

**MECHANISTIC INVESTIGATION INTO THE SOMMELET-HAUSER
REARRANGEMENT OF AN ALLYL AMMONIUM YLIDE THROUGH
DETERMINATION OF ^{13}C KIES**

A Thesis

by

SEAN CHRISTOPHER COLLINS

Submitted to the Office of Graduate Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of
MASTER OF SCIENCE

August 2010

Major Subject: Chemistry

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ABSTRACT

Mechanistic Investigation into the Sommelet-Hauser Rearrangement of an Allyl
Ammonium Ylide Through Determination of ^{13}C KIEs. (August 2010)

Sean Christopher Collins, B.S., Schreiner University

Chair of Advisory Committee: Dr. Daniel A. Singleton

The [2,3]-sigmatropic rearrangement is a pericyclic reaction of great synthetic utility to organic chemists. Within the scope of this reaction exist some cases in which the product corresponding to a [1,2] rearrangement is formed, despite the fact this is a forbidden process. Generally this is explained by a radical dissociation-recombination pathway; however, studies into the failure of transition state theory and the necessity to incorporate dynamic effects into mechanistic theory lead us to believe such products may arise from these phenomena. In particular, the possibility that many of these products result from an “unsymmetrical bifurcating surface” in the potential energy landscape is intriguing. To investigate this possibility, the Sommelet-Hauser rearrangement of *N*-allyl-*N,N*-dimethylglycine methyl ester was explored. The combined use of experimental and theoretically predicted kinetic isotope effects (KIEs) has been previously shown to deliver great mechanistic insight into reactions. The combination of these techniques, however, has found little employ in studying [2,3] rearrangements. This combination was used to study this reaction, using the Singleton method for determining small heavy-atom isotope effects.

Resulting experimental KIEs suggest the reaction proceeds by an asynchronous, concerted, early transition state, and is relatively exothermic. This agrees with previous studies and Hammond's postulate. Predicted theoretical KIEs are in good agreement with experimental KIEs, and the associated transition structure confirms the results suggested by experiment. Interestingly, as calculations proceed from gas phase to solvent models, the activation barrier of the reaction increases, while its exothermicity decreases. The energy difference determined between the lowest and second lowest energy transition structures decreases to 0.81 kcal/mol in the PCM model, so we cannot exclude the contribution of this transition structure to the reaction. However, qualitative results from the associated KIEs and energetics are consistent with the lowest energy transition structure. This reaction does not seem to afford the [1,2] product, and most likely dynamic effects are insignificant in determining product distribution. However, the study has validated, with respect to this body of reactions, both the use of the Singleton method for KIE determination and the combination of these experimental and theoretical techniques.

To the glory of God, the Author of knowledge.

ACKNOWLEDGEMENTS

I would like to thank Dr. Singleton for his advice, guidance, and commitment to his students. His vast knowledge, desire to teach, passion, and open door policy despite his busy schedule fostered a dynamic learning environment that is difficult to describe. I especially would like to express my gratitude for his faith and persistence in helping me develop as a student.

I would also like to thank my committee members, Dr. Bergbreiter, Dr. Liu, and Dr. Pellois for their time and guidance throughout the course of this thesis.

I would like to thank Erik Plata, Ollie Gonzalez-James, Yatsandra Oyola, Matt Vetticat, Xavier Bogle, Zhuo Chen, Larisamae Quijano, Diana Sepulveda, Ivonne Andujar and the rest of the Singleton group for their friendship and advice on this project.

Lastly, I would like to thank my family and friends for their continued support through all circumstances. I would like to thank in particular my parents for their love and encouragement during difficult times. I must especially thank my fiancée Christina for her love, support, self-sacrifice, patience and commitment through these years of study.

TABLE OF CONTENTS

		Page
ABSTRACT		iii
DEDICATION		v
ACKNOWLEDGEMENTS		vi
TABLE OF CONTENTS		vii
LIST OF FIGURES.....		ix
LIST OF TABLES		xi
CHAPTER		
I	INTRODUCTION.....	1
	General Overview	1
	Dynamic Effects.....	2
	Kinetic Isotope Effects.....	4
II	[2,3]-SIGMATROPIC REARRANGEMENTS.....	9
	[2,3]-Sigmatropic Rearrangement of <i>N</i> -alkyl ammonium salt 1	10
	Background and Significance.....	11
III	RESULTS AND DISCUSSION	21
	Experimental KIEs	23
	Theoretical Studies.....	25
	Discussion.....	30
IV	EXPERIMENTAL	31
	General Computational Procedures	31
	General Experimental Procedures.....	31
	Synthesis of <i>N,N</i> -dimethylglycine methyl ester 4.....	33
	Synthesis of <i>N</i> -allyl- <i>N,N</i> -dimethylglycine methyl ester 1	34
	DBU-Induced Rearrangement of 1	34

CHAPTER	Page
Results for ^{13}C Determination of KIE Sets 1 and 2.....	38
V CONCLUSIONS.....	47
REFERENCES.....	49
APPENDIX.....	53
VITA.....	98

LIST OF FIGURES

FIGURE	Page
1 a) Symmetrical PES which results in a bifurcating MEP, yielding two products from the same transition state. b) Unsymmetrical PES, leading to one product or two nonequivalent products	4
2 An illustration of the primary isotope effect between protium and deuterium	6
3 Two depictions of a generic Wittig rearrangement with emphasis on the envelope nature of the five-membered transition state	18
4 Rearrangement of ammonium salt 1 . a) The concentration of DBU was varied; for the standard reactions, 4 eq of DBU were used. For sample reactions, 15-20 mol% DBU were used	22
5 Experimental and computational intermolecular KIEs. Experimental KIEs represent measurements obtained from two independent experiments, with the standard deviations of these measurements included in parentheses. The methoxy methyl was chosen as a standard as its isotopic composition was not expected to change during the course of the reaction. Computational KIEs are indicated by italicized brackets	24
6 Sample ^{13}C NMR of 2 (CDCl_3); δ_{C} 33.7, 41.3, 50.6, 67.2, 116.8, 134.0, 171.7	40
7 Sample ^1H NMR of 2 (CDCl_3); δ_{H} 2.26 (s, 6H), 2.35 (m, 2H), 3.1 (dd, 1H), 3.6 (s, 3H), 5.0 (m, 2H), 5.7 (m, 1H)	41
8 Expanded regions for ^1H spectrum of 2	42
9 Sample ^{13}C NMR of 1 (CDCl_3); δ_{C} 50.7, 52.9, 60.6, 66.5, 123.9, 130.3, 164.9	43
10 Sample ^1H NMR of 1 (CDCl_3); δ_{H} 3.56 (s, 6H), 3.8 (s, 3H), 4.6 (d, 2H), 5.0 (s, 2H), 5.8 (m, 2H), 6.0 (m, 1H)	44

FIGURE	Page
11 Expanded regions for ^1H spectrum of 1	45
12 Sample ^1H NMR of 4 (CDCl_3); δ_{H} 2.26 (s, 6H), 3.1 (s, 2H), 3.6 (s, 3H).....	46

LIST OF TABLES

TABLE		Page
1	Relative energetics of the four lowest energy transition structures	27
2	Predicted theoretical and experimental KIEs for several transition structures	28
3	Calculated gas phase and solvent model ΔG^{\ddagger} 's/ ΔG^{\ddagger} 's	29
4	^{13}C Integrations for Methyl-2-(<i>N,N</i> -dimethylamino)-4-pentenoate 2 , KIE set 1	38
5	^{13}C Integrations for Methyl-2-(<i>N,N</i> -dimethylamino)-4-pentenoate 2 , KIE set 2	39

CHAPTER I

INTRODUCTION

General Overview

Understanding how reactions operate can easily be considered the fundamental objective of physical organic chemistry. Chemists pursue this goal various ways, but the essential focus lies in understanding reaction mechanisms. Within organic chemistry, considerable effort has been directed toward understanding why reactions often give a mixture of products. Chemical reactions are understood to generate multiple products in various ways, and understanding the distribution of products in a reaction can offer clear insight into the mechanism of their formation. Often in reactions, the primary product is formed through a specific reaction mechanism, which then can undergo potential side reactions or equilibration, yielding different products. However, some reactions have been shown to operate under multiple pathways, giving multiple products. This generally occurs through competition amongst several pathways whose energy barriers are relatively close in energy, leading to a kinetic competition between these pathways.

This thesis follows the style and format of *The Journal of the American Chemical Society*.

Such competition is generally understood throughout organic chemistry within the framework of transition state theory (TST). TST operates by considering the potential energy surface (PES) of a reaction, in which changes in reactants increase or decrease a system's potential energy, creating a theoretical landscape connecting reactants and products. As a reaction proceeds along a given pathway, it eventually reaches the highest point, or transition state, along the potential energy path taken. TST states that the rate by which products form will be governed by the relative heights of the energy barriers associated with the transition states in each pathway involved. This transition state, including associated enthalpy and entropy, is derived from the PES of the reaction. TST uses this PES to calculate the rate of a reaction. TST also assumes that the intramolecular vibrational energy redistribution (IVR) of a molecule will occur very rapidly in comparison with motion along the reaction pathway. Therefore, TST assigns the relative rates of reactions to the differing heights of the energy barriers involved, rather than atomic motion. Thus, the distribution of products arises from kinetic competition between the various pathways, with the fastest pathway giving the predominant product. However, there have been cases documented in which TST fails to account for the experimental results obtained from a reaction.¹

Dynamic Effects

In order to properly understand the reaction in such cases, it is necessary to employ alternative theory, to which end dynamic effects, that is, the physical vectors associated with atomic motion and momenta, must be taken into consideration. Investigation into the failure of transition state theory has led to several primary

dynamic effects which result in discrepancies between experiment and TST's predictions. Some of these effects, as detailed by Carpenter, occur when the assumptions of TST regarding the rate of IVR are invalid, and relatively slow IVR allows products to form before the redistribution is complete.²

Of particular interest to this study are other dynamic effects which cause a single transition state to give rise to multiple products. This phenomenon has been referred to as a bifurcating energy surface (Figure 1). In such cases, a reactant following the minimum energy path (MEP) can enter a flat region of the PES after passing through an initial transition state, and can then proceed to form two different products without encountering an additional energy barrier. This process occurs on a symmetrical PES, and such cases are generally associated with symmetry breaking in a reaction, giving indistinguishable products (Figure 1a). However, a far less understood process occurs with an "unsymmetrical bifurcating surface" (Figure 1b), possibly generating two nonequivalent products. In this case, similarly to a bifurcating energy surface, the reaction coordinate encounters an adjacent saddle point subsequent to the transition state without passing through an intermediate; however, the MEPs in such surfaces do not bifurcate. Instead, some trajectories can stray from the expected MEP and produce an alternative product.³

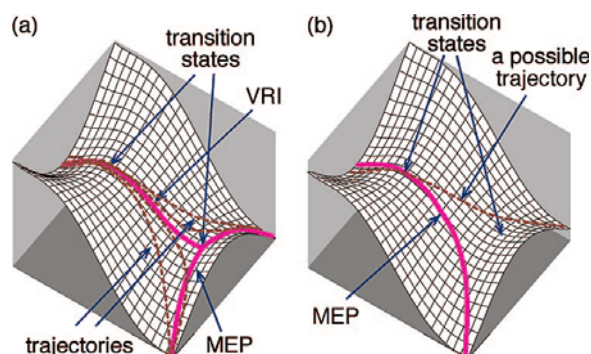


Figure 1. a) Symmetrical PES which results in a bifurcating MEP, yielding two products from the same transition state. b) Unsymmetrical PES, leading to one product or two nonequivalent products.³

In order to explore the mechanism of the reaction investigated herein and determine if such dynamic effects contributed significantly, it was necessary to first gain an idea of the nature of the reaction at the transition state. To accomplish this, measurement of experimental kinetic isotope effects (KIEs) and calculation of predicted theoretical KIEs for the reaction system were employed.

