Assessing and Characterizing the Inductive Effect Through Silicon-Containing Backbones and On Silicon Reactivity

By

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Dedication

This thesis is dedicated to my family who made me who I am.

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Abstract

This thesis describes a study of the inductive effect in derivatives of bicyclo[1.1.1]pentane; chosen because it eliminates any possibility of conjugation between the substituent and probe, and keeps the steric effect constant by providing a rigid backbone. The substituent effects, both upon a silicon center and transmitting through silicon atoms, in these systems were studied using Density Functional Theory and the isodesmic reaction approach to Hammett's methods. The electron density distribution was analyzed using the Quantum Theory of Atoms in Molecules.

Although less sensitive to substitution, it was discovered that the effect as measured on a Si-probe ($–Si(OH)_3$) is the same as that measured using a C-probe (–COOH). In both cases, the transmission of the "so-called" inductive effect appears to operate in the same fashion: through the molecule using the atomic dipole moment. The x-component (axis connecting the substituent and probe) of the substituent dipole was determined to be the controlling property. Despite minor differences in structure, replacing the backbone atoms with silicon appears to have little effect upon the mechanism of transmission, but a general decrease in sensitivity, to the effect of substitution, is apparent. As the atomic dipole moment conforms to the principle of atomic transferability, it is possible to describe the inductive effect in terms of the substituent-only dipole ($\mu_x(R_H)$; determined for the RH system). In fact, we were able to replace the substituent constant, an empirically derived parameter, with $\mu_x(R_H)$, a quantum mechanically derived parameter. Linear free energy relationships to describe the inductive effect with $\mu_x(R_H)$, as well as an electronegativity term and steric terms to

describe the backbone and probe, were developed that essentially recreate the entire substituent effect.

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List of Abbreviations

AIL: Atomic interaction line

AO: Atomic orbital

B: Backbone

BCP: Bond critical point

BO: Born-Oppenheimer

B3LYP: Three-parameter Exchange-Correlation Functional created by Becke; with the Lee, Yang and Parr correlation functional

CB: Conjugate base

CBS: Complete basis set

CC: Coupled cluster

CCP: Cage critical point

CGTO: Contracted Gaussian type orbital

CI: Configuration interaction

CP: Critical point

DFT: Density Functional Theory

DI: Delocalization index

EDG: Electron donating group

ELF: Electron localization function

EWG: Electron withdrawing group

GGA: Generalized gradient approximation

GIAO: Gauge including atomic orbitals

GTO: Gaussian type orbital

HA: Acid

HF: Hartree-Fock

HOMO: Highest occupied molecular orbital

IAS: Interatomic surface

IUPAC: International Union of Pure and Applied Chemistry

KS: Kohn-Sham

LCAO: Linear combination of atomic orbitals

LDA: Local density approximation

LSDA: Local spin density approximation

LUMO: Lowest unoccupied molecular orbital

MO: Molecular orbital

MP: Møller-Plesset

NA: Nuclear attractor

NCP: Nuclear critical point

NMR: Nuclear magnetic resonance

NNA: Non-nuclear attractor

P: Probe

PBE0: Parameter-free hybrid exchange-correlation functional developed by Perdew, Burke, and Ernzerhof

PES: Potential energy surface

PGTO: Primitive Gaussian type orbital

PT: Perturbation theory

QTAIM: Quantum Theory of Atoms in Molecules

R: Substituent

RCP: Ring critical point

SCF: Self-consistent field

SD: Slater determinant

STO: Slater type orbital

TBP: Trigonal bipyramidal

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Note on Formatting

The thesis is formatted such that Chapters 3 through 5 are manuscripts that have been or will be submitted to be published in a journal. Therefore, each has its own Introduction and Methods sections, in addition to the results.

Chapter 1: General Introduction

Silicon chemistry is a vast and diverse field with possible applications in biological fields (e.g. in plant[1] and animal life,[2,3] and drug design[4]) and in manufacturing (e.g. ceramics,[5] polymer chemistry[6] and lasers[7]). The most interesting aspects of Si chemistry are also what make it so complicated. Unlike its first row analog, carbon, Si can adopt coordination schemes ranging from 2- to 6-coordinate geometries. Although it is isoelectronic with C, Si has a greater atomic radius, a greater polarizability, and the opportunity to employ (p–d)π, (p–d–d)π, etc. interactions.[8] In addition, silicon compounds like silicates have a tendency to oligomerize[9] under ambient conditions making preparation and characterization extremely difficult. Investigations of silicon systems tend to rely on phenomena observed for their carbon based counterparts and relationships developed for organic reactions (e.g. the Hammett equation[10-12]), an approach that, historically,[13,14] does not perform particularly well.

1.1 Substituent Effects

Substituent effects continue to be one of the most ubiquitous and least understood concepts in chemistry. In general terms, substituent effects refer to the changes in chemical properties, such as reactivity, of a molecule due to a group, or atom, when compared to its unsubstituted counterpart (when the substituent is simply a hydrogen atom).[15] This overall effect is generally divided into different contributions: steric, resonance, and inductive effects are most common.

The International Union of Pure and Applied Chemistry (IUPAC) defines the steric effect as the resulting change in a property upon the introduction of a substituent with a different steric requirement and is generally related to the overall size of the substituent itself.[16] Steric effects, or strain in a molecule, tend to come from non-bonded repulsions, bond angle strain, and bond stretches or compressions. Steric effects can be avoided by increasing the distance between the substituent and the probe (where the effect is being measured) such that they no longer spatially interact. This is generally achieved by using some sort of molecular linker, or backbone, to transmit the effect.

Resonance effects describe the effect a substituent has on reactivity through electron delocalization, and thus require a conjugated network of π-bonds.[16] Substituents can be placed into two groups based on the type of effect they exert: electron withdrawing groups (EWGS, which are said to have a negative effect, and electron donating groups (EDGs), which are said to have a positive effect.[17] Resonance effects can be easily avoided by employing a fully saturated backbone.

The inductive effect is arguably the most important of all substituent effects because it is always in operation. The concept, originally introduced by Ingold,[18] is now defined by IUPAC as an experimentally observable effect of the transmission of electron density through σ-bonds via electrostatic induction.[16] Classically suggested to propagate via consecutive polarizations of bonds, the electron density is said to flow from a substituent of lower electronegativity to one with higher electronegativity.[19] Simultaneously, the transmission of electron density can occur through space and this mechanism is termed the field effect.[16] Field effects are generally described in terms of induced dipole interactions, or even dispersion forces. The separation of the inductive and field effects is problematic as both occur simultaneously and most often operate in the same direction. Both are defined by Coulombic relationships and therefore decay with distance.[19,20] The indivisibility of the two effects has led many groups to combine both under the inductive effect title, regardless of the mechanism of operation, and invoke the term “the so-called inductive effect”.[21]

1.2 Quantifying Substituent Effects

To simplify studies of substituent effects, most molecules are separated into three parts: the substituent (designated as R through this discussion), a backbone (B) through which the effect is transmitted, and a probe (P) where the effect is measured.

One of the first methods to calculate substituent effects, now most widely used for organic reactions,[20] was postulated by Hammett.[10-12] He was the first to systematically study the effects of substituents on the properties of a functional group, and his simple empirical relationship became known as the Hammett equation. Hammett noticed a relationship between the acid-dissociation constant for the substituted benzoic acid (K_R) and that of the unsubstituted acid (K_H) according to equation 1.1, where σ is the substituent constant, which depends on the nature of the substituent and on its position on the ring.

$$log\left(\frac{K_R}{K_H}\right) = \sigma\rho \tag{1.1}$$

Ortho-substitution was not used because of the addition of steric complications between the substituent and probe. The values of the constants were determined using the results of 52 different reaction series. ρ is the reaction constant, which depends on the reaction conditions and the nature of the probe group. Hammett suggested his reaction constants take the form of equation 1.2,[22] where **R** is the universal gas constant, **T** is the absolute temperature, **d** is the distance between substituent and probe, and **D** is the dielectric constant of the solvent.

$$\rho = \frac{\left(\frac{B_1}{D}\right) + B_2}{RTd^2} \tag{1.2}$$

The constants $\mathbf{B_1}$ and $\mathbf{B_2}$ are more ambiguous. $\mathbf{B_1}$ is said to depend on the electrostatic interaction between the compound and solvent, while $\mathbf{B_2}$ is taken as a measure of the sensitivity of the reaction to changes in charge density at the probe. A positive ρ implies that the reaction is favoured by low electron density at the probe, while a negative ρ requires high electron density. For benzoic acids in water, at 25°C ρ was defined as 1.000.[23] The use of the relationship in Equation 1.1 has been criticized due to its empirical nature,[20] but the constants have been used to describe a large body of data with a mean deviation of only 15%.[22]

Although it was originally developed using the equilibrium constants of benzoic acids, the Hammett equation has since been extended to other organic systems, and to other properties such as infrared frequencies,[24] nuclear magnetic resonance (NMR) chemical shifts,[25] polarographic electroreductions,[26] isotropic effects,[27], and mass spectra.[28] The Hammett equation has also been extended via the separation of inductive (σ_I) and resonance (σ_R) effects according to equation 1.3.[20]

$$\sigma = \sigma_I - \sigma_R \tag{1.3}$$

With the separation of constants, the Hammett equation can be rewritten for any property (Y) according to equation 1.4.[29]

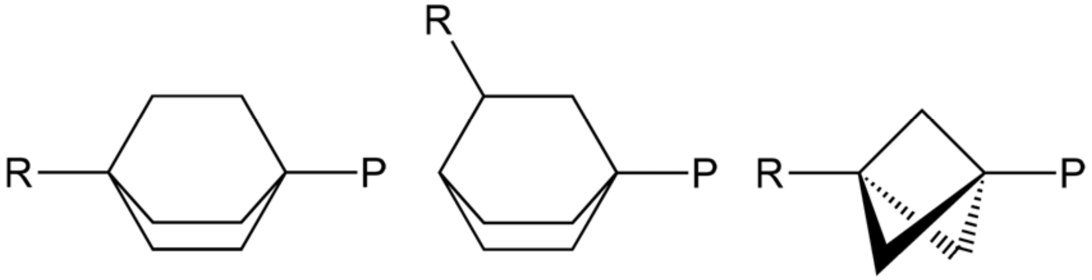
$$Y_R - Y_H = \rho_I \sigma_I + \rho_R \sigma_R \tag{1.4}$$

Y_R represents the property in the substituted compound and Y_H that in the unsubstituted compound, and the proportionality constants ρ_I and ρ_R are obtained through multiple linear regression analysis.[29,30]

Separation of resonance and inductive effects is important as each can have a different, and sometimes even opposite, effect upon reactivity. Alkyl groups are electron donating, but can only add density through the inductive effect. Substituents like the halogens or hydroxyl are electron withdrawing though σ-bonds, but actually donate density via n-π interactions. Separation of these effects is also important with respect to the structure of a molecule. Using the *para*- and *meta*-substituted benzoic acids as an example, the same substituent in each could have a different effect. The distance between the substituent and probe group (carboxylic acid) is longer in *p*-substitution, and the angular direction through-space is also different.

1.3 Bicyclic Hydrocarbons

Bicyclic hydrocarbons have been used as a backbone to separate substituents by ensuring only the inductive effect is in operation. The saturated σ-bond network makes resonance impossible, and the substituent and probe are held at a distance to keep steric interaction constant (which can then become a part of the reaction constant).[31] The bicyclo[2.2.2]octane structure, shown in Figure 1.1, was originally suggested because substitution at the 4-position ensured the number of C–C bonds between substituent and probe was essentially the same as in the *p*-substituted benzoic acids,[32]



4-substituted
bicyclo[2.2.2]octane

3-substituted
bicyclo[2.2.2]octane

3-substituted
bicyclo[1.1.1]pentane

Figure 1.1. Common bicyclic hydrocarbons used in inductive effect studies: bicyclo[2.2.2]octane and bicyclo[1.1.1]pentane.

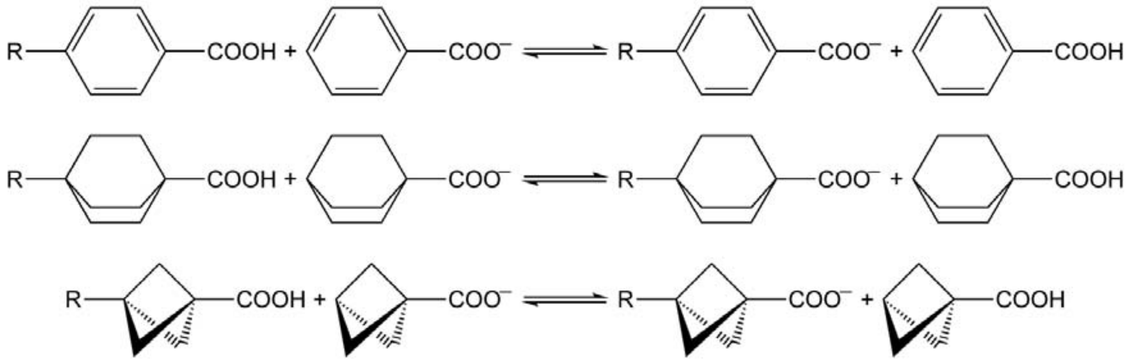
while substitution at the 3-position is related to the *m*-substituted benzoic acids.[33] The rigid backbones also force the substituent and probe to be coplanar, thus removing any angle dependence of the distance. Bicyclo[1.1.1]pentane (see Figure 1.1) has also been used as a backbone in inductive effect studies. The main advantage of using the bicyclo[1.1.1]pentane backbone over the bicyclo[2.2.2]octane backbone is that the shorter distance between the substituents and probe should lead to a more sensitive effect.[33]

1.4 Isodesmic Reactions

In order to investigate a substituent effect, or in this case the inductive effect, it is more efficient to use isolated molecules than rely on solution reactivities.[30] Isolated molecules would be more sensitive to minute changes in structure and electron density; one could avoid any artificial changes due to system interaction, such as solvent stabilization. This fact leads to the usefulness of quantum chemical calculations: their ability to accurately determine the thermochemistry of single, isolated, molecules. Quantum calculations also make it possible to test systems that are difficult or impossible to synthesize, as well as study microscopic properties that may not be resolvable experimentally.

An important tool in the study of substituents via quantum chemical or computational calculations is the isodesmic reaction:[30] a special category of reactions where the number and types of bonds are the same on both sides of the reaction.[16] Three examples using systems already discussed are shown in Scheme 1.1. An

SCHEME 1.1



isodesmic reaction is particularly useful as it functions to reduce the errors associated with some common approximations like incomplete basis sets, the set of function used to create the molecular orbital that must be truncated in order to calculate, and incomplete correction for electron correlation.[34] Electron correlation errors are related to the fact that in simple Hartree-Fock theory the motion of electrons is considered correlated even at long distances, and thus bond breaking reactions, like acid-base dissociations, are problematic. It is possible to correct for this, but complete corrections are impossible (discussed in more detail in Chapter 2). The use of an isodesmic reaction treats this error as systematic, and therefore it cancels.

Isodesmic reactions are also important in that they exploit the relationship of the Hammett equation to linear free energies. Equation 1.1 is a linear free energy relationship,[22] and equation 1.4 can be related to isodesmic reactions. This stems from the proportionality between the left hand side of the equations ($\log K_R - \log K_H$) and the differences in the free energies for the substituted and unsubstituted compounds. Using the first reaction in Scheme 1.2 for substituted benzoic acid, the derivation in equation 1.5 shows how the isodesmic reaction energy can be directly related to the Hammett relationship of equation 1.1. HA refers to the acid species, CB refers to the conjugate base species, and the subscripts R and H corresponding to the substituted and unsubstituted species, respectively.

$$log(K_R) - log(K_H) = \sigma\rho$$

$$log\left(e^{-\Delta_R G/_{RT}}\right) - log\left(e^{-\Delta_H G/_{RT}}\right) = \sigma\rho$$

$$\Delta_H G - \Delta_R G = \sigma\rho \tag{1.5}$$

$$[G(HA_H) - G(CB_H)] - [G(HA_R) - G(CB_R)] = \sigma\rho$$

$$[G(HA_H) + G(CB_R)] - [G(CB_H) + G(HA_R)] = \sigma\rho$$

$$\Delta_{iso} G = \sigma\rho$$

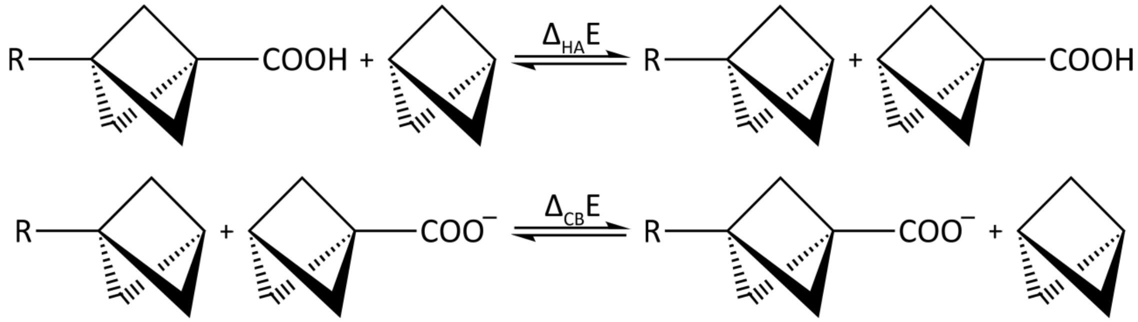
One potential problem with the isodesmic reaction approach is that the reactions shown in Scheme 1.1 all involve two separate, but simultaneous interactions: the effect of R on the carboxylic acid probe in its protonated state, and that on its deprotonated state. These two interactions can be separated by splitting the overall reaction into two separate isodesmic reactions,[30] one for each effect. In Scheme 1.2, HA refers to the effect upon the acid species only and CB refers to the effect upon the conjugate base only.

1.5 Substitution and Silicon Systems

The majority of substituent effect studies involving silicon treat the center as a substituent and not as a probe. Work involving the effect upon a center began with Taft, who measured the effect in organic carbonyls.[35] It was Taft who first suggested the requirement of a term to describe the steric effect to the original Hammett equation as in equation 1.6.

$$log(K_R) - log(K_H) = \sigma\rho + \delta E_s \tag{1.6}$$

SCHEME 1.2



Cartledge defined a series of steric parameters specifically for silicon, $E_s(Si)$, due to the size difference between C and Si.[13] These steric parameters were calculated using the acid-catalyzed hydrolysis of silanes (R_3SiH) with a variety of alkyl groups.

More recently, Ploom and Tuulmets investigated the inductive effect in Si chemistry[14] using the method described by Exner and Böhm.[36] They discovered that the addition of an electronegativity term, as outlined in equation 1.7, was needed to fully describe the effect.

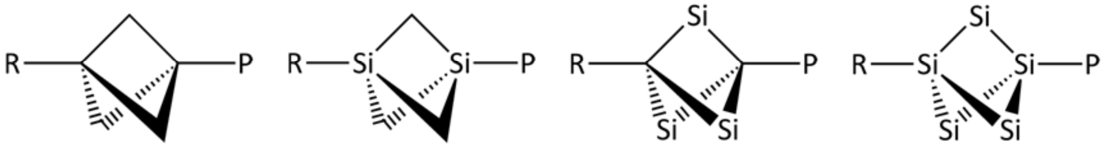
$$log(K_R) - log(K_H) = \sigma\rho + \zeta\chi + \delta E_s(Si) \tag{1.7}$$

Most of their organosilicon centers take the form $RSi(CH_3)_2Cl$ and therefore do include steric effects at the Si center. To date there has been no study of the inductive effect at Si that removes the complicating steric hindrance.

Another aspect of substituent effects in silicon systems is the manner in which the effect transmits through a Si atom. One of the few studies of this nature was undertaken by Yoder *et al.*[8] They studied the transmission of substituent effects though a disilane bond using the NMR coupling constants and chemical shifts as probes in molecules of the form $RSi(CH_3)_2Si(CH_3)_3$ and $RSi(CH_3)_2Si(CH_3)_2N(CH_3)_2$. They found that the Si–Si bonds was less effective at transmitting substituent effects than the C–C counterpart, and even behaved as an insulator rather than a conductor in some cases.

In this investigation we aim to answer two main questions: what is the effect of substituents on a silicon center and how does the effect transmit through silicon containing backbones. To do this, we will use the bicyclo[1.1.1]pentane backbone to ensure only the “so-called” inductive effect is operating and employ a variety of substituents (chosen to cover a range of electronegativity, χ). Li is electropositive (χ=1.00) and has been previously shown to adopt bonds that are highly ionic in nature. However, it is commonly referred to as an electron donating group in substituent effect studies,[37] and will be used as such here due to the small number of inductively donating substituents. Using the well documented carboxylic acid probe as a benchmark, a silicic acid type probe ($Si(OH_3)$) will be used to measure the effect of the substituents on silicon using the isodesmic reaction approach to solving the Hammett equation. The Quantum Theory of Atoms in Molecules (see Chapter 2) will be employed to determine how the substituents perturb the electron density distribution. As illustrated in Scheme 1.3, we will systematically replace the carbon atoms within the bicyclo[1.1.1]pentane backbone with silicon atoms to determine the effect upon the mechanism of transmission.

SCHEME 1.3



Full Carbon Analog 1 Analog 2 Analog 3

R = H, Li, CH_3, NH_2, OH, F, CF_3, NF_2, CN, NO_2
P = COOH, $Si(OH)_3$

Chapter 2: Computational Theory and Methods

Throughout this thesis, Density Functional Theory (more specifically the parameter-free hybrid functional PBE0) was used to optimize the structure for and determine the energy of the bicyclo[1.1.1]pentane systems. The accuracy of the resultant energies was confirmed using a composite method, known for achieving highly accurate thermochemistries (CBS-QB3). The same model chemistry (PBE0/6-31++G(d,p)) was used in all calculations to ensure consistency. Central to any study of the "so-called" inductive effect, the electron density distribution was analyzed according to Bader's Quantum Theory of Atoms in Molecules.

2.1 Density Functional Theory

Conventional quantum chemistry, uses the wavefunction (Ψ_i) because it includes all information about the specific state of the system and can be used to determine any physically observable property of the system if one knows the appropriate operator ($\hat{Q}$ for a general operator).[38] For example, in equation 2.1 the Hamiltonian operator, $\hat{H}$, for a molecular system described by the function of the q_i and q_A electronic and nuclear coordinates – which includes M nuclei and N electrons – returns the total energy, E_i, of the system.

$$\hat{H}\Psi_i(q_i, q_A) = E_i\Psi_i(q_i, q_A) \tag{2.1}$$

Unfortunately, the wavefunction is a vastly complex quantity: it depends on 4N variables, one spin variable and three spatial variables for each of N electrons (after the nuclear positions have been fixed), and is almost completely uninterpretable. Density Functional Theory (DFT) stemmed from the idea that a simpler, physical observable could be used to determine the energy of the system. The basic premise behind DFT is that the electron density can be used, instead of the wavefunction, to determine the energy, and thereby other properties, of a molecule.[38-40] The electron density, ρ(r), is given by a multiple integral over the spin coordinates of all electrons and all but one of the spatial variables because electrons are indistinguishable:[40]

$$\rho(r) = N \int \dots \int |\Psi(x_1, x_2, \dots x_N)|^2 ds_1 dx_2 \dots x_N \tag{2.2}$$

ρ(r) is a non-negative function, which goes to zero at infinity and integrates to give the total number of electrons, N.

$$N = \int \rho(r) dr \tag{2.3}$$

While there were previous approximations which used the electron density, contemporary DFT got its roots with Hohenberg and Kohn in 1964.[41] The two theorems presented in their paper (the proof of existence and the variational principle) form the basis for all DFT.

2.1.1 Hohenberg-Kohn Theorems

The first theorem states that "the external potential $V_{ext}(r)$ is (to within a constant) a unique functional of ρ(r); since, in turn $V_{ext}(r)$ fixes $\widehat{H}$ we see that the full many particle ground state functional of ρ(r)" (sic).[41] In DFT the electrons interact not only with one another, but also an external potential. In a uniform electron gas, as was used in the proof of the existence theorem, the external potential is defined as a uniform positive charge. In a molecular system, the external potential is the attractive forces between the nuclei and electrons. The electron density determines not only the external potential, the Hamiltonian and the ground-state wavefunction, but also the excited-state wavefunctions.[39]

Although the existence theorem shows the utility of the density, it does not describe how to predict the density. In the second theorem, Hohenberg and Kohn showed that the density obeys the variational principle.[41] One can evaluate the expectation value of the energy, by optimizing the orbital coefficients, which must be greater than or equal to the true energy.

2.1.2 Kohn-Sham Approach

Kohn and Sham proposed to simplify the Hamiltonian by treating the system as if the electrons were non-interacting.[42] If this was the case, the Hamiltonian could be expressed as a sum of one-electron operators. The Kohn-Sham (KS) approach takes a fabricated system of non-interacting electrons with the same density as the real system as the starting point, and uses this to separate the energy into components according to:[39]

$$E[\rho(r)] = T_{ni}[\rho(r)] + V_{ne}[\rho(r)] + V_{ee}[\rho(r)] + \Delta T[\rho(r)] + \Delta V_{ee}[\rho(r)] \qquad (2.4)$$

The terms in equation 2.4 correspond to the kinetic energy of the non-interacting electrons, the nuclei-electron interaction, the classical electron-electron repulsion, the correction to the kinetic energy of the electrons required because of their interactions in the real system, and all non-classical corrections to the electron-electron repulsion, respectively. The attraction between nuclei and electrons is defined as[39]

$$V_{ne}[\rho(r)] = \sum_{A}^{nuclei} \int \frac{Z_A}{|r - r_A|} \rho(r)\, dr \tag{2.5}$$

where Z_A is the atomic number of atom A, and r_A is the radial distance from atom A. The classical electron-electron repulsion is given by:[39]

$$V_{ee}[\rho(r)] = \frac{1}{2} \int \int \frac{\rho(r_1)\rho(r_2)}{|r_1 - r_2|} dr_1 dr_2 \tag{2.6}$$

where r_1 and r_2 are dummy integration variables, which run over all space. Using bra-ket notation in terms of orbitals, equation 2.4 can be rewritten as

$$\begin{aligned} E[\rho(r)] = {} & \sum_{i}^{N} \left(\langle \phi_i \left| -\frac{1}{2} \nabla_i^2 \right| \phi_i \rangle - \langle \phi_i \left| \sum_{A}^{nuclei} \frac{Z_A}{|r_i - r_A|} \right| \phi_i \rangle \right) \\ & + \sum_{i}^{N} \langle \phi_i \left| \frac{1}{2} \int \frac{\rho(r')}{|r_i - r'|} dr' \right| \phi_i \rangle + E_{xc}[\rho(r)] \end{aligned} \tag{2.7}$$

Where N is the total number of electrons and the density, ρ, is given by

$$\rho = \sum_{i=1}^{N} \langle \phi_i | \phi_i \rangle \tag{2.8}$$

In equation 2.7 the two correction terms have been combined in $E_{xc}[\rho(r)]$, which is generally termed the so-called exchange-correlation energy (discussed in Section 2.1.3).[39]

The KS approach follows a Self-Consistent Field (SCF) method. The many-electron operator can be described as a product of one-electron operators, or orbitals. These orbitals are assumed to be orthonormal and are given as a linear combination of atomic orbitals (LCAO), χ_i, weighted by coefficients c_{ij} as in equation 2.9 (discussed in more detail in Section 2.2).

$$\phi_i = \sum_{i=1}^{N} c_{ij}\chi_i \tag{2.9}$$

The Hamiltonian operator can then be rewritten as:

$$\widehat{H} = \sum_{i=1}^{N} h_i^{KS} \tag{2.10}$$

where h_i^{KS} is the KS one-electron operator and is defined as:

$$h_i^{KS} = -\frac{1}{2}\nabla_i^2 - \sum_{k}^{nuclei} \frac{Z_k}{|r_i - r_k|} + \int \frac{\rho(r')}{|r_i - r'|} dr' + V_{xc} \tag{2.11}$$

and V_{xc} is a functional-derivative given in equation 2.12.

$$V_{xc} = \frac{\partial E_{xc}}{\partial \rho} \tag{2.12}$$

The orbitals that minimize the energy can be found using the following relationship, where ε_i is the energy:

$$h_i^{KS}\phi_i = \varepsilon_i\phi_i \tag{2.13}$$

To determine the KS orbitals, they are expressed as a set of basis functions (Section 2.2) and then the orbital coefficients are determined iteratively by solving the secular equation, represented by a Slater determinant as in equation 2.14, to determine a set of orbital energies.[39]

$$\Phi_{SD} = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(1) & \phi_2(1) & \dots & \phi_N(1) \\ \phi_1(2) & \phi_2(2) & \dots & \phi_N(2) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_1(N) & \phi_2(N) & \dots & \phi_N(N) \end{vmatrix} \tag{2.14}$$

DFT, by definition, is an exact theory and all that must be known is how E_{xc} depends on ρ(r).[40] Unfortunately, the theorems give no indication as to the functional form or how to discover it. Consequently much time has gone into determining the exact or best form for E_{xc}.

2.1.3 Exchange-Correlation Functionals

The so-called exchange-correlation energy accounts for the differences between the classical and quantum descriptions of electron-electron repulsion, and the kinetic energies of the non-interacting and interacting systems. Our work employs hybrid approaches (Section 2.1.3.3), which depend on the local and generalized gradient approximations. Therefore, these three methods will now be discussed: the local density approximation, the generalized gradient approximation, and hybrid methods. Most functionals use the following syntax to define E_{xc}:[39]

$$E_{xc}[\rho(r)] = \int \rho(r)\varepsilon_{xc}[\rho(r)]dr \tag{2.15}$$

where E_{xc} is described as an interaction between an energy density (ε_{xc}; which depends on the electron density) and ρ(r). The energy density is a sum of exchange and correlation contributions and, as an example, the Slater exchange energy density is defined as:

$$\varepsilon_x[\rho(r)] = -\frac{9\alpha}{8}\left(\frac{3}{\pi}\right)^{1/3}\rho^{1/3}(r) \tag{2.16}$$

Spin densities are depicted in terms of ζ (equation 2.17), where individual functionals of the α and β densities are used.[39]

$$\zeta(r) = \frac{\rho^{\alpha}(r) - \rho^{\beta}(r)}{\rho(r)} \tag{2.17}$$

2.1.3.1 Local Density Approximation (LDA)

Originally the LDA referred only to those functionals where ε_{xc} at any position could be determined from the electron density at that position (the local density). The local density is treated as a uniform electron gas, which leads to $\alpha=2/3$ in equation 2.16 (other models yield different α values; for example, the Slater model has $\alpha=1$, and the Xα model has $\alpha=3/4$). The LDA can be extended to include spin polarization with:[39]

$$\varepsilon_x[\rho(r),\zeta] = \varepsilon_x^0[\rho(r)] + \{\varepsilon_x^1[\rho(r)] - \varepsilon_x^0[\rho(r)]\}\left[\frac{(1+\zeta)^{4/3} + (1-\zeta)^{4/3} - 2}{2\left(2^{1/3}-1\right)}\right] \tag{2.18}$$

ε_x^0 is given in equation 2.16, and ε_x^1 is derived from considering a uniform electron gas where all electrons have the same spin. In this case, the approximation takes the title Local Spin Density Approximation (LSDA).[39] The correlation energy is more complex as there is no analytical derivation for even the simple uniform electron gas. Monte Carlo methods were used to estimate the correlation energy of the uniform gas; by subtracting the analytical exchange energy from the total energy at several densities. Local functionals, including one analogous to equation 2.18, were designed by Vosko, Wilk, and Nusair[43] using a fitting scheme to the correlation energies. The fitting scheme interpolates within the unpolarized ($\zeta=0$) and polarized ($\zeta=1$) limits, and is expressed in terms of r_s instead of ρ (equation 2.19).[38]

$$\varepsilon_C^{VWN}(r_s,\zeta) = \varepsilon_c(r_s,0) + \varepsilon_a(r_s)\left[\frac{f(\zeta)}{f''(0)}\right][1-\zeta^4] + [\varepsilon_c(r_s,1) - \varepsilon_c(r_s,0)]f(\zeta)\zeta^4 \tag{2.19}$$

$$f(\zeta) = \frac{(1+\zeta)^{4/3} + (1-\zeta)^{4/3} - 2}{2(2^{1/3} - 1)}$$

In general, LSDA underestimates the exchange energy by approximately 10%, and overestimates electron correlation by a factor of 2. This leads to unrealistically strong bonds.[38]

2.1.3.2 Generalized Gradient Approximation (GGA)

The most intuitive way to improve the LSDA would be to consider a non-uniform electron gas. In this type of approach, the exchange and correlation energies are also dependent on the derivatives of the electron density, and is thus termed the Generalized Gradient Approximation (GGA).[38] In general, GGA functionals add a correction to the LDA functional as in equation 2.20.

$$\varepsilon_{xc}^{GGA}[\rho(r)] = \varepsilon_{xc}^{LDA}[\rho(r)] + \Delta\varepsilon_{xc}\left[\frac{|\nabla\rho(r)|}{\rho^{4/3}(r)}\right] \tag{2.20}$$

This correction is dependent on a dimensionless reduced gradient.[39] One of the first popular exchange functionals was proposed by Becke.[44] It takes the abbreviation B, or B88, and has the correct asymptotic behaviour for the energy density (-r $^{-1}$).[38]

$$\begin{gathered}\varepsilon_x^{B88} = \varepsilon_x^{LDA} + \Delta\varepsilon_x^{B88} \\ \Delta\varepsilon_x^{B88} = -\beta\rho^{1/3}(r)\frac{x^2}{1+6\beta x sinh^{-1}x}\end{gathered} \tag{2.21}$$

Where β is a fitting parameter (determined to by 0.0042 using a least-squares fit to the exact exchange energies for noble gas atoms He through Rn)[40] and x is defined as:

$$x = \frac{|\nabla\rho(r)|}{\rho^{4/3}(r)} \tag{2.22}$$

In GGAs, corrections to the correlation energy density are also calculated following equation 2.20, but have very complicated analytical forms.[40] Some functions do not correct the LDA expression, but actually calculate the total energy. The LYP correlation functional was developed on the basis of an accurate expression for the correlation energy of the helium atom, and takes the form of equation 2.23, where a, b, c and d are fitting parameters.[38]

$$\begin{aligned}\varepsilon_c^{LYP} = -a\frac{\gamma}{(1+d\rho^{-1/3})} - ab\frac{\gamma e^{-c\rho^{-1/3}}}{9(1+d\rho^{-1/3})\rho^{8/3}} \\ \times\Big[18\big(2^{2/3}\big)C_F\Big(\rho_\alpha^{8/3}+\rho_\beta^{8/3}\Big) - 18\rho t_w + \rho_\alpha(2t_w^\alpha + \nabla^2\rho_\alpha) \\ + \rho_\beta\Big(2t_w^\beta + \nabla^2\rho_\beta\Big)\Big]\end{aligned} \tag{2.23}$$

$$\gamma = 2\left[1 - \frac{\rho_\alpha^2 + \rho_\beta^2}{\rho^2}\right]$$

$$t_w^\sigma = \frac{1}{8}\left(\frac{|\nabla\rho_\sigma|^2}{\rho_\sigma} - \nabla^2\rho_\sigma\right)$$

2.1.3.3 Hybrid Methods

Exchange contributions tend to be significantly larger than correlation effects, and can therefore be considered the most important part in developing a functional. In the Hartree-Fock (HF) regime, the exchange energy is defined exactly. Hybrid functionals use this exact HF exchange and make approximations to compute the correlation energy.[40]

$$E_{xc} = (1-a)E_{xc}^{DFT} + aE_{x}^{HF} \tag{2.24}$$

This approach was taken in the creation of the B3LYP functional (used in the composite method described in Section 2.3), which uses Becke's exchange correction and the LYP correlation functional:

$$E_{xc}^{B3LYP} = (1-a)E_{x}^{LDA} + aE_{x}^{HF} + b\Delta E_{x}^{B88} + (1-c)E_{c}^{LDA} + cE_{c}^{LYP} \tag{2.25}$$

where a, b, and c have values of 0.20, 0.72, and 0.81, respectively. B3LYP has proven to be the most popular functional to date.[39] There are also so-called parameter-free hybrid functionals, where the fitting parameters are not empirical. One example is PBE0 (equation 2.26; used in this study), whose contribution of HF exchange (25%, a=0.25) was chosen based on perturbation theory arguments.

$$\begin{gathered} E_{xc}^{PBE0} = (1-a)E_{xc}^{PBE} + aE_{x}^{HF} \\ E_{xc}^{PBE} = \frac{cx^2}{1+bx^2} \end{gathered} \tag{2.26}$$

In equation 2.26, c and b have values of 0.00336 and 0.00449, respectively, and x is given in equation 2.22. It is suggested that the inclusion of HF exchange makes up for the underestimation of the importance of polar terms as occurs in 'pure' functionals.[39]

2.2 Basis Sets

One approximation essential to *ab initio* calculations is the basis functions or set used to create the MO in equation 2.9.[38] It is not an approximation if a complete set is used, but this means an infinite number of functions must also be used and this becomes impossible in a real calculation. The smaller the set of functions used to represent the MO is, the poorer the representation will be.

The type of function used in the representation can also affect its accuracy. In general one can use any type of function that fits the boundary conditions, but the most commonly used are the Slater type orbital (STO) and the Gaussian type orbital (GTO). These basis functions are referred to as atomic orbitals (AOs) because they are used to represent the MO, but they do not correspond to solutions of the atomic wavefunction (although STOs do resemble the atomic orbitals).[38] STOs take the following form, where N is a normalization constant and $Y_{l,m}$ are spherical harmonic functions:[38]

$$\chi_{\zeta,n,l,m}(r,\theta,\varphi) = NY_{l.m}(\theta,\varphi)r^{n-1}e^{-\zeta r} \tag{2.27}$$

The exponential term ($e^{-\zeta r}$) recreates the distance dependence between the electrons and the nucleus. One disadvantage of STOs is that they do not have any radial nodes as in true orbitals, but this can be overcome by using a linear combination of STOs. The main problem is that a calculation using STOs cannot be solved analytically.[38]

GTOs take the following form (equation 2.28), and can also be written in terms of Cartesian coordinates (equation 2.29):[38]

$$\chi_{\zeta,n,l,m}(r,\theta,\varphi) = NY_{l.m}(\theta,\varphi)r^{(2n-2-l)}e^{-\zeta r^2} \tag{2.28}$$

$$\chi_{\zeta,l_x,l_y,l_z}(x,y,z) = Nx^{l_x}y^{l_y}z^{l_z}e^{-\zeta r^2} \tag{2.29}$$

The sum of the l_x, l_y, and l_z terms gives the type of orbital the GTO is describing. The r^2 dependence of the exponential terms leads to an unrealistic negative slope at the nucleus. In general, GTOs do a poor job at representing what happens near the nucleus, and at the other distance extreme; the GTO falls off far too quickly. However, the benefit to using GTOs is that the pertinent integrals can be calculated. GTOs are the most widely used functions in basis sets, but a linear combination of GTOs is used to recreate the desired properties of an STO as described in equation 2.30.

$$\chi(CGTO) = \sum_{i}^{k} a_i \chi_i(PGTO) \tag{2.30}$$

This is referred to as a contracted basis function (CGTO), and the original GTOs that are combined are now called primitive GTOs (PGTOs).[39] When two CGTOs are used it is termed a double-zeta (because of the use of ζ in the exponent) basis set, and when three are used it is termed a triple-zeta basis set.

Basis sets can also be improved by separately describing the valence and core orbitals, and are referred to as split-valence basis sets.[38] Pople *et al.* have designed split valence basis sets, designated *k-nlmG*. The *k* corresponds to the number of PGTOs used to describe the core orbitals and *nlm* is used for the valence orbitals. One of the most common (and that used in this study) Pople-style basis sets is 6-31G.[45,46] In this set, a contraction of six PGTOs is used for the core orbitals; and the valence is split into two functions, one described by three PGTOs and one represented by one PGTO.

Additionally, diffuse and/or polarization functions can be added to each basis set. The presence of diffuse functions in the Pople-style basis sets are indicated by '+' before the G. A single '+' indicates that a set of s and p functions have been added to the heavy atoms, and a second '+' indicates that a set of s functions have been added to hydrogen.[38,39] Diffuse functions are used to improve the density farther from the nucleus as required in complexes that have more spatially diffuse molecular orbitals (such as anions and highly excited electronic states).[39] Polarization functions, which allow flexibility in the molecular orbitals required for asymmetry, are designated after the G in a similar manner. In the most simple additions, the designation '**' is used. This corresponds to the addition of a d function on heavy atoms and a p function on hydrogen. Polarization functions must be designated explicitly when more are added, thus '**' is equivalent to (d,p). The largest standard Pople-style basis set is 6-311++G(3df,3pd).[38]

2.3 Composite Methods

Composite methods are multilevel, or multistep, approaches to achieving highly accurate results (most often thermochemical quantities). They generally assume that basis-set, and correlation energy, incompleteness can be dealt with in an additive manner as calculations to achieve the exact answer are impossible.[39] In one of the most common composite methods (used in this study), CBS-QB3,[47,48] energies computed at different levels of theory are extrapolated to a complete basis set (CBS) limit. Differing techniques for calculating electron correlation are also used to determine correction terms to the overall energy. The CBS-QB3 approach involves lower level calculations on large basis sets for the SCF and zero-point energies, medium sized basis set for second order corrections, and small size basis sets for higher-level corrections. The specific steps are:[49]

(i) B3LYP/6-311G(2d,d,p) geometry optimization

(ii) B3LYP/6-311G(2d,d,p) vibrational frequency analysis, with a 0.99 scaling factor to correct for the harmonic approximation

(iii) UMP2/6-311+G(3df,2df,2p) energy calculation, and a CBS extrapolation

(iv) MP4(SDQ)/6-31+G(d(f),p) energy calculation

(v) CCSD(T)/6-31+G† energy calculation

The total energy of the system is calculated by adding corrections to that determined at the MP2 level of theory according to equation 2.31.

$$E_{CBS-QB3} = E_{MP2} + \Delta E_{MP4} + \Delta E_{CCSD(T)} + \Delta E_{ZPE} + \Delta E_{CBS} + \Delta E_{emp} + \Delta E_{spin} \tag{2.31}$$

ΔE_{CBS} represents the correction for the basis set truncation, ΔE_{MP4} and $\Delta E_{CCSD(T)}$ are defined in equations 2.32 and 2.33 (respectively), ΔE_{ZPE} is obtained from the frequency calculation in step (ii), the empirical correction is given in equation 2.34, and the spin contamination correction is given by equation 2.35.[49]

$$\Delta E_{MP4} = E_{MP4(SDQ)/6-31+G(d(f),p)} - E_{MP2/6-31+G(d(f),p)} \tag{2.32}$$

$$\Delta E_{CCSD(T)} = E_{CCSD(T)/6-31+G\dagger} - E_{MP4(SDQ)/6-31+G\dagger} \tag{2.33}$$

$$\Delta E_{emp} = -0.00579 \sum_{i=1}^{n_\beta} \left(\sum_{\mu=1}^{N_{virt}+1} C_{\mu ii} \right)^2 |S|_{ii}^2 \tag{2.34}$$

$$\Delta E_{spin} = -0.00954[\langle S^2 \rangle - S_z(S_z - 1)] \tag{2.35}$$

The numerical coefficients in equations 2.34 and 2.35 are determined from experimental data.[47] The CBS-QB3 method provides very accurate thermochemistries (maximum error for the test set was 2.8 kcal/mol corresponding to the electron affinity of Cl_2), while reducing the computational cost associated with very high level calculations.

MP2, MP4, and CCSD(T) are all examples of post-HF methods developed to correct for electron correlation in the HF method. In HF theory, each electron feels an average, static field of all others. This average field does not cover the instantaneous electron-electron repulsions. All post-HF methods to correct for electron correlation have a similar approach: the use of multiple determinants (and excited states) to describe the wavefunction. As the HF wavefunction is generally able to account for ~99% of the total energy,[38] it is used as a starting point as in equation 2.36.

$$\Psi = c_0\Phi_{HF} + \sum_{i=1} c_i\Phi_i \tag{2.36}$$

In equation 2.36, c_0 is generally taken to be close to one. Fundamentally, electron correlation methods differ in how they determine c_i.

MP2 and MP4 employ Perturbation Theory (PT), which functions by removing a difficult to calculate section of the operator and adding a correction term in its place. In equation 2.37, $\hat{H}$ is the Hamiltonian operator, which has been separated into a simplified operator $\hat{H}_0$ and a perturbing operator V.

$$\hat{H} = \hat{H}_0 + \lambda V \tag{2.37}$$

Møller and Plesset[50] proposed choices for $\widehat{H}_0$ and V, and their method is now referred to as MP*n* (where *n* is the order at which the Taylor expansion is truncated). By default, HF theory is correct to first order. Thus the lowest level of correction from Møller-Plesset is MP2.

Solving the HF equations for N electrons and M basis functions will obtain N/2 occupied MOs and (M – N/2) virtual MOs. The occupied MOs used to build the determinant can be replaced by virtual MOs to create a whole new set of determinants. These determinants can correspond to single-, double-, or triple-excitations, up to N excited electrons.[38] These excited state determinants are referred to as Singles (S), Doubles (D), and Triples (T), etc. Theoretically, PT includes all corrections to a given order, whereas, Coupled Cluster (CC) theory includes all corrections of a given type to an infinite order.[38] In CC, the full wavefunction is expressed as:

$$\Psi_{\mathrm{CC}} = e^{\hat{T}}\Psi_{HF} \tag{2.38}$$

where the cluster operator, $\hat{T}$, is a summation of the operators which generate all possible determinants (equation 2.39). The subscripts in equation 2.39 correspond to the number of excitations for that term, and N is the total number of electrons.

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \cdots + \hat{T}_N \tag{2.39}$$

Since including all operators up to $\hat{T}_N$ is impossible, one must truncate the expansion at some point. Just as in PT, the accuracy of the calculation increases with the number of terms included. Inclusion of only the $\hat{T}_1$ operator yields the HF results, thus the lowest level correction, $\hat{T}_2$, is termed Coupled Cluster Doubles (CCD). Single excitations can be included (CCSD), as well as triple excitations (CCSDT). The CCSDT level is very computationally demanding, thus it is more efficient, and common practice, to add in the Triples term as a correction (given the acronym CCSD(T)).

2.4 Quantum Theory of Atoms in Molecules

Bader's Quantum Theory of Atoms in Molecules (QTAIM)[51,52] is founded on the idea that the electron density can explain experimental observations in chemistry. QTAIM relates intuitive chemical concepts, such as chemical structure and bonding, to the electron density distribution. According to the theory, the electron density can also be used to define an atom within a molecule and its corresponding energy. One consequence of the theory is the additivity of atomic properties. This can be used to sum over the whole molecule (to get the molecular property) or over a functional group to determine how it is affected in the system (particularly useful in the study of substituent effects). One of the many advantages of using the electron density to gain information about a chemical system is that it can be obtained both by quantum calculations and experimental means.[53]

2.4.1 Topology of the Electron Density

The molecular electron density, derived from calculation or experiment, is a three-dimensional function with large maxima at the nuclei and minima in between. Generally these maxima are so large that they dwarf any other meaningful characteristics. One way to expose the underlying features is to use the gradient of the electron density. The gradient, ∇, of a 3D function is defined as:[53,54]

$$\nabla\rho = i\frac{d\rho}{dx} + j\frac{d\rho}{dy} + k\frac{d\rho}{dz} \tag{2.40}$$

where i, j, and k are the three unit vectors. The gradient points in the direction of the greatest increase in ρ(r) and the magnitude is equal to the rate of the increase. The gradient must begin at a minimum or saddle point, and end at saddle point.[51,53,55] Just as in a simple 3D function, maxima, minima, and saddle points (referred to as critical points) can be defined by setting the gradient equal to zero. Discrimination between these types of critical points is a simple matter of calculating the second derivative or tensor $\nabla\nabla\rho$. The second derivatives of ρ(r) can be arranged in a Hessian matrix for a particular critical point (CP) at position r_c:[54]

$$\nabla\nabla\rho(r_c) = \begin{pmatrix} \frac{\partial^2\rho}{\partial x^2} & \frac{\partial^2\rho}{\partial x\partial y} & \frac{\partial^2\rho}{\partial x\partial z} \\ \frac{\partial^2\rho}{\partial y\partial x} & \frac{\partial^2\rho}{\partial y^2} & \frac{\partial^2\rho}{\partial y\partial z} \\ \frac{\partial^2\rho}{\partial z\partial x} & \frac{\partial^2\rho}{\partial z\partial y} & \frac{\partial^2\rho}{\partial z^2} \end{pmatrix}_{r=r_c} \tag{2.41}$$

The Hessian matrix can be diagonalized, which leads to a rotation of the coordinate system and the superimposition of the new axes (x’, y’, z’) with the principal curvature axes of the CP.[53]

$$\nabla\nabla\rho(r_c) = \begin{pmatrix} \frac{\partial^2\rho}{\partial x'^2} & 0 & 0 \\ 0 & \frac{\partial^2\rho}{\partial y'^2} & 0 \\ 0 & 0 & \frac{\partial^2\rho}{\partial z'^2} \end{pmatrix}_{r'=r_c} = \begin{pmatrix} \lambda_1 & 0 & 0 \\ 0 & \lambda_2 & 0 \\ 0 & 0 & \lambda_3 \end{pmatrix} \tag{2.42}$$

where λ_1, λ_2, and λ_3 are the curvatures of the density. By convention, $\lambda_1 \geq \lambda_2 \geq \lambda_3$.[55] The trace of the Hessian is known as the Laplacian of the electron density, $\nabla^2\rho(r)$, which is equal to the sum of the curvatures.[54]

CPs are classified according to a rank (σ) and a signature (λ) expressed as (σ, λ).[51] σ corresponds to the number of non-zero curvatures at that CP. λ is comprised of the sum of the values given to each curvature, which will be positive or negative one depending sign of that curvature. There are four types of stable critical points [(3, -3), (3, -1), (3, +1), and (3, +3)] each attributed to a component of chemical structure. A (3, -3) CP is a local maximum which occurs at nuclei and corresponds to a nuclear critical point (NCP). The NCP is also referred to as a nuclear attractor (NA).[53] Rarely, a maximum can be found at a point which does not contain a nucleus; in this case the CP is called a non-nuclear attractor (NNA).[53] The (3, +3) CP is a local minimum and represents a cage critical point (CCP). The final two CPs, (3, -1) and (3, +1), are saddle points and correspond to a bond critical point (BCP) and a ring critical point (RCP), respectively. The four main types of critical points are present in the bicyclo[1.1.1]pentane system shown in Figure 2.1. The number of CPs that can exist in a system at any time is given by the following relationship:[56]

$$n_{NCP} - n_{BCP} + n_{RCP} - n_{CCP} = x \tag{2.43}$$

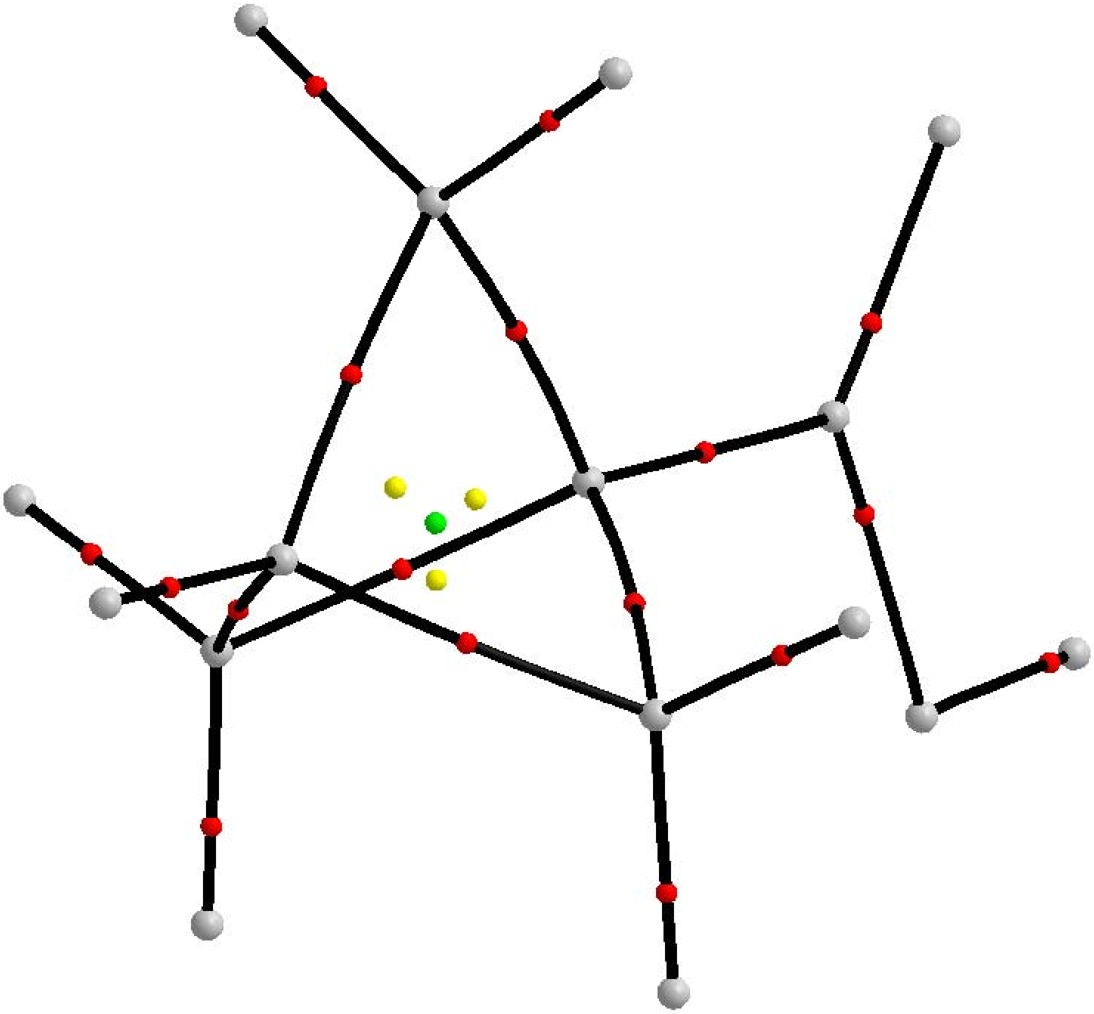


Figure 2.1. Molecular graph of bicyclo[1.1.1]pentane-1-carboxylic acid. All four main types of critical points are present: the nuclear critical points shown in grey, bond critical points are shown in red, ring critical points are shown in yellow, and the cage critical point is shown in green. Bond paths are denoted by black lines.

where n is the number of the specific CP. x is equal to one for isolated molecules and zero for infinite crystals.[54]

2.4.2 Atomic Partitioning and Atomic Properties

Another consequence of using the gradient of the electron density is the ability to define gradient paths and thereby the gradient vector field.[53] A gradient path, defined as a curve to which a gradient vector is tangential at each point, is orthogonal to the original surface and do not cross one another except when $\nabla\rho = 0$. The collection of all gradient paths makes up the gradient vector field, which partitions a molecule into its constituent atoms. The boundary between atoms, or the interatomic surface (IAS), is made of gradient paths which begin at infinity and terminate at the CP between two nuclei. The IAS is a zero-flux surface because $\nabla\rho = 0$ for every point, which means that no gradient vectors cross the surface. A large amount of an atom may be open to infinity (not bound by an IAS on some side). In order to define an atom's volume within a molecule (the atomic basin), the atom is generally capped by a 0.001au envelope of electron density (chosen to represent the van der Waals surface).[53]

The atomic basin, denoted by Ω, can be used to define properties by integrating over the volume. The average of a property over the basin, A(Ω), can be determined using the one- electron operator, or sum of operators, which corresponds to the property according to:[54]

$$A(\Omega) = \frac{N}{2}\int_{\Omega} dr \int d\tau' \left[\Psi^* \hat{A}\Psi + \left(\hat{A}\Psi\right)\Psi^*\right] \tag{2.44}$$

In this way, the total electron population can be defined by setting $\hat{A} = \hat{1}$:[53,54]

$$N(\Omega) = \int_{\Omega} \rho(r) d\tau \tag{2.45}$$

The population integral extends past the 0.001 au electron density envelope to provide an accurate representation. In this case, the envelope is extended to a point where $\rho=10^{-6}$ au.[53] The atomic charge [$q(\Omega)$] is calculated by subtracting the electron population from the nuclear charge (Z_Ω):[54]

$$q(\Omega) = Z_\Omega - N(\Omega) = Z_\Omega - \int_{\Omega} \rho(r) d\tau \tag{2.46}$$

The electronic energy of an atom in a molecule, $E_e(\Omega)$, is defined by:[51]

$$E_e(\Omega) = T(\Omega) + V(\Omega) \tag{2.47}$$

where $T(\Omega)$ is the kinetic energy and $V(\Omega)$ is the total virial for the atom. As the atom is bound by a zero-flux surface, the atomic virial theorem is satisfied and $E_e(\Omega)$ can be rewritten as:[51]

$$E_e(\Omega) = -T(\Omega) = \frac{1}{2} V(\Omega) \tag{2.48}$$

In reality, the atomic virial theorem may not be exactly satisfied due to the approximations used in the calculations, but corrections for this deviation from exactness can be incorporated, as done in several software programs. As an example, the integration software PROAIM[56,57] multiplies each atomic kinetic energy by [1-(-V/T)] instead of simply (-1).[54]

A crucial consequence of the IAS is the concept of atomic additivity. As the atoms do not overlap, and no volume is lost between them, the atomic properties can be summed to give the molecular property (such as electron population, charge or energy):[51,53]

$$A_{molecule} = \sum_{\Omega} A(\Omega) \tag{2.49}$$

where A is any given property. This also allows for the definition of a functional group within a molecule.[53]

2.4.3 Bond Paths and Molecular Graphs

The point at which the electron density reaches a maximum on the IAS is the BCP. It is also the termination point of a number of gradient paths which originate at infinity and thus is a maximum in that coordinate. However, in comparison to the nuclei (here called A and B for clarity), the BCP is a minimum in electron density. There are two gradient paths which begin at the BCP; one path terminates at nucleus A and one at B, and together these form the atomic interaction line (AIL). An AIL becomes a bond path when one more criterion is satisfied: the forces on the nuclei vanish. In other words, a bond path occurs where there is an attractive stability between nuclei and due to this condition the system must be at its equilibrium geometry. The full set of bond paths gives the molecular graph, the QTAIM expression of which nuclei are bonded.[53] Figure 2.1 shows the molecular graph for bicyclo[1.1.1]pentane-1-carboxylic acid, where the bond paths are shown in black.

Just as it is possible to use the electron density to determine atomic properties, it is possible to determine properties related to the bonds. The electron density at the BCP has often been related to the bond order or strength of a bond according to:[53,54]

$$Bond\ Order = e^{[A(\rho_{BCP} - B)]} \tag{2.50}$$

where A and B are constants which depend on the identity of the atoms. In general, covalent bonds occur when ρ_{BCP} is greater that 0.20 au, and closed-shell interactions (such as ionic, van der Waals and hydrogen bonds) occur for ρ_{BCP} less than 0.10 au.[54] Perhaps a more direct measure of the bond order is to use the average number of electron pairs shared between two atoms, referred to as the delocalization index (DI; equation 2.51) in QTAIM.

$$DI(A,B) = 2|F^{\alpha}(A,B)| + 2\left|F^{\beta}(A,B)\right| \tag{2.51}$$

The F^{σ} (σ=α, β) functions, or Fermi correlations (equation 2.52) are related to the sum of the overlap integrals (S_{ij}) for atoms A and B.

$$\begin{aligned} F^{\sigma}(A,B) &= -\sum_i \sum_j \int_A dr_1 \int_B dr_2 \left\{\phi_i^*(r_1)\phi_j(r_1)\phi_j^*(r_2)\phi_i(r_2)\right\} \\ &= -\sum_i \sum_j S_{ij}(A)S_{ij}(B) \end{aligned} \tag{2.52}$$

As the electron density within the bonds and bond order are related, it has been suggested that the DI be used to replace bond order in equation 2.50 to form a fully QTAIM based description.

The bond ellipticity (ε), which measures how symmetrically the density is distributed about a bond, can be determined using a ratio the curvatures perpendicular to the bond path:[54]

$$\varepsilon = \frac{\lambda_1}{\lambda_2} - 1 \tag{2.53}$$

A large ellipticity value (5 or greater) indicates that the bond is structurally unstable.[53]

Chapter 3: The Inductive Effect – A Quantum Theory of Atoms in Molecules Perspective

Bicyclo[1.1.1]pentane-1-carboxylic Acid Derivatives

3.1 Introduction

Although substituent effects are used to explain many phenomena in chemistry, only the inductive effect is omnipresent. IUPAC defines the inductive effect as the effect of "the transmission of charge through a chain of atoms via electrostatic induction."[16] It is said to decay with distance and is intimately related to the electronegativity of the substituent.[17] Deceptively simple, the inductive effect is always complicated by a competing mechanism: the field effect, which is defined as the transmission of charge through-space rather than through bonds.[16] As both effects follow the same decay with distance, and generally exert their influence in the same direction, they are said to be inseparable. This has led to the use of the phrase "so-called" inductive effect to encompass both mechanisms (used interchangeably with the inductive effect).[16]

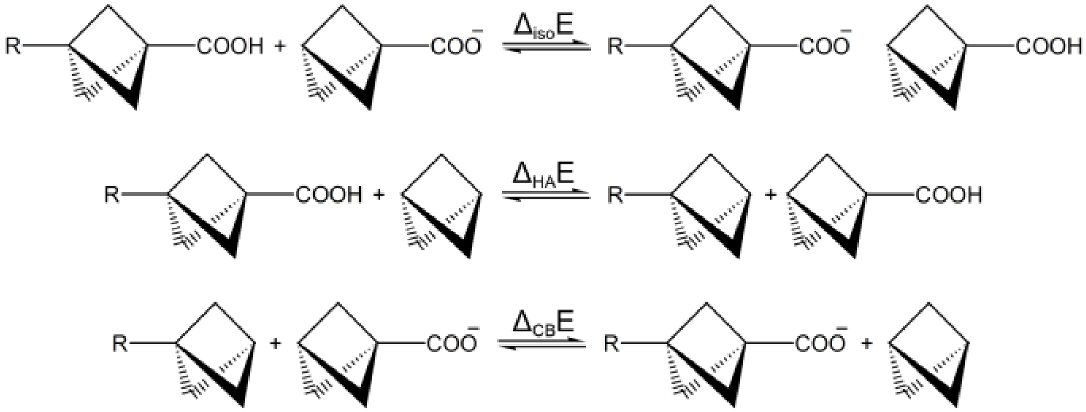
The most common method to study the inductive effect is still the Hammett formulation.[10-12] Originally used to describe the acid dissociation constants of substituted benzoic acids, the Hammett formulation has since been extended to a wide variety of organic reations.[20] Central to this approach is the use of a substituent and a reaction constant, σ_I and ρ_I, respectively. Recently it was suggested that the addition of an electronegativity term and corresponding proportionality constant (χ and ζ, respectively), in the manner of equation 3.1, was needed to accurately describe the inductive effect.[36]

$$\Delta E - \Delta E^0 = \Delta_{iso} E = \rho_I \sigma_I + \zeta \chi \tag{3.1}$$

This relationship was developed using an isodesmic reaction approach, an important tool for the theoretical estimation of substituent effects. An isodesmic reaction, such as those shown in Scheme 3.1, is useful such that the energy of that reaction can be related directly to the substituent effect in Hammett's relationship.[30] Bicycloalkanes have been used as a model to study the inductive effect without complication of other substituent effects. The saturated cage is used as a backbone because it removes any possibility of conjugation or steric interaction between the substituent and probe (the group used to measure the effect; most often a carboxylic acid). The bicyclo[2.2.2]octane backbone is the most used,[30] but recently the bicyclo[1.1.1]pentane backbone has been applied as it exhibits a more sensitive effect.[33]

Studies of the inductive effect using the bicyclo[1.1.1]pentane backbone began as a comparison to bicyclo[2.2.2]octane. Wiberg studied both systems computationally and determined the substituent effect upon the acidities of the substituted carboxylic acids,[33] obtaining a good agreement with experimentally observed values. Using Hirshfeld charges, Wiberg determined that the electron density at the carbon connected to the substituent was invariant with substitution, and that the C–R bond dipoles formed a good linear relationship (r^2=0.987) with the acidity. These two observations were used as proof that the through-space mechanism of transmission was operating. A more recent study by Adcock *et al.* corroborates these findings and suggests that an electrostatic field model can be used to describe the acidities.[58] A phenyl group has also been used as a probe to determine electronic effects through the bicyclo[1.1.1]pentane backbone.[59] Campanelli *et al.* determined that although this backbone is known and used for its rigidity, it deforms according to the electronegativity of the substituent. As the electronegativity increase, there is an associated increase in **α1** and decrease in **a**

SCHEME 3.1



with corresponding changes in the other internal coordinates (labels changed to conform to our study, see Scheme 3.2).

Fourré *et al*. investigate the electron density distribution in substituted bicyclo[1.1.1]pentanes using both the Quantum Theory of Atoms in Molecules (QTAIM) and the Electron Localization Function (ELF).[60] They focused primarily on the atomic charges and atomic basin populations to study the transmission of electron density. Their analysis supported the through-space mechanism, but their study was very limited as they only used two extreme substituents: fluorine and lithium, with comparison to the unsubstituted species. Fourré observed little perturbation of the electron density past the valence shell of $\mathbf{C_a}$ (see Scheme 3.2), just as Wiberg noted. Although this represents the first attempt to use QTAIM to describe the inductive effect in the bicyclo[1.1.1]pentane systems, a systematic study using the full complement of properties available from a topological analysis of the electron density has not been completed.

QTAIM[51,52] is a perfect tool for the study of the inductive effect and specifically the transmission of charge though a molecule because it focuses on the electron density ($\rho(r)$).[15] In QTAIM, a molecule is partitioned into a series of atomic basins using the zero-flux surface created by the gradient of the electron density ($\nabla\rho(r)$). Integration of $\rho(r)$ over the basin can yield atomic properties such as energy and charge. As each adjacent atom shares an infinitely thin surface, the interatomic surface (IAS), and no volume is lost, the sum of a property over all atoms yields the corresponding molecular property. Critical points in $\rho(r)$ can be used to identify structural features, such as the bond critical point (BCP), which is the identifying characteristic of a bonding interaction between two atoms. The BCP lies on the IAS and corresponds to the point along the bond path where ∇ρ(r) is equal to zero.

In this paper we present a systematic study of the substituent effects in the bicyclo[1.1.1]pentane-1-carboxylic acid system shown in Scheme 3.1, using the isodesmic reaction energy ($\Delta_{iso}E$) as a measure of the substituent effect. The substituents employed in this discussion were chosen to cover a wide range of possible electronegativities. Although small data sets may lead to limitations within the scope of a regression based analysis, a smaller set was used due to the extent of computational calculations and analysis involved. We examine the electron density with QTAIM and relate it to the structural features, frontier molecular orbitals, and nuclear magnetic resonance shielding parameters within the system. Studying the electron density itself helps resolve which properties are related to the inductive effect and give insight into the mechanism of transmission.

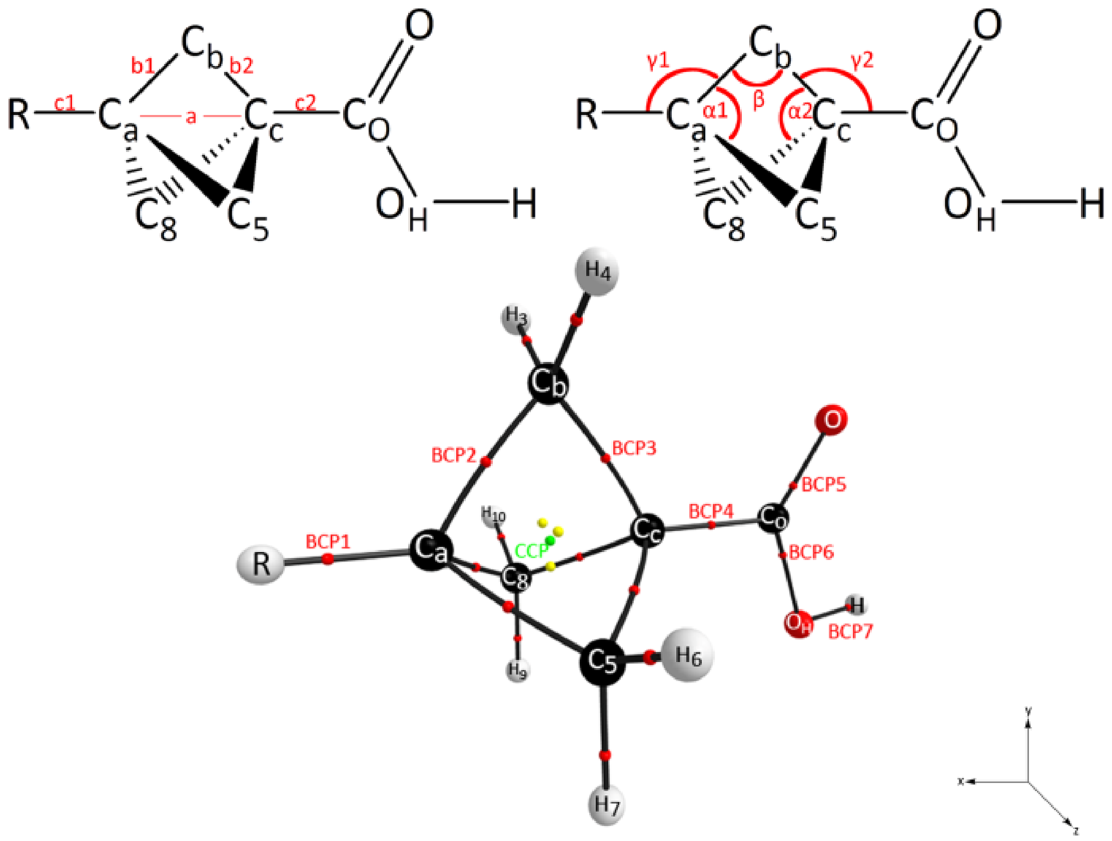
3.2 Methods

All calculations were performed using the Gaussian suite of programs.[61,62] The composite method CBS-QB3[47,48] was used to determine accurate thermochemistries for the reactions shown in Scheme 3.1 and to confirm the validity of the chosen model chemistry: the hybrid functional, PBE0, developed by Perdew, Burke and Ernzerhof,[63,64] combined with the Pople-style 6-31++G(d,p) basis set.[45,46] Geometries for all species were optimized and vibrational frequency analysis was used to confirm minima suitable for analysis using the Quantum Theory of Atoms in Molecules (QTAIM),[51,52] which was performed using the AIMALL suite of programs.[65] Stationary points are required to ensure the forces are equal to zero and thus, the zero-flux boundary conditions are met.

Chemical shielding tensors were calculated at the same level of theory, using the gauge including atomic orbital's (GIAO) method,[66-68] which was determined to be a compromise between accuracy and efficiency as it reproduces the trends from higher levels of theory: PBE0/6-311++G(2df,pd) and PBE0/aug-cc-pVTZ. The calculated relative shieldings were converted to chemical shifts using the unsubstituted system as an internal standard.

To simplify the following discussion the labeling and axis system described in Scheme 3.2, consistent with Levin *et al.*,[69] will be used throughout.

SCHEME 3.2


R
c1
b1
C_a
a
C_b
b2
C_c
c2
C_O
O
O_H
H
C_8
C_5
γ1
α1
β
α2
γ2
H_4
H_3
C_b
BCP2
BCP3
O
BCP5
H_10
BCP4
C_O
C_c
CCP
BCP1
C_a
C_8
BCP6
R
O_H
H
BCP7
H_9
C_5
H_6
H_7
y
x
z

3.3 Results

3.3.1 Energies

In order to determine the effect of the substituent, the isodesmic reaction energy was calculated for all reactions in Scheme 3.1; Table 3.1 shows the values determined at the CBS-QB3 and PBE0/6-31++G(d,p) levels of theory. The order of substituents, conserved throughout this discussion and between methods, is based on $\Delta_{iso}E$ for the CBS-QB3 method. The electron donating groups, lithium and methyl, result in a positive $\Delta_{iso}E$ suggesting a stabilization of the substituted acid species; whereas, the electron withdrawing groups have a negative $\Delta_{iso}E$, which is indicative of a stabilization of the conjugate base molecules. In addition to providing accurate thermochemistries, the CBS-QB3 method was used to validate the use of the chosen model chemistry. The PBE0 energies recreate the CBS-QB3 energies almost perfectly ($\Delta_{iso,CBS}E = 1.03\ \Delta_{iso,PBE0}E + 0.46$; $r^2=0.995$) with an average deviation of only 0.48kcal/mol, and will be used for the remainder of this discussion.

One complication associated with using $\Delta_{iso}E$ as a measure of substituent effects is that $\Delta_{iso}E$ is actually a measure of two simultaneous effects: the effect of the substituent on the protonated probe and the effect of the substituent on the deprotonated probe.[30] To separate these effects, we have broken the overall isodesmic reaction into two constituent reactions to observe the effect on the acid (HA) and on the conjugate base (CB; Scheme 3.1). The reactions have been formed such that the energies of the constituent reactions sum to give the overall reaction energy ($\Delta_{iso}E = \Delta_{HA}E + \Delta_{CB}E$). Both the effect on the acid and on the conjugate base, also outlined in

Table 3.1. Isodesmic reaction energies (kcal/mol), calculated at both the CBS-QB3 and PBE0/6-31++G(d,p) levels of theory, for the reactions outlined in Scheme 1. Shown is the overall reaction energy ($\Delta_{iso}E$), as well as the energy for the separate effects on the acid ($\Delta_{HA}E$) and conjugate base species ($\Delta_{CB}E$).

Substituents	CBS-QB3			PBE0/6-31++G(d,p)		
	$\Delta_{iso}E$	$\Delta_{HA}E$	$\Delta_{CB}E$	$\Delta_{iso}E$	$\Delta_{HA}E$	$\Delta_{CB}E$
Li	13.85	2.70	11.15	12.04	2.58	9.46
CH_3	0.44	0.32	0.13	0.53	0.26	0.27
H	0.00	0.00	0.00	0.00	0.00	0.00
NH_2	-0.48	0.10	-0.57	-0.21	0.08	-0.29
OH	-2.60	-0.46	-2.14	-2.54	-0.51	-2.03
F	-5.94	-1.17	-4.78	-6.30	-1.24	-5.06
CF_3	-7.94	-0.77	-7.17	-8.23	-0.97	-7.27
NF_2	-9.33	-1.04	-8.29	-9.77	-1.31	-8.46
CN	-10.61	-1.17	-9.44	-11.07	-1.35	-9.72
NO_2	-12.35	-1.39	-10.96	-12.88	-1.65	-11.22

Table 3.1, affect the overall $\Delta_{iso}E$, but the contribution from CB is greater ($\Delta_{iso}E = 1.19\ \Delta_{CB}E + 0.26$; r^2=0.998) than for HA ($\Delta_{iso}E = 5.78\ \Delta_{HA}E - 1.46$; r^2=0.955). According to the energies of the constituent reactions, electron donating groups stabilize HA molecules and destabilize CB, while electron withdrawing substituents destabilize HA and stabilize CB with the effect increasing with the strength (e.g., the move from NH_2 to NO_2). The only exception is for amino substitution, which results in an almost negligible stabilization of HA.

The “so-called” inductive effect comprises two mechanisms of transmission: through-bond and through-space. The through-bond mechanism is traditionally linked to the substituent’s electronegativity; therefore, if the charge was transmitting through-bonds we would expect to see a good correlation between $\Delta_{iso}E$ and the substituent electronegativity (χ). Figure 3.1a shows this comparison using χ calculated at the PBE0/6-31++G(d,p) level of theory using Boyd *et al.*’s bond critical point method.[70,71] As apparent by the lack of relationship, a simple through-bond model cannot be used. The field effect substituent constant, σ_F (which has also been labeled as σ_I by some,[31,72,73] further highlighting the use of the phrase “so-called inductive effect”), has been used to describe the though-space mechanism. Figure 3.1b shows the comparison between $\Delta_{iso}E$ and σ_F calculated using our level of theory according to the method prescribed by Topsom.[74] Although $\Delta_{iso}E$ and σ_F do show a good correlation, it is evident that the substituent effect in this system cannot be fully described by this simple Hammett equation. One implication is that the description of charge transmission requires more than a simple field model. As both contributions are important to accurately

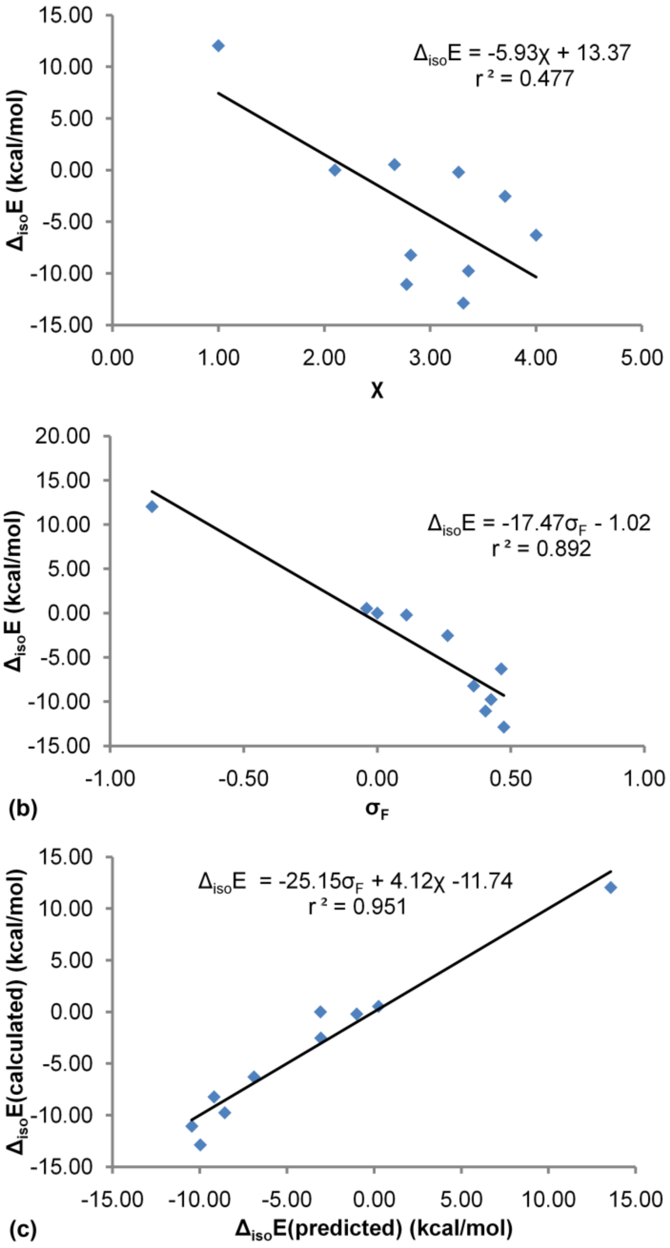


Figure 3.1. Relationships between the overall isodesmic reaction energy and (a) the substituent electronegativity, χ, (b) the substituent constant, σ_F, and (c) the reaction energy predicted by the two term expression using σ_F and χ; all calculated at the PBE0/6-31++G(d,p) level of theory.

describe the "so-called" inductive effect, it is not surprising that a two-term expression, using both a substituent constant and an electronegativity term has been suggested.[36] As shown in Figure 3.1c, this expression represents an improvement over the correlations with σ_F and χ individually, but it still does not fully recreate the overall effect. Furthermore, there appears to be some linear dependence between σ_F and χ ($\sigma_F = 0.40\chi - 1.00$; $r^2=0.743$), suggesting that σ_F already incorporates some aspects of the inductive effect, consistent with its formulation (see Supplemental Information), and thus the dual parameter expression should not be used.

Through the application of QTAIM the overall stabilization by a substituent can be examined at the individual atom or group levels. The kinetic energy, given in equation 3.2 as it depends on the electron density, can be defined for an atom if the zero-flux boundary conditions are met (the integral of the Laplacian term, $\nabla^2(\rho(r))$, over the atomic basin is equal to zero).[54]

$$K(r) = G(r) - \frac{\hbar^2}{4m}\nabla^2\rho(r) \tag{3.2}$$

How close the integral is to zero is often used as a measure of accuracy of the integration. In equation 3.2, K(r) is the Schrödinger kinetic energy and G(r) is the kinetic energy density. Using the atomic virial theorem, the energy of an atom can be related to its atomic energy at equilibrium as described in equation 3.3.[54]

$$E(\Omega) = -T(\Omega) = \frac{1}{2}V(\Omega) \tag{3.3}$$

Figure 3.2a shows the relationship between $\Delta_{iso}E$ and the total energy of the probe. As expected, $\Delta_{iso}E$ is related completely to the energy of the probe, $\Delta_{Probe}E$

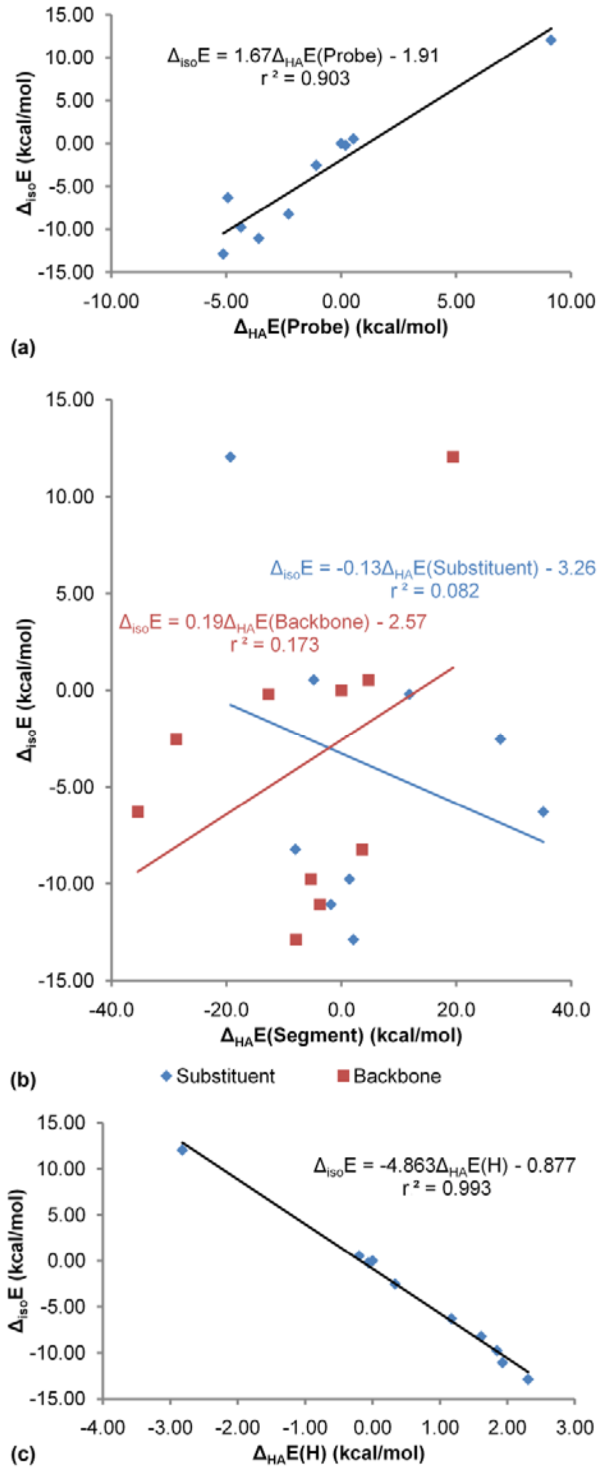


Figure 3.2. Relationships between the overall isodesmic reaction energy and (a) the energy of the probe, (b) the energy of the substituent and backbone, and (c) the energy of the acidic proton; all calculated at the PBE0/6-31++G(d,p) level of theory.

(calculated in the same manner as $\Delta_{iso}E$, but using the sum of the energies for all atoms in the probe instead of the molecular energy), which becomes more stabilized as electron-withdrawing strength increases. The order of substituents, however, is not conserved between probe systems. NH_2 substitution now results in a positive $\Delta_{Probe}E$, CN and NF_2 exchange places and F has the second most negative value. The total energies of both the substituent and backbone, $\Delta_{Substituent}E$ and $\Delta_{Backbone}E$, show no relationship with $\Delta_{iso}E$, as displayed in Figure 3.2b. However, they appear to be reflections of one another in accordance with the atomic transferability present in QTAIM.[75] This reflection implies that an energy transfer occurs between the substituent and backbone.

Within the probe itself, the effect is primarily centered on the acidic proton (see Figure 3.2c). The negative slope indicates that H is destabilized with an increase in electron withdrawing ability. The carboxyl carbon, C_O, in HA also shows a fair correlation to $\Delta_{iso}E$ (r^2=0.746), with the same general trend. Due to this observation we have limited our discussion mainly to the effect on HA and its properties.

3.3.2 Nuclear Magnetic Resonance Chemical Shifts

The NMR chemical shift of a probe group (most commonly fluorine) has been used in the past to determine the substituent effect[76] and it was suggested that this method is more sensitive than using proton-transfer equilibria.[20] We have calculated the absolute chemical shielding for each nucleus and converted them to relative NMR chemical shifts using the internal unsubstituted species as a standard to determine the relationship with the substituent effect. We find that only the NMR chemical shift changes in the acid species, and in particular the probe group itself, correlate with $\Delta_{iso}E$. The relationship between the NMR chemical shift of the acidic proton and $\Delta_{iso}E$ is shown in Figure 3.3a. As expected, $\Delta\delta^1H$ shows a downfield shift with increasing strength of electron-withdrawing substituents and thus increasing acidity. By convention, this is commonly explained as the substituents withdraw the electron density surrounding the proton, which results in a greater level of deshielding. Our findings support this description (see later for a discussion of electron density). $\Delta\delta^1H$ also shows a very good relationship with the atomic energy of that atom (which also depends on the electron density assigned to the atom, see equation 3.2). As apparent in Figure 3.3b, the proton is destabilized as the nucleus becomes more deshielded. This suggests that the increased acidity present in the substitution by electron withdrawing groups can be linked to perturbations in the electron density in the probe.

Unexpectedly, with the exception of the carbonyl oxygen which exhibits the same general trend as for H (see Figure 3.3c), no other atom's NMR chemical shift correlates with $\Delta_{iso}E$. This seems very peculiar as the transmission of charge, regardless of mechanism, should have an effect on the environment surrounding each nucleus in the molecule. Since the NMR chemical shift (shielding) is actually a tensor, we also examined the three diagonalized principal components as well as the nine tensor components. Certain components for both H and O (Scheme 3.2) exhibit good relationships with $\Delta_{iso}E$, but there are still no common relationships for any of the other nuclei in the molecule.

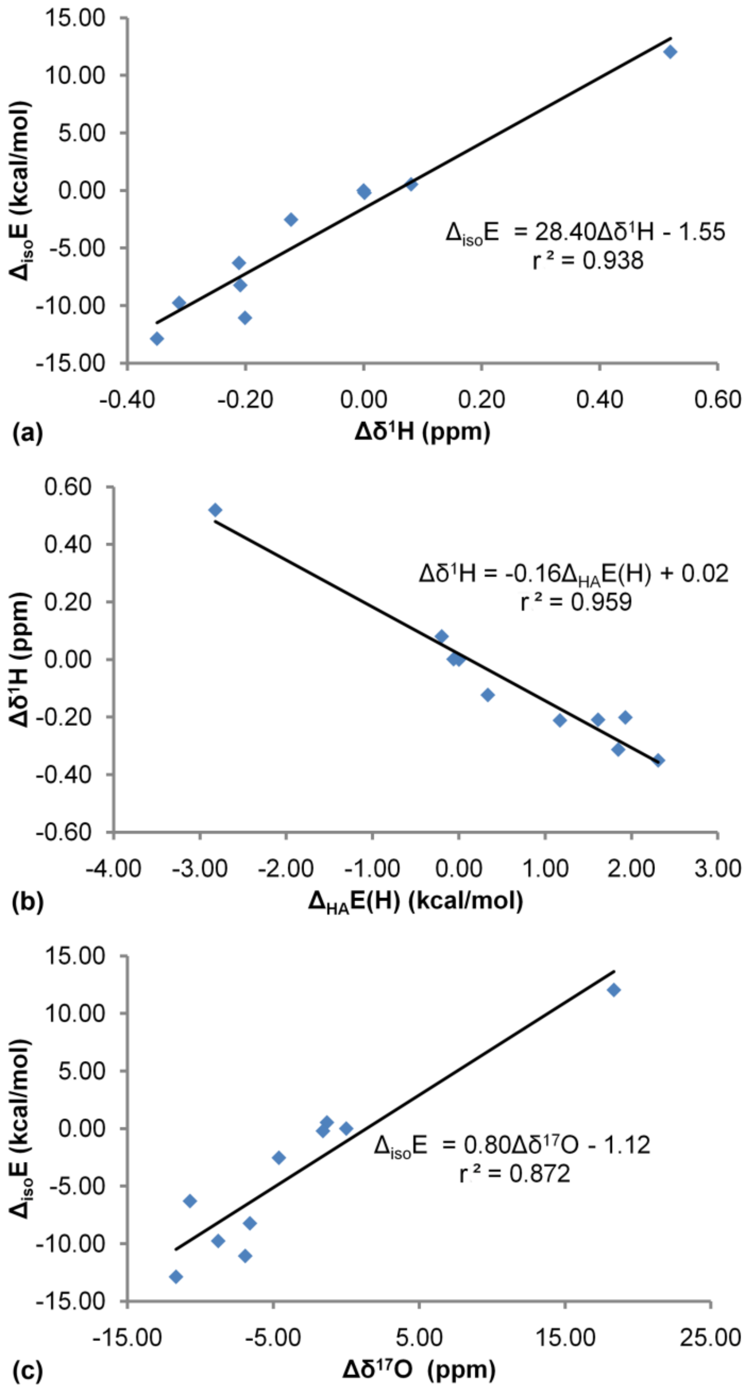


Figure 3.3. Linear correlations between the relative NMR chemical shift of the acidic proton and (a) the overall isodesmic reaction energy, (b) its atomic energy; (c) shows the relationship between the relative chemical shift of the carbonyl oxygen and the overall reaction energy. All values are calculated at the PBE0/6-31++G(d,p) level of theory.

3.3.3 Molecular Orbitals

Frontier molecular orbitals (MOs), such as the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), are often used as descriptors of chemical reactivity in a system, something that should be perturbed by a substituent. Figure 3.4 shows visualization of the frontier MOs for the unsubstituted system. The HOMO, in both acid and conjugate base molecules, appears to be mainly associated with the probe segment; although the HOMO in the acid includes some contribution from the backbone. The general shape of the orbitals is conserved through substitution (apart from the density associated with the substituent group), with a few exceptions. In order to allow for comparison with the series, the exceptions were replaced with the conserved orbital (see footnotes in Table 3.2 for details). As described in Table 3.2, ε_{HOMO} shows a very good correlation with $\Delta_{iso}E$ for HA (r^2=0.937) and a minor correlation for CB (r^2=0.799). The HOMO appears to be more stable with increasing acidity in both cases. The same trend is seen for the LUMO in HA (r^2=0.986).

In addition to the orbital energies, derived properties, such as the electronic chemical potential and the chemical hardness (denoted μ and η respectively), can provide insight into the reactivity of a molecule. The electronic chemical potential is a measure of the tendency of electrons to escape a system, and can be related to the energies of the HOMO and LUMO via Koopmans' theorem[77] according to equation 3.4 where I is the ionization potential and A is the electron affinity.[78-80]

$$\mu = \left(\frac{\partial E}{\partial N}\right)_{\nu} \approx -\frac{1}{2}(I + A) \approx \frac{1}{2}(\varepsilon_{HOMO} + \varepsilon_{LUMO}) \tag{3.4}$$

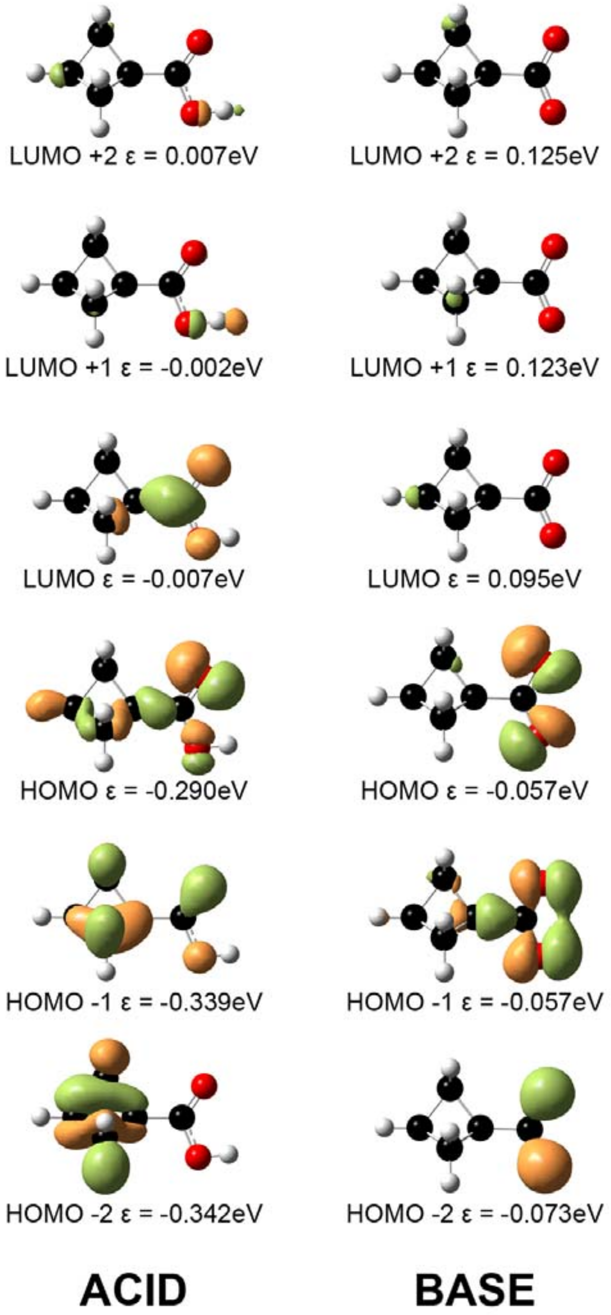


Figure 3.4. Isosurfaces (0.05 au) of the frontier molecular orbitals for bicyclo[1.1.1]pentane-1-carboxylic acid and its conjugate base and the energies for each orbital with the different phases shown in orange and green; determined at the PBE0/6-31++G(d,p) level of theory.

Table 3.2. Frontier molecular orbital energies, electronic chemical potential (μ), and chemical hardness (η), in eV, for the 3-substituted acid species; calculated at the PBE0/6-31++G(d,p) level of theory. Squared correlation coefficients are calculated for linear relationships with $\Delta_{iso}E$.

Substituent	ε_{HOMO}	ε_{LUMO}	μ	η
Li[a]	0.014	0.027	0.020	0.012
CH_3	0.002	0.003	0.003	0.001
H	0.000	0.000	0.000	0.000
NH_2[b]	-0.003	0.003	0.000	0.006
OH	-0.001	-0.002	-0.001	-0.001
F	-0.015	-0.008	-0.012	0.007
CF_3	-0.016	-0.013	-0.015	0.003
NF_2	-0.014	-0.016	-0.015	-0.002
CN	-0.022	-0.021	-0.022	0.001
NO_2[c]	-0.021	-0.019	-0.020	0.002
r^2	0.937	0.986	0.982	0.409

In order to compare equivalent orbitals (a) ε_{HOMO} was replaced with ε_{HOMO-1} and ε_{LUMO} was replaced with ε_{LUMO+5}, (b) ε_{HOMO} was replaced with ε_{HOMO-1} and ε_{LUMO} was replaced with ε_{LUMO+1}, and (c) ε_{LUMO} was replaced with ε_{LUMO+1}.

μ is also equal to the negative of Mulliken's electronegativity: the average of I and A.[81] Outlined in Table 3.2, μ shows a very good relationship with $\Delta_{iso}E$ (r^2=0.982), but appears to be reflecting the LUMO correlation. The chemical potential becomes more negative with increased acidity, suggesting the system has a smaller pull toward electrons. The chemical hardness has been used to describe the resistance of a system to charge transfer. Defined in equation 3.5 and listed in Table 3.2, the chemical hardness shows no relationship to $\Delta_{iso}E$.

$$\eta = \left(\frac{\partial^2 E}{\partial N^2}\right)_\nu \approx (I - A) \approx -(\varepsilon_{HOMO} - \varepsilon_{LUMO}) \tag{3.5}$$

Neither μ nor η show a relationship with $\Delta_{Substituent}E$ or $\Delta_{Backbone}E$.

3.3.4 Structure and Critical Points in the Electron Density

Although the bicyclo[1.1.1]pentane backbone is used for its rigidity,[58] there is still a significant variation in structural parameters with substitution. The largest variation occurs between the substituent and backbone. Thus, given the implied rigidity of the remainder of the molecule, one would expect to see some relationship between this distance and $\Delta_{iso}E$, but none is observed. Figure 3.5 (3.5a is for HA and 3.5b is for CB) shows the relative changes in bond distance within the backbone using the labels outlined in Scheme 3.2. In HA both **a** and **b2** show reasonable relationships with $\Delta_{iso}E$ (r^2=0.712 and 0.844 respectively). **a** appears to be mainly governed by pyramidalization at $\mathbf{C_a}$. The distance decrease as $\mathbf{C_a}$ becomes more planar, which corresponds to an increase in strength of electron-withdrawing group. The opposite trend is observed for

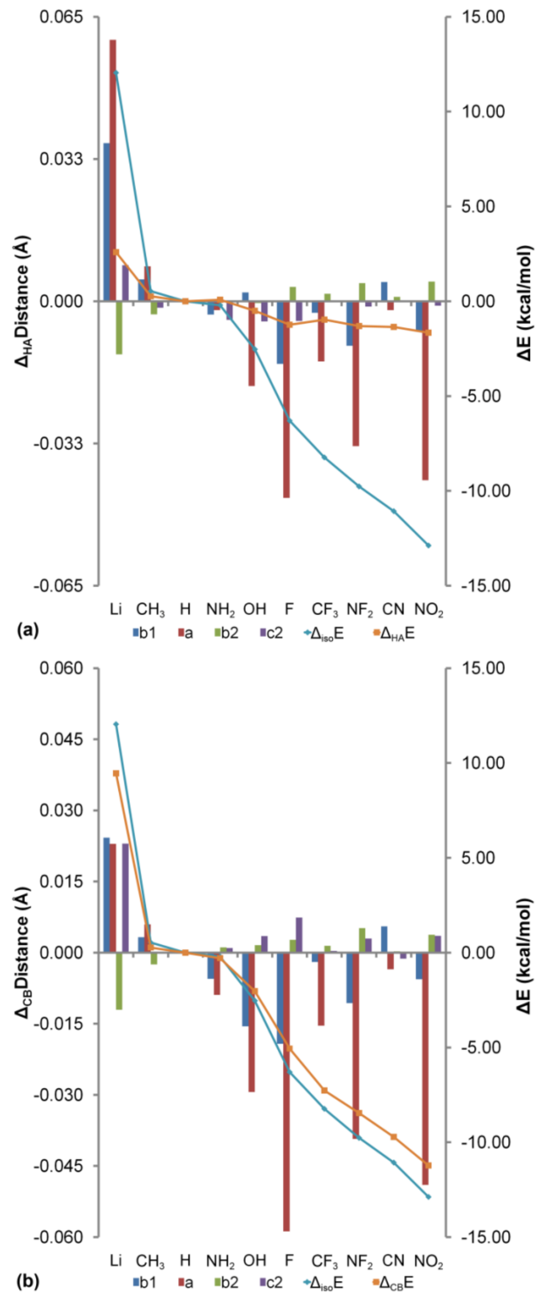


Figure 3.5. Relative length of the structural coordinates, for (a) the acid species and (b) the conjugate base, as compared to the corresponding reaction energies. All geometries were optimized at the PBE0/6-31++G(d,p) level of theory. Squared correlation coefficients for the linear relationships to $\Delta_{iso}E$ are (a) **b1**: 0.619, **a**: 0.712, **b2**: 0.844, **c2**: 0.276, and (b) **b1**: 0.356, **a**: 0.505, **b2**: 0.749, **c2**: 0.258.

b2: an increase in distance with increasing acidity. Distance **b2** also shows a fair relationship in CB (r^2=0.749).

As suggested by Campanelli *et al.*,[59] the cage in bicyclo[1.1.1]pentane deforms with the electronegativity of the substituent. In both HA and CB the internal coordinates (**b1**, **a**, and **b2**) show good correlation to the substituent electronegativity. Interestingly, in HA the link between the backbone and probe (**c2**) also shows a good relationship with χ (r^2=0.843).

The structural parameters within the probe group alone show good relationships with $\Delta_{iso}E$. Figure 3.6 shows these relationships. As expected from the acid-base nature of the reaction, the O_H–H distance shows a good correlation with $\Delta_{iso}E$ (the distance increases with the strength of the electron-withdrawing group); however, it does not exhibit the best relationship (Figure 3.6b). Both C_O–O and C_O–O_H decrease in length with increase in acidity. The re-distribution of charge accompanying deprotonation appears to cause this shortening. It also induces a widening in θ(O–C_O–O_H) (Figure 3.6c). In reality, all angles about the C_O atom are affected, but they are all linearly dependent as there is essentially no deviation from planarity. Thus, just like in the atomic energies, the substituent effect (with respect to $\Delta_{iso}E$) on the structural features is localized on the probe.

As the electron density is a topological function it has critical points (CPs) where the first derivative ($\nabla\rho$) goes to zero. CPs in a molecular system correspond to structural features and can be used to discern properties of the molecule. The maximum in density at the nuclei actually corresponds to a nuclear critical point (although it actually

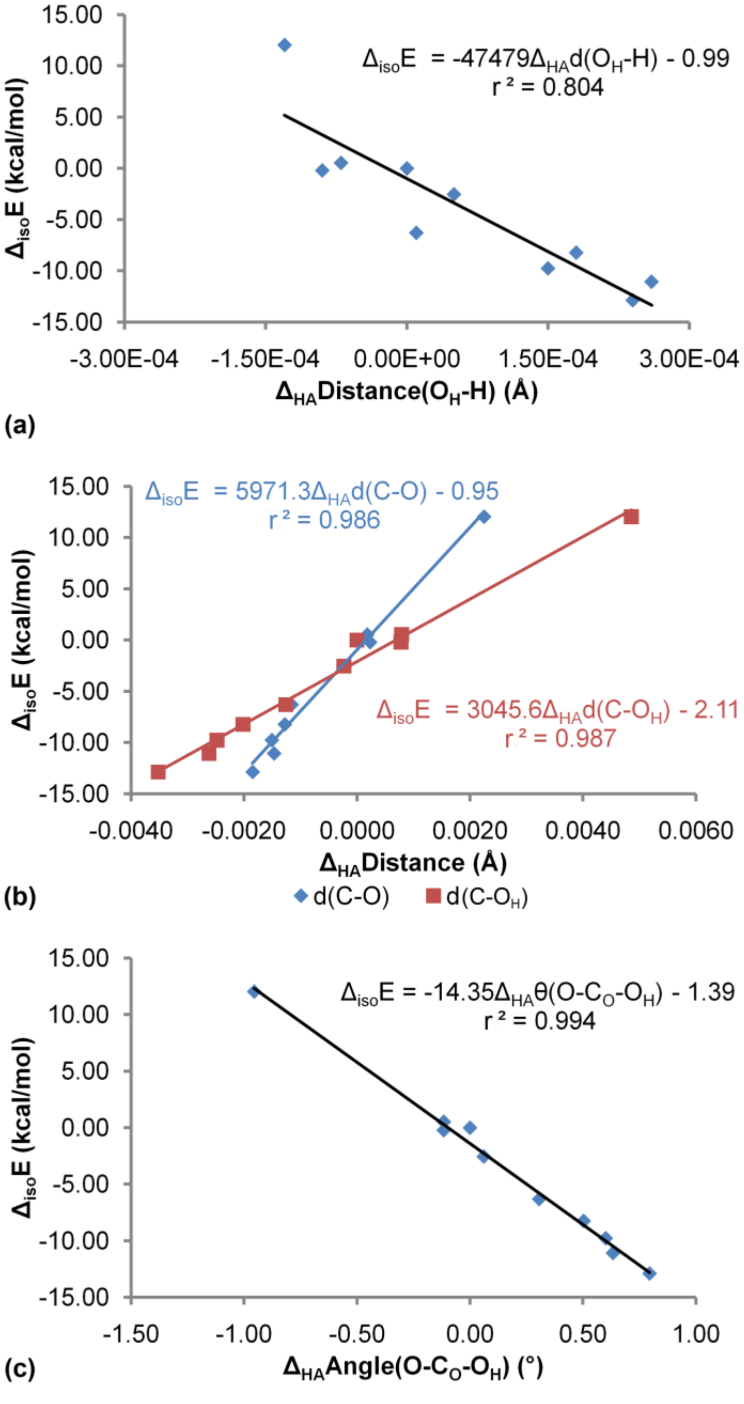


Figure 3.6. Relationships between the overall isodesmic reaction energy and (a) the O_H–H bond length, (b) the bond lengths between the carbonyl carbon and both oxygen atoms, and (c) the O–C_O–O_H angle; all calculated at the PBE0/6-31++G(d,p) level of theory.

forms a cusp, it behaves as a CP).[54] The bond critical point (BCP; shown in red in Scheme 3.2) is found along the atomic interaction line, falls on the interatomic surface, and is one indication of a bonding interaction between two atoms. It is commonly known that there is a relationship between the length of a bond and the electron density at the BCP.[82,83] In general, a decrease in ρ(BCP) corresponds to an increase in the length of the corresponding bond. Due to this relationship, it may be possible to use ρ(BCP) to investigate more subtle effects upon the structure of the system. Furthermore, as it occurs within a bond path, it is uniquely suited to give information about the through-bond transmission of electron density within the system.

The electron density at all BCPs within the probe group show very good relationships with $\Delta_{iso}E$, as evident in Figure 3.7. ρ(BCP7) shows a very good relationship with an expected decrease in density with increasing acidity. Both ρ(BCP5) and ρ(BCP6) show an increase in density. The increase is expected for ρ(BCP6), but counter to the traditional picture of deprotonation (as seen in the bond distance). It appears that the electron withdrawing groups function by pulling electron density from the O_H–H region and redistributing it within the rest of the probe. Once again there are no relationships with the bond between substituent and backbone and the bond between backbone and probe. However, very good correlations are present between ρ in the bonds between the bridging carbons and their attached hydrogen atoms (e.g., BCP(C_b–H_3) and BCP(C_b–H_4)).

Two other critical points are present in the bicyclo[1.1.1]pentane structure (Scheme 3.2): the ring critical points (yellow) and the cage critical point (CCP; green).

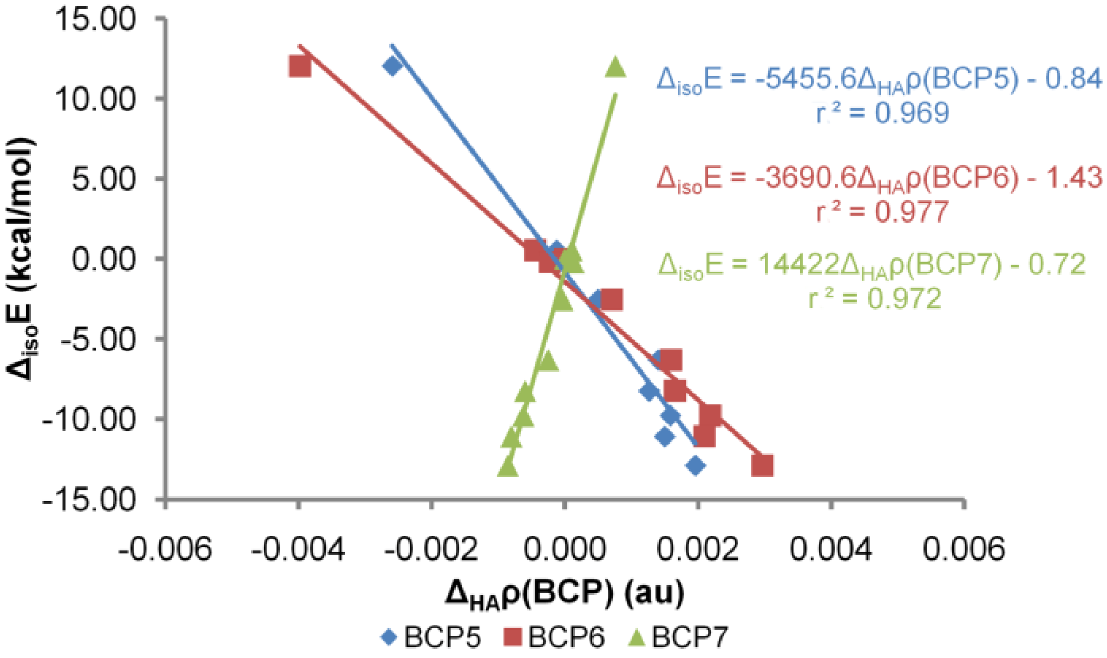


Figure 3.7. Linear relationships between the electron density at the bond critical points within the probe group (BCP5, BCP6, and BCP7, see Scheme 3.2) and the isodesmic reaction energy; all calculated at the PBE0/6-31++G(d,p) level of theory.

The CCP is analogous to a BCP between C_a and C_c (length **a**) and one would expect it to give information about transmission of charge, or electron density, through-space, but no apparent relationship between $\Delta_{iso}E$ and the electron density at the CCP exists. Thus, there appears to be no evidence of transmission through-bonds (e.g., no relationships between $\Delta_{iso}E$ and the electron density along the bond path), and evidence of through-space transmission is also missing, as if there is no transmission whatsoever.

3.3.5 Atomic Charges and Delocalization Index

Both mechanisms in the "so-called" inductive effect are defined by the transmission of electron density. Although each may perturb different atoms, there should be an effect of the substituent on the atomic charges. In QTAIM, the atomic charge is defined as the difference between the nuclear charge, Z_Ω, and the total number of electrons within the basin according to equation 3.6.[51,52]

$$q(\Omega) = Z_\Omega - N(\Omega) = Z \quad - \int_\Omega \rho(r) d\tau \tag{3.6}$$

Just as in the atomic energies, the total charge on the probe shows a good relationship to $\Delta_{iso}E$ (Figure 3.8a). Other than for O_H, which is essentially invariant with substitution, the charges on the individual atoms in the probe also show very good correlations as apparent in Figure 3.8b. In all cases the atoms are becoming more positive, or less negative, as the electron withdrawing strength of the substituent increases.

Unexpectedly, the overall charge, or the change in charge, on the substituent shows no relationship to $\Delta_{iso}E$, nor does the charge on the adjacent bridgehead carbon.

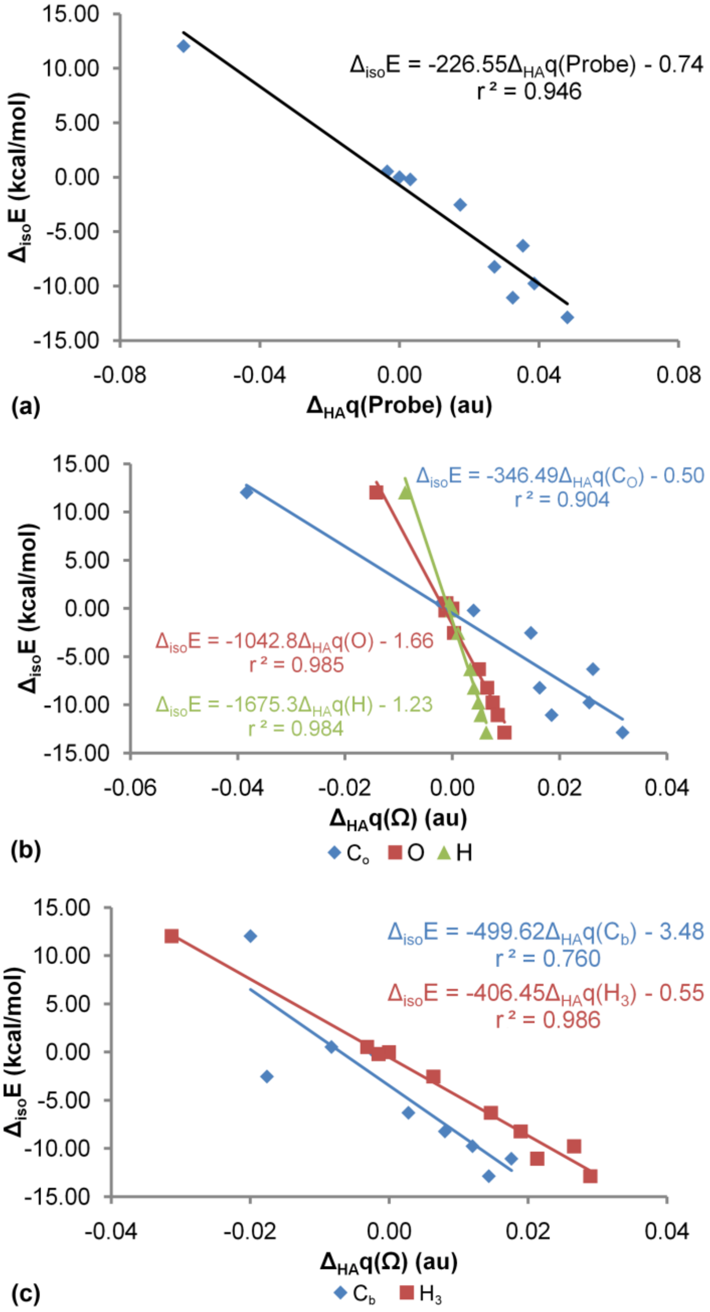


Figure 3.8. Linear correlations between the overall isodesmic reaction energy and (a) the relative charge on the probe segment, (b) the relative charge on the carbonyl carbon, the carbonyl oxygen, and the acidic hydrogen within the probe, and (b) the relative charge on a representative sample of the atoms within the backbone: C_b and H_3; all calculated at the PBE0/6-31++G(d,p) level of theory.

However, both show very good correlations with χ. This is due to the manner in which χ is calculated within the BCP model. The QTAIM definition of χ depends on the position of the BCP, which lies on the interatomic surface, and thus a change in distance between the substituent and BCP1 would have a direct effect on the atomic basin. The reflective pattern seen in the relationships between the charge on R and C_a, and the electronegativity, mimic those seen for the atomic energies of the substituent and backbone (see Figure 3.2b). The charge on the substituent increases with increasing electronegativity (as expected), but the charge on C_a decreases in a mirrored fashion as if a complete charge transfer is occurring. Interestingly, the charge on O_H (which shows no relationship with $\Delta_{iso}E$) also appears to be governed by the electronegativity of the substituent.

In general, the effect on the charge does decay with distance along the molecule, but there is no apparent relationship to the substituent effect. Figure 3.9 shows that the effect upon C_a is the largest in magnitude and the effect decreases along the molecule. The effect upon H is greater than that on O_H due to the invariance mentioned above. It is also evident in Figure 3.9 that the charge on C_c is not affected by substitution, even though it is the other bridgehead carbon. While the decay itself shows no relationship to $\Delta_{iso}E$, the charges on the bridging carbons and their associated hydrogen atoms show reasonable relationships. Figure 3.8c shows the best relationships in the bridging group. Just as for the atoms in the probe, all atoms are becoming more positive with increasing strength of electron withdrawing group. This is consistent with the substituent pulling density from, or through, the backbone. The lack

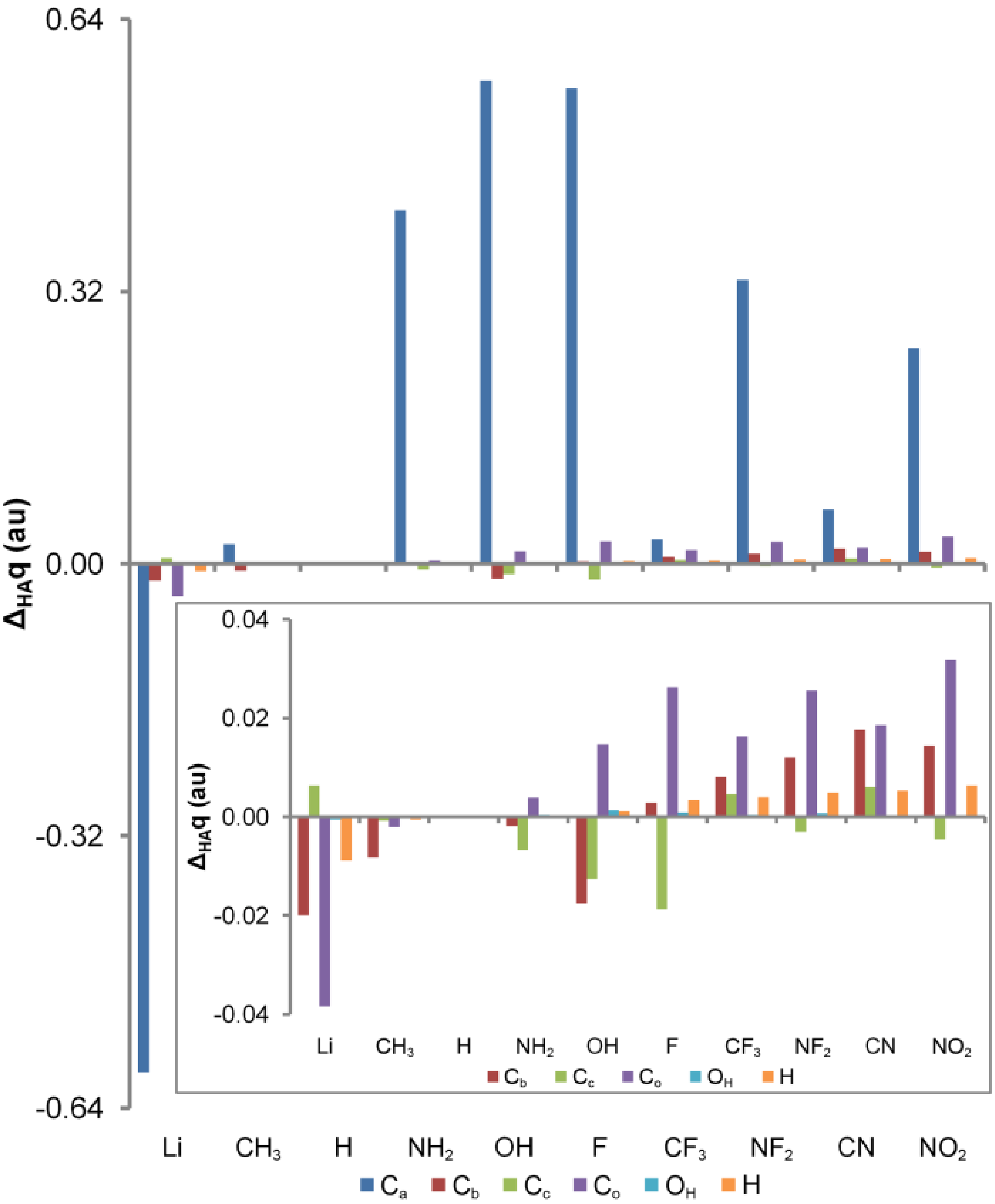


Figure 3.9. Graphical representation of the decay in the relative charge with increasing distance from the substituent group. Inset is a larger version from atom C_b to H to show detail masked by the large changes on C_a. All values were calculated from wave functions generated at the PBE0/6-31++G(d,p) level of theory.

of relationship between the substituent effect and the charge on C_c, and the presence of good correlations in the off-axis hydrogen atoms, however, would suggest a through-space mechanism.

The atomic charges explain some of the effects observed in the other properties. The charge on C_O appears to be controlling the $O–C_O–O_H$ angle, and consequently the $O_H–H$ bond length. As the carbonyl carbon becomes more positive, the angle opens to mimic the deprotonated state, which in turn results in the lengthening of the $O_H–H$ bond. Expectedly, the atomic charge also clarifies the downfield shift of the carboxyl hydrogen seen in Figure 3.3a and the carbonyl oxygen in Figure 3.3c, as both atoms become more positive with substitution of an electron withdrawing group. The most intuitive link is between the atomic energy and charge on the atom. As the QTAIM energy is based on the electron density, it follows that a good relationship should be apparent between q and E(Ω). For the carboxyl hydrogen a very good correlation is evident (r^2=0.995), which describes the destabilization of the atom within the molecule with the increase in positive charge.

The lack of transmission along the bond path, or relationship between $\Delta_{iso}E$ and the charge on the bridgehead atoms (as might be expected for through-space transmission) would suggest that the effect is not transmitting at all. The delocalization index, a property derived from QTAIM, can be used to describe the communication between atoms, and should give insight into the mechanism of transmission. The delocalization index (DI) is the average number of electrons shared between two atoms

(A and B) and is defined by equation 3.7[51,52] where the F^{σ} functions ($\sigma = \alpha$ or β) correspond to the sum of the overlap integrals for the atoms involved.

$$DI(A,B) = 2|F^{\alpha}(A,B)| + 2|F^{\beta}(A,B)| \tag{3.7}$$

The DI has also been used as a direct measure of covalent bond order.[84-86] Due to the atomic additivity inherent in QTAIM, it is possible to determine the DI between a group and an atom, or even two groups. Unexpectedly, there appears to be no relationship between $\Delta_{iso}E$ and the DI between the substituent and probe group, as if there is no communication at all. The relationship between $\Delta_{iso}E$ and DI(Substituent, H) is also quite weak with a squared correlation coefficient of only 0.615. Fortunately there exist fair relationships with the DI between substituent and the bridging carbons (e.g., C_b) and far bridgehead $\mathbf{C_c}$. The number of electrons shared with these atoms increases with increasing acidity, as if the increased strength of electron withdrawing group affords better communication. As the DI(Probe, C_b) also shows a good relationship to $\Delta_{iso}E$, it is possible that communication is occurring in a stepwise fashion: first the substituent communicates with a bridging carbon of the backbone, which passes the “information” on to the probe segment.

3.3.6 Dipole Moment Contributions

Wiberg suggested that a relationship between the substituent effect and the R–C_a bond dipole (using the labels in Scheme 3.2) in the bicyclo[1.1.1]pentane system is an indication of through-space transmission.[33] The overall molecular dipole, values given in Table 3.3, shows no relationship to $\Delta_{iso}E$. However, a weak relationship with the x-component of the dipole indicates the possibility of substituent-dependence along the bond axis (all molecules were rotated to ensure conformity to the axis system presented in Scheme 3.2). Using the topology of the electron density it is possible to determine the dipole moment vector for each atom within the molecule according to equation 3.8, which can also be summed to give the overall dipole moment of the group.

$$\mu(\Omega) = -e \int_{\Omega} r_{\Omega}\rho(r)d\tau \tag{3.8}$$

It has been suggested in the literature that through-space transmission is related to the substituent dipole moment, whereas through-bond transmission is related to the substituent electronegativity.[87] Therefore, if the charge transmission were occurring through-space, it is expected that the x-component of the substituent dipole moment (the direction of the probe) would show a good relationship to $\Delta_{iso}E$.

$\mu_x(R_{HA})$ for the substituent shows a remarkably good relationship with $\Delta_{iso}E$ as seen in Figure 3.10a (see Table 3.3 for values). As the electron-withdrawing strength of the substituent increases, $\mu_x(R_{HA})$ becomes more negative or more concentrated in the direction of the probe. Li is the only substituent which results in a positive μ_x due to its very great electron-donating ability, or least electronegativity. Even $\mu_x(R_{CB})$ shows a good correlation to $\Delta_{iso}E$. The x-component of the atomic dipole moment (μ_x) for all atoms along the bond path also shows good relationships with $\Delta_{iso}E$ (with r^2 ranging from 0.834 to 0.985). The off-axis hydrogens, and the carbonyl oxygen, do not show any relationship to $\Delta_{iso}E$ due to their off-axis orientation, which is why the molecular μ_x is only weakly correlated.

Table 3.3. Molecular and atomic dipole moment contributions (in debyes), calculated at the PBE0/6-31++G(d,p) level of theory, for the bicyclo[1.1.1]pentane-1-carboxylic acid systems and simpler models. Squared correlation coefficients are calculated for linear relationships with $\Delta_{iso}E$.

Substituent	Molecular			Atomic				
	$\lvert\mu\rvert$ (R_{HA})	$\mu_x(R_{HA})$	$\mu_x(R_{CB})$	$\mu_x(R_{HA})$	$\mu_x(R_{CB})$	$\mu_x(R_{B[1]P})^a$	$\mu_x(R_{CH3})^b$	$\mu_x(R_H)^c$
Li	8.13	7.97	10.50	3.00	1.00	2.94	3.00	3.16
CH_3	2.12	-1.53	10.26	-0.47	0.01	-0.54	-0.61	-0.34
H	1.90	-1.18	8.29	-0.33	-0.46	-0.36	-0.34	-0.29
NH_2	2.62	1.41	9.84	-0.72	-0.54	-0.80	-1.18	-0.52
OH	1.36	0.52	8.99	-1.42	-1.45	-1.50	-1.60	-1.07
F	1.67	0.88	7.62	-2.31	-2.48	-2.36	-2.47	-1.82
CF_3	2.25	1.74	11.38	-2.29	-1.90	-2.39	-2.42	-1.84
NF_2	2.45	-2.02	9.47	-2.77	-2.60	-2.86	-2.87	-1.96
CN	3.69	-3.40	6.22	-3.71	-3.91	-3.80	-3.86	-3.00
NO_2	3.67	-3.37	7.81	-3.58	-3.47	-3.69	-3.66	-2.68
r^2	0.274	0.641	0.236	0.982	0.892	0.982	0.969	0.957

Dipole moment contribution calculated for the substituent with (a) the bicyclo[1.1.1]pentane backbone attached, (b) a methyl group, and (c) only a hydrogen atom.

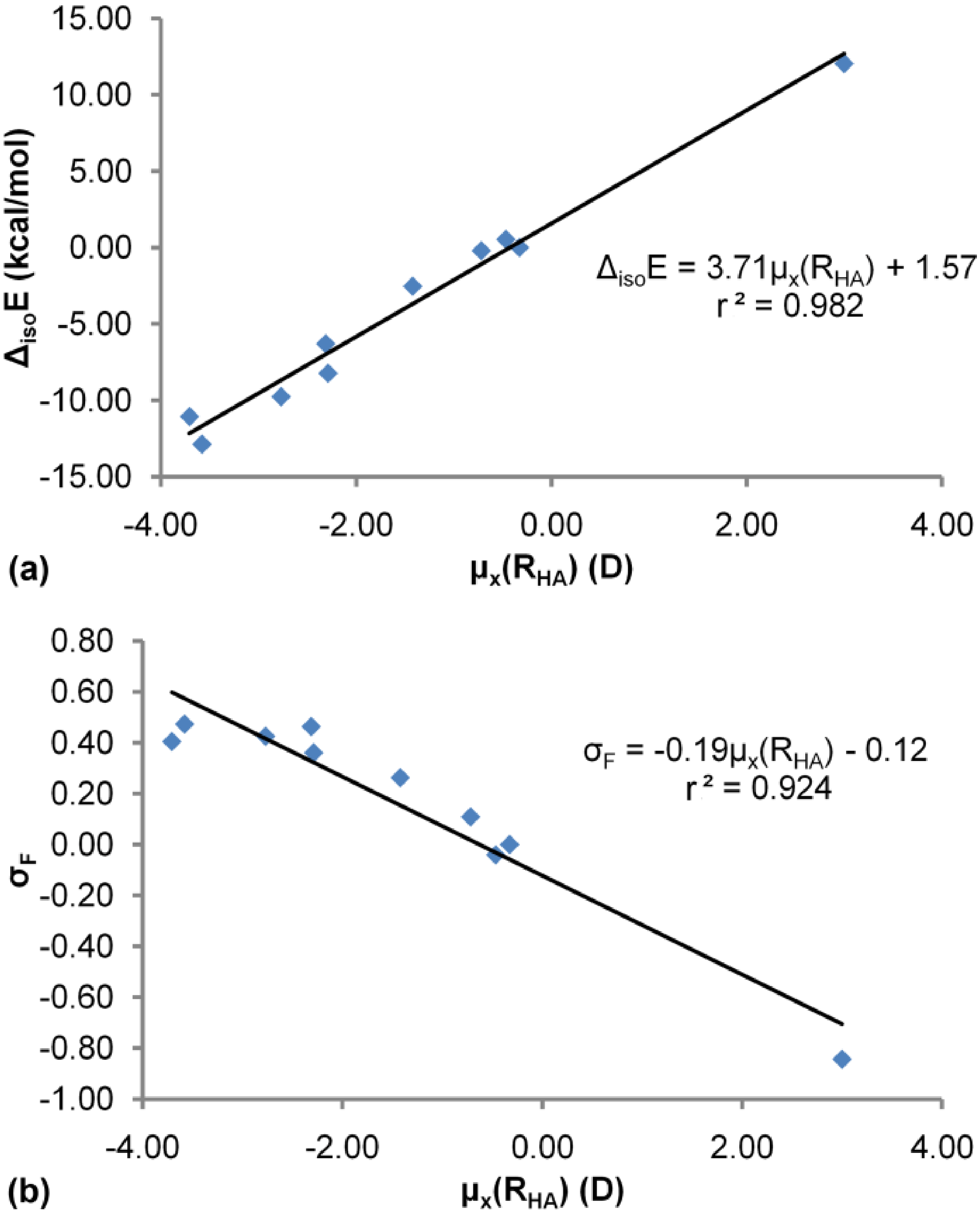


Figure 3.10. Linear correlations between the x-component of the substituent dipole moment and (a) the overall isodesmic reaction energy, and (b) the substituent constant; all values calculated at the PBE0/6-31++G(d,p) level of theory. All species were rotated to conform to the axis system outlined in Scheme 3.2.

It is very important to note that this is the only property which shows consistent relationship to the substituent effect across the entire molecule. μ_x for each of the bond path atoms correlates very well with that of the substituent (r^2 ranges from 0.872 to 0.969) and thus μ_x for the substituent appears to be controlling the μ_x value for the atoms along the bond path. Therefore, it appears that the mode of transmission of charge in this system is through the manipulation of atomic dipoles along the bond path controlled by the substituent dipole. As might be expected, $\mu_x(R_{HA})$ also forms a very good relationship with the substituent constant, σ_F, as visible in Figure 3.10b. When a two-termed expression for the energy was created using σ_F and χ the relationship did a better job of recreating $\Delta_{iso}E$. However, adding an electronegativity term to μ_x results in a worse relationship, further proof that μ_x is dictating the substituent effect. All other properties related to the substituent effect also appear to be controlled by $\mu_x(R)$. Figure 3.11 shows the relationship between $\mu_x(R)$ and the chemical shifts of the acidic hydrogen and the carbonyl oxygen. As expected, the more negative $\mu_x(R_{HA})$ corresponds to the downfield shift evident for both atoms.

The dipole moment has been shown to be one property of functional groups that is transferable between molecules within normal hydrocarbons.[88] In order to determine if this is also true for substituents within this system, the atomic dipole moments were calculated for the substituents with progressively simpler backbones: the bicyclo[1.1.1]pentane (without probe), a methyl group, and a hydrogen atom. As evident in Table 3.3, $\mu_x(R_{HA})$ and $\mu_x(R_{B[1]P})$ form a virtually perfect 1:1 relationship (r^2=0.9999) suggesting that the probe has little effect upon the molecule and that any

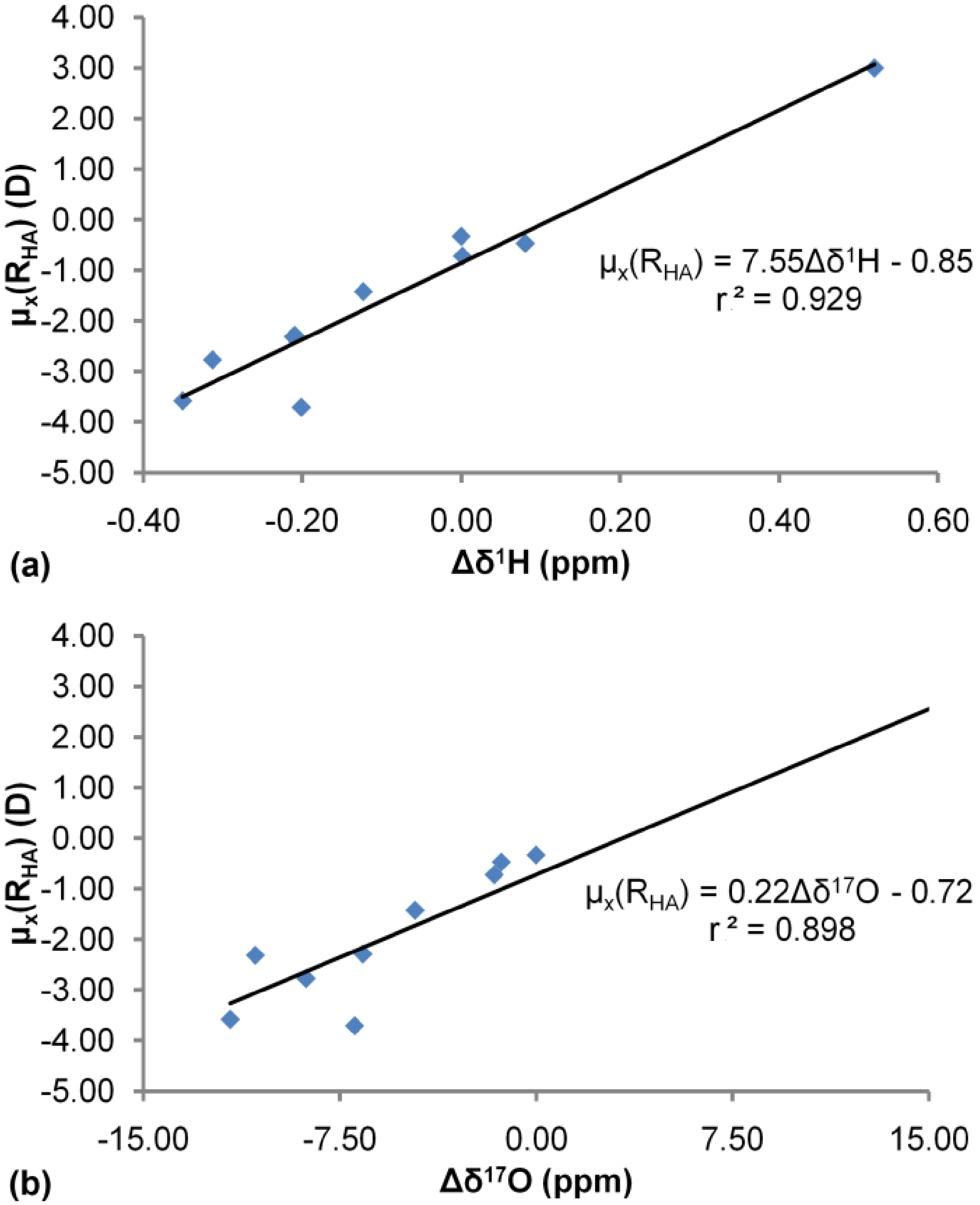


Figure 3.11. Relationships between the x-component of the substituent dipole moment and (a) the relative chemical shift of the acidic proton, and (b) the relative chemical shift of the carbonyl oxygen; all values calculated at the PBE0/6-31++G(d,p) level of theory. All species were rotated to conform to the axis system outlined in Scheme 3.2.

change can be attributed to the substituent alone. $\mu_x(R)$ is transferable between "backbones" as apparent with further simplification. Therefore, $\mu_x(R_H)$ can be used as a simple model to predict the substituent dipole moment in the bicyclo[1.1.1]pentane-1-carboxylic acid systems and all other properties which relate to the substituent effect.

3.4 Summary and Conclusion

We have presented a systematic study of the electron density in derivatives of bicyclo[1.1.1]pentane-1-carboxlic acid as it pertains to the "so-called" inductive effect. Using the CBS-QB3 method for accurate thermochemistries, it was determined that the substitution with an electron donating group results in a positive isodesmic reaction energy and lead to stabilization of the substituted acid species. In contrast, the electron withdrawing groups stabilize the substituted conjugate base species, which results in a negative overall reaction energy. As expected due to the nature of the acid-base reaction, the substituent's effect upon the energy of the system is centered completely on the probe. The effect of substituent upon the NMR chemical shifts in the system was also centered mainly on the acidic proton.

Some distance related decay was observed in the charges of the atoms along the bond path, but it was not related to the substituent effect. This is in direct contrast to the definition of the "so-called" inductive effect, which cites strict distance dependence. Although the effect doesn't appear to propagate through the bonds (looking at either the atomic charges or electron density at the bond critical points), the delocalization index seems to suggest that the mechanism of transmission is stepwise. The only property that appears to be consistently related to the substituent effect is the atomic dipole moment (most specifically the x-component of that lying on the bond axis). It appears that μ_x of the substituent is controlling all other properties deemed related to the “so-called” inductive effect.

Using QTAIM is was possible to conclude that the transmission of charge in the bicyclo[1.1.1]pentane system is controlled by the x-component of the substituent dipole, consistent with the field effect, but propagates along the bond path connecting the substituent and probe, as the classic picture of the inductive effect suggests. As transferability of properties is conserved within this system, it is possible to recreate the substituent effect using μ_x for the simplest of substituents, RH.

Chapter 4: The Effect of Substitution on a Silicon Center: Using a Silicic Acid Probe

4.1 Introduction

Substituent effects are used to explain many phenomena in chemistry and are therefore vital. Steric effects require close contact between groups and resonance effects require a conjugated π network, thus only the “so-called” inductive effect is omnipresent. IUPAC defines the inductive effect as the transmission of charge through σ-bonds.[16] In constant simultaneous operation is the field effect: the transmission of charge through space.[16] As both effects tend to operate in the same direction and suffer from distance related decay, they are often impossible to separate. This has led many groups to amalgamate the two mechanisms and use the term the “so-called” inductive effect.

Studies of “so-called” inductive effect (or any substituent effect in fact) can be simplified by separating the system into three segments: the substituent, which is having the effect; the backbone, which transmits the effect; and the probe, on which the effect is measured. Electronegativity is especially important to the inductive effect because it also relates to the transmission of electron density (IUPAC defines this as the power of an atom to attract electrons,[17] but it has also been extended to groups[70,71]). Thus, the substituents in this study were chosen to cover a wide range of electronegativities. The backbone employed in this study is bicyclo[1.1.1]pentane. This segment is used to avoid π-conjugation, thus removing the possibility of a resonance effect, and to separate the substituent and probe enough to remove complications due to inconsistent steric effects. Bicyclo[1.1.1]pentane is generally considered to be rather rigid and the substituent and probe are generally coplanar, avoiding potential angle dependence of the effect.[58,59] To study the inductive effect on silicon we have chosen silicic acid (– $Si(OH)_3$) as a silicon counterpart of the previously studied carboxylic acid probe.[89] Silicic acid, common and naturally occurring, is used over the direct analog silanoic acid (–Si(=O)OH)) as silanoic acids are generally unstable and limited to very lower temperature studies.[90]

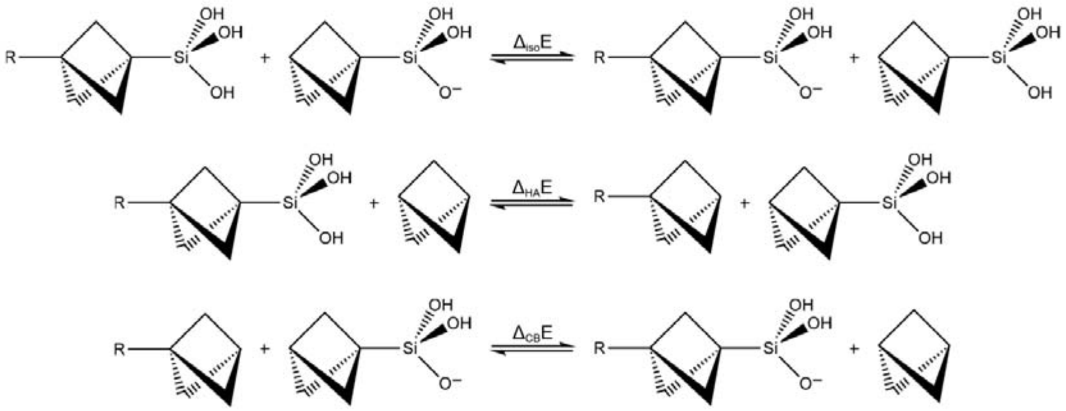
Most studies of substituent effects use the formulation outlined by Hammett,[10] which is readily extended to computational calculations via an isodesmic reaction[30] (a reaction with the same number and types of bonds on both sides[16]). As the Hammett relationship is a linear free energy relationship, the isodesmic reaction can be used as a direct measure of the substituent effect. Central to this study are the isodesmic reactions shown in Scheme 4.1.

Studies of substituent effects on silicon began with Taft[35] and the study of aliphatic substituents on the reactivity of organosilicon compounds using Ingold's original method.[91] The relationship gleaned from this study, in the Hammett formulation, is shown in equation 4.1, where σ^* is an inductive effect constant and E_s is a steric parameter.

$$logk - logk_0 = \rho^* \sigma^* + \delta E_s \tag{4.1}$$

Although this relationship performs relatively well, its parameters were based on reactions of organic carbonyls. The steric parameter has been the subject of many studies and has been redefined for silicon.[92] Recently Ploom and Tuulmets discovered that there was a significant relationship between the inductive and steric parameters, and thus suggested that only steric effects were being measured.[14] In the manner of

SCHEME 4.1



Exner and Bohm,[36,72] they suggest that an electronegativity parameter ζχ, as in equation 4.2, is needed to adequately describe the inductive effect.

$$logk - logk_0 = \rho_I\sigma_I + \zeta\chi + \delta E_s(Si) \tag{4.2}$$

However the inductive effect, without complication from steric effects, has not yet been studied. Herein we describe the effect of substitution in a silicon system, by replacing the traditional carboxylic acid probe (-COOH) with a silicic acid based probe (-$Si(OH)_3$) using the same approach used earlier.[89]

4.2 Methods

All calculations were performed using the Gaussian 03[61] and Gaussian 09 programs.[62] The geometries were optimized at the PBE0[63,93]/6-31++G(d,p)[45,94] level of theory and vibrational frequency analysis was performed to confirm the presence of a stationary point. The chosen level of theory is a reliable compromise of accuracy and efficiency in the bicyclo[1.1.1]pentane-1-carboxylic acid systems previously studied.[89] To further confirm the validity of the model chemistry, reaction energies (Scheme 4.1) are also determined using a composite method, CBS-QB3,[47,48] known for achieving accurate thermochemistries. In order to maintain consistency, this model chemistry was also used to calculate group electronegativities, χ, according to the method described by Boyd *et al.*[70,71]

Nuclear magnetic resonance data was generated at the PBE0/6-31++G(d,p) level of theory using the gauge-independent atomic orbitals (GIAO) method.[68,95] This level was confirmed to be sufficient for the calculation of NMR shielding tensors in the bicyclo[1.1.1]pentane-1-carboxylic acid systems[89] reproducing the relative values from larger basis sets, and is known for achieving accurate NMR data,[96] and is used here for consistency.

Wavefunctions, generated at the PBE0/6-31++G(d,p) level of theory, were used to determine the electron density distribution which was analyzed according to the Quantum Theory of Atoms in Molecules[51,52,54] (QTAIM) using the AIMALL program suite.[65] Integration for the lithium-substituted conjugate base resulted in a potentially significant error, even at the most accurate integration levels. Regardless, the results follow expected trends and are therefore included in our analysis.

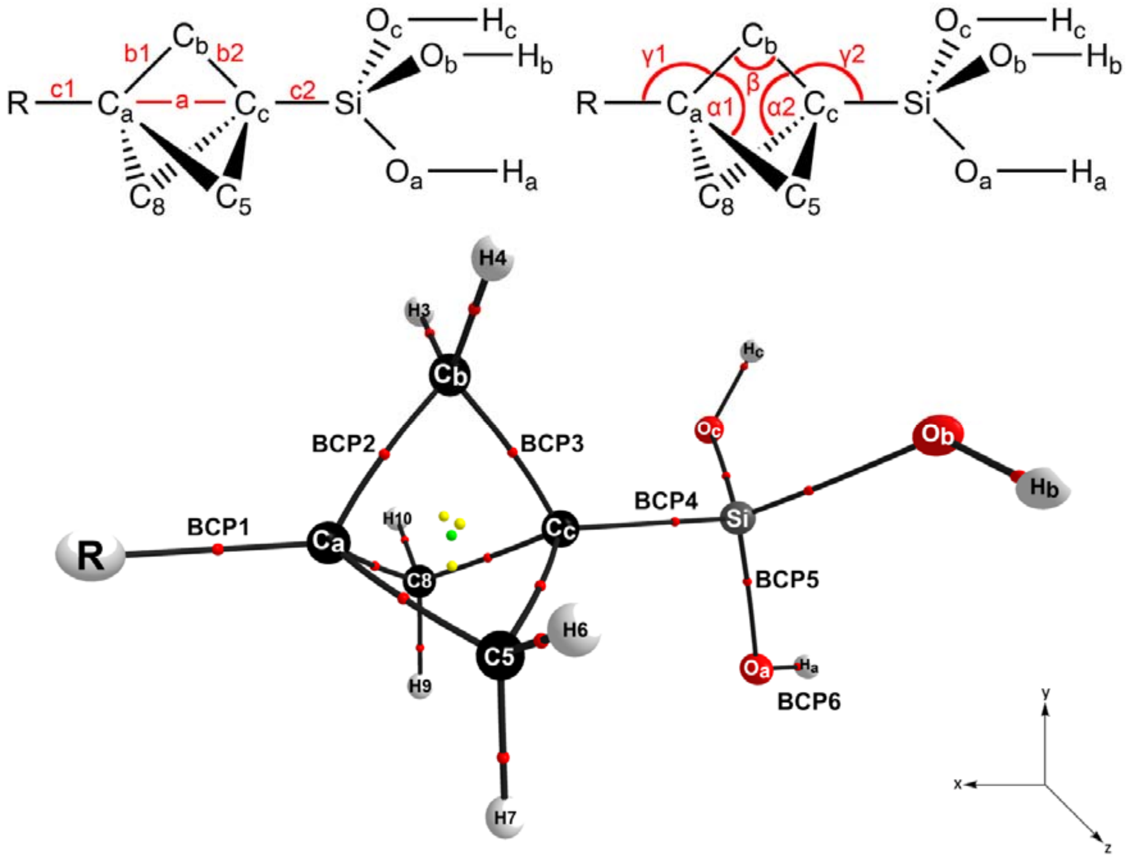
To simplify the following discussion, the labeling and axis system (consistent with Levin *et al.*[69]) described in Scheme 4.2, will be used throughout. The proton involved in deprotonation has been labelled $\mathbf{H_a}$ for consistency. For the asymmetric systems (e.g., NR_2 and OH), each proton was removed and the structure was allowed to relax. The lowest energy structure was used as the deprotonated species, and the corresponding hydrogen atom was renamed $\mathbf{H_a}$.

4.3 Results

4.3.1 Energies

The first isodesmic reaction described in Scheme 4.1 was used to compute the inductive effect on the silicic acid probe (–$Si(OH)_3$; referred to as the Si-Probe for brevity) in the same manner as was employed in the bicyclo[1.1.1]pentane-1-carboxylic

SCHEME 4.2



R
c1
Ca
b1
Cb
b2
a
Cc
c2
Si
Oc
Hc
Ob
Hb
Oa
Ha
C8
C5
γ1
β
γ2
α1
α2
H4
H3
Cb
BCP2
BCP3
Hc
Oc
Ob
Hb
BCP4
Si
BCP1
R
Ca
H10
Cc
C8
BCP5
H6
C5
Oa
Ha
H9
BCP6
H7
y
x
z

acid system (referred to as the C-Probe for brevity). Using the CBS-QB3 composite method for accurate thermochemistries, it was determined that the substituents affect the Si-Probe in the same manner as the C-Probe. As shown in Table 4.1, electron donating substituents yield a positive $\Delta_{iso}E$ and electron withdrawing groups result in a negative $\Delta_{iso}E$. The CBS-QB3 energies were also used to determine if the PBE0/6-31++G(d,p) model chemistry is sufficiently accurate for the Si system. As indicated in equation 4.3 the reaction energy computed at the lower level of theory forms an almost perfect one to one relationship with that obtained using the composite method.

$$\Delta_{PBE0}E = 0.994\Delta_{CBS-QB3}E - 0.155 \quad (r^2 = 0.999) \tag{4.3}$$

The order of the substituents in Table 4.1 is based on their $\Delta_{iso}E$ values. It is apparent that the order of substituents is the same for both probe systems, confirming that the effect is the same. This is consistent with Hammett's formulation, where any differences in the magnitude of the substituent effect are attributable to the reaction constant ρ (Equation 4.1). By plotting $\Delta_{iso}E$ for both systems (Figure 4.1) and setting ρ=1 for the carbon system, the slope of the linear relationship (0.843) is equal to the relative reaction constant for the Si-system. The same types of relationships between $\Delta_{iso}E$ and both σ_F and χ as seen for the C-system are observed in the Si-system (Figure 4.2). Although the magnitudes of the slope and intercept are different, due to ρ, the r^2 values are the same in both cases. Multiple linear regression using both parameters does improve the correlation, but once again by the same amount as in the C-system. This strengthens the idea that the substituents have the same effect on the reactivity of a carboxylic acid probe and a silicic acid probe.

Table 4.1. Isodesmic reaction energies (kcal/mol) for the silicon system (Scheme 4.1), calculated at both the CBS-QB3 composite method and PBE0/6-31++G(d,p) level of theory. The overall reaction energy ($\Delta_{iso}E$) is shown with its constituent effects: the effect upon the protonated species ($\Delta_{HA}E$) and upon the deprotonated species ($\Delta_{CB}E$).

Probe	Substituents	CBS-QB3			PBE0/6-31++G(d,p)		
		$\Delta_{iso}E$	$\Delta_{HA}E$	$\Delta_{CB}E$	$\Delta_{iso}E$	$\Delta_{HA}E$	$\Delta_{CB}E$
$Si(OH)_3$	Li	10.79	-0.46	11.25	10.09	0.05	10.04
	CH_3	0.27	0.48	-0.21	0.37	0.49	-0.12
	H	0.00	0.00	0.00	0.00	0.00	0.00
	NH_2	-0.47	1.21	-1.68	-0.16	1.10	-1.27
	OH	-2.36	1.68	-4.04	-2.11	1.52	-3.63
	F	-5.20	2.26	-7.45	-5.48	1.83	-7.32
	CF_3	-6.80	0.65	-7.45	-6.99	0.42	-7.41
	NF_2	-7.90	1.43	-9.33	-8.18	1.03	-9.21
	CN	-9.13	0.40	-9.54	-9.42	0.27	-9.68
	NO_2	-10.59	1.72	-12.30	-10.87	1.24	-12.11

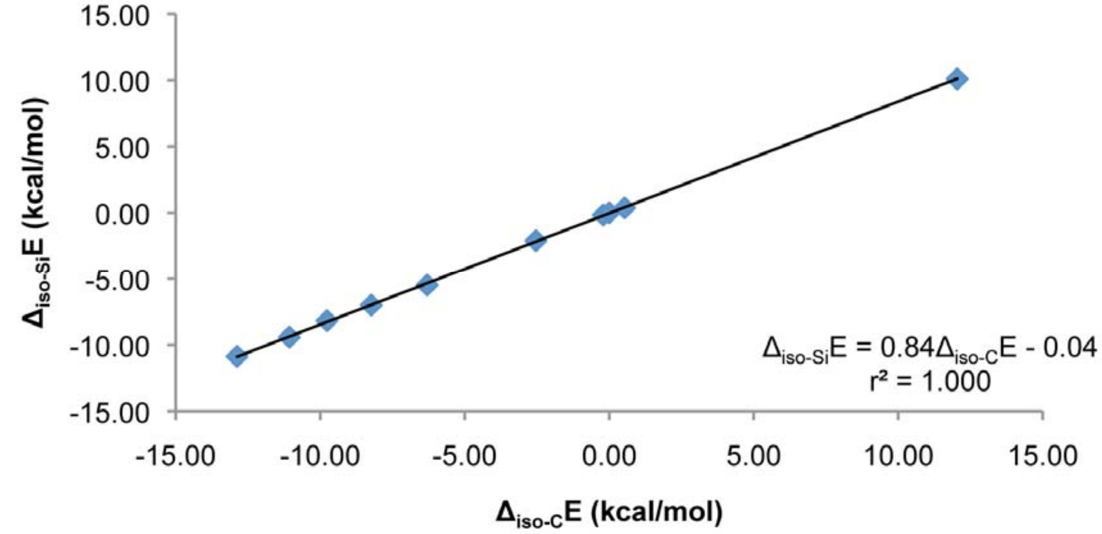


Figure 4.1. Relationship between the overall isodesmic reaction energy in the silicon system and the carbon system; all calculated at the PBE0/6-31++G(d,p) level of theory.

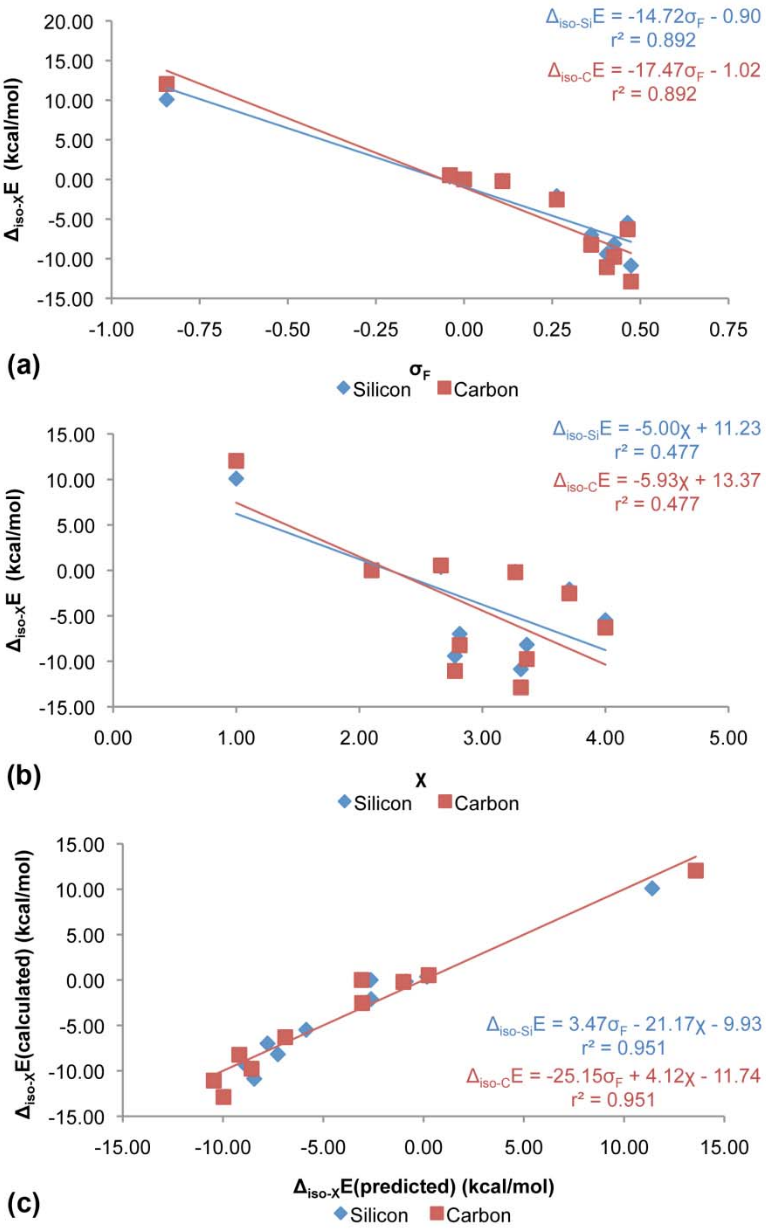


Figure 4.2. Relationships between the overall isodesmic reaction energy in both the silicon system and the carbon system, and (a) the substituent constant, σ_F, and (b) the substituent electronegativity, χ, and (c) the result of multiple linear regression using both parameters; all calculated at the PBE0/6-31++G(d,p) level of theory. χ was calculated, according to the QTAIM model described by Boyd,[70,71] under the PBE0 model chemistry for consistency.