Kinetic Isotope Effects

KIEs arise from the difference in reaction rate associated with isotopic substitution at a rate-limiting position of a molecule. A simplistic model of this effect is that substitution anywhere in a molecule by an isotopomer produces differences in the frequencies of vibrational modes associated with that atom. This substitution causes little difference in the potential energy of the system, i.e., the relative minima and maxima of the PES remain constant. However, changes in the vibrational modes of a molecule

affect the shape of the potential energy well associated with any point on the PES. These changes are dominated by the vibrational modes undergoing the most change during a reaction. Considering, for instance, a bonding change at the rate-limiting step during a reaction, the reaction coordinate can be defined as the stretching vibration of the bond(s) being broken or formed. At ambient temperature, the quantized energies of the vibrational modes for bond stretches are dominated by $n = 0$, referred to as the zero-point energy (ZPE, eq. 1).

$$e_n = (n + \frac{1}{2}) h\nu \quad n = 0, 1, 2, 3, \dots \quad (1)$$

Stretching vibrations are modeled by the classic equation for the stretching of a spring with a mass attached at both ends, and the frequency is therefore directly proportional to the square root of the force constant k for the bond, and inversely proportional to the square root of the reduced mass m_r . This reduced mass is greatly affected when D replaces H in a bond between this light atom and a heavy atom like C. Because the heavier mass of D reduces the stretching frequency of a bond, the ZPE of the bond upon substitution with D is also reduced (eq. 2). The magnitude of the resulting KIE will be dependent upon the relative shapes of the potential energy wells in the starting material and transition state. As bonds are formed or broken at the transition state, the potential energy wells of the associated stretching vibrations in the transition state are generally wider than those of the starting material. This has a tendency to lower the gap between the ZPE of the lighter isotope and the heavier isotope at the transition state as the change in the degree of bonding causes the associated k to approach 0. The result is a lower activation energy for the lighter isotope when compared to the heavier

isotope. These differences in activation energy between competing isotopes produce differing rates of reaction arising from the differences in associated ZPEs (Figure 2).⁴

$$v = \frac{1}{2}\pi (k/m_r)^{1/2} \text{ where } m_r = (m_1m_2)/(m_1+m_2) \quad (2)$$

The measurement of KIEs has been previously used to investigate the transition states of reactions. The predominant methods for these measurements involve measurement of the rate of reaction for a reactant specifically labeled with an isotope in question, and comparison of that rate against the rate of reaction for unlabeled material. However, this results in a severe limitation in the use of KIEs to study reaction mechanisms, necessitating the selection of reaction systems and conditions conducive to isotopic labeling. Often labeled material is very expensive, and can be cost-prohibitive, particularly because generally only one atom may be studied at a time. In addition, most labeling studies require the use of radioactive isotopes.

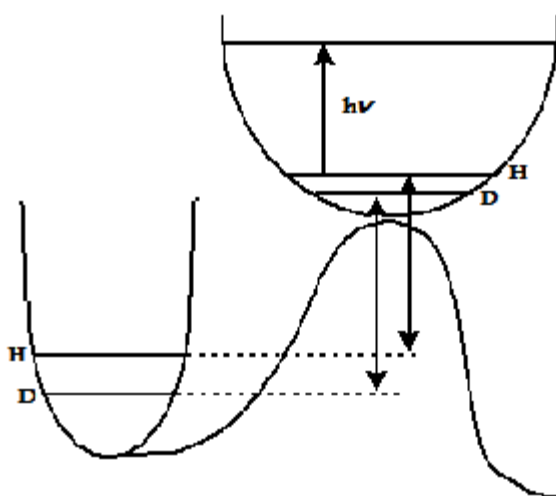


Figure 2. An illustration of the primary isotope effect between protium and deuterium.

Singleton has instead shown that using methodology involving nuclear magnetic resonance (NMR) spectroscopy can permit the study of KIEs at isotopic natural abundance, which has found employ in permitting the simultaneous investigation of numerous positions within a molecule. For this reason, all KIE measurements in this thesis have been performed using the Singleton method. As a reaction proceeds, the unreacted starting material becomes fractionatively enriched in the slower reacting (minor) isotopic component. The proportion (R/R_0) of the minor isotopic component in residual starting material at a given conversion can be determined by comparison to unreacted starting material from the same synthetic lot. Equation 3 relates this proportion to the fractional conversion (F) of the reactants and the KIE. As a reaction proceeds toward completion, F approaches 1 and $R/R_0 \rightarrow \infty$, greatly enhancing the KIE observed from R/R_0 . KIEs can be calculated from these measurements (eq. 4), with uncertainty arising primarily from the measurement of $\Delta R/R_0$ (ΔKIE_R) and ΔF (ΔKIE_F) (eq. 5 and 6, respectively) as equation 7. In cases where KIEs are large or measurement of the isotopic proportion is very precise, ΔKIE_F dominates and therefore high conversion does little to improve accuracy. However, in cases using NMR integration, precision in measuring R/R_0 is relatively low, ΔKIE_F is negligible, and uncertainty is dominated by ΔKIE_R , which decreases as a reaction approaches completion (Equations 3-7 are taken from: Thomas, A. A.; Singleton, D. A. *J. Am. Chem. Soc.* **1995**, *117*, 9357-9358, its references, and supporting information).

$$(R/R_0) = (1 - F)^{(1/KIE)-1} \quad (3)$$

$$KIE_{calcd} = \frac{\ln(1-F)}{\ln[(1-F)R/R_0]} \quad (4)$$

$$\Delta KIE_F = \frac{\partial KIE}{\partial F} \Delta F = \frac{-\ln(R/R_0)}{(1-F)\ln^2[(1-F)R/R_0]} \Delta F \quad (5)$$

$$\Delta KIE_R = \frac{\partial KIE}{\partial (R/R_0)} \Delta(R/R_0) = \frac{-\ln(1-F)}{(R/R_0)\ln^2[(1-F)R/R_0]} \Delta(R/R_0) \quad (6)$$

$$\Delta KIE = KIE \cdot ((KIE_R/KIE)^2 + (KIE_F/KIE)^2)^{1/2} \quad (7)$$

Singleton has demonstrated this principle through the measurement of starting material KIEs. Using careful acquisition and integration in ^{13}C NMR, ^{13}C quantities can be measured in both the sample (a reaction taken to 80-99% conversion) and standard by comparing peak integrations to an internal standard; this is a position in the molecule expected to remain constant in isotopic composition. Differences in isotopic composition can be used to calculate the associated KIEs (eq. 4).⁵ For this thesis, due to the nature of the reaction involved, product KIEs, in which product obtained from a low conversion reaction is compared with that of a reaction driven to completion, were used rather than the starting material KIEs just described, though through an analogous method.⁶ Subsequently, theoretical calculations were used to model the reaction transition state, and the calculated frequencies of the normal vibrational modes associated with these transition states used to predict KIEs. Comparison of predicted KIEs to those obtained experimentally, as well as the use of potential energy surfaces and dynamic trajectories, has in the past allowed for detailed investigation of reaction mechanisms, and has been demonstrated to be a versatile tool for the exploration of organic reactions.⁷

CHAPTER II

[2,3]-SIGMATROPIC REARRANGEMENTS

The [2,3]-sigmatropic rearrangement is a reaction class that has found great synthetic utility within the toolbox of organic chemistry. These pericyclic reactions have been extensively employed, and a fair amount of mechanistic investigation directed toward them.⁸ Some heteroatomic [2,3]-sigmatropic rearrangements have produced the Stevens rearranged [1,2] product in addition to the predicted [2,3] rearrangement.⁹ As the [1,2] rearrangement is a forbidden process according to the conservation of orbital symmetry as outlined by Woodward and Hoffman,¹⁰ the formation of [1,2] rearranged products is generally explained via a dissociation-recombination stepwise mechanism. However, the generation of the [1,2] product from an expected [2,3] rearrangement provides a striking case in which dynamic effects in atomic motion may play a critical role in product determination. Despite the intrigue of these reactions, and the combined experimental and theoretical investigation employed in attempts to elucidate the reaction mechanism,¹¹ there have been, so far as we are aware, no attempts to directly investigate these transition states using heavy-atom KIEs, with the exception of an associated [2,3]-sigmatropic rearrangement in the ene reaction of selenium dioxide with 2-methyl-2-butene.¹² To this end, this thesis addresses several primary objectives. First, to investigate the potential of an example of the Sommelet-Hauser rearrangement as a subject in the aforementioned discrepancy, ¹³C KIE measurements and subsequent

theoretical calculations were used to explore the reaction's transition state. Subsequently, the energetics of the rearrangement from the deprotonated starting material were analyzed by calculational methodology to further investigate the rearrangement. Finally, the efficacy of the Singleton method was evaluated against the results obtained from the experiments herein described, as justification for the application of such physical organic techniques to future systems within the body of [2,3]-sigmatropic rearrangements.

[2,3]-Sigmatropic Rearrangement of *N*-alkyl ammonium salt 1

Coldham *et al.* have demonstrated the [2,3] rearrangement of *N*-allyl α -aminoesters.^{13,14} This rearrangement of a quaternary ammonium salt was used to generate experimental intermolecular KIEs; as mentioned previously, heavy-atom intermolecular KIEs have proven effective tools in generating information about the transition state of a reaction at the rate-limiting step. The particular reaction studied was selected for several reasons. Although apparent that this rearrangement would yield identical products via either the [1,2] or [2,3] rearrangement, it was noted that dynamic methods, that is, the analysis of atomic motion along the trajectory followed by the reactants over the PES, could be used to investigate the transition state for this reaction, should it appear conducive to the generation of a [1,2] rearrangement in addition to the expected [2,3] rearrangement. Furthermore, the facile nature of this reaction, and the significance of the Sommelet-Hauser rearrangement of ammonium ylides as an original instance of the [2,3]-sigmatropic rearrangement,^{15,16} brought the reaction to light as an introductory system in our investigations. Also, this system appeared to be an excellent

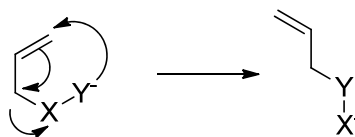
opportunity to validate whether or not the Singleton method would be effectively applicable to these reactions, from the standpoint of whether theoretical KIEs accurately predict experimental data. Finally, data obtained from this reaction will hopefully provide a basis for future investigation into dynamic effects in [2,3]-sigmatropic rearrangements.

Background and Significance

Since their inception in the early 20th century, heteroatomic [2,3]-sigmatropic rearrangements, such as the Sommelet-Hauser,^{15,16} Wittig,¹⁷ aza-Wittig,¹⁸ and thio-Wittig,¹⁹ as well as rearrangements of selenium,²⁰ have found considerable employ within the toolbox of modern organic chemistry. These reactions continue to serve as objects of study from the perspective of general methodology,²¹ especially with regards to asymmetric synthesis.²² Continued development of the [2,3]-sigmatropic rearrangement has led to two classes of rearrangements: those involving oxides or onium ylides, such as the Mislow-Evans²³ or Sommelet-Hauser rearrangements, and those such as the Wittig rearrangement which involve anionic species. As the atom X (Scheme 1) in the rearrangement must be able to function as a leaving group, it is generally an electronegative atom, hence the widespread development of heteroatomic rearrangements. In the most facile [2,3] reactions, atom Y is also stabilized, as with onium ylides, or through the addition of an electron withdrawing group. In addition, as sigmatropic rearrangements such as the [2,3] rearrangement remain one of the primary methods of carbon-carbon bond formation, direct application of [2,3] rearrangements has also found employ within the context of projects such as natural product total synthesis,

in order to affect addition to existing carbon skeletons, as well as generate functionalities in locations that would be otherwise difficult or impossible to produce.²⁴

Scheme 1



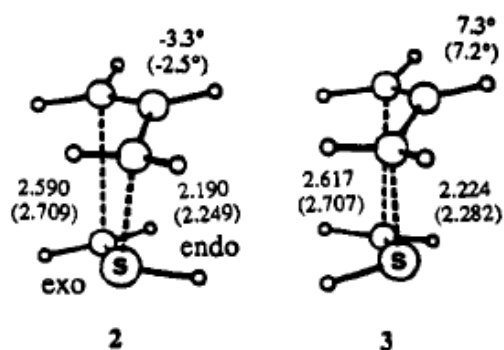
Because of the utility of [2,3]-sigmatropic rearrangements, these reactions have undergone considerable mechanistic study in terms of the nature of the rearrangement and its transition structure, as well as to the influencing factors toward stereochemical and regiochemical control. The transition states involved in these rearrangements, while similar, show unique properties depending on the heteroatom involved. In the late 1960's and early 1970's, groups such as Sharpless, Baldwin, and Rautenstrauch²⁵ worked on investigating and classifying various sigmatropic rearrangements and their associated mechanisms.

Subsequent expansion of computational chemistry would later allow in-depth analysis of transition states and mechanisms. Research into reaction mechanisms of [2,3]-sigmatropic rearrangements follows along the lines of the general divide between the two major classes of the rearrangement. Among the oxide and ylide compounds which undergo [2,3]-sigmatropic rearrangement, much of the focus has been on nitrogen and sulfur containing compounds. Following research by Raustenstrauch into the mechanism of ammonium ylide rearrangements,^{25d} Jursic investigated the

rearrangements of ammonium and sulfonium ylides using *ab initio* calculations. This study concluded that both rearrangements would occur through a concerted pathway, rather than a dissociation mechanism into an ion pair. The ammonium rearrangement is expected to proceed through an early transition state according to Hammond's postulate, with a relatively low energy barrier. The sulfonium system could proceed through either an *exo* or an *endo* configuration, with the *exo* configuration predicted to be slightly lower in energy.²⁶ In 1996, Heard and Yates investigated the concerted Sommelet-Hauser mechanism versus the radical dissociation-recombination mechanism of *N*-methyl-3-propenylammonium methylene, noting that both pathways were relatively close in energy, and that influences from substituents, solvent effects, various basis sets and electron correlation were unable to predict rules by which each mechanism would be preferred.^{11a} Work by Wu and Houk in 1991 investigated the transition states of sulfur ylides, noting that the preference for *exo* and *endo* (Scheme 2, respectively 2 and 3) configurations within the transition state varied depending upon the nature of the substituents involved. The transition states in all cases appear to be concerted and asynchronous, demonstrating relatively early transition states, in agreement with predicted exothermicity and activation energies. Stabilization advances the transition state along the reaction pathway, with a tendency to orient in such a way that the forming and breaking bonds are partially eclipsed, promoting orbital overlap, particularly in stabilized systems.^{8c} In 2003, a study by Okada *et al.* investigated the rearrangement of a cyclic sulfonium salt, substituted in the ring with either a sulfur or sulfonium moiety. The inclusion of the sulfonium yielded the expected [2,3]

rearrangement, while inclusion of the donating sulfur atom decreased the electrophilicity of the alkyl group, converting the mechanism into a [1,4]-sigmatropic shift.²⁷ An interesting example of *in situ* generation of ammonium ylides was accomplished by Blid *et al.* in 2007 by the complexation of a Lewis acid to a tertiary amine; the subsequent [2,3] rearrangement of these compounds was investigated by DFT calculations and spectroscopic means, with the high diastereoselectivity being explained by *exo* complexation of the Lewis acid at the transition state.^{9c}

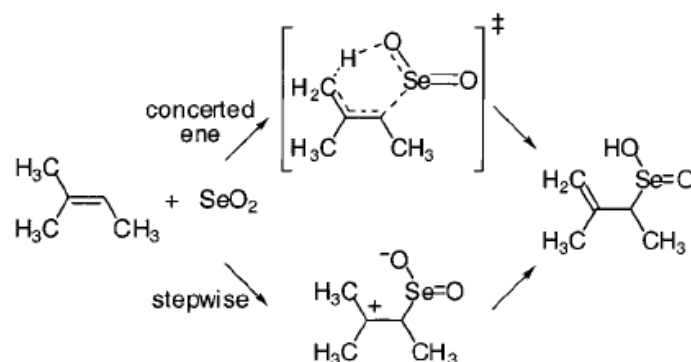
Scheme 2^{8c}



In 1995, the Mislow-Evans rearrangement of allylic sulfoxides was investigated by Jones-Hertzog and Jorgensen. It was determined that the transition state appeared to resemble the sulfenate product, as the rate of the forward reaction was slowed by polar solvent, while the reverse reaction remained unaffected. Calculations revealed that the dipole moment of the system as the reaction approaches the transition state highly resembles the sulfenate, with the exception of the sulfoxide oxygen, which remains more reactant-like in its configuration. The resulting substantial decrease in hydrogen bonding explains the apparent solvent effects. Regioselectivity in the reaction was analyzed as a

product of four possible transition states originating from two diastereomeric configurations for the sulfur atom. However, in both cases the configuration leading to the *E*-product is favored, though this leads to the *exo* product from one epimer and the *endo* from the other.^{28,8d} In 2006, a study relating to the apparent discrepancy between experimental and calculational studies of the Mislow-Evans rearrangement, and the question of a concerted versus a radical dissociation mechanism, was conducted by Freeman *et al.*, in which alkyl-3-propenyl sulfoxides were studied. The rearrangements of these compounds were confirmed to be concerted, with small differences between the barriers for *exo* and *endo* transition states. Barriers for these allylic sulfoxide rearrangements were also smaller than those of the corresponding non-allylic aryl sulfoxide rearrangements.²⁹ Further studies in 2000 investigated the Mislow-Evans rearrangement as an entry to allylic alcohols, using DFT calculations to compute energy barriers and the nucleus-independent chemical shifts (NICSSs) for the transition states of various rearrangements, determining that there was strong aromatic character at the transition states.³⁰

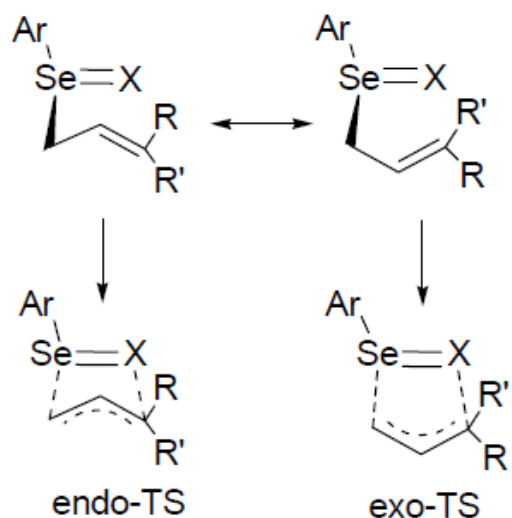
Scheme 3¹²



Also in 2000, a study performed by Singleton and Hang addressed the ene reaction of selenium dioxide with 2-methyl-2-butene, using experimental and calculated KIEs to evaluate between a concerted and stepwise mechanism (Scheme 3). Using DFT methods, the study ruled out the involvement of selenium esters as the oxidant because of higher activation barriers, and reversible electrophilic attack by HSeO_2^+ because the reaction showed no dependence on basicity. Calculations predicted the concerted mechanism was dominant, but the KIEs suggested the possibility of a mixture of concerted and stepwise mechanisms, with the stepwise giving the minor products observed experimentally.¹² A related study in 2003 addressed the same reaction from the perspective of overall stereochemical control. The *anti-endo* or *syn-endo* were determined to be the preferred configurations for addition, with the *anti-endo* preferred by 0.76 kcal/mol. The pseudo-equatorial position of the methyl group of the allyl moiety within the transition state is preferred over the axial position by 2.96 kcal/mol, accounting for the retention in stereochemistry of the double bond.³¹ Work by Bayse in 2009 investigated the rearrangements of aryl allyl selenoxides and selenimides via DFT calculations, modeling the transition states and comparing the results to experimental data by Reich, as well as previously estimated barriers. *Ortho* substitution by nitro groups was also investigated. In each case, the *endo* and *exo* transition state configurations were explored (Scheme 4), yielding general agreement between calculated barriers and those obtained experimentally. Substitution by a nitro group lowered the relative energies of the conformations leading to the *endo* and *exo* transition states, as well as increased the barrier of the *exo* relative to the *endo*, with an overall

increase in reaction exothermicity. Unsubstituted selenoxides and compounds substituted at the 1 or 3 position of the allyl group favored the *endo* configuration, while selenimides and compounds substituted at the 2 position of the allyl group favored the *exo* TS.³²

Scheme 4³²



In addition to investigations of various ylides, theoretical work has also explored anionic species; notably, the Wittig rearrangement of anionic oxygen-containing species is among the most ubiquitous of the [2,3]-sigmatropic rearrangements. A 1983 study of diastereoselectivity in the Wittig rearrangement rationalized that both the *E* and *Z* isomers reacted via an envelope transition state (Figure 3). Reaction of the *Z*-isomer produced a diaxial interaction that disfavored the *threo* product, while in the *E*-isomer the gauche interactions are minimized in the transition state, leading to the *threo* product. This results in the preference of the *Z*-isomer for *erythro* and the *E*-isomer for *threo*.³³ In

1990, computational studies performed by Wu *et al.* probed the transition structure of the Wittig rearrangement, focusing on the necessity of the lithium (Li^+) counterion in order to locate a concerted reaction pathway. The overall transition state located for the concerted pathway produced the expected envelope configuration, and provided rationale for the observed stereoselectivity in the reactions.^{8b} In 1994, a study investigating the Wittig rearrangement was published, comparing several allyloxy anion species. It was rationalized that the diastereoselectivity is due to differences in the transition states for stabilized versus unstabilized systems, with various substituents altering the transition state configurations.^{8c} These theoretical calculations on the Wittig rearrangement consistently included the Li^+ counterion, and a subsequent study in 2001 noted that the presence of explicit tetrahydrofuran (THF) solvent molecules altered chelation to the Li^+ .³⁴

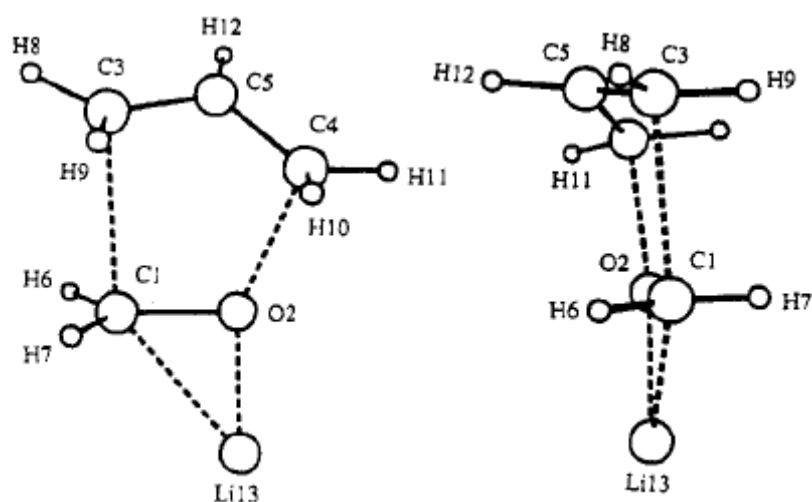


Figure 3. Two depictions of a generic Wittig rearrangement with emphasis on the envelope nature of the five-membered transition state.^{8b}

Similar exploration has been undertaken for anionic rearrangements involving other heteroatoms. A mechanistic study in 1971 investigated rearrangements of lithiated allyl sulfides; in analogous cases involving sulfonium ylides or allylic oxygen ethers, competition ensues between the [2,3] shift and the [1,2] shift; again, the mechanism of the latter is rationalized as a dissociation-recombination mechanism to produce the alternative product. The apparent absence of this competition in the case of these allyl sulfides is explained by the instability of the thioaldehyde anion radical fragments that would be involved in this pathway.¹⁹ While, until recently, difficulty in accessing the rearrangement of tertiary amines has primarily required nitrogen-bearing compounds to be ammonium ylides,³⁵ studies of the aza-Wittig reaction have also been undertaken. In 2003, a study by Haeffner *et al.* delved the mechanisms of various [2,3] rearrangements, including the Wittig, aza-Wittig, thio-Wittig, and carba-Wittig rearrangements. The researchers used homolytic and heterolytic bond cleavage energies, compared with the proton affinity of the heteroatom involved, to explore the reactions. It was determined that less basic atoms like sulfur and oxygen could promote the concerted [2,3] rearrangement, while the instability of atoms like nitrogen tended to promote a heterolytic cleavage-recombination pathway. The presence of a counterion again provided a stabilizing effect that promoted the concerted pathway, but still produced cleavage in the aza-Wittig and carba-Wittig structures.^{8a}

Some mechanistic research has targeted the formation of the [1,2] product in [2,3] rearrangements. One example studied the transition states of [1,2] and [2,3] rearrangements of α -allyloxycarbenes, noting that the [1,2] shift was expectedly higher

in energy, although it was speculated that methyl substitution may lower the gap between the two transition states.^{11b} A later study by Zipse investigated the [1,2] shift in acyloxy radicals, exploring substituent and solvent effects, as well as the possible influence of other mechanisms besides the [2,3] and [1,2] rearrangements. It was determined that the [2,3] shift was the most favorable in all cases, with the [1,2] slightly less favorable; in addition, solvent effects seemed to be under-predicted in the models investigated.^{11c}

Despite such studies targeted at [2,3]-sigmatropic rearrangements, this class of reaction has still received relatively little attention from the perspective of physical organic techniques, such as the measurement of experimental KIEs, prediction of theoretical KIEs, and the investigation of dynamic effects; this thesis aims at a preliminary address of these deficiencies.