The overall reaction energy is a combination of two effects: the substituent acting on the protonated silicic acid and the substituent acting on the deprotonated form. In order to determine if it is an acid stabilization or base destabilization, the overall isodesmic reaction has been broken into its constituent reactions (Table 4.1; Scheme 4.1), where $\Delta_{HA}E$ shows the effect on only the protonated species, and conversely $\Delta_{CB}E$ shows the effect on only the deprotonated species. For the most part the PBE0 energies recreate the CBS-QB3 energies for the constituent reactions as well (r^2=0.942 for HA and r^2=0.997 for CB). Although small, the only exception is the effect of lithium substitution on the protonated reaction. Using the CBS-QB3 method yields a negative $\Delta_{HA}E$, whereas the PBE0 model chemistry results in a small positive $\Delta_{HA}E$. The difference apparent in the $\Delta_{CB}E$ for both methods compensates in the opposite direction to yield a similar $\Delta_{iso}E$.

The effect of the substituent on the conjugate base dominates and dictates the overall substituent effect in the Si-system. $\Delta_{iso}E$ and $\Delta_{CB}E$ show a very good linear relationship (r^2=0.992), whereas $\Delta_{HA}E$ is relatively poor (r^2=0.155) as apparent in Figure 4.3. This is in contrast to the C-system, where both effects correlate with $\Delta_{iso}E$ and contribute to the overall effect.

Analysing the electron density distribution allows us to determine the energy of individual atoms or groups within the molecule, thus providing further insight into the stabilization energy. Figure 4.4 shows the relationships between the energies of the three molecular segments and the overall isodesmic reaction energy, or substituent effect. $\Delta_{iso}E$ is completely related to the energy in the probe segment. $\Delta_{iso}E$(Probe) was

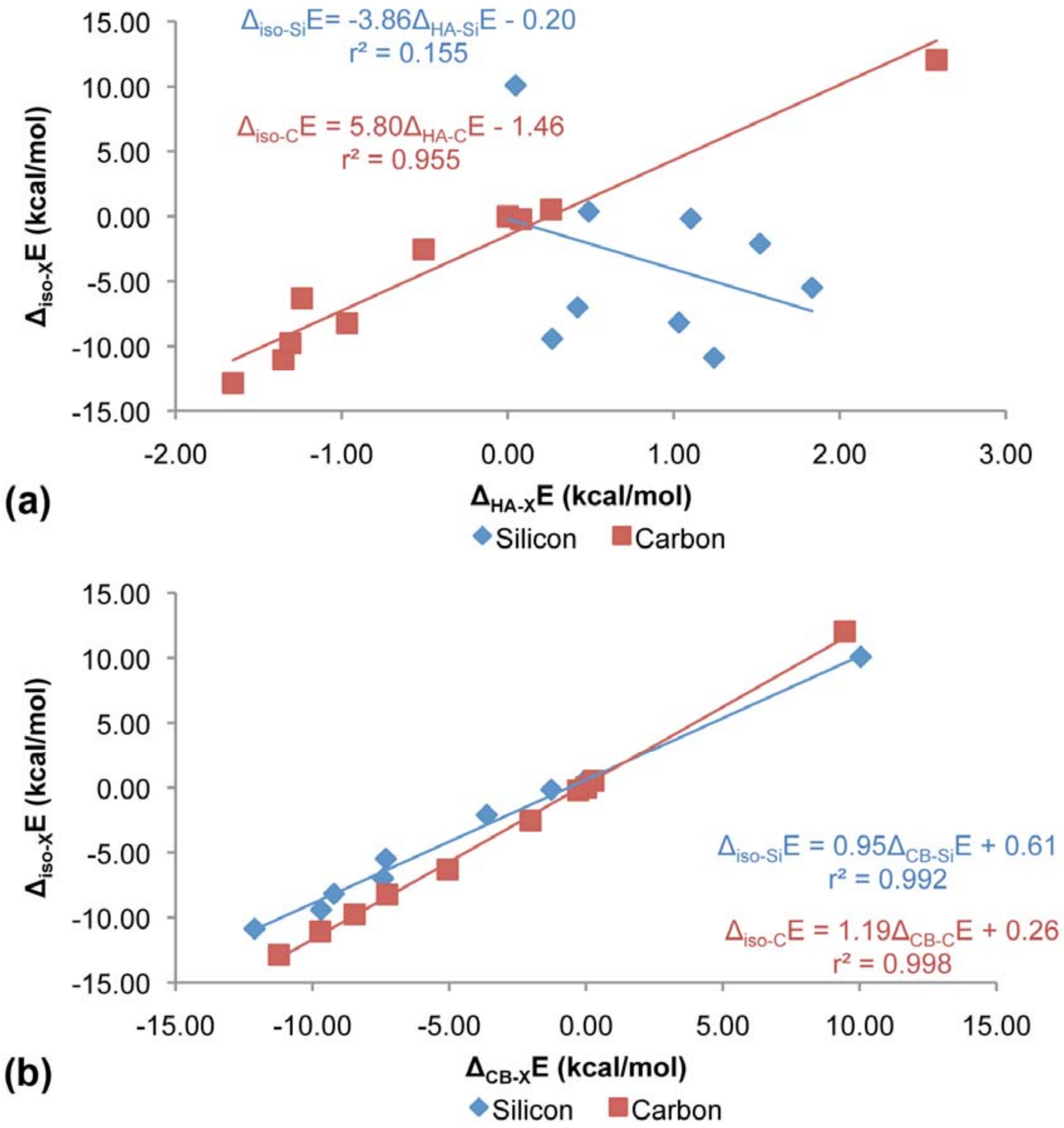


Figure 4.3. Relationships between the overall isodesmic reaction energy in both the silicon and carbon system, and the effect upon each of the constituent reactions: (a) the effect upon the protonated species and (b) the effect upon the deprotonated species. All energies were calculated at the PBE0/6-31++G(d,p) level of theory.

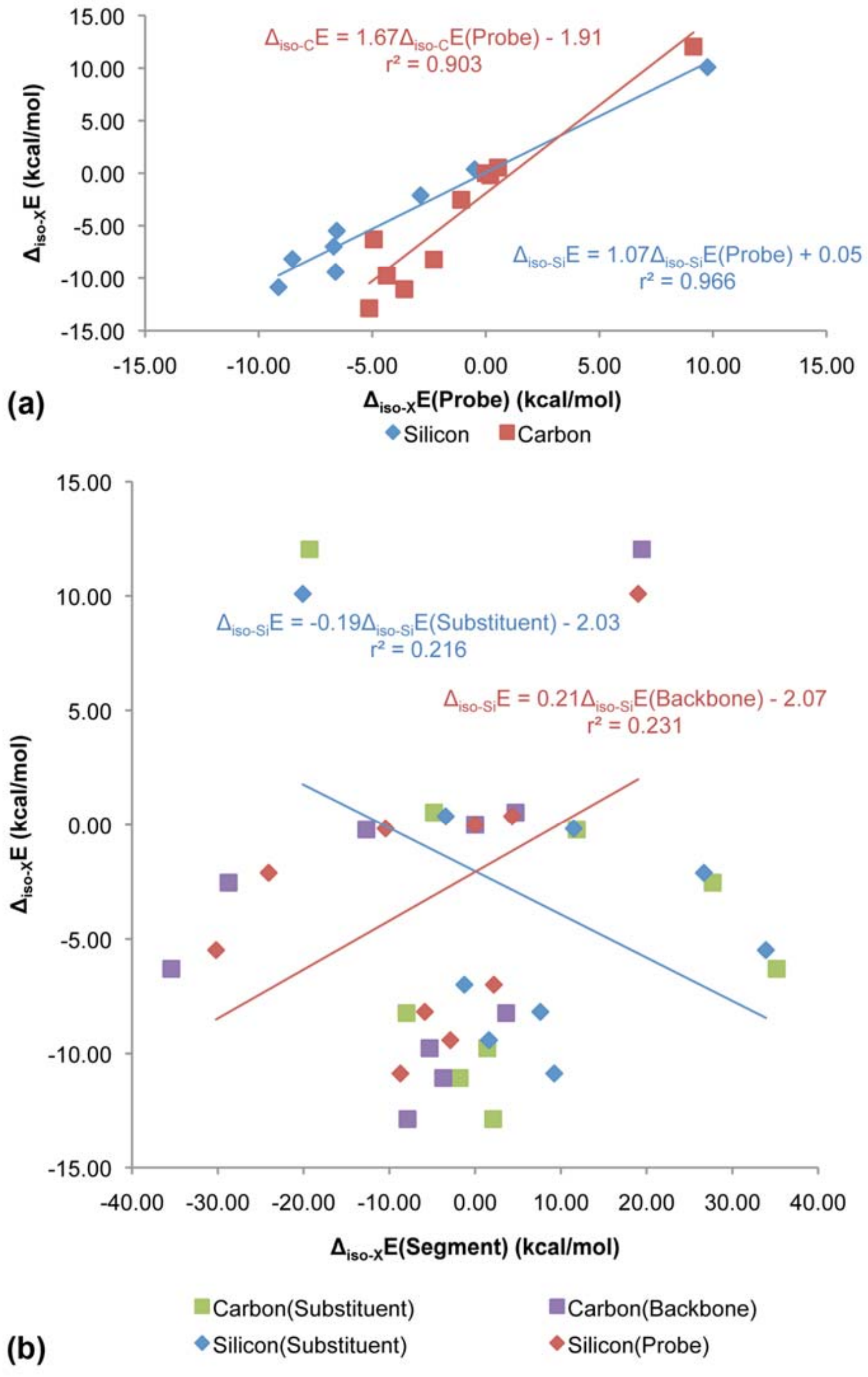


Figure 4.4. Relationships between the overall isodesmic reaction energies in both systems and (a) the energy of the probe, and (b) the energy of the substituent and backbone; all calculated at the PBE0/6-31++G(d,p) level of theory.

calculated in the same manner as $\Delta_{iso}E$, but using the energies of the probe atoms instead of the overall molecule. The same trend is evident for both probe systems, the probe segment becomes more stabilized as the strength of electron withdrawing group increases, but the correlation is significantly stronger in the Si-system. The energies of neither the substituent segment nor the backbone show any relationship to the overall substituent. Once again they appear to be mirror images (Figure 4.4b), implying an energy transfer between the substituent and backbone.

In the C-system, the effect within the probe segment was centered mainly on the acidic proton. In the Si-system, it is mainly centered on the remaining hydrogen atoms in the conjugate base (minor relationships with the oxygen atoms; average r^2 between O_a, O_b and O_c is 0.699). As visible in Figure 4.5, the hydrogen atoms are destabilized as the electron withdrawing strength of the substituent increases, making them more acidic.

4.3.2 Nuclear Magnetic Resonance Chemical Shifts

The NMR nuclear shielding tensor,[97,98] a 3x3 matrix describing the magnitude and orientation dependence of the interaction between the nuclei and external magnetic field, is intimately related to the electron density surrounding nuclei and consequently should be related to the inductive effect. Diagonalization of the matrix yields three principal components denoted σ_{11}, σ_{22}, and σ_{33} where, by convention, $\sigma_{11} < \sigma_{22} < \sigma_{33}$. An average of the principle components gives the isotropic shielding of the nucleus (σ_{iso}) and is related to the chemical shift. We have converted the calculated

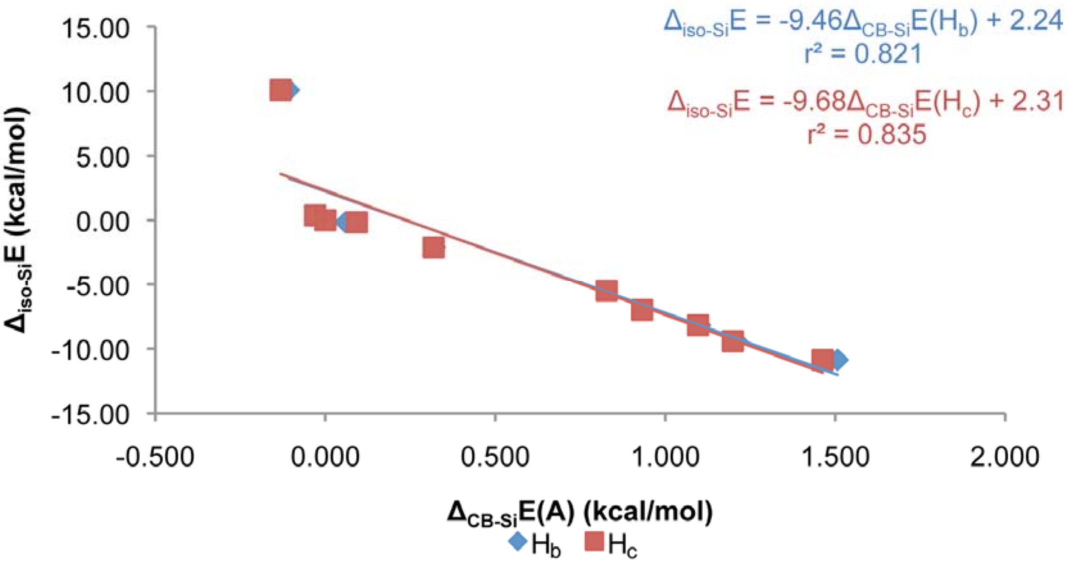


Figure 4.5. Relationships between the overall isodesmic reaction energy in the silicon system and the energies of the $\mathbf{H_b}$ and $\mathbf{H_c}$ atoms within the probe; all calculated at the PBE0/6-31++G(d,p) level of theory.

isotropic shielding for each nucleus into relative NMR chemical shifts using the unsubstituted species as an internal standard.

Just as in the C-system, we find that only NMR chemical shift changes in the probe segment correlate with $\Delta_{iso}E$. As expected in HA, the absolute shielding for the proton involved in the acid-base reaction studied shows a good relationship with the substituent effect exhibiting a downfield shift with increasing strength of electron withdrawing substituent. Interestingly, $\Delta\delta^1H$ for H_c, see Scheme 4.2, relates better to $\Delta_{iso}E$ (Figure 4.6a), with the same general relationship. In the deprotonated species it is the remaining protons within the probe, H_b and H_c, which show good relationships with $\Delta_{iso}E$ (see Figure 4.6b) and also correspond to an increase in deshielding at the nucleus.

Also similar to the C-system, the σ_{11} principal component (mainly associated with the σ_{xx} matrix component, see Scheme 4.2 for axis definition) shows good relationships for almost every atom within the deprotonated probe, O_a being the only exception.

4.3.3 Molecular Orbitals

The shape and order of the frontier molecular orbitals is conserved with substitution, with a few exceptions as listed in the footnote to Table 4.2, and for the most part with the change in probe group. This is consistent with the observation that the reactivity is similar as the HOMO and LUMO are often used as descriptors of chemical reactivity.

Just as in the C-system, ε_{HOMO} and ε_{LUMO} in the protonated species show a good linear correlation with $\Delta_{iso}E$, but there is no relationship present in the conjugate base

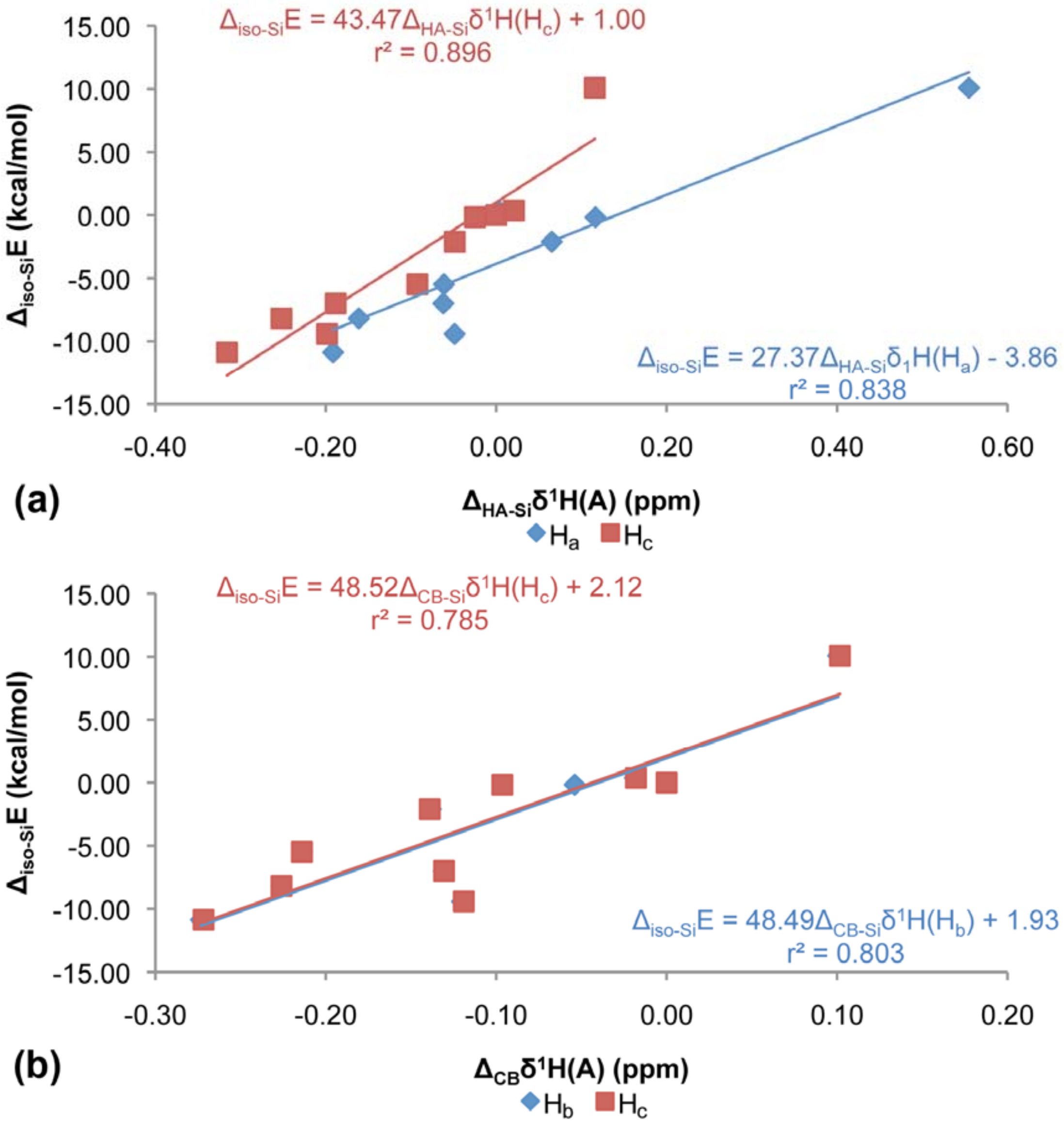


Figure 4.6. Relationships between the overall isodesmic reaction energy in the silicon system and the relative NMR chemical shifts of specific protons in the probe of the (a) protonated species, and (b) deprotonated species; all calculated at the PBE0/6-31++G(d,p) level of theory.

Table 4.2. Energies of the frontier molecular orbitals, electronic chemical potential (μ), and chemical hardness (η) for the silicon system calculated at the PBE0/6-31++G(d,p) level of theory (all in eV). To afford comparison to the substituent effect, squared correlation coefficients are calculated for the linear relationships with $\Delta_{iso}E$.

Substituent	ε_{HOMO}	ε_{LUMO}	μ	η
Li[a]	-0.170	0.000	-0.085	0.085
CH_3	-0.281	-0.012	-0.147	0.135
H	-0.282	-0.013	-0.148	0.135
NH_2[b]	-0.297	-0.012	-0.155	0.143
OH[b]	-0.304	-0.015	-0.159	0.145
F	-0.316	-0.019	-0.168	0.149
CF_3	-0.303	-0.021	-0.162	0.141
NF_2[b]	-0.327	-0.022	-0.174	0.152
CN	-0.315	-0.024	-0.169	0.145
NO_2[c]	-0.299	-0.025	-0.162	0.137
r^2	0.730	0.998	0.795	0.634

In order to compare equivalent orbitals (a) ε_{LUMO} was replaced with ε_{LUMO+3}, (b) ε_{HOMO} was replaced with ε_{HOMO-1}, (c) and ε_{LUMO} was replaced with ε_{LUMO+1}.

species (as such only the values for HA are shown in Table 4.2). This is highly unexpected given that the overall reaction energy is governed almost entirely by $\Delta_{CB}E$. The magnitudes of the orbital energies are different in the Si-system than in the C-system, but not by a great deal and not in any consistent manner. However, the HOMO-LUMO gap appears to be essentially the same between systems and centered around 0.28 eV. The value of the gap does not appear to vary with substitution.

The molecular orbital energies can be related to the reactivity via Pearson's Hard and Soft Acids and Bases theory.[78,80] The electronic chemical potential (μ) describes the escaping tendency of electrons from the system, which is also the negative of Mulliken's electronegativity[81] (but is not discussed here) and should be related to the inductive effect. The chemical hardness, η, is also used as a descriptor of chemical reactivity as it corresponds to the resistance of a system to charge transfer. μ and η can be defined in terms of orbital energies using Koopmans' theorem,[77] as given in equations 4.4 and 4.5.

$$\mu = \left(\frac{\partial E}{\partial N}\right)_{\upsilon(\vec{r})} \approx -\frac{1}{2}(I + A) \approx \frac{1}{2}(\varepsilon_{HOMO} + \varepsilon_{LUMO}) \tag{4.4}$$

$$\eta = \left(\frac{\partial^2 E}{\partial N^2}\right)_{\upsilon(\vec{r})} \approx (I - A) \approx -(\varepsilon_{HOMO} - \varepsilon_{LUMO}) \tag{4.5}$$

Just as in the carbon system μ shows a reasonable correlation to the reaction energy (r^2=0.795), exhibiting a decreased tendency for electrons to escape with the increased electron withdrawing strength of substituent, but the correlation is significantly worse (r^2=0.982 in the C-system). μ in the Si-system is always more negative than in the C-system by an average of 0.147 eV. Although the magnitude of μ in the silicic acid molecules is not identical to that of the carbon system, the trend is the same.

4.3.4 Structure and Critical Points in the Electron Density

One of the main structural differences between the two probe systems is the atomic radius of the central probe atom (Si or C). Consequently the **c2** length is on average 0.364 Å longer in the protonated Si-system and 0.357 Å longer in the deprotonated Si-Probe. As apparent in Figure 4.7, the effect of substitution on $\mathbf{\Delta_{Si\text{-}C}c2}$ (value in the carbon system subtracted from the value in the silicon system) is minimal, varying by 0.004 Å in HA and 0.011 Å in CB. This may be the reason for the smaller reaction constant (ρ=0.84, see Figure 4.1). As shown in equation 4.6, using $\mathbf{\Delta_{Si\text{-}C}c2}$ as a parameter essentially recreates the relationship from Figure 4.1, with ρ≅2.31 $\mathbf{\Delta_{Si\text{-}C}c2}$.

$$\Delta_{iso-Si}E = 2.31\Delta_{Si-C}c2 \cdot \Delta_{iso-C}E - 0.05 \quad (r^2 = 0.9999) \tag{4.6}$$

All lengths in the backbone, except **b2** and **a**, are consistently longer in the Si-system. These structural features exhibit a worse relationship with $\Delta_{iso}E$ than that seen in the C-system, but are still dictated by the group electronegativity of substituent as noted previously.[59,89] Length **a** appears to be governed by the pyramidalization of $\mathbf{C_a}$ (also observed in the C-system), where a decrease in length is caused by a more planar atom. Variations between HA and CB in the Si-system are not consistent or significant.

The structural parameters of the Si-probe group in its acidic form unexpectedly show less correlation with $\Delta_{iso}E$, which was not the case in the protonated C-probe. The bond lengths Si-O_a and Si-O_c show the best relationships to $\Delta_{iso}E$ (r^2=0.865 and r^2=0.795, respectively) with a decrease in length as the electron withdrawing group strength increases. In the C-system, all angles within the probe showed a relationship with the reaction energy.[89] In the Si-system, only θ(Si-O_b-H_b) shows a good correlation with $\Delta_{iso}E$

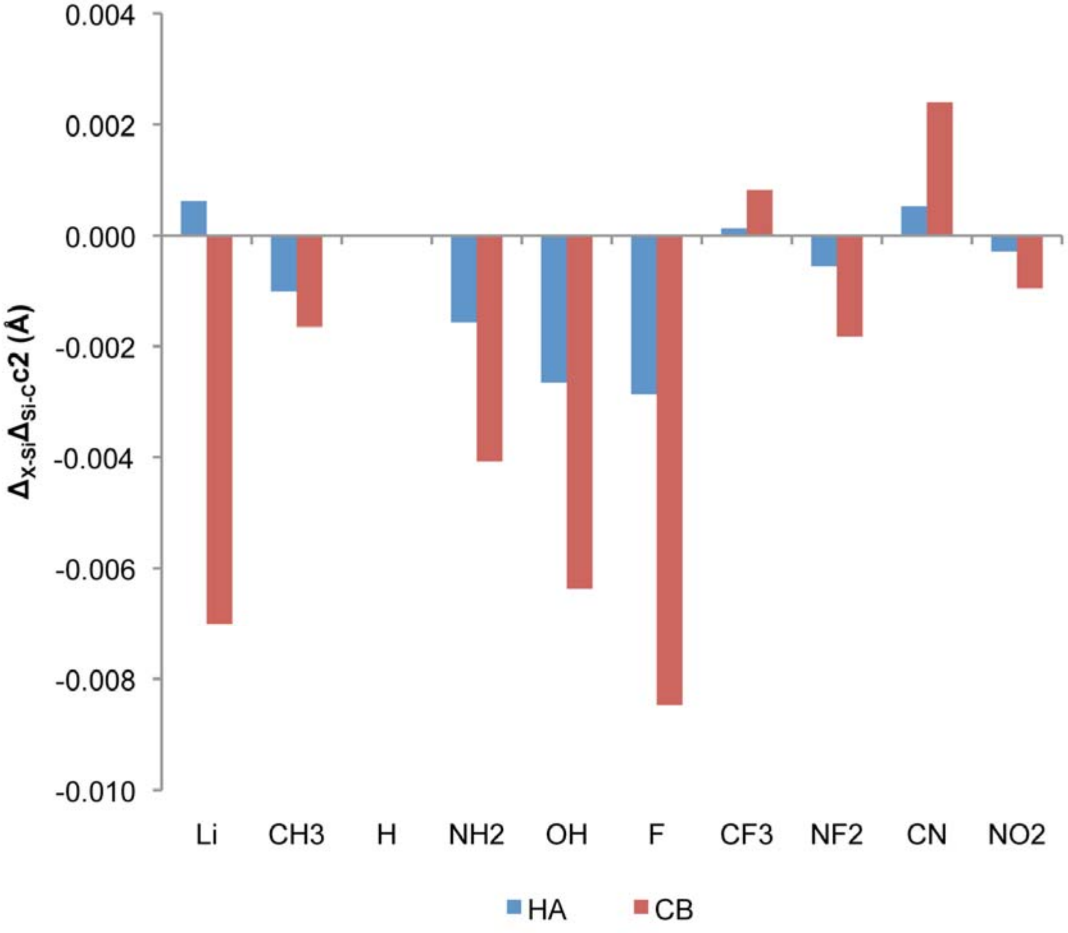


Figure 4.7. Graphical representation of the effect of substitution on the difference between **c2** (Å) in the Si-system and the C-system. All geometries were optimized at the PBE0/6-31++G(d,p) level of theory.

(r^2=0.807). In direct contrast to the C-system, whose best relationships were for the acid species, every structural parameter within the deprotonated Si-probe group (except c2 and γ2) shows good linear correlations with $\Delta_{iso}E$ ($r^2 \geq 0.814$). All bond lengths for the deprotonated molecules show a decrease in length with increasing electron withdrawing group strength. Therefore the same probe-central effect is apparent in the Si-system, but it appears to be associated with the conjugate base, consistent with the relationships between $\Delta_{iso}E$ and $\Delta_{CB}E$. The electron density at the bond critical point (BCP) is generally related to the length of the corresponding bond.[99,100] For the most part this is conserved in the Si-system, although the bonds within the probe group do not follow this general trend.

In addition to a larger atomic radius, Si has the ability to expand its coordination to 5 or 6. We examined the effect of substitution on the pyramidalization (termed **Dev** for brevity) of the Si-center using equation 4.7, where 31.5 ° corresponds to an ideal tetrahedral structure and 0 ° corresponds to a planar trigonal bipyramidal (TBP) center.

$$Dev(Si_O) = 360° - [\theta(O_a - Si_O - O_b) + \theta(O_b - Si_O - O_c) + \theta(O_c - Si_O - O_a)] \tag{4.7}$$

As the TBP structure has a larger spatial effect on the rest of the system, **Dev(Si_O)** may be related to the steric parameter, E_s, in equation 4.1. This measure of pyramidalization at the Si-center shows an almost perfect linear relationship with $\Delta_{iso}E$ (r^2=0.999 in HA). As is apparent in Figure 4.8, in both the protonated and deprotonated forms, electron withdrawing groups “planarize” Si, giving it more TBP character. Replacing E_s with **Dev(Si_O)** in equation 4.1 results in a marked improvement (equation 4.8) over the

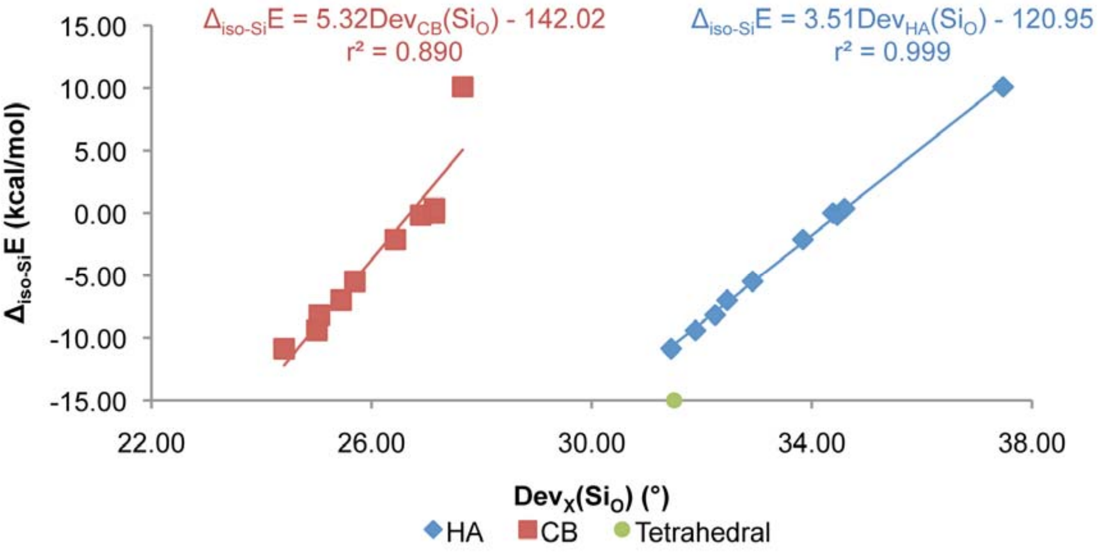


Figure 4.8. Relationship between the overall isodesmic reaction energy and the pyramidalization of the probe group in the silicon system; all calculated at PBE0/6-31++G(d,p) level of theory.

relationship depicted in Figure 4.2a. Despite the increase in TBP character, the valence shell charge concentrations (critical points in the Laplacian of the electron density, often used as an indication of the electron pairs around an atom in QTAIM[53]) indicated that Si remains 4-coordinate.

$$\Delta_{iso-Si}E = 1.12\sigma_F + 3.74\Delta_{HA}Dev(Si_O) - 0.41 \quad (r^2 = 0.999) \tag{4.8}$$

If the “so-called” inductive effect is transmitting through-bonds (as opposed to through-space) the electron density along the shortest bond path between substituent and probe would be perturbed. The expected bond path in this system is denoted by the numbered bond critical points (BCPs) in Scheme 4.2. Just as in the C-system, although with smaller correlations, the electron density at the relevant BCPs within the probe group, of the acidic species, (5 and 6 in Scheme 4.2) show fair relationships to Δ_{iso}E. ρ(BCP6) shows an expected decrease in density with increasing strength of electron withdrawing group, evident in Figure 4.9, and ρ(BCP5) shows an increase in density consistent with the redistribution of charge. Unlike the C-system, the electron density in the bond linking the backbone and probe (BCP4) also shows a fair relationship with Δ_{iso}E decreasing as the electron withdrawing strength of substituent increases. Once again there are no relationships with the bond between substituent and backbone or the BCPs within the backbone (1, 2 and 3), and correlations are present only for ρ(BCP) between the bridging carbons and their attached hydrogen atoms (e.g., BCP(Cb–H4)).

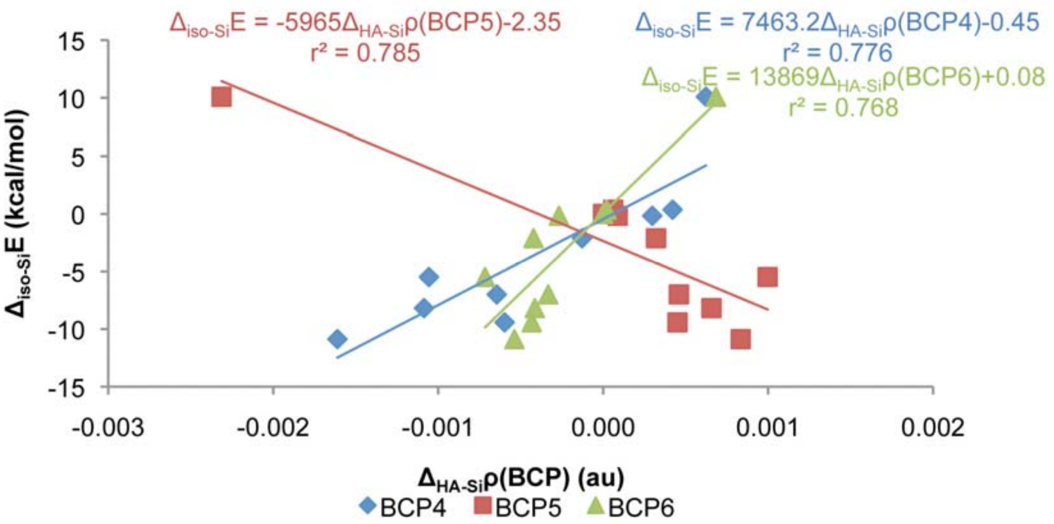


Figure 4.9. Relationships between the electron density at the bond critical points in the probe group of the silicon system (see Scheme 4.2) and the overall reaction energy; all calculated at the PBE0/6-31++G(d,p) level of theory.

4.3.5 Atomic Charges and Delocalization Index

The transmission of electron density through-bonds, or even through-space, should affect not only the bonds, but also the atoms themselves. Although each mechanism could influence different atoms, the effect of substituent should be apparent on the charges of the atoms. The QTAIM atomic charge is defined using the nuclear charge, Z_Ω, and the total number of electrons according to equation 4.9.

$$q(\Omega) = Z_\Omega - N(\Omega) = Z_\Omega - \int_\Omega \rho(r)d\tau \tag{4.9}$$

As expected, the overall charge on the Si-probe shows a good correlation to $\Delta_{iso}E$ just like the C-probe. This time the overall charge in both the protonated and the deprotonated forms show good relationships, although the correlations are poorer than in C-system (r^2=0.946). As depicted in Figure 4.10, the charge on the deprotonated probe correlates better with $\Delta_{iso}E$ (r^2=0.928 versus r^2=0.849 in the acid species). Within the protonated form, the charge on Si and O_a show the expected good relationship (r^2=0.814 and 0.871, respectively). The charge on H_a, however, shows very little relationship (r^2=0.441). In addition the charges on H_b and H_c show fair relationships (r^2=0.802 and 0.702, respectively). This is in contrast to the C-system where the acidic proton showed a very good linear relationship with $\Delta_{iso}E$ (r^2=0.984).

Given our findings for the C-probe, it is no surprise that there is no significant relationship between the overall charge on the substituent and the reaction energy (r^2=0.652 in the protonated species and r^2=0.681 in the deprotonated species). Lithium has an overall positive charge and all electron withdrawing groups have a negative total

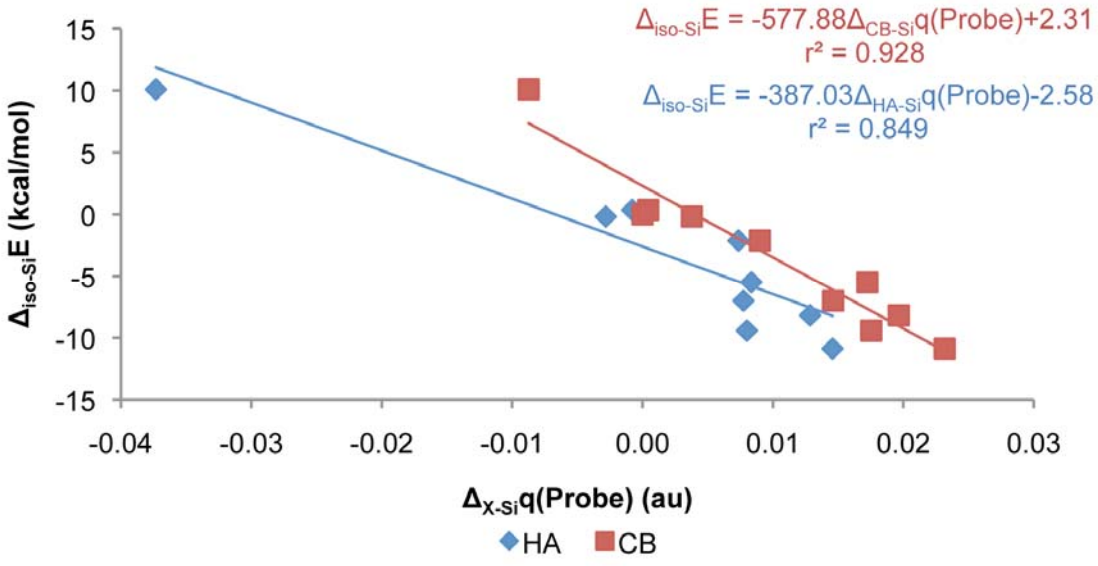


Figure 4.10. Relationships between the overall reaction energy and the QTAIM charge of the probe group within the molecules of the silicon system; all calculated at the PBE0/6-31++G(d,p) level of theory.

charge thus, qualitatively, reflecting their electron withdrawing or donating nature. The methyl substituent has an overall positive charge of 0.01 au in the protonated form and an overall negative charge of -0.01 au in the conjugate base. The same trends were observed in the C-system, even the unexpected change of the methyl substituent in the deprotonated species. The differences in charge of the substituents are almost negligible, which once again points to a similar effect in both systems. The largest variation between systems is for the CF_3-substituted acids. The CF_3 group in the Si-system is 0.021 au more negative than the corresponding group in the C-system. The effect upon the charge does appear to decay with distance, although there is again no relationship to the substituent effect. Figure 4.11 shows the relative charges of the atoms along the bond path (a shows the effect on the protonated species and b shows the effect on the deprotonated species); as expected, **C_a** has the largest variation in charge with substitution and this variation decreases with increased distance from the substituent.

Once again the overall charge on the substituent, and on **C_a**, has a very good relationship to the QTAIM group electronegativity, consistent with its formulation. Interestingly, the charge on the acidic hydrogen within the Si-probe, **H_a**, appears to be governed by the electronegativity of the substituent (as shown in Figure 4.12) instead of the isodesmic reaction energy, with the acidic hydrogen becoming more positive as the electronegativity of the substituent increases. This dependence on the electronegativity hints toward a through-bond mechanism of transmission not seen in the C-system.

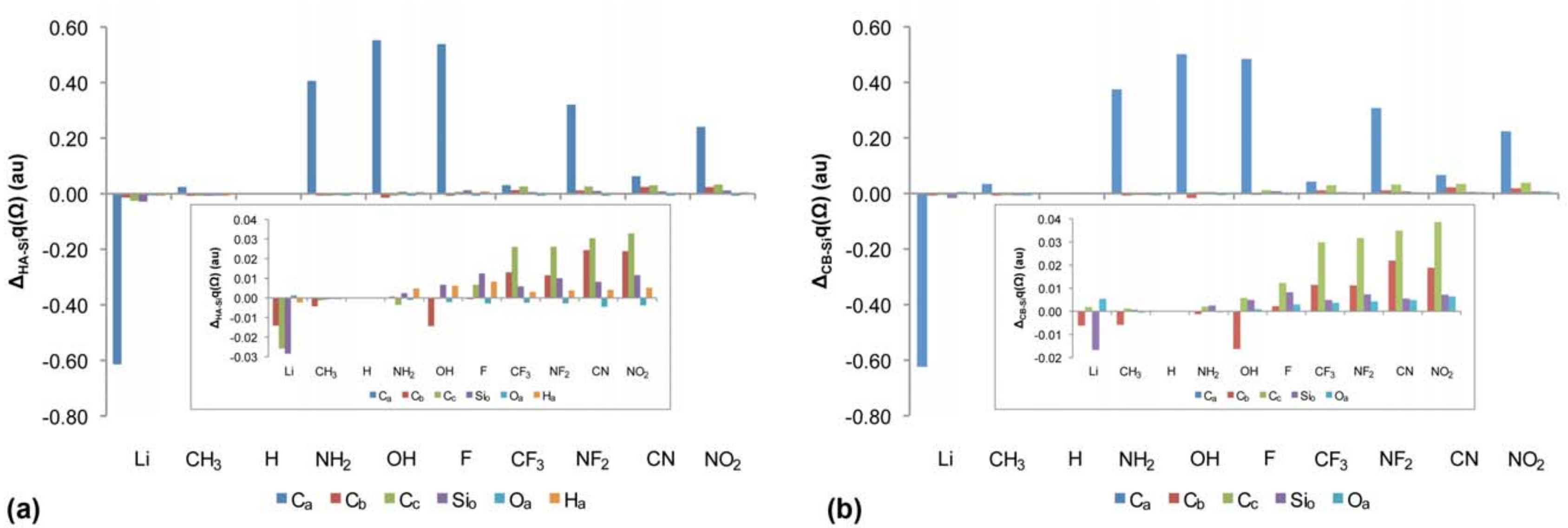


Figure 4.11. Graphical representation of the decay in the relative charges of the atoms along the bond path (see Scheme 4.2) in the silicon system for the (a) protonated species and (b) deprotonated species. Inset is the effect upon the atoms from $\mathbf{C_b}$ to $\mathbf{H_a}$ to show the detail masked by the effects at $\mathbf{C_a}$. All values calculated from wavefunctions created at the PBE0/6-31++G(d,p) level of theory.

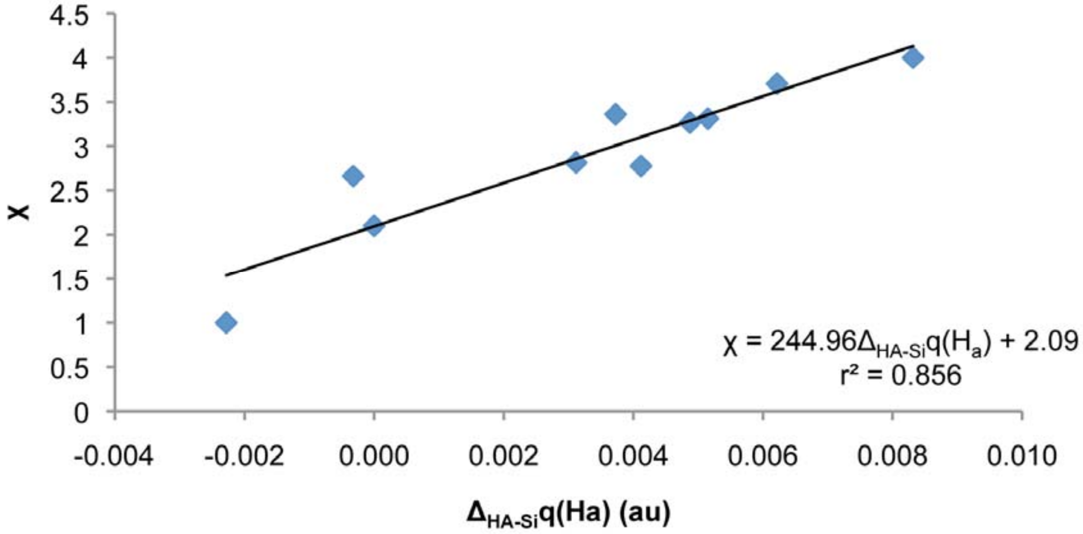


Figure 4.12. Relationship between the QTAIM substituent electronegativity and the relative charge of the acidic proton in the silicon system; all calculated at the PBE0/6-31++G(d,p) level of theory.

Evidence for transmission should also be apparent in the delocalization index (DI): the average number of electrons shared between two atoms (A and B). As described in equation 4.10, the DI depends on the overlap integrals for the atoms involved (F^{α} and F^{β}). Using the principle of atomic additivity, the DI can also be used to describe the communication between two groups within the molecule.

$$DI(A,B) = 2|F^{\alpha}(A,B)| + 2\left|F^{\beta}(A,B)\right| \tag{4.10}$$

There is no significant correlation between the isodesmic reaction energy and DI(Substituent, Probe), similar to that seen in the C-system suggesting that there is no direct communication between the substituent and probe. Although a weak relationship between DI(Substituent, H_a) and $\Delta_{iso}E$ was noted in the C-system, no relationship exists in the Si-system. In fact, the only relationship within the probe segment occurs for DI(Substituent, O_a) in the protonated species, which shows an increase in shared electrons with the increasing electron withdrawing strength.

Just as was apparent in the carbon system, there is evidence of a step-wise transmission of electron density. Fair relationships between $\Delta_{iso}E$ and electrons shared between the substituent and $\mathbf{C_b}$ (r^2=0.700), as well as the far bridgehead carbon ($\mathbf{C_c}$, r^2=0.775), indicating some level of transmission into the backbone. Corresponding relationships between the DI of the same atoms and the probe group appear to complete the stepwise transmission ($r^2(C_b)$=0.854 and $r^2(C_c)$=0.905); suggesting that once again the substituent communicates with the bridging carbon, which in turn passes the information to the probe.

4.3.6 Dipole Moment Contributions

The dipole moment has been used as proof of through space transmission of electron density, as in the traditional field effect, in previous studies[33] and in our analysis of the bicyclo[1.1.1]pentane-1-carboxylic acid system.[89] As it was determined that the effect of substitution in the carbon system transmits via the x-component of the atomic dipole moments along the bond path linking the substituent and probe, a careful analysis of all components was also performed for the silicon system. As determined in the C-system, the overall molecular dipole moment for the Si-system, as described in Table 4.3, shows no linear relationship with the reaction energy. Although only a weak correlation in the carbon system (r^2=0.641), the x-component of the molecular dipole, μ_x, in the acidic species shows a strong correlation with the substituent effect (r^2=0.985). As all molecules conform to the axis system described in Scheme 4.2, it appears that the overall charge distribution is skewed toward the probe segment in the electron withdrawing substituted molecules.

QTAIM provides a way to determine the individual atomic dipole moments according to equation 4.11 and, through summation, the group dipole moment.

$$\mu(\Omega) = -e\int_{\Omega} r_{\Omega}\rho(r)d\tau \tag{4.11}$$

As observed for the C-probe, the x-component of the substituent dipole shows a very good relationship to $\Delta_{iso}E$ (see Table 4.3 for values and Figure 4.13a). The dipole becomes greater in the direction of the probe segment as the strength of electron withdrawing group increases in both the protonated and deprotonated species. Owing

Table 4.3. Molecular and atomic dipole moment contributions (in debyes) calculated at PBE0/6-31++G(d,p) in accordance with the axis system described in Scheme 4.2. Shown are the contributions for the silicon system, and simpler models: 3-substituted-bicyclo[1.1.1]pentane, r-CH_3 and R-H. Squared correlation coefficients for the linear correlation to $\Delta_{iso}E$ are shown for comparison purposes.

Substituent	Molecular				Atomic				
	$\lvert\mu\rvert$ (R_{HA})	$\mu_x(R_{HA})$	$\lvert\mu\rvert$ (R_{CB})	$\mu_x(R_{CB})$	$\mu_x(R_{HA})$	$\mu_x(R_{CB})$	$\mu_x(R_{B[1]P})$[a]	$\mu_x(R_{CH3})$[b]	$\mu_x(R_H)$[c]
Li	7.54	7.43	7.86	7.68	2.94	1.05	2.94	3.00	3.16
CH_3	1.40	0.36	6.97	6.78	-0.53	-0.12	-0.54	-0.61	-0.34
H	1.36	0.01	5.22	4.95	-0.37	-0.49	-0.36	-0.34	-0.29
NH_2	0.32	0.19	6.51	6.34	-0.79	-0.63	-0.80	-1.18	-0.52
OH	1.42	-0.91	5.45	5.44	-1.55	-1.51	-1.50	-1.60	-1.07
F	2.92	-2.61	4.27	3.95	-2.39	-2.54	-2.36	-2.47	-1.82
CF_3	3.67	-3.44	7.85	7.68	-2.39	-2.04	-2.39	-2.42	-1.84
NF_2	4.06	-3.86	5.99	5.86	-2.85	-2.70	-2.86	-2.87	-1.96
CN	5.50	-5.35	2.94	2.45	-3.81	-4.00	-3.80	-3.86	-3.00
NO_2	5.57	-5.43	4.32	4.01	-3.68	-3.56	-3.69	-3.66	-2.68
r^2	0.001	0.985	0.370	0.366	0.982	0.911	0.983	0.969	0.958

Dipole moment contribution calculated for the substituent with (a) with the bicyclo[1.1.1]pentane backbone attached, (b) with a methyl group, and (c) only a hydrogen atom. Squared correlation coefficients are calculated for linear relationships with $\Delta_{iso}E$.

to lithium's electron donating properties and low electronegativity it is the only substituent to have a positive $\mu_x(R_{HA})$. Consistently, μ_x is lower (or more negative by an average of 0.08 D) in the Si-system than the C-system presumably due to the different dipole moments of the probe segment ($\mu_x(COOH)=+0.46D$ and $\mu_x(Si(OH)_3)=-0.75D$).

There are good correlations between $\Delta_{iso}E$ and μ_x for all atoms along the bond path. In fact, the x-component of the atomic dipole moment is the only property related to the substituent effect that is consistent along the bond path, and $\mu_x(R)$ appears to be the controlling factor. Figure 4.13b shows the relationship between $\mu_x(R_{HA})$ and the substituent constant (σ_F) for both the Si- and the C-systems. Not only does $\mu_x(R_{HA})$ in the silicon system show a very good correlation to σ_F, but the relationship is almost identical to that in the C-system. This strengthens the idea that the substituent effect is the same in both systems. As observed before for the C-system, all other properties which relate to the substituent effect are controlled by $\mu_x(R_{HA})$, two examples of which are shown in Figure 4.14: (a) the relative NMR chemical shift of the acidic proton and (b) the pyramidalization of the probe group. The downfield shift apparent in the NMR chemical shift of the acidic proton is controlled by the more negative $\mu_x(R_{HA})$. The more negative $\mu_x(R_{HA})$ also results in a greater pyramidalization of the probe group.

In the carbon system it was determined that because transferability of QTAIM properties is conserved within the system, it is possible to recreate the substituent effect using more simple backbones. As evident in Table 4.3, this is also the case in the silicon system. The substituent effect in this case can be recreated with $\mu_x(R_{HA})$ in the

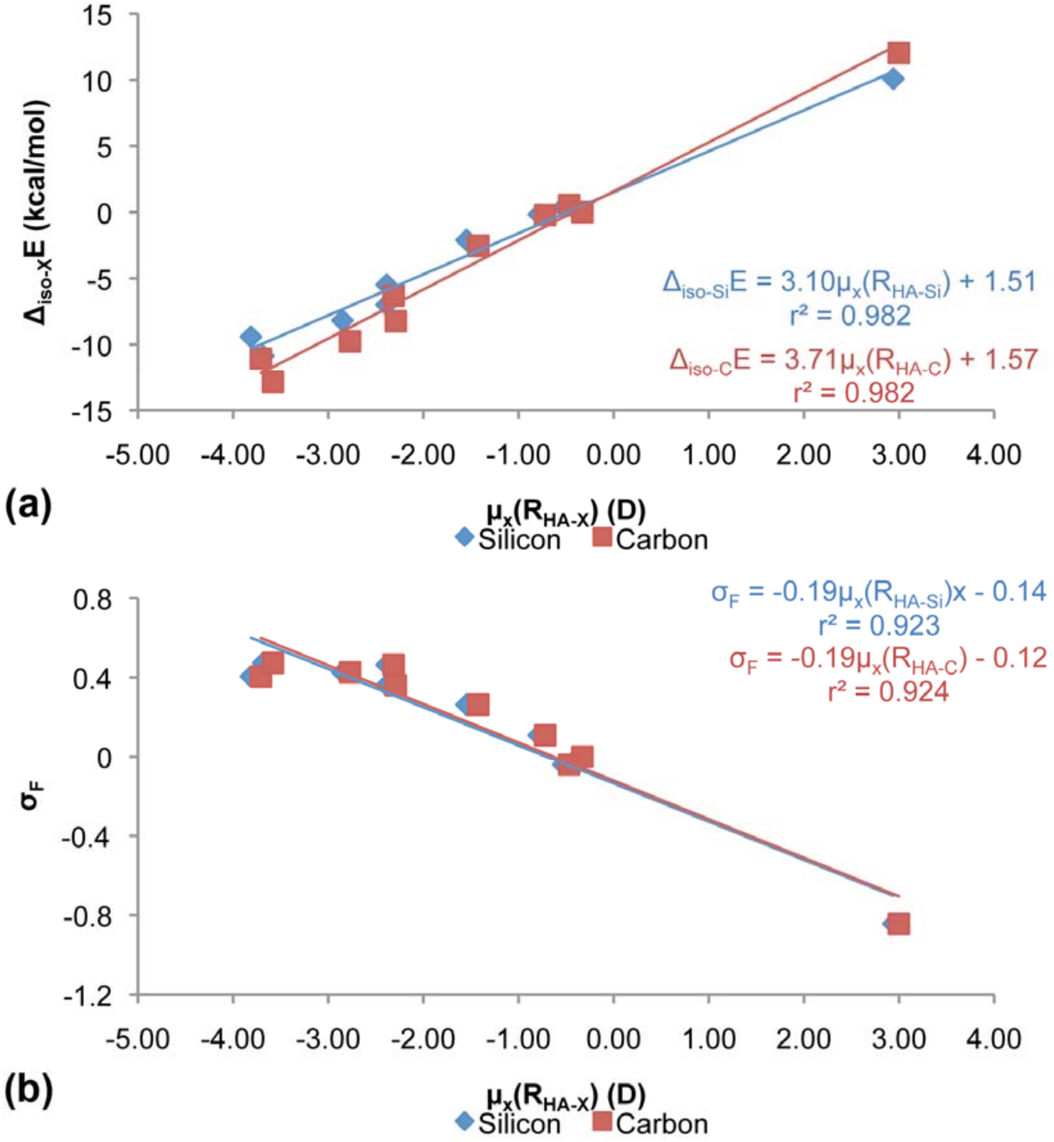


Figure 4.13. Relationships between the overall isodesmic reaction energy and (a) the x-component of the substituent dipole in the silicon system, and (b) and the x-component of the substituent dipole in both protonated silicon and carbon systems, as well as the (c) the relationship between the substituent constant and the x-component of the substituent dipole in both protonated systems; all calculated at the PBE0/6-31++G(d,p) level of theory. All species were rotated to conform to the axis system outlined in Scheme 4.2.

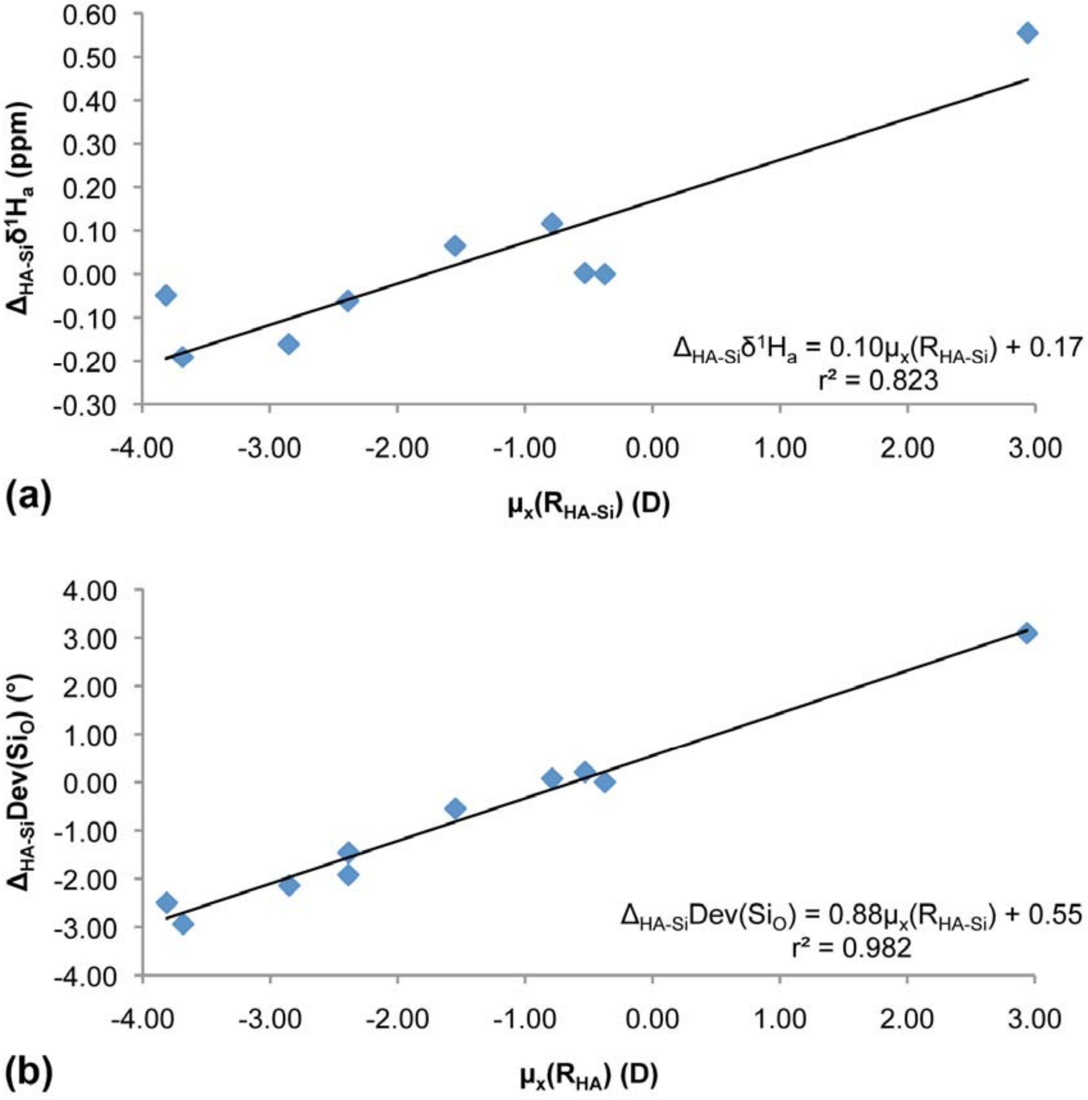


Figure 4.14. Relationships between the x-component of the substituent dipole in the protonated silicon system and (a) the relative NMR chemical shift of the acidic proton and (b) the pyramidalization of the probe group; all calculated at the PBE0/6-31++G(d,p) level of theory. All species were rotated to conform to the axis system outlined in Scheme 4.2.

carbon system as well as in the RH system. Yet again, it appears the mode of transmission is through variations in the atomic dipole moments. As such we can use $\mu_x(R_{HA})$ to create an expression akin to equation 4.1 to describe the substituent effect in the Si-system. As is apparent in equation 4.12, the only improvement over equation 4.8 is that the intercept, sometimes considered the error in the relationship, is lower.

$$\Delta_{iso-Si}E = 0.11\mu_x(R_{HA-Si}) + 3.39\Delta_{HA-Si}Dev(Si_O) - 0.36 \quad (r^2 = 0.999) \tag{4.12}$$

4.4 Summary and Conclusion

We present a systematic study of the effect of a variety of substituents on a silicon based probe: silicic acid. The essentially perfect linear relationship between the isodesmic reaction energy of the silicon system and that of the previously studied carbon system[89] implies that the effect of the substituent on the reactivity is the same, consistent with the substituent constant concept proposed by Hammett. The silicon probe system is less sensitive to the effect of substitution as suggested by ρ. The reaction constant is directly related to **$\Delta_{Si\text{-}C}$c2**, the change in distance between the two probes (C and Si) and the backbone.

In Hammett's formulation, a steric parameter was required to correctly describe the effects of substitution. We find that this correction is related to the effect of substitution on Si pyramidalization, **Dev(Si_O)**. Thus, even when the substituent has no direct steric interaction it still has an effect.

Just as in the carbon system, distance related decay is apparent, but it does not relate to the substituent effect. Analysis of the atomic charges and electron density at the bond critical points provides no significant insight into the transmission of the effect, although there does appear to be more evidence for a through-bond than a through-space connection. The delocalization indices point to a stepwise transmission with communication between the substituent and backbone atoms and the same backbone atoms and the probe segment. The key substituent property is the x-component of the dipole moment as it controls all other properties related to the substituent effect, also observed in the C-system. The x-component of the substituent dipole, which appears to be a conserved property, causes a change in the atomic dipole moments along the bond path, resulting in an effect that appears to pass through-bonds. A linear equation has been developed, using $\boldsymbol{\mu}_{\mathbf{x}}(\mathbf{R}_{\mathbf{HA}})$ and $\mathbf{Dev}_{\mathbf{HA}}(\mathbf{Si}_{\mathbf{O}})$ as parameters, to describe the “so-called” inductive effect of substituents on silicic acid reactivity.

Chapter 5: The Transmission of the Inductive Effect Through Silicon Containing Backbones

5.1 Introduction

The “so-called” inductive effect comprises two mechanisms for the transmission of charge through a molecule: the through σ-bonds mechanism termed the (traditional) inductive effect and the through-space mechanism termed the field effect.[16] Both mechanisms generally operate in the same direction and therefore tend to be inseparable. Transmission through carbon-carbon bonds has been widely studied; however this is not the case with silicon-silicon bonds.

In one of the first substituent effect studies, Hammett used a benzene moiety as the transmitting segment. He discovered that the acid dissociation constants of the substituted and unsubstituted acids (according to $\log K_R - \log K_H$) could be related to a substituent (σ) and a reaction (ρ) constant. Since then almost every other type of carbon based backbone has been tested according to his method.[20] Just as the benzene backbone has been used to describe how the resonance effect transmits, saturated systems have been employed to describe how the inductive effect transmits. Acetic acids have been used as one of the simplest systems to study the inductive effect,[21] but their smaller size can lead to steric complications. Bicyclic alkanes have become the standard for inductive effect studies because they exclude any possibility of resonance and due to their rigidity maintain an approximately constant steric effect.[36] The bicyclo[2.2.2]octane backbone was originally introduced because it the number of C–C bonds between the substituent and probe is the same as in benzene.

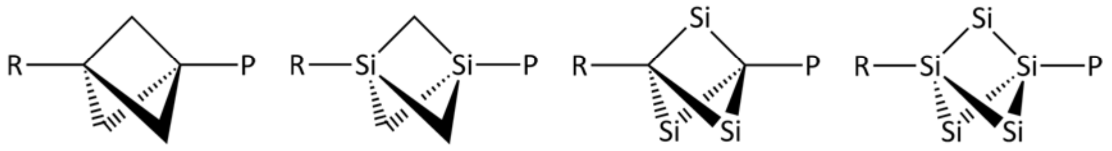
Bicyclo[1.1.1]pentane is becoming more popular because it has the same attractive qualities, but results in a more sensitive system as the substituent and probe are closer together and the effect transmits through fewer bonds.[33]

Although Si is isoelectronic to C, it has an increased atomic radius, greater polarizability, and low-lying d orbitals which may allow for (p–d)π, (p–d–d)π, etc., interactions.[8] Unlike carbon, Si has been found to expand beyond 4-coordinate to include 5- and 6-coordinate species[101] and 2- and 3-coordinate species, like alkene and alkyne analogs, which exhibit a "lone pair" effect where Si is pyramidal. This is generally attributed to the presence of some lone pair density on the Si atoms.[102,103]

Yoder *et al.*[8] undertook one of the few studies of the transmission of substituent effects through the disilane bond using NMR chemical shifts and coupling constants. Using the ^{13}C–^{1}H coupling constants, as they are the least sensitive to external effects, it was determined that transmission was more effective through a C-C linkage than a Si-Si linkage, despite the greater polarizability. The authors attributed this to a shorter distance between the substituent and probe with the C-C linkage and intramolecular interactions between the β-Si and electron rich substituents. Using the Hammett approach, Yoder *et al.* determined that the NMR parameters correlated well with substituent constants as expected for carbon systems.

Herein we investigate the transmission of substituent effects through silicon atoms by extending our previous method using the bicyclo[1.1.1]pentane backbone to include silicon based analogs.[89] The carbon atoms within the backbone were systematically replaced by silicon, according to Scheme 5.1, to develop three analog systems. Each analog was subsequently compared to the original all-carbon backbones,

SCHEME 5.1



Full Carbon Analog 1 Analog 2 Analog 3

both with carbon and silicon probes, to determine the effect of transmission through silicon. Applying the isodesmic reaction approach to Hammett's method and the Quantum Theory of Atoms in Molecules (QTAIM), we have examined the transmission of the "so-called" inductive effect to determine if transmission occurs differently in a Si-based bicyclo[1.1.1]pentane structure.

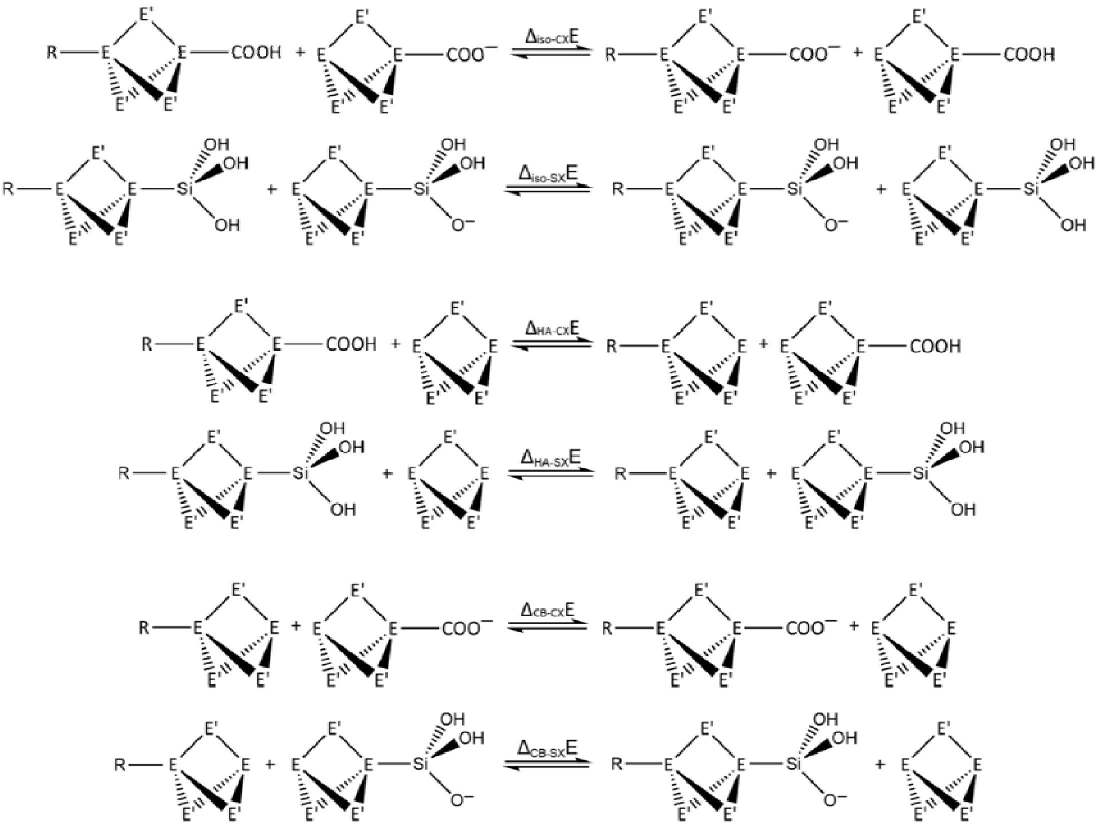
5.2 Methods

All calculations were performed using the Gaussian 03[61] and 09[62] versions of the program suite. Geometry optimization was performed at the PBE0[63,93]/6-31++G(d,p)[45,94] level of theory followed by vibrational frequency analysis, with the same model chemistry, to confirm the presence of a stationary point. This model chemistry was previously shown to be a compromise between accuracy and efficiency in the 3-substituted-bicyclo[1.1.1]pentane-1-carboxylic acid system.[89] The accuracy of the isodesmic reaction energies (reactions shown in Scheme 5.2), were assessed using a complete basis set method, CBS-QB3,[47,48,104] known for achieving highly accurate thermochemistries.

Nuclear magnetic resonance (NMR) data was generated at the PBE0/6-31++G(d,p) level of theory using the gauge-independent atomic orbitals (GIAO) method.[68,95] PBE0 has been proven to be accurate in the prediction of NMR shielding tensors,[96] and the basis set was confirmed to be sufficient via comparison to larger basis sets.[89]

Wavefunctions were generated at the PBE0/6-31++G(d,p) level of theory to ensure a stationary point was used, and the electron density distribution was analyzed

SCHEME 5.2



where X refers to the Analog
Analog 1: E=Si; E’=C
Analog 2: E=C; E’=Si
Analog 3: E=E’=Si

using the AIMALL program suite[65] according to Bader's Quantum Theory of Atoms in Molecules.[51,52] The integration for the lithium and CF_3-substituted conjugate base molecules with backbone 1, and the carboxylic acid probe, resulted in a potentially significant error even at the most accurate levels. As the results follow expected trends, they will be included in the analysis. The molecular graph for the lithium-substituted acid with backbone 2 (both probes) includes a non-nuclear attractor (see Figure A1.2) near the lithium substituent and was not used in the analysis.

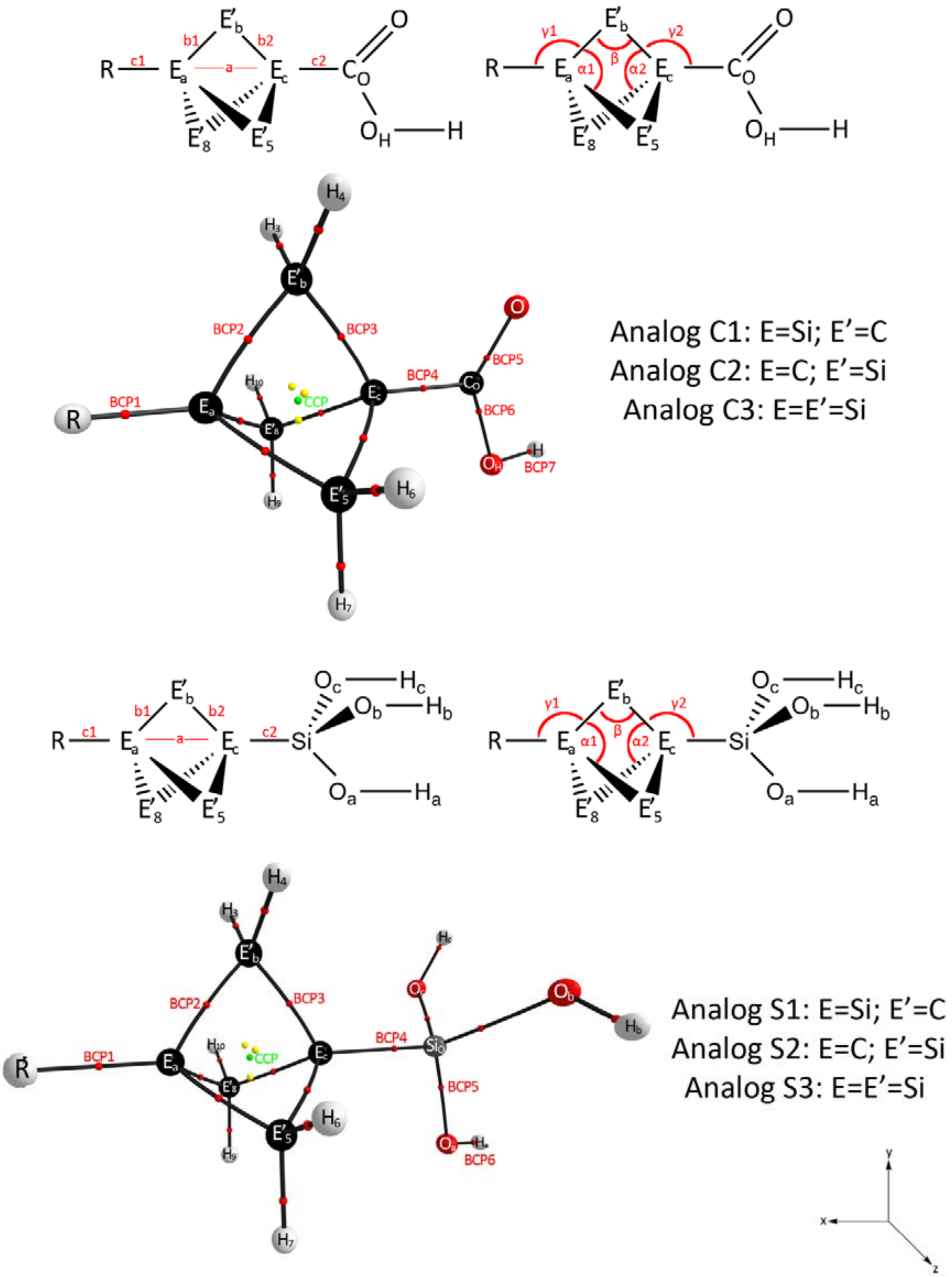
Scheme 5.3 shows the labeling and axis systems used in this discussion, chosen to be consistent with Levin *et al.*[69] Those with the carboxylic acid probe will be referred to as simply analogs C1, C2, and C3 depending on their backbone, and those with the silicic acid type probe will be referred to as analog S1, S2, and S3; each will be compared to their all-carbon backbone (E=E'=C) counterparts to determine the effect on transmission.

5.3 Results

5.3.1 Energies

To study how the "so-called" inductive effect transmits through silicon, the isodesmic reaction energies ($\Delta_{iso\text{-}X}E$, where X=AC1, AC2, AC3, or AS1, AS2, AS3. A indicates an analog system, C specifies the carboxylic acid probe and S specifies the use of the silicic acid probe) obtained from the reactions described in Scheme 5.2 were compared to that determined for the all carbon backbone (for COOH probe see Section 3.4.1; for $Si(OH)_3$ probe see Section 4.4.1). The substituents have been ordered based

SCHEME 5.3



Analog C1: E=Si; E′=C
Analog C2: E=C; E′=Si
Analog C3: E=E′=Si

Analog S1: E=Si; E′=C
Analog S2: E=C; E′=Si
Analog S3: E=E′=Si

on the $\Delta_{iso}E$, calculated using the composite CBS-QB3 method, for the bicyclo[1.1.1]pentane-1-carboxylic acid system.

5.3.1.1 Analogs C1 and S1

It is apparent in Table 5.1 that there are some important differences in the reactivity with the introduction of silicon within the backbone. The backbone promotes electron donating character in the amino-substituted analog 1 (both probes; positive $\Delta_{iso}E$ using CBS-QB3 method versus a negative $\Delta_{iso}E$ in the all carbon backbone) and CN-substitution yields a smaller $\Delta_{iso}E$ than NF_2-substitution and therefore a weaker electron withdrawing group in the C-probe system, but the ordering is conserved within the Si-probe. Regardless of the changes in substituent ordering, the PBE0/6-31++G(d,p) energies recreate the CBS-QB3 energies well, as described in equations 5.1 and 5.2.

$$\Delta_{iso-AC1(CBS)}E = 1.02\Delta_{iso-AC1(PBE0)}E + 0.76 \quad (r^2 = 0.993, n = 10) \tag{5.1}$$

$$\Delta_{iso-AS1(CBS)}E = 1.02\Delta_{iso-AC1(PBE0)}E + 0.34 \quad (r^2 = 0.997, n = 10) \tag{5.2}$$

Using the PBE0/6-31++G(d,p) values we find that $\Delta_{iso}E$ of the analog systems form very good linear relationships with the reaction energy of the carbon backbone systems, shown in Figure 5.1a. According to the slope and intercept of the linear equation, the change in backbone has the same effect on both probes. They are both more sensitive to substitution than the all-carbon backbones, by approximately the same amount (ρ=1.11).

Separating the overall isodesmic reaction into their constituent parts (Scheme

Table 5.1. Isodesmic reaction energies, in kcal/mol, for the analog 1 systems, calculated using the CBS-QB3 composite method and the PBE0/6-31++G(d,p) level of theory (see Scheme 5.2 for reactions).

Species	Substituent	CBS-QB3	PBE0/6-31++G(d,p)		
		$\Delta_{iso}E$	$\Delta_{iso}E$	$\Delta_{HA}E$	$\Delta_{CB}E$
Analog C1	Li	16.68	14.49	2.69	11.80
	CH_3	1.87	2.07	0.25	1.82
	H	0.00	0.00	0.00	0.00
	NH_2	1.65	1.46	0.07	1.40
	OH	-1.27	-2.04	-0.46	-1.58
	F	-5.26	-6.42	-1.04	-5.38
	CF_3	-7.72	-7.96	-0.64	-7.32
	NF_2	-9.28	-10.21	-0.97	-9.24
	CN	-9.22	-9.69	-0.82	-8.86
	NO_2	-12.62	-13.81	-1.21	-12.60
Analog S1	Li	13.56	12.42	-0.80	13.22
	CH_3	1.52	1.76	0.15	1.61
	H	0.00	0.00	0.00	0.00
	NH_2	1.48	1.47	0.62	0.84
	OH	-1.01	-1.37	1.10	-2.47
	F	-4.20	-4.85	1.46	-6.31
	CF_3	-6.71	-6.71	0.83	-7.55
	NF_2	-8.05	-8.37	1.35	-9.72
	CN	-8.06	-8.23	0.83	-9.06
	NO_2	-10.87	-11.37	1.64	-13.01

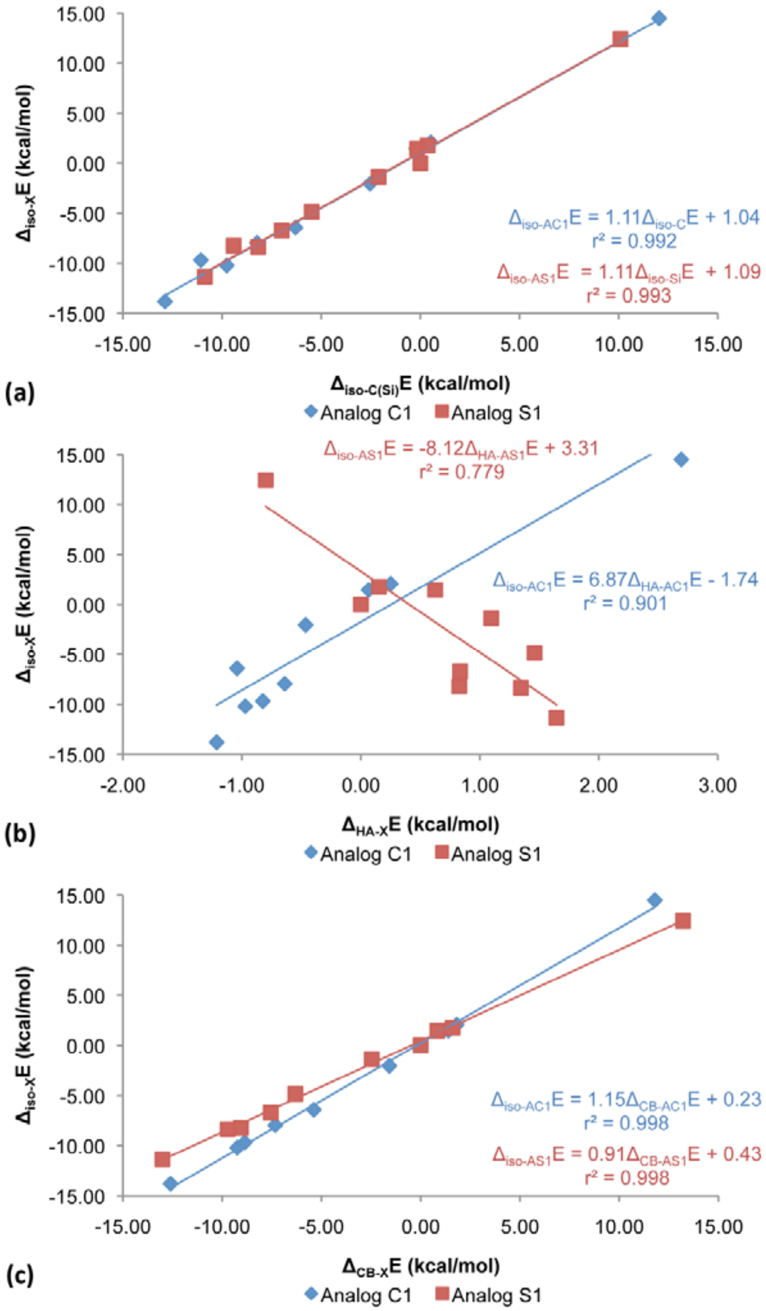


Figure 5.1. Graphical representation of the relationships between the overall reaction energy and (a) the overall reaction energies of the corresponding carbon-backbone systems, (b) the effect upon the protonated probe groups, and (c) the effect upon the deprotonated probe groups, for analogs C1 and S1. All values were calculated at the PBE0/6-31++G(d,p) level of theory.

5.2) describes the two simultaneous effects: the effect of the substituent on the protonated probe and the effect of the substituent on the deprotonated probe. In the carbon backbone systems, $\Delta_{CB}E$ dictates the overall reaction energy. $\Delta_{HA}E$ does contribute to the overall effect with the C-probe, but not in the Si-system (r^2 between $\Delta_{HA\text{-}Si}E$ and $\Delta_{iso\text{-}Si}E$ is only 0.155). Electron donating groups appear to stabilize HA and destabilize CB, whereas electron withdrawing groups do the opposite (with the exception of NH_2 substitution, which shows a very small stabilization of HA) in the C-system. All groups appear to stabilize HA within the Si-system, but only Li substitution destabilizes the CB. In both analogs C1 and S1, $\Delta_{CB}E$ shows the most control over the overall reaction energies (see Figure 5.1c and Table 5.1 for values), with smaller contributions from $\Delta_{HA}E$ (Figure 5.1b). This is consistent with the result for the all-carbon backbones with one exception: Analog S1 shows a fair relationship between $\Delta_{HA}E$ and $\Delta_{iso}E$.

In general for both analogs, the electron donating groups yield a stabilization of the acid species and a destabilization of the conjugate base, whereas the withdrawing groups show the opposite result. Li-substitution in analog S1 leads to a destabilization of the protonated species in direct contrast to the all-carbon backbone. Within the deprotonated species, NH_2 substitution leads to destabilization in both analogs and CH_3 substitution also leads to a destabilization for analog S1.

Using QTAIM to analyze the electron density distribution allows us to dissect $\Delta_{iso}E$ past its constituent parts into the energies of the atoms or groups, themselves. The atomic energy can be used to determine if a single atom, or group, is stabilized or destabilized with respect to a change in substituent. The energies of the substituent or backbone show no relationship to the substituent effect in the all carbon systems. However, as expected given the acid- base nature of the reaction, the effect is centered mainly upon the probe segment. The same trend occurs for both probe systems: the probe segment is stabilized with increased acidity. Within the C-probe the effect was centered on the acidic hydrogen, but in the Si-probe it was the remaining hydrogen atoms in CB that correlated best with $\Delta_{iso}E$. In the analog 1 systems there are also no relationships between $\Delta_{iso}E$ and the energy of the substituent or the backbone as a whole. The isodesmic energy of the probe (calculated in the same manner as $\Delta_{iso}E$, but using the energy of the probe segment instead of the energy of the entire compound) in analog S1 correlates very well with $\Delta_{iso}E$. Although there is no correlation between the energy of the probe segment and $\Delta_{iso}E$ for analog C1, the energy of the acidic hydrogen does relate well to the overall reaction energy (see Figure 5.2). As the acidity of the system increases, the acidic hydrogen becomes more destabilized within the molecule. Although it is in contrast to the all-carbon backbone, this trend is followed in analog S1. The acidic hydrogen is less stable in the analog systems (by 0.0007 au in AC1 and 0.002 au in AS1) than in the all-carbon backbones.

5.3.1.2 Analogs C2 and S2

Replacement of the all-carbon backbone with analog 2 (Scheme 5.1) leads to significant rearrangement in the structure of the deprotonated systems for the most electron withdrawing substituents (CF_3, NF_2, CN and NO_2 in analog C2; CN and NO_2 in

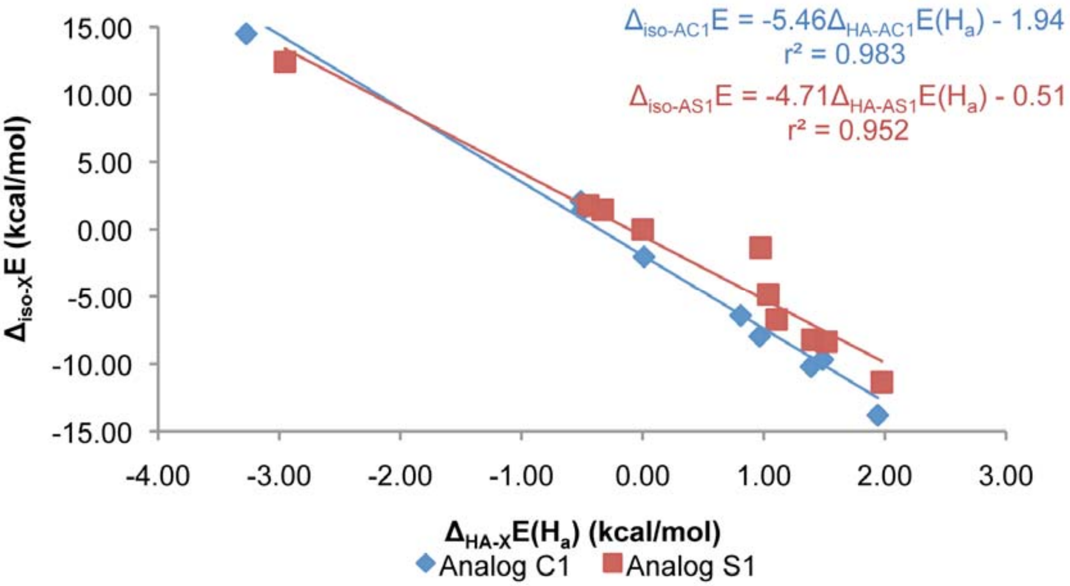


Figure 5.2. Graphical representation of the relationship between the overall reaction energy and the energy of the acidic hydrogen within analogs C1 and S1. All values were calculated at the PBE0/6-31++G(d,p) level of theory.

analog S2) as depicted in Figure 5.3 (see Table 5.2 for values). Si–O affinity leads to the breaking of one of the bridging silicon atoms from the cage and the formation of two four-membered rings. In all cases, this structure is a stationary point. An elongation of **b1** and a decrease in the length of the **b2** is apparent, in the weaker electron withdrawing groups, leading up to the breaking of b1 and subsequent rearrangement to a difference bicyclic structure. As an example, for NF_2 substituted analog C1, **b1** is 0.024 Å longer and **b2** is 0.012 Å shorter in CB (values come from the PBE0 optimized geometry). The PBE0/6-31++G(d,p) optimizations appear to be less sensitive to rearrangement and therefore only the CN- and NO_2-substituted analog C2 species, and the NO_2-substituted analog S2 species, must be removed from the data set in this case. In spite of the structural issues, the PBE0/6-31++G(d,p) energies recreate the available CBS-QB3 energies very well (relationships described in equation 5.3 and 5.4).

$$\Delta_{iso-AC2(CBS)}E = 1.00\Delta_{iso-AC2(PBE0)}E - 0.03 \quad (r^2 = 0.9995, n = 6) \tag{5.3}$$

$$\Delta_{iso-AS2(CBS)}E = 0.96\Delta_{iso-AS2(PBE0)}E + 0.05 \quad (r^2 = 0.996, n = 8) \tag{5.4}$$

Using the PBE0/6-31++G(d,p) energies, it is apparent that the order of substituents is conserved with a single exception: substitution with NH_2 leads to a positive $\Delta_{iso}E$. The reaction energies for the analog systems correlate very well with that for the all-carbon backbones (see Sections 3.4.1 and 4.4.1), although, analog 2 has a different effect upon the reaction constant for each probe system. As illustrated in Figure 5.4a, according to their respective ρ values analog C2 is less sensitive to substitution, whereas analog S2 is actually more sensitive.

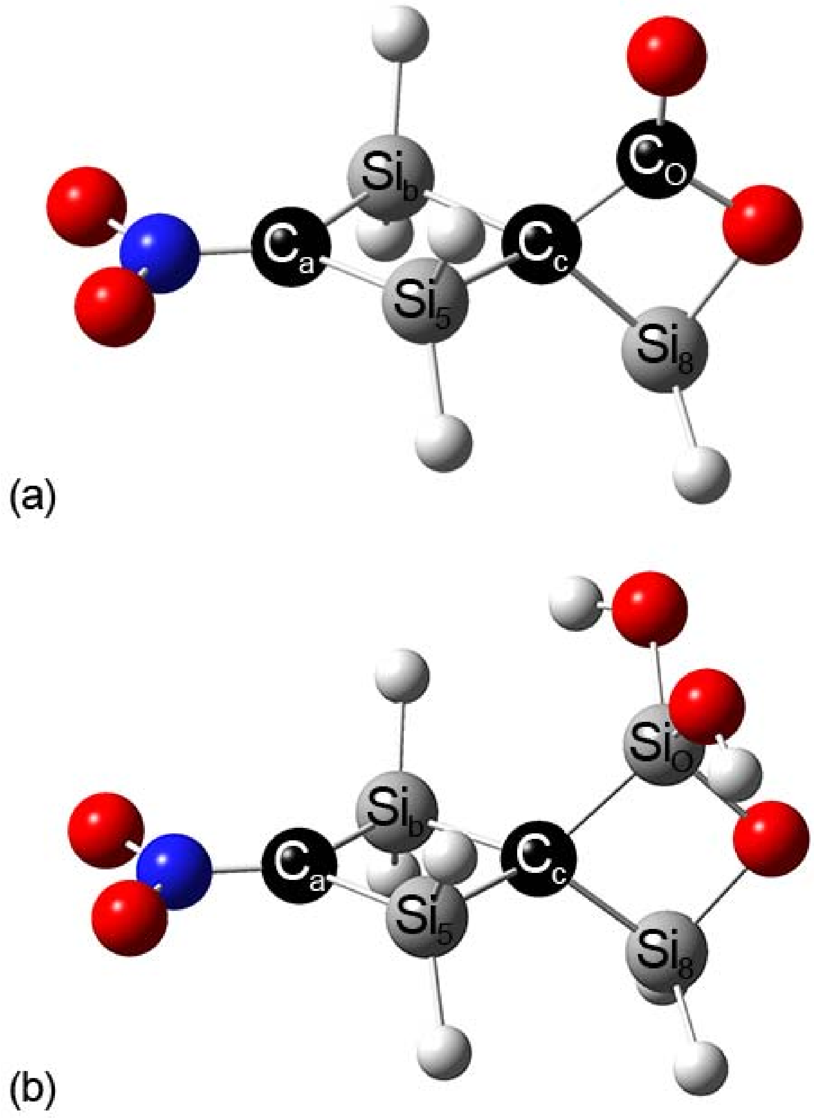


Figure 5.3. Geometry optimization of the CF_3, NF_2, CN and NO_2 substituted conjugate base of analog C2, and CN and NO_2 substituted conjugate base of analog S2, using the CBS-QB3 composite method (CN and NO_2, and NO_2 substitution, respectively, at the PBE0/6-31++G(d,p) level of theory) results in the rearrangement of one of the bridging silicon atoms to form two four-membered rings. Shown is (a) NO_2 substitution with analog C1 and (b) NO_2 substitution with analog S2.

Table 5.2. Isodesmic reaction energies, in kcal/mol, for the analog 2 systems, calculated using the CBS-QB3 composite method and the PBE0/6-31++G(d,p) level of theory (see Scheme 5.2 for reactions).

Species	Substituent	CBS-QB3	PBE0/6-31++G(d,p)		
		$\Delta_{iso}E$	$\Delta_{iso}E$	$\Delta_{HA}E$	$\Delta_{CB}E$
Analog C2	Li	12.52	12.40	2.01	10.39
	CH_3	0.27	0.22	-0.08	0.30
	H	0.00	0.00	0.00	0.00
	NH_2	-0.19	0.03	-0.11	0.14
	OH	-1.81	-1.63	-0.51	-1.13
	F	-4.39	-4.49	-0.95	-3.54
	CF_3	^{a}	-8.37	-0.86	-7.51
	NF_2	^{a}	-9.11	-0.95	-8.16
	CN	^{a}	^{a}	-1.22	^{a}
	NO_2	^{a}	^{a}	-1.09	^{a}
Analog S2	Li	11.47	11.48	0.14	11.34
	CH_3	0.23	0.31	0.48	-0.18
	H	0.00	0.00	0.00	0.00
	NH_2	-0.15	0.26	1.09	-0.83
	OH	-1.60	-1.22	1.37	-2.58
	F	-3.74	-3.91	1.38	-5.29
	CF_3	-6.89	-7.48	0.14	-7.62
	NF_2	-7.47	-8.35	0.55	-8.90
	CN	^{a}	-10.23	0.11	-10.34
	NO_2	^{a}	^{a}	0.71	^{a}

(a) Values missing due to rearrangement to a different bicyclic structure (see Figure 5.2).

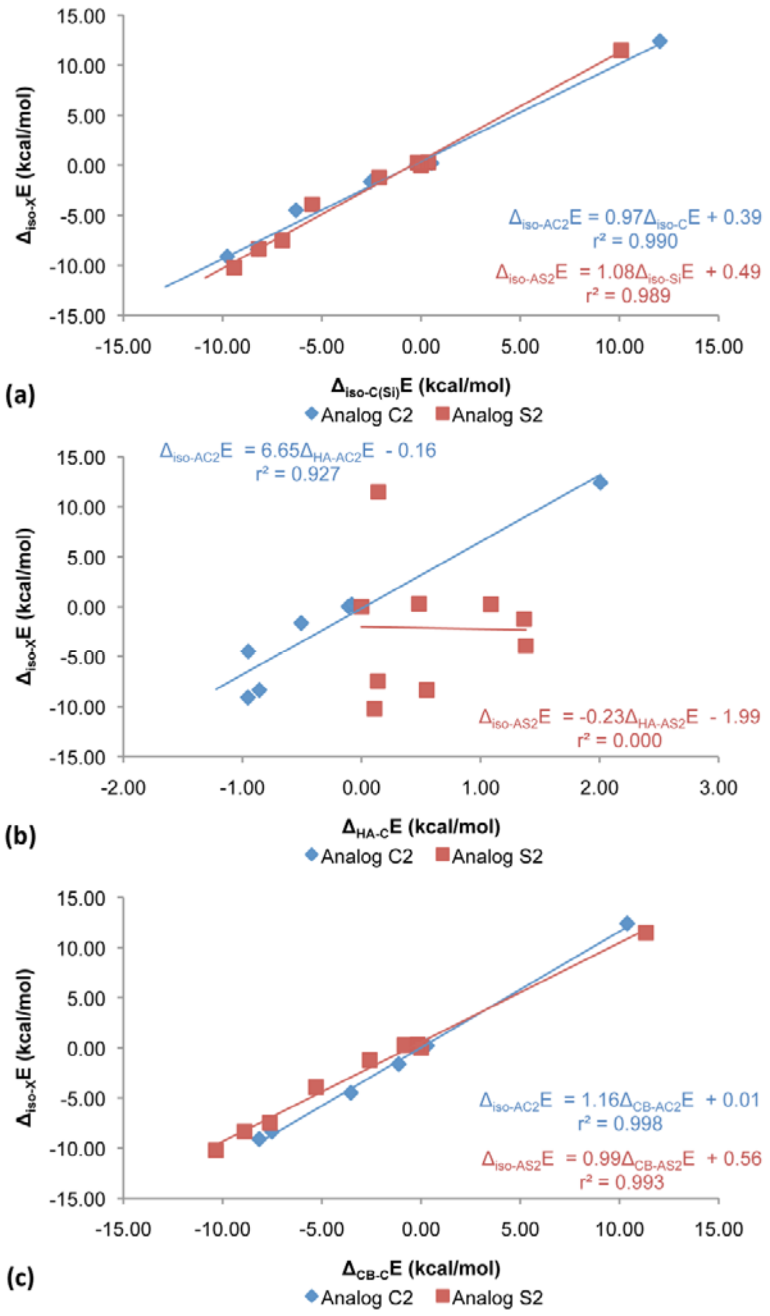


Figure 5.4. Graphical representation of the relationships between the overall reaction energy and (a) the overall reaction energies of the corresponding carbon-backbone systems, (b) the effect upon the protonated probe groups, and (c) the effect upon the deprotonated probe groups, for analogs C2 and S2. All values were calculated at the PBE0/6-31++G(d,p) level of theory.

The effect upon the deprotonated probe once again yields the best linear correlations to $\Delta_{iso}E$ (Figure 5.4c), and therefore the most control over the overall reaction. $\Delta_{HA}E$ for the analogs follows the same trends as for the all-carbon backbones (Figure 5.4b): a good relationship between $\Delta_{iso}E$ and $\Delta_{HA}E$ for the C-probe system, and no relationship for the Si-probe. However, in analog C2, $\Delta_{HA}E$ shows a destabilization in both the CH_3 and NH_2 substituted species not apparent in the carbon backbone system; there is also a destabilization of the NH_2 substituted analog C2 apparent in $\Delta_{CB}E$. The effect of substitution upon the protonated and deprotonated versions of analog S2 is the same as in the all-carbon backbone.

Similar to the all-carbon backbone systems the energy of the substituent and backbone do not appear to be affected by the substituent effect. However, the isodesmic energy of the probe group does correlate well to $\Delta_{iso}E$ (r^2=0.846 for analog C2 and 0.851 for analog S2). As seen previously, the effect in the carbon probe appears to be centered on the acidic hydrogen as shown in Figure 5.5, but there is no correlation present for analog S2. The acidic hydrogen is becoming destabilized within analog C2 as the strength of electron withdrawing group increases, but in this case the atom is more stable than in the all-carbon system by an average of 0.0005 au. **H_a** is less stable in analog S2 by an average of 0.001 au, similar to analog S1.

5.3.1.3 Analogs C3 and S3

Optimization of analog C3 under the CBS-QB3 method [B3LYP/6-311G(2d,d,p)] also results in an unexpected “rearrangement”. There is a very significant elongation in

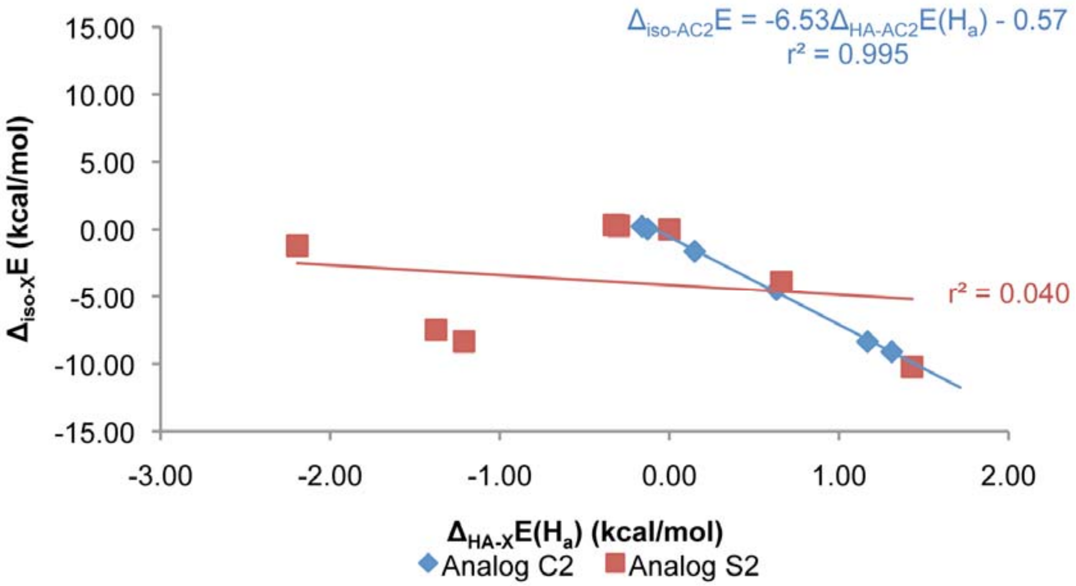


Figure 5.5. Graphical representation of the relationship between the overall reaction energy and the energy of the acidic hydrogen within analogs C2 and S2. All values were calculated at the PBE0/6-31++G(d,p) level of theory.

the backbone-probe linkage, **c2**, which resembles the loss of the probe group as carbon dioxide. This leads to difficulties in the structural optimization of the most highly electron withdrawing substituents. The elongation is also present in analog S3, but it is not as severe (lengths of the **c2** bond are given in brackets in Table 5.3). Figure 5.6 shows the elongation with comparison to the PBE0/6-31++G(d,p) structure. Although the bond length is dramatically longer (Figure 5.6a), QTAIM analysis indicates there is still a bond path between **Si$_c$** and **C$_O$**. In some cases it was still possible to solve the SCF equations, and thereby obtain an optimized structure. Table 5.3 shows the isodesmic reaction energies for those systems, and the corresponding **c2** bond length. For those systems where it was not possible to obtain a structure, the bond length is shown for the last possible optimization step. The **c2** bond length increases from minor elongation with Li (2.079 Å) to a very severe elongation with NO_2 substitution (3.695 Å, which is 1.257 Å longer than the equivalent Si–Si bond in analog S3). $\Delta_{iso}E$ for those "rearranged" systems is more negative than expected, and this difference increases with increased strength of electron withdrawing substituent. NF_2 and CN substitution is very highly negative as compared to the equivalent all-carbon backbone structure: 7.99 kcal/mol more negative for NF_2 and 5.33 kcal/mol for CN (as compared to the expected 0.86 kcal/mol and 2.67 kcal/mol, respectively, extrapolated from the PBE0/6-31++G(d,p) energies). Interestingly, we do not see this type of rearrangement in analog 1, which also features a Si atom at the **E$_c$** position. The bond lengths in the rearranged species are significantly longer in the equivalent analog 3 species. For the substituents NH_2 through NO_2 (see Table 5.3 for ordering), **c2** is an average of 1.639 Å longer than in

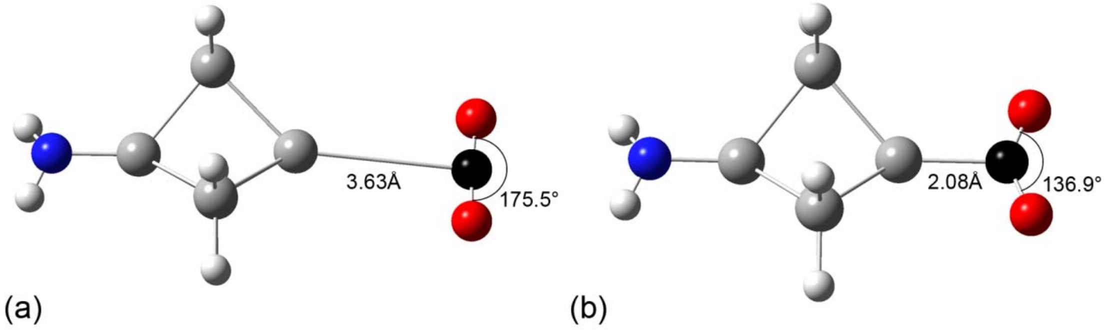


Figure 5.6. Apparent removal of the deprotonated probe segment of substituted analog C3 molecules. Shown as the NH_2-substituted CB with optimized using the (a) CBS-QB3 composite method and (b) the PBE0/6-31++G(d,p) level of theory.

Table 5.3. Isodesmic reaction energies, in kcal/mol, for the analog 3 systems, calculated using the CBS-QB3 composite method and the PBE0/6-31++G(d,p) level of theory (see Scheme 5.2 for reactions). Shown in brackets are the lengths (Å) of the backbone-probe linkage in the deprotonated species, which is elongated in the CBS-QB3 optimized structures.

Species	Substituent	CBS-QB3	PBE0/6-31++G(d,p)		
		$\Delta_{iso}E$	$\Delta_{iso}E$	$\Delta_{HA}E$	$\Delta_{CB}E$
Analog C3	Li	14.61 (2.079)	13.76 (2.024)	1.76	12.01
	CH_3	1.50 (2.167)	1.63 (2.056)	0.06	1.56
	H	0.00 (2.156)	0.00 (2.050)	0.00	0.00
	NH_2	-5.39 (3.632)	0.73 (2.080)	-0.09	0.82
	OH	-9.87 (3.651)	-2.52 (2.111)	-0.43	-2.09
	F	[a] (3.670)	-6.38 (2.143)	-0.74	-5.63
	CF_3	[a] (3.658)	-6.64 (2.083)	-0.33	-6.30
	NF_2	-17.32 (3.676)	-8.91 (2.120)	-0.51	-8.40
	CN	-15.94 (3.666)	-8.40 (2.080)	-0.51	-7.89
	NO_2	[a] (3.695)	-12.08 (2.149)	-0.60	-11.49
Analog S3	Li	12.32 (2.420)	11.64 (2.391)	-0.91	12.55
	CH_3	1.59 (2.422)	1.66 (2.395)	0.20	1.46
	H	0.00 (2.420)	0.00 (2.393)	0.00	0.00
	NH_2	1.68 (2.429)	1.58 (2.400)	0.83	0.75
	OH	-0.36 (2.435)	-0.87 (2.405)	1.26	-2.13
	F	-3.10 (2.442)	-3.79 (2.410)	1.58	-5.37
	CF_3	-5.23 (2.426)	-5.36 (2.399)	0.57	-5.93
	NF_2	-6.16 (2.435)	-6.63 (2.404)	1.13	-7.76
	CN	-6.82 (2.424)	-7.02 (2.396)	0.60	-7.62
	NO_2	[a] (2.438)	-9.19 (2.407)	1.35	-10.54

(a) Values missing due to apparent removal of deprotonated probe leading to optimization difficulties.

analog C1. The distances in the Si-probe systems are essentially equivalent with a difference of only 0.036 Å.

The PBE0/6-31++G(d,p) optimized structures do not appear to be as affected by this elongation. Although the elongation does appear to be present, all structures were able to be optimized and led to reaction energies within the expected range. The difference in the **c2** bond length between methods is significant and increases qualitatively with the strength of electron withdrawing group ($\Delta_{\text{CBS-PBE0}}$c2(Li)=0.055 Å and $\Delta_{\text{CBS-PBE0}}$c2(CN)=1.586 Å). Once again this elongation is less severe in analog S3. Even with these drastic structural differences, good correlations exist between the CBS-QB3 and PBE0/6-31++G(d,p) energies (equation 5.5 and 5.6), but the CBS-QB3 energies cannot be used as a benchmark in this case.

$$\Delta_{iso-AC3(CBS)}E = 1.43\Delta_{iso-AC3(PBE0)}E - 3.87 \quad (r^2 = 0.948, n = 7) \tag{5.5}$$

$$\Delta_{iso-AS3(CBS)}E = 1.01\Delta_{iso-AS3(PBE0)}E + 0.31 \quad (r^2 = 0.998, n = 9) \tag{5.6}$$

Just as in all other analog systems, the NH_2 group in both analog C3 and analog S3 acts as an electron donating group with a positive Δ_{iso}E. The order, and thus reactivity, of substituents is conserved with only one other exception: CN substitution of analog C3 results in a smaller negative Δ_{iso}E than NF_2 substitution. The reaction energies for the analogs show good correlation to their carbon-backbone counterparts. The reaction constant (Figure 5.7a) indicates that analog 3 is less sensitive to substitution than the all-carbon backbones. Similar to analog 1, ρ for analog C3 and S3 are comparable in magnitude. As in all other systems, the overall reaction energy is

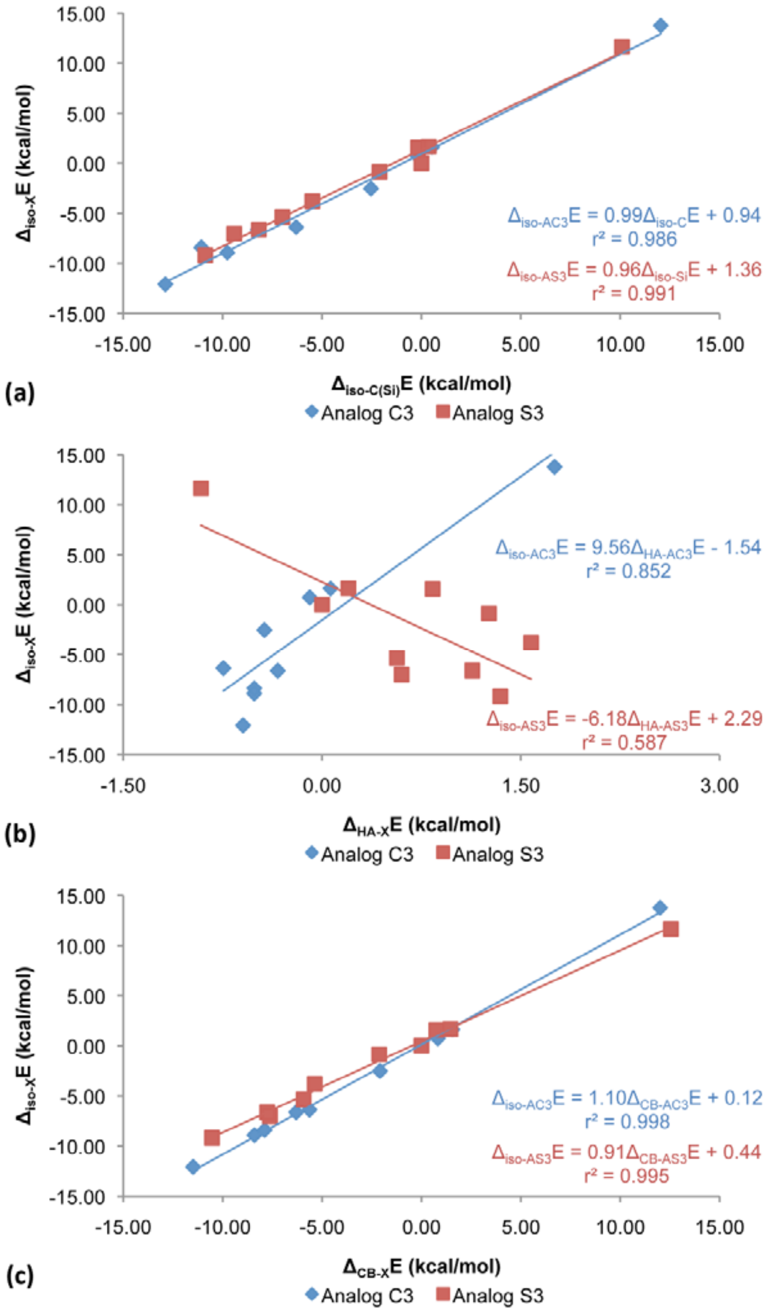


Figure 5.7. Graphical representation of the relationships between the overall reaction energy and (a) the overall reaction energies of the corresponding carbon-backbone systems, (b) the effect upon the protonated probe groups, and (c) the effect upon the deprotonated probe groups, for analogs C3 and S3. All values were calculated at the PBE0/6-31++G(d,p) level of theory.

controlled by the effect on the deprotonated probe, as apparent by the almost perfect correlations between $\Delta_{iso}E$ and $\Delta_{CB}E$ (Figure 5.7c, r^2=0.998 for analog C3 and r^2=0.995 for analog S3). NH_2 substitution in both analog C3 and S3 result in the destabilization of the conjugate base species as previously observed. The swap in ordering of CN and NF_2 is also apparent in $\Delta_{CB}E$ for both species. Analog C3 shows a good relationship between $\Delta_{HA}E$ and the reaction energy (see Figure 5.7b), analog S3 does not, consistent with the effect on the all-carbon backbone. Contrary to the result in the all-carbon backbone, NH_2 substitution in analog C3 and Li substitution in analog S3 cause a destabilization of the acid species.

The atomic energies in analog 3 behave in essentially the same fashion as in the all-carbon backbone systems. There is no relationship between $\Delta_{iso}E$ and the energy of either the substituent or the backbone, but the isodesmic energy of the probe does relate well. The relationship is good in analog S3 (r^2=0.868), but only fair within analog C3 (r^2=0.699). Again the effect on the probe is mainly centered on the energy of the acidic hydrogen. Although the trend is the same as observed in the all-carbon backbone (the destabilization with increased strength of electron withdrawing group, see Figure 5.8), the acidic hydrogen within analog C3 is less stable by an average of 0.001 au. A fair relationship exists between $\Delta_{iso}E$ and the energy of $\mathbf{H_a}$ in analog S3 (r^2=0.772), in contrast to the all-carbon backbone (r^2=0.522). $\mathbf{H_a}$ is also less stable by an average of 0.003 au. As a whole, the probe segment in analog S3 is becoming more stabilized within the molecule as the strength of electron withdrawing group, or acidity of the system, increases.

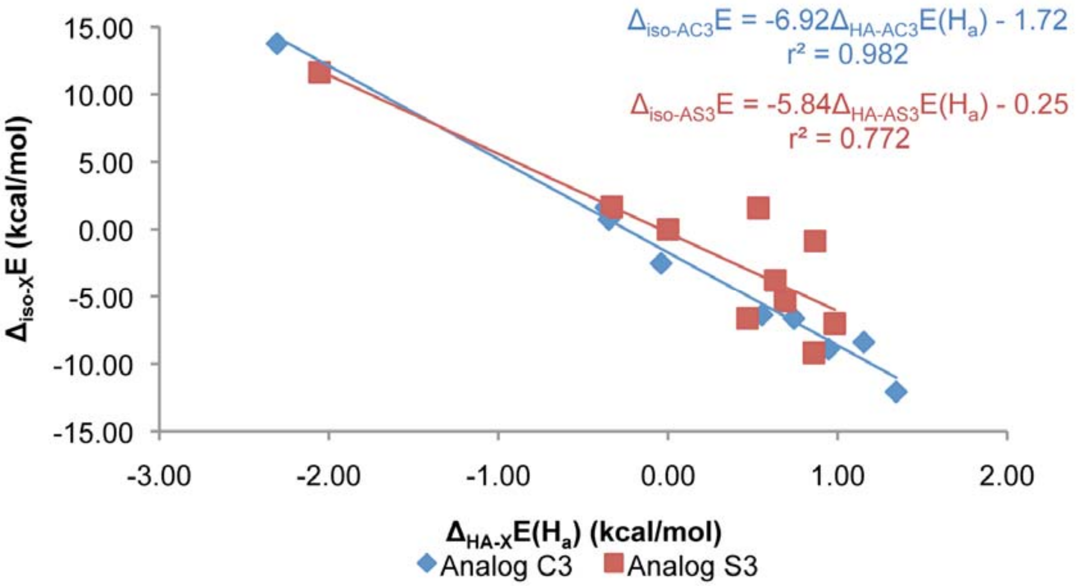


Figure 5.8. Graphical representation of the relationship between the overall reaction energy and the energy of the acidic hydrogen within analogs C3 and S3. All values were calculated at the PBE0/6-31++G(d,p) level of theory.

5.3.2 Structure and Critical Points in the Electron Density

5.3.2.1 Analogs C1 and S1

Structurally silicon differs from carbon in that it has a greater atomic radius and, therefore, should form bonds with longer lengths. In analog 1, the bonds between the silicon at the bridgehead position and the carbon at the bridging position (**b1** and **b2**, see Scheme 5.3) are both on average 0.364 Å longer than their counterparts in the all-carbon backbone. Figure 5.9a shows the relative **b1** distance for each probe (value for the all-carbon system subtracted from the value for the analog system); **b2** shows essentially the same trend. These two distances both show good correlation to $\Delta_{iso}E$ (for both probes) corresponding to a decrease in length for **b1** and an increase in length for **b2** with increasing strength of electron withdrawing group. The trend is the same as seen in the carbon backbones, but the relationship with **b1** in the C-system is missing (see Section 3.4.4), and the relationships are only minor in the Si-system (see Section 4.4.4).

As a result, the interbridgehead distance, **a**, is also longer in the analog system by an average of 0.407 Å in analog C1 and 0.414 Å in analog S1 (Figure 5.9b; the differences between probe systems are mainly attributable to the Li-substitution, the backbone rigidity is maintained for all other substituents). Although unrelated in analog C1, **a** forms a good relationship with $\Delta_{iso}E$ in analog S1, in both cases opposite to what is seen for the all-carbon backbone. In the all carbon system length **a** was controlled by the pyramidalization at $\mathbf{E_a}$ (termed Dev(E_a) for brevity, see equation 5.7 and Figure 5.10), which appears to be the case for analog S1 only.

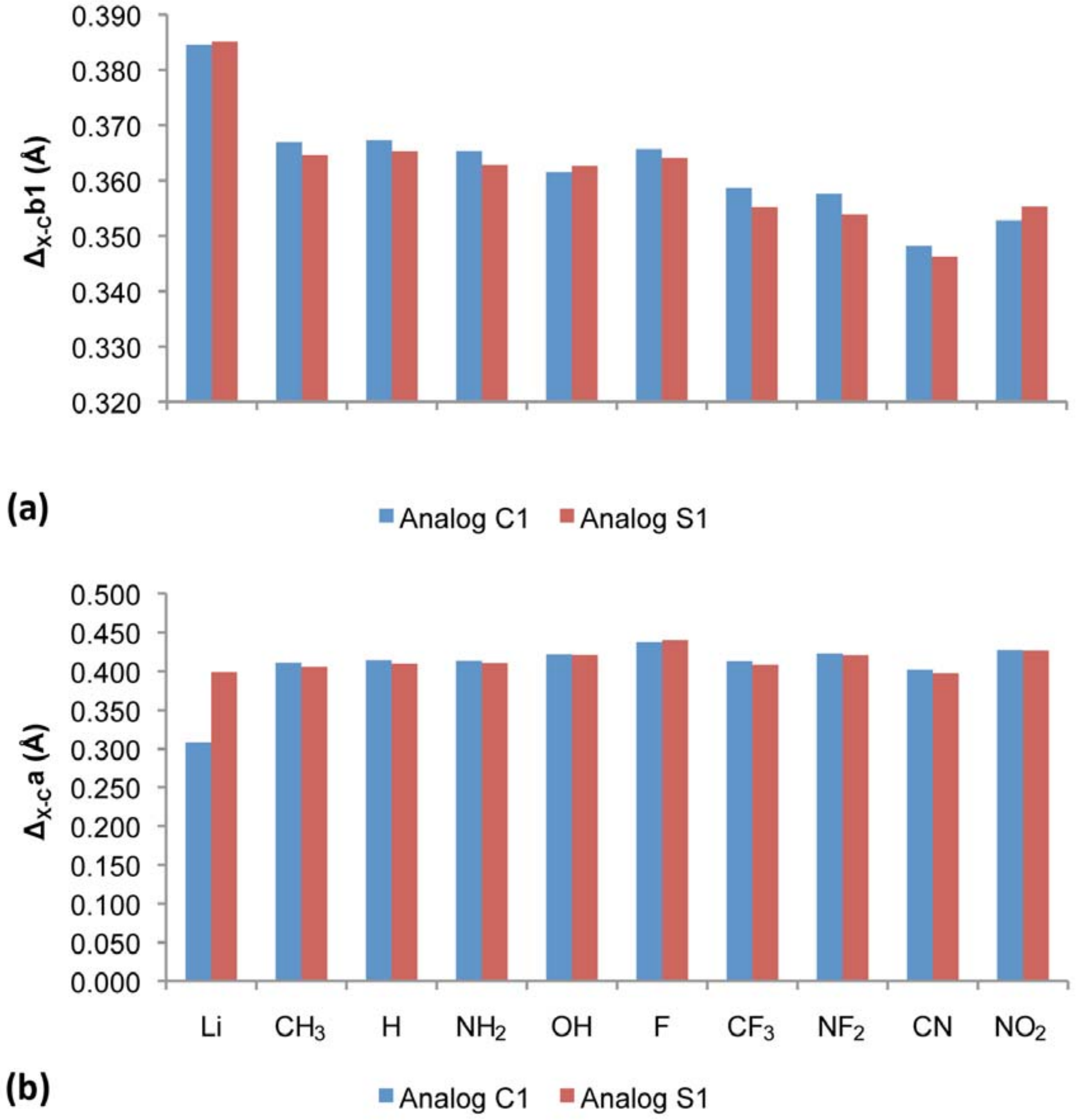


Figure 5.9. Graphical representations of the differences between the lengths (a) **b1**, and (b) **a**, in analog C1 and S1 as compared to the all-carbon backbones (see Scheme 5.3 for labelling). All values were optimized at the PBE0/6-31++G(d,p) level of theory.

$$\begin{aligned} Dev(E_a) = 360^\circ \\ - [\theta(E'_b - E_a - E'_5) + \theta(E'_5 - E_a - E'_8) \\ + \theta(E'_8 - E_a - E'_b)] \end{aligned} \tag{5.7}$$

However, as illustrated in Figure 5.10a, the pyramidalization is related to $\Delta_{iso}E$ for both analogs and follows the trend outlined by the all-carbon backbone: $\mathbf{E_a}$ is more planar in those species with stronger electron withdrawing groups. Replacement with analog 1 leads to a less pyramidal $\mathbf{E_a}$ as apparent in Figure 5.10b. As expected, the linkage between the backbone and probe (**c2**) is also longer by an average of 0.438 Å in analog C1 and 0.484 Å in analog S1. All bond length increases are in contrast to the reaction constant, which suggests that the reactions with analog 1 are more sensitive to substitution, given that the inductive effect is supposed to diminish with distance.

It is generally accepted that there exists a relationships between the length of a bond and the electron density (ρ) at the bond critical point (BCP; shown in red in Scheme 5.3),[82,83] and therefore it should be possible to use ρ(BCP) to examine subtle structural effects. In the carbon system, the only BCPs that had a relationship between their electron density and the substituent effect were those between the bridging carbons and their attached hydrogen atoms.[89] These relationships are also present in the silicon analogs, but they are not the only ones. ρ along the backbone in analog 1 shows good relationships at almost every BCP. ρ(BCP2) and its equivalents (between E_a and E_5, and E_a and E_8) all show good relationships which correspond to an increase in density with increasing strength of electron withdrawing group; whereas, ρ(BCP3) and its equivalents show the opposite trend. Even the density at BCP4 shows a good

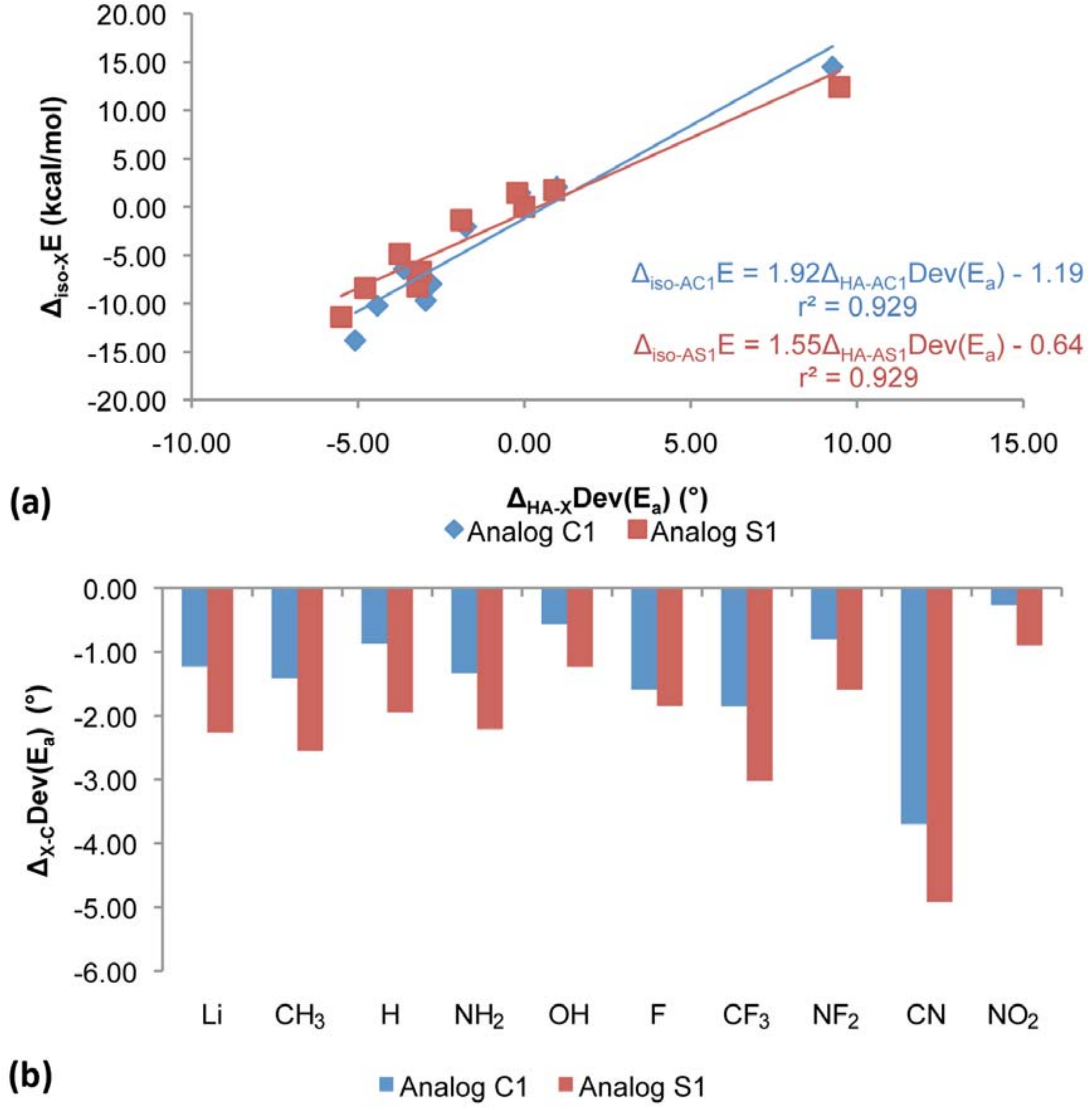


Figure 5.10. Graphical representations of (a) the relationship between the overall reaction energy and the deviation of $\mathbf{E_a}$ from planarity, and (b) the difference, between the analog systems and the all-carbon system, of the deviation of $\mathbf{E_a}$ from planarity, in both analog C1 and analog S1. All values calculated at the PBE0/6-31++G(d,p) level of theory.

relationship to the substituent effect in analog C1 (absent in the all-carbon system and analog S1). Just as with length **a**, the electron density at the cage critical point (CCP; shown in green in Scheme 5.3) correlates well with $\Delta_{iso}E$, this time for both probe groups. With very few exceptions, the analog systems appear to have less density within the bonds than the all-carbon systems.

Although the probe segment was kept constant through all systems, any difference in transmission through the backbone should be reflected within the probe. All structural features within the probe group of analog C1 show good relationships with $\Delta_{iso}E$, as expected from the all carbon system. Although the strength of the linear correlations may not be the same, the trends in bonds lengths are conserved through all replacement of the backbone. Both the C_O–O and the C_O–O_H bonds decrease in length with increasing strength of electron withdrawing group, or acidity, corresponding to the redistribution of charge upon deprotonation. As expected the length of the O_H–H bond increases with increasing acidity, congruent with the destabilization of the acidic hydrogen. The C–O bond lengths are minutely shorter in the analog system as in the all-carbon, and the O–H bond lengths are minutely longer. All bonds show a decrease in density with respect to the all-carbon system, regardless of effect upon length.

In analog S1, the only bond length which forms a good relationship to $\Delta_{iso}E$ is between $\mathbf{Si_O}$ and $\mathbf{O_a}$, consistent with the all-carbon backbone. The use of the silicon based backbone results in a decrease in the length as compared to the all-carbon backbone. Another difference between Si and C is silicon’s ability to expand its coordination to 5 or 6, moving from a tetrahedral structure to a trigonal bipyramidal

(TBP) center. The pyramidalization at **Si$_O$**, defined in equation 5.8, can be used as a measure of this, with 31.5 ° corresponding to an ideal tetrahedral structure and 0 ° corresponding to a TBP center.

$$\begin{aligned} Dev(Si_O) = 360° \\ - [\theta(O_a - Si_O - O_b) + \theta(O_b - Si_O - O_c) \\ + \theta(O_c - Si_O - O_a)] \end{aligned} \tag{5.8}$$

In the all-carbon backbone, an increase in the strength of electron withdrawing group resulted in a more planar **Si$_O$**, suggesting an increase in TBP character. This is conserved in analog S1, but the use of a silicon based backbone results in a more tetrahedral probe, as seen in Figure 5.11, with the exception of the unsubstituted species.

5.3.2.2 Analogs C2 and S2

Although unrelated to $\Delta_{iso}E$, the linkage between substituent and backbone (**c1**; see Scheme 5.3) in analog 2 is generally shorter than in the all carbon system by an average of 0.022 Å in analog C2 and 0.007 Å in analog S2 as illustrated in Figure 5.12a. The shorter bond length is accompanied by a greater electron density at the bond critical point (BCP1). Although the difference in bond length shows no relationship to the substituent effect, $\Delta_{X-C}\rho$(BCP1) in the acid molecules does show a fair linear correlation (r^2=0.766 for analog C2 and r^2=0.882 for S2). This is surprising given that no relationship is present for BCP1 in the all-carbon system or any other analog. Just as with **c1**, **c2** is shorter in analog 2 by an average of 0.019 Å with the C-probe and 0.026 Å with the Si-probe.

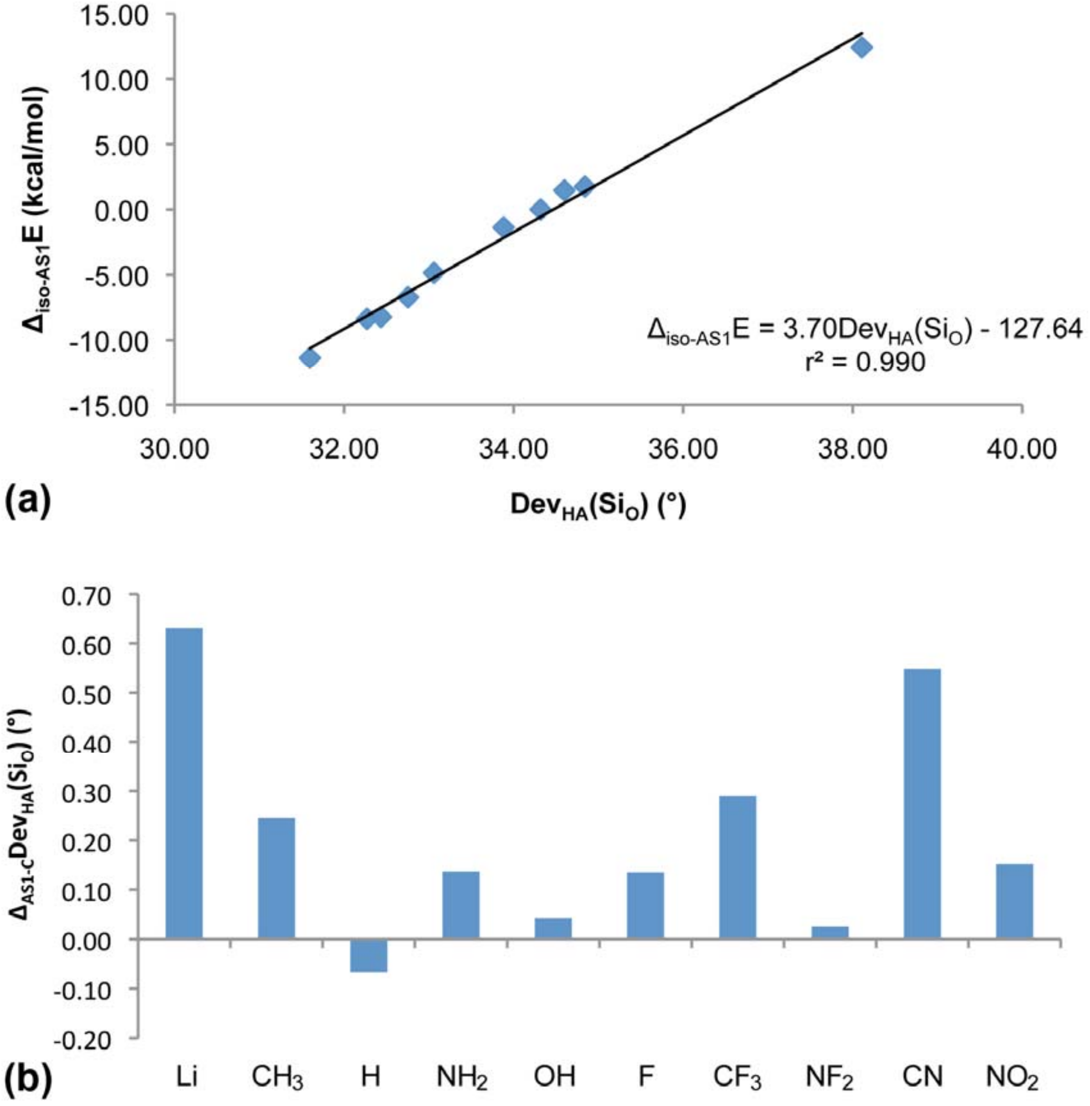


Figure 5.11. Graphical representations of (a) the relationship between the overall reaction energy and the deviation of **Si_O** from planarity, and (b) the difference, between the analog system and the all-carbon system, of the deviation of **Si_O** from planarity, in analog S1. All values calculated at the PBE0/6-31++G(d,p) level of theory.

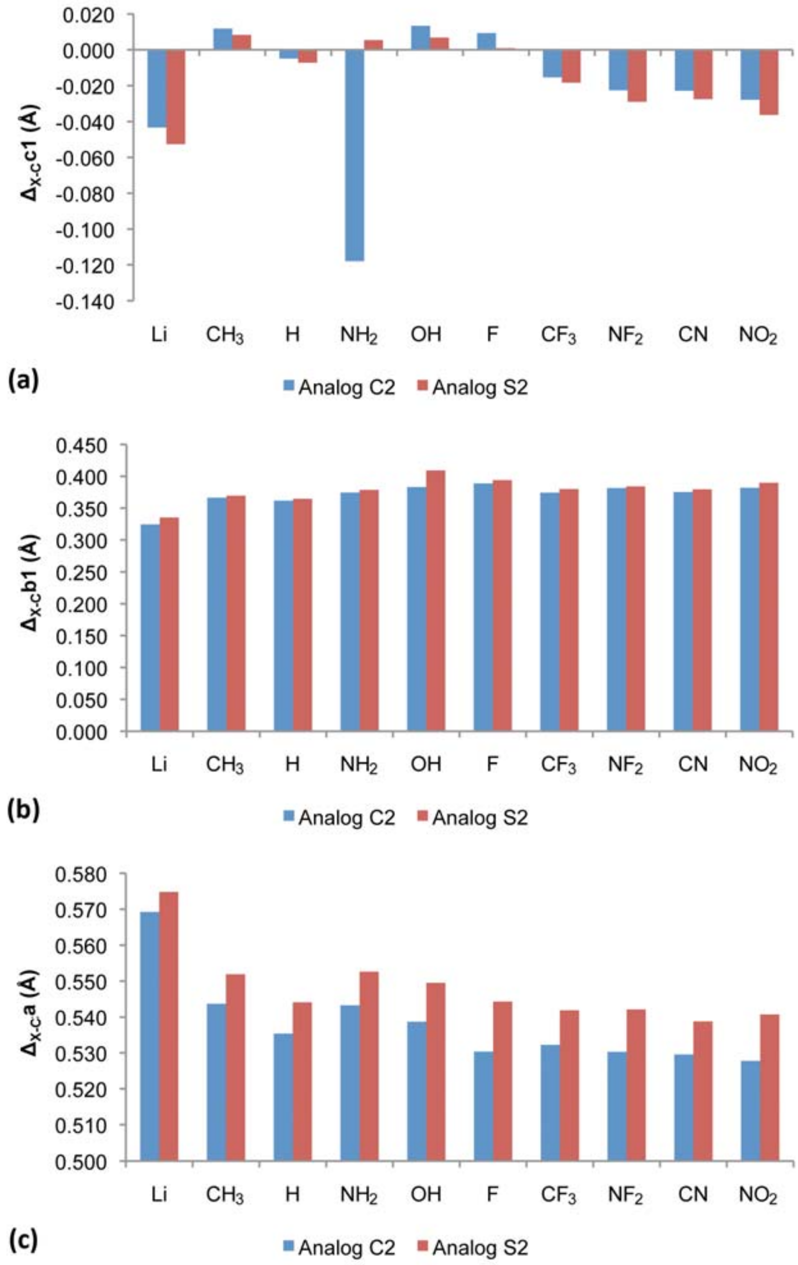


Figure 5.12. Graphical representations of the differences between the lengths (a) **c1**, (b) **b1**, and (c) **a**, in analogs C2 and S2 as compared to the all carbon backbones (see Scheme 5.3 for labelling). All values were optimized at the PBE0/6-31++G(d,p) level of theory.

The Si–C bonds in analog 2 (**b1** and **b2**) are both longer than their C–C counterparts in the all-carbon backbone, as expected due to the increase in atomic radius (by an average of 0.371 Å in analog C2 and 0.365 Å in analog S2). The relative **b1** distance for each probe is shown in Figure 5.12b. Just as in the all-carbon system, these two distances do not show correlation to $\Delta_{iso}E$. The only internal coordinate to show any relationship to the reaction energy is the distance between bridgehead atoms, **a**. In analog C2 the relationship is better than in the all-carbon system (r^2=0.843), but corresponds to the same trend: a decrease in length as the strength of electron withdrawing group increases. As expected, **a** is longer in the analogs than in the all carbon system by an average of 0.538 Å in analog C2 and 0.548 Å in S2 (Figure 5.12c). **a** is controlled by the pyramidalization at $\mathbf{E_a}$: as $\mathbf{E_a}$ becomes more planar, **a** decreases. The correlation between $\Delta_{iso}E$ and **Dev($\mathbf{E_a}$)** for analog C2 is good (r^2=0.842), as shown in Figure 5.13a, but poor for analog S2 (r^2=0.654). As illustrated in Figure 5.13b, $\mathbf{E_a}$ becomes more planar with the use of the analog 2 backbone.

The relationships with the structure of the probe segment are conserved upon replacement with analog C2. Both C–O bonds decrease in length and the O_H–H bond increases in length with the electron withdrawing strength of substituent. The use of analog 2 causes an elongation of the C–O bonds and a reduction in the length of the O_H–H bond as compared to the all-carbon backbone. The only property conserved within analog S2 is the pyramidalization at $\mathbf{Si_O}$, which results in a more planar probe with the silicon-based backbone, as shown in Figure 5.14. This suggests the silicon in the backbone induces more tetrahedral structure in the probe. In the same manner as the

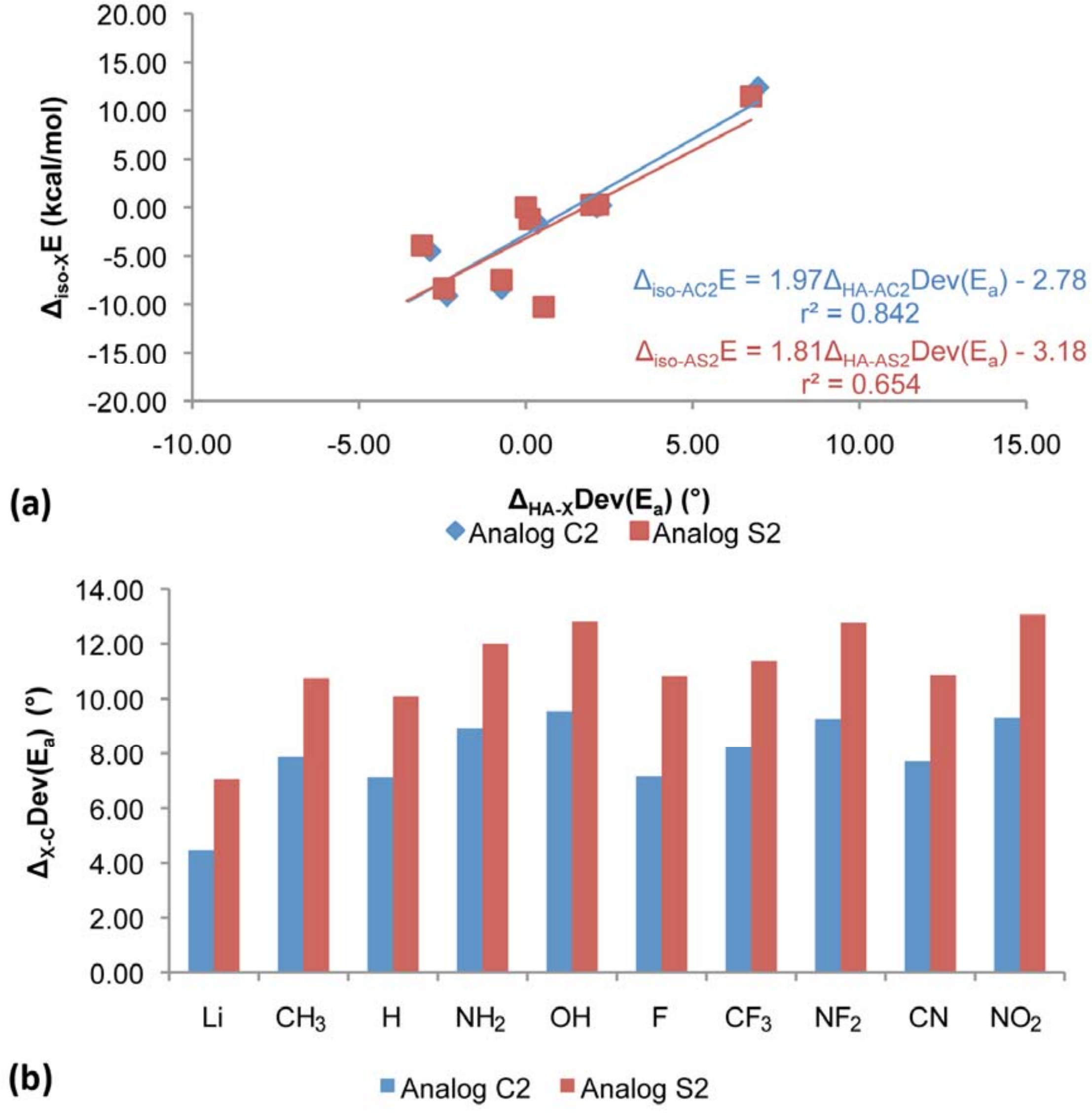


Figure 5.13. Graphical representations of (a) the relationship between the overall reaction energy and the deviation of $\mathbf{E_a}$ from planarity, and (b) the difference, between the analog systems and the all-carbon system, of the deviation of $\mathbf{E_a}$ from planarity, in both analog C2 and analog S2. All values calculated at the PBE0/6-31++G(d,p) level of theory.

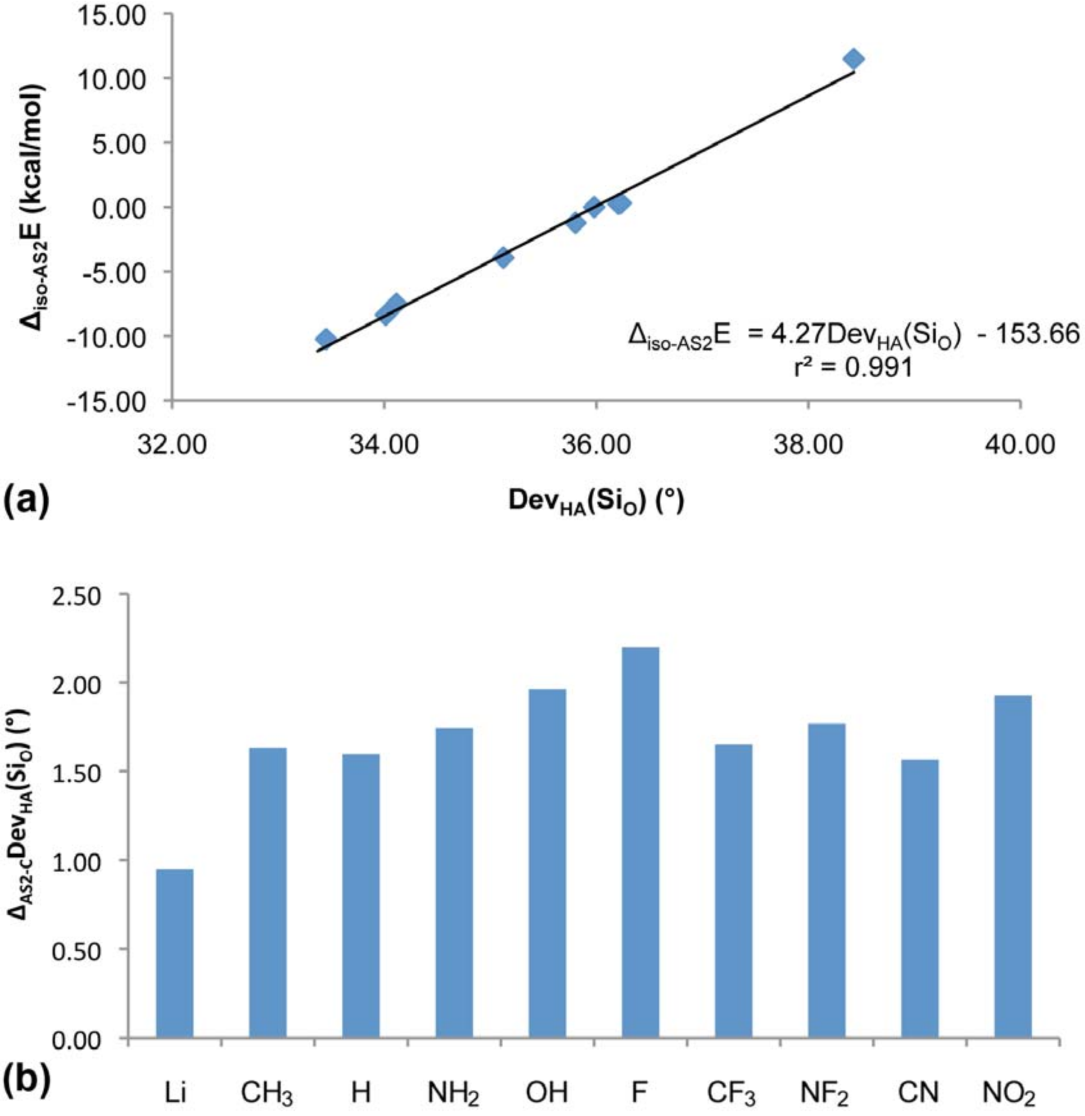


Figure 5.14. Graphical representations of (a) the relationship between the overall reaction energy and the deviation of **Si_O** from planarity, and (b) the difference, between the analog systems and the all-carbon system, of the deviation of **Si_O** from planarity, in analog S2. All values calculated at the PBE0/6-31++G(d,p) level of theory.

other systems, as the substituent becomes more electron withdrawing, the probe group becomes more planar. Analog 2 is more similar to the all-carbon system in that, apart from the bonds between the bridging atoms and hydrogen atoms, only ρ(BCP2) within the backbone shows a good relationship to $\Delta_{iso}E$. The BCPs within the probe of analog C2 also show good correlations, corresponding to an increase in density at BCP5 and BCP6, and a decrease in density at BCP7, with increase strength of electron withdrawing group. Unlike in the all-carbon system, there are no relationships between $\Delta_{iso}E$ and the BCPs within the probe group of analog S2.

5.3.2.3 Analogs C3 and S3

As analog 3 represents the complete conversion from a carbon-based backbone to a silicon-based backbone, it is expected that all bond length should be longer. In fact, the lengths of the Si–Si bonds are about twice as long as the C–Si bonds present in the other analogs. The **b1** and **b2** bonds are an average of 0.799 Å longer in analog C3 and 0.795 Å in analog S3 (Figure 5.15a shows the trend for **b1**). These two distances both show good correlations with $\Delta_{iso}E$, even though that is not true in the all-carbon backbone (relationships for **b1** in the C-probe and both in the Si-probe are missing). With increased strength of electron withdrawing substituent it is evident that **b1** decreases in length while **b2** increases in length.

The distance between bridgehead atoms, **a**, is also longer by an average of 1.003 Å in analog C3 and 1.033 Å in analog S3. The difference decreases with increased acidity, as detailed in Figure 5.15b, and forms a good linear correlation with $\Delta_{iso}E$. The

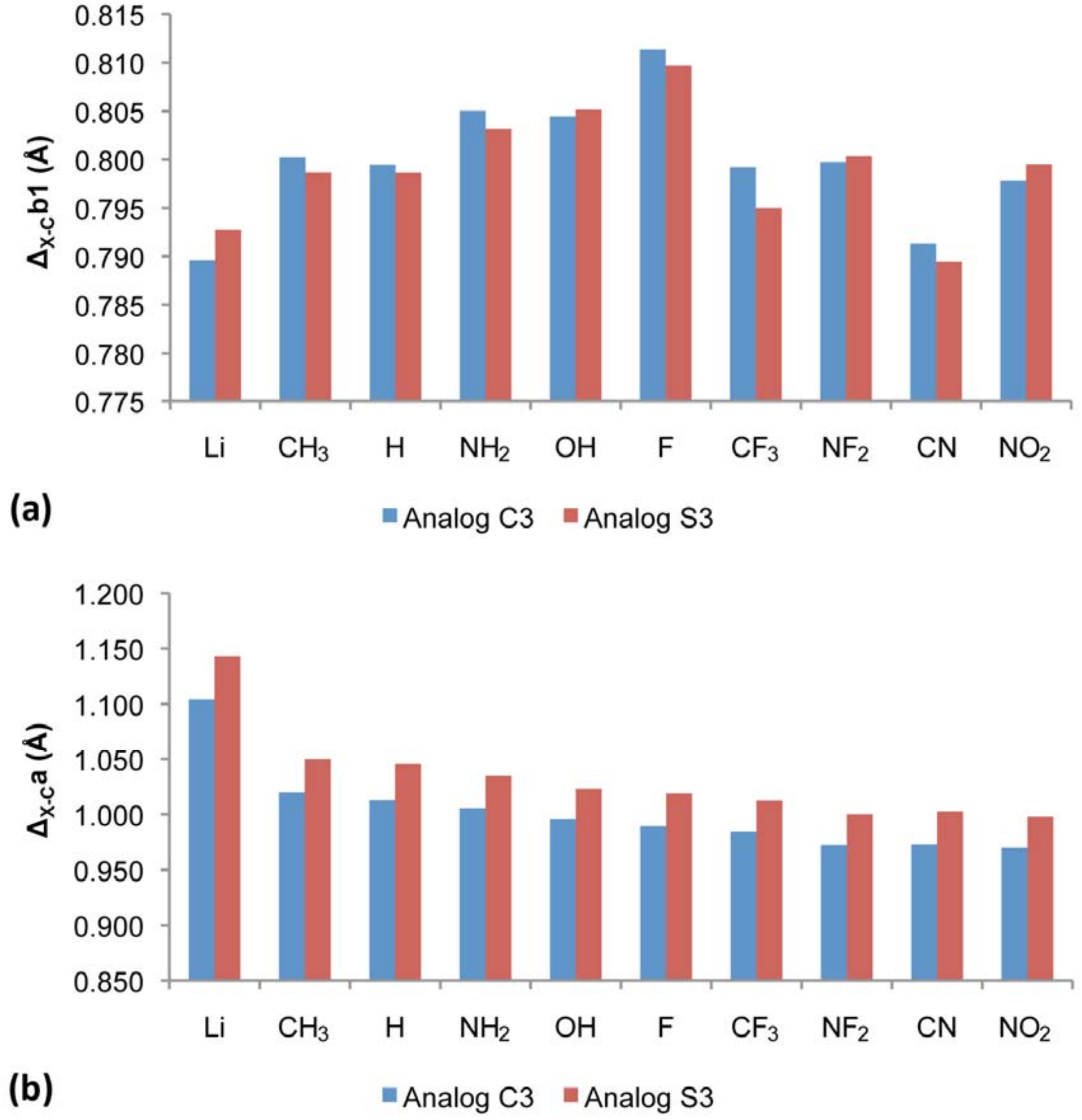


Figure 5.15. Graphical representations of the differences between the lengths (a) **b1**, and (b) **a**, in analog C3 and S3 as compared to the all carbon backbones (see Scheme 5.3 for labelling). All values were optimized at the PBE0/6-31++G(d,p) level of theory.

absolute distance also correlates well with the reaction energy in both cases, something not observed in the all- carbon backbone with Si-probe. The length of **a** decreases with increased strength of electron withdrawing group, controlled by a decrease in the pyramidalization at $\mathbf{E_a}$ (r^2 between **a** and $\mathbf{Dev(E_a)}$ is 0.996 for analog C3 and 0.997 in analog S3). As shown in Figure 5.16a, $\mathbf{Dev(E_a)}$ forms very good relationships with $\Delta_{iso}E$ in analog 3. In both systems, an increased electron withdrawing character of the substituents leads to a more planar bridgehead atom. The replacement of silicon atoms within the probe yields a less planar, or more tetrahedral, $\mathbf{E_a}$.