CHAPTER III

RESULTS AND DISCUSSION

In order to initiate such investigation into [2,3]-sigmatropic rearrangements, the base-induced rearrangement of *N*-allyl-*N,N*-dimethylglycine methyl ester bromide (Figure 4) was explored, using 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU). Coldham reports optimal synthesis of the rearranged product as a one-pot reaction, in which the ammonium salt was generated and subsequently rearranged. To accomplish this, the *N*-allyl α -aminoester of glycine was combined with iodomethane, dimethyl formamide (DMF), potassium carbonate (K_2CO_3), and DBU, and reacted at 40°C.¹³ Because measurement of KIEs at natural abundance requires the initial isotopic composition of the starting material in both the experimental and standard to be uniform, it was instead necessary to form and isolate the ammonium salt separately, prior to subjecting the compound to conditions by which to induce the rearrangement. To accomplish this, *N,N*-dimethylglycine methyl ester **4** was generated from a glycine methyl ester hydrochloride salt **3** using the Eschweiler-Clarke reaction, then reacted with allyl bromide to generate the starting material **1** for the reactions (Scheme 5).

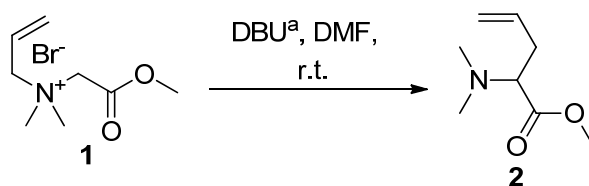
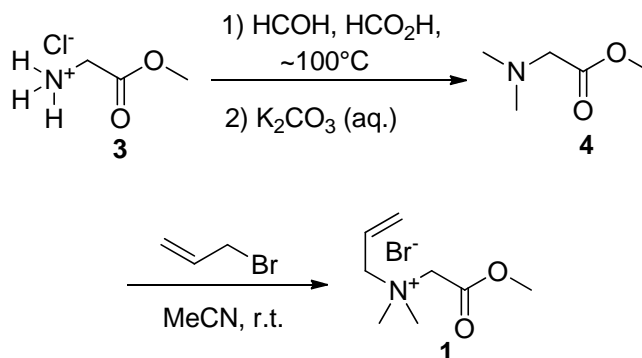


Figure 4. Rearrangement of ammonium salt **1**. a) The concentration of DBU was varied; for the standard reactions, 4 eq of DBU were used. For sample reactions, 15-20 mol% DBU were used.

Subsequent experiments with this starting material led us to evaluate the rearrangement conditions given by Coldham. In particular, it was decided to carry out the reaction at room temperature, rather than 40°C, as the increase in temperature was noted to have little effect on the net yield of the reaction. It was discovered, however, that discernable quantities of water in the reaction mixture tended to reduce the yield dramatically, forming a byproduct that was presumed to be the hydrolysis of the methyl ester of the ammonium salt. K_2CO_3 seemed to play no substantial role in the reaction or in minimizing this effect, and so was not included in our experiments. In order to combat the apparent starting material decomposition, 4Å powdered molecular sieves were included in the reaction mixture. Because of the possibility of starting material decomposition, *trans*-stilbene was included as a standard against which to quantify the conversion of the reaction.

Scheme 5



Experimental KIEs

The nature of the ammonium salt as starting material proved to be unfeasible for the measurement of starting material KIEs, as recovery of the starting material from the protonated DBU was nearly impossible. Instead, product KIEs were measured. Optimization of the reaction conditions described above necessitated the use of excess base in order to drive conversion to 100%. Formation of product at low conversion was affected by using 15-20 mol% DBU. The reaction of **1** with ≈ 15 mol % DBU afforded **2** in 11.7% yield, while the equivalent reaction with ≈ 20 mol % DBU afforded **2** in 21.3% yield. Product from these reactions was isolated using column chromatography. The ^{13}C in the low conversion samples was compared with the ^{13}C in the standards that had been driven to 100% conversion, using NMR methodology.⁶ Because the methyl group of the methoxy was not expected to change in composition, it was selected as the internal standard for measurement of ^{13}C composition. Intermolecular isotope effects are shown in Figure 5.

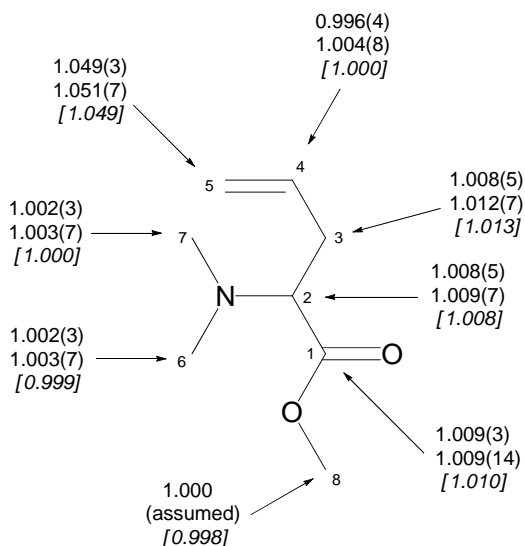


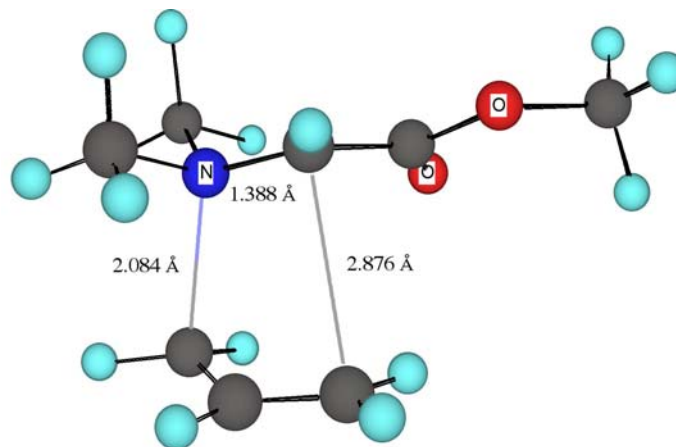
Figure 5. Experimental and computational intermolecular KIEs. Experimental KIEs represent measurements obtained from two independent experiments, with the standard deviations of these measurements included in parentheses. The methoxy methyl was chosen as a standard as its isotopic composition was not expected to change during the course of the reaction. Computational KIEs are indicated by italicized brackets.

Interestingly, the resulting KIEs show a small isotope effect at C1, the carbonyl carbon, which may reflect a change from the enolate in the deprotonated intermediate to a carbonyl at the transition state, as the oxygen no longer greatly assists in the stabilization of the anion at C2. There is a large primary isotope effect at C5, indicating cleavage of the C5-N bond at the transition state, while small isotope effects on C6 and C7 may reflect the changing environment from the formerly cationic nitrogen. C4 interestingly shows results that are unclear, giving equally a small inverse and small normal isotope effect, while C3 shows a small isotope effect, possibly indicating only a

small degree of bond formation between C2 and C3 at the transition state. These results seem to indicate an early transition state.

Theoretical Studies

In order to further evaluate the transition state and reaction mechanism of this rearrangement, theoretical calculations were employed, using the program Gaussian03 (G03).³⁶ All calculations were performed in the gas phase at the Becke3LYP³⁷/6-31+G** level. Several transition structures were located, and the four lowest energy transition structures modeled using an Onsager solvent model. The lowest energy transition structure is given as structure **5**; Table 1 contains the relative ΔG s of the different transition structures versus **5**. Scaled theoretical vibrational frequency calculations were performed on all four transition structures.³⁸ These frequency calculations were used to calculate predicted theoretical KIEs using conventional transition state theory by the method of Bigeleisen and Mayer.^{39,40} The KIEs associated with structure **5** are shown in Figure 5 and in Table 2, which also contains KIEs associated with the other three transition structures for both the gas phase and solution phase calculations. It is interesting to note that all predicted isotope effects from this structure are within experimental error of those obtained experimentally.



5

The predicted KIEs, coupled with transition structure **5**, further confirm the character of the transition state for this rearrangement. Examining the data, several points of interest are apparent. Interestingly, the isotope effect at C4 is predicted at unity, a result possibly extrapolated from the experimental isotope effects in that both measurements were off from unity by the same degree in opposite directions. The C5-N bond in the transition state is elongated to 2.084 Å from the more typical ammonium C-N bond length of 1.564 Å in the intermediate, while the C2-C3 bond length is still 2.876 Å, much greater than the C-C single bond length of 1.542 Å in the product (structural information regarding the deprotonated intermediate and the rearranged product are included in the Appendix). The transition structure suggests a concerted, though highly asynchronous, mechanism, and, according to Hammond's postulate, a relatively early transition state. The C2-N bond length is also shortened in the transition state, from 1.479 Å in the intermediate to 1.388 Å at the transition state, consistent with the

transition from a C-N charge separated bond to a formal C-N single bond described by Heard and Yates.^{11a}

Table 1. Relative energetics of the four lowest energy transition structures.

Calculated Structure	Gas Phase $\Delta\Delta G^\ddagger$ (kcal/mol)	G03 Onsager $\Delta\Delta G^\ddagger$ (kcal/mol)	G09 PCM $\Delta\Delta G^\ddagger$ (kcal/mol)
Transition Structure 5	0	0	0
Transition Structure 6 (Alt TS 1)	1.82	1.50	0.81
Transition Structure 7 (Alt TS 2)	6.06	4.40	—
Transition Structure 10 (Alt TS 5)	3.84	2.76	2.11

Table 2. Predicted theoretical and experimental KIEs for several transition structures.