Just as in analog 1, both **c1** and **c2** are longer than in the all-carbon backbone. As if unaffected by the nature of the bridging atom the relative values of **c1** are very similar (0.373 Å versus 0.378 Å with the C-probe and 0.373 Å versus 0.375 Å for the Si-probe, in analog 1 and analog 3, respectively). Neither shows any relationship to the substituent effect. Within the probe segment itself, analog C3 follows the same trends as in the all-carbon backbone, but analog S3 does not. Just as in analog S2, the only parameter which shows a good relationship to $\Delta_{iso}E$ is $\mathbf{Dev(Si_O)}$. This relationship corresponds to an increase in the TBP character of the probe group as the electron withdrawing strength of the substituent increases (Figure 5.17a). With respect to the all-carbon backbone, the relative $\mathbf{Dev(Si_O)}$ also shows a good relationship with the substituent effect, moving from more planar to more tetrahedral with increased acidity (Figure 5.17b).

The trends for the electron density at the BCPs appear to be conserved within analog C3, apart from the addition of a relationship at BCP4 and the CCP. Both

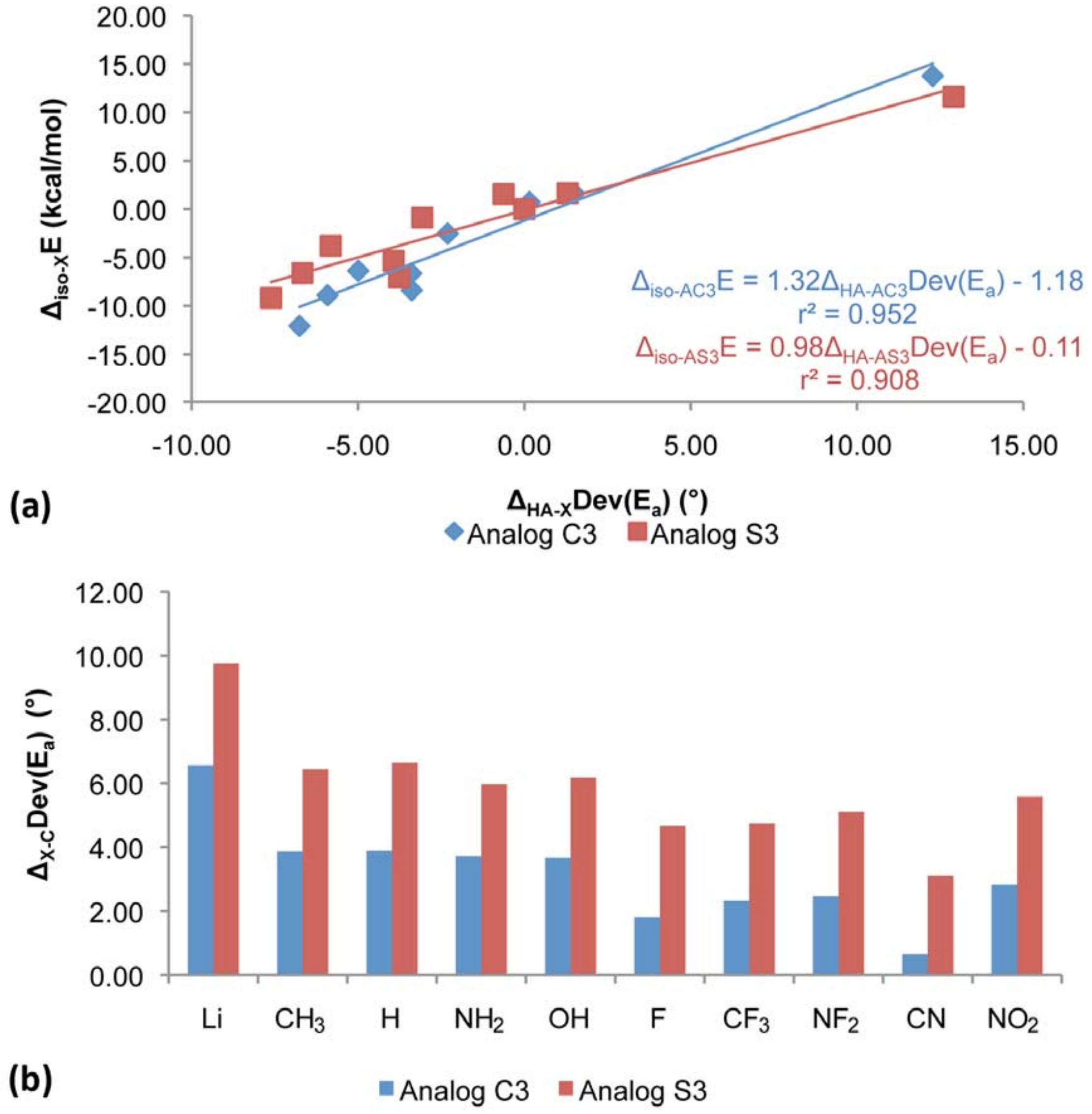


Figure 5.16. Graphical representations of (a) the relationship between the overall reaction energy and the deviation of $\mathbf{E_a}$ from planarity, and (b) the difference, between the analog systems and the all-carbon system, of the deviation of $\mathbf{E_a}$ from planarity, in both analog C3 and analog S3. All values calculated at the PBE0/6-31++G(d,p) level of theory.

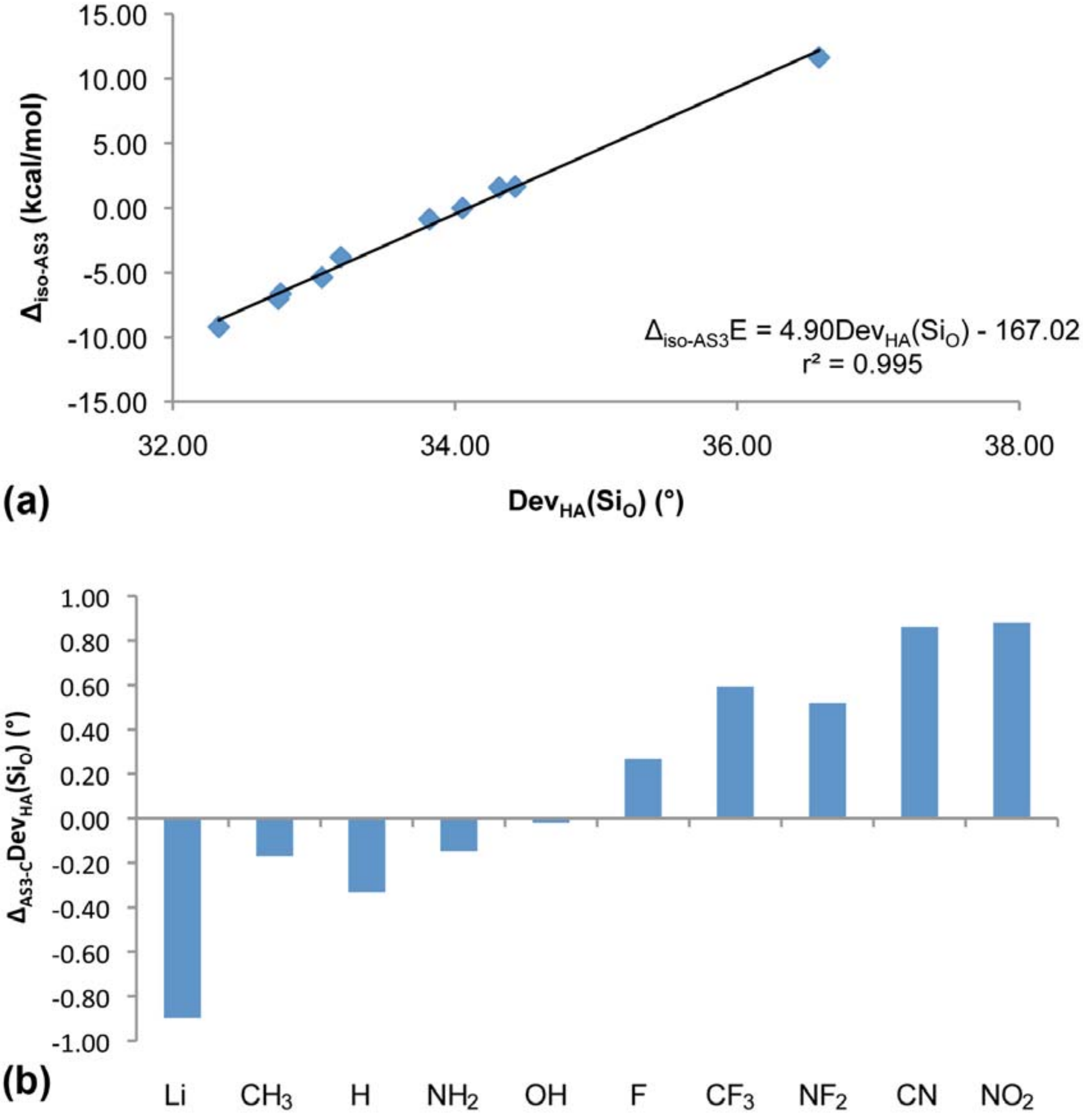


Figure 5.17. Graphical representations of (a) the relationship between the overall reaction energy and the deviation of **Si_O** from planarity, and (b) the difference, between the analog systems and the all-carbon system, of the deviation of **Si_O** from planarity, in analog S3. All values calculated at the PBE0/6-31++G(d,p) level of theory.

relationships correspond to an increase in density with increased acidity. ρ(CCP) also correlates well with the substituent effect in analog S3, but the relationships within the probe segment are missing. Just as in the other analog systems, replacement with silicon atoms within the backbone results in less density within the bonds as compared to the all-carbon system.

5.3.3 Atomic Charges and Delocalization Index

Since the "so-called" inductive effect is the transmission of electron density through a molecular system, the charges on the atoms should be affected as well as the bonds. There should be a large effect on the terminal atom, **E$_a$**, but according to the definitions of both mechanisms of transmission the effect should decay with increasing distance from the substituent. This is seen in all analog systems, but it does not relate to the substituent effect (see Figures A1.3 to A1.5). In QTAIM, the atomic charge is defined as in equation 5.9, where Z_Ω is the nuclear charge and N(Ω) gives the total number of electrons.

$$q(\Omega) = Z_\Omega - N(\Omega) = Z_\Omega - \int_\Omega \rho(r)d\tau \tag{5.9}$$

We have previously used the delocalization index (DI) as a description of communication between the substituent and probe. Defined in equation 5.10 where F^α and F^β are the sum of the overlap integrals for atoms A and B, the DI represents the average number of electrons shared between two atoms. As with all other QTAIM properties, the specific atomic values can be summed to give the value over a segment within the molecule.

$$DI(A,B) = 2\left|F^{\alpha}(A,B)\right| + 2\left|F^{\beta}(A,B)\right| \tag{5.10}$$

5.3.3.1 Analogs C1 and S1

The overall charge of the substituent also has little relationship with the reaction energies of the systems. However, the charge of the substituent in the all-carbon backbone appears to be indicative of the electron donating or electron withdrawing nature of the substituent. Both Li and CH_3 have an overall positive charge, consistent with an electron donating effect; whereas all other substituents have an overall negative charge, consistent with an electron withdrawing effect. Interestingly, the methyl group appears to be acting as an electron withdrawing group in the both analog 1 conjugate base molecules. With analog 1, the Li group is the only substituent to have an overall positive charge and all others are operating to withdraw electron density to themselves. In both cases the analog backbone appears to decrease the charge on the substituent, with respect to the all-carbon backbone, as if the bridgehead silicon atom is donating more electron density to the substituent.

Due to the atomic replacements, there are significant differences between the charges on the backbone atoms and which charges correlate well with the reaction energy. Although the backbone as a whole does not relate to the reaction energy, the charges of the hydrogen atoms attached to the bridging carbons ($\mathbf{H_3}$, $\mathbf{H_4}$, and equivalents) in the all-carbon backbones all show good linear correlations with $\Delta_{iso}E$. This trend is conserved within all analogs, and corresponds to the atom becoming more positive with increased acidity. The main differences occur within the $\mathbf{E}^{(\prime)}$ atoms themselves. In the carbon system the charges on the bridging atoms show fair relationships with the reaction energy. This is not the case in analog 1. The Si bridgehead atoms (**E$_a$** and **E$_c$**) have a positive charge of about 2.7 au, but the neighbouring C atoms feature a negative charge (approximately -1.3 au), consistent with the electronegativity difference between both atoms. As may be expected, the bridgehead atoms have a more positive charge in analog 1, as shown in Figure 5.18a for **E$_a$** and Figure 5.19a for **E$_c$**, as compared to the all-carbon backbone. With replacement of the bridgehead atoms, the remaining carbon atoms (**C$_b$**, **C$_5$**, and **C$_8$**), have a significantly decreased charge as illustrated in Figure 5.18b (in the all-carbon system the atoms have a positive charge). Although their absolute values do not, the relative (all-carbon value subtracted from analog value) charges in the bridging atoms do show good relationships to the substituent effect.

Both species of analog 1 also show good relationships with the charge at the opposite bridgehead atom, **E$_c$**, and the reaction energy, something not seen in the all carbon system with C-probe **E$_c$** is becoming more negative with increase acidity as detailed in Figure 5.19b, suggesting that some aspect of the charge transmission is passing through this atom. Both bridgehead Si atoms are more positive than their carbon backbone counterparts by approximately 2.4 au at **E$_a$** and 2.7 au at **E$_c$**.

Any change in the transmission of the substituent effect should also be reflected in the charge on the probe segment. Similar to the carbon system, the total charge on the protonated probe group shows very good linear correlations with $\Delta_{iso}E$ as illustrated in Figure 5.20a. The probe group is becoming more positive, or less negative, with

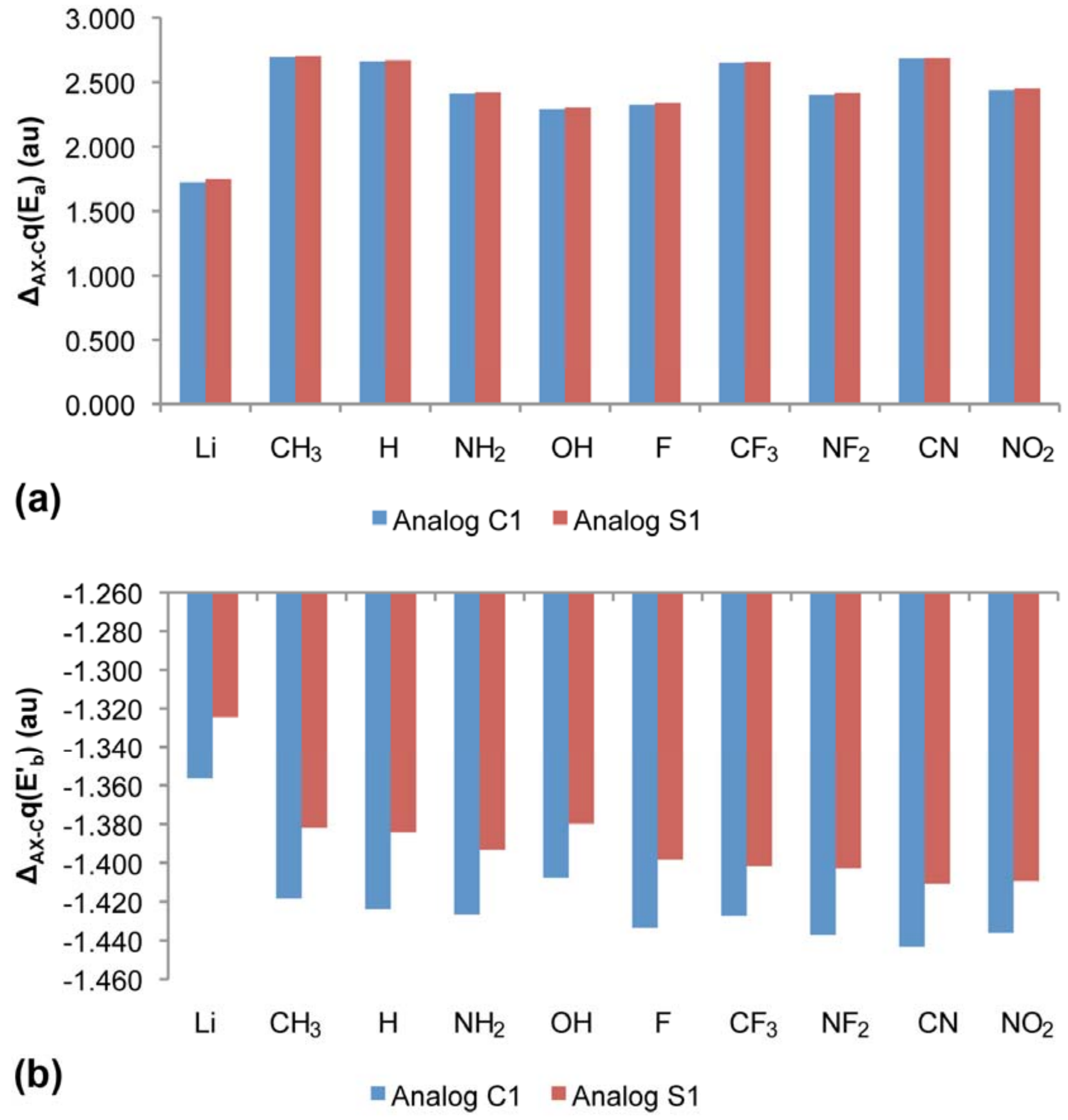


Figure 5.18. Graphical representations of the differences, between the analog systems and the all-carbon backbones, of the charges of (a) the forward bridgehead atom, E_a, and (b) the bridging atom, E'_b, in both analog C1 and analog S1. All values calculated at the PBE0/6-31++G(d,p) level of theory.

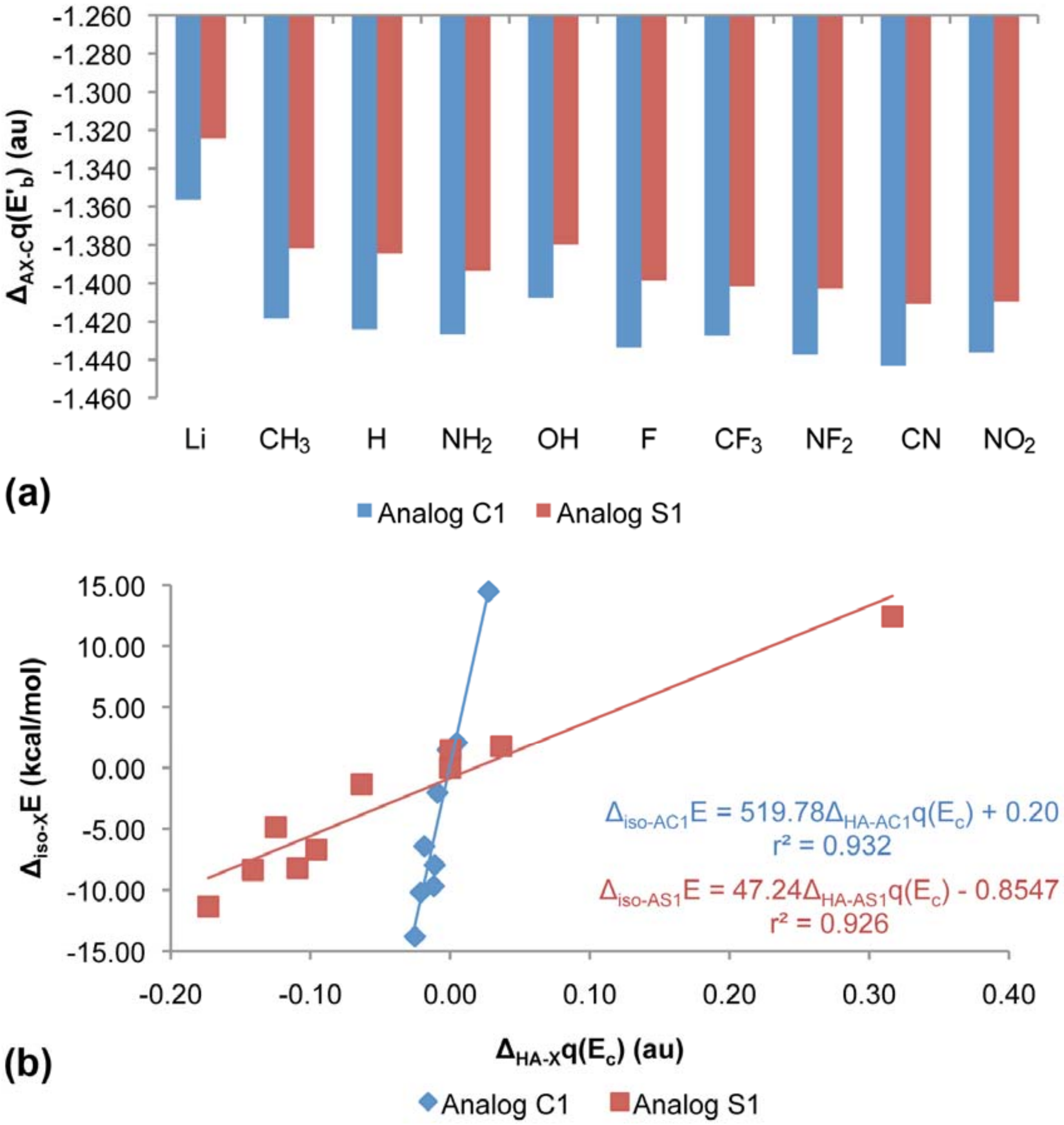


Figure 5.19. Graphical representations of (a) the difference, between the analog systems and the all-carbon system, of the charge on $\mathbf{E_c}$, and (b) the relationship between the overall reaction energy and the charge on $\mathbf{E_c}$, in both analog C1 and analog S1. All values calculated at the PBE0/6-31++G(d,p) level of theory.

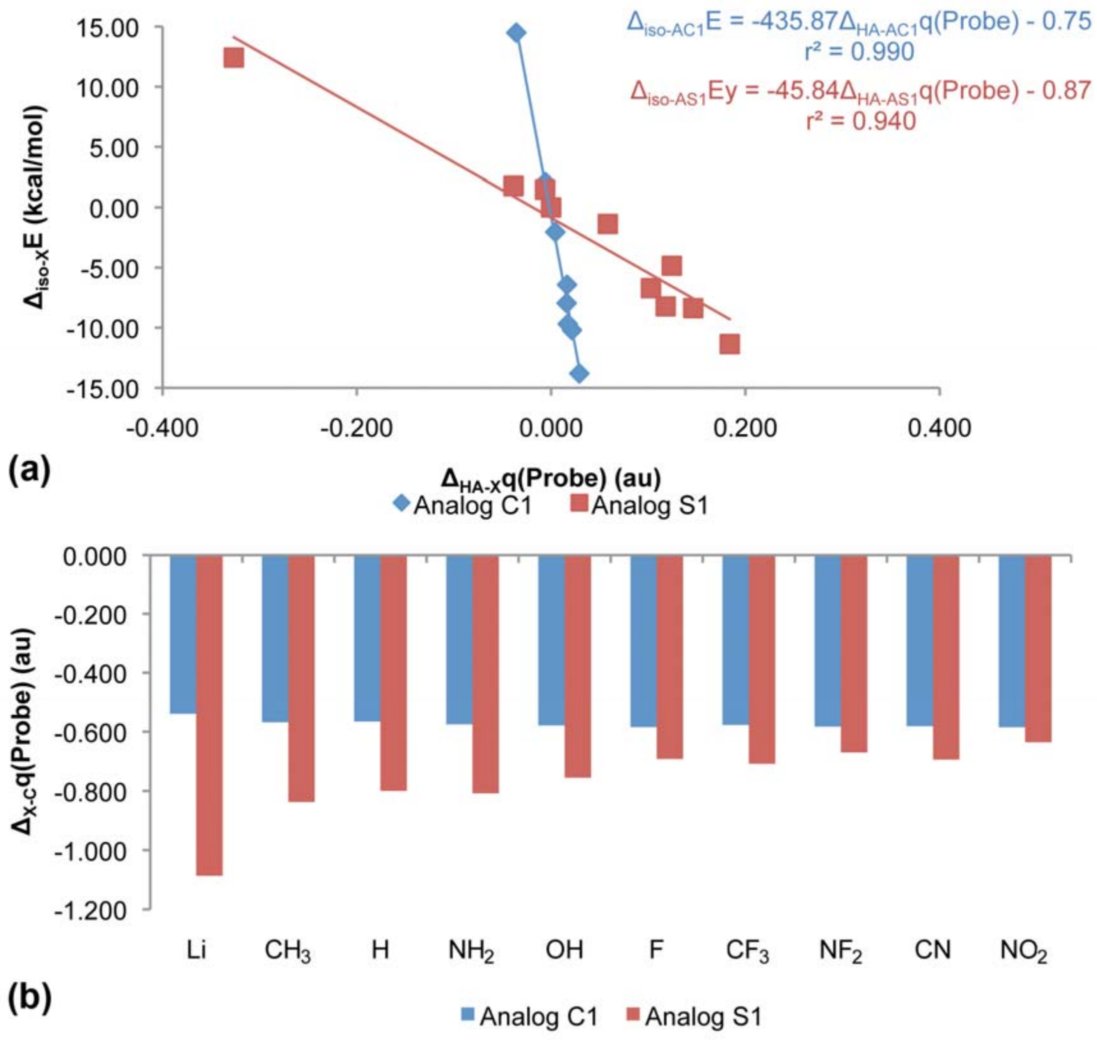


Figure 5.20. Graphical representations of (a) the relationship between the overall reaction energy and the charge of the probe group, and (b) the difference, between the analog systems and the all-carbon system, of the charge of the probe group, in both analog C1 and analog S1. All values calculated at the PBE0/6-31++G(d,p) level of theory.

increased acidity. In both cases the probe group has a more negative charge than in the all-carbon backbone, with a more pronounced effect in analog S1 (see Figure 5.20b).

In the all-carbon systems, the DI was used to describe the communication between the substituent and probe groups. There was no evidence of direct communication (the number of electrons shared between the substituent and probe did not correlate with $\Delta_{iso}E$), but it did appear that transmission occurred in a stepwise fashion. There are good relationships between the reaction energy and the DI between the bridging atoms, as well as $\mathbf{E_c}$, and both the substituent and probe. The substituent communicates with those atoms, and in turn they pass on the information to the probe group. With analog C1 there is no correlation between the DI of the substituent, or probe, and any other atom as if there is no communication occurring. Analog S1 acts more similarly to the all-carbon system. There is a good relationship between $\Delta_{iso}E$ and both DI(Substituent, $\mathbf{E_c}$) and DI(Probe, $\mathbf{E_c}$) in the acid species. This suggests the stepwise communication is occurring more directly through the system than in the all carbon backbone. In each case, the average number of electron shared with $\mathbf{E_c}$ increases with the acidity of the system (r^2[DI(Substituent, $\mathbf{E_c}$)]=0.741 and r^2[DI(Probe, $\mathbf{E_c}$)]=0.755).

5.3.3.2 Analogs C2 and S2

The overall charge of the substituent has little relationship with the reaction energies of the system, as expected, but does appear to point qualitatively to the electron donating or withdrawing character of the substituent. In acid molecules of analog C2, CH_3 has an overall positive charge, but in the conjugate base molecules all substituents except Li possess a negative charge, just as in the all-carbon backbone. With respect to the all-carbon backbone, analog 2 does not affect the substituent in the same manner. For substituents CH_3 through F, the analog system results in a more positive charge, but for the remaining substituents it yields a more negative charge.

The Si bridging atoms have charges of approximately 2.7 au, essentially equivalent to the bridgehead atoms within analog 1, and the carbon bridgeheads possess a negative charge, consistent with the differences in electronegativity between atoms. As expected, the Si atoms have a more positive charge than the equivalent carbon atoms in the original backbone. The relative charge on $\mathbf{E'_b}$ is shown in Figure 5.21a. The bridging atoms, $\mathbf{E_a}$ and $\mathbf{E_c}$ (Figure 5.21b and 5.21c, respectively), experience a large decrease in charge due to the move from a positive to a negative value. In contrast to the original systems, no atoms within the backbone of analog 2 show correlation to $\Delta_{iso}E$.

The same trend for the charge of the probe group found in the all-carbon backbone is present in analog 2. In both cases, the probe group becomes more positive as the electron withdrawing strength of the substituent increases (see Figure 5.22a), but the correlation is much better for the carbon-based probe. Use of the analog backbone causes a different effect in the C-probe as in the Si-probe (not observed in the other analog systems). In analog C2, the charge of the probe is more negative for all substituents (only by an average of 0.02 au), but there is no consistency within analog S2 as depicted in Figure 5.22b.

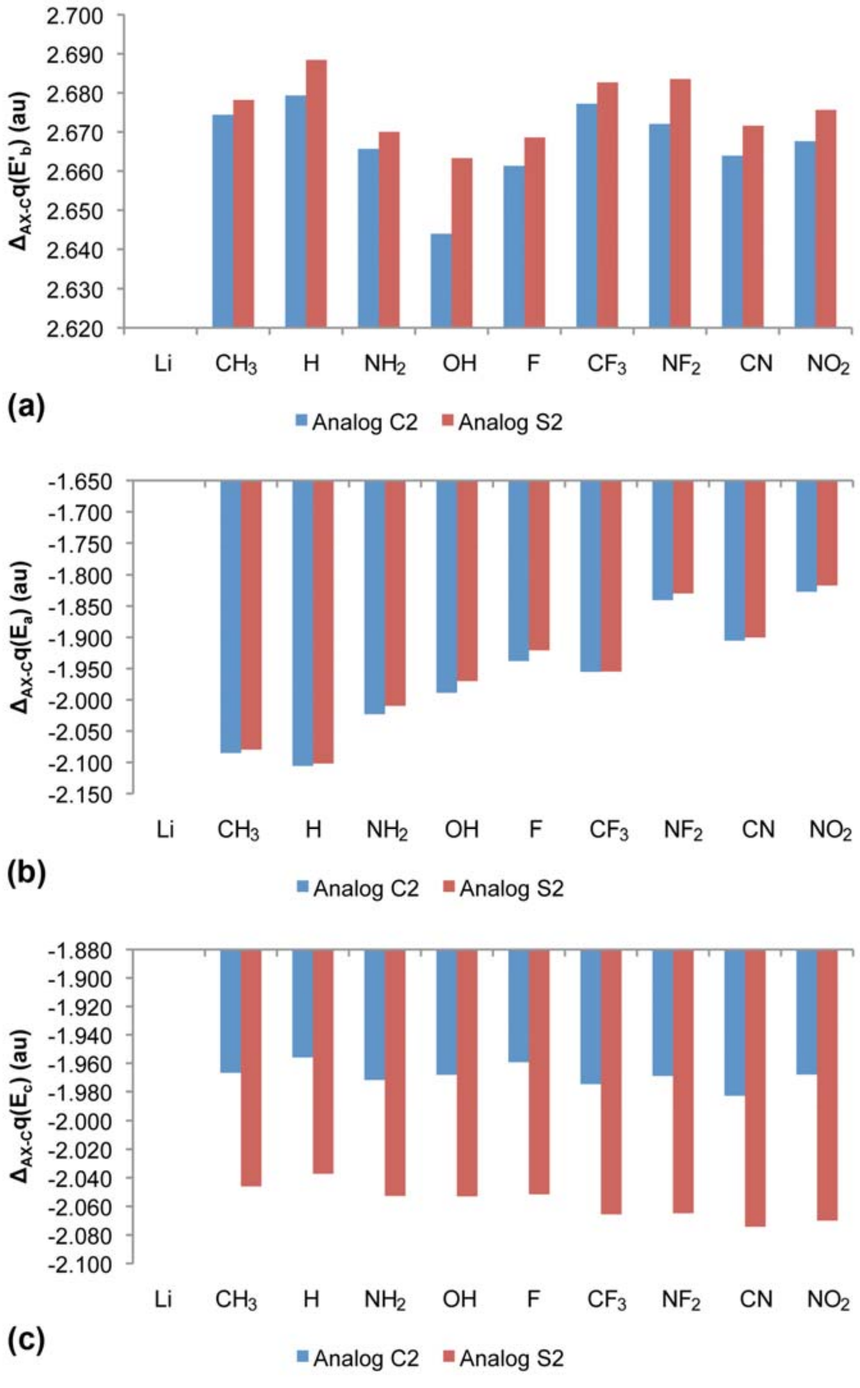


Figure 5.21. Graphical representations of the differences, between the analog systems and the all-carbon backbones, of the charges of (a) the bridging atom, **E'$_b$**, (b) the forward bridgehead atom, **E$_a$**, and (c) the opposite bridgehead atom, **E$_c$**, in both analog C2 and analog S2. All values calculated at the PBE0/6-31++G(d,p) level of theory.

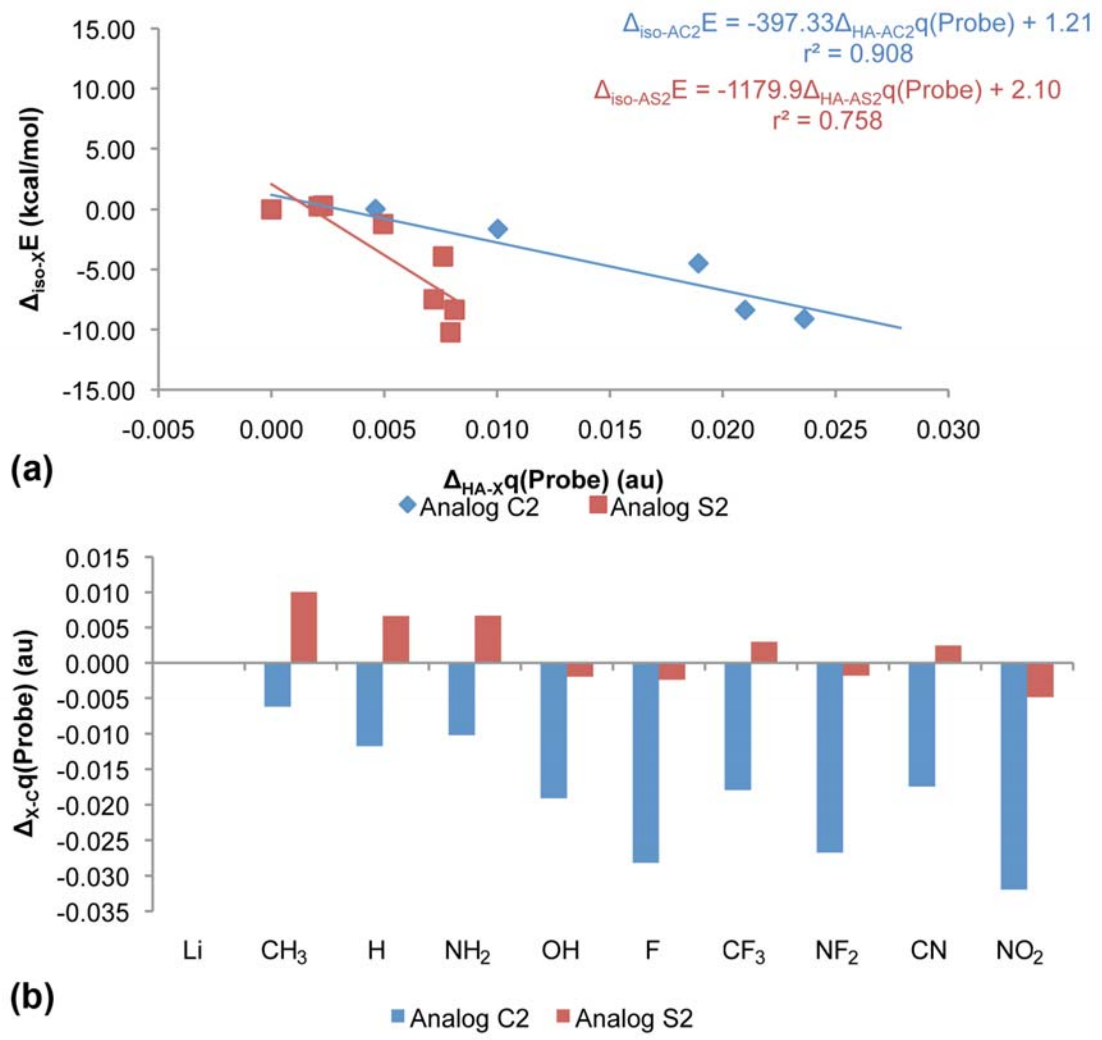


Figure 5.22. Graphical representations of (a) the relationship between the overall reaction energy and the charge of the probe group, and (b) the difference, between the analog systems and the all-carbon system, of the charge of the probe group, in both analog C2 and analog S2. All values calculated at the PBE0/6-31++G(d,p) level of theory.

For analog 2, there are no relationships between $\Delta_{iso}E$ and the delocalization indices within the system, indicating the absence of any communication between the substituent and probe. This is unexpected given the result for the all-carbon backbone, and also the relationships between properties of the probe group and $\Delta_{iso}E$.

5.3.3.3 Analogs C3 and S3

The overall charges of the substituent groups for analog C3 follow the same trends as the all-carbon backbone: both Li and CH_3 have overall positive charges in the acids, whereas only Li has a positive charge in the conjugate bases. In analog S3, the methyl substituent appears to be acting as an electron withdrawing group in that it has an overall negative charge in the acid species. Similarly to analog 1, the backbone appears to make the charge of the substituent more negative with reference to the all-carbon backbone.

As all atoms have been replaced with Si, it follows that the charges of all $E^{(\prime)}$ atoms within the backbone have more positive charge than their carbon counterparts, shown in Figure 5.23. The charge on $\mathbf{E_a}$ is greater by an average of 0.28 au in both systems, and the charge on $\mathbf{E_c}$ is greater by 0.46au in analog C3 and 0.74au in analog S3. This points to a greater amount of charge transfer from the backbone to the probe in the Si-probe system. In both probes the relative charge on the bridging atoms is very similar (average of 1.40 au in analog C3 and 1.35au in S3). The charges on all bridging atoms correlate well with $\Delta_{iso}E$ (see Figure 5.24) and the charge on $\mathbf{E_c}$ shows a minor

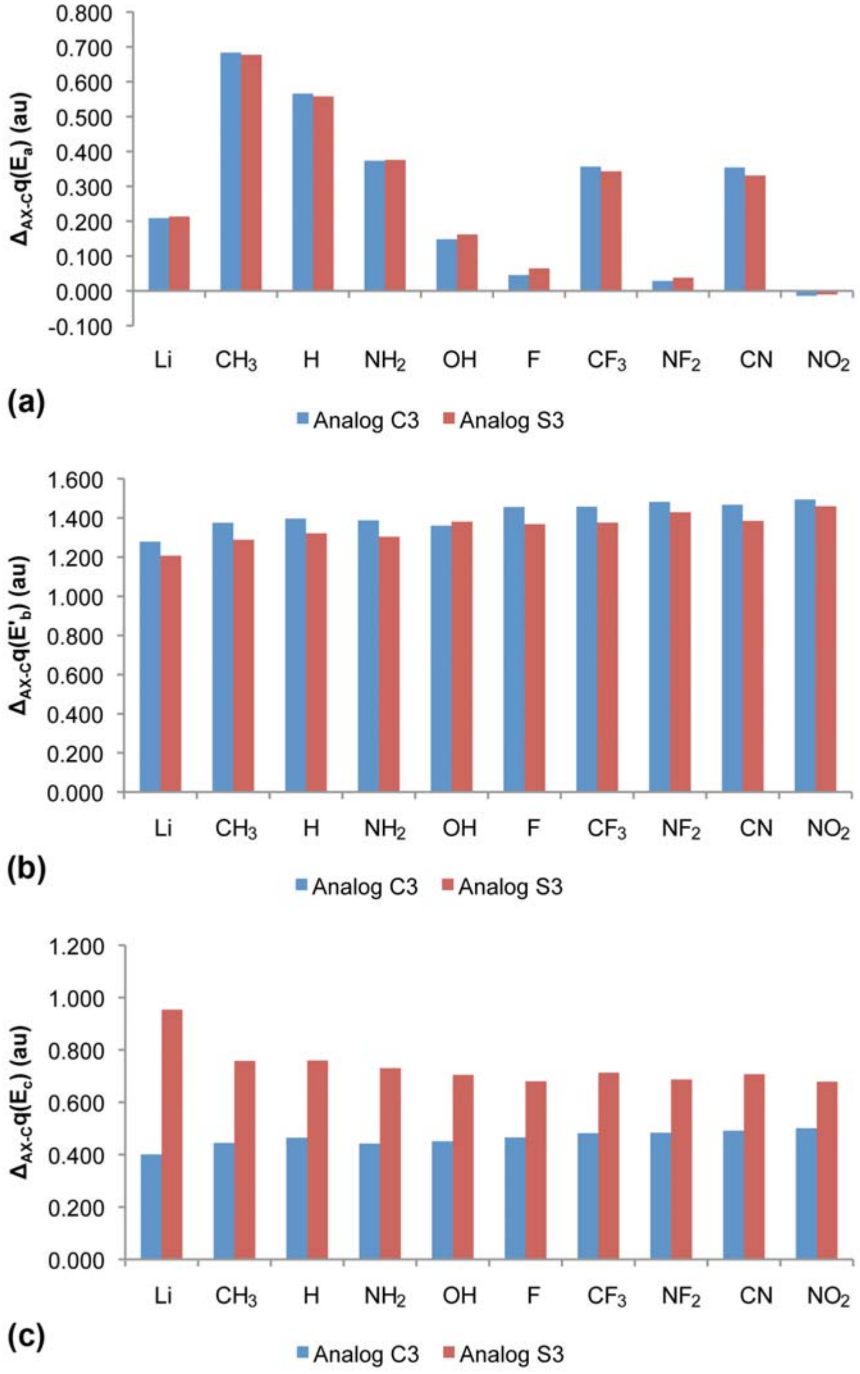


Figure 5.23. Graphical representations of the differences, between the analog systems and the all-carbon backbones, of the charges of (a) the forward bridgehead atom, $\mathbf{E_a}$, (b) the bridging atom, $\mathbf{E'_b}$, and (c) the opposite bridgehead atom, $\mathbf{E_c}$, in both analog C3 and analog S3. All values calculated at the PBE0/6-31++G(d,p) level of theory.

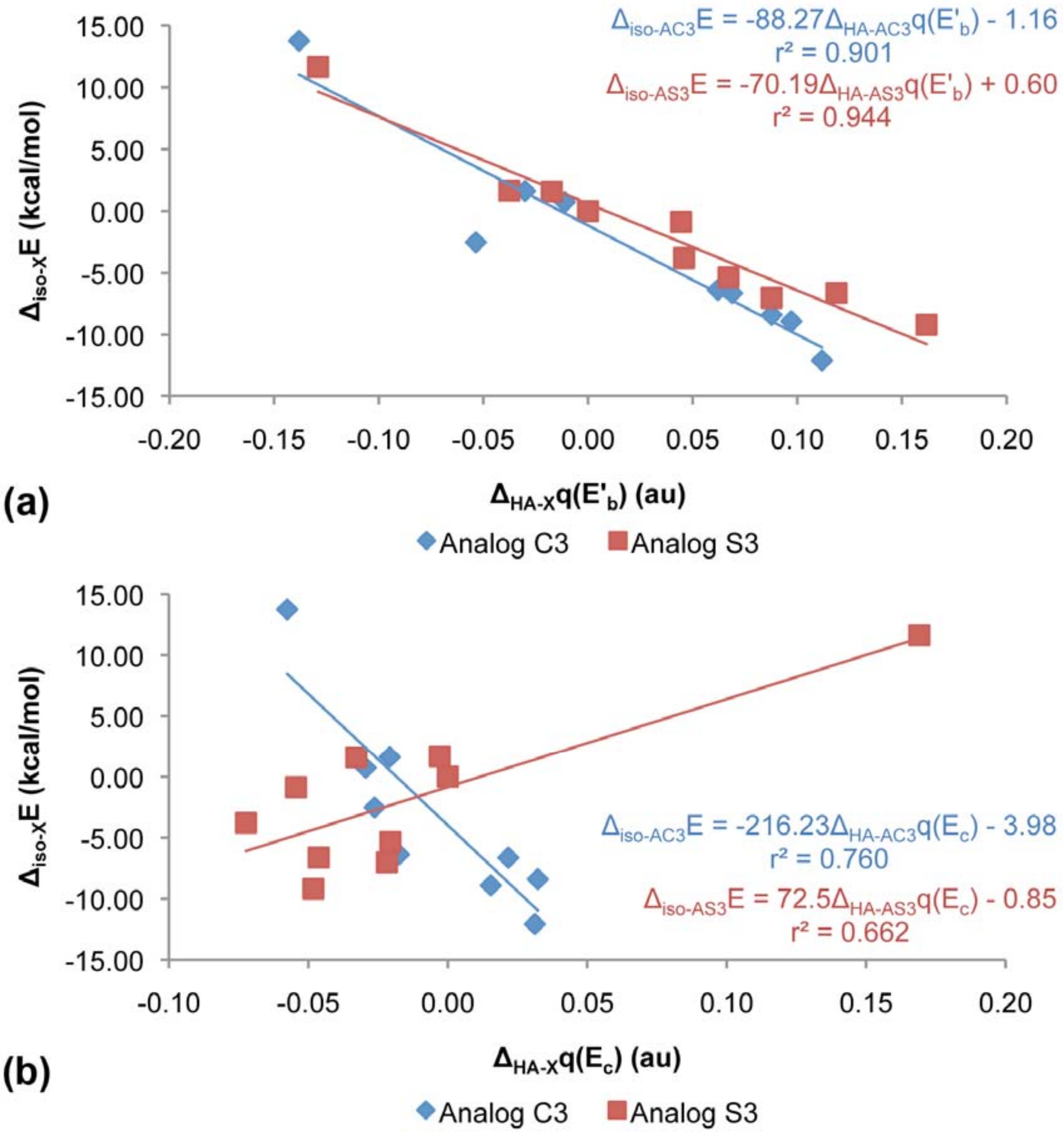


Figure 5.24. Graphical representations of the relationship between the overall reaction energy and (a) the charge on **E’$_b$**, and (b) the charge on **E$_c$**, in both analog C3 and analog S3. All values calculated at the PBE0/6-31++G(d,p) level of theory.

correlation; all corresponding to an increase in charge with increased electron withdrawing strength of the substituent, apart from the charge on $\mathbf{E_c}$ in analog S3.

Just as in all other analogs, the trends observed in the charge of the probe group in the all-carbon backbone are conserved in analog 3: as the strength of electron withdrawing substituent increases, the charge on the probe segment becomes more positive as illustrated in Figure 5.25a. For the most part the probe group is more negative in the analog than in the carbon system, by an average of 0.57 au for the C-probe and 0.73 au for the Si-probe. As apparent in Figure 5.25b, the Si-probe appears to be more sensitive to the change in backbone. Given that there is a larger, and more consistent, effect in analogs 1 and 3, it appears that the main effect upon transmission is by the Si atoms at the bridgehead positions.

In analog C3, the only atom along the bond path that communicates with the substituent is $\mathbf{E_c}$. DI(Substituent, $\mathbf{E_c}$) forms a good relationship with the reaction energy (r^2=0.811), and corresponds to an increased number of electrons shared between the substituent and $\mathbf{E_c}$ with increased strength of electron withdrawing group. There are no relationships between DI(Probe, B) and the substituent effect. In analog S3 the stepwise transmission using $\mathbf{E_c}$ is conserved. As this relationship is also present in analog 1, it appears that Si atoms in the bridgehead positions promote a more direct mode of transmission through the molecule.

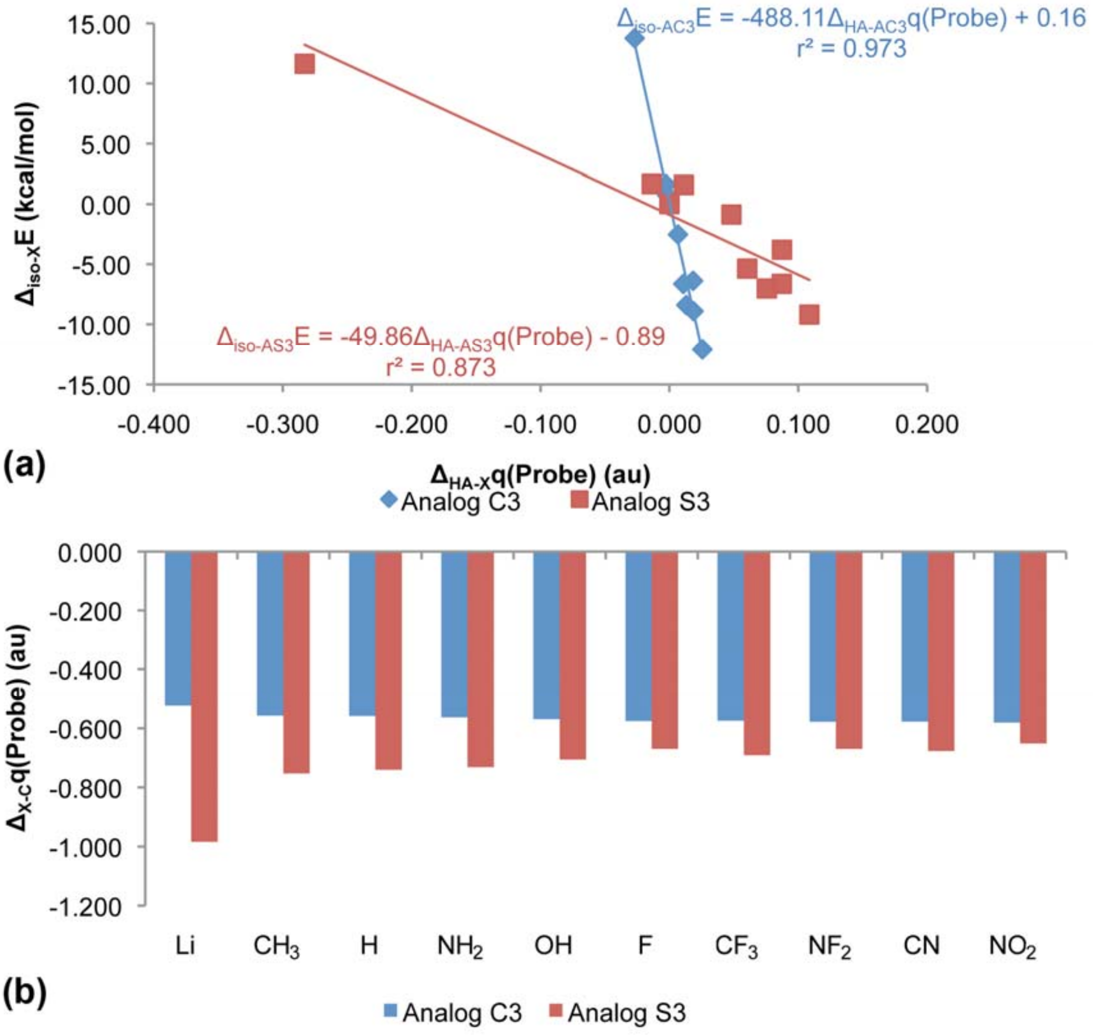


Figure 5.25. Graphical representations of (a) the relationship between the overall reaction energy and the charge of the probe group, and (b) the difference, between the analog systems and the all-carbon system, of the charge of the probe group, in both analog C3 and analog S3. All values calculated at the PBE0/6-31++G(d,p) level of theory.

5.3.4 Dipole Moment Contributions

In previous studies the dipole moment has been used as proof of the through-space mechanism of the “so-called” inductive effect.[33] QTAIM can be used to determine the specific atomic contributions to the molecular dipole moment. The atomic dipole moment, and its components, is determined according to equation 5.11.

$$\mu(\Omega) = -e \int_{\Omega} r_{\Omega}\rho(r)d\tau \tag{5.11}$$

We have shown that the effect in the bicyclo[1.1.1]pentane carboxylic acids, and silicic acids, operates through the substituent dipole moment (Sections 3.4.6 and 4.4.6). The x-component of the dipole moment was the only property to consistently relate to the substituent effect along the bond path, and appeared to be controlled by the x-component of the substituent dipole, $\mu_x(R)$. The dipole moment was shown to be transferrable between systems, and the substituent only value (determined from RH; shown in Table 5.4) was used to recreate the value. The relationship for the C-system is shown in equation 5.12.

$$\Delta_{iso-C}E = 1.13\mu_x(R_H) - 0.29 \quad (r^2 = 0.989, n = 10) \tag{5.12}$$

$\mu_x(R_H)$ was used to successfully replace the substituent constant in both all-carbon systems; however, the addition of an electronegativity term in the C-system led to a worse relationship (lowered r^2 value to 0.962). In the Si-system, a steric parameter was required to describe the effect upon the probe. The best descriptor was determined to be the pyramidalization of **Si$_{\mathbf{O}}$**, as described in equation 5.13.

Table 5.4. X-components of the atomic dipole moments (in debyes) for the substituent-only value, as well as all analog systems, calculated using the PBE0/6-31++G(d,p) level of theory. Squared correlation coefficients are calculated for linear relationships to the corresponding $\Delta_{iso}E$.

Substituent	$\mu_x(R_H)$[a]	Analog C1		Analog S1		Analog C2		Analog S2		Analog C3		Analog S3	
		$\mu_x(R_{HA})$	$\mu_x(R_{CB})$	$\mu_x(R_{HA})$	$\mu_x(R_{CB})$	$\mu_x(R_{HA})$	$\mu_x(R_{CB})$	$\mu_x(R_{HA})$	$\mu_x(R_{CB})$	$\mu_x(R_{HA})$	$\mu_x(R_{CB})$	$\mu_x(R_{HA})$	$\mu_x(R_{CB})$
Li	3.16	3.27	1.09	3.18	1.50	[b]	2.98	[b]	2.98	3.38	2.69	3.35	2.94
CH3	-0.34	-0.90	-0.32	-1.02	-0.51	-0.48	0.05	-0.51	-0.08	-0.86	-0.14	-0.93	-0.30
H	-0.29	-1.38	-1.64	-1.45	-1.67	-0.26	-0.34	-0.29	-0.36	-1.35	-1.53	-1.40	-1.54
NH2	-0.52	-0.61	-0.52	-0.72	-0.65	-0.68	-0.36	-0.72	-0.50	-0.69	-0.48	-0.71	-0.52
OH	-1.07	-1.52	-1.71	-1.63	-1.75	-1.40	-1.25	-1.48	-1.41	-1.58	-1.69	-1.63	-1.63
F	-1.82	-2.66	-2.88	-2.72	-2.90	-2.32	-2.42	-2.35	-2.45	-2.72	-2.91	-2.76	-2.89
CF3	-1.84	-3.08	-2.53	-3.22	-2.76	-2.57	-2.21	-2.64	-2.32	-3.12	-2.47	-3.21	-2.65
NF2	-1.96	-3.33	-3.14	-3.40	-3.24	-3.19	-3.00	-3.24	-3.20	-3.43	-3.14	-3.51	-3.24
CN	-3.00	-4.20	-4.45	-4.35	-4.58	-4.12	[c]	-4.19	-4.43	-4.38	-4.49	-4.45	-4.56
NO2	-2.68	-4.26	-4.17	-4.41	-4.32	-4.02	[c]	-4.10	[c]	-4.35	-4.18	-4.45	-4.27
r^2		0.972	0.906	0.977	0.939	0.954	0.953	0.945	0.959	0.974	0.947	0.988	0.967

(a) Calculated as a substituent-only value in the complex RH. Values missing due to (b) the presence of a non-nuclear attractor in the molecular graph, and (c) rearrangement to a different bicyclic structure.

$$\Delta_{iso-Si}E = -0.24\mu_x(R_H) + 0.04\chi + 3.75\Delta_{HA-Si}Dev(Si_O) - 0.59 \quad (r^2 = 0.999, n = 10) \tag{5.13}$$

Therefore, we have used this approach upon the analog systems to determine how introduction of Si into the backbone changes the mode of transmission. The dipole moment data for all systems, including the substituent-only value, is given in Table 5.4. For the most part, the substituent-only values do a very good job of recreating the x-component of the substituent dipole in the analog systems, as illustrated in Figure 5.26, with the exception of analog 2.

5.3.4.1 Analogs C1 and S1

As shown in Table 5.4, the x-components of the atomic dipole moments of the substituents ($\mu_x(R)$) show good linear correlations with the reaction energy. Just as in the all-carbon system, $\mu_x(R_{HA})$ becomes more negative (negative x is an indication of direction toward the probe; Scheme 5.3) with increasing strength of electron withdrawing group. The correlation coefficient for the relationship with the acid species is stronger, and thus will be discussed here. In both analog C1 and S1, Li substitution results in the only positive $\mu_x(R_{HA})$, which would explain the large positive $\Delta_{iso}E$ value. The use of the analog 1 backbone generally produces a larger magnitude of $\mu_x(R_{HA})$ (in the corresponding direction), with NH_2 substitution as the only exception, as compared to both the all-carbon backbone and the substituent-only value.

Within the carbon system, $\mu_x(R_{HA})$ was the only property which showed a consistent relationship to the reaction energy across the entire molecule (analog S1 has relationships between $\Delta_{iso}E$ and only $\mu_x(\mathbf{E_a})$, $\mu_x(\mathbf{E'_b})$ within the backbone), and therefore

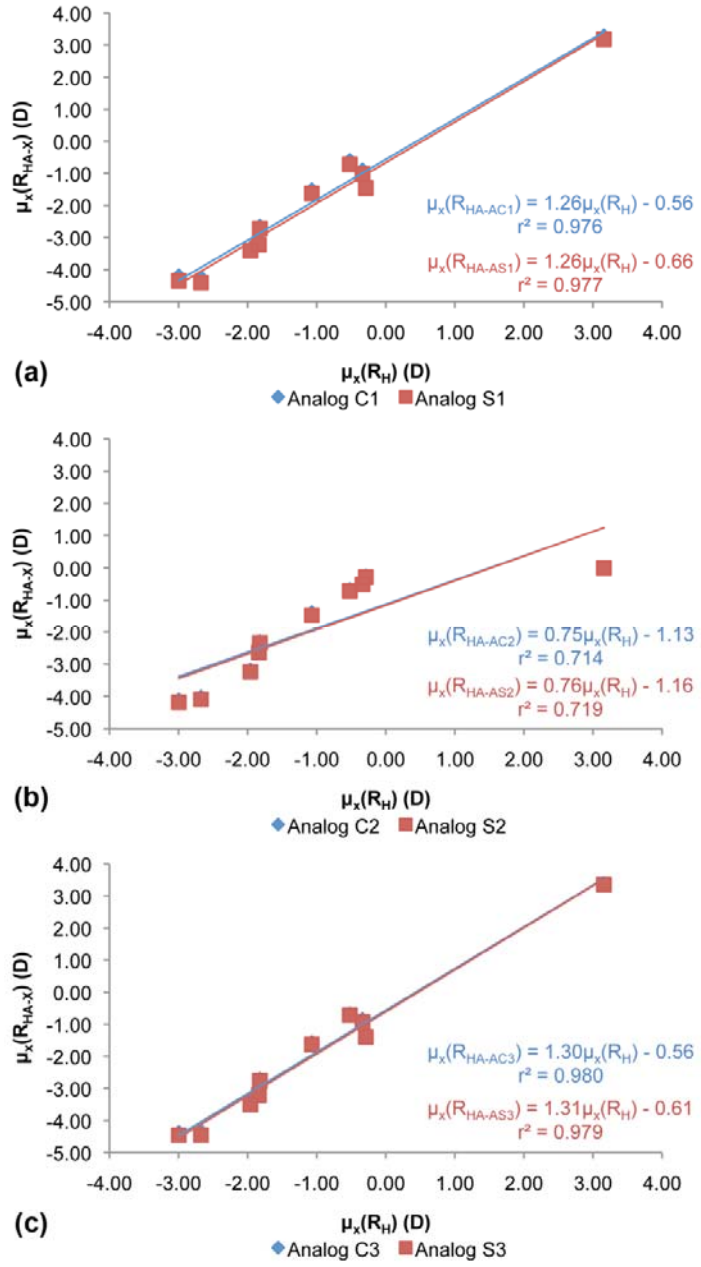


Figure 5.26. Graphical representation of the relationships between the x-component of the substituent-only dipole and the x-component of the substituent dipole in the acid species of (a) analogs C1 and S1, (b) analogs C2 and S2, and (c) analogs C3 and S3. All values were calculated at the PBE0/6-31++G(d,p) level of theory.

was determined to be the method of transmission for the substituent effect. Although correlations are missing for some individual atoms (**O_H** in analog C1, and **O_a** and **H_a** in analog S1), the relationship is still present for the probe as a whole. The lack of relationship at the acidic hydrogen in the Si-probe may be due to the non-planarity of the probe group (as opposed to the carboxylic acid probe). $\mu_x(R_{HA})$ still appears to be controlling the substituent effect and again correlates very well with the substituent constants. It can be used to describe the properties that are affected by the substituent. The NMR chemical shift of the acidic hydrogen can be recreated very well using $\mu_x(R_{HA})$. A more negative $\mu_x(R_{HA})$ corresponds to a downfield shift in $\Delta\delta^1$**H_a** (r^2=0.875 for analog C1 and r^2=0.819 for analog S1).

Using $\mu_x(R_H)$ to replace the substituent constant in the Hammett equation creates a much better relationship for the substituent effect. It is suggested that in systems involving Si, a steric parameter must be added to the Hammett expression.[29] Using the pyramidalization of **E_a** in the analog systems and that in the carbon systems to describe the steric component of the backbone, and the O–C_O–O_H angle to describe the effect of the backbone upon the probe , a four-term Hammett relationship was created (equation 5.14) , where χ is the electronegativity of the substituent.

$$\begin{aligned}\Delta_{iso-AC1}E = 0.98\mu_x(R_H) + 0.36\chi - 1.31\Delta_{HA-AC1}Dev(E_a) \\ - 19.20\Delta_{HA-AC1}\theta(O - C_O - O_H) \\ - 0.67 \quad (r^2 = 0.999, n = 10)\end{aligned} \tag{5.14}$$

The pyramidalization at **Si_O** is required to describe the effect in the Si-probe, as in the all carbon backbone, as shown in equation 5.15.

$$\Delta_{iso-AS1}E = -0.57\mu_x(R_H) - 1.01\chi - 1.55\Delta_{HA-AS1}Dev(E_a) + 7.41\Delta_{HA-AS1}Dev(Si_O) + 1.86 \quad (r^2 = 0.999, n = 10) \tag{5.15}$$

5.3.4.2 Analogs C2 and S2

Just as in the all-carbon system, the x-component of the substituent dipole relates very well to the substituent effect in both species, as described in Table 5.4, despite the missing values. As the electron withdrawing strength of the substituent increases, the $\mu_x(R)$ becomes more negative (seen for both HA and CB). Comparison of analog 2 to the carbon system does not yield a consistent trend: H, NH_2, and OH result in a smaller magnitudes (also CH_3 and F with the Si-probe), but all others show an increase in the magnitude of $\mu_x(R_{HA})$. Apart from the unsubstituted species, all substituents show an increase in the magnitude in the negative direction with respect to the substituent only value.

μ_x is the only property to show consistent correlations to $\Delta_{iso}E$ along the bond path, as expected given the results for the all-carbon backbone, and therefore was determined to be the method of transmission for the substituent effect. μ_x for all backbone atoms show very good correlations to the reaction energy, as well as the probe as a whole. Just as seen in analog 1, some relationships for the individual atoms with the probe group, which are present in the all-carbon backbones, are missing in the analog systems: $\mathbf{O_H}$ in analog C2, and $\mathbf{O_a}$ and $\mathbf{H_a}$ in analog S2. Despite these differences, $\mu_x(R_{HA})$ can still be used to describe the effect of substituent on all properties that relate to the reaction energy. The dipole moment contribution does a good job of predicting the NMR chemical shift of the acidic hydrogen in analog C2 (r^2=0.924), but the same quantity does not relate to the substituent effect in the Si-probe system (r^2=0.488).

In the all-carbon backbone, $\mu_x(R_{HA})$ was used as a substituent for Hammett's substituent constant to great success. The same can be performed in the analog 2 systems. As was suggested for analog 1, the use of a steric term for the backbone (the pyramidalization of $\mathbf{E_a}$, given by **Dev($\mathbf{E_a}$)**) and a steric term for the probe (the O–C_O–O_H angle) is required to accurately describe the substituent effect. The Hammett relationship determined for analog C2 is shown in equation 5.16.

$$\begin{aligned}\Delta_{iso-AC2}E &= 0.53\mu_x(R_H) - 1.05\chi - 0.09\Delta_{HA-AC2}Dev(E_a) \\ &\quad - 16.68\Delta_{HA-AC2}\theta(O - C_O - O_H) \\ &\quad + 2.22 \quad (r^2 = 0.9996, n = 8)\end{aligned} \tag{5.16}$$

As determined in the all-carbon backbone, a different steric term (the pyramidalization at $\mathbf{Si_O}$) is also required when the silicic acid probe is used. Consequently, the improved Hammett relationship for analog S2 is shown in equation 5.17.

$$\begin{aligned}\Delta_{iso-AS2}E &= 0.74\mu_x(R_H) - 0.20\chi + 0.01\Delta_{HA-AS2}Dev(E_a) \\ &\quad + 3.36\Delta_{HA-AS2}Dev(Si_O) + 0.73 \quad (r^2 = 0.998, n = 9)\end{aligned} \tag{5.17}$$

5.3.4.3 Analogs C3 and S3

As with all other systems, the x-component of the substituent dipole correlates very well with $\Delta_{iso}E$. As is apparent in Table 5.4, $\mu_x(R)$ follows the same trends previously described: a more negative dipole with increased strength of electron withdrawing substituent. Analog 3 behaves in the same manner as Analog 1. With respect to the all-carbon backbone and the substituent-only value, $\mu_x(R_{HA})$ has a larger magnitude in both analog C3 and analog S3 (NH_2 substitution is the only exception for comparison to the all-carbon backbone).

In keeping with the trends previously observed, μ_x consistently relates well with $\Delta_{iso}E$ along the bond path. In analog C3, μ_x has very good correlations for the backbone and probe as a whole, but appears to transmit in a slightly different fashion (all backbone atoms and $\mathbf{Si_O}$ show very good relationships in analog S3). Very strong correlations are apparent for both bridgehead atoms, but the bridging atoms only form weak relationships (average $r^2=0.626$). For the bridging atoms it is actually μ_y and μ_z which show strong correlations. Replacing the entire backbone with Si appears to result in a path of transmission directly through the molecule (explaining the very good relationship between $\Delta_{iso}E$ and $\rho(CCP)$), but also results in a greater diffusion of charge.

Even with slight differences in transmission, $\mu_x(R_{HA})$ still appears to be controlling the substituent effect. It can be used to describe any of the properties associated with the reaction energy (e.g. $\Delta\delta^1\mathbf{H_a}$ and $\mu_x(R_{HA})$ have a linear squared correlation coefficient of 0.817 in analog C3 and 0.876 in analog S3). Replacement of the substituent constant with the dipole moment contribution, as well as using the pyramidalization at $\mathbf{E_a}$ to describe the steric contribution of the backbone, and the two terms to describe the steric contribution of the probes [$\boldsymbol{\theta(O\text{–}C_O\text{–}O_H)}$ for the C-probe and $\mathbf{Dev(Si_O)}$ for the Si-probe), leads to better Hammett-type relationships overall (see equations 5.18 and 5.19).

$$\begin{aligned}\Delta_{iso-AC3}E = &-0.29\mu_x(R_H) - 0.18\chi - 0.38\Delta_{HA-AC3}Dev(E_a) \\ &- 24.74\Delta_{HA-AC3}\theta(O - C_O - O_H) \\ &- 0.32 \quad (r^2 = 0.996, n = 10)\end{aligned} \tag{5.18}$$

$$\begin{aligned}\Delta_{iso-AS3}E = &-0.63\mu_x(R_H) - 0.50\chi - 0.47\Delta_{HA-AS3}Dev(E_a) \\ &+ 7.70\Delta_{HA-AS3}Dev(Si_O) + 0.69 \quad (r^2 = 0.999, n = 10)\end{aligned} \tag{5.19}$$

5.4 Summary

Herein we have presented a systematic study on the transmission of electron density through silicon, upon both a carbon based probe and a silicon based probe, by replacing the carbon atoms in the bicyclo[1.1.1]pentane backbone. The isodesmic reaction approach was used to determine the effect of substitution using Hammett's method. In general, reactivity and the ordering of substituents is conserved between the all-carbon and analog systems. In all analog systems, NH_2 substitution results in a positive $\Delta_{iso}E$ and consequently appears to act as an electron donating group. In analog 1 and analog 3, the order of the CN and NF_2 substituents is swapped; NF_2 substitution leads to a greater electron withdrawing effect.

Unexpected structural changes occurred with the conjugate bases of analogs 2 and 3 with highly electron withdrawing groups (CF_3 through NO_2 with the CBS-QB3 method, and CN and NO_2 with the PBE0 level of theory), and was more severe in the CBS-QB3 method than the PBE0/6-31++G(d,p) level of theory. For analog 2, a different bicyclic structure was located, while the probe group was prone to leaving in analog 3.

One of the most obvious differences between Si and C is their atomic radii. Consequently the structure within the backbone segments varies with each replacement of a carbon atom with silicon. As expected, all Si–C and Si–Si bonds are longer than their carbon counterparts. Length **a**, the interbridgehead distance, shows this variation best and the relative distance (carbon value subtracted from the analog value) generally shows very good correlation to $\Delta_{iso}E$. With each addition of more Si atoms, **a** increases in length by an average of 0.41 Å in analog 1, 0.54 Å in analog 2 and 1.02 Å in analog 3. Just as in the carbon systems, **a** appears to vary with the pyramidalization at $\mathbf{E_a}$. We have used the pyramidalization at $\mathbf{E_a}$ successfully as the structural parameter for the backbone, required in the Hammett relationships for silicon systems. The use of the silicic acid probe also requires a second structural parameter, the pyramidalization of $\mathbf{Si_O}$, to accurately describe the substituent effect.

Bader's Quantum Theory of Atoms in Molecules was used to analyze minute variations in the electron density distribution between systems, and thus give insight into the mechanism of transmission. The all-carbon system appears to be operating solely through the substituent dipole moment, but when silicon atoms are introduced into the backbone some degree of through-bond transmission is induced. However, the x-component of the substituent dipole is still the property most consistently related to the substituent effect. There does not appear to be a clear relationship between the number of silicon atoms introduced and the change in substituent effect. $\mu_x(R_H)$ was used to replace the traditional substituent constant, σ_F, in the Hammett-based relationship to achieve a better description of the effect.

Chapter 6: Summary and Conclusions

We have investigated the “so-called” inductive effect with respect to silicon on two fronts: the effect of substitution on a silicon probe and the transmission of the effect through a silicon center. To that end we have employed a silicic acid based probe and a carboxylic acid probe, for comparison. To ensure it is only the “so-called” inductive effect being studied, we have used bicyclo[1.1.1]pentane as the backbone segment to link the substituent and probe. The bicyclo[1.1.1]pentane cage structure removes any possibility of conjugation or steric interaction between the substituent and probe.[33] In order to study the transmission through silicon, the atoms within the backbone were systematically replaced with silicon atoms (see Scheme 1.3). Finally, the substituents utilized were chosen to cover a wide range of possible electronegativities, while still remaining manageable with respect to computational cost. Bader’s Quantum Theory of Atoms in Molecules[51,52,75] was used to examine the effect of substituents on the electron density distribution in the system.

Derivatives of 3-substituted-bicyclo[1.1.1]pentane-1-carboxylic acid were employed to determine a benchmark and method for studying the inductive effect in the proposed systems. Our QTAIM results confirm that, qualitatively, the inductive effect does decay with distance, but the decay does not relate to the inductive effect as suggested by definition. Consistent with Hammett’s formulation, the substituents have the same effect upon the silicic acid probe as they have upon the carboxylic acid probe. The order of substituents, based on the isodesmic reaction energy, is conserved and the reactions energies between the C- and Si-systems show a remarkable linear correlation.

With respect to the C-system, the silicic acid probe is less sensitive to substitution (ρ=0.84, see Figure 6.1).

Introduction of silicon atoms into the backbone results in some important differences in reactivity. In all three analog systems, substitution with NH_2 results in a positive reaction energy, as if the change in backbone promotes electron donating character in the amino group. When the bridgehead atoms are replaced by Si (analog 1 and analog 3) the NF_2 yields a more negative $\Delta_{iso}E$ than CN substitution and it appears the change in backbone promotes the electron withdrawing nature of NF_2. Analog 1 is more sensitive to substitution, ρ=1.11 for the C-probe and ρ=0.93 with the Si-probe (see Figure 6.1), but the Si-probe is still less sensitive. Analog 2 has a different effect on the two probe groups. Analog C2 is less sensitive to substitution (ρ=0.97), while analog S2 is more sensitive (ρ=1.08) with respect to the Si-system. Overall analog S2 yields a reaction less sensitive to substitution (ρ=0.91 with respect to the C-system). Replacement of all C atoms within the backbone with Si, results in a less sensitive reaction with the Si-probe (as expected given Yoder *et al.*'s findings[8]), but an essentially equivalent effect in the C-probe: analog C3 has ρ=0.99 and analog S3 has ρ=0.81. Therefore, it can be concluded that the transmission of the inductive effect through a Si-center is diminished.

The intercept of a regression line is generally used to refer to the error within a relationship. For the Si-system the intercept is essentially zero (0.04, see Figure 6.1a) on this scale, and thus the relationship can be said to be very accurate. In the analog systems the intercepts are higher. This is expected as the squared correlation

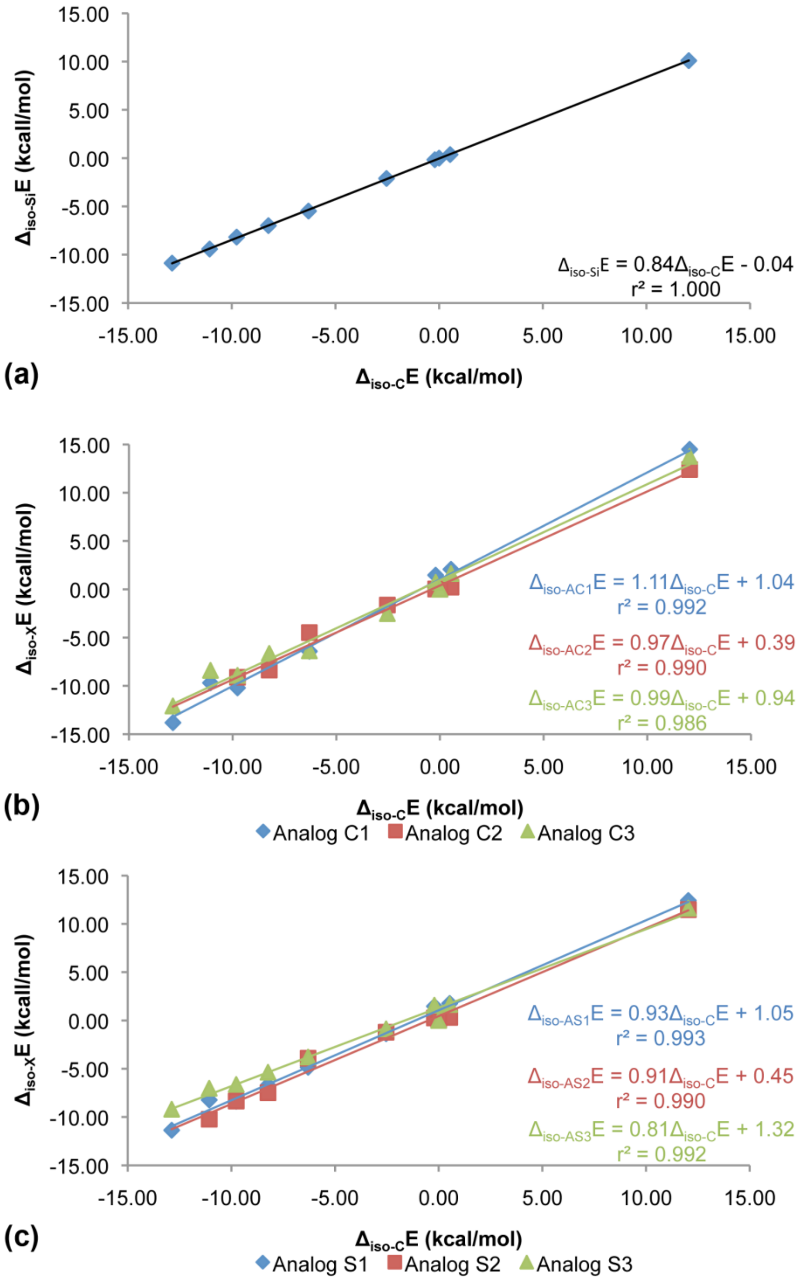


Figure 6.1. Graphical representations of the relationships between the isodesmic reaction energy in the C-system and the reaction energies in the (a) Si-system, (b) analogs C1, C2 and C3, and (c) analogs S1, S2 and S3, to determine the value of the reaction constant in each case. All values were calculated at the 6-31++G(d,p) level of theory.

coefficients indicate that the relationships are not perfect. Regardless, the largest intercept is only 1.32 in the relationship describing the effect in analog S3 (see Figure 6.1c). This represents, approximately, a 6% error overall, indicating that the relationships are still adequate in describing the substituent effect.

The greater atomic radius found in Si leads to an increase in bond lengths within the analog backbones (specifically **b1** and **b2**). In analogs 1 and 2, the Si–C bonds are on average 0.36 Å longer than their C–C counterparts. This difference increases to an average 0.70 Å in analog 3 with the move to pure Si–Si bonds. The most dramatic effects upon the structure occur within the conjugate base species of analogs 2 and 3. In analog 2, the high Si–O affinity between the Si atom, now at a bridging position, and the deprotonated O atom in the probe group leads to the rearrangement to a different bicyclic structure. In analog 3 the elongation of the linkage between the backbone and the probe is so severe that it appears to lead to the dissociation of the C-probe group in the conjugate base species as CO_2 (no dissociation apparent for the Si-probe). Although the elongation did lead to optimization issues, a bond path was still present between the backbone and probe. These rearrangements occur with the most electron withdrawing substituents, and are more severe with the C-probe than the Si-probe.

According to the Hammett approach, a steric term should be required to describe the inductive effect in Si systems. It was discovered that the pyramidalization of the forward bridgehead atom, $\mathbf{E_a}$, could be used to describe the steric component of the backbone. An additional term was required to describe the effect within the probe group. For the Si-probes, the pyramidalization of $\mathbf{Si_O}$ within the probe, as used in the Si-system, was determined to be the best parameter. For the C-probe systems, the O–C_O–O_H angle was the most useful for recreating the effect of substituent.

The reaction constants can be related to the relative (value for the C-system subtracted from the value for the Si-system) length of **c2**. This appears to be consistent through all analog systems. Figure 6.2 shows the relationships between the reaction energies, and that in the C-system, using $\mathbf{\Delta_{X\text{-}C}c2}$ as a parameter within ρ. As apparent in Figure 6.2a, the only relationship that is not fully recovered (in comparison to the relationships outlined in Figure 6.1) is for analog C2. This may be due to the fact that the **c2** distance is shorter than in the C-system due to the Si atoms at the bridging positions, and consequently the high Si–O attraction. However, the absolute distance **c2** does recreate the relationship as described in equation 6.1.

$$\Delta_{iso-A2}E = 0.66c2(A2) \cdot \Delta_{iso-C}E + 0.39 \quad r^2 = 0.990 \tag{6.1}$$

Although $\mathbf{\Delta_{X\text{-}C}c2}$ does not return the full value of ρ, it shows that the reaction constant does relate to some property of the system not controlled by the substituent.

Hammett suggested that the reaction constants can take the form of equation 6.2 and depend upon the universal gas constant (R), the temperature (T), the distance between substituent and probe (d), and the dielectric constant of the solvent (D).

$$\rho = \frac{\left(\frac{B_1}{D}\right) + B_2}{RTd^2} \tag{6.2}$$

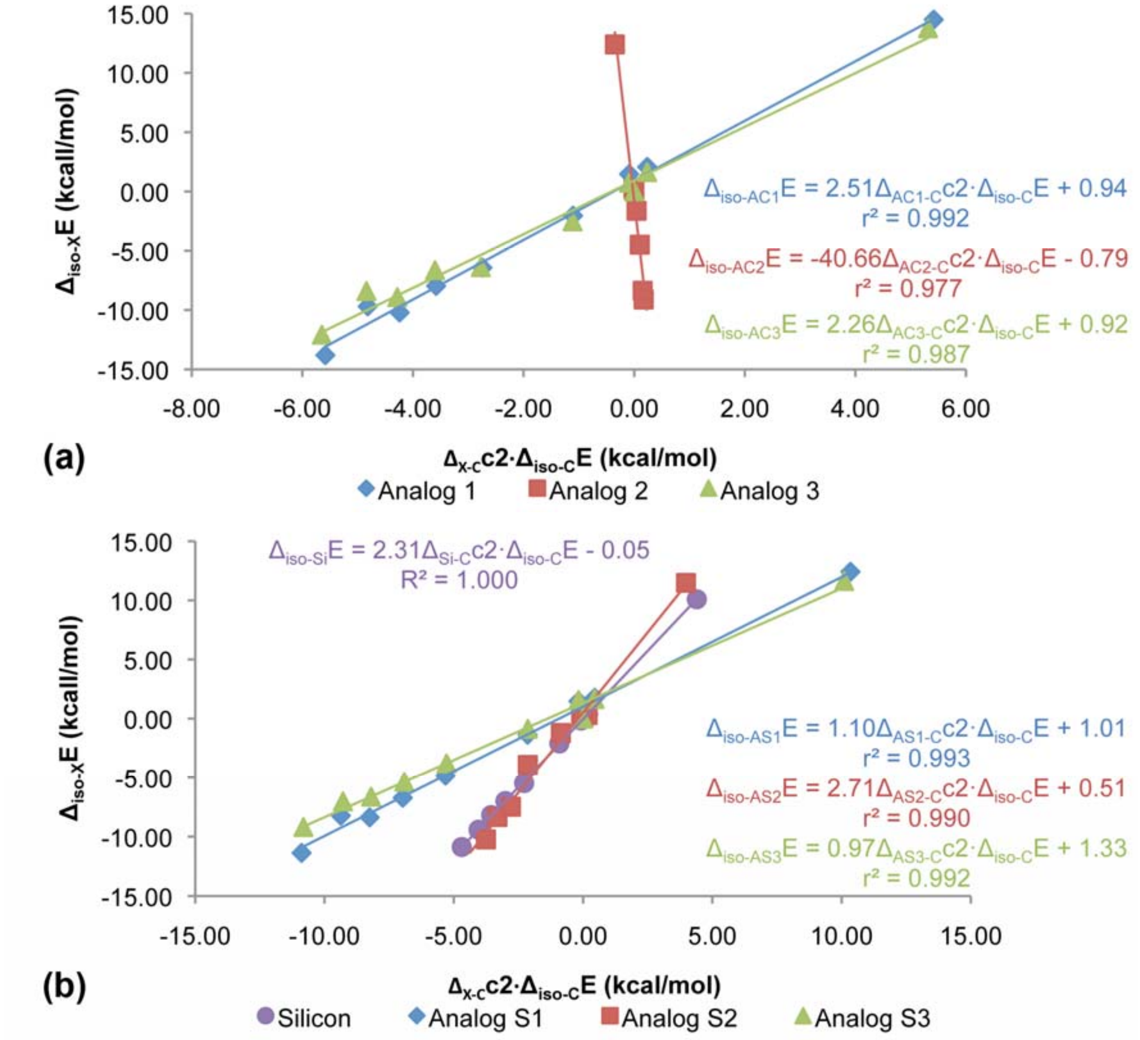


Figure 6.2. Graphical representation between the isodesmic reaction energy of the C-system, using $\mathbf{\Delta_{X\text{-}C}c2}$ as a parameter within the reaction constant, and the isodesmic reaction energy of (a) analogs C1, C2 and C3, and (b) the Si-system, and analogs S1, S2 and S3. All values were calculated at the PBE0/6-31++G(d,p) level of theory.

The constants in equation 6.2, B_1 and B_2, are said to be related to the electrostatic interaction between the molecule and the solvent, and the sensitivity of the reaction to changes in electron density at the probe, respectively. As the calculations in this study were performed in gas phase under constant temperature, equation 6.2 should reduce to:

$$\rho \cong \frac{B_2}{d^2} \tag{6.3}$$

Unfortunately, no simple relationship was found to allow for the *a priori* estimation of ρ.

The delocalization index alludes to a stepwise mechanism of transmission. Within the C-system, the substituent communicates with both **E'$_b$** and **E$_c$**, and these atoms pass the information on to the probe. Within the silicon systems (apart from analog 2, which shows no substituent-probe communication whatsoever), stepwise transmission involving **E$_c$** is conserved, suggesting that the Si atoms encourage a more direct transmission through the molecule. The average number of electrons shared between **E$_c$** and both the substituent and probe, increases with the electron withdrawing strength of the substituent, as if they promote greater communication.

The only property which consistently related to the substituent effect throughout all systems (with both backbone and probe substitutions) is the x-component of the dipole moment. It appears that for all systems, μ_x of the substituent dipole is controlling the effect upon the entire molecule. This consistency suggests that the dipole moment is the mechanism of transmission. Analogs 1 and 3 generally have a larger magnitude in the corresponding direction (e.g., μ_x for Li is more positive and the μ_x of NO_2 is more negative) of $\mu_x(R_{HA})$ than the all-carbon backbone. NH_2 substitution represents the only exception within analog 3, as it has a smaller magnitude. In analog 2 there is no consistency with respect to the original systems. The H, NH_2 and OH (also F and CF_3 in analog S2) substituents all result in a smaller μ_x, and all other substituents have a larger magnitude.

The atomic dipole moment has previously been shown to conform to the principle of atomic transferability,[88,89] and thus the substituent-only dipole moment [$\mu_x(R_H)$] recreates the substituent dipole moment within the systems very well. We were able to replace the traditional substituent constant, σ, with $\mu_x(R_H)$ to achieve a better representation of the substituent effect in the form of equation 6.2.

$$\Delta_{iso}E = \rho_\mu \mu_x(R_H) + \zeta\chi + \delta_1 E_s(B) + \delta_2 E_s(P) \tag{6.4}$$

This is also attractive as it replaces a compounded empirical term with one determined by quantum mechanical means. The substituent effect in all analog systems was described using $\mu_x(R_H)$, as well as the electronegativity and steric terms, to essentially recreate the entire effect (equations 5.14 through 5.19; all r^2 values at least 0.996). This approach can also be used to describe effect upon the all-carbon backbones according to equations 6.3 and 6.4.

$$\begin{aligned}\Delta_{iso-C}E = -0.65\mu_x(R_H) - 1.65\chi - 0.48\Delta_{HA-C}Dev(E_a)\\ - 18.15\Delta_{HA-C}\theta(O - C_O - O_H)\\ + 3.12 \quad (r^2 = 0.999, n = 10)\end{aligned} \tag{6.5}$$

$$\begin{aligned}\Delta_{iso-Si}E = -0.59\mu_x(R_H) - 0.37\chi - 0.13\Delta_{HA-Si}Dev(E_a)\\ + 4.25\Delta_{HA-Si}Dev(Si_O) + 0.51 \quad (r^2 = 0.999, n = 10)\end{aligned} \tag{6.6}$$

Although both relationships return a very good squared correlation coefficient, the intercept in the relationship describing the C-system, equation 6.3, is significant and represents a 12.5% error on the scale of the reaction energy. Both all-carbon backbones have negative ρ_{μ} values (following the form in equation 6.2) and are within the same order of magnitude, as are all values. The small differences in the prefactor magnitudes reinforces the transferability of $\mu_x(R_H)$. Use of analog 2, and analog 1 with the C-probe only, results in a positive value for the prefactor. Describing ρ_{μ} in terms of a pseudo-reaction constant for $\mu_x(R_H)$, and setting the value for the C-system equal to 1.00, returns essentially the same trend observed in the full reaction constant. Apart from an obvious change in sign, those systems that result in a more sensitive reaction to substitution also have a more sensitive dipole moment [ρ_{μ}(Si)=0.91, ρ_{μ}(AC1)=-1.51, ρ_{μ}(AC2)=-0.82, ρ_{μ}(AC3)=0.45, ρ_{μ}(AS1)=0.87, and ρ_{μ}(AS3)=0.97]. The only exception to this is for analog S2, which appears to be more sensitive [ρ_{μ}(AS2)=-1.14].

Although linear free energy relationships were derived, via quantum mechanical means, to describe the “so-called” inductive effect in these systems, future work must be undertaken to confirm their validity. To provide a more complete the picture, the list of substituents should be expanded to include more electron donating groups and at least one Si-based substituent, such as SiH_3. The same approach should be applied to another backbone system to determine if the mode of transmission is the same. Bicyclo[2.2.2]octane represents the next logical choice for a backbone moiety. The substituent–probe distance will be longer, but any issues surrounding the potential overlap between orbitals on the bridgehead atoms, as possible in the bicyclo[1.1.1]pentane system,[33,105] can be avoided.

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Appendix 1: Supplemental Information and Figures

Topsom's method for calculating σ$_F$ as used in this discussion (Original reference: Topsom, R. D. *Prog. Phys. Org. Chem.* **1987**, *16*, 125.)

The structures of H_2 and HR were optimized separately at the PBE0/6-31++G(d,p) level of theory. A single point energy calculation was performed for the "complex" outlined in Scheme A1.1 at the same level of theory.

Mulliken populations were used in equation A1.1 to determine the difference in charge on H_α when "complexed".

$$\Delta q_{H\alpha} = q_{H\alpha}(H_2 \cdots HR) - q_{H\alpha}(H_2 \cdots H_2) \tag{A1.1}$$

$$\sigma_F = -35.5\Delta q_{H\alpha} \tag{A1.2}$$

Equation A1.2 was used to convert the relative charge to σ$_F$.

SCHEME A1.1

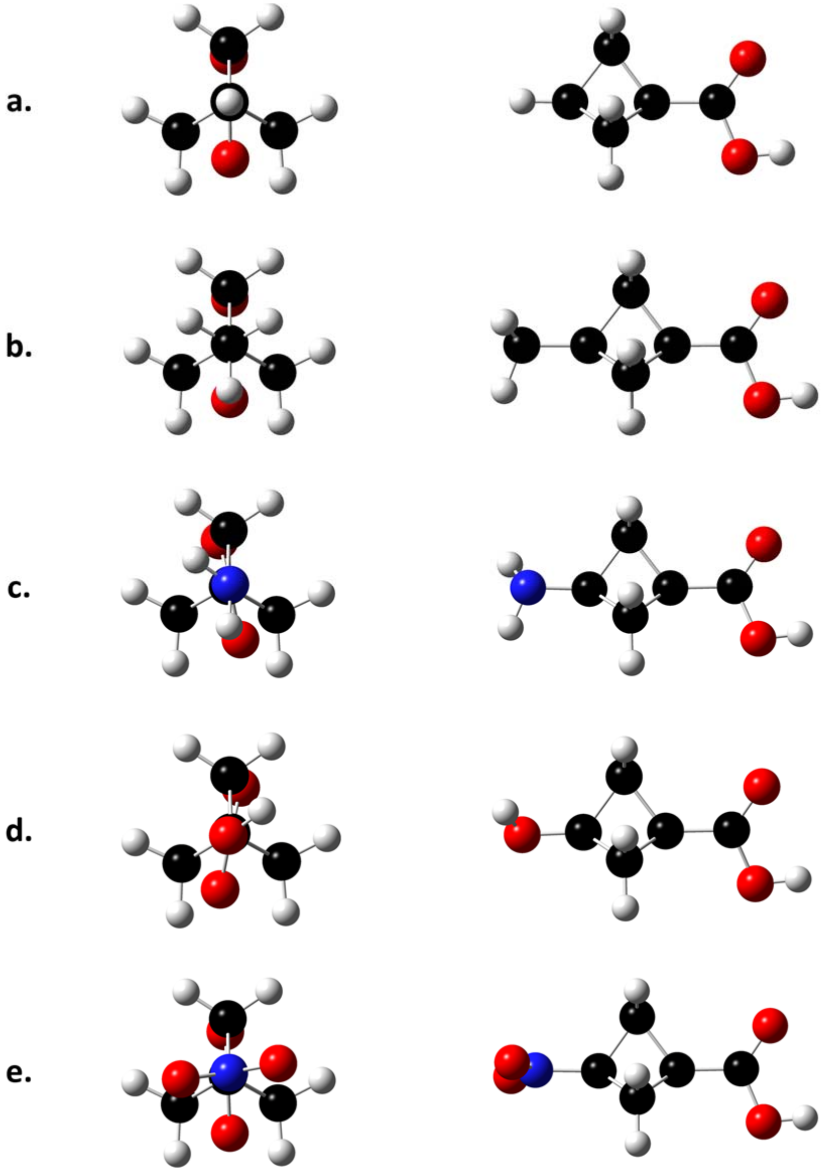


Figure A1.1. Angular orientation of the substituent with respect to the backbone and probe. Also included in each grouping are: (a) F, Li, and CN, (b) CF_3, (c) NF_2. OH and NO_2 are in groups of their own (c and d, respectively). All geometries optimized at the PBE0/6-31++G(d,p) level of theory.

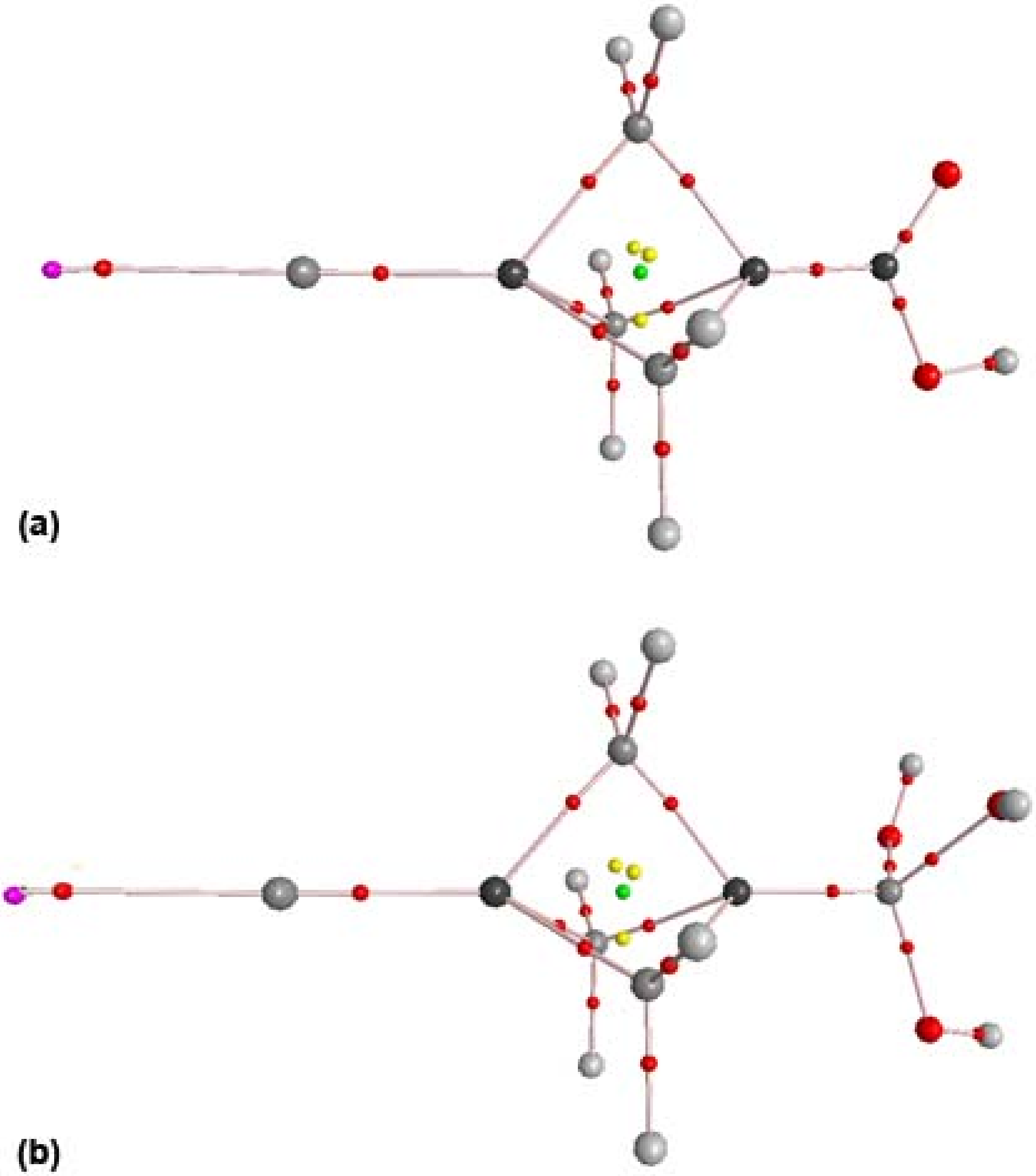


Figure A1.2. Molecular graphs for the acid species with backbone 2, and (a) the carboxylic acid probe and (b) the silicic acid probe, showing the presence of a non-nuclear attractor (NNA) in each case. The molecular graphs were determined using wavefunctions generated at the PBE0/6-31++G(d,p) level of theory.

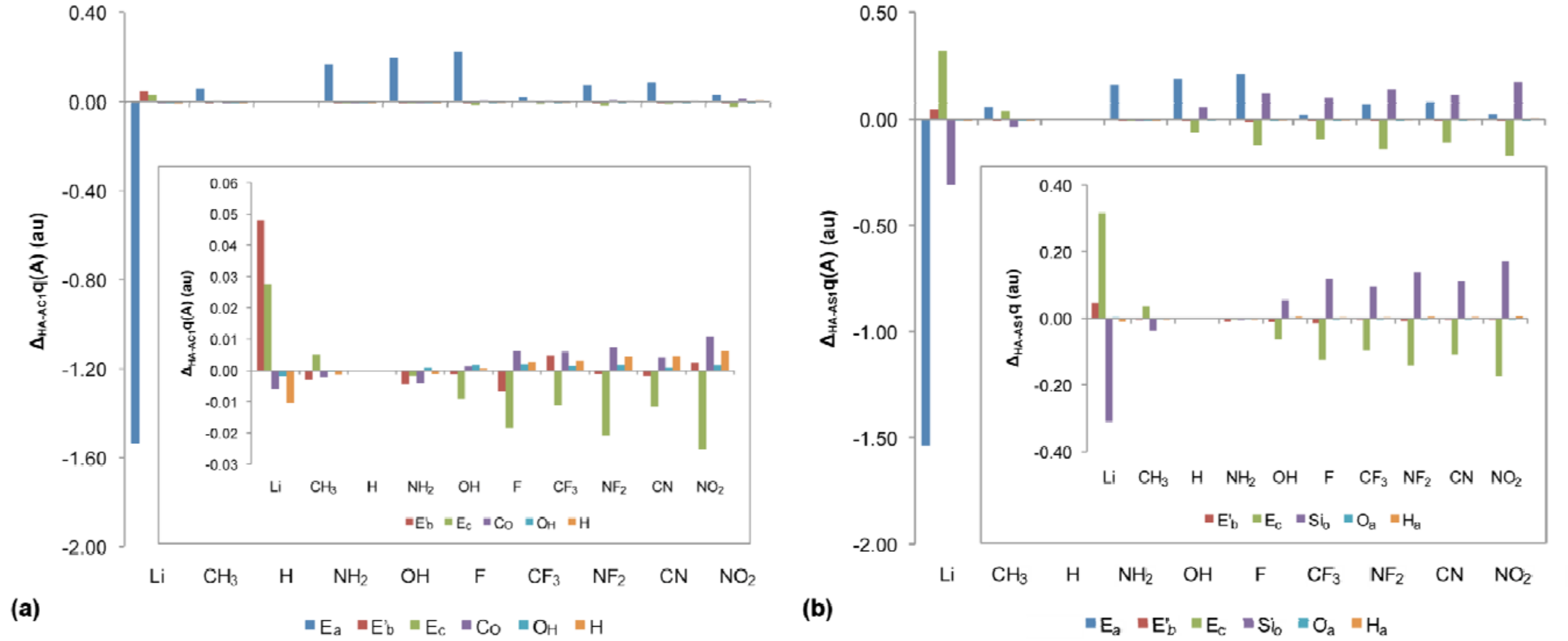


Figure A1.3. Graphical representation of the decay in the relative charge with increasing distance from the substituent group for analogs C1 and S1. Inset is a large version from atom C_b to H_a to show detail masked by the large changes on Si_a. All values were calculated from wavefunctions generated at the PBE0/6-31++G(d,p) level of theory.

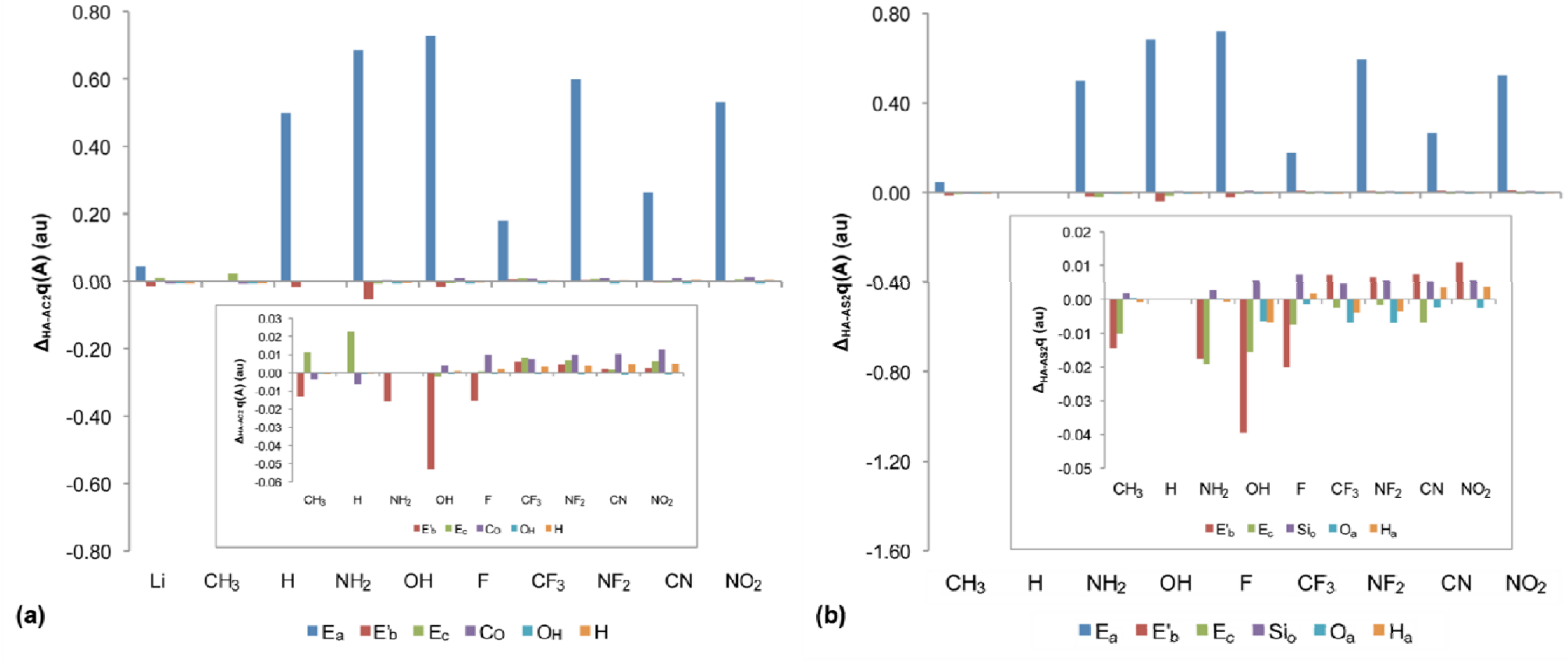


Figure A1.4. Graphical representation of the decay in the relative charge with increasing distance from the substituent group for analogs C2 and S2. Inset is a large version from atom C_b to H_a to show detail masked by the large changes on C_a. All values were calculated from wavefunctions generated at the PBE0/6-31++G(d,p) level of theory.

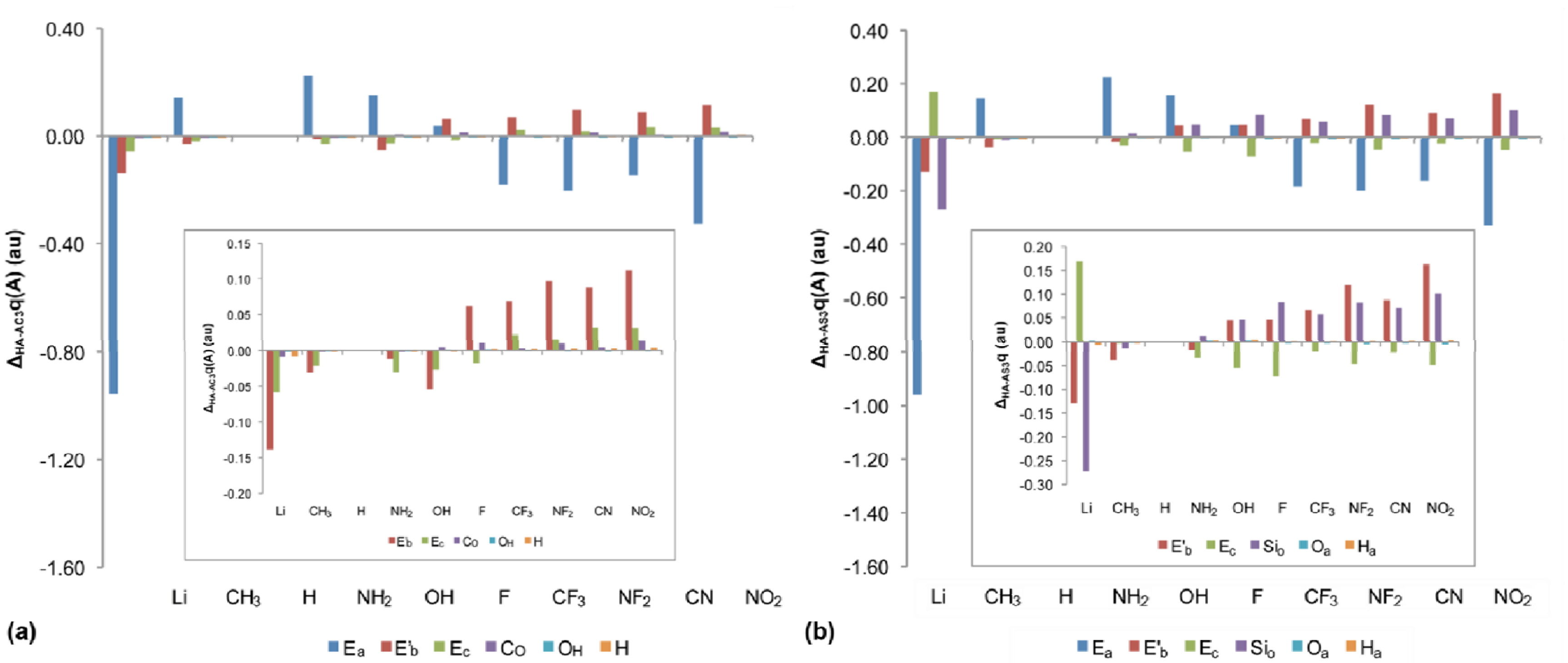
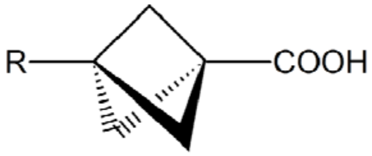
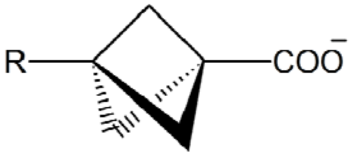


Figure A1.5. Graphical representation of the decay in the relative charge with increasing distance from the substituent group for analogs C3 and S3. Inset is a large version from atom C_b to H_a to show detail masked by the large changes on Si_a. All values were calculated from wavefunctions generated at the PBE0/6-31++G(d,p) level of theory.

Appendix 2: Cartesian Coordinates and Absolute Energies





Acid R=H
E = -383.43599987 au

C	2.01432800	-0.05122200	0.00007000
H	3.10485900	-0.10133000	0.00014700
C	1.13806800	1.22704800	-0.00125700
H	1.15760300	1.84093700	0.90421200
H	1.15767300	1.83938100	-0.90775700
C	1.05509300	-0.63177200	-1.06773400
H	1.06684600	-0.15591500	-2.05360400
H	0.99031500	-1.72173600	-1.13667400
C	1.05506300	-0.62951200	1.06900500
H	0.99030700	-1.71934900	1.14016300
H	1.06672000	-0.15175800	2.05396300
C	0.15205000	0.04348300	-0.00009600
C	-1.33629300	0.13140800	-0.00012500
O	-1.97670500	1.15810700	0.00000100
O	-1.91473100	-1.08644100	0.00002000
H	-2.87268300	-0.94015600	0.00019800

Conjugate Base R=H
E = -382.87683447 au

C	1.97342900	-0.00667300	0.00013500
H	3.07219900	-0.02022000	0.00024400
C	1.05543300	1.23608900	-0.00043800
H	1.04889500	1.85438300	0.90502400
H	1.04916600	1.85347200	-0.90648900
C	1.03301600	-0.61637400	-1.06228100
H	1.02934800	-0.14219400	-2.05232500
H	0.99773100	-1.70919200	-1.13450300
C	1.03274700	-0.61554400	1.06278300
H	0.99748300	-1.70833800	1.13584800
H	1.02877200	-0.14048500	2.05239800
C	0.08965300	0.02079600	-0.00013600
C	-1.44423700	0.00479500	-0.00007000
O	-2.00432300	1.12769000	-0.00003400
O	-1.95365600	-1.14343500	0.00001400

Acid R=CH_3
E = -422.71139320 au

C	1.58500100	-0.00875300	0.00000700
C	0.67704700	1.25336000	-0.00010500
H	0.68749200	1.86753700	0.90612400
H	0.68752900	1.86730300	-0.90648800
C	0.62478100	-0.60323300	-1.06701100
H	0.62965300	-0.12657800	-2.05329300
H	0.57914800	-1.69472200	-1.13730400
C	0.62474900	-0.60305500	1.06710200
H	0.57911500	-1.69453600	1.13758000
H	0.62959100	-0.12619300	2.05328200
C	-0.28656900	0.05533100	-0.00002900
C	-1.77481600	0.11597900	-0.00000900
O	-2.43592500	1.12969100	0.00000500
O	-2.33136000	-1.11289800	0.00000800
H	-3.29159000	-0.98286500	0.00003400
C	3.08495000	-0.05232500	0.00002400
H	3.48963000	0.44893900	-0.88587300
H	3.48961700	0.44896700	0.88591200
H	3.44723700	-1.08602000	0.00004800

Conjugate Base R=CH_3
E = -422.15133572 au

C	-1.53907100	0.00219700	-0.00003800
C	-0.60918800	1.24019600	-0.00001400
H	-0.60317400	1.85840100	-0.90630200
H	-0.60335700	1.85842500	0.90622700
C	-0.59297300	-0.60930500	1.06134100
H	-0.59037100	-0.13425300	2.05160300
H	-0.56369200	-1.70286700	1.13418300
C	-0.59278900	-0.60941600	-1.06117000
H	-0.56351700	-1.70301100	-1.13386200
H	-0.58996200	-0.13446300	-2.05147500
C	0.35077000	0.02348400	0.00014000
C	1.88434300	0.00091600	0.00002600
O	2.44967000	1.12113800	-0.00004600
O	2.38854000	-1.14959600	-0.00005100
C	-3.04618600	-0.01058700	-0.00013600
H	-3.44412300	0.49821600	0.88726200
H	-3.44405000	0.50005300	-0.88651500
H	-3.43287200	-1.03774600	-0.00123200

Acid R=CN
E = -475.57594475 au

C	1.31800800	0.00518100	0.00001800
C	0.40812100	1.26516000	-0.00056800
H	0.42578200	1.87389600	0.90679100
H	0.42586100	1.87305900	-0.90848300
C	0.37203100	-0.59997600	-1.07135400
H	0.38622300	-0.11993400	-2.05361700
H	0.34906000	-1.69056600	-1.13627200
C	0.37195300	-0.59899100	1.07187200
H	0.34897500	-1.68952600	1.13778900
H	0.38604600	-0.11802300	2.05368200
C	-0.54404000	0.05293400	-0.00008600
C	-2.03387900	0.10759100	-0.00003000
O	-2.68864500	1.12345100	0.00001500
O	-2.57955300	-1.12242500	0.00002600
H	-3.54196700	-1.00689000	0.00011700
C	2.76068600	-0.02577200	0.00003700
N	3.92118900	-0.05242500	0.00004800

Conjugate Base R=CN
E = -475.03468744 au

C	-1.27145700	0.00470200	-0.00000600
C	-0.34367700	1.24707900	-0.00038200
H	-0.34987300	1.85812700	-0.90812200
H	-0.34990100	1.85863700	0.90700900
C	-0.33271800	-0.61194900	1.06636400
H	-0.34252600	-0.13324200	2.05164300
H	-0.32013900	-1.70368000	1.13258000
C	-0.33267900	-0.61265700	-1.06593700
H	-0.32009300	-1.70443700	-1.13144000
H	-0.34244100	-0.13456700	-2.05151400
C	0.60891800	0.02105800	0.00002300
C	2.14145200	-0.00069600	-0.00000600
O	2.69676900	1.12223500	-0.00001900
O	2.63870700	-1.15196200	-0.00000600
C	-2.71781400	-0.00338400	-0.00000800
N	-3.88156900	-0.00970600	-0.00003500

Acid R=CF_3
E = -720.18741268 au

C	0.63523400	-0.01367200	-0.00001000
C	-0.26462000	-1.27219800	-0.00026500
H	-0.25305800	-1.88019700	-0.90822700
H	-0.25312800	-1.88052000	0.90748700
C	-0.29695200	0.59336800	1.07230000
H	-0.28839800	0.11222100	2.05408200
H	-0.32299300	1.68388100	1.13734400
C	-0.29690100	0.59378600	-1.07213800
H	-0.32292300	1.68432000	-1.13676900
H	-0.28829800	0.11301200	-2.05410300
C	-1.21517200	-0.05777800	-0.00007500
C	-2.70544000	-0.10793400	-0.00001300
O	-3.36535800	-1.12068100	0.00002900
O	-3.24802400	1.12409700	0.00002800
H	-4.21049300	1.00970100	0.00010300
C	2.13135400	0.01404500	0.00001800
F	2.60434900	1.27580400	-0.00046600
F	2.63787100	-0.60233300	1.08537300
F	2.63792800	-0.60318800	-1.08482500

Conjugate Base R=CF_3
E = -719.64148793 au

C	0.58667200	-0.00610100	0.00000000
C	-0.32774800	-1.24908200	0.00052900
H	-0.32791800	-1.86065900	-0.90687700
H	-0.32802500	-1.85977900	0.90852500
C	-0.33895500	0.61175200	1.06670600
H	-0.33501000	0.13324300	2.05209200
H	-0.35819100	1.70343700	1.13176500
C	-0.33885700	0.61083500	-1.06732600
H	-0.35803600	1.70247500	-1.13334300
H	-0.33481800	0.13146900	-2.05229700
C	-1.28183700	-0.02275600	-0.00008200
C	-2.81599700	0.00053700	0.00000500
O	-3.37420800	-1.12116800	-0.00000200
O	-3.31293100	1.15216900	0.00005000
C	2.07860300	0.00200000	0.00001800
F	2.59360300	1.25585900	-0.00138800
F	2.60139500	-0.62010600	1.08508000
F	2.60142700	-0.62256400	-1.08361900

Acid R=NH_2
E = -438.73887749 au

C	1.59400200	-0.01256500	-0.00069100
C	0.70025900	1.21824700	-0.28117300
H	0.70758200	2.01749200	0.46676600
H	0.72065100	1.61042800	-1.30234500
C	0.64527700	-0.83118200	-0.90677300
H	0.66285900	-0.58503000	-1.97305300
H	0.59756200	-1.91053100	-0.73066900
C	0.62746600	-0.35184000	1.18360600
H	0.57361300	-1.39969100	1.49652300
H	0.62399500	0.33820100	2.03414200
C	-0.26754800	0.04956000	-0.01690600
C	-1.75267500	0.11746200	-0.00884300
O	-2.40756700	1.13525100	-0.00516000
O	-2.31622300	-1.10802400	0.01220300
H	-3.27527200	-0.97149400	0.03439500
N	3.01078600	-0.02482000	-0.08191500
H	3.39397400	-0.93828700	0.13461900
H	3.42915800	0.65674300	0.54137100

Conjugate Base R=NH_2
E = -438.18017610 au

C	1.54449200	-0.00001200	-0.00844300
C	0.62701300	1.06967700	-0.62826100
H	0.60038100	2.05268100	-0.14399900
H	0.64135600	1.15275900	-1.72155200
C	0.62690500	-1.06770700	-0.63152900
H	0.64123700	-1.14734900	-1.72509500
H	0.60011500	-2.05212100	-0.15017800
C	0.59144200	-0.00185100	1.21743100
H	0.56537700	-0.91319400	1.82838800
H	0.56556100	0.90780500	1.83088000
C	-0.33039900	0.00015200	-0.03450200
C	-1.86507400	0.00000200	-0.00707100
O	-2.39811600	1.13566800	0.01772400
O	-2.39772700	-1.13584700	0.01784200
N	2.98413500	0.00007200	-0.06782700
H	3.34877100	-0.81821900	0.41186000
H	3.34872100	0.81700200	0.41421200

Acid R=NO_2
E = -587.74345529 au

C	-0.93719700	-0.01129100	0.00190800
C	-0.07122200	1.13049400	-0.56965600
H	-0.09258100	1.25947200	-1.65393400
H	-0.09702500	2.07719500	-0.02629100
C	-0.02780900	-0.05151400	1.23532700
H	-0.04855000	0.82395300	1.88716500
H	0.00463200	-0.99458300	1.78546800
C	-0.02699600	-1.02566300	-0.69369100
H	0.00633500	-2.02871800	-0.26301000
H	-0.04251300	-1.03052600	-1.78523200
C	0.88549900	0.04732600	-0.02345000
C	2.37427300	0.09845300	-0.05285400
O	3.02484500	0.99211300	-0.54059400
O	2.92091000	-0.98126600	0.53337300
H	3.88320200	-0.88046300	0.47534600
N	-2.41352600	-0.02331300	0.01172500
O	-2.96167000	0.60910800	0.89878800
O	-2.97134900	-0.64370100	-0.87745400

Conjugate Base R=NO_2
E = -587.20493332 au

C	-0.88529000	-0.02469500	0.00204700
C	-0.00975600	1.23830100	-0.08829200
H	-0.02566300	1.77600300	-1.03982400
H	-0.02265500	1.90536200	0.77758600
C	0.01618300	-0.54590900	1.11674900
H	0.00518500	0.00847100	2.05876700
H	0.04445800	-1.62924500	1.26048200
C	0.01461600	-0.69731100	-1.03089500
H	0.04361900	-1.78996800	-1.02078300
H	0.00085700	-0.28113600	-2.04151700
C	0.94925900	0.01585000	-0.00324500
C	2.48676100	0.00790800	-0.00106300
O	3.02702500	1.13585600	-0.04259300
O	2.99178100	-1.13700900	0.04485500
N	-2.36977000	-0.01107800	0.00147400
O	-2.94049800	0.05430300	1.08222900
O	-2.93931300	-0.03774900	-1.08159500

Acid R=NF_2
E = -636.91358374 au

C	-0.89875200	0.06591400	0.21539900
C	0.03522300	1.26430000	0.46438200
H	-0.02631500	2.08548000	-0.25262800
H	0.12332800	1.61128300	1.49662900
C	0.06996400	-0.81993600	1.01535300
H	0.16010700	-0.60612400	2.08351800
H	0.04760900	-1.88906600	0.79464600
C	-0.09797400	-0.26280500	-1.06052000
H	-0.12356300	-1.29931900	-1.40246600
H	-0.16095400	0.45953800	-1.87745700
C	0.92671400	0.06753000	0.06596900
C	2.41096400	0.08128700	-0.06054300
O	3.10793800	1.06144900	0.05825500
O	2.89953600	-1.14269200	-0.33300500
H	3.86184100	-1.05395800	-0.40698300
N	-2.32565400	0.09710700	0.43483300
F	-2.77828000	-1.15008700	-0.01517800
F	-2.81495400	0.95949000	-0.55385900

Conjugate Base R=NF_2
E = -636.36992683 au

C	-0.84651900	0.00095900	0.21548700
C	0.10248300	1.07853000	0.75641400
H	0.06851900	2.05512600	0.26801500
H	0.19296700	1.15397200	1.84475400
C	0.10226100	-1.07381200	0.76246000
H	0.19270000	-1.14320200	1.85121500
H	0.06806900	-2.05308400	0.27946100
C	-0.04913200	-0.00294500	-1.09571400
H	-0.09245000	-0.91635900	-1.69519700
H	-0.09237400	0.90699600	-1.70051100
C	0.99243800	0.00032300	0.07000700
C	2.52109900	-0.00047900	-0.08963000
O	3.04345000	1.13623000	-0.15297200
O	3.04104500	-1.13793300	-0.15966700
N	-2.27642000	0.00175600	0.45418700
F	-2.77853600	-1.09233200	-0.28715700
F	-2.77860000	1.09038100	-0.29507500

Acid R=OH
E = -458.59021320 au

C	-1.59200300	-0.01889900	-0.00063400
C	-0.64602000	-0.34987100	1.18417200
H	-0.64222900	0.34420600	2.03125000
H	-0.59517100	-1.39632300	1.49759800
C	-0.66048400	-0.83916200	-0.90517200
H	-0.61687800	-1.91566300	-0.72009800
H	-0.67738000	-0.59746900	-1.97212200
C	-0.70927500	1.22424300	-0.28942200
H	-0.72391900	1.61118700	-1.31246700
H	-0.71229200	2.02503600	0.45667200
C	0.25184600	0.05155900	-0.01957500
C	1.73658700	0.11931800	-0.00894700
O	2.39041800	1.13724300	-0.00679100
O	2.29714500	-1.10634900	0.01644400
H	3.25657900	-0.97183100	0.04003500
O	-2.96507300	-0.12462200	-0.05049100
H	-3.35254600	0.52754700	0.54331500

Conjugate Base R=OH
E = -458.03517749 au

C	1.54109500	0.01788000	-0.00000200
C	0.62206100	-0.60093400	1.07069500
H	0.58623100	-1.69429600	1.13853200
H	0.61815500	-0.12067200	2.05611900
C	0.64317600	1.25608400	-0.00138300
H	0.63946700	1.86889000	0.90605700
H	0.63960200	1.86691100	-0.91016100
C	0.62219100	-0.60325700	-1.06946000
H	0.61842300	-0.12516100	-2.05594100
H	0.58634800	-1.69675800	-1.13492700
C	-0.31342100	0.03153700	-0.00014300
C	-1.85041300	-0.00542300	-0.00007900
O	-2.33813300	-1.16158600	0.00022800
O	-2.42355600	1.10857100	-0.00004900
O	2.94441500	0.07318900	0.00002100
H	3.26183300	-0.83562900	0.00095600

Acid R=F
E = -482.59478998 au

C	1.57866400	-0.01166800	0.00002600
C	0.72315700	1.26339900	-0.00042400
H	0.73625600	1.86938100	0.90879600
H	0.73635100	1.86877600	-0.91004200
C	0.66522600	-0.61094100	-1.07762300
H	0.67352100	-0.12767000	-2.05827600
H	0.61701800	-1.70079800	-1.13876100
C	0.66513000	-0.61025200	1.07796700
H	0.61691600	-1.70007800	1.13979000
H	0.67330400	-0.12634400	2.05830400
C	-0.23976400	0.05677900	-0.00009900
C	-1.72492100	0.11822100	-0.00002700
O	-2.38128500	1.13341400	0.00003200
O	-2.27643400	-1.11067700	0.00001000
H	-3.23750400	-0.98641900	0.00010000
F	2.93788200	-0.05688600	0.00009300

Conjugate Base R=F
E = -482.04568398 au

C	-1.52517700	0.00104500	-0.00000300
C	-0.65537100	1.25466000	-0.00022500
H	-0.64977200	1.86259800	-0.90987100
H	-0.64976900	1.86291200	0.90921100
C	-0.63381700	-0.61435100	1.07351500
H	-0.63184800	-0.13110200	2.05632300
H	-0.59863300	-1.70552400	1.13602300
C	-0.63381800	-0.61475600	-1.07328700
H	-0.59862600	-1.70595200	-1.13539000
H	-0.63184400	-0.13186900	-2.05627200
C	0.29982100	0.02758900	-0.00000500
C	1.84095500	0.00101600	-0.00000500
O	2.40140400	1.12014800	-0.00000400
O	2.33328500	-1.15122600	0.00000700
F	-2.91917500	-0.01485200	0.00000100

Acid R=Li
E = -390.29839018 au

C	1.93298500	-0.03492400	0.00001900
C	0.97901600	1.23198400	-0.00031700
H	0.98434600	1.85510600	0.90274500
H	0.98436700	1.85463600	-0.90370400
C	0.90841400	-0.61420600	-1.05986600
H	0.90529700	-0.14477100	-2.05249000
H	0.84027200	-1.70630800	-1.13869300
C	0.90839300	-0.61365300	1.06018200
H	0.84024900	-1.70571600	1.13957600
H	0.90524800	-0.14369600	2.05255900
C	0.01041900	0.04978000	-0.00002800
C	-1.48690000	0.12468200	-0.00002600
O	-2.14915600	1.14011900	-0.00002700
O	-2.06308600	-1.09961000	0.00003200
H	-3.02019400	-0.94870200	0.00006700
Li	3.91479500	-0.08220000	0.00004000

Conjugate Base R=Li
E = -389.72009516 au

C	1.86066500	-0.00717900	0.00001200
C	0.90257900	1.23571300	-0.00032200
H	0.89361000	1.85809300	0.90390400
H	0.89364700	1.85762700	-0.90487000
C	0.87897000	-0.61387600	-1.06153300
H	0.87230800	-0.14170900	-2.05408700
H	0.83845800	-1.70730200	-1.13988200
C	0.87892900	-0.61332500	1.06183300
H	0.83841800	-1.70671200	1.14074700
H	0.87222600	-0.14063800	2.05413800
C	-0.04604800	0.02223600	-0.00003600
C	-1.60289100	0.00369500	-0.00003400
O	-2.15907300	1.12616800	0.00000700
O	-2.10609800	-1.14449300	0.00004500
Li	3.89316100	-0.01211500	0.00003700

All-Carbon Backbone R=H

E = -195.04455759 au

C	0.00001500	-0.00000100	-0.93503600
H	-0.00022100	0.00000200	-2.02858500
C	1.23345200	-0.00440700	-0.00011500
H	1.84662700	-0.91241200	-0.00017700
H	1.85306200	0.89921500	-0.00017700
C	-0.61303800	1.07041200	0.00002600
H	-0.13293800	2.05519700	0.00000400
H	-1.70544100	1.15455000	0.00018500
C	-0.62067500	-1.06600700	0.00002500
H	-1.71365300	-1.14233100	0.00018500
H	-0.14761300	-2.05419200	0.00000300
C	0.00021200	-0.00000100	0.93510200
H	0.00038000	-0.00000400	2.02855500

All-Carbon Backbone R=CH_3

E = -234.31969159 au

C	0.48338500	-0.00036900	-0.00051600
C	-0.46319100	-0.72000600	-0.99925400
H	-0.46211100	-0.34570900	-2.02971800
H	-0.46202700	-1.81587400	-0.96941900
C	-0.46197100	-0.50546900	1.12336200
H	-0.46080900	-1.58510100	1.31361100
H	-0.45960500	0.06823900	2.05754200
C	-0.46192100	1.22571400	-0.12388000
H	-0.45959900	1.93027300	0.71605800
H	-0.46063800	1.74762400	-1.08793100
C	-1.39499300	0.00041200	0.00049100
H	-2.48758100	0.00069800	0.00092700
C	1.98560100	-0.00025700	-0.00032200
H	2.37728400	-1.01829700	0.10285900
H	2.37737500	0.41978400	-0.93336800
H	2.37625100	0.59821700	0.83014400

All-Carbon Backbone R=CN

E = -287.18696178 au

C	0.19313500	0.00005200	0.00012200
C	-0.74390800	-0.01706900	1.23695000
H	-0.73005300	-0.93287500	1.83515300
H	-0.73017100	0.88190000	1.86017900
C	-0.74357800	1.08010900	-0.60375500
H	-0.72996200	2.05582200	-0.10925900
H	-0.72953800	1.17030500	-1.69389800
C	-0.74344300	-1.06307200	-0.63329600
H	-0.72939000	-1.12318800	-1.72550600
H	-0.72969900	-2.05203700	-0.16587200
C	-1.67492700	-0.00006100	-0.00025300
H	-2.76544400	-0.00013000	-0.00040600
C	1.63790200	0.00012500	0.00017000
N	2.79902600	-0.00004300	-0.00000400

All-Carbon Backbone R=CF_3

E = -531.79790401au

C	-0.38066200	0.00000900	0.00003800
C	-1.30464000	0.88169200	0.86909000
H	-1.29539300	0.67993200	1.94431300
H	-1.29587700	1.95358700	0.65042200
C	-1.30509300	0.31229200	-1.19809400
H	-1.29659400	1.34472900	-1.55997600
H	-1.29632100	-0.41232800	-2.01762000
C	-1.30433800	-1.19384700	0.32872500
H	-1.29531100	-2.02323400	-0.38457900
H	-1.29511300	-1.54156100	1.36594200
C	-2.23696400	-0.00038800	0.00050500
H	-3.32814500	-0.00062700	0.00092100
C	1.11596300	0.00003600	-0.00015900
F	1.61475400	-0.89210300	-0.87959500
F	1.61469800	1.20790000	-0.33255300
F	1.61467700	-0.31571500	1.21214200

All-Carbon Backbone R=NH_2

E = -250.34740752 au

C	-0.50208500	0.00023200	-0.00338600
C	0.43141500	-1.06357100	-0.62370300
H	0.43134300	-2.05293400	-0.15129700
H	0.42242900	-1.13350800	-1.71650600
C	0.43177600	1.07021000	-0.61251500
H	0.42288300	1.15172700	-1.70456500
H	0.43207400	2.05458600	-0.12984800
C	0.44675000	-0.00676500	1.24063000
H	0.45020200	0.89743500	1.86045800
H	0.44987100	-0.91775900	1.85050300
C	1.36544800	-0.00017900	0.00129300
H	2.45599200	-0.00006900	-0.00427700
N	-1.92270600	0.00066400	-0.09997000
H	-2.32299400	0.81959400	0.34524200
H	-2.32268200	-0.82328600	0.33616200

All-Carbon Backbone R=NO_2
E = -399.35497541 au

C	0.12668900	0.01588300	-0.00016300
C	1.02024100	-0.62174600	1.07554500
H	1.01035800	-0.13855300	2.05627200
H	0.99444800	-1.71203700	1.13967600
C	1.02075700	-0.62530400	-1.07339800
H	0.99471400	-1.71560000	-1.13312600
H	1.01160200	-0.14693700	-2.05652200
C	1.02984800	1.24880700	-0.00214800
H	1.02340900	1.85408900	-0.91163000
H	1.02303900	1.85822300	0.90486100
C	1.95317300	-0.00174400	0.00036600
H	3.04240400	-0.00668100	0.00054500
N	-1.35309300	0.00337300	-0.00024600
O	-1.88907700	-1.09294900	0.00003100
O	-1.92749300	1.07901300	0.00002300

All-Carbon Backbone R=NF_2
E = -448.52447342 au

C	-0.16176200	-0.00003500	-0.15440900
C	-1.17581400	1.07453800	-0.57742800
H	-1.06206400	2.05528500	-0.10826900
H	-1.39306000	1.14451300	-1.64696200
C	-1.17610400	-1.07411900	-0.57812800
H	-1.39335400	-1.14339200	-1.64771500
H	-1.06262800	-2.05520900	-0.10962800
C	-0.79360600	-0.00043100	1.25184400
H	-0.66054700	-0.90963700	1.84347100
H	-0.66030800	0.90837000	1.84406800
C	-1.95766100	0.00008400	0.22523700
H	-3.02425400	0.00009700	0.44837200
N	1.22834400	-0.00004400	-0.55451000
F	1.79154500	-1.08951100	0.12531800
F	1.79151000	1.08951700	0.12529800

All-Carbon Backbone R=OH
E = -270.19966311 au

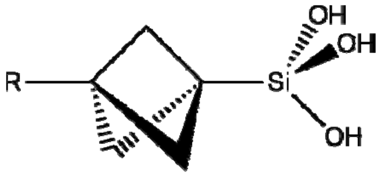
C	-0.50825100	0.01093500	0.00003900
C	0.41186800	-0.62557100	-1.07367100
H	0.40614000	-1.71924200	-1.14601100
H	0.41446800	-0.14773900	-2.05857900
C	0.41878800	1.23417700	-0.00452100
H	0.41802800	1.84183400	-0.91494800
H	0.41825200	1.84859900	0.90144500
C	0.41184300	-0.61756400	1.07822500
H	0.41467900	-0.13253400	2.05960800
H	0.40623400	-1.71070900	1.15839300
C	1.34066000	-0.01138100	-0.00003200
H	2.42983200	-0.01990700	0.00017000
O	-1.88689100	0.10924000	-0.00034800
H	-2.26194800	-0.77779700	0.00246200

All-Carbon Backbone R=F
E = -294.20543787 au

C	0.50091300	0.00008200	-0.00004400
C	-0.39485000	1.23239000	-0.17582100
H	-0.39234700	1.96205100	0.63900800
H	-0.39227800	1.70586000	-1.16189200
C	-0.39501600	-0.76867200	-0.97905800
H	-0.39257800	-0.42821700	-2.01852000
H	-0.39267300	-1.85929700	-0.89512700
C	-0.39502400	-0.46396600	1.15488000
H	-0.39266200	-1.53448600	1.37933500
H	-0.39255400	0.15344300	2.05774700
C	-1.32111900	0.00027000	-0.00006200
H	-2.40909000	0.00035200	-0.00002900
F	1.86608400	-0.00003700	0.00001200

All-Carbon Backbone R=Li
E = -201.90269378 au

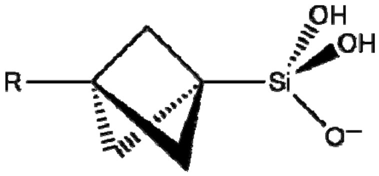
C	0.81932600	-0.00018000	0.00036500
C	-0.18335900	-0.49471900	1.11960700
H	-0.19341900	-1.57405800	1.32794200
H	-0.19354100	0.07888200	2.05721900
C	-0.18283600	1.21714300	-0.13147600
H	-0.19281600	1.93692700	0.69926000
H	-0.19245800	1.74251300	-1.09693600
C	-0.18296200	-0.72240400	-0.98840500
H	-0.19272300	-0.36245200	-2.02701800
H	-0.19317900	-1.82124800	-0.96067200
C	-1.11107600	0.00011200	-0.00010300
H	-2.21604500	0.00033900	-0.00033800
Li	2.80654200	-0.00020600	0.00020400



Acid R=H

E = -711.21752087 au

C	2.59950700	-0.03091700	-0.02489300
C	1.68571400	0.34262300	1.16227500
H	1.68497400	-0.34567100	2.01596700
H	1.69580200	1.38835700	1.48709400
C	1.67265600	0.82436200	-0.91661500
H	1.67835500	1.90589700	-0.74699900
H	1.65213300	0.58262400	-1.98454200
C	1.64913900	-1.21858300	-0.29451900
H	1.62900400	-1.61344800	-1.31608000
H	1.64045900	-2.02374400	0.44873400
C	0.71096700	-0.00427200	-0.00896800
Si	-1.14436500	0.02326200	0.00165000
O	-1.56383200	1.59747700	0.27729900
O	-1.78071800	-1.02506300	1.12657300
O	-1.82359100	-0.47618400	-1.42169700
H	-2.47879100	1.84026900	0.11115100
H	-1.52387800	-0.90729400	2.04433600
H	-2.21435800	-1.35403300	-1.41053900
H	3.69464500	-0.04775100	-0.03330000



Conjugate Base R=H

E = -710.64730223 au

C	-2.57567900	0.00004300	0.00248100
C	-1.65704800	1.06365600	0.63732400
H	-1.63426000	2.05142800	0.16041500
H	-1.66797300	1.14558900	1.73113600
C	-1.65724000	-1.06407100	0.63685200
H	-1.66818300	-1.14641900	1.73062900
H	-1.63466300	-2.05162000	0.15947800
C	-1.61766500	0.00023500	-1.20545400
H	-1.58996200	-0.90616400	-1.82260200
H	-1.58977300	0.90693900	-1.82214700
C	-0.67661900	-0.00015200	0.04506900
Si	1.21649500	-0.00002700	0.10773200
O	1.92847800	-0.00012600	1.50925600
O	1.59594500	1.36256600	-0.85229800
O	1.59658100	-1.36215000	-0.85270600
H	2.28446100	1.83909000	-0.37818200
H	2.28454600	-1.83915900	-0.37829200
H	-3.67764800	0.00011100	-0.02032900

Acid R=CH_3

E = -750.49332194 au

C	-2.20590900	-0.01190300	0.01326800
C	-1.25267000	-1.19923600	0.30318300
H	-1.24036000	-1.58005200	1.33090600
H	-1.24718200	-2.01570500	-0.42866400
C	-1.27464900	0.33928300	-1.17411600
H	-1.27629100	-0.36152100	-2.01844700
H	-1.27889800	1.38079200	-1.51444400
C	-1.26737400	0.84991900	0.89520400
H	-1.26790400	1.92963000	0.71041800
H	-1.25386700	0.62353900	1.96728400
C	-0.30920300	0.00427000	0.00464600
Si	1.54384400	0.01952300	0.00031400
O	1.97865400	1.58661300	-0.29225800
O	2.17486800	-1.04798800	-1.11003700
O	2.21890400	-0.46509400	1.43112900
H	2.89657000	1.82036600	-0.12937200
H	1.90398200	-0.95023300	-2.02617900
H	2.58381300	-1.35404100	1.43812700
C	-3.70895000	-0.02639000	0.01954000
H	-4.09739700	-0.73910000	-0.71657300
H	-4.09258100	-0.31464300	1.00453600
H	-4.11057400	0.96373800	-0.22300400

Conjugate Base R=CH_3

E = -749.92240764 au

C	2.17703900	0.00000000	0.01280600
C	1.21585100	-0.00042900	-1.19714100
H	1.19286800	0.90640600	-1.81485000
H	1.19293500	-0.90765900	-1.81427900
C	1.24831400	-1.06243700	0.64369000
H	1.22994800	-2.05080000	0.16651500
H	1.25758600	-1.14413600	1.73809800
C	1.24822600	1.06268100	0.64309000
H	1.25750400	1.14507900	1.73745100
H	1.22971700	2.05076700	0.16533900
C	0.27170700	-0.00009800	0.04829800
Si	-1.61970700	0.00001500	0.10524900
O	-2.33476700	-0.00027700	1.50524900
O	-1.99755500	-1.36207000	-0.85611100
O	-1.99724200	1.36244700	-0.85565900
H	-2.68633900	-1.83921100	-0.38298900
H	-2.68586300	1.83982000	-0.38255900
C	3.68634400	0.00004100	-0.01313400
H	4.07097600	-0.88772800	-0.53133200
H	4.07089900	0.88691900	-0.53292000
H	4.09729400	0.00097900	1.00456700

Acid R=CN
E = -803.36008600 au

C	1.95998300	-0.00962200	-0.00334700
C	1.02054200	-1.23980200	0.01544600
H	1.02189400	-1.86152000	-0.88452500
H	1.02943100	-1.83989800	0.93027500
C	1.03660700	0.62943000	1.06157300
H	1.05144400	0.16117200	2.05097500
H	1.04904900	1.72133800	1.12126000
C	1.02880000	0.60156700	-1.07851200
H	1.03878600	1.69149200	-1.16539000
H	1.02869600	0.10829300	-2.05460600
C	0.07435800	0.00137300	0.00233800
Si	-1.78157000	0.01438700	-0.00720100
O	-2.19282900	1.61278300	-0.02089600
O	-2.42877400	-0.80528200	1.28275900
O	-2.38754200	-0.76279900	-1.33093200
H	-3.09158000	1.84473600	-0.26980000
H	-2.35671200	-0.41284200	2.15617300
H	-2.91052300	-1.55047500	-1.15838400
C	3.40811300	-0.01988600	-0.00459700
N	4.56917700	-0.02852800	-0.00428700

Conjugate Base R=CN
E = -802.80507893 au

C	1.92844700	-0.00001600	0.01947200
C	0.97850300	-0.00013000	-1.19987800
H	0.97163400	0.90815000	-1.81110100
H	0.97166500	-0.90846200	-1.81101300
C	1.00413200	-1.06737000	0.64927000
H	1.00085900	-2.05056400	0.16727400
H	1.02195900	-1.14306200	1.74131400
C	1.00408200	1.06740900	0.64905500
H	1.02191600	1.14334400	1.74108600
H	1.00075900	2.05052600	0.16689500
C	0.03274500	-0.00004100	0.04727500
Si	-1.86169600	-0.00005700	0.10346900
O	-2.55196500	-0.00040400	1.51206200
O	-2.21806800	-1.35973700	-0.86108600
O	-2.21775700	1.36034100	-0.86038500
H	-2.90117600	-1.85811400	-0.40226200
H	-2.90082400	1.85844200	-0.40117900
C	3.38063600	-0.00001400	-0.00170500
N	4.54400000	-0.00001400	-0.02074900

Acid R=CF$_3$
E = -1047.97116535 au

C	1.26930200	-0.00223700	-0.00356800
C	0.34516000	-1.23469700	-0.05110000
H	0.34298800	-1.80634900	-0.98359500
H	0.34999100	-1.88339700	0.83005300
C	0.35755500	0.57774500	1.09497600
H	0.36891500	0.05650000	2.05759300
H	0.36252500	1.66494800	1.21282900
C	0.35015800	0.66464500	-1.04563100
H	0.35274900	1.75761700	-1.07331900
H	0.34627800	0.22458200	-2.04678200
C	-0.60413800	0.00484800	0.00194400
Si	-2.45996100	0.01491200	-0.00592700
O	-2.87716400	1.61044300	0.06482300
O	-3.10320300	-0.87804600	1.23750400
O	-3.08027000	-0.68536400	-1.36641800
H	-3.78148300	1.84606600	-0.15936800
H	-2.97644000	-0.56620700	2.13681000
H	-3.56376900	-1.50572700	-1.23652500
C	2.76873600	-0.01053000	-0.00423100
F	3.27417200	1.23812300	0.04291400
F	3.26265000	-0.67995500	1.05749800
F	3.26341700	-0.59946900	-1.11111500

Conjugate Base R=CF$_3$
E = -1047.41217609 au

C	-1.23408400	-0.00020000	0.02123900
C	-0.29634400	-0.00039600	-1.19874300
H	-0.28234600	-0.90905100	-1.80914600
H	-0.28242600	0.90794500	-1.80962000
C	-0.32372900	1.06859800	0.65218500
H	-0.31415500	2.05129500	0.16946200
H	-0.33657200	1.14426400	1.74426400
C	-0.32365300	-1.06861900	0.65266200
H	-0.33648800	-1.14355600	1.74478100
H	-0.31401500	-2.05160500	0.17052700
C	0.64920600	-0.00014200	0.05081700
Si	2.54378500	0.00000000	0.10444200
O	3.24309300	-0.00073100	1.50932800
O	2.90160000	1.36113800	-0.85918600
O	2.90213200	-1.36006200	-0.86051900
H	3.58590800	1.85541700	-0.39763500
H	3.58609200	-1.85490000	-0.39905000
C	-2.73069900	-0.00001000	-0.00126100
F	-3.26873800	-0.00042800	1.24235300
F	-3.23976300	1.08454000	-0.63487600
F	-3.24014200	-1.08388500	-0.63571600

Acid R=NH$_2$
E = -766.52203730 au

C	2.20725300	-0.01599900	-0.00911500
C	1.26784700	-1.23372700	-0.11578100
H	1.25420700	-1.76527000	-1.07420500
H	1.27078700	-1.92556900	0.73350500
C	1.28892400	0.51225900	1.11085700
H	1.29925500	-0.05544900	2.04848000
H	1.29010500	1.59342900	1.28795400
C	1.26681900	0.70870600	-1.02152500
H	1.26203300	1.80377300	-0.99977900
H	1.24810100	0.32058300	-2.04607800
C	0.32335000	0.00272300	-0.00617100
Si	-1.52633200	0.01966200	-0.00277400
O	-1.95392700	1.61182200	0.10267400
O	-2.16230200	-0.90661300	1.22369200
O	-2.19941800	-0.62972900	-1.36725700
H	-2.87703700	1.82601900	-0.05728400
H	-1.87138400	-0.72462900	2.12054800
H	-2.56547700	-1.51274500	-1.26798700
N	3.62806000	-0.08571500	0.06650200
H	4.03948600	0.83616400	0.16748800
H	4.02216200	-0.51918200	-0.76179000

Conjugate Base R=NH$_2$
E = -765.95219876 au

C	-2.17542700	-0.01181900	0.00482400
C	-1.26292100	-1.10642100	0.58056800
H	-1.26956500	-1.24204800	1.66949700
H	-1.25127100	-2.06536500	0.04983500
C	-1.23072500	0.05102400	-1.20536400
H	-1.21468100	-0.82403600	-1.86491400
H	-1.20598600	0.99015200	-1.77236300
C	-1.25142800	1.02511300	0.69440400
H	-1.22816200	2.03542500	0.26617900
H	-1.25598300	1.04785900	1.79148300
C	-0.28725700	-0.01076000	0.04154400
Si	1.60265700	-0.00460500	0.10613600
O	1.97277300	1.41330400	-0.77289000
O	1.99662600	-1.30480100	-0.92858500
O	2.30449500	-0.07727900	1.51046100
H	2.65086600	1.87127500	-0.26665100
H	2.68556600	-1.80566300	-0.48112500
N	-3.61630100	-0.07533200	-0.06178500
H	-3.97722400	0.77239200	-0.49093400
H	-4.00126000	-0.12081500	0.87785000

Acid R=NO$_2$
E = -915.52958653 au

C	1.56936100	-0.00892500	-0.00284300
C	0.68095100	0.55489200	1.11058900
H	0.68565300	0.01279300	2.05950400
H	0.68858000	1.63920700	1.23956000
C	0.67621100	0.68730200	-1.03512100
H	0.68646700	1.77934100	-1.02928400
H	0.68335300	0.26866000	-2.04529900
C	0.68545500	-1.24773500	-0.07660700
H	0.69655600	-1.79707300	-1.02165600
H	0.69067000	-1.90916400	0.79261400
C	-0.27090000	-0.00620000	0.00023300
Si	-2.12513100	-0.00218300	0.01477100
O	-2.76618200	-0.60003600	-1.39285000
O	-2.72552900	1.52965400	0.12646800
O	-2.53471000	-0.89548600	1.33950500
H	-2.70023200	-1.54308700	-1.56157200
H	-3.24085900	1.84232100	-0.62208400
H	-3.43031800	-0.81503900	1.67850500
N	3.05571800	0.00931900	-0.00917300
O	3.58827500	1.10383600	0.07261300
O	3.63258000	-1.06154800	-0.09703400

Conjugate Base R=NO$_2$
E = -914.97685375

C	1.52938000	-0.01590700	0.03592100
C	0.65132500	0.88041500	0.90467500
H	0.65880100	0.68032900	1.98014600
H	0.65245000	1.94767800	0.67118800
C	0.63180100	0.30375100	-1.16233400
H	0.63217400	1.33836100	-1.51435900
H	0.62512600	-0.42560300	-1.97733600
C	0.64888900	-1.20894400	0.36898800
H	0.63983100	-2.03362800	-0.34787000
H	0.65428600	-1.55346700	1.40663400
C	-0.31378800	-0.01218600	0.04976700
Si	-2.20987600	-0.02460000	0.09834200
O	-2.55807200	-1.11612500	-1.16160200
O	-2.55862000	1.52282800	-0.52063700
O	-2.89477100	-0.35789400	1.46829900
H	-3.22566600	-1.72542700	-0.83233300
H	-3.23771200	1.90716400	0.04194800
N	3.02810400	-0.00056900	0.00338200
O	3.57683200	1.08871400	-0.09238400
O	3.61670400	-1.07124800	0.05500100

Acid R=NF_2
E = -964.69872026 au

C	-1.52941600	-0.00471500	0.22873500
C	-0.59308200	1.07090000	0.78956800
H	-0.64770600	2.05359000	0.31249500
H	-0.51203000	1.13525200	1.87775500
C	-0.58381700	-1.07672700	0.78180300
H	-0.50021300	-1.14694800	1.86925800
H	-0.62114900	-2.05556700	0.29765500
C	-0.72304200	0.00296700	-1.07961900
H	-0.76761600	-0.90473700	-1.68618300
H	-0.77637100	0.91342200	-1.68182400
C	0.31545300	0.00265600	0.09073800
Si	2.16440500	-0.00548400	-0.04275200
O	2.72298600	-1.33948100	-0.83721500
O	2.70183500	0.00300700	1.51748800
O	2.73744600	1.27166600	-0.93376000
H	3.12637200	-1.18445500	-1.69561600
H	3.62125300	-0.22948400	1.67333000
H	2.64019300	2.15842100	-0.57847300
N	-2.96614700	-0.00761400	0.43599200
F	-3.42751300	-1.09296000	-0.32128200
F	-3.42983000	1.08613400	-0.30997100

Conjugate Base R=NF_2
E = -964.14164675 au

C	-1.49080400	-0.00002100	0.24259600
C	-0.55666500	1.07153200	0.80899700
H	-0.58892100	2.05262900	0.32669500
H	-0.48163000	1.13933900	1.89840200
C	-0.55671600	-1.07187800	0.80849300
H	-0.48168800	-1.14020200	1.89786600
H	-0.58901400	-2.05273200	0.32570500
C	-0.67376700	0.00027000	-1.05304500
H	-0.70619400	-0.90947700	-1.65845200
H	-0.70615500	0.91030400	-1.65801900
C	0.36111400	-0.00002400	0.12645800
Si	2.25455900	0.00001200	0.04195800
O	2.54014100	-1.35985200	-0.94476400
O	3.04630400	-0.00015900	1.39617300
O	2.53988900	1.36010000	-0.94450100
H	3.25176400	-1.85886800	-0.53235200
H	3.25186300	1.85893600	-0.53249400
N	-2.93470700	-0.00003800	0.45211300
F	-3.41558400	-1.09164900	-0.30428700
F	-3.41558900	1.09167000	-0.30413800

Acid R=OH
E = -786.37488275 au

C	2.19920000	-0.01275300	-0.00348700
C	1.26747800	-1.23921500	-0.14711600
H	1.24794700	-1.73973600	-1.12158200
H	1.26348800	-1.95323300	0.68291100
C	1.30125900	0.48237800	1.13342200
H	1.30867200	-0.11302300	2.05291800
H	1.31046600	1.55737000	1.33623200
C	1.28241100	0.73910600	-0.99533600
H	1.28278000	1.83153300	-0.93854800
H	1.26155400	0.37825600	-2.02952200
C	0.33563400	0.00172200	0.00036700
Si	-1.51256400	0.01979100	-0.00372300
O	-1.93787700	1.61026300	0.12271400
O	-2.15478700	-0.92208800	1.20607900
O	-2.16422200	-0.61759200	-1.38315000
H	-2.85353900	1.83469000	-0.06378500
H	-1.92317700	-0.71017100	2.11360300
H	-2.57285500	-1.48227000	-1.28913100
O	3.58081800	0.00663700	0.07168200
H	3.94320400	-0.32568100	-0.75667700

Conjugate Base R=OH
E = -785.80821107 au

C	-2.16525600	0.00032100	-0.00345700
C	-1.26463900	-1.07263900	0.63223300
H	-1.26433100	-1.14829800	1.72654400
H	-1.24705400	-2.05604900	0.14960600
C	-1.24288600	0.00043000	-1.21925600
H	-1.22485800	-0.90853300	-1.82998700
H	-1.22380400	0.90988700	-1.82921500
C	-1.26352300	1.07190800	0.63311200
H	-1.24487100	2.05559400	0.15115400
H	-1.26310000	1.14675400	1.72746900
C	-0.30003500	-0.00069500	0.03238100
Si	1.58972400	-0.00019400	0.10740600
O	1.97501000	1.36124700	-0.84735300
O	1.97620400	-1.36020900	-0.84871300
O	2.27386400	-0.00039800	1.52153400
H	2.65079000	1.84672800	-0.36431600
H	2.65148400	-1.84646000	-0.36575700
O	-3.57045600	0.00085100	-0.09160100
H	-3.90933900	-0.00478800	0.80981500

Acid R=F
E = -810.38119915 au

C	2.17857600	-0.01587300	-0.01011100
C	1.30395000	0.50036500	1.13287200
H	1.30978400	-0.08394400	2.05835800
H	1.30799100	1.57819000	1.31554500
C	1.29134900	0.72291200	-1.01184400
H	1.29154300	1.81497600	-0.96726000
H	1.27596100	0.34274100	-2.03680700
C	1.28023300	-1.24726500	-0.13256800
H	1.26687100	-1.75595700	-1.10043700
H	1.27884800	-1.94612600	0.70895000
C	0.34465400	-0.00169200	0.00146700
Si	-1.50342300	0.01893000	-0.00269400
O	-2.14109200	-0.60311000	-1.39294000
O	-1.91585700	1.60994200	0.14544600
O	-2.14624500	-0.93349900	1.19574100
H	-2.58451300	-1.45162700	-1.30982600
H	-2.82226000	1.85235100	-0.06246400
H	-1.97594400	-0.69257600	2.10949400
F	3.54806800	-0.02893200	-0.01585600