Structure	C	Gas Phase KIE	G03 Onsager KIE	G09 PCM KIE	Experimental KIE 1	Experimental KIE 2
Transition Structure 5	1	1.009	1.010	1.012	1.009(3)	1.009(14)
	2	1.008	1.008	1.009	1.008(5)	1.009(7)
	3	1.013	1.013	1.015	1.008(5)	1.012(7)
	4	1.000	1.000	1.000	0.996(4)	1.004(8)
	5	1.049	1.049	1.048	1.049(3)	1.051(7)
	6	0.999	0.999	1.000	1.002(3)	1.003(7)
	7	1.000	1.000	1.001	1.002(3)	1.003(7)
	8	0.997	0.998	0.998	1.000	1.000
Transition Structure 6 (Alt TS 1)	1	1.008	1.011	1.013	1.009(3)	1.009(14)
	2	1.006	1.007	1.008	1.008(5)	1.009(7)
	3	1.010	1.011	1.012	1.008(5)	1.012(7)
	4	1.001	1.002	1.002	0.996(4)	1.004(8)
	5	1.050	1.051	1.051	1.049(3)	1.051(7)
	6	0.999	0.999	1.000	1.002(3)	1.003(7)
	7	1.000	1.000	1.000	1.002(3)	1.003(7)
	8	0.997	0.998	0.998	1.000	1.000
Transition Structure 7 (Alt TS 2)	1	1.010	1.010	—	1.009(3)	1.009(14)
	2	1.009	1.008	—	1.008(5)	1.009(7)
	3	1.008	1.009	—	1.008(5)	1.012(7)
	4	1.001	1.000	—	0.996(4)	1.004(8)
	5	1.050	1.049	—	1.049(3)	1.051(7)
	6	0.999	0.999	—	1.002(3)	1.003(7)
	7	1.000	0.998	—	1.002(3)	1.003(7)
	8	0.997	0.996	—	1.000	1.000
Transition Structure 10 (Alt TS 5)	1	1.009	1.010	1.012	1.009(3)	1.009(14)
	2	1.008	1.008	1.009	1.008(5)	1.009(7)
	3	1.011	1.013	1.015	1.008(5)	1.012(7)
	4	1.000	1.000	1.000	0.996(4)	1.004(8)
	5	1.050	1.048	1.048	1.049(3)	1.051(7)
	6	0.999	0.999	1.000	1.002(3)	1.003(7)
	7	1.000	1.000	1.001	1.002(3)	1.003(7)
	8	0.997	0.997	0.998	1.000	1.000

Further calculations into the energetics of the rearrangement were performed and are shown in Table 3. Structure 5 and the two lowest energy alternate structures were further evaluated at the Becke3LYP/6-31+G** level using Gaussian09⁴¹ (G09) and a PCM solvent model for comparison. Structural information is included in the Appendix.

Table 3. Calculated gas phase and solvent model ΔG 's/ ΔG^\ddagger 's.

Calculated Structure	Gas Phase $\Delta G/\Delta G^\ddagger$ (kcal/mol)	G03 Onsager $\Delta G/\Delta G^\ddagger$ (kcal/mol)	G09 PCM $\Delta G/\Delta G^\ddagger$ (kcal/mol)
Deprotonated Intermediate for 5	0	0	0
Transition Structure 5	5.13	7.42	9.87
Product from 5	-38.75	-35.66	-32.07
Deprotonated Intermediate for 6	3.24	2.83	2.49
Transition Structure 6 (Alt TS 1)	6.95	8.92	10.68
Product from 6	-36.17	-33.33	-23.22
Deprotonated Intermediate for 7	5.95	3.26	—
Transition Structure 7 (Alt TS 2)	11.19	11.82	—
Product from 7	-38.40	-35.16	—
Deprotonated Intermediate for 10	5.25	3.08	2.21
Transition Structure 10 (Alt TS 5)	8.98	10.17	11.98
Product from 10	-35.67	-32.57	-29.52

Discussion

Examining **5**, the transition state is indeed early, as expected from the experimental KIEs. Interestingly, the barrier of the rearrangement from the ylide structure increases from the gas phase to the solution phase, from 5.13 kcal/mol to 7.42 kcal/mol, further increasing to 9.87 kcal/mol in the G09 calculations (structure **5**). The barrier in each case is relatively low, while the reaction is highly exothermic, as expected from Hammond's postulate, and in agreement with previous work by Heard and Yates^{11a}, as well as calculations by Jursic.²⁶ The exothermicity, however, does decrease with the solvent model, similarly to how the barrier increases. The second lowest energy transition structure (**6**) shows a lower barrier for rearrangement from the corresponding starting material than does structure **5**; in addition, the difference in energy between the two transition structures drops from 1.82 kcal/mol in the gas phase down to 0.81 kcal/mol in the G09 calculations. It is therefore likely that structure **6** contributes to the actual nature of the reaction; however, in looking at the predicted versus experimental KIEs for both **5** and **6**, one notes that the KIEs are relatively similar between the two, and so a weighted average of the KIEs would make little difference; in addition, in comparing transition structures **5** and **6**, one notes the two structures are very similar, with difference resulting from the orientation of the allyl group, as might be expected in order to generate alternate configurations of the product. In addition, the qualitative results from the associated KIEs and energetics do not differ from those of the lowest energy transition state, and the KIEs for both structures agree with experimental values.

CHAPTER IV

EXPERIMENTAL

General Computational Procedures

Standard procedures using Gaussian 03³⁶ and Gaussian 09⁴¹ were performed for optimization of structures and energies. Vibrational frequency analyses were performed for all stationary points and used to calculate predicted KIEs.

General Experimental Procedures

Materials for all reactions were purchased from Sigma-Aldrich and used without further purification unless otherwise specified.

General NMR Methodology. ¹H and ¹³C spectra were recorded on Mercury 300, Inova 300, NMRS 300, and Unity 500 spectrometers. Simultaneous determination of kinetic isotope effects used identical techniques in all cases. All KIE measurements were performed using product KIEs. This procedure involves running a reaction to 100% conversion, then running a reaction under identical conditions to low (10-20%) conversion. Product from both reactions is isolated and NMR samples prepared. Starting material for both high and low conversion reactions was obtained from the same synthetic lot. NMR samples for both high and low conversion reactions were prepared in an identical fashion. This involves filling a 5 mm NMR tube containing an identical quantity of material, on the order of 300-500 mg, to a height of 5 cm with deuterated

solvent. Inclusion of the deuterated solvent assists in shimming during NMR acquisitions.

In order to perform measurements using inverse-gated decoupling, and to avoid integration errors from paramagnetic impurities in the sample, T1 values were determined for each sample by the inversion-recovery method. The ^{13}C spectra for KIE determination were recorded on a Unity 500 NMR at constant temperature, with delays of at least $5xT1$ between pulses. ^{13}C integrations for each spectrum were determined numerically using a constant integration for each peak based upon the peak width at half height, generally $\approx 10x$ half height, but in some cases reduced to $\approx 5x$ half height in order to prevent integration of minor impurities in the sample. In all cases, a zeroth order baseline correction was applied, but a first order (tilt) correction was not applied. Six spectra were recorded for each sample of rearranged product. The acquisition time, spectra width, and number of points was optimized to obtain necessary resolution.

Determination of Kinetic Isotope Effects. The ratio of integrations (R/R_0) was taken from the NMR spectra of the full conversion and low conversion samples, with standard deviations calculated from equation 8. General uncertainty from the measurement of R/R_0 using this method is minimal at low conversion, and increases as conversion increases. Uncertainty in the measurement of F was not expected to play a significant role in the uncertainty of the KIE determination, and no allowance was made for this factor. KIEs were calculated from the fractionation (F) and the ratio of integrations (R/R_0) using equation 9, with the standard deviations calculated from equations 10 and 11. Equation 9 is a perturbation of equation 4 from Chapter I, taken

from *Reaction Rates of Isotopic Molecules*, Melander and Saunders.⁴² Equation 10 and 11 are derived from equations 6 and 7, respectively, in Chapter I. Equations 3-7 are taken from: Thomas, A. A.; Singleton, D. A. *J. Am. Chem. Soc.* **1995**, *117*, 9357-9358, its references, and supporting information.

$$\Delta(R/R_0) = (R/R_0) \cdot ((\Delta \text{IntSample} / \text{IntSample})^2 + (\Delta \text{IntStandard} / \text{IntStandard})^2)^{1/2} \quad (8)$$

$$KIE_{\text{calcd}} = \frac{\ln(1-F)}{\ln[1-(FR/R_0)]} \quad (9)$$

$$\Delta KIE_R = \frac{\partial KIE}{\partial (R/R_0)} \Delta(R/R_0) = \frac{F \ln(1-F)}{[1-(FR/R_0)] \ln^2[1-(FR/R_0)]} \Delta(R/R_0) \quad (10)$$

$$\Delta KIE = \Delta KIE_R \quad (11)$$

Synthesis of *N,N*-dimethylglycine methyl ester **4**

Experimental Procedure. To a clean 250-mL round-bottomed flask equipped with a condenser were added 15.07 g (120 mmol) of glycine methyl ester hydrochloride **3**, 35 mL (465 mmol) of formaldehyde (37% solution in water), and 40 mL (917 mmol) of formic acid. The solution was allowed to reflux while stirring with a magnetic stirrer for 4 h. The hydrochloride salt was concentrated under reduced pressure, free-based with saturated K_2CO_3 solution, and extracted with methylene chloride (DCM). The organic layer was dried with sodium sulfate (Na_2SO_4) and concentrated under reduced pressure, then purified via short-path distillation (60°C, 26.7 mbars), giving **4** as a clear oil, which was obtained in $\approx 30\%$ yield. Generally several reactions were run, and the crude product collected combined on the order of 20-30 grams prior to distillation.

Synthesis of *N*-allyl-*N,N*-dimethylglycine methyl ester **1**

Experimental Procedure. To a 250-mL round-bottomed flask containing 19.07 g (163 mmol) of **4** were added 40 mL of acetonitrile, and then the sample was dissolved to form a solution. Then 19.72 g (163 mmol) of allyl bromide were added and the reaction mixture stirred with a magnetic stirrer at room temperature (r.t.) for 20 h. The solution was concentrated under reduced pressure until **1** was crystallized as an off-white solid, which was obtained in $\approx 70\%$ yield.

DBU-Induced Rearrangement of **1**

General Methodology. All glassware, magnetic stirring bars, and molecular sieves used in these reactions were oven-dried overnight. Glassware was used and/or placed under nitrogen (N_2) as quickly as possible after being removed from the oven. All DMF used in these reactions was dried using 4Å molecular sieves in the following manner: approximately 500 mL of DMF were added to a bottle containing ≈ 30 g of molecular sieves and allowed to dry for 24 h. A 250-mL three-necked flask was fitted with a ≈ 15 cm long, 0.75 cm diameter straight condenser packed with molecular sieves, and sealed with septa and parafilm. Approximately 100 mL of DMF were then passed through the condenser under N_2 , then the condenser was removed and the flask sealed. DMF added to reactions was removed from the flask via syringe. Procedures for working up the reactions, as well as the amount of base added to the sample reactions, varied between sets 1 and 2 of KIE samples. The procedures for purifying the material were altered for sample and standard 2 in order to gain better purity; the increase in the mol% of base added was undertaken in an attempt to increase the yield of product from

the reactions vs. the amount recovered from the first set of reactions. Workup conditions were identical for each set of sample and standard to maintain the integrity of the NMR measurements.

Experimental Procedure Sample 1. A 250-mL round-bottomed flask containing a magnetic stirrer was placed under N₂, then 20.18 g (84.8 mmol) of **1** and 1.81 g (10.0 mmol) of *trans*-stilbene were added, working as quickly as possible, and the flask returned to N₂. 25 mL of DMF were added via an oven-dried syringe to the flask under N₂, and the reactants dissolved. Then ≈15 mol% DBU (1.98 g, 14.8 mmol) and 24 g of 4Å powdered molecular sieves were added and the mixture left stirring for 30 min at r.t., allowing the reaction to proceed to 11.7% conversion. The reaction mixture was diluted by the sequential addition of 40 mL of chloroform (CHCl₃) and 70 mL of water, and then the organic layer was extracted with CHCl₃. The organic layer was washed with water, then dried with Na₂SO₄ and concentrated under reduced pressure. The residual organics were dissolved in 150 mL of diethyl ether (Et₂O), washed twice with water, then dried with Na₂SO₄ and concentrated under reduced pressure. The crude compound **2** was purified by flash chromatography using 1% methanol (MeOH) in DCM. The results were then analyzed by NMR using CDCl₃ as a solvent. Isolated product was then used to prepare a low-conversion KIE sample by the addition of 0.30 g of product to a 5 mm NMR tube, which was filled to 5.5 cm with CDCl₃.

Experimental Procedure Sample 2. A 250-mL round-bottomed flask containing a magnetic stirrer was placed under N₂, then 17.67 g (74.3 mmol) of **1** and 1.82 g (10.1 mmol) of *trans*-stilbene were added, working as quickly as possible, and the

flask returned to N₂. 30 mL of DMF were added via an oven-dried syringe to the flask under N₂, and the reactants dissolved. Then ≈20 mol% DBU (2.33 g, 15.3 mmol) and 35 g of 4Å powdered molecular sieves were added and the mixture left stirring for 30 min at r.t., allowing the reaction to proceed to 21.3% conversion. The reaction mixture was diluted by the sequential addition of 40 mL of DCM and 70 mL of water, and then the organic layer was extracted with DCM. The organic layer was washed twice with water and once with a saturated solution of sodium carbonate (Na₂CO₃), then was dried with Na₂SO₄ and concentrated under reduced pressure. The residual organics were dissolved in 180 mL of Et₂O, washed twice with water and once with brine, then dried with Na₂SO₄ and concentrated under reduced pressure. The crude compound **2** was purified by flash chromatography using a gradient of DCM followed by 1% MeOH in DCM. The results were then analyzed by NMR using CDCl₃ as a solvent. Isolated product was then used to prepare a low-conversion KIE sample by the addition of 0.50 g product to a 5 mm NMR tube, which was filled to 5 cm with CDCl₃.

Experimental Procedure Standard 1. A 100-mL round-bottomed flask containing a magnetic stirrer was placed under N₂, then 3.57 g (15 mmol) of **1** and 0.90 g (5 mmol) of *trans*-stilbene were added, working as quickly as possible, and the flask returned to N₂. 15 mL of DMF were added via an oven-dried syringe to the flask under N₂, and the reactants dissolved. Then 9.13 g (60 mmol, 4 eq.) of DBU and 12 g of 4Å powdered molecular sieves were added and the mixture left stirring for 3h at r.t., allowing the reaction to proceed to 100% conversion. The reaction mixture was diluted by the sequential addition of 40 mL of CHCl₃ and 70 mL of water, and then the organic

layer was extracted with CHCl_3 . The organic layer was washed with water, then dried with Na_2SO_4 and concentrated under reduced pressure. The residual organics were dissolved in 150 mL of Et_2O , washed twice with water, then dried with Na_2SO_4 and concentrated under reduced pressure. The crude compound **2** was purified by flash chromatography using 1% MeOH in DCM. The results were then analyzed by NMR using CDCl_3 as a solvent. Isolated product was then used to prepare a low-conversion KIE sample by the addition of 0.30 g of product to a 5 mm NMR tube, which was filled to 5.5 cm with CDCl_3 .

Experimental Procedure Standard 2. A 100-mL round-bottomed flask containing a magnetic stirrer was placed under N_2 , then 3.57 g (15 mmol) of **1** and 0.90 g (5 mmol) of *trans*-stilbene were added, working as quickly as possible, and the flask returned to N_2 . 15 mL of DMF were added via an oven-dried syringe to the flask under N_2 , and the reactants dissolved. Then 9.13 g (60 mmol, 4 eq.) of DBU and 12 g of 4Å powdered molecular sieves were added and the mixture left stirring for 3h at r.t., allowing the reaction to proceed to 100% conversion. The reaction mixture was diluted by the sequential addition of 40 mL of DCM and 70 mL of water, and then the organic layer was extracted with DCM. The organic layer was washed twice with water and once with a saturated solution of sodium carbonate (Na_2CO_3), then was dried with Na_2SO_4 and concentrated under reduced pressure. The residual organics were dissolved in 180 mL of Et_2O , washed twice with water and once with brine, then dried with Na_2SO_4 and concentrated under reduced pressure. The crude compound **2** was purified by flash chromatography using a gradient of DCM followed by 1% MeOH in DCM. The results

Table 5. ^{13}C Integrations for Methyl-2-(*N,N*-dimethylamino)-4-pentenoate **2**, KIE set 2.

% Conv.	C	Fid 1	Fid 2	Fid 3	Fid 4	Fid 5	Fid 6	Avg
21.3	1	1035.73	1033.27	1035.52	1035.63	1033.52	1034.98	1034.78
	2	982.88	982.34	981.27	984.17	981.50	983.51	982.61
	3	978.47	978.82	978.29	980.28	975.52	979.46	978.47
	4	1006.73	1006.10	1008.43	1008.49	1007.56	1007.77	1007.51
	5	939.80	938.98	940.83	938.42	938.25	938.22	939.08
	6	1939.59	1937.62	1939.77	1939.37	1938.43	1940.70	1939.25
	7	1939.59	1937.62	1939.77	1939.37	1938.43	1940.70	1939.25
	8	1000.00	1000.00	1000.00	1000.00	1000.00	1000.00	1000.00
100	1	1034.30	1042.44	1063.81	1038.86	1051.07	1028.33	1043.14
	2	991.15	983.71	998.23	983.32	995.26	990.64	990.38
	3	988.68	979.68	996.14	984.43	992.64	989.61	988.53
	4	1012.56	1000.84	1018.52	1003.42	1013.83	1014.73	1010.65
	5	979.83	973.19	989.73	978.11	986.39	981.49	981.46
	6	1945.72	1929.62	1961.08	1931.93	1952.09	1944.54	1944.16
	7	1945.72	1929.62	1961.08	1931.93	1952.09	1944.54	1944.16
	8	1000.00	1000.00	1000.00	1000.00	1000.00	1000.00	1000.00

Figures 6 through 12 contain spectral information regarding the different materials synthesized; figures 6-8 detail compound 2, figures 9-11 detail compound 1, and figure 12 details compound 4.

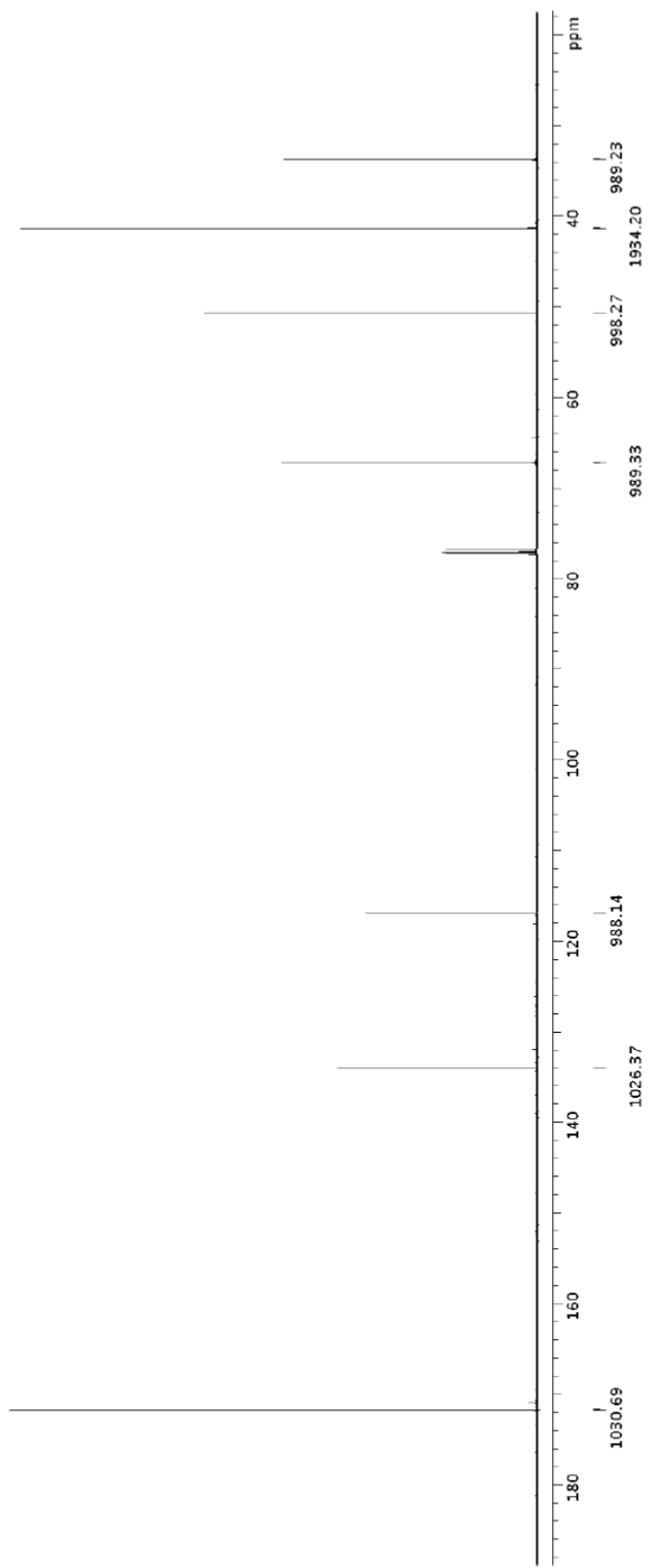


Figure 6. Sample ¹³C NMR of **2**; (CDCl₃); δ_c 33.7, 41.3, 50.6, 67.2, 116.8, 134.0, 171.7.

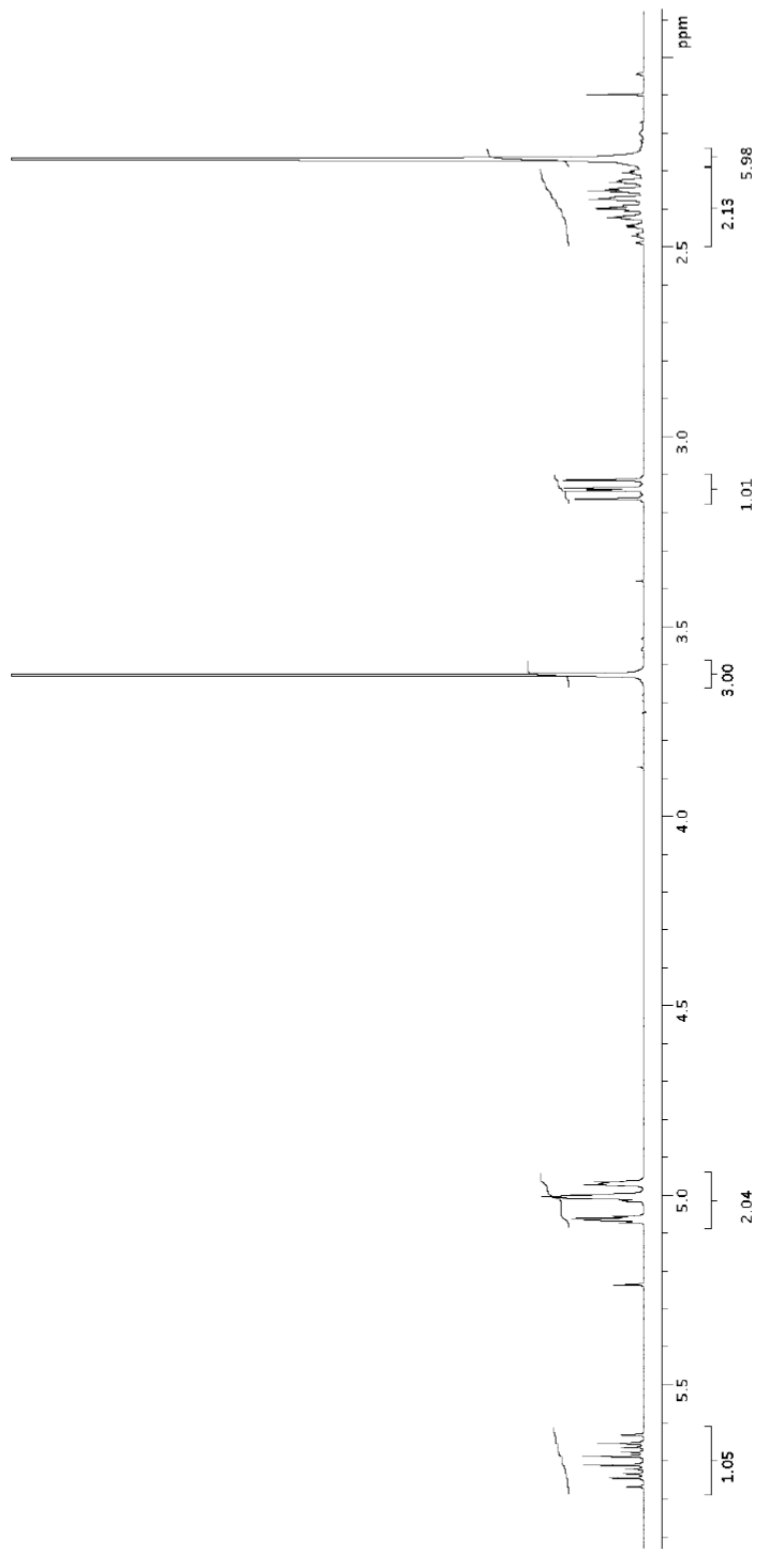


Figure 7. Sample ¹H NMR of **2** (CDCl₃); δ_H 2.26 (s, 6H), 2.35 (m, 2H), 3.1 (dd, 1H), 3.6 (s, 3H), 5.0 (m, 2H), 5.7 (m, 1H).