Conjugate Base R=F
E = -809.81986003 au

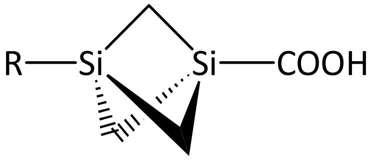
C	-2.14052700	-0.00000900	0.01201100
C	-1.23940400	0.00015500	-1.21399200
H	-1.21414000	-0.91059900	-1.81979900
H	-1.21409000	0.91112600	-1.81947300
C	-1.27416200	1.07610400	0.65059800
H	-1.25344100	2.05625000	0.16429100
H	-1.28290000	1.14622300	1.74250400
C	-1.27423200	-1.07634300	0.65030200
H	-1.28296600	-1.14677700	1.74218700
H	-1.25357400	-2.05633400	0.16367900
C	-0.30898700	-0.00006100	0.04846500
Si	1.58322400	-0.00003200	0.10549900
O	2.28218200	-0.00044200	1.51028500
O	1.94545800	1.36019600	-0.85700900
O	1.94574800	-1.35958300	-0.85780900
H	2.62418400	1.85435600	-0.38717700
H	2.62394900	-1.85428300	-0.38777800
F	-3.54171100	0.00000500	-0.01371700

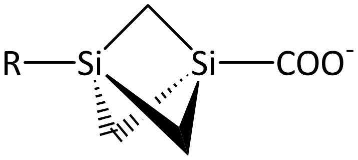
Acid R=Li
E = -718.07602335 au

C	-2.54197100	-0.01777600	0.02457400
C	-1.55255200	0.12788900	-1.19635800
H	-1.53696800	-0.70576400	-1.91498500
H	-1.55169700	1.09098100	-1.72440200
C	-1.55193700	0.98560100	0.73795500
H	-1.54864900	2.02247300	0.37658200
H	-1.52797700	0.95952500	1.83597200
C	-1.52328900	-1.11998300	0.51313600
H	-1.49890000	-1.32747900	1.59206400
H	-1.50003400	-2.05870000	-0.05905200
C	-0.59076700	0.01253600	0.01492400
Si	1.27352400	0.02332400	-0.00582100
O	2.01526700	-0.24522200	1.45676000
O	1.75119500	1.52497600	-0.51715200
O	1.87608900	-1.20671700	-0.96398900
H	2.25751100	-1.16014600	1.62285400
H	2.68112700	1.73383000	-0.39139600
H	1.42839500	-1.34782800	-1.80217300
Li	-4.53648300	-0.01577400	0.05856300

Conjugate Base R=Li
E = -717.48973410 au

C	-2.47827600	0.00001400	0.00433400
C	-1.48018600	-0.00081600	-1.19933000
H	-1.44695600	-0.90668800	-1.81882500
H	-1.44703000	0.90415900	-1.82014100
C	-1.52400800	1.06401500	0.64176400
H	-1.49669500	2.05384600	0.16682500
H	-1.53524800	1.15079500	1.73631900
C	-1.52395200	-1.06301200	0.64326700
H	-1.53516700	-1.14828300	1.73793900
H	-1.49657500	-2.05351700	0.16973300
C	-0.56063300	0.00010700	0.05344100
Si	1.34877200	-0.00000400	0.10592600
O	2.07194300	0.00024900	1.50290500
O	1.72990500	1.36146700	-0.85626600
O	1.72944400	-1.36194700	-0.85571800
H	2.40532300	1.84452400	-0.36969400
H	2.40549000	-1.84442600	-0.36944100
Li	-4.52798500	-0.00011700	-0.03463700





Acid R=H
E = -886.08042563 au

Si	2.18482000	-0.03224400	0.00008000
C	1.07687200	1.53231500	-0.00154000
H	1.09066800	2.15211900	0.89896000
H	1.09075600	2.15033400	-0.90326700
C	1.01571400	-0.77332100	-1.32746800
H	1.02733900	-0.30557000	-2.31577600
H	0.97949600	-1.86310000	-1.40725500
C	1.01558800	-0.77063700	1.32901200
H	0.97936600	-1.86024900	1.41100900
H	1.02710200	-0.30087500	2.31636800
Si	-0.09339900	0.03363500	-0.00010000
C	-2.02295200	0.12078500	-0.00004900
O	-2.66355700	1.14634500	0.00004500
O	-2.59822400	-1.09789700	-0.00001700
H	-3.56207700	-0.96576700	0.00011700
H	3.67036700	-0.06881200	0.00017100

Conjugate Base R=H
E = -885.54219802 au

Si	2.13837300	-0.03074600	0.00015500
C	1.08508000	1.54162900	-0.00056000
H	1.09146500	2.16446500	0.89994100
H	1.09162000	2.16375300	-0.90155300
C	0.99790700	-0.75782800	-1.32404000
H	1.00141700	-0.29224400	-2.31512500
H	0.93193100	-1.84735700	-1.40492700
C	0.99768800	-0.75676000	1.32474400
H	0.93170600	-1.84622200	1.40650500
H	1.00102600	-0.29037000	2.31545100
Si	-0.18508100	0.05527800	-0.00007600
C	-2.15968500	0.00856000	-0.00012400
O	-2.74893800	1.10270800	-0.00015300
O	-2.57185500	-1.16882500	-0.00007300
H	3.64514200	-0.08015400	0.00028600

Acid R=CH_3
E = -925.36685936 au

Si	1.78550600	-0.01086000	0.00002900
C	0.65825000	1.54556400	-0.00012400
H	0.66337600	2.16575300	0.90064900
H	0.66340900	2.16558600	-0.90101200
C	0.61250100	-0.75762600	-1.32764800
H	0.61623000	-0.28892600	-2.31599500
H	0.57899700	-1.84763600	-1.41032800
C	0.61247000	-0.75739200	1.32780900
H	0.57896800	-1.84738600	1.41068400
H	0.61616800	-0.28851200	2.31607100
Si	-0.49757300	0.03984800	-0.00000600
C	-2.42762900	0.10975600	-0.00002600
O	-3.08087900	1.12774000	-0.00004000
O	-2.99247700	-1.11474600	-0.00001900
H	-3.95712200	-0.98915500	-0.00002400
C	3.65679900	-0.04472000	0.00000800
H	4.04913400	0.46147600	-0.88754400
H	4.04917900	0.46153500	0.88750500
H	4.02308500	-1.07601700	0.00002800

Conjugate Base R=CH_3
E = -924.82526858 au

Si	1.73431000	-0.00461700	0.00015500
C	0.66051500	1.55718700	0.00009800
H	0.65570300	2.18052900	0.90069100
H	0.65585100	2.18056900	-0.90046700
C	0.59611500	-0.74126500	-1.32434900
H	0.58992100	-0.27443500	-2.31524100
H	0.53564900	-1.83126700	-1.40777900
C	0.59592800	-0.74132200	1.32445000
H	0.53546100	-1.83132800	1.40782200
H	0.58955800	-0.27453600	2.31536200
Si	-0.59155500	0.05901200	-0.00003500
C	-2.56773600	-0.00702900	-0.00015900
O	-3.16611000	1.08228800	-0.00016700
O	-2.97099000	-1.18734600	-0.00021900
C	3.63003500	-0.04993300	0.00009600
H	4.02760200	0.45337700	-0.88857000
H	4.02776700	0.45465800	0.88796200
H	3.99156700	-1.08447900	0.00080400

Acid R=CN

E = -978.23140756 au

Si	1.52244000	-0.00153800	0.00000500
C	0.42281400	1.55085000	-0.00072600
H	0.43274600	2.16953300	0.90012700
H	0.43279800	2.16871600	-0.90213900
C	0.38986100	-0.75678500	-1.32941800
H	0.39924900	-0.28759400	-2.31660400
H	0.37065000	-1.84656000	-1.40967300
C	0.38980400	-0.75557400	1.33005900
H	0.37059500	-1.84527200	1.41132000
H	0.39913800	-0.28547000	2.31681200
Si	-0.74216500	0.03675400	-0.00007200
C	-2.66707800	0.10441200	-0.00001500
O	-3.31197500	1.12557500	0.00002600
O	-3.22318200	-1.12066400	0.00002300
H	-4.18959100	-1.00729400	0.00009700
C	3.36850700	-0.02573500	0.00005500
N	4.53119600	-0.04305600	0.00012500

Conjugate Base R = CN

E = -977.70870797 au

Si	-1.46851000	0.00585100	-0.00001200
C	-0.43583400	1.57234700	-0.00050300
H	-0.44327400	2.19200000	-0.90204100
H	-0.44326600	2.19255900	0.90064900
C	-0.36749300	-0.73223700	1.32765900
H	-0.37240600	-0.26416000	2.31644600
H	-0.31590100	-1.82173500	1.40711000
C	-0.36750000	-0.73307600	-1.32722400
H	-0.31590300	-1.82262400	-1.40597800
H	-0.37242400	-0.26563200	-2.31631100
Si	0.83745900	0.07156000	-0.00004300
C	2.82091400	-0.01812300	0.00003800
O	3.42766600	1.06133700	-0.00000700
O	3.18611700	-1.20713900	0.00015500
C	-3.35082400	-0.03670800	-0.00000800
N	-4.51542300	-0.06299500	-0.00000800

Acid R = CF_3

E = -1222.82116223 au

Si	0.82062300	0.00271700	-0.00166300
C	-0.30423200	-0.86933000	-1.26758600
H	-0.29867900	-0.48423400	-2.29050600
H	-0.31776400	-1.96193100	-1.25508600
C	-0.31213800	-0.65059900	1.38301900
H	-0.32684700	-1.73030400	1.55048800
H	-0.31281500	-0.10029500	2.32753200
C	-0.29418400	1.54282800	-0.13259600
H	-0.29431300	2.23306400	0.71491700
H	-0.28760800	2.08369000	-1.08227600
Si	-1.44346300	0.01731800	-0.01026000
C	-3.36537100	-0.10845200	0.00033200
O	-3.94727100	-1.16792100	0.00691800
O	-3.99469200	1.07908800	0.00780300
H	-4.95209000	0.90433000	0.01996200
C	2.76158600	0.00055000	0.00414500
F	3.26261700	0.70141700	1.04371300
F	3.26244900	-1.25008700	0.09367800
F	3.26733400	0.54821200	-1.12181000

Conjugate Base R = CF_3

E = -1222.29557257 au

Si	-0.76106300	0.01799400	0.00014400
C	0.28072500	1.58014200	0.00082200
H	0.28081700	2.20030500	-0.90040300
H	0.28091100	2.19947300	0.90262000
C	0.33717900	-0.72718900	1.32830900
H	0.33901400	-0.25906100	2.31710600
H	0.38663500	-1.81684800	1.40720300
C	0.33708500	-0.72593300	-1.32881200
H	0.38652800	-1.81551500	-1.40875300
H	0.33884200	-0.25685800	-2.31716100
Si	1.54311100	0.07175700	0.00006800
C	3.52973700	-0.02256400	-0.00011900
O	4.13546000	1.05765100	-0.00009700
O	3.89662900	-1.21078000	-0.00028700
C	-2.72186600	-0.01934800	-0.00000800
F	-3.22781800	-1.28137800	-0.00109200
F	-3.26370500	0.59570300	1.08513000
F	-3.26350800	0.59749600	-1.08422300

Acid R = NH_2
E = -941.41529009 au

Si	-1.79603900	0.00471800	0.03244700
C	-0.68055500	-1.27207200	-0.85157800
H	-0.64761100	-2.28793800	-0.44819000
H	-0.71556500	-1.28352600	-1.94451000
C	-0.66451700	1.38964000	-0.64670700
H	-0.69902300	1.56945900	-1.72476000
H	-0.62325800	2.33146500	-0.09223600
C	-0.59928400	-0.11877600	1.53716200
H	-0.56339800	0.73194300	2.22390100
H	-0.57299800	-1.06610900	2.08347000
Si	0.47941800	-0.00572600	-0.02858300
C	2.40163800	-0.10886500	-0.02154600
O	3.01696100	-1.15021000	0.00276900
O	3.00789200	1.09432100	-0.01477300
H	3.96689800	0.93403400	0.01953900
N	-3.50947800	0.02364600	-0.05957100
H	-4.03883400	0.84813000	0.18288800
H	-4.04968300	-0.82131000	0.05484200

Conjugate Base R = NH_2
E = -940.87493657 au

Si	-1.74759100	-0.01255500	0.02054000
C	-0.64234500	-1.08001800	-1.07374800
H	-0.56530100	-2.15062600	-0.85832300
H	-0.66723200	-0.90062100	-2.15357400
C	-0.69148800	1.49651900	-0.38801000
H	-0.71679000	1.87702000	-1.41431200
H	-0.65754500	2.32189900	0.33086800
C	-0.58583100	-0.38108400	1.47693000
H	-0.55926500	0.32958300	2.31017500
H	-0.51690200	-1.41137800	1.84193800
Si	0.57037900	0.04426500	-0.03393800
C	2.55410900	-0.00000800	-0.01203600
O	2.98295400	-1.16823100	0.02580700
O	3.11981000	1.10558700	-0.01466400
N	-3.50051700	-0.00921800	-0.06851400
H	-3.98551700	0.73357900	0.41914900
H	-3.97564900	-0.89017600	0.08329600

Acid R = NO_2
E = -1090.39982855 au

Si	1.15166100	-0.01694200	-0.02816900
C	0.06969000	-0.75015000	1.34483900
H	0.05058500	-1.83787600	1.44489100
H	0.10700800	-0.25846500	2.31975700
C	0.06613200	1.53831800	-0.02747500
H	0.10470400	2.16779000	0.86444400
H	0.04867500	2.13895900	-0.93997500
C	0.00812500	-0.79382300	-1.32233100
H	-0.01027700	-0.33500800	-2.31366200
H	-0.01101300	-1.88447000	-1.38612800
Si	-1.09876600	0.01254200	0.02941900
C	-3.01934200	-0.09034400	0.05748700
O	-3.62094800	-1.04399100	0.48938900
O	-3.61650600	0.98762500	-0.47606800
H	-4.57782500	0.83887000	-0.44710700
N	3.03213000	0.00060700	-0.01382700
O	3.54480700	0.56740900	0.94263700
O	3.63953200	-0.53560100	-0.92821600

Conjugate Base R = NO_2
E = -1089.88353196 au

Si	-1.09366700	-0.03048100	0.00468400
C	-0.10431100	1.49083800	-0.45348700
H	-0.11942600	1.82084800	-1.49587200
H	-0.12640500	2.34197200	0.23256400
C	-0.00234000	-0.32777600	1.49164800
H	-0.02389400	0.41277700	2.29555800
H	0.07066900	-1.34365500	1.88886400
C	0.00494600	-1.10345900	-1.05795600
H	0.07828400	-2.16802400	-0.82003500
H	-0.00954000	-0.93808500	-2.13844500
Si	1.19576400	0.07172100	-0.01904600
C	3.20266100	-0.00174800	0.00176900
O	3.78191100	1.03074700	-0.34810400
O	3.57134900	-1.12397900	0.37632300
N	-3.02005000	-0.02717700	0.00734300
O	-3.59159700	0.37932400	1.01486500
O	-3.60721600	-0.39360200	-1.00618700

Acid R = NF$_2$

E = -1139.56207931 au

Si	-1.11363100	0.03182300	-0.17345900
C	0.03485700	-1.17615100	-1.07968200
H	0.01592100	-2.22163100	-0.76281400
H	0.09535100	-1.09035300	-2.16750200
C	0.03639600	1.45827100	-0.66789800
H	0.09653600	1.70746900	-1.73029900
H	0.01348700	2.35864900	-0.04923200
C	-0.08733100	-0.21874900	1.40468000
H	-0.11923100	0.57570700	2.15425300
H	-0.11530000	-1.20757600	1.86863500
Si	1.13756800	0.01172800	-0.05624900
C	3.04995300	-0.12533600	0.10413800
O	3.61615200	-1.17572800	0.29253800
O	3.68747700	1.05307400	0.00593000
H	4.63931000	0.88353000	0.11747400
N	-2.93538300	0.07194700	-0.41806600
F	-3.39059200	1.04442900	0.48925900
F	-3.39227400	-1.12955500	0.15037200

Conjugate Base R = NF$_2$

E = -1139.04010360 au

Si	-1.05687600	0.05538800	-0.16406100
C	0.07737400	-1.01138600	-1.20228400
H	0.10381700	-2.08628500	-1.00430500
H	0.14412600	-0.80355000	-2.27409800
C	0.01199000	1.55643500	-0.49963600
H	0.07664900	1.92656000	-1.52687400
H	-0.01977800	2.38340600	0.21534800
C	-0.06127600	-0.34262000	1.37077600
H	-0.10150200	0.36138800	2.20656400
H	-0.04633200	-1.37752500	1.72280000
Si	1.23568800	0.08075100	-0.04673800
C	3.22536100	-0.05126300	0.10632700
O	3.54733900	-1.22241100	0.36183900
O	3.85675500	0.99859000	-0.06010700
N	-2.91404300	0.08699000	-0.42002700
F	-3.41030000	0.95181100	0.58536200
F	-3.36920100	-1.17795700	0.02430200

Acid R = OH

E = -961.28183205 au

Si	1.80073800	0.00679200	0.00014800
C	0.66084900	-0.76678900	1.32792400
H	0.62824700	-1.85714400	1.40536400
H	0.65780400	-0.30056200	2.31710400
C	0.68098900	1.54341100	0.00012400
H	0.67992900	2.16157400	0.90175100
H	0.68011400	2.16177700	-0.90135800
C	0.66067900	-0.76688800	-1.32749000
H	0.65748900	-0.30060200	-2.31664600
H	0.62815400	-1.85723400	-1.40502500
Si	-0.46619900	0.01625900	0.00011000
C	-2.38556300	-0.10956200	-0.00004000
O	-2.97509100	-1.16546100	-0.00013600
O	-3.01439700	1.07986100	-0.00018400
H	-3.97112100	0.90221800	-0.00037600
O	3.45233900	0.09695600	-0.00046500
H	3.95130800	-0.72462500	-0.00125900

Conjugate Base R = OH

E = -960.74697406 au

Si	1.75503800	0.00449600	0.00004600
C	0.63331500	-0.73989700	1.32439100
H	0.55537500	-1.82931600	1.40021700
H	0.62989600	-0.27771300	2.31694500
C	0.71196800	1.56562600	-0.00125500
H	0.71124100	2.18772000	0.89924500
H	0.71137300	2.18630100	-0.90273500
C	0.63348200	-0.74201800	-1.32325200
H	0.63020600	-0.28145000	-2.31655700
H	0.55552900	-1.83155900	-1.39731900
Si	-0.55456900	0.06983900	-0.00016300
C	-2.54601900	-0.01267800	-0.00001000
O	-2.93061000	-1.19536500	0.00003300
O	-3.14162300	1.07406700	0.00011500
O	3.44322400	0.02531400	0.00009600
H	3.83541300	-0.85299900	0.00065100

Acid R = F
E = -985.30086899 au

Si	-1.80015000	0.00255000	0.00007100
C	-0.67957600	-0.76163500	-1.33047400
H	-0.65641000	-1.85145200	-1.41060700
H	-0.67394200	-0.29133700	-2.31730500
C	-0.69267000	1.54784200	-0.00027800
H	-0.68826000	2.16550900	-0.90212100
H	-0.68805800	2.16579600	0.90136600
C	-0.67936100	-0.76119800	1.33064700
H	-0.67352500	-0.29050000	2.31728900
H	-0.65617300	-1.85098100	1.41122000
Si	0.45698200	0.01815600	-0.00015300
C	2.37475200	-0.11034500	-0.00001600
O	2.95965600	-1.16776000	0.00006600
O	3.00105700	1.07896900	0.00003300
H	3.95852800	0.90489900	0.00015500
F	-3.41582100	-0.00216500	0.00012100

Conjugate Base R = F
E = -984.77282132 au

Si	-1.75704500	-0.01066800	0.00000100
C	-0.72954600	1.56113500	-0.00029000
H	-0.72748500	2.18199300	-0.90151200
H	-0.72747200	2.18231700	0.90070800
C	-0.65036300	-0.74177500	1.32803500
H	-0.64542400	-0.27236400	2.31665100
H	-0.58005800	-1.83047400	1.41005400
C	-0.65038000	-0.74225900	-1.32778300
H	-0.58007300	-1.83098900	-1.40940100
H	-0.64545600	-0.27321400	-2.31657300
Si	0.54346300	0.06817600	-0.00003100
C	2.54359000	-0.00794600	0.00001200
O	3.12720800	1.08314500	0.00000000
O	2.92789300	-1.18843100	0.00006400
F	-3.40272000	-0.05944700	0.00001600

Acid R = Li
E = -892.98595432 au

Si	2.11242200	-0.02662000	0.00002000
C	0.91297100	1.53663900	-0.00039800
H	0.93338000	2.15865600	0.89955600
H	0.93340100	2.15819000	-0.90067300
C	0.85475400	-0.76492100	-1.32632900
H	0.87389400	-0.29906400	-2.31650400
H	0.82812500	-1.85561400	-1.41024200
C	0.85472400	-0.76423000	1.32672400
H	0.82809300	-1.85487800	1.41121000
H	0.87383600	-0.29785200	2.31665400
Si	-0.21745300	0.03668600	-0.00002500
C	-2.16478900	0.11637400	-0.00001700
O	-2.82325500	1.13424900	-0.00002700
O	-2.74961400	-1.10398700	0.00002700
H	-3.71120800	-0.95713000	0.00005300
Li	4.58263700	-0.05950000	0.00004400

Conjugate Base R = Li
E = -892.42502256 au

Si	2.04859700	-0.01680600	0.00001800
C	0.90375300	1.54497200	-0.00039700
H	0.91817900	2.17012800	0.89927300
H	0.91820600	2.16967000	-0.90038400
C	0.83862600	-0.74977300	-1.32308300
H	0.85346000	-0.28427000	-2.31496600
H	0.79674700	-1.84074400	-1.40979800
C	0.83858900	-0.74909100	1.32346100
H	0.79671100	-1.84001600	1.41074400
H	0.85338900	-0.28307000	2.31510200
Si	-0.31185800	0.04891600	-0.00003400
C	-2.30256700	-0.00090700	-0.00000400
O	-2.88241200	1.09904400	-0.00002100
O	-2.72437900	-1.17415400	0.00005200
Li	4.57762900	-0.07051600	0.00004600

Analog 1 Backbone R=H

E = -697.6935918au

Si	-1.14483900	0.00000400	0.00003400
C	-0.00014500	-0.01486400	1.53284500
H	-0.00003000	0.88017500	2.16154900
H	-0.00003100	-0.92199200	2.14400000
C	0.00005600	-1.32060600	-0.77914500
H	0.00010400	-2.31192600	-0.31693400
H	-0.00054100	-1.39835000	-1.87016300
C	0.00005400	1.33545900	-0.75342100
H	-0.00054200	1.43443300	-1.84269200
H	0.00010500	2.31761300	-0.27201500
Si	1.14491800	0.00000400	-0.00046400
H	2.63369200	0.00000400	0.00181300
H	-2.63364700	-0.00000100	-0.00122500

Analog 1 Backbone R=CH$_3$

E = -736.97961761au

Si	-0.73523300	-0.00115300	0.00080300
C	0.41688100	1.46766600	-0.43935300
H	0.41962600	1.80423000	-1.48046700
H	0.42036600	2.32089900	0.24564600
C	0.42020900	-0.35371700	1.49125200
H	0.42434700	0.37911500	2.30371200
H	0.42537400	-1.37391400	1.88673300
C	0.41922200	-1.11580900	-1.05074800
H	0.42432600	-2.18527700	-0.81977800
H	0.42243700	-0.95093200	-2.13243500
Si	1.55801100	0.00107100	-0.00093400
H	3.04706100	0.01021800	-0.00424000
C	-2.60970000	0.00059700	-0.00033300
H	-2.99324600	0.74731100	0.70217100
H	-2.99243000	0.23736200	-0.99814600
H	-2.99642100	-0.98028300	0.29373300

Analog 1 Backbone R=CN

E = -789.84596563au

Si	-0.45751800	-0.00014700	0.00046000
C	0.66006700	-0.01089800	1.53526100
H	0.65654200	0.88644800	2.15967700
H	0.65677600	-0.91702000	2.14687600
C	0.66021500	-1.32438300	-0.77722600
H	0.65696000	-2.31376400	-0.31227900
H	0.65581900	-1.40134000	-1.86772700
C	0.65985800	1.33528400	-0.75835200
H	0.65543100	1.42770900	-1.84765100
H	0.65634100	2.31796400	-0.27940700
Si	1.81603800	0.00015200	-0.00060300
H	3.30019800	0.00035500	0.00402800
C	-2.30750400	-0.00035200	0.00055200
N	-3.47045200	0.00023800	-0.00041700

Analog 1 Backbone R=CF$_3$

E = -1034.43537062au

Si	0.17814500	0.00414400	0.00397800
C	1.29776000	1.43878800	-0.53925200
H	1.29498200	1.70131700	-1.60055400
H	1.30202300	2.33446700	0.08793100
C	1.29887700	-0.25152800	1.51602200
H	1.30253600	0.53619700	2.27410400
H	1.29707100	-1.24230000	1.97829600
C	1.29304900	-1.18683600	-0.97511000
H	1.28954300	-2.23692100	-0.67102800
H	1.28895400	-1.09320400	-2.06447700
Si	2.45148000	-0.00266700	-0.00319500
H	3.93659300	-0.00039200	-0.00158800
C	-1.76414600	-0.00010800	0.00001600
F	-2.26830600	-1.17793300	0.42975200
F	-2.27297000	0.96064700	0.80293500
F	-2.26757800	0.21487200	-1.23532000

Analog 1 Backbone R=NH$_2$

E = -753.02831040au

Si	-0.75336000	0.00047500	0.03449900
C	0.35939400	-1.33093500	-0.75976900
H	0.39304200	-2.31521600	-0.28313200
H	0.31698000	-1.42433100	-1.84870900
C	0.35987700	1.33373100	-0.75515500
H	0.31782900	1.43089600	-1.84378000
H	0.39466800	2.31633100	-0.27515500
C	0.44965900	-0.00265900	1.53404900
H	0.47978800	0.89726700	2.15583800
H	0.47881000	-0.90483100	2.15262800
Si	1.53132800	-0.00037700	-0.03801100
H	3.01633700	-0.00000200	-0.09326200
N	-2.47119400	-0.00020100	-0.04656900
H	-3.00246500	0.83586500	0.14813600
H	-3.00176000	-0.83677900	0.14783200

Analog 1 Backbone R=NO$_2$
E = -902.01491373au

Si	0.12347000	0.03267400	-0.01006600
C	-0.94984000	-0.65785100	1.38749400
H	-0.91639900	-1.73777300	1.55032500
H	-0.95431000	-0.11181000	2.33422100
C	-1.00990500	1.54082100	-0.12154700
H	-1.01539800	2.22684000	0.72895000
H	-1.02766900	2.08454800	-1.06933500
C	-0.96622600	-0.86817100	-1.26697400
H	-0.98402100	-0.47890000	-2.28802100
H	-0.93267400	-1.96030500	-1.25735000
Si	-2.13371800	-0.01888100	0.00879900
H	-3.61484800	-0.04394400	0.01784700
N	2.00700300	0.00797200	-0.00427100
O	2.61915000	1.06564400	0.00288000
O	2.51780000	-1.10518700	0.00176600

Analog 1 Backbone R=NF$_2$
E = -951.17683578au

Si	0.09225900	-0.00056500	-0.14506300
C	-1.10276200	1.33091300	-0.76522700
H	-1.03985600	2.31727500	-0.29866400
H	-1.24668500	1.41156100	-1.84577700
C	-1.10399600	-1.33074500	-0.76570100
H	-1.24833300	-1.41066900	-1.84625700
H	-1.04294500	-2.31745000	-0.29962300
C	-0.80292900	-0.00042200	1.52504300
H	-0.72107300	-0.90280900	2.13607200
H	-0.71976000	0.90178600	2.13619300
Si	-2.14985700	0.00048800	0.14994500
H	-3.61930800	0.00029000	0.34581700
N	1.89365200	-0.00005900	-0.52761100
F	2.40317300	-1.10049700	0.18520900
F	2.40203600	1.10083200	0.18506500

Analog 1 Backbone R=OH
E = -772.89563024au

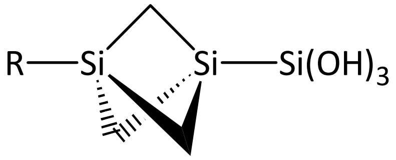
Si	0.76401500	0.00292400	0.00014700
C	-0.36865500	-0.77170400	1.32835300
H	-0.38731300	-1.86241000	1.41162400
H	-0.37245800	-0.30314900	2.31668800
C	-0.35718900	1.53264800	-0.00148500
H	-0.35997300	2.15231200	0.89948800
H	-0.35970500	2.15053500	-0.90368000
C	-0.36837400	-0.77431900	-1.32680800
H	-0.37191900	-0.30773700	-2.31607600
H	-0.38702400	-1.86519200	-1.40790500
Si	-1.51142800	0.00155500	-0.00014200
H	-2.99510500	0.00384900	-0.00024000
O	2.41804100	0.09665900	-0.00003900
H	2.91825500	-0.72393200	-0.00000600

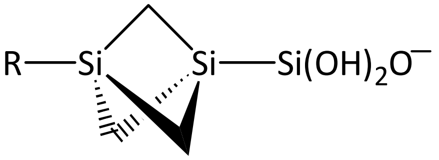
Analog 1 Backbone R=F
E = -796.91562225au

Si	-0.76821300	-0.00024000	0.00035800
C	0.34378200	1.53657500	-0.01286300
H	0.35087100	2.14714600	-0.91987700
H	0.35163300	2.16312600	0.88315300
C	0.34424700	-0.75681200	1.33720400
H	0.35204400	-0.27711800	2.31970600
H	0.35189400	-1.84612300	1.43089100
C	0.34349100	-0.77938300	-1.32395700
H	0.35121400	-1.87013100	-1.39925900
H	0.35062100	-0.31620400	-2.31440100
Si	1.49686900	-0.00001100	-0.00038700
H	2.97817600	-0.00003900	-0.00091900
F	-2.38630700	0.00006400	-0.00013200

Analog 1 Backbone R=Li
E = -704.59482715au

Si	1.04991700	-0.00682800	0.00098800
C	-0.17573900	1.51417800	-0.21848000
H	-0.16346900	2.25973600	0.58335200
H	-0.16347300	2.00263700	-1.19838500
C	-0.18765800	-0.94726500	-1.20251000
H	-0.17606000	-0.62649100	-2.24930100
H	-0.18359900	-2.04011900	-1.13480700
C	-0.18767200	-0.56865900	1.42124700
H	-0.18362500	-1.63605200	1.66529900
H	-0.17610500	0.03499300	2.33463800
Si	-1.29418800	0.00539400	-0.00078700
H	-2.79961900	0.01911500	-0.00276100
Li	3.52405300	0.00557800	-0.00079800





Acid R=H
E = -1213.86894439 au

Si	2.81539800	-0.02647700	-0.01121300
C	1.67570700	0.07434900	1.51884500
H	1.65826200	-0.79582100	2.18191800
H	1.68836200	1.00479000	2.09371000
C	1.70652800	1.28372100	-0.84719900
H	1.71512600	2.29358600	-0.42803500
H	1.70158900	1.31348300	-1.94042400
C	1.64855700	-1.36909400	-0.70726500
H	1.64353000	-1.51526500	-1.79121100
H	1.62402400	-2.32935300	-0.18380200
Si	0.51756700	0.02536000	-0.01827200
Si	-1.82242900	0.01974900	0.00649300
O	-2.26650600	1.53701100	0.48139200
H	-3.17523700	1.80366100	0.30872400
O	-2.41329300	-1.18879000	0.98482500
H	-2.10766000	-1.22482000	1.89511600
O	-2.52085500	-0.28442700	-1.46235800
H	-2.78160800	-1.19573500	-1.62457900
H	4.30659600	-0.05959900	-0.00667300

Base R = H
E = -1213.31273667 au

Si	-2.78309900	0.01616000	0.03566100
C	-1.66136700	-1.18489400	0.97201200
H	-1.61666900	-1.09991900	2.06286100
H	-1.65559800	-2.23495600	0.66301600
C	-1.71156600	-0.23521900	-1.50229600
H	-1.70724700	-1.22249900	-1.97466900
H	-1.70048500	0.55702800	-2.25785700
C	-1.64335600	1.43303100	0.55720200
H	-1.62994500	2.33672100	-0.06103700
H	-1.59647900	1.68951000	1.62081500
Si	-0.45362000	-0.01223000	-0.02357100
Si	1.91381100	-0.13519400	-0.10498400
O	2.39268700	-1.52751600	-0.62190700
O	2.42666000	0.27908100	1.47567300
H	2.77945600	-0.51901200	1.88208200
O	2.33441900	1.29122500	-0.92248900
H	2.80727800	1.87575600	-0.32201600
H	-4.29199200	0.03522000	0.07559200

Acid R = CH_3
E = -1253.15519941 au

Si	2.43694200	-0.00869100	-0.00966900
C	1.26881000	-1.33703900	-0.74216600
H	1.26330900	-1.45813700	-1.82956500
H	1.24068900	-2.31005400	-0.24227400
C	1.28338000	0.05008200	1.51791000
H	1.26254200	-0.83675200	2.15912600
H	1.28690700	0.96528100	2.11749200
C	1.31827600	1.31824200	-0.81616800
H	1.31784700	2.31786500	-0.37219200
H	1.31260000	1.37673600	-1.90854500
Si	0.13527900	0.03661200	-0.02361900
Si	-2.20331600	0.01458600	0.00636500
O	-2.66544400	1.51880000	0.50739700
O	-2.77784700	-1.21632300	0.96827600
O	-2.91472300	-0.27052800	-1.46126200
H	-3.58048600	1.77047100	0.34591000
H	-2.44402600	-1.27675900	1.86735700
H	-3.14909200	-1.18528900	-1.64292900
C	4.31245800	-0.04246600	0.00051800
H	4.67958600	-0.92249000	0.53841300
H	4.70163700	-0.07650700	-1.02222700
H	4.71036900	0.85204600	0.49051000

Base R = CH_3
E = -1252.59606068 au

Si	-2.39999500	0.00604500	0.01329100
C	-1.26287800	1.42900400	0.53346800
H	-1.24314900	2.32950700	-0.08984900
H	-1.21859900	1.69267600	1.59580400
C	-1.27643400	-1.18556000	0.96436400
H	-1.23411800	-1.09380700	2.05510800
H	-1.26052300	-2.23806500	0.66292100
C	-1.31320500	-0.25162500	-1.51579900
H	-1.29798400	-1.24172800	-1.98278900
H	-1.29393400	0.53563100	-2.27689400
Si	-0.06875000	-0.01614400	-0.03063900
Si	2.29967200	-0.13240000	-0.09730700
O	2.79056500	-1.52416500	-0.60503000
O	2.80133900	0.29048200	1.48528600
O	2.72358900	1.29181200	-0.91809400
H	3.15494400	-0.50508900	1.89590400
H	3.17890200	1.88447500	-0.31206100
C	-4.29658200	0.02290000	0.04957300
H	-4.66248100	0.18381300	1.07013100
H	-4.68805500	0.82478200	-0.58681900
H	-4.69733100	-0.93056400	-0.31320600

Acid R = CN
E = -1306.02244195 au

Si	2.18727600	-0.00140200	-0.00960200
C	1.06226100	-1.43398200	-0.52935100
H	1.06044600	-1.71089500	-1.58705400
H	1.05171400	-2.32077200	0.11002400
C	1.07862800	0.28066700	1.50135700
H	1.07494100	-0.49912600	2.26805500
H	1.08596300	1.27665300	1.95191400
C	1.09275600	1.18397400	-1.00132800
H	1.09663200	2.23778100	-0.71126600
H	1.08894600	1.07422600	-2.08886400
Si	-0.09565300	0.02624400	-0.01541100
Si	-2.43255800	0.00998200	0.00499100
O	-2.85955800	1.55489000	0.38760800
O	-3.02271100	-1.13390500	1.05169300
O	-3.09469900	-0.38921300	-1.45343500
H	-3.75836800	1.83584600	0.18783100
H	-2.80612600	-1.06313200	1.98515900
H	-3.40086400	-1.29570700	-1.55149800
C	4.04254200	-0.02607000	-0.00279700
N	5.20549100	-0.04344700	0.00311400

Base R = CN
E = -1305.47961184 au

Si	-2.14575700	0.00069700	0.00174700
C	-1.06268400	1.44743200	0.50112600
H	-1.05773500	2.33225400	-0.14229000
H	-1.03776700	1.72987900	1.55790000
C	-1.05672100	-1.16531900	0.98547900
H	-1.03188900	-1.04949500	2.07310400
H	-1.03976800	-2.22126400	0.70121700
C	-1.08684500	-0.27909700	-1.51925600
H	-1.06937500	-1.27867400	-1.96233100
H	-1.08046200	0.49428000	-2.29281500
Si	0.16489500	-0.00263000	-0.02851200
Si	2.53357200	-0.13189700	-0.08972200
O	2.97044600	-1.54013300	-0.59210600
O	3.02608900	0.29956700	1.48620700
O	2.95697700	1.27565100	-0.92669800
H	3.34585300	-0.49323100	1.92842800
H	3.40998500	1.88604000	-0.33682300
C	-4.03191400	0.00872900	0.03165200
N	-5.19655700	0.01752500	0.05302800

Acid R = CF_3
E = -1550.61184162 au

Si	-1.47824300	0.00824700	0.00936500
C	-0.35389500	-1.40019400	0.59953600
H	-0.35142800	-1.62597500	1.66929400
H	-0.33989500	-2.31664300	0.00339300
C	-0.36481400	0.21768500	-1.51228000
H	-0.35738200	-0.59748500	-2.24122300
H	-0.36777600	1.19154000	-2.00904800
C	-0.38209300	1.23906100	0.94712000
H	-0.38118600	2.27809900	0.60806900
H	-0.37776700	1.17978700	2.03862600
Si	0.80305500	0.03424800	0.01855700
Si	3.14057000	0.00793500	-0.00524700
O	3.57861200	1.54256700	-0.41689100
O	3.71923300	-1.15992800	-1.03282200
O	3.81236600	-0.36587000	1.45612300
H	4.48191600	1.81642300	-0.22780500
H	3.47332200	-1.11992600	-1.96086400
H	4.09479100	-1.27736600	1.57629000
C	-3.42392000	-0.01566600	0.00112100
F	-3.94396200	1.13602200	-0.47885800
F	-3.91365700	-1.01559700	-0.76634000
F	-3.93385800	-0.18864000	1.24092600

Base R = CF_3
E = -1550.06647443 au

Si	-1.43125200	-0.00228600	-0.01004100
C	-0.34682700	1.44713500	0.48465300
H	-0.33527200	2.32809400	-0.16396800
H	-0.32007500	1.73499800	1.53991800
C	-0.34464600	-1.16519800	0.98337300
H	-0.31889900	-1.04293300	2.07027300
H	-0.32460700	-2.22262200	0.70484500
C	-0.36795200	-0.29143400	-1.52840400
H	-0.34714400	-1.29331200	-1.96611000
H	-0.35493000	0.47815700	-2.30565900
Si	0.87710000	-0.00823300	-0.03470500
Si	3.24780500	-0.13142100	-0.08650300
O	3.69812700	-1.53849700	-0.58067900
O	3.73011700	0.30906700	1.49079400
O	3.67136400	1.27491700	-0.92651100
H	4.05097100	-0.48094200	1.93718000
H	4.10841800	1.89294800	-0.33257700
C	-3.39400600	0.00609200	0.01842600
F	-3.93699800	-1.17138700	-0.39063800
F	-3.90285500	0.23742400	1.25863800
F	-3.93191100	0.96166400	-0.78617100

Acid R = NH_2

E = -1269.20471253 au

Si	2.44253500	0.00576000	-0.02047100
C	1.29523400	-1.45243500	-0.44990200
H	1.27550300	-1.80115700	-1.48683200
H	1.28317600	-2.29543000	0.24712500
C	1.30533200	0.40605600	1.45516000
H	1.30172800	-0.31323000	2.27976300
H	1.28993900	1.43357900	1.83045800
C	1.31633500	1.12089200	-1.10170400
H	1.30626100	2.19424600	-0.89068200
H	1.30514700	0.93576700	-2.17996600
Si	0.14834000	0.03849400	-0.04070100
Si	-2.18429600	0.00857300	0.00931400
O	-2.64836800	1.58012000	0.20901800
O	-2.74545800	-1.01089400	1.19830600
O	-2.89990000	-0.56275900	-1.36913500
H	-3.56635900	1.79327400	0.01284800
H	-2.39752900	-0.89838500	2.08697000
H	-3.12981200	-1.49650600	-1.36587500
N	4.15705600	-0.11447900	0.08150600
H	4.70364600	0.60985900	0.52465600
H	4.68520600	-0.59905100	-0.62983600

Base R = NH_2

E = -1268.64633072 au

Si	-2.40679200	0.00604600	0.00151800
C	-1.28515500	1.40972400	0.57255700
H	-1.24768200	2.32766800	-0.02371600
H	-1.25774500	1.63942000	1.64275400
C	-1.30396700	-1.23197400	0.89829200
H	-1.27884000	-1.19391600	1.99227100
H	-1.27449400	-2.26711100	0.54302700
C	-1.31364500	-0.19102300	-1.53665100
H	-1.29254600	-1.16125900	-2.04378200
H	-1.28400600	0.62707600	-2.26432900
Si	-0.08435400	-0.01810400	-0.03443800
Si	2.28469900	-0.12940400	-0.09495900
O	2.77617200	-1.50416600	-0.64453200
O	2.77820400	0.24794900	1.50012400
O	2.70386300	1.31959500	-0.87132700
H	3.12303000	-0.55935100	1.89479800
H	3.13755100	1.90417900	-0.24205600
N	-4.15508400	0.03486700	0.15763300
H	-4.65176900	-0.82559700	-0.03704600
H	-4.64696700	0.81789200	-0.25436100

Acid R = NO_2

E = -1418.19281623 au

Si	1.81048400	-0.04544700	0.00180300
C	0.71695100	0.77184300	1.30541700
H	0.71071200	0.33401200	2.30680300
H	0.72222200	1.86380400	1.34743700
C	0.72264600	0.68745800	-1.35542800
H	0.73385300	1.77479800	-1.46496300
H	0.71839500	0.18770000	-2.32736700
C	0.72012600	-1.58271500	0.04946600
H	0.71226900	-2.22788100	-0.83218700
H	0.71466400	-2.16959000	0.97108400
Si	-0.45669600	-0.04796900	-0.00141400
Si	-2.79130600	0.00343800	-0.00768100
O	-3.22156700	-1.02960800	-1.21484400
O	-3.35102000	1.55083400	-0.20061800
O	-3.45612500	-0.50763600	1.41177700
H	-4.12442300	-1.36354900	-1.22424900
H	-3.11665600	2.03386300	-0.99761200
H	-3.74244000	0.17563400	2.02525200
N	3.69898600	0.02584700	0.01140000
O	4.18249200	1.14744400	-0.08723600
O	4.33939600	-1.00972700	0.11859200

Base R = NO_2

E = -1417.65492949 au

Si	1.76398900	-0.02956700	-0.02737900
C	0.72204100	0.37138400	1.47231300
H	0.71854300	-0.34017200	2.30271600
H	0.71646600	1.40391800	1.83191900
C	0.69211400	1.05865600	-1.10077400
H	0.68767600	2.13231000	-0.89516200
H	0.65513900	0.85811000	-2.17480100
C	0.70371000	-1.51716000	-0.40726600
H	0.66765300	-1.88379100	-1.43626000
H	0.69926100	-2.34302800	0.30875600
Si	-0.52857200	-0.03511500	-0.00481200
Si	-2.90341200	-0.06996300	-0.13207700
O	-3.32758300	-0.44346000	-1.58172500
O	-3.37520300	1.46194000	0.44311200
O	-3.32388100	-1.02959100	1.19152200
H	-3.67036900	1.99360900	-0.30275400
H	-3.74266000	-0.49428200	1.87255000
N	3.69016700	0.02957600	0.00803900
O	4.21164100	1.14051000	0.05503000
O	4.32526000	-1.02014300	0.01092000

Acid R = NF$_2$

E = -1467.35426464 au

Si	-1.76868600	0.00358300	0.19218500
C	-0.65088300	1.34456800	0.91424500
H	-0.67546900	2.33234400	0.44771700
H	-0.58838300	1.42046900	2.00272600
C	-0.61919000	-1.31902100	0.89911900
H	-0.55842600	-1.40655200	1.98702400
H	-0.62839400	-2.30233000	0.42190500
C	-0.74955100	0.02076900	-1.40036000
H	-0.77431400	-0.88143100	-2.01719300
H	-0.78669900	0.92432100	-2.01396600
Si	0.49897400	0.03369900	0.08148300
Si	2.82875100	0.00943400	-0.07040300
O	3.35700800	-1.28779600	-0.95771000
O	3.58231800	-0.15534300	1.38830100
O	3.21983800	1.47444900	-0.71344300
H	3.05911500	-1.38058200	-1.86655600
H	3.87727300	-1.04062300	1.62142900
H	4.12712000	1.78076800	-0.61484000
N	-3.60031000	-0.02571900	0.42253500
F	-4.02850800	-1.12567300	-0.34485800
F	-4.06391100	1.07581200	-0.32035500

Base R = NF$_2$

E = -1466.81150707 au

Si	-1.72419100	0.01516900	0.17837900
C	-0.60689900	1.38589300	0.78716500
H	-0.60098300	2.33098800	0.23672600
H	-0.52829100	1.55380100	1.86472100
C	-0.64118400	-1.26499700	1.00665200
H	-0.56171800	-1.25513500	2.09705000
H	-0.65805500	-2.28748200	0.61955200
C	-0.73226000	-0.12777800	-1.40253900
H	-0.75965000	-1.07766800	-1.94378400
H	-0.73633800	0.72138700	-2.09161500
Si	0.57062200	-0.02460700	0.07666500
Si	2.94786800	-0.03369000	0.08854200
O	3.31891000	-1.37709200	-0.86728400
O	3.46581800	0.08731300	1.55155300
O	3.36888700	1.22330100	-0.98411800
H	3.66055700	-1.09167100	-1.72021200
H	3.70501400	1.96345700	-0.46905000
N	-3.58590400	0.06149400	0.41052100
F	-4.06361600	-1.10248200	-0.23869500
F	-4.03485600	1.09012400	-0.45309500

Acid R = OH

E = -1289.07271726 au

Si	2.44214900	-0.01113600	-0.00584600
C	1.29338000	-1.35360800	-0.72051300
H	1.27377200	-1.49017700	-1.80584100
H	1.26537000	-2.31764500	-0.20419600
C	1.32144700	0.08082300	1.51781900
H	1.30100900	-0.79256100	2.17610700
H	1.32814200	1.00923800	2.09553200
C	1.34637400	1.29929900	-0.85014700
H	1.34857900	2.30936200	-0.43124300
H	1.32591300	1.32841500	-1.94351400
Si	0.15832900	0.03662900	-0.02190200
Si	-2.17285900	0.01491300	0.00715200
O	-2.62562600	1.52719300	0.48465300
O	-2.74349800	-1.20082200	0.98546500
O	-2.86978700	-0.29105600	-1.46054400
H	-3.53799900	1.78598000	0.31953500
H	-2.42279100	-1.24277800	1.89038900
H	-3.10258900	-1.20775400	-1.63455800
O	4.09713400	-0.03958300	0.09827600
H	4.60094500	-0.07270300	-0.71962100

Base R = OH

E = -1288.51878446 au

Si	-2.40882400	0.01643500	0.02055500
C	-1.34005900	-0.34845500	-1.49042100
H	-1.30425800	-1.36966400	-1.88308400
H	-1.32567600	0.38325700	-2.30453000
C	-1.30505000	1.47329800	0.44566900
H	-1.29225400	2.32797500	-0.23797400
H	-1.26427800	1.80562500	1.48779700
C	-1.30060600	-1.11569000	1.04555000
H	-1.26115700	-0.95757500	2.12829200
H	-1.26616100	-2.18330700	0.80552600
Si	-0.09580100	-0.00274600	-0.02165600
Si	2.27313000	-0.14156800	-0.09089100
O	2.77780000	0.37662900	1.45802500
O	2.70404400	1.21832800	-1.00447600
O	2.72833500	-1.57073900	-0.51573300
H	3.10270800	-0.39378200	1.93463600
H	3.12686600	1.86914200	-0.43583400
O	-4.09423700	0.09583800	0.06556100
H	-4.52812100	-0.70673200	-0.23874000

Acid R = F
E = -1313.09325989 au

Si	2.43856700	-0.01133500	-0.00901200
C	1.31089600	-1.37300200	-0.68563800
H	1.30122100	-1.53496200	-1.76695100
H	1.28124800	-2.32343200	-0.14559500
C	1.32962200	0.11198400	1.52081300
H	1.30703900	-0.74684300	2.19768500
H	1.33125400	1.05313200	2.07740400
C	1.35987500	1.28297500	-0.87089800
H	1.35772500	2.29912100	-0.46799800
H	1.34962800	1.29269100	-1.96409900
Si	0.16469200	0.03278300	-0.02061100
Si	-2.16575000	0.01415500	0.00674200
O	-2.60347400	1.53211100	0.47490600
O	-2.73705900	-1.19224700	0.99239600
O	-2.85053400	-0.29939400	-1.46253600
H	-3.50752900	1.80917300	0.29439200
H	-2.44790000	-1.21067800	1.90863400
H	-3.10021200	-1.21269800	-1.63115400
F	4.05873100	-0.04216000	-0.00064200

Base R = F
E = -1312.54484617 au

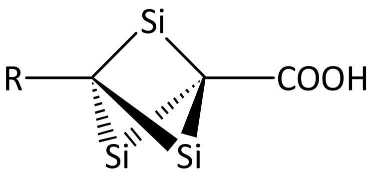
Si	-2.40622200	0.00618400	0.01459200
C	-1.30830300	1.45331600	0.48564800
H	-1.28992400	2.32859900	-0.17107000
H	-1.26259000	1.75177800	1.53767500
C	-1.31630700	-1.15219000	1.00896000
H	-1.27144600	-1.02029200	2.09449000
H	-1.29631100	-2.21281300	0.74140600
C	-1.35688400	-0.30227300	-1.50918400
H	-1.33717000	-1.30781800	-1.93935600
H	-1.33852000	0.45997300	-2.29403100
Si	-0.10280300	-0.01235900	-0.03012000
Si	2.26972000	-0.13532600	-0.09439100
O	2.73198700	-1.54100400	-0.58034400
O	2.74852800	0.31983600	1.48004200
O	2.68942400	1.26548700	-0.94570600
H	3.07088300	-0.46599100	1.93257600
H	3.07223500	1.91103300	-0.34370400
F	-4.05193700	0.02098500	0.04849000

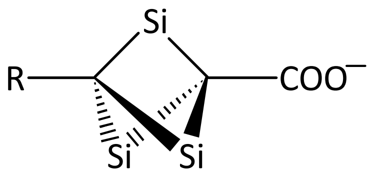
Acid R = Li
E = -1220.76901904 au

Si	2.76182400	-0.02188600	-0.00747800
C	1.50548000	-1.25009800	-0.88374100
H	1.51919800	-1.25629500	-1.97857600
H	1.48018200	-2.27296300	-0.49369500
C	1.51655500	-0.11541000	1.50855200
H	1.49931000	-1.06649800	2.05178200
H	1.53747600	0.72707900	2.20738200
C	1.57642200	1.39320500	-0.67448000
H	1.59406300	2.34270000	-0.13035300
H	1.59113600	1.56855400	-1.75486000
Si	0.41253700	0.04639700	-0.02960700
Si	-1.94526000	0.02074400	0.00573300
O	-2.45823700	1.48796900	0.58248800
O	-2.50800900	-1.26717200	0.91404900
O	-2.70905700	-0.19721600	-1.45631500
H	-3.38833200	1.69331700	0.44179600
H	-2.07559800	-1.41715800	1.75918700
H	-2.88358600	-1.11295300	-1.69160200
Li	5.24347500	-0.06472700	0.00136900

Base R = Li
E = -1220.19318307 au

Si	-2.70781300	0.01676200	0.02892600
C	-1.48918400	1.43127700	0.53024300
H	-1.48567600	2.32985400	-0.09692300
H	-1.45367400	1.70359500	1.59115900
C	-1.51771700	-1.17743000	0.97566300
H	-1.48552700	-1.08171600	2.06682700
H	-1.53084800	-2.23280400	0.68262700
C	-1.56529400	-0.25768300	-1.50656800
H	-1.57933000	-1.24953000	-1.97088300
H	-1.56513900	0.52509600	-2.27314100
Si	-0.34062000	-0.02293200	-0.03225100
Si	2.04037700	-0.13445000	-0.10196100
O	2.55344900	-1.52102400	-0.60836300
O	2.54413600	0.28913300	1.48373300
O	2.47100800	1.29367000	-0.91913900
H	2.90489200	-0.50690900	1.88729200
H	2.90530400	1.88957800	-0.30083900
Li	-5.23760000	0.04009700	0.08066900





Acid R = H
E = -1137.36993829 au

C	2.03620600	-0.04668400	0.00001300
Si	0.89366100	1.48578400	-0.00101700
H	0.91885100	2.33725600	1.21842100
H	0.91880400	2.33561500	-1.22160200
Si	0.82102500	-0.76357500	-1.28137900
H	0.80684600	-0.14089800	-2.63352100
H	0.75888100	-2.24490400	-1.40725200
Si	0.82104400	-0.76175800	1.28242000
H	0.75884800	-2.24291400	1.41034600
H	0.80684700	-0.13720600	2.63369500
C	-0.36219900	0.04169500	-0.00005300
C	-1.82930400	0.14025000	-0.00001000
O	-2.47041600	1.17137200	-0.00003400
O	-2.43817900	-1.06957000	0.00000900
H	-3.39107900	-0.89446000	0.00004300
H	3.12233600	-0.08478200	0.00003500

Base R = H
E = -1136.81472958 au

C	2.02044000	0.08465800	-0.00000200
Si	0.70832400	1.48952600	-0.00005200
H	0.71213200	2.36737900	1.20963100
H	0.71202600	2.36731300	-1.20978000
Si	0.84156500	-0.73348200	-1.26675900
H	0.82429700	-0.13376300	-2.63869300
H	0.97855700	-2.21422900	-1.43047900
Si	0.84157000	-0.73337100	1.26679500
H	0.97855900	-2.21410600	1.43064400
H	0.82440000	-0.13353500	2.63868100
C	-0.40782700	-0.05220800	0.00000500
C	-1.94462500	-0.04352100	0.00000500
O	-2.44708700	1.10855200	-0.00002600
O	-2.50620000	-1.16219000	0.00004600
H	3.10797500	0.13905700	0.00001500

Acid R = CH_3
E = -1176.63615176 au

C	1.72561600	-0.01574400	0.00000200
Si	0.54490900	1.49984100	-0.00014000
H	0.56085700	2.35457800	1.21880600
H	0.56092200	2.35437400	-1.21923000
Si	0.49924600	-0.74539100	-1.27978100
H	0.47736700	-0.12500700	-2.63430400
H	0.45584100	-2.22831700	-1.40949500
Si	0.49921700	-0.74517700	1.27987000
H	0.45580300	-2.22808000	1.40984400
H	0.47727600	-0.12455100	2.63428100
C	-0.69002300	0.04353300	-0.00004000
C	-2.15756100	0.12114000	-0.00004400
O	-2.81465100	1.14227100	0.00003500
O	-2.74926100	-1.09763600	0.00005300
H	-3.70437000	-0.93528000	0.00012000
C	3.23770200	-0.04743700	0.00005100
H	3.65138100	0.45478200	-0.88190200
H	3.65132200	0.45492200	0.88195100
H	3.62328000	-1.07326900	0.00014400

Base R = CH_3
E = -1176.08052409 au

C	1.70578300	0.02747400	0.00006100
Si	0.41471700	1.46188000	0.00002200
H	0.44493900	2.34120700	1.20974100
H	0.44495400	2.34116800	-1.20972600
Si	0.49003600	-0.76011300	-1.26536700
H	0.49148000	-0.16078300	-2.63866400
H	0.59389400	-2.24449500	-1.42981500
Si	0.48997800	-0.76007900	1.26545700
H	0.59381000	-2.24446200	1.42994200
H	0.49133900	-0.16073000	2.63874600
C	-0.73802400	-0.04827700	0.00000500
C	-2.27613000	-0.00342400	-0.00010800
O	-2.75213800	1.15935600	-0.00011700
O	-2.86200700	-1.10921800	-0.00021300
C	3.21662600	0.07186400	0.00011800
H	3.60863100	0.59538900	-0.88233000
H	3.60856900	0.59531000	0.88263900
H	3.65978700	-0.93316200	0.00008800

Acid R = CN
E = -1229.51349429 au

C	1.51854800	-0.00350000	0.00006800
Si	0.33012300	1.51643100	-0.00065200
H	0.36405700	2.34946700	1.22698200
H	0.36417400	2.34836600	-1.22903100
Si	0.30558200	-0.75071300	-1.29151300
H	0.30551100	-0.11238700	-2.63248100
H	0.30300100	-2.23124800	-1.39921400
Si	0.30545100	-0.74955200	1.29219400
H	0.30283400	-2.22999100	1.40121900
H	0.30522400	-0.11002800	2.63259100
C	-0.87337900	0.03342100	-0.00007900
C	-2.34411800	0.11164500	-0.00015000
O	-2.99060900	1.13797900	-0.00017900
O	-2.93314600	-1.10481600	0.00018200
H	-3.88993900	-0.95031900	0.00024800
C	2.93861900	-0.02295700	0.00015100
N	4.10299600	-0.03816300	-0.00009700

Base R = CN
Not optimized.

Acid R = CF_3
E = -1474.11895641 au

C	-0.93800600	0.00433700	0.00000400
Si	0.24146800	1.52117300	-0.00030200
H	0.21750400	2.35578700	-1.22754200
H	0.21774900	2.35613200	1.22670900
Si	0.26198200	-0.74456400	1.29126500
H	0.27293000	-0.10733000	2.63307100
H	0.27096900	-2.22521100	1.40101000
Si	0.26173200	-0.74491600	-1.29128500
H	0.27068000	-2.22559200	-1.40063600
H	0.27243300	-0.10804000	-2.63326300
C	1.44493700	0.03692000	-0.00023800
C	2.91560600	0.10857400	-0.00040300
O	3.56920500	1.13065100	0.00007000
O	3.49988000	-1.11101300	0.00040100
H	4.45702100	-0.95916800	0.00079400
C	-2.41893000	-0.01287400	0.00010500
F	-2.92265300	-1.26980000	0.00007200
F	-2.94227600	0.60655600	1.08368800
F	-2.94242300	0.60667400	-1.08333900

Base R = CF_3
E = -1473.57720322 au

C	0.91292000	-0.01136400	0.00000000
Si	-0.40302300	1.41923000	-0.00004200
H	-0.36180200	2.27267400	1.21943900
H	-0.36179700	2.27259800	-1.21957500
Si	-0.27472800	-0.82070400	-1.27732900
H	-0.27293800	-0.20409900	-2.63666100
H	-0.13064100	-2.29848000	-1.42824700
Si	-0.27473300	-0.82063400	1.27737500
H	-0.13065000	-2.29840100	1.42836800
H	-0.27293800	-0.20395600	2.63667400
C	-1.49507000	-0.12685800	-0.00000100
C	-3.02300900	0.03030700	0.00000200
O	-3.37179300	1.24175400	0.00001200
O	-3.71548300	-1.00678200	-0.00001500
C	2.37982100	0.05109100	-0.00000400
F	2.98167200	-1.17372000	0.00009000
F	2.89338000	0.69958500	-1.08340400
F	2.89337100	0.69972900	1.08331200

Acid R = NH_2
E = -1192.65516982 au

C	1.73794900	-0.02027700	0.00204400
Si	0.56197900	1.47765200	-0.25138700
H	0.60182700	2.51512600	0.81586900
H	0.55165800	2.12313600	-1.59232800
Si	0.51087000	-0.94698900	-1.14556100
H	0.47017700	-0.56349600	-2.58392800
H	0.48579900	-2.43093900	-1.01955400
Si	0.49047600	-0.52570900	1.40689800
H	0.42961500	-1.96666300	1.78057800
H	0.45037800	0.31301200	2.63812000
C	-0.66727200	0.03781500	-0.00262900
C	-2.13324600	0.12398400	-0.00585100
O	-2.78522800	1.14855600	0.00070400
O	-2.73183900	-1.09165000	-0.01443200
H	-3.68589400	-0.92345600	-0.01111100
N	3.16503500	-0.01954000	-0.09103000
H	3.56839600	-0.93573000	0.06592300
H	3.59819400	0.63206200	0.55278400

Base R = NH_2
E = -1192.10004611 au

C	1.71481700	0.02982600	-0.01634700
Si	0.42599400	1.44917500	-0.21255200
H	0.48154300	2.48389700	0.86644600
H	0.41547400	2.15121600	-1.53191500
Si	0.49936800	-0.93175900	-1.15413800
H	0.46840500	-0.53935500	-2.59815600
H	0.62407300	-2.42280500	-1.09657800
Si	0.49215600	-0.57203400	1.37449700
H	0.59307000	-2.01836900	1.75060500
H	0.49078400	0.21903100	2.64734300
C	-0.71515600	-0.05358100	0.01502000
C	-2.25631000	-0.00481300	0.00328900
O	-2.72845100	1.15887500	-0.00161100
O	-2.84303700	-1.10932600	-0.00222500
N	3.15451700	0.10367400	-0.10986300
H	3.57998000	-0.80254100	0.05821800
H	3.53160100	0.74287000	0.58269600

Acid R = NO_2
E = -1341.67055970 au

C	-1.20198800	-0.00041600	0.00756100
Si	-0.03271500	1.34688600	-0.71507500
H	-0.08846900	1.49257700	-2.19023500
H	-0.05390500	2.65811400	-0.02277500
Si	-0.01471500	-0.02707200	1.50860100
H	0.01509400	1.17688300	2.37467400
H	-0.03908300	-1.27834700	2.30646600
Si	-0.03237500	-1.27725300	-0.79610000
H	-0.03218000	-2.62988200	-0.18662200
H	-0.00836400	-1.33601300	-2.27787700
C	1.14939400	0.02165900	-0.01284600
C	2.61971800	0.08397400	-0.06158800
O	3.26597300	0.94324500	-0.62341500
O	3.20891200	-0.93844000	0.59690600
H	4.16549500	-0.81217200	0.50624500
N	-2.65044600	-0.01817100	0.00825400
O	-3.23091700	0.72711900	0.78577000
O	-3.20533600	-0.77831200	-0.77555900

Base R = NO_2
Not optimized.

Acid R = NF_2

E = -1390.83913922 au

C	1.16453100	0.05413600	-0.21257400
Si	-0.06876100	1.50014700	-0.49346400
H	0.03201700	2.61910500	0.47452400
H	-0.19303700	1.98852000	-1.89001800
Si	-0.09420500	-1.03024300	-1.16544000
H	-0.24604600	-0.75594100	-2.61774000
H	-0.03201800	-2.48747900	-0.89395900
Si	0.11496600	-0.36828500	1.34764400
H	0.15706800	-1.77320200	1.82296200
H	0.16313000	0.59343800	2.47730300
C	-1.18816000	0.03156400	-0.00596000
C	-2.65480800	0.07230500	0.11339400
O	-3.34056500	1.06823600	0.01424800
O	-3.19413800	-1.14402500	0.35400500
H	-4.15220300	-1.01374900	0.41883700
N	2.56835000	0.09287800	-0.43217100
F	3.06248200	-1.14828000	0.03700500
F	3.08339600	0.97214500	0.54919000

Base R = NF_2

E = -1390.29842478 au

C	-1.14555700	-0.20653900	0.00001200
Si	-0.00702900	1.37118400	-0.00004800
H	-0.11495400	2.21466500	-1.22119600
H	-0.11493700	2.21475500	1.22104000
Si	0.11908800	-0.89579700	1.27819800
H	0.03640900	-0.28856500	2.63752500
H	0.14120100	-2.38130900	1.41397100
Si	0.11907800	-0.89588300	-1.27813900
H	0.14119400	-2.38140200	-1.41381300
H	0.03639000	-0.28874300	-2.63750600
C	1.24188300	-0.05755500	-0.00000300
C	2.76532600	0.17699900	-0.00001000
O	3.07361600	1.39509000	-0.00005000
O	3.48872300	-0.84060200	0.00001700
N	-2.54132700	-0.43167200	0.00002400
F	-3.06891900	0.32814900	1.09800400
F	-3.06892000	0.32806400	-1.09801300

Acid R = OH

E = -1212.50077118 au

C	-1.73467100	-0.01556800	0.00250700
Si	-0.50444800	-0.60737100	1.37472600
H	-0.47779800	0.17036200	2.64533300
H	-0.43185500	-2.06424800	1.66744200
Si	-0.52374400	-0.89637100	-1.19257500
H	-0.47680400	-2.38183500	-1.13607900
H	-0.49425300	-0.43302300	-2.60678800
Si	-0.55614300	1.50858400	-0.17727800
H	-0.54378400	2.21786500	-1.48490800
H	-0.58413800	2.48774100	0.94386400
C	0.64851800	0.04530200	-0.00362000
C	2.11573300	0.12388100	-0.00342100
O	2.77293100	1.14465400	0.00875200
O	2.70635900	-1.09506000	-0.01630000
H	3.66167500	-0.93400700	-0.01147000
O	-3.12048200	-0.11622700	-0.07094900
H	-3.52027800	0.48074700	0.56956400

Base R = OH

E = -1211.94838318 au

C	-1.71286500	0.04171800	-0.00001400
Si	-0.50402300	-0.75944100	-1.28469000
H	-0.62613900	-2.24413200	-1.43674000
H	-0.47529500	-0.16341400	-2.65677700
Si	-0.43004000	1.47554400	0.00006700
H	-0.43917300	2.34692800	-1.21310000
H	-0.43903900	2.34690600	1.21324700
Si	-0.50407900	-0.75956300	1.28468200
H	-0.47522600	-0.16371000	2.65684200
H	-0.62623200	-2.24426900	1.43656700
C	0.69540000	-0.05619100	0.00003200
C	2.24072300	-0.01179200	0.00000200
O	2.82349000	-1.11745100	-0.00008800
O	2.71309100	1.15100500	0.00004200
O	-3.11580000	0.16723700	-0.00008600
H	-3.49070100	-0.71861600	0.00006300

Acid R = F

E = -1236.50260277 au

C	1.71757900	-0.01700400	0.00004300
Si	0.56781100	1.52619400	-0.00047500
H	0.57815900	2.36681100	1.22479600
H	0.57825200	2.36603400	-1.22627900
Si	0.51784700	-0.76131000	-1.30279700
H	0.48994500	-0.13061100	-2.64931400
H	0.46427700	-2.24245000	-1.41447000
Si	0.51774900	-0.76048300	1.30326200
H	0.46415000	-2.24155200	1.41586500
H	0.48971700	-0.12893500	2.64937800
C	-0.63169900	0.04396200	-0.00007400
C	-2.09992700	0.12440700	-0.00011700
O	-2.75345900	1.14693700	-0.00010900
O	-2.69142800	-1.09349500	0.00010200
H	-3.64688600	-0.93275700	0.00016200
F	3.08645100	-0.05043200	0.00010500

Base R = F

E = -1235.95462404 au

C	-1.69692000	0.04349000	0.00006000
Si	-0.41359900	1.48446600	-0.00011400
H	-0.42034000	2.34975700	-1.21584100
H	-0.42039300	2.35000200	1.21543800
Si	-0.52019500	-0.77391300	1.28692400
H	-0.50117500	-0.16586700	2.65249700
H	-0.63412900	-2.25580100	1.43593100
Si	-0.52025100	-0.77421200	-1.28668600
H	-0.63423500	-2.25612900	-1.43533000
H	-0.50123400	-0.16648200	-2.65239800
C	0.67718000	-0.06530200	0.00002400
C	2.22551000	-0.01120900	-0.00009600
O	2.68533800	1.15662100	-0.00030200
O	2.81589400	-1.11125600	-0.00006800
F	-3.08626100	0.09677300	0.00011300

Acid R = Li

E = -1144.25646638 au

C	1.98952100	-0.03771500	0.00002400
Si	0.80120100	1.45811000	-0.00036400
H	0.81199200	2.33667200	1.20787700
H	0.81201800	2.33606200	-1.20904800
Si	0.73845800	-0.73876200	-1.25197700
H	0.70723600	-0.13647800	-2.62016200
H	0.66952600	-2.22322900	-1.40904600
Si	0.73842700	-0.73811900	1.25235100
H	0.66948000	-2.22250500	1.41017800
H	0.70716600	-0.13513300	2.62022600
C	-0.50275700	0.04575200	-0.00003300
C	-1.97038900	0.13242100	-0.00005100
O	-2.62864900	1.15481500	-0.00012800
O	-2.57470200	-1.08341600	0.00011800
H	-3.52705500	-0.90629000	0.00012700
Li	3.92833100	-0.06674400	0.00004600

Base R = Li

E = -1143.68157885 au

C	-1.96936300	0.03296600	0.00000100
Si	-0.67133000	1.44924900	-0.00005000
H	-0.68952300	2.35214900	-1.19988600
H	-0.68951000	2.35222900	1.19972600
Si	-0.73040100	-0.73251600	1.24233500
H	-0.72270500	-0.15028100	2.62949000
H	-0.80912600	-2.22088700	1.43316300
Si	-0.73041300	-0.73260600	-1.24228100
H	-0.80913200	-2.22099200	-1.43299700
H	-0.72272300	-0.15047300	-2.62947900
C	0.54913900	-0.02889200	-0.00000400
C	2.08395100	-0.01096000	-0.00000300
O	2.59528300	1.13769100	-0.00000300
O	2.64922200	-1.13088400	-0.00000200
Li	-3.88189100	0.08245100	0.00000200

Analog 2 Backbone R=H
E = -948.97747394au

C	-0.00020600	-0.00036300	-1.20426900
Si	0.95981200	-1.12910600	-0.00002500
H	0.59695500	-2.57546800	0.00032700
H	2.44576800	-1.00420000	-0.00007200
Si	0.49834900	1.39547500	0.00001700
H	1.93232800	1.80478500	-0.00022100
H	-0.35233900	2.62029200	-0.00023000
Si	-1.45799500	-0.26625700	-0.00003000
H	-2.52887500	0.77148200	-0.00007600
H	-2.09350900	-1.61527100	0.00032400
C	-0.00016300	-0.00021200	1.20434100
H	-0.00019200	0.00022000	2.29174900
H	-0.00023400	0.00003900	-2.29170500

Analog 2 Backbone R=CH_3
E = -988.24375371au

C	-0.88584900	0.00018400	0.00001100
Si	0.33805900	1.35235300	-0.60058100
H	0.33663500	1.65642700	-2.06173800
H	0.33755600	2.64042900	0.15331200
Si	0.33924100	-0.15589800	1.47114700
H	0.33879400	0.95762600	2.46492500
H	0.33931600	-1.45318000	2.20903000
Si	0.33849000	-1.19667300	-0.87055300
H	0.33798600	-2.61366500	-0.40208400
H	0.33705900	-1.18741500	-2.36297000
C	1.53890600	0.00063300	-0.00102100
H	2.62554600	0.00089200	-0.00126300
C	-2.39753200	-0.00026200	0.00067400
H	-2.80286800	0.10753300	-1.01205700
H	-2.80177000	-0.93164000	0.41374600
H	-2.80245000	0.82271700	0.60093400

Analog 2 Backbone R=CN
E = -1041.12308410au

C	-0.66983200	-0.00057900	0.00022600
Si	0.54805000	-1.20859900	-0.87694700
H	0.52299200	-2.61232200	-0.38705100
H	0.52127100	-1.17820700	-2.36338200
Si	0.54686100	1.36384000	-0.60819100
H	0.51952000	1.64177500	-2.06871900
H	0.51980200	2.63614500	0.16099700
Si	0.54806700	-0.15508300	1.48508900
H	0.52126900	0.97108200	2.45577800
H	0.52279200	-1.45741600	2.20233200
C	1.73156300	0.00081700	-0.00044000
H	2.81800000	0.00154300	-0.00074800
C	-2.08956400	-0.00014600	0.00006200
N	-3.25433300	-0.00076600	0.00034200

Analog 2 Backbone R=CF_3
E = -1285.72799651au

C	0.13572800	0.00000900	0.00001000
Si	-1.07000600	-1.25201300	-0.81232800
H	-1.05099200	-1.30183400	-2.29874000
H	-1.05258500	-2.62982000	-0.25229900
Si	-1.07110000	-0.07764600	1.49026800
H	-1.05332100	-1.34013900	2.27647300
H	-1.05342500	1.09625200	2.40349200
Si	-1.06997700	1.32965200	-0.67789600
H	-1.05244800	2.64175300	0.02236400
H	-1.05101100	1.53377300	-2.15108200
C	-2.25713300	0.00008900	-0.00113000
H	-3.34377100	0.00012600	-0.00128400
C	1.61574300	-0.00001000	0.00024900
F	2.13506500	-1.11377700	0.56983500
F	2.13509300	1.05021800	0.67990500
F	2.13502900	0.06349900	-1.24910800

Analog 2 Backbone R=NH_2
E = -1004.26291274au

C	-0.90427200	0.03149900	-0.00014900
Si	0.29098800	-0.75898400	1.27941200
H	0.29621900	-0.13880400	2.63727700
H	0.26092600	-2.24244800	1.42915300
Si	0.29127000	-0.76040700	-1.27853900
H	0.26131800	-2.24406700	-1.42649200
H	0.29724500	-0.14182400	-2.63712500
Si	0.39103800	1.48725600	-0.00076600
H	0.43186300	2.35488800	-1.21481100
H	0.43170900	2.35651300	1.21210600
C	1.50797500	-0.04497900	0.00023100
H	2.59277200	-0.09048200	0.00031800
N	-2.33491800	-0.02222600	-0.00024600
H	-2.73804900	0.41643700	0.81966500
H	-2.73793700	0.41615100	-0.82036500

Analog 2 Backbone R=NO_2

E = -1153.28000915au

C	-0.38202200	-0.00169700	0.00002800
Si	0.82122100	-0.75500000	1.29320400
H	0.76544000	-0.12327100	2.63788600
H	0.82884000	-2.23604000	1.40595300
Si	0.82120100	-0.75586000	-1.29266600
H	0.82888800	-2.23698800	-1.40426000
H	0.76544900	-0.12530000	-2.63789400
Si	0.77794000	1.51800900	-0.00053700
H	0.75360900	2.35788300	-1.22563900
H	0.75363200	2.35952500	1.22342700
C	1.97840100	0.03190100	0.00002300
H	3.06463300	0.04707100	-0.00003100
N	-1.83082400	-0.01295000	0.00001400
O	-2.40473000	1.06947800	0.00011500
O	-2.39627800	-1.09866900	-0.00009900

Analog 2 Backbone R=NF_2

E = -1202.44835461au

C	0.32790800	0.00034000	-0.21748800
Si	-1.01124700	1.29572000	-0.67390700
H	-0.83906200	2.64165400	-0.06755100
H	-1.34213200	1.41634500	-2.11932800
Si	-1.01099000	-1.29536900	-0.67457900
H	-1.34153100	-1.41537300	-2.12011900
H	-0.83793500	-2.64154100	-0.06896900
Si	-0.49140900	-0.00042900	1.53121600
H	-0.29670500	-1.22396900	2.35209000
H	-0.29730700	1.22251700	2.35316800
C	-1.97794800	-0.00023900	0.33417200
H	-3.03586800	-0.00056400	0.58101400
N	1.68319000	0.00011100	-0.64558800
F	2.29420200	-1.09133800	0.01940300
F	2.29463200	1.09140900	0.01954200

Analog 2 Backbone R=OH

E = -1024.10917819au

C	-0.90769400	0.00020800	-0.02011300
Si	0.33361100	1.30371700	-0.73677200
H	0.36116300	1.44516700	-2.22200000
H	0.34589500	2.65931500	-0.11710100
Si	0.26840400	-0.00044700	1.49446900
H	0.25976200	1.21467100	2.35711900
H	0.25923300	-1.21600700	2.35649400
Si	0.33305000	-1.30344300	-0.73743700
H	0.34476900	-2.65937700	-0.11848000
H	0.36047600	-1.44415000	-2.22273800
C	1.48294500	-0.00030900	0.02647300
H	2.56839300	-0.00055400	0.05309300
O	-2.29727700	0.00047400	0.05353300
H	-2.66389400	0.00016700	-0.83644400

Analog 2 Backbone R=F

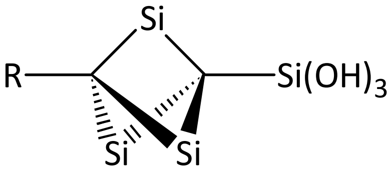
E = -1048.11163680au

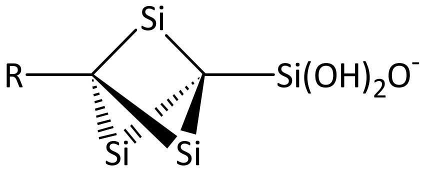
C	0.89647400	-0.00268700	0.00020000
Si	-0.30278100	-0.70906400	1.32890800
H	-0.31585300	-2.18707600	1.50992900
H	-0.30844300	-0.03769700	2.65808700
Si	-0.29572200	1.50651100	-0.04983000
H	-0.30028400	2.40304600	1.13915700
H	-0.29990200	2.32244700	-1.29550400
Si	-0.30240300	-0.79530000	-1.27922200
H	-0.30769500	-0.21319300	-2.64984000
H	-0.31547000	-2.28202600	-1.36227400
C	-1.46145700	0.00484600	-0.00040500
H	-2.54667900	0.00800800	-0.00068900
F	2.26632300	-0.00627900	0.00048700