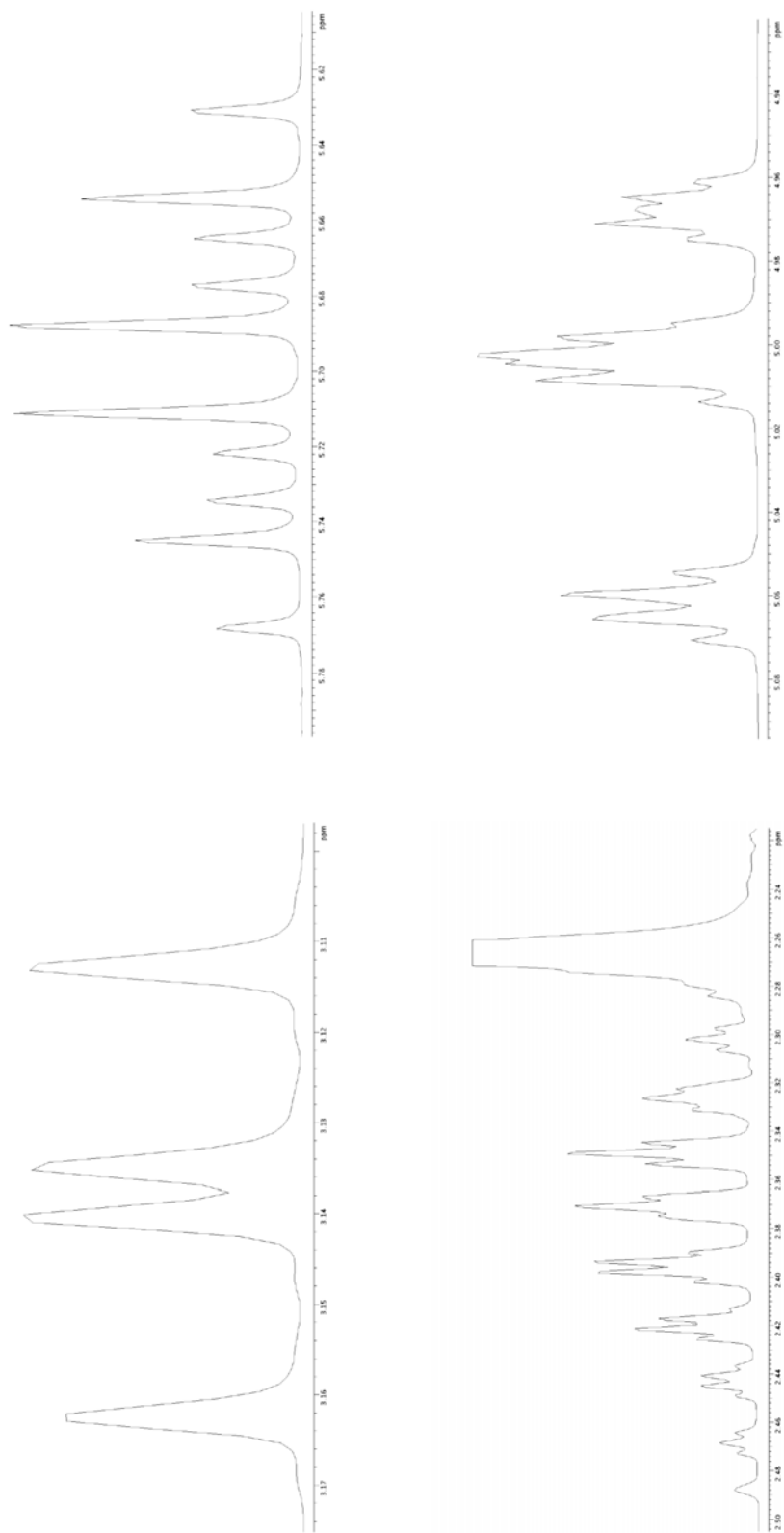


Figure 8. Expanded regions for ^1H spectrum of **2**.

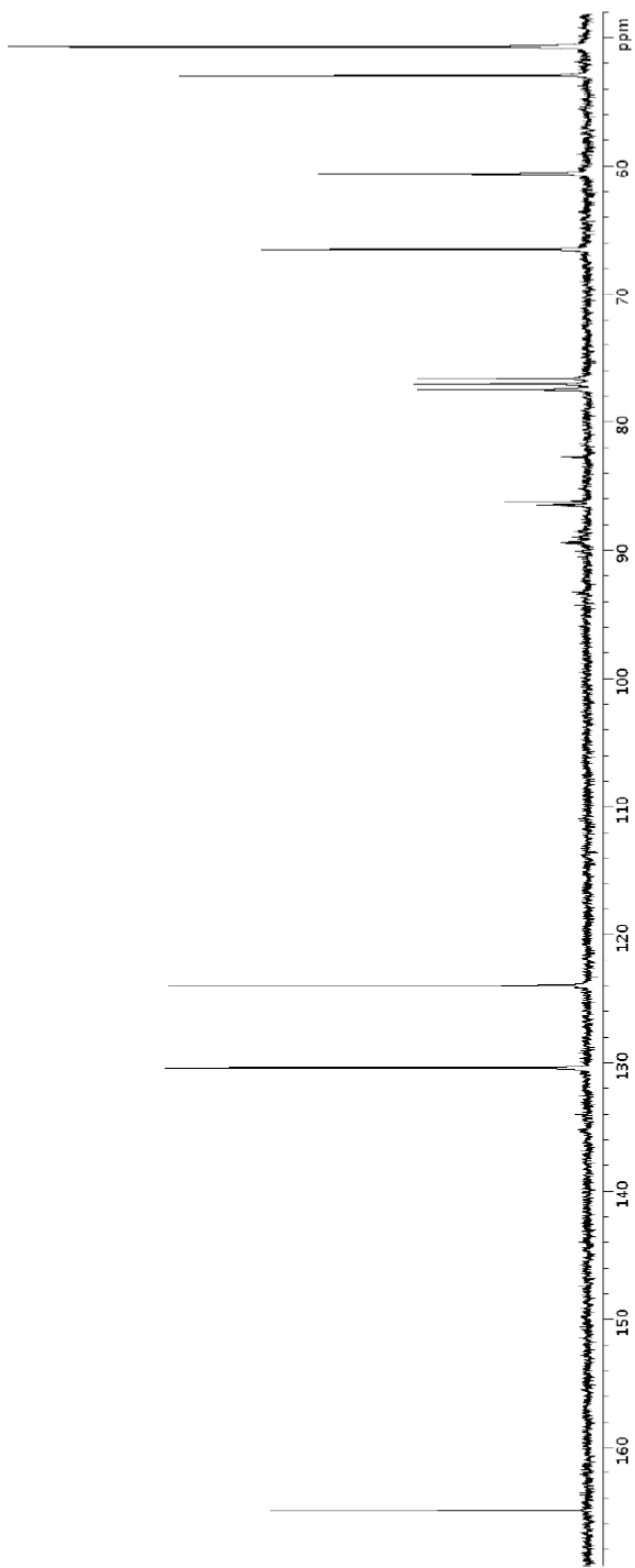


Figure 9. Sample ^{13}C NMR of **1** (CDCl_3); δ_{C} 50.7, 52.9, 60.6, 66.5, 123.9, 130.3, 164.9.

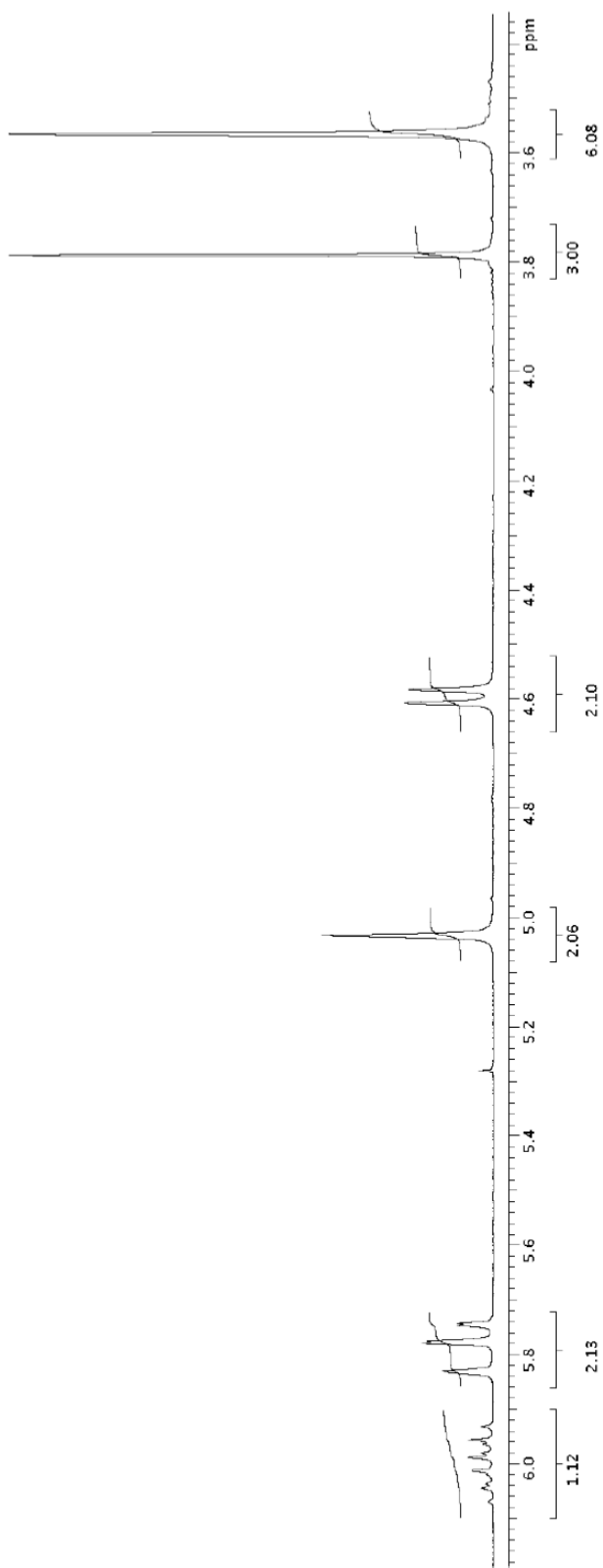


Figure 10. Sample ¹H NMR of **1** (CDCl₃); δ_H 3.56 (s, 6H), 3.8 (s, 3H), 4.6 (d, 2H), 5.0 (s, 2H), 5.8 (m, 2H), 6.0 (m, 1H).