Analog 2 Backbone R=Li

E = -955.86068022au

C	-0.00212000	-0.00312000	1.13259300
Si	1.44594800	-0.09464400	-0.10674700
H	2.41842600	1.04500600	-0.11328100
H	2.25910200	-1.35289100	-0.12145700
Si	-0.80490200	-1.20356600	-0.11548000
H	-0.30340900	-2.61526800	-0.13071500
H	-2.30110600	-1.27951300	-0.13088100
Si	-0.64004000	1.29969400	-0.10692500
H	-2.11342600	1.57079500	-0.12174200
H	0.04168500	2.63371000	-0.11333300
C	0.00337800	0.00488600	-1.36750300
H	0.00562500	0.00796000	-2.45951500
Li	-0.00951200	-0.01372200	3.06950400





Acid R = H

E = -1465.16108146 au

C	2.58392600	0.02597900	0.01529200
Si	1.36502400	-0.45113400	1.40974500
H	1.36733600	-1.87454700	1.84598000
H	1.33464400	0.43543700	2.60552300
Si	1.36301100	1.45966000	-0.29177000
H	1.33225000	2.55571800	0.71686700
H	1.34911200	2.05557700	-1.65861100
Si	1.39119000	-0.97336400	-1.09152400
H	1.37917200	-0.63671300	-2.54490100
H	1.39881900	-2.45276800	-0.93185100
C	0.15119100	0.00355400	-0.00440500
Si	-1.67695300	-0.02379000	-0.00120000
O	-2.34904300	0.53305500	1.40636500
H	-2.82399400	1.36545900	1.33642200
O	-2.10812700	-1.60800200	-0.21526400
H	-3.02786000	-1.82833000	-0.04342800
O	-2.35212200	0.97240500	-1.15334900
H	-2.10961100	0.82718400	-2.07102200
H	3.67196600	0.03690900	0.02416700

Base R = H

E = -1464.59458974 au

C	2.57640400	0.00001200	-0.00303200
Si	1.35001300	-0.00035000	1.47496900
H	1.39416300	-1.20788600	2.35513200
H	1.39396700	1.20658200	2.35595900
Si	1.33044500	1.26912000	-0.72336300
H	1.36891900	2.63686400	-0.11882600
H	1.35062700	1.43271000	-2.20978600
Si	1.33047900	-1.26879000	-0.72391300
H	1.35071200	-1.43161300	-2.21042100
H	1.36903700	-2.63685500	-0.12010500
C	0.12668500	-0.00004200	0.02010800
Si	-1.75737100	-0.00003300	0.10813900
O	-2.43275100	-0.00063100	1.52573000
O	-2.15482300	-1.36224900	-0.84343100
H	-2.86244100	-1.82284700	-0.38202600
O	-2.15460700	1.36299600	-0.84233700
H	-2.86262400	1.82301100	-0.38096900
H	3.66662400	0.00003800	-0.01275700

Acid R = CH_3

E = -1504.42809911 au

C	2.28565900	0.01494400	0.00919800
Si	1.06931000	-0.83656300	-1.20762600
H	1.05420800	-0.32752000	-2.61157500
H	1.07198300	-2.32559700	-1.23415000
Si	1.04864100	-0.62886100	1.33484200
H	1.04936600	-2.09620300	1.59398800
H	1.02417400	0.10091000	2.63401500
Si	1.04837900	1.47550400	-0.11412000
H	1.02366800	2.44069300	1.02219300
H	1.03399800	2.24020100	-1.39564300
C	-0.16296700	0.00100700	-0.00757100
Si	-1.98995500	-0.01969600	-0.00096100
O	-2.66672600	0.47121800	1.42887600
O	-2.43101000	-1.59062900	-0.27887200
O	-2.65685000	1.03193500	-1.10778600
H	-3.08885900	1.33424300	1.41097500
H	-3.35333500	-1.80864400	-0.11808000
H	-2.36983700	0.96176800	-2.02146100
C	3.79697800	0.02358900	0.02128600
H	4.20611900	-0.98984200	0.10573300
H	4.20700600	0.46371300	-0.89514000
H	4.19092800	0.60346100	0.86401100

Base R = CH_3

E = -1503.86114758 au

C	-2.27271400	-0.00010300	0.00344000
Si	-1.01461800	1.26771400	-0.72092700
H	-1.04471800	1.43258800	-2.20818500
H	-1.05480300	2.63704100	-0.11739800
Si	-1.02509100	-0.00030100	1.47497100
H	-1.06972900	1.20660700	2.35782200
H	-1.06940600	-1.20771200	2.35715000
Si	-1.01439600	-1.26731100	-0.72148800
H	-1.05420000	-2.63696600	-0.11870100
H	-1.04445600	-1.43125400	-2.20884900
C	0.18895100	0.00015900	0.01671900
Si	2.07266100	-0.00002300	0.10556600
O	2.74407200	-0.00070800	1.52502000
O	2.47234600	1.36271500	-0.84388500
O	2.47216700	-1.36202900	-0.84499200
H	3.17831900	1.82335900	-0.37999400
H	3.17763900	-1.82339200	-0.38103800
C	-3.78420700	-0.00016500	-0.00429100
H	-4.19562500	0.88247400	0.50373300
H	-4.18810300	0.00018300	-1.02568200
H	-4.19556000	-0.88320000	0.50309900

Acid R = CN
E = -1557.30679659 au

C	-2.08796600	-0.00845600	-0.00415000
Si	-0.86817100	1.41981500	-0.43734400
H	-0.88594300	1.86822700	-1.85519200
H	-0.89383100	2.58490300	0.48240200
Si	-0.85718800	-0.33716700	1.44618800
H	-0.87623700	0.66617600	2.54159200
H	-0.86883300	-1.71840500	1.99206000
Si	-0.86285700	-1.09688800	-1.01387100
H	-0.87504000	-2.54849100	-0.69632500
H	-0.87487400	-0.88615500	-2.48595900
C	0.33642400	-0.00021100	-0.01068300
Si	2.16648700	0.01057400	0.01084900
O	2.75230000	-0.95727300	1.21598000
O	2.59427400	1.59396400	0.24197500
O	2.86253100	-0.60738500	-1.36698600
H	3.41805800	-1.59999700	0.95626100
H	3.49893900	1.77835200	0.50894700
H	2.86372100	-0.05986400	-2.15601500
C	-3.50860400	-0.01433500	-0.00151700
N	-4.67338600	-0.01854900	0.00015200

Base R = CN
E = -1556.75687754 au

C	2.07542300	-0.00000100	0.00790200
Si	0.80887600	-0.00011000	1.48039200
H	0.87219200	-1.21542800	2.33953900
H	0.87218100	1.21511600	2.33967100
Si	0.82279400	1.27846500	-0.73500200
H	0.88176000	2.63221600	-0.11320700
H	0.89500600	1.42256900	-2.21707600
Si	0.82281000	-1.27837000	-0.73518800
H	0.89502000	-1.42228800	-2.21727900
H	0.88178900	-2.63220100	-0.11356700
C	-0.36622700	-0.00001300	-0.00481900
Si	-2.25020600	0.00000100	0.10527800
O	-2.86878300	-0.00000700	1.54598000
O	-2.64670800	-1.36145500	-0.84052600
H	-3.34380100	-1.84033100	-0.38199800
O	-2.64665900	1.36148500	-0.84050500
H	-3.34380200	1.84033200	-0.38202500
C	3.49188900	0.00000600	0.01308600
N	4.66007300	0.00001100	0.01608700

Acid R= CF_3
E = -1801.91172860 au

C	-1.49875400	-0.00436400	-0.00132300
Si	-0.28163300	-0.10466000	1.48181900
H	-0.29246700	1.05392200	2.41211100
H	-0.28501600	-1.38495200	2.23525000
Si	-0.28535400	-1.23351500	-0.83270700
H	-0.28750500	-2.62150800	-0.30071800
H	-0.28942300	-1.24986600	-2.32001000
Si	-0.29172000	1.34076900	-0.64826600
H	-0.29895400	1.56744100	-2.11880000
H	-0.30833300	2.63534100	0.07884200
C	0.91655100	0.00317700	-0.00776100
Si	2.74620700	0.01099700	0.00929100
O	3.43173300	-0.72101300	-1.31812000
O	3.35208000	-0.85326400	1.28236500
O	3.18263300	1.60477700	0.11760900
H	3.37556800	-0.26714600	-2.16258200
H	3.96291500	-1.56027100	1.05710100
H	4.09246800	1.79784000	0.35995000
C	-2.97984000	-0.01030600	0.00040500
F	-3.49951700	0.05927200	-1.24864500
F	-3.49357500	-1.12997800	0.56287200
F	-3.50174800	1.03335900	0.68734800

Base R = CF_3
E = -1801.35725746 au

C	-1.48132800	0.00007800	0.00565700
Si	-0.23791600	1.27859800	-0.72964800
H	-0.29180600	1.42388200	-2.21270100
H	-0.29207400	2.63414900	-0.11018200
Si	-0.23854600	-0.00004000	1.48490800
H	-0.29724800	1.21388100	2.34746500
H	-0.29687200	-1.21465700	2.34650100
Si	-0.23731200	-1.27758600	-0.73020100
H	-0.29065400	-2.63337300	-0.11121500
H	-0.29130400	-1.42231200	-2.21328900
C	0.95032300	0.00067000	0.00849300
Si	2.83507000	-0.00013600	0.10571300
O	3.47760800	-0.00197100	1.53634500
O	3.22603700	1.36222500	-0.84317200
O	3.22481500	-1.36109400	-0.84573200
H	3.92694300	1.83759400	-0.38676600
H	3.92502400	-1.83798400	-0.38982700
C	-2.95178100	-0.00022600	0.00233600
F	-3.49468200	-1.08400600	0.62516800
F	-3.49514500	1.08221500	0.62711000
F	-3.49029600	0.00075800	-1.24997200

Acid R = NH_2
E = -1520.44830976 au

C	2.29281400	0.01330000	0.01286100
Si	1.05874700	1.48059600	-0.05080100
H	1.04850300	2.38686800	1.13383100
H	1.02494200	2.30821500	-1.29131600
Si	1.07880500	-0.77282500	-1.25038000
H	1.04187700	-0.20170000	-2.62887600
H	1.09598000	-2.25959400	-1.34035400
Si	1.03484600	-0.70218300	1.32402500
H	1.02198400	-2.18073000	1.51059100
H	0.99946500	-0.03324200	2.65566400
C	-0.14374500	-0.00136600	0.00048300
Si	-1.96873900	-0.01909900	-0.00358700
O	-2.40854100	-1.57228700	-0.36971300
O	-2.63182300	1.09092300	-1.05405100
O	-2.65024400	0.39794000	1.44721000
H	-3.33256800	-1.79719600	-0.22982100
H	-2.33957900	1.07325200	-1.96862300
H	-3.09230400	1.25106100	1.46283500
N	3.71946500	0.06971300	-0.06585900
H	4.14487200	-0.85019600	-0.07422500
H	4.12979000	0.60019700	0.69406900

Base R = NH_2
E = -1519.88157392 au

C	2.27646600	-0.00019100	-0.00340400
Si	1.02132800	1.26726400	-0.73010700
H	1.07711100	2.63292300	-0.11824400
H	1.02311200	1.43652700	-2.21546900
Si	1.02069700	-1.26594300	-0.73201500
H	1.02250900	-1.43375400	-2.21753100
H	1.07590600	-2.63226200	-0.12153400
Si	1.02172400	-0.00098800	1.49041800
H	1.06405700	-1.20971600	2.37155800
H	1.06469600	1.20731300	2.37216800
C	-0.17028000	0.00037900	0.02648800
Si	-2.05439600	0.00001300	0.10752800
O	-2.44578600	-1.36226200	-0.84572700
O	-2.44617400	1.36370300	-0.84338900
O	-2.73685700	-0.00163300	1.52138100
H	-3.15629100	-1.82229900	-0.38816500
H	-3.15831200	1.82190700	-0.38657000
N	3.71758700	-0.00044800	-0.10068900
H	4.11308600	-0.81718100	0.35448100
H	4.11349500	0.81525700	0.35597000

Acid R = NO_2
E = -1669.46466408 au

C	1.76334400	0.00296500	0.00630200
Si	0.56589100	-0.68191500	-1.33238800
H	0.60909600	0.03486400	-2.63402800
H	0.57501700	-2.15208000	-1.52815000
Si	0.55460200	-0.83872100	1.23981300
H	0.54318200	-2.32232600	1.25431000
H	0.58767300	-0.28308500	2.61647200
Si	0.58534000	1.50357900	0.08830500
H	0.59412400	2.26993400	1.35995700
H	0.58205600	2.41262700	-1.08650900
C	-0.61758100	0.01676100	-0.00702000
Si	-2.44662900	-0.00718100	0.00072800
O	-3.02326000	-0.35049700	1.51139200
O	-2.87254600	-1.17340800	-1.09658900
O	-3.15138700	1.45171700	-0.37114400
H	-3.69961500	0.24174200	1.85142400
H	-3.77934000	-1.49161700	-1.08383300
H	-3.15580100	1.72814300	-1.29091100
N	3.21349000	0.01124300	0.01057400
O	3.79320000	-1.06262200	0.10401500
O	3.77221100	1.09781900	-0.08252900

Base R = NO_2
Not optimized.

Acid R = NF_2
E = -1718.63283146 au

C	-1.72591900	-0.02625900	-0.21162800
Si	-0.47198100	-1.38298900	-0.72987500
H	-0.53540700	-2.64802900	0.04803600
H	-0.37078800	-1.66193900	-2.18496100
Si	-0.46562300	1.18281200	-1.01175200
H	-0.35795300	1.13307300	-2.49300400
H	-0.52787500	2.58520100	-0.52911800
Si	-0.63618500	0.15425800	1.36905600
H	-0.68649500	1.46229000	2.07055600
H	-0.68005800	-0.97036700	2.33996900
C	0.65923100	-0.01172200	-0.02892900
Si	2.48518500	0.01020300	0.07242400
O	3.08924600	1.53275800	-0.15352900
O	3.00313200	-1.01713700	-1.11937800
O	3.08677300	-0.42982400	1.55898000
H	3.66516800	1.86365300	0.54117200
H	3.93330500	-0.98361300	-1.35905600
H	3.01690100	-1.35105900	1.82108400
N	-3.13376100	-0.04457400	-0.41513500
F	-3.62304700	1.13419600	0.19849500
F	-3.63396600	-1.03149100	0.46906800

Base R = NF_2
E = -1718.07957769 au

C	1.70784500	-0.00030700	-0.20052800
Si	0.40960900	1.27949500	-0.83681800
H	0.52827200	2.63344700	-0.22692300
H	0.33040600	1.41418300	-2.31939500
Si	0.41082500	-1.28153300	-0.83589100
H	0.33165100	-1.41716100	-2.31839600
H	0.53008200	-2.63514600	-0.22528500
Si	0.60618900	-0.00007600	1.39742500
H	0.71796400	-1.21697900	2.24824100
H	0.71696800	1.21746200	2.24745900
C	-0.69176300	-0.00122400	0.01560100
Si	-2.57126100	-0.00001400	0.19598100
O	-2.98543600	-1.36041600	-0.74732600
O	-2.98145100	1.36472500	-0.74287300
O	-3.17790200	-0.00184600	1.64079500
H	-3.67683700	-1.83691400	-0.27779700
H	-3.67344000	1.84053900	-0.27353600
N	3.09967300	0.00017100	-0.45138100
F	3.64411200	-1.09590200	0.29649000
F	3.64299600	1.09797200	0.29465800

Acid R = OH
E = -1540.29501163 au

C	2.28540100	0.01821900	0.01137400
Si	1.04489800	1.50060000	-0.08075400
H	1.02116900	2.42573200	1.08851000
H	1.00706100	2.29787000	-1.33971600
Si	1.08909400	-0.80612600	-1.23888900
H	1.06370700	-0.25039700	-2.62299800
H	1.08531700	-2.29249600	-1.29951800
Si	1.04827800	-0.68195200	1.33191300
H	1.02526100	-2.15468000	1.54680700
H	1.02718500	0.01875400	2.64717500
C	-0.12766800	0.00368200	-0.00414200
Si	-1.95223700	-0.02074300	-0.00024300
O	-2.38503200	-1.59217800	-0.28787800
O	-2.62841600	1.02889000	-1.10209200
O	-2.61642700	0.47275300	1.43380500
H	-3.30626600	-1.81830200	-0.13248400
H	-2.38577700	0.93070300	-2.02596000
H	-3.10139600	1.30166600	1.39955200
O	3.67329100	-0.02488400	-0.06366600
H	4.04955800	0.44819100	0.68551500

Base R = OH
E = -1539.73063442 au

C	-2.26979200	-0.00285700	0.00180700
Si	-1.02298300	-0.03392800	1.49020300
H	-1.07100600	1.16721900	2.38110700
H	-1.04503800	-1.25249400	2.35397100
Si	-1.03605600	-1.27046900	-0.74936600
H	-1.06448900	-2.64402700	-0.16014200
H	-1.05548900	-1.40447700	-2.23773200
Si	-1.01274700	1.28708900	-0.72100800
H	-1.02020400	1.47385400	-2.20380200
H	-1.05530900	2.64249900	-0.08660500
C	0.15392400	-0.00442900	0.01287900
Si	2.03822900	-0.00126300	0.10656000
O	2.44461400	-1.33947800	-0.87201300
O	2.70188700	-0.02886200	1.52868100
O	2.43050600	1.38419100	-0.81131100
H	3.14627000	-1.81306300	-0.41472400
H	3.13954000	1.83441800	-0.34191700
O	-3.67581300	-0.06598600	-0.04213900
H	-4.01882200	0.70089000	0.42653500

Acid R = F
E = -1564.29758583 au

C	-2.26490700	-0.01763200	0.00493000
Si	-1.07806500	1.07572500	-1.04092600
H	-1.05574300	0.83776400	-2.51180200
H	-1.07511300	2.53539700	-0.76032400
Si	-1.05765200	0.36070200	1.45731400
H	-1.04959100	1.75184300	1.98323000
H	-1.02583200	-0.61744300	2.57715600
Si	-1.05557200	-1.45246700	-0.40975700
H	-1.02231000	-2.60933400	0.52556400
H	-1.03585500	-1.93601100	-1.81800000
C	0.11333000	-0.00030600	-0.00916200
Si	1.93856500	0.01921900	0.00463500
O	2.57701100	-0.68060600	1.36115800
O	2.37131100	1.61558500	-0.06293500
O	2.62200000	-0.86276400	-1.23002900
H	3.11751000	-1.46084300	1.21066900
H	3.28686700	1.82413900	0.14254100
H	2.46307700	-0.57741400	-2.13297700
F	-3.63533300	-0.02918700	0.01178600

Base R = F
E = -1563.73742778 au

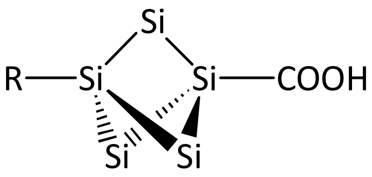
C	2.24951600	0.00000900	0.00142000
Si	1.03601400	-0.00010100	1.50198100
H	1.07284300	-1.21291200	2.37111800
H	1.07278800	1.21255800	2.37133000
Si	1.01928700	1.29015000	-0.73351300
H	1.05058400	2.65089000	-0.11882300
H	1.03502700	1.44057400	-2.21893500
Si	1.01933800	-1.29009600	-0.73365600
H	1.03508600	-1.44031700	-2.21909900
H	1.05067700	-2.65092300	-0.11915700
C	-0.13968900	-0.00004100	0.02067100
Si	-2.02590200	-0.00001300	0.10701500
O	-2.69440700	-0.00028200	1.52604800
O	-2.41385000	-1.36148600	-0.84613500
H	-3.12185000	-1.82818500	-0.39163400
O	-2.41364300	1.36186800	-0.84562800
H	-3.12194600	1.82824800	-0.39127400
F	3.64008000	0.00003200	-0.00843700

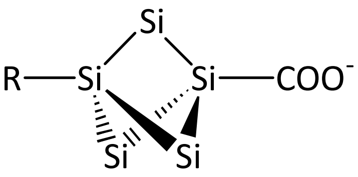
Acid R = Li
E = -1472.04482802 au

C	-2.55159800	0.01666600	-0.02157500
Si	-1.29780200	-0.96756600	-1.08025400
H	-1.29368900	-2.45484700	-0.93027000
H	-1.25623200	-0.66543500	-2.54439900
Si	-1.28991700	1.41496700	-0.31529100
H	-1.24354300	2.03727000	-1.67560000
H	-1.25671000	2.53667400	0.67714000
Si	-1.32115700	-0.44077400	1.36178100
H	-1.28664900	0.43845100	2.57582600
H	-1.31676700	-1.85407600	1.84750200
C	-0.02552400	-0.00486900	0.00230200
Si	1.80416800	-0.02199800	0.01039000
O	2.44079000	1.20805500	0.94495100
O	2.53594500	0.22052300	-1.46137500
O	2.28101600	-1.52167400	0.52967800
H	1.98690600	1.39654900	1.77020400
H	2.80151900	1.12741300	-1.63490100
H	3.21243300	-1.72369700	0.40379400
Li	-4.49354900	0.01696000	-0.05082000

Base R = Li
E = -1471.45989684 au

C	2.54103700	-0.00000500	-0.00690000
Si	1.28739700	-0.00001400	1.44784400
H	1.32396600	-1.19791800	2.35270400
H	1.32396300	1.19789500	2.35269900
Si	1.25944900	1.24434600	-0.70773500
H	1.28923000	2.62832700	-0.12314900
H	1.26261500	1.43271000	-2.19806800
Si	1.25945400	-1.24434800	-0.70775200
H	1.26262000	-1.43270000	-2.19808700
H	1.28923500	-2.62833700	-0.12318200
C	0.00538000	-0.00000900	0.02767000
Si	-1.88125900	-0.00000300	0.10770300
O	-2.58364000	-0.00013800	1.51545900
O	-2.29341600	-1.36324100	-0.84225700
H	-2.99765000	-1.81177000	-0.36361800
O	-2.29332600	1.36342300	-0.84201800
H	-2.99777000	1.81174800	-0.36349700
Li	4.45925700	0.00000700	-0.02357600





Acid R = H
E = -1639.97708821 au

Si	2.29782500	-0.03568900	0.00008800
H	3.78443600	-0.07454900	0.00017900
Si	0.90279600	1.85451100	-0.00182500
H	0.93197300	2.70170900	1.22127900
H	0.93206100	2.69927100	-1.22661600
Si	0.83230200	-0.94146200	-1.59277900
H	0.83740500	-0.32470000	-2.94782200
H	0.78193800	-2.42553000	-1.69561300
Si	0.83216600	-0.93824300	1.59463500
H	0.78176000	-2.42210000	1.70047200
H	0.83711000	-0.31873800	2.94842500
Si	-0.57873900	0.04701100	-0.00013600
C	-2.50670400	0.13264300	-0.00005600
O	-3.15177100	1.15461000	-0.00001700
O	-3.07521700	-1.08920500	0.00003400
H	-4.03945600	-0.96024800	0.00014500

Conjugate Base R = H
E = -1639.45046210 au

Si	2.33271500	-0.04484500	0.00018000
Si	0.91245300	1.81125000	-0.00067700
H	0.99827000	2.69592000	1.20461000
H	0.99847900	2.69495600	-1.20665500
Si	0.81507900	-0.90910500	-1.55152800
H	0.87150000	-0.32149900	-2.92821600
H	0.80537500	-2.39811500	-1.70224900
Si	0.81481300	-0.90782200	1.55233400
H	0.80507200	-2.39670900	1.70427900
H	0.87097800	-0.31907500	2.92854400
Si	-0.69271600	0.06263000	-0.00013000
C	-2.74199600	0.01704600	-0.00015200
O	-3.26451000	1.13196900	-0.00013600
O	-3.14612300	-1.14853300	-0.00014400
H	3.83455800	-0.09474900	0.00031800

Acid R = CH_3
E = -1679.26006507 au

Si	1.98577400	-0.01562400	-0.00003100
Si	0.56424200	1.86192800	-0.00019700
H	0.57952800	2.71366500	1.22143300
H	0.57954600	2.71344500	-1.22198000
Si	0.51124400	-0.92661200	-1.59049200
H	0.50343300	-0.31250200	-2.94803800
H	0.46106500	-2.41131100	-1.70098400
Si	0.51126400	-0.92632300	1.59058700
H	0.46108500	-2.41100200	1.70135500
H	0.50344400	-0.31196400	2.94802100
Si	-0.90608900	0.04974800	-0.00002800
C	-2.83421900	0.11711100	0.00002700
O	-3.49131200	1.13152900	0.00004700
O	-3.39100700	-1.11068500	0.00006200
H	-4.35619300	-0.98953300	0.00010400
C	3.87329000	-0.04943800	0.00013000
H	4.26295200	0.45694200	-0.88777100
H	4.26275700	0.45702500	0.88806900
H	4.23642000	-1.08119000	0.00021800

Conjugate Base R = CH_3
E = -1678.73075628 au

Si	2.00939800	-0.01673900	0.00009700
Si	0.56261400	1.82196100	0.00005400
H	0.63455000	2.71110200	1.20432000
H	0.63465600	2.71114700	-1.20417100
Si	0.49266900	-0.89302900	-1.54955800
H	0.53796200	-0.30666700	-2.92838200
H	0.49260100	-2.38258600	-1.70630400
Si	0.49250600	-0.89307700	1.54956400
H	0.49243600	-2.38264200	1.70624600
H	0.53765000	-0.30677600	2.92841800
Si	-1.02522400	0.06088500	-0.00005800
C	-3.08010300	-0.00574600	-0.00013700
O	-3.61096200	1.10479000	-0.00005900
O	-3.47286100	-1.17457400	-0.00024700
C	3.91404200	-0.06054000	0.00018900
H	4.30844700	0.44329800	-0.88852100
H	4.30838400	0.44421100	0.88840900
H	4.27279300	-1.09511800	0.00073000

Acid R = CN

E = -1732.12697257 au

Si	1.75117100	-0.00382900	0.00002800
Si	0.36113900	1.88535900	-0.00085300
H	0.39341600	2.71902300	1.22882700
H	0.39347200	2.71789700	-1.23129600
Si	0.32445000	-0.93428000	-1.60733400
H	0.33522300	-0.30540500	-2.95430900
H	0.30463600	-2.41779100	-1.69699200
Si	0.32437300	-0.93280100	1.60817000
H	0.30453900	-2.41622900	1.69920100
H	0.33506100	-0.30268000	2.95456400
Si	-1.08402300	0.04395500	-0.00007200
C	-3.01114100	0.10906300	-0.00003200
O	-3.66239300	1.12584600	-0.00002000
O	-3.56221100	-1.11891100	0.00001700
H	-4.52866800	-1.00643500	0.00006800
C	3.59231900	-0.03032200	0.00007600
N	4.75607500	-0.04770800	0.00007900

Conjugate Base R = CN

E = -1731.61382462 au

Si	-1.77701000	-0.00831700	-0.00001300
Si	-0.36973100	1.84863100	-0.00058700
H	-0.46464400	2.71953500	-1.21143200
H	-0.46464300	2.72027700	1.20972300
Si	-0.29801000	-0.89457100	1.56530500
H	-0.36743500	-0.29546900	2.93302100
H	-0.32124200	-2.38173100	1.70334000
Si	-0.29802100	-0.89558100	-1.56477200
H	-0.32126000	-2.38282900	-1.70184600
H	-0.36746400	-0.29736600	-2.93287600
Si	1.20588600	0.06771200	-0.00005000
C	3.28405300	-0.01839400	0.00005800
O	3.81163400	1.08882300	0.00005000
O	3.64748300	-1.19238700	0.00013300
C	-3.64570900	-0.04795500	-0.00000800
N	-4.81141600	-0.07229100	-0.00000700

Acid R = CF$_3$

E = -1976.71642333 au

Si	-1.13933000	0.00544100	0.00013300
Si	0.25396200	1.88996900	-0.00025900
H	0.22918400	2.72627700	-1.22893700
H	0.22927800	2.72672400	1.22812000
Si	0.28407900	-0.92654100	1.60695400
H	0.28104200	-0.29907900	2.95524900
H	0.30599600	-2.41017400	1.70212600
Si	0.28393900	-0.92710800	-1.60647600
H	0.30583000	-2.41077700	-1.70112400
H	0.28080800	-0.30012900	-2.95499500
Si	1.69597300	0.04688600	-0.00000800
C	3.62356100	0.10287900	-0.00004000
O	4.28189000	1.11544500	-0.00004200
O	4.16931300	-1.12837500	-0.00005500
H	5.13605000	-1.01889500	-0.00006600
C	-3.08399100	-0.01799900	-0.00007500
F	-3.57381600	-1.27657600	-0.00041100
F	-3.59744600	0.60133600	1.08454900
F	-3.59717500	0.60181400	-1.08455100

Conjugate Base R = CF$_3$

E = -1976.20033440 au

Si	1.15004500	0.00950800	-0.00011900
Si	-0.26645400	1.85632600	-0.00093800
H	-0.18593200	2.73115700	1.20862200
H	-0.18602700	2.72997800	-1.21135800
Si	-0.31963700	-0.88777200	-1.56452800
H	-0.26374700	-0.29086500	-2.93431200
H	-0.29479600	-2.37524400	-1.70351500
Si	-0.31956000	-0.88621400	1.56524800
H	-0.29476200	-2.37355000	1.70570000
H	-0.26363600	-0.28794800	2.93443600
Si	-1.83198400	0.06586300	-0.00008100
C	-3.91234100	-0.02976000	0.00016400
O	-4.44286300	1.07598900	0.00017400
O	-4.27219200	-1.20453900	0.00029700
C	3.11036100	-0.02600600	0.00000900
F	3.61455500	-1.28754100	0.00067300
F	3.65099800	0.58887100	-1.08422700
F	3.65083000	0.58995000	1.08371700

Acid R = NH$_2$
E = -1695.30348502 au

Si	1.98642700	-0.01629600	0.03841200
Si	0.58929400	1.68954600	-0.77937800
H	0.57636900	2.97114900	-0.02157000
H	0.62893400	1.95176100	-2.24455100
Si	0.55366800	-1.53270500	-1.04322100
H	0.58469000	-1.55858900	-2.53192500
H	0.50182500	-2.91935000	-0.50209600
Si	0.47842800	-0.15466400	1.85499800
H	0.38558600	-1.44532900	2.59414500
H	0.41408000	0.98851700	2.80857800
Si	-0.88025700	0.02716200	-0.04648600
C	-2.80354700	0.11823300	-0.03117900
O	-3.44193800	1.14431000	-0.01302100
O	-3.38096900	-1.09956000	-0.01834600
H	-4.34331700	-0.96085300	0.01241000
N	3.71441100	-0.02619100	-0.05262900
H	4.22718600	-0.87962600	0.11687100
H	4.24245800	0.78565000	0.23400100

Conjugate Base R = NH$_2$
E = -1694.77580331 au

Si	2.01430500	-0.00009900	0.03748100
Si	0.56883300	1.57659600	-0.89798600
H	0.58731100	2.93853600	-0.27449100
H	0.65864000	1.76804300	-2.38110500
Si	0.56839500	-1.57373900	-0.90237900
H	0.65813700	-1.76111100	-2.38601700
H	0.58651500	-2.93738400	-0.28261600
Si	0.45943100	-0.00248900	1.79755000
H	0.43350100	-1.20910000	2.68621000
H	0.43388200	1.20138800	2.68992900
Si	-0.99656200	0.00045400	-0.06871400
C	-3.07579000	-0.00008500	-0.01617200
O	-3.52744200	1.14226800	0.00579300
O	-3.52646500	-1.14283700	0.00579800
N	3.77661400	-0.00036800	-0.02913000
H	4.24478800	-0.82978800	0.31425100
H	4.24527400	0.82690900	0.31873500

Acid R = NO$_2$
E = -1844.29367780 au

Si	-1.41556200	-0.02534200	-0.02274500
Si	-0.06615700	1.88711100	-0.01626900
H	-0.08663800	2.70323000	-1.25696900
H	-0.11853900	2.72354100	1.20963700
Si	-0.03642300	-0.91771900	1.64052900
H	-0.07582100	-0.25268600	2.96794700
H	-0.01684300	-2.39871200	1.75577600
Si	0.00993600	-0.95332200	-1.61867900
H	0.05659300	-2.43587800	-1.70321400
H	0.03258700	-0.31499700	-2.95954000
Si	1.37693000	0.04003800	0.02473400
C	3.30319500	0.10974100	-0.03216700
O	3.93759400	1.05403700	-0.43492800
O	3.86925600	-1.02715100	0.41057100
H	4.83372800	-0.92418200	0.33291200
N	-3.30698800	-0.02335900	-0.01127800
O	-3.84311100	0.44498200	0.98368100
O	-3.89592000	-0.47511500	-0.98189700

Conjugate Base R = NO$_2$
E = -1843.78624560 au

Si	-1.44088300	-0.03904500	0.01131000
Si	-0.07848900	1.81055800	-0.35775400
H	-0.17681900	2.42798900	-1.71418000
H	-0.16986200	2.89486300	0.66545400
Si	0.02622300	-0.56753700	1.72935100
H	-0.02661400	0.30711400	2.93829100
H	0.03682500	-1.99405900	2.17030600
Si	0.01633200	-1.18357700	-1.38575600
H	0.02367300	-2.67072800	-1.25074300
H	-0.04577400	-0.83524700	-2.83641900
Si	1.50180500	0.06773200	-0.01959400
C	3.64958000	-0.01096600	0.00176600
O	4.13634800	1.09346900	-0.16739400
O	3.99525000	-1.16704700	0.18455600
N	-3.37694700	-0.03900300	0.01065700
O	-3.95869600	0.14946200	1.07424000
O	-3.95416600	-0.20400600	-1.05936700

Acid R = NF$_2$
E = -1893.45476082 au

Si	1.38282300	0.01370500	-0.16952400
Si	-0.04840700	1.69912100	-0.93329900
H	-0.00078000	2.99081100	-0.20155500
H	-0.11993700	1.89644700	-2.40457900
Si	-0.06013900	-1.55829100	-1.12431100
H	-0.13945500	-1.58797000	-2.60827000
H	-0.02930700	-2.92620900	-0.54520300
Si	0.08487500	-0.10500200	1.77263900
H	0.10325900	-1.38938800	2.51979200
H	0.11709600	1.06734600	2.68484200
Si	-1.41785300	0.02041100	-0.03537300
C	-3.33800100	0.09727200	0.12347000
O	-3.97799800	1.12077300	0.14343500
O	-3.89481500	-1.12275100	0.23330400
H	-4.85492500	-0.99787200	0.33003300
N	3.21762000	0.02164100	-0.40338300
F	3.67396800	-1.13628000	0.25207900
F	3.68525800	1.05276400	0.43148000

Conjugate Base R = NF$_2$
E = -1892.94220051 au

Si	1.40510200	0.00030700	-0.15559400
Si	-0.05880600	1.58874300	-1.01371200
H	0.01385100	2.94749000	-0.39791600
H	-0.06655900	1.74375500	-2.50045700
Si	-0.05921100	-1.58428800	-1.02005200
H	-0.06698300	-1.73348100	-2.50738200
H	0.01343400	-2.94543500	-0.40958300
Si	0.02788000	-0.00337400	1.71717100
H	0.09081100	-1.21767500	2.58476500
H	0.09103200	1.20728400	2.58982800
Si	-1.54629800	0.00044400	-0.06152300
C	-3.65485300	-0.00059200	0.15572100
O	-4.08388300	1.14373900	0.20503600
O	-4.08111900	-1.14560300	0.21336300
N	3.27420700	0.00199100	-0.39035800
F	3.75004300	-1.10121700	0.35962700
F	3.74915100	1.09865500	0.36966900

Acid R = OH
E = -1715.16795745 au

Si	1.97922600	0.00743100	0.01534600
Si	0.51430700	-0.38916500	1.81507800
H	0.46241200	-1.76560200	2.38053500
H	0.45689800	0.62826800	2.90040000
Si	0.56923400	1.78191600	-0.57703100
H	0.54073000	2.95297700	0.33999300
H	0.58743700	2.21804600	-1.99953600
Si	0.57216500	-1.40673800	-1.23848000
H	0.57611400	-1.25041800	-2.71887200
H	0.53794900	-2.84581100	-0.85950100
Si	-0.86132800	0.00566800	-0.04507900
C	-2.78342100	-0.10930200	-0.01324800
O	-3.40060500	-1.14761700	0.00700100
O	-3.38058600	1.09758200	0.00420200
H	-4.34064900	0.94356000	0.03852900
O	3.64510500	0.10889400	0.01100100
H	4.13786900	-0.68364200	0.24264600

Conjugate Base R = OH
E = -1714.64540194 au

Si	2.01485200	-0.01544400	0.00013400
Si	0.51595400	-0.89459100	1.56379200
H	0.48671600	-2.38497100	1.70880600
H	0.55090700	-0.31138800	2.94298400
Si	0.61373400	1.84134200	-0.00159500
H	0.68310200	2.72442100	1.20508400
H	0.68334700	2.72229800	-1.20981300
Si	0.51627400	-0.89731500	-1.56231500
H	0.55156100	-0.31651900	-2.94251600
H	0.48709000	-2.38794400	-1.70474500
Si	-0.97547800	0.07702600	-0.00026700
C	-3.08424000	-0.01122500	-0.00001200
O	-3.44490100	-1.18255800	0.00001300
O	-3.59775900	1.09989100	0.00012400
O	3.71330800	0.00091300	0.00024300
H	4.10280500	-0.87877600	0.00071700

Acid R = F
E = -1739.18659867 au

Si	1.96394200	-0.02335800	0.00004200
Si	0.60907600	1.89291400	-0.00060300
H	0.62485900	2.72880100	1.22882900
H	0.62492300	2.72799700	-1.23058300
Si	0.53749300	-0.94220400	-1.61495100
H	0.52787300	-0.31744600	-2.96475900
H	0.46946500	-2.42520600	-1.70272600
Si	0.53741200	-0.94116100	1.61554700
H	0.46936600	-2.42410500	1.70428000
H	0.52770300	-0.31552900	2.96494900
Si	-0.84387000	0.05997200	-0.00006700
C	-2.76967900	0.12261000	-0.00003200
O	-3.42920400	1.13359500	0.00000100
O	-3.31315600	-1.10955100	-0.00002000
H	-4.27979400	-1.00006800	0.00002500
F	3.59286900	-0.06097000	0.00008800

Conjugate Base R = F
E = -1738.67008589 au

Si	-2.01100600	-0.03317000	0.00000500
Si	-0.62906600	1.84543500	-0.00034300
H	-0.69743300	2.72433600	-1.20947200
H	-0.69741300	2.72477800	1.20846600
Si	-0.52590800	-0.89824000	1.57143800
H	-0.56591000	-0.29835400	2.94210200
H	-0.48915400	-2.38572300	1.72274200
Si	-0.52592900	-0.89882100	-1.57113300
H	-0.48918300	-2.38635900	-1.72188800
H	-0.56596200	-0.29944200	-2.94201800
Si	0.95357100	0.08114200	-0.00004000
C	3.09494800	-0.00765900	0.00005200
O	3.59284200	1.10629400	0.00002800
O	3.44243800	-1.17884000	0.00004600
F	-3.66779100	-0.08908300	0.00002100

Acid R = Li
E = -1646.89777913 au

Si	2.30412100	-0.02424500	0.00001900
Si	0.79256400	1.80830900	-0.00045900
H	0.81157400	2.68453600	1.20913000
H	0.81159300	2.68390600	-1.21050400
Si	0.73930000	-0.90937500	-1.54832600
H	0.73542000	-0.31920900	-2.92131700
H	0.69516000	-2.39662700	-1.68387000
Si	0.73927100	-0.90856600	1.54879600
H	0.69512100	-2.39574700	1.68511900
H	0.73535900	-0.31767900	2.92147600
Si	-0.72366000	0.04365300	-0.00002900
C	-2.66249600	0.12286400	-0.00002200
O	-3.31842700	1.14056400	-0.00005300
O	-3.23829000	-1.09951500	0.00003800
H	-4.20101400	-0.96039600	0.00005200
Li	4.74105000	-0.06041200	0.00004800

Conjugate Base R = Li
E = -1646.34940015 au

Si	2.31973600	-0.02417200	0.00002100
Si	0.78085800	1.77273200	-0.00044700
H	0.85375300	2.68139600	1.19441100
H	0.85378600	2.68079300	-1.19576200
Si	0.71675600	-0.88131400	-1.51230900
H	0.76343500	-0.31306400	-2.90340200
H	0.72408600	-2.37264300	-1.68988500
Si	0.71671700	-0.88052300	1.51275500
H	0.72403600	-2.37175900	1.69111300
H	0.76334900	-0.31154000	2.90354900
Si	-0.83905900	0.04971400	-0.00004000
C	-2.86249600	0.00483300	-0.00000600
O	-3.40087100	1.11845900	-0.00001800
O	-3.28644900	-1.15949500	0.00003900
Li	4.75365800	-0.06800300	0.00004400

Analog 3 Backbone R=H

E = -1451.59078694au

Si	-0.00001000	-0.00019500	-1.45209200
Si	0.00320400	1.84154400	0.00003200
H	1.22464800	2.69442900	0.00042300
H	-1.21458000	2.69965600	0.00042200
Si	-1.59735900	-0.91781600	-0.00003200
H	-2.94623600	-0.28528900	-0.00013000
H	-1.73289200	-2.40144900	-0.00021100
Si	1.59412700	-0.92340500	-0.00003400
H	1.72449000	-2.40751000	-0.00021000
H	2.94516800	-0.29554100	-0.00013600
Si	-0.00000800	-0.00033000	1.45211500
H	0.00002800	-0.00112300	2.93979800
H	0.00002900	-0.00033900	-2.93980900

Analog 3 Backbone R=CH_3

E = -1490.87363212au

Si	1.13439200	-0.00001800	0.00109100
Si	-0.33334600	-0.02561000	1.83734600
H	-0.34346600	-1.25518300	2.68067000
H	-0.34348700	1.17971900	2.71498700
Si	-0.33086000	1.60493300	-0.89649500
H	-0.33982600	2.94933600	-0.25168700
H	-0.33760000	1.76395200	-2.37905200
Si	-0.33091300	-1.57933300	-0.94082900
H	-0.33770300	-1.69704900	-2.42723900
H	-0.33996500	-2.94114100	-0.33364600
Si	-1.78406400	0.00006600	-0.00168700
H	-3.27169000	0.00011100	-0.00336800
C	3.02174500	-0.00003100	0.00093800
H	3.40389000	0.88063600	0.52550500
H	3.40392000	-0.89494800	0.50078500
H	3.40255200	0.01422200	-1.02454000

Analog 3 Backbone R=CN

E = -1543.74149020au

Si	0.89375600	0.00118200	-0.00003800
Si	-0.52926900	1.85917600	-0.00191800
H	-0.51660400	2.70243500	1.22323300
H	-0.51668100	2.69987000	-1.22883400
Si	-0.52756800	-0.93150000	-1.60907700
H	-0.51544500	-0.29256700	-2.95222100
H	-0.51343500	-2.41449500	-1.72320500
Si	-0.52747600	-0.92817100	1.61100600
H	-0.51332900	-2.41092500	1.72819200
H	-0.51527400	-0.28646500	2.95282900
Si	-1.96492600	-0.00083200	0.00004400
H	-3.45008400	-0.00106000	0.00009400
C	2.73614600	0.00065900	-0.00005900
N	3.90010600	0.00018400	0.00000500

Analog 3 Backbone R=CF_3

E = -1788.33066495au

Si	0.31524000	0.00232400	0.00040200
Si	-1.10302400	-1.43515700	-1.18089200
H	-1.09494800	-1.31341700	-2.66359600
H	-1.09476500	-2.86382900	-0.76571100
Si	-1.10725900	-0.30743800	1.83169000
H	-1.09918000	-1.65663700	2.45858700
H	-1.10210400	0.76016100	2.86771200
Si	-1.10717400	1.74213700	-0.64956300
H	-1.10220200	2.95840900	0.20720600
H	-1.09894600	2.10873400	-2.09136300
Si	-2.54352600	-0.00130100	-0.00264900
H	-4.02975200	-0.00247900	-0.00335400
C	2.26034500	0.00058100	0.00026800
F	2.76825200	0.94886700	0.81724900
F	2.76514500	-1.18228200	0.41339400
F	2.76662800	0.23315400	-1.23030100

Analog 3 Backbone R=NH_2

E = -1506.91718781au

Si	1.13966300	-0.00269400	0.06446200
Si	-0.26155600	1.64271400	-0.85178900
H	-0.30722500	2.96121900	-0.15744900
H	-0.19085900	1.84994100	-2.32574200
Si	-0.26286400	-1.55208200	-1.00736200
H	-0.19401100	-1.61725900	-2.49442000
H	-0.30912400	-2.93086200	-0.44213700
Si	-0.41267200	-0.09016600	1.84386500
H	-0.49187200	-1.35143700	2.63550400
H	-0.49590700	1.08402700	2.75925500
Si	-1.74852200	0.00384000	-0.07884400
H	-3.23213300	0.01657300	-0.14657700
N	2.87056400	-0.00184400	0.01134900
H	3.38521300	-0.84483000	0.22253000
H	3.38527600	0.82296800	0.28494500

Analog 3 Backbone R=NO_2
E = -1655.90830772au

Si	-0.57822100	0.03794900	-0.00274000
Si	0.79240200	-0.91547000	1.63114300
H	0.78775100	-0.25912200	2.96494400
H	0.74993300	-2.39621700	1.74727900
Si	0.79679500	-0.98112700	-1.59235300
H	0.75537400	-2.46536600	-1.64785400
H	0.79648900	-0.37978300	-2.95185000
Si	0.84779500	1.88311500	-0.03768200
H	0.86654400	2.69047500	-1.28523500
H	0.86393000	2.74274400	1.17436800
Si	2.23370700	-0.01995800	0.00247400
H	3.71800200	-0.04415300	0.00464700
N	-2.47035700	0.01532500	-0.00167500
O	-2.99896600	-1.08842700	-0.00257800
O	-3.06856200	1.08105600	0.00178200

Analog 3 Backbone R=NF_2
E = -1705.06923307au

Si	-0.54153600	-0.00003400	-0.17933900
Si	0.97940100	-1.61323200	-0.91330100
H	0.88312600	-2.95958900	-0.28980100
H	1.19427100	-1.71156300	-2.38156000
Si	0.97894100	1.61483900	-0.91057200
H	1.19378600	1.71570000	-2.37866500
H	0.88225500	2.96012300	-0.28482700
Si	0.57351100	-0.00160100	1.87618700
H	0.45155700	1.22573600	2.70632700
H	0.45195400	-1.23039500	2.70423100
Si	2.25347700	0.00002500	0.22902400
H	3.72251900	0.00007600	0.44506800
N	-2.34723000	0.00001800	-0.58414600
F	-2.87565000	1.09867100	0.11896200
F	-2.87567900	-1.09869000	0.11884500

Analog 3 Backbone R=OH
E = -1526.78216221au

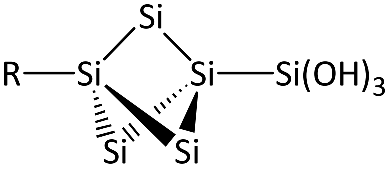
Si	1.13806500	-0.00823100	0.00253600
Si	-0.31146400	-0.91984600	1.61641200
H	-0.35294900	-2.40398800	1.74625500
H	-0.32761400	-0.28535600	2.96393000
Si	-0.27065300	1.86001600	-0.01308400
H	-0.27608200	2.71799700	1.20373400
H	-0.27091800	2.69988400	-1.24251000
Si	-0.30588100	-0.94150800	-1.60417500
H	-0.31645600	-0.32601800	-2.96053300
H	-0.34657800	-2.42734500	-1.71369900
Si	-1.72424600	0.01857200	-0.00278100
H	-3.20835200	0.02843300	-0.00509700
O	2.80574900	0.07775000	0.00484400
H	3.29146200	-0.75164800	-0.01555200

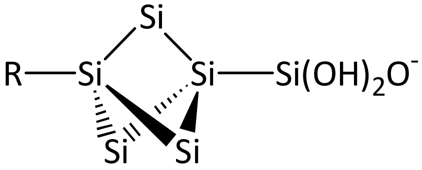
Analog 3 Backbone R=F
E = -1550.80133305au

Si	1.12785500	-0.00005400	0.00003800
Si	-0.28107900	1.87071800	-0.00060900
H	-0.29578500	2.71472900	1.22492100
H	-0.29570200	2.71394100	-1.22668300
Si	-0.28200900	-0.93601200	-1.61896000
H	-0.29595800	-0.29909200	-2.96383000
H	-0.29735800	-2.41975400	-1.73330300
Si	-0.28211200	-0.93497200	1.61954400
H	-0.29746900	-2.41864000	1.73484100
H	-0.29615000	-0.29718600	2.96400300
Si	-1.70141000	0.00100700	-0.00005600
H	-3.18457800	0.00033500	-0.00009200
F	2.75839500	-0.00043800	0.00008300

Analog 3 Backbone R=Li
E = -1458.50872143au

Si	-1.43786700	0.00002100	-0.00351300
Si	0.11804700	-0.00880200	1.78684600
H	0.12162100	1.19218800	2.67862800
H	0.12161500	-1.21851500	2.66676500
Si	0.12341300	-1.54380100	-0.90069100
H	0.12785200	-2.91615700	-0.30549500
H	0.13213100	-1.70121000	-2.38830700
Si	0.12341800	1.55259500	-0.88545800
H	0.13213500	1.72464200	-2.37145200
H	0.12785800	2.91902700	-0.27678200
Si	1.62569800	-0.00001300	0.00276800
H	3.12390500	-0.00002900	0.00603000
Li	-3.87501200	0.00001900	-0.00290900





Acid R = H

E = -1967.77108811 au

Si	-2.89737200	0.02869900	-0.01435700
Si	-1.44254500	-0.10785300	1.81700400
H	-1.41305100	1.06051900	2.74361300
H	-1.45712700	-1.37067800	2.60710600
Si	-1.46254100	-1.52898100	-1.02225800
H	-1.48247700	-2.91471500	-0.47665600
H	-1.45464300	-1.57018600	-2.51142000
Si	-1.40394800	1.64680700	-0.81623300
H	-1.39105200	1.89070900	-2.28640500
H	-1.37860300	2.95062800	-0.09380500
Si	0.03641300	-0.02851200	-0.01190200
Si	2.36608700	-0.02036400	0.01056800
O	2.80071700	-1.47629800	0.65256000
H	3.70626500	-1.76597800	0.50074200
O	2.95821700	1.29030700	0.84125500
H	2.62302200	1.45870000	1.72586900
O	3.06383600	0.10498900	-1.48270700
H	3.30741800	0.99195400	-1.76329800
H	-4.38723700	0.05992400	-0.01410400

Base R = H

E = -1967.22269464 au

Si	2.91668600	0.01789400	-0.03320100
Si	1.41346300	-1.35883500	-1.17928700
H	1.42202000	-1.23537600	-2.67206700
H	1.47581400	-2.81739800	-0.85359000
Si	1.45859200	-0.33242900	1.76267700
H	1.52461700	-1.67870700	2.41046900
H	1.50747100	0.69343500	2.85163700
Si	1.39779400	1.70104600	-0.59973500
H	1.44448000	2.94006900	0.24025500
H	1.40805300	2.14028300	-2.03153100
Si	-0.11465500	-0.01376400	0.02589200
Si	-2.50280400	-0.14254200	0.09609800
O	-2.94355800	-1.56550600	0.54388500
O	-2.97590000	0.36677900	-1.45874000
H	-3.25583200	-0.40220900	-1.96476100
O	-2.91428100	1.22478800	0.99659000
H	-3.24174900	1.91942400	0.41700900
H	4.41796600	0.03281600	-0.06550500

Acid R = CH$_3$

E = -2007.05424439 au

Si	2.59182400	-0.01474700	-0.00985200
Si	1.09125600	-1.60953500	-0.85895900
H	1.07359300	-1.81834200	-2.33574500
H	1.05674200	-2.93523200	-0.17532300
Si	1.11827300	0.06670100	1.81691800
H	1.07909200	-1.12693800	2.71243700
H	1.12027100	1.30367300	2.64906700
Si	1.14426400	1.56624400	-0.97513800
H	1.15283800	2.93799200	-0.39216600
H	1.13157700	1.65667600	-2.46327600
Si	-0.35446200	0.03831300	-0.01452000
Si	-2.68243500	0.01324700	0.00924500
O	-3.13539900	1.45337500	0.67466300
O	-3.25883400	-1.31750200	0.82010600
O	-3.38808400	-0.09217100	-1.48256700
H	-4.04550700	1.73066000	0.52713000
H	-2.89673400	-1.50952400	1.68921500
H	-3.60129200	-0.97905800	-1.78697000
C	4.47987200	-0.04810000	-0.00774000
H	4.84690100	-0.92434500	0.53505700
H	4.86180500	-0.08978300	-1.03226600
H	4.87795000	0.85008200	0.47394200

Base R = CH$_3$

E = -2006.50309496 au

Si	2.60189300	0.01119200	-0.01700600
Si	1.07887300	1.70208300	-0.56017700
H	1.11596500	2.93012000	0.29828100
H	1.08625800	2.16819800	-1.98465100
Si	1.09451900	-1.34380400	-1.18876900
H	1.10064300	-1.19846300	-2.68073600
H	1.14787300	-2.80983300	-0.89073600
Si	1.13173200	-0.36643200	1.76702500
H	1.18870100	-1.72262500	2.39737200
H	1.17171300	0.64033100	2.87552200
Si	-0.43605100	-0.01984700	0.03307200
Si	-2.82753500	-0.13919900	0.08615400
O	-3.28248400	-1.56202100	0.51947000
O	-3.27998200	0.38628800	-1.46946100
O	-3.24308900	1.22137400	0.99478300
H	-3.54700000	-0.37757200	-1.98992000
H	-3.52127000	1.93738200	0.41548700
C	4.50487200	0.02697000	-0.05134100
H	4.86817000	0.23275100	-1.06364800
H	4.89459900	0.79919600	0.62012500
H	4.90152900	-0.94233300	0.26844600

Acid R = CN
E = -2059.92272921 au

Si	-2.36077600	0.00455300	-0.00951300
Si	-0.91777100	1.73900000	-0.62020200
H	-0.92427900	2.13871300	-2.05349600
H	-0.91991300	2.93962300	0.25942300
Si	-0.93472400	-0.33606100	1.81089600
H	-0.93377900	0.72350100	2.85730500
H	-0.94755600	-1.68680600	2.43360000
Si	-0.94002700	-1.41842800	-1.20428900
H	-0.95894500	-2.85337300	-0.81407200
H	-0.94596900	-1.26954400	-2.68434300
Si	0.52739900	-0.01783900	-0.01074800
Si	2.85702700	-0.01019800	0.00743100
O	3.27075000	-1.49698200	0.58480300
O	3.45707900	1.25636500	0.89315900
O	3.53039500	0.18398100	-1.48671100
H	4.16969200	-1.80065000	0.42114300
H	3.18228400	1.35466900	1.80857700
H	3.82362000	1.07185800	-1.71192700
C	-4.20760000	0.02309400	-0.00677200
N	-5.37159000	0.03459300	-0.00509000

Base R = CN
E = -2059.38571975 au

Si	2.37007900	0.00283500	-0.00545500
Si	0.90639200	1.71075400	-0.61285900
H	0.97065900	2.94669400	0.22495800
H	0.95214700	2.11971800	-2.04967900
Si	0.90100900	-1.38768900	-1.16510500
H	0.94348300	-1.26644500	-2.65434400
H	0.96145800	-2.83577800	-0.80830300
Si	0.92265800	-0.31972600	1.79538300
H	0.98446000	-1.66362500	2.44141900
H	0.98331700	0.72473000	2.86161600
Si	-0.61106600	-0.00159300	0.01931300
Si	-3.00274300	-0.13783500	0.08219600
O	-3.40681300	-1.57126100	0.52549400
O	-3.47432200	0.37600200	-1.46705700
O	-3.41089500	1.21885600	0.99325800
H	-3.74088100	-0.38833100	-1.98717600
H	-3.76169100	1.91453900	0.42874900
C	4.23655200	0.00712100	-0.02734700
N	5.40219700	0.01179400	-0.04219200

Acid R = CF_3
E = -2304.51180944 au

Si	-1.73985400	-0.00472800	-0.00760900
Si	-0.30064400	1.70967800	-0.67641500
H	-0.30263500	2.06352700	-2.12198800
H	-0.29580400	2.93987700	0.16182700
Si	-0.31339700	-0.28522500	1.82110300
H	-0.30526000	0.80577000	2.83507900
H	-0.31755800	-1.61547900	2.48713900
Si	-0.32121400	-1.46476600	-1.15802200
H	-0.33163300	-2.88740900	-0.72405700
H	-0.32325400	-1.36395400	-2.64236400
Si	1.14630100	-0.02535300	-0.01226900
Si	3.47660100	-0.00575000	0.00738000
O	3.90405700	-1.48277000	0.60047200
O	4.06520700	1.27579700	0.88034100
O	4.15664900	0.17460900	-1.48614500
H	4.80611200	-1.77807300	0.43874100
H	3.76886100	1.39268000	1.78684000
H	4.42493700	1.06581800	-1.72849900
C	-3.68777200	0.01633900	-0.00338800
F	-4.20811200	-1.13681600	0.47148600
F	-4.18249300	1.01254200	0.76447700
F	-4.19534300	0.19140000	-1.24352700

Base R = CF_3
E = -2303.97202785 au

Si	1.73805000	-0.00006100	0.00329100
Si	0.27549700	1.70905200	-0.59543300
H	0.32854100	2.94112100	0.24931000
H	0.31323900	2.12753200	-2.02999000
Si	0.27645000	-1.38666500	-1.16694300
H	0.31196600	-1.25612900	-2.65584200
H	0.33137400	-2.83792500	-0.82098400
Si	0.29409000	-0.33612200	1.80213200
H	0.35045400	-1.68369900	2.44169700
H	0.34415300	0.70179500	2.87561900
Si	-1.23830900	-0.01072200	0.02609200
Si	-3.63331100	-0.13551200	0.07683700
O	-4.05517500	-1.56757800	0.50799300
O	-4.08889000	0.39314800	-1.47277800
O	-4.04055500	1.21778300	0.99409400
H	-4.35098800	-0.36619200	-2.00233500
H	-4.35979800	1.92750300	0.42834100
C	3.69644200	0.00815800	-0.01802000
F	4.23478000	-1.16327200	0.40952500
F	4.20892800	0.22193700	-1.25786500
F	4.22905200	0.97362900	0.77547000

Acid R = NH_2
E = -2023.09886893 au

Si	-2.58558200	-0.00193000	-0.01744500
Si	-1.10780400	1.62558000	-0.83034700
H	-1.08660800	1.86427300	-2.30230900
H	-1.08105100	2.93326500	-0.11422900
Si	-1.13137900	-0.11299000	1.81859400
H	-1.09801100	1.06550600	2.73283800
H	-1.12235600	-1.36753400	2.62346200
Si	-1.13518500	-1.57107100	-1.02735100
H	-1.11325400	-2.95544400	-0.47475000
H	-1.09389100	-1.62493500	-2.51692800
Si	0.33274400	-0.04562400	-0.02024500
Si	2.65635000	-0.00425900	0.01458100
O	3.11368200	-1.44277300	0.67935700
O	3.21954200	1.32814000	0.83095000
O	3.36741100	0.10915500	-1.47354500
H	4.02587900	-1.71467000	0.53493700
H	2.84107400	1.52322900	1.69239400
H	3.57684800	0.99831800	-1.77391700
N	-4.31159000	0.13261700	0.04897000
H	-4.85432000	-0.52868900	0.58613900
H	-4.82628400	0.46630200	-0.75354500

Base R = NH_2
E = -2022.54820641 au

Si	2.59623000	0.00548800	-0.02401500
Si	1.14723100	-0.48998800	1.74072800
H	1.20104300	-1.88729200	2.27336500
H	1.18903600	0.44166900	2.91138300
Si	1.09143200	1.73811100	-0.45182700
H	1.12698300	2.90304500	0.48873400
H	1.09209800	2.29410100	-1.84343700
Si	1.09173700	-1.27910500	-1.29559400
H	1.07241700	-1.03103000	-2.77400200
H	1.12196700	-2.76245600	-1.09574300
Si	-0.41288700	-0.02984100	0.02631500
Si	-2.80989900	-0.13824800	0.08416300
O	-3.25288200	0.47772200	-1.43879500
O	-3.21456100	1.16885400	1.06976500
O	-3.26755500	-1.57980400	0.44299400
H	-3.49491000	-0.25287100	-2.01597000
H	-3.42646500	1.94078400	0.53608800
N	4.35296900	0.10758300	0.03132400
H	4.82096200	0.47885800	-0.78557700
H	4.85225400	-0.70190100	0.37739200

Acid R = NO_2
E = -2172.09087286 au

Si	-2.01417600	0.02655300	-0.02624500
Si	-0.62186700	-0.49939900	1.77122300
H	-0.64214000	0.43706700	2.92602700
H	-0.63423400	-1.91618800	2.22255000
Si	-0.60976000	-1.29364700	-1.33530500
H	-0.60368900	-2.75224800	-1.04369500
H	-0.60142400	-1.03509600	-2.79919700
Si	-0.61867900	1.84372500	-0.45987800
H	-0.61083100	2.36978700	-1.84972700
H	-0.61787100	2.94090600	0.54231300
Si	0.82377800	0.03429800	-0.01134300
Si	3.15316900	-0.00634500	-0.00326300
O	3.57461400	0.41410600	-1.53886800
O	3.72658600	-1.48157800	0.48644500
O	3.83352800	1.06785000	1.04700500
H	4.47569800	0.72215200	-1.68146200
H	3.43720200	-2.27057800	0.02060900
H	4.11616700	0.71669600	1.89667700
N	-3.91085000	-0.01620700	0.01524000
O	-4.44245100	-1.11487600	-0.07359000
O	-4.50695800	1.04304500	0.14983100

Base R = NO_2
E = -2171.55724988 au

Si	-2.01488700	0.02058100	-0.02648100
Si	-0.58135900	-1.34272200	-1.24707200
H	-0.62441700	-2.79685100	-0.91310900
H	-0.62489000	-1.18053200	-2.72912200
Si	-0.58727000	1.77956000	-0.54172100
H	-0.62295600	2.26589000	-1.95071100
H	-0.62809300	2.94688200	0.38615900
Si	-0.60050200	-0.40325800	1.76954200
H	-0.66352800	0.57804200	2.89352100
H	-0.65568500	-1.78451800	2.33301200
Si	0.90962900	0.02220500	-0.01263700
Si	3.31325100	0.05331200	-0.14011500
O	3.71074200	1.16612300	1.05624700
O	3.71651600	0.26654000	-1.62403900
O	3.76224300	-1.39673800	0.61667700
H	4.01595600	0.72092000	1.85272400
H	4.00427100	-2.04730800	-0.04952500
N	-3.93957700	-0.02197800	0.01014900
O	-4.55366100	1.03952600	-0.01301100
O	-4.48180100	-1.12097200	0.07472200

Acid R = NF$_2$

E = -2221.25138889 au

Si	1.97927700	0.03084300	-0.16333500
Si	0.51138600	1.72546200	-0.80486800
H	0.54186500	2.98582100	-0.01561500
H	0.41864300	2.01258700	-2.26204900
Si	0.53083000	-1.44988100	-1.23404900
H	0.43452700	-1.34020600	-2.71563400
H	0.56982800	-2.87373600	-0.80795600
Si	0.68437000	-0.24738300	1.76246500
H	0.73255500	-1.57990200	2.41953100
H	0.72015100	0.85119500	2.76371100
Si	-0.86547200	-0.00750000	0.00555500
Si	-3.19310500	-0.02348900	0.08556400
O	-3.58261000	-1.50251100	0.69777000
O	-3.84574900	0.29258000	-1.40535500
O	-3.83565800	1.13678300	1.06720500
H	-4.46811600	-1.60905400	1.06063400
H	-3.57906900	-0.25241200	-2.15044300
H	-4.12971500	1.94576600	0.63814000
N	3.81710100	0.07424200	-0.40990100
F	4.28883400	-1.11424300	0.17879400
F	4.27669300	1.06232000	0.48158100

Acid R = OH

E = -2042.96457495 au

Si	-2.57149200	0.01593400	-0.01130500
Si	-1.09762700	1.63869100	-0.85785000
H	-1.05722100	1.84294600	-2.33417600
H	-1.05401600	2.95657300	-0.16298300
Si	-1.14686000	-0.08184800	1.83762200
H	-1.10852100	1.10954000	2.73263800
H	-1.14810300	-1.33131000	2.64720600
Si	-1.15032100	-1.57314700	-1.00425400
H	-1.14890900	-2.94914600	-0.43505000
H	-1.11524800	-1.63225800	-2.49298900
Si	0.31494200	-0.03541400	-0.00635500
Si	2.63852100	-0.01444500	0.01200700
O	3.08456000	-1.46076800	0.66521400
O	3.21751500	1.30824300	0.83031500
O	3.33074700	0.09927600	-1.48371700
H	3.99222300	-1.74403400	0.51400100
H	2.86531400	1.49105000	1.70548600
H	3.53834000	0.98750000	-1.78824000
O	-4.23946700	0.04093300	0.08526000
H	-4.73098200	0.07086400	-0.74057300

Base R = NF$_2$

E = -2220.71369494 au

Si	1.98191000	0.01730700	-0.15884800
Si	0.49808300	1.64930200	-0.89570200
H	0.55380100	2.95973600	-0.18016900
H	0.47454300	1.90688200	-2.36544300
Si	0.52294400	-1.49789800	-1.15351600
H	0.50162200	-1.50888600	-2.64532100
H	0.60412900	-2.90455300	-0.65969800
Si	0.62502500	-0.14580200	1.72350800
H	0.71022800	-1.42391700	2.49177500
H	0.69107300	0.99362500	2.68706800
Si	-0.95499800	-0.01722000	-0.04417800
Si	-3.35934200	-0.02712300	-0.06637700
O	-3.71496800	-1.41210300	0.82124700
O	-3.84472000	0.14768500	-1.53124400
O	-3.76110200	1.17821300	1.05973600
H	-3.96342800	-1.18601900	1.72284200
H	-4.03461400	1.97406500	0.59341700
N	3.84561700	0.05986700	-0.38627900
F	4.32973200	-1.10724400	0.25217800
F	4.30570600	1.08054800	0.48039300

Base R = OH

R = -2042.41758609 au

Si	2.58538600	0.02249800	-0.02082100
Si	1.14668800	-0.45557600	1.76510900
H	1.19003900	-1.84703600	2.31250800
H	1.17325800	0.49381300	2.92127000
Si	1.09811200	1.75143400	-0.48392500
H	1.12739200	2.92669100	0.44218600
H	1.09663200	2.27718500	-1.88502100
Si	1.10738700	-1.29684100	-1.26922500
H	1.09635800	-1.08111100	-2.75097400
H	1.14560000	-2.77271300	-1.02617800
Si	-0.39375400	-0.01776200	0.03054200
Si	-2.79458400	-0.14656500	0.07930300
O	-3.23319700	0.46298000	-1.44540900
O	-3.20846300	1.15757400	1.06204100
O	-3.23174900	-1.59309500	0.44011200
H	-3.45691500	-0.26867000	-2.02856400
H	-3.41623100	1.93147100	0.52955200
O	4.27841200	0.10501400	-0.06833200
H	4.71456200	-0.72004400	0.16416500

Acid R = F
E = -2066.98429927 au

Si	-2.55274100	0.01403500	-0.01110000
Si	-1.11278300	1.66539500	-0.82907300
H	-1.08745100	1.89447300	-2.29989100
H	-1.07761900	2.96212400	-0.09767600
Si	-1.14139000	-0.11585300	1.84881800
H	-1.10180900	1.06001600	2.76281700
H	-1.13341400	-1.38351200	2.62817100
Si	-1.15832600	-1.56191100	-1.03498600
H	-1.15668900	-2.94055900	-0.47563500
H	-1.13659600	-1.59272800	-2.52268000
Si	0.29988000	-0.02898800	-0.01133900
Si	2.62399500	-0.01392900	0.00978900
O	3.05519300	-1.46841200	0.65239500
O	3.20438500	1.29899100	0.83966900
O	3.31165700	0.10958600	-1.48568800
H	3.95730800	-1.76555800	0.49455200
H	2.87268700	1.46312700	1.72646600
H	3.53736000	0.99683600	-1.78011300
F	-4.18494700	0.04021800	-0.01072600

Base R = F
E = -2066.44199858 au

Si	2.56951200	0.01178000	-0.01680500
Si	1.09859400	1.74041700	-0.54249000
H	1.12230400	2.94222400	0.34771700
H	1.09495100	2.21518300	-1.96085900
Si	1.11697000	-1.34516400	-1.23556500
H	1.11216700	-1.15752600	-2.71978100
H	1.16007000	-2.81097800	-0.95027700
Si	1.15277200	-0.40210900	1.78964400
H	1.19991300	-1.77171400	2.38346400
H	1.18148200	0.59701900	2.90123500
Si	-0.37769700	-0.02163600	0.03009900
Si	-2.78366900	-0.14060800	0.08470100
O	-3.21809500	-1.56891600	0.51129900
O	-3.21412900	0.40228700	-1.46520900
O	-3.18570200	1.20627500	1.01019300
H	-3.43351100	-0.35202200	-2.02048100
H	-3.37619700	1.96361000	0.44822900
F	4.22350100	0.02883600	-0.04596600

Acid R = Li
E = -1974.68761674 au

Si	2.92400700	-0.03315300	-0.00860800
Si	1.31637400	-1.48695800	-0.97028800
H	1.30462700	-1.59387500	-2.46252400
H	1.26788400	-2.88051500	-0.42638500
Si	1.34731600	-0.09412200	1.76111600
H	1.29442800	-1.35490000	2.56760200
H	1.36003400	1.04713100	2.72767000
Si	1.39824300	1.59754300	-0.81420400
H	1.41922100	2.93017600	-0.13686000
H	1.39598800	1.84321900	-2.28948300
Si	-0.16917500	0.05460400	-0.01965800
Si	-2.50654200	0.01966000	0.00994700
O	-2.99952000	1.42783000	0.72327200
O	-3.06722700	-1.34808300	0.78125800
O	-3.24880800	-0.04206200	-1.47247700
H	-3.92035500	1.67200600	0.58391600
H	-2.62807500	-1.60225100	1.59743900
H	-3.41013100	-0.92486200	-1.81754500
Li	5.36590100	-0.08121800	-0.00550700

Base R = Li
E = -1974.12057993 au

Si	2.92999400	0.02664100	-0.03564700
Si	1.29826100	1.65712900	-0.55484800
H	1.33454800	2.90405500	0.28448200
H	1.29488800	2.14279700	-1.97778800
Si	1.33105100	-1.30937600	-1.15791800
H	1.32852500	-1.19291100	-2.65712900
H	1.40096800	-2.78257300	-0.87509700
Si	1.37918500	-0.34884900	1.71389600
H	1.45400200	-1.69730900	2.36982700
H	1.42274300	0.64704600	2.83839500
Si	-0.24915600	-0.02902400	0.03838000
Si	-2.63720700	-0.14197800	0.09459200
O	-3.12454800	-1.55316200	0.54074500
O	-3.10027600	0.36581000	-1.46975500
O	-3.06344400	1.23506600	0.98256600
H	-3.38536800	-0.40743500	-1.96630900
H	-3.34444000	1.93470000	0.38486200
Li	5.35683000	0.03543500	-0.06935500

Simple Structures for Dipole Moment Comparison

H – H

E = -1.16732679 au

H	0.00000000	0.00000000	0.37232900
H	0.00000000	0.00000000	-0.37232900

CH_3 – H

E = -40.45841854 au

C	0.00000000	0.00000000	0.00000000
H	0.63139400	0.63139400	0.63139400
H	-0.63139400	-0.63139400	0.63139400
H	-0.63139400	0.63139400	-0.63139400
H	0.63139400	-0.63139400	-0.63139400

CN – H

E = -93.31193730 au

C	0.00000000	0.00000000	-0.50112600
N	0.00000000	0.00000000	0.65434700
H	0.00000000	0.00000000	-1.57367400

CF_3 – H

E = -337.93033096 au

C	-0.00000900	-0.00005800	0.33931800
F	1.08902000	-0.62182000	-0.12838700
F	-1.08310900	-0.63205000	-0.12838700
F	-0.00590600	1.25388100	-0.12840700
H	0.00001500	0.00025500	1.43071600

NH_2 – H

E = -56.48488809 au

N	0.00000000	0.00000000	0.11071100
H	0.00000000	0.94618800	-0.25832600
H	-0.81942300	-0.47309400	-0.25832600
H	0.81942300	-0.47309400	-0.25832600

NO_2 – H

E = -205.48821943 au

N	-0.00000200	0.30865300	0.00000000
H	0.00003800	1.34960100	0.00000000
O	-0.00000200	-0.21938600	1.09250800
O	-0.00000200	-0.21938600	-1.09250800

NF_2 – H

E = -254.65769087 au

N	-0.03797500	0.58495000	0.00000000
H	0.94937900	0.87112400	0.00000000
F	-0.03797500	-0.27587600	1.09163100
F	-0.03797500	-0.27587600	-1.09163100

OH – H

E = -76.33712419 au

O	0.00000000	0.00000000	0.11697600
H	0.00000000	0.76760600	-0.46790500
H	0.00000000	-0.76760600	-0.46790500

F – H

E = -100.34510073 au

F	0.00000000	0.00000000	0.09331600
H	0.00000000	0.00000000	-0.83984700

Li – H

E = -8.04631142 au

Li	-1.97991100	2.34072300	0.00000000
H	-3.60984700	2.35322200	0.00000000

H – CH$_3$
E = -40.45841854 au

C	0.00000000	0.00000000	0.00000000
H	0.63139400	0.63139400	0.63139400
H	-0.63139400	-0.63139400	0.63139400
H	-0.63139400	0.63139400	-0.63139400
H	0.63139400	-0.63139400	-0.63139400

CH$_3$ – CH$_3$
E = -79.72214639 au

C	0.00000000	0.00000000	0.76189500
H	0.51019000	0.88403500	1.16156900
H	0.51050200	-0.88385500	1.16156900
H	-1.02069200	-0.00018000	1.16156900
C	0.00000000	0.00000000	-0.76189500
H	1.02069200	-0.00018000	-1.16156900
H	-0.51050200	-0.88385500	-1.16156900
H	-0.51019000	0.88403500	-1.16156900

CN – CH$_3$
E = -132.59594660 au

C	0.00000000	0.00000000	-1.17748700
H	0.00000000	1.02689400	-1.55510600
H	-0.88931600	-0.51344700	-1.55510600
H	0.88931600	-0.51344700	-1.55510600
C	0.00000000	0.00000000	0.27811700
N	0.00000000	0.00000000	1.43736200

CF$_3$ – CH$_3$
E = -377.20887986 au

C	1.47508300	-0.00010900	-0.00007800
H	1.83805200	0.88185100	0.53193300
H	1.83835500	0.01958300	-1.02979500
H	1.83813500	-0.90176700	0.49778500
C	-0.02430200	-0.00002200	-0.00006100
F	-0.52680000	-1.07247600	-0.64503700
F	-0.52654700	-0.02240900	1.25129900
F	-0.52656800	1.09500900	-0.60615900

NH$_2$ – CH$_3$
E = -95.73903776 au

C	-0.70380400	-0.00000100	0.01802900
H	-1.11199900	-0.88077800	-0.48883300
H	-1.11198400	0.88084800	-0.48871900
H	-1.07963900	-0.00006300	1.05506200
N	0.74614100	-0.00000100	-0.12047800
H	1.15172900	0.81550700	0.32883000
H	1.15173200	-0.81550700	0.32883000

NO$_2$ – CH$_3$
E = -244.75977273 au

C	1.31593300	-0.00021600	-0.00301100
H	1.65872800	0.90598900	-0.49954700
H	1.65853400	-0.90818800	-0.49641900
H	1.62291700	0.00166600	1.04538300
N	-0.17109500	0.00000000	-0.01121200
O	-0.72760200	-1.08416900	0.00294600
O	-0.72716300	1.08439800	0.00294500

NF$_2$ – CH$_3$
E = -293.93023241 au

C	1.29172800	0.00000800	0.10254400
H	1.79834600	-0.89332700	-0.26841500
H	1.24410800	-0.00023400	1.19566000
H	1.79815600	0.89361000	-0.26802400
N	-0.04009800	0.00000100	-0.48578300
F	-0.68391400	1.08730800	0.11811200
F	-0.68389600	-1.08731900	0.11811000

OH – CH$_3$
E = -115.58803434 au

C	0.66168200	-0.02080900	0.00000000
H	1.07828400	0.98926800	-0.00000200
H	1.02532600	-0.54578600	-0.89515500
H	1.02532700	-0.54578300	0.89515700
O	-0.74398300	0.12268100	0.00000000
H	-1.14716200	-0.75429600	0.00000000

F – CH$_3$
E = -139.59938370 au

C	0.00000000	0.00000000	-0.63425300
H	0.00000000	1.03647700	-0.98453200
H	-0.89761500	-0.51823900	-0.98453200
H	0.89761500	-0.51823900	-0.98453200
F	0.00000000	0.00000000	0.75101200

Li – CH$_3$
E = -47.31802480 au

C	0.00000000	0.00000000	0.38945200
H	0.00000000	1.01826200	0.81252900
H	-0.88184100	-0.50913100	0.81252900
H	0.88184100	-0.50913100	0.81252900
Li	0.00000000	0.00000000	-1.59143400