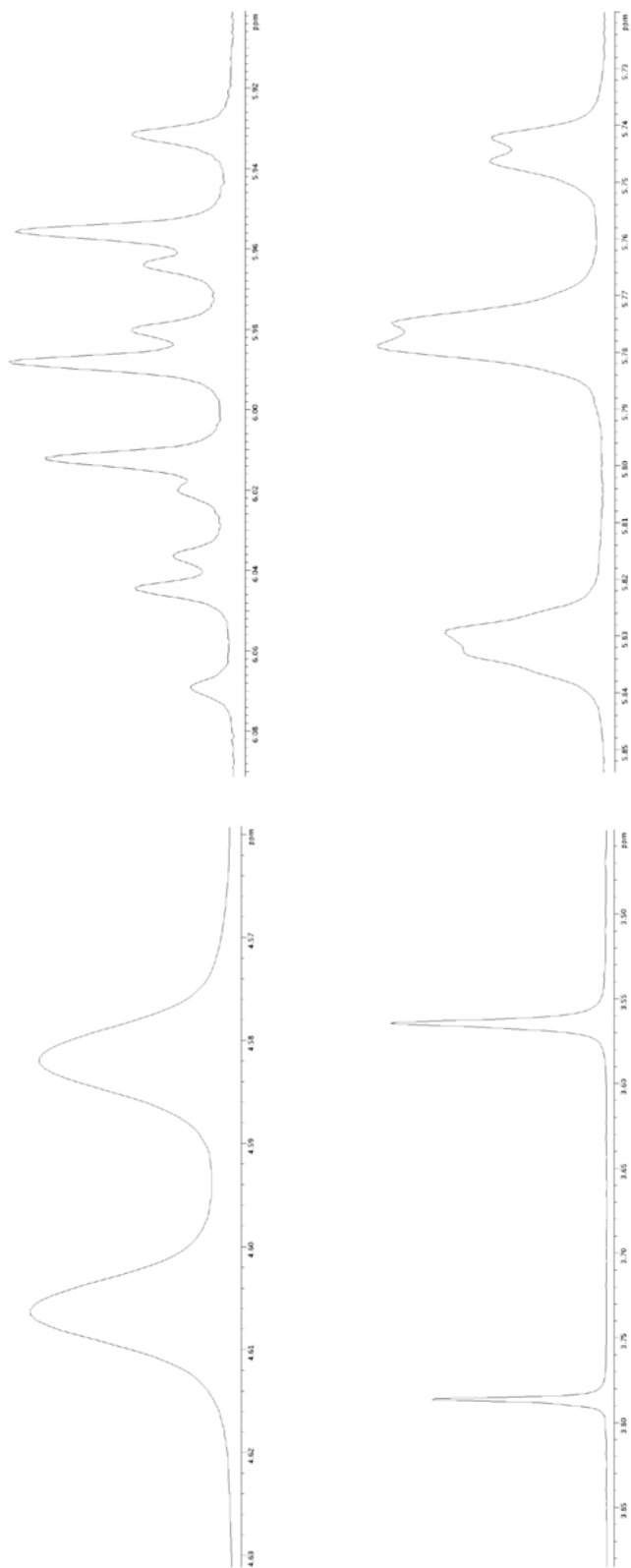


Figure 11. Expanded regions for ^1H spectrum of **1**.

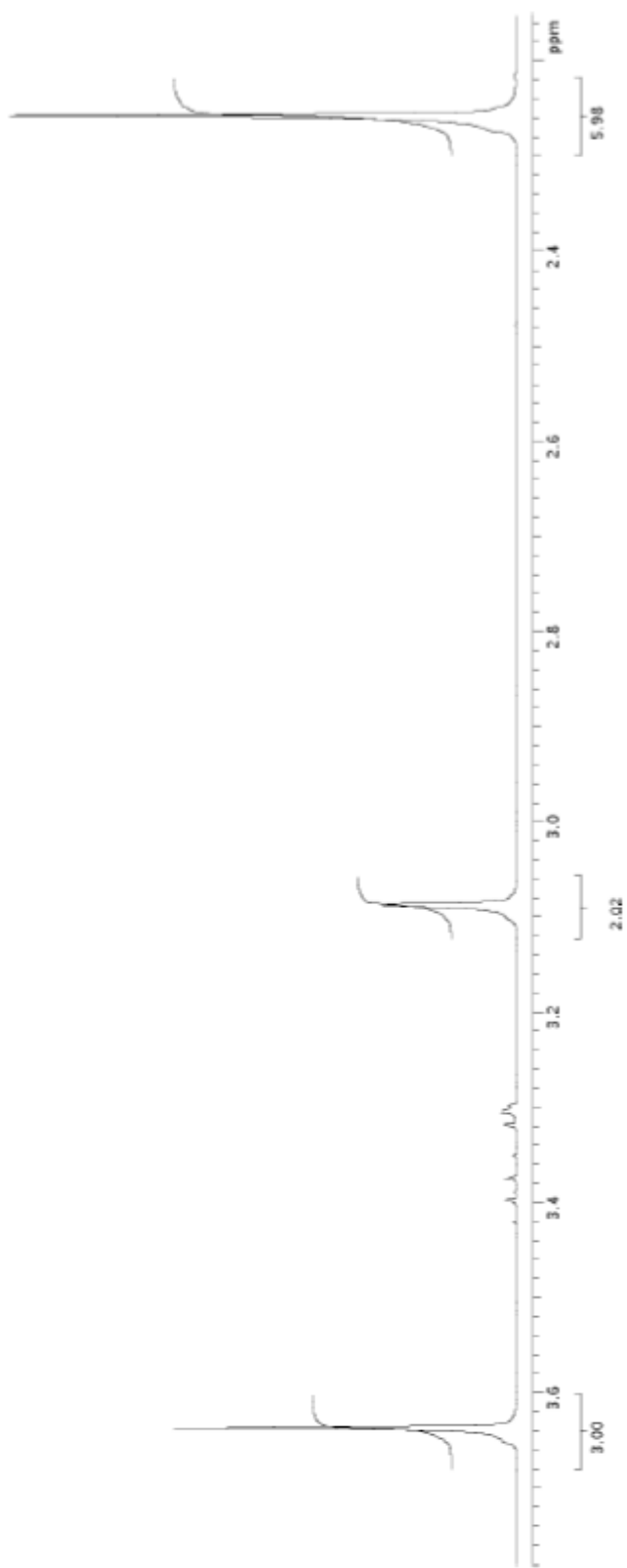


Figure 12. Sample ^1H NMR of **4** (CDCl_3); δ_{H} 2.26 (s, 6H), 3.1 (s, 2H), 3.6 (s, 3H).

CHAPTER V

CONCLUSIONS

In physical organic chemistry, the ability to measure experimental kinetic isotope effects and the power of theoretical calculations are particularly effective tools. Determination of KIEs alone can yield valuable insight into the general mechanism of a reaction. When compared with theoretically predicted heavy-atom KIEs, this tool becomes still more effective, permitting evaluation between correct and incorrect transition structures. This is important, because an understanding of the transition structure and the associated mechanism involved in a reaction allows chemists to push forward reaction optimization, as well as develop new synthetic strategies to affect various synthetic goals.

Exploring the Sommelet-Hauser [2,3]-sigmatropic rearrangement of this glycine-derived ammonium ylide, the combined use of experimental and theoretically predicted KIEs allowed for in-depth analysis of the reaction. As evidenced by the results shown in Figure 5, the predicted theoretical KIEs match very well with experimental data. Examining the lowest-energy transition structure (**5**), the bond changes occurring between the deprotonated intermediate and the transition structure reflect an early transition state. Furthermore, subsequent calculations of energetics have demonstrated that the reaction is highly exothermic, with a relatively small energy barrier to the rearranged product, as expected for an early transition state according to Hammond's

postulate. This matches well with the geometry of the transition structure, with minor bond dissociation and little bond formation at the transition state. The difference in energy determined between the lowest energy and second lowest energy transition structures decreases to 0.81 kcal/mol in the PCM solvent model, so we cannot exclude the contribution of this transition structure to the reaction. However, qualitative results of the associated KIEs and energetics do not differ from those of the lowest energy transition structure. Overall, our results are in agreement with previous work by previous researchers such as Heard and Yates.^{11a}

The ability of the computational methods used to replicate experimental results, as well as the relatively harmonious nature of the experimental KIE measurements, has demonstrated that, at least for such ammonium ylide type starting materials, the Singleton method has proven successful in addressing the nature of the transition state geometry involved in the reaction. While the particular reaction studied does not appear to generate multiple products from the same transition state, and so does not seem to be a case in which dynamic effects are particularly contributing in terms of the reaction selectivity, nevertheless, it has demonstrated that the Singleton method should be effective in evaluating future [2,3]-sigmatropic rearrangements, which would likely exhibit such dynamic effects. Furthermore, this study has again validated the ability of KIE measurements to elucidate the mechanism of an organic reaction, and is, so far as we know, among the only studies to make such an evaluation of this particular class of pericyclic reactions.

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APPENDIX

TABLE OF CONTENTS

Terms:	54
Theoretical Structures from Chapter III.....	54
G03 Calculations: Gas Phase Structures.....	54
Glycine Salt 1 Rearrangement Transition Structures.....	54
Structure 5 B3LYP/6-31+G**, File glycinetsgp.....	54
Structure 6 B3LYP/6-31+G**, File glycinets2gp.....	56
Structure 7 B3LYP/6-31+G**, File glycinets3gp.....	57
Structure 8 B3LYP/6-31+G**, File glycinets4gp.....	58
Structure 9 B3LYP/6-31+G**, File glycinets5gp.....	59
Structure 10 B3LYP/6-31+G**, File glycinets6gp.....	60
Glycine Salt 1 Starting Material Optimized Structure.....	61
Structure 5 SM B3LYP/6-31+G**, File glycinesmgp.....	61
Structure 6 SM B3LYP/6-31+G**, File glycinesm2gp.....	62
Structure 7 SM B3LYP/6-31+G**, File glycinesm3gp.....	63
Structure 10 SM B3LYP/6-31+G**, File glycinesm6gp.....	64
Deprotonated Glycine Salt 1 Starting Material Optimized Structure	65
Structure 5 Int B3LYP/6-31+G**, File glydeprotonsmgp.....	65
Structure 6 Int B3LYP/6-31+G**, File glydeprotonsm2gp.....	66
Structure 7 Int B3LYP/6-31+G**, File glydeprotonsm3gp.....	67
Structure 10 Int B3LYP/6-31+G**, File glydeprotonsm6gp.....	67
Rearranged Product 2 Optimized Structure	68
Structure 5 Prod B3LYP/6-31+G**, File productoptgp.....	68
Structure 6 Prod B3LYP/6-31+G**, File productopt2gp.....	69
Structure 7 Prod B3LYP/6-31+G**, File productopt3gp.....	70
Structure 10 Prod B3LYP/6-31+G**, File productopt6gp.....	71
G03 Calculations: Solution Phase Structures.....	72
Glycine Salt 1 Rearrangement Transition Structures.....	72
(5) B3LYP/6-31+G**, Onsager, $\epsilon=37.219$, $a_0=4.71$, File glycinetsdielec.....	72
(6) B3LYP/6-31+G**, Onsager, $\epsilon=37.219$, $a_0=4.71$, File glycinets2dielec.....	73
(7) B3LYP/6-31+G**, Onsager, $\epsilon=37.219$, $a_0=4.71$, File glycinets3dielec	74
(10) B3LYP/6-31+G**, Onsager, $\epsilon=37.219$, $a_0=4.71$, File glycinets6dielec.....	75
Glycine Salt 1 Starting Material Optimized Structure	76
(5) B3LYP/6-31+G**, Onsager, $\epsilon=37.219$, $a_0=4.58$, File glycinesmdielec.....	76
(6) B3LYP/6-31+G**, Onsager, $\epsilon=37.219$, $a_0=4.58$, File glycinesm2dielec.....	77
(7) B3LYP/6-31+G**, Onsager, $\epsilon=37.219$, $a_0=4.58$, File glycinesm3dielec	78
(10) B3LYP/6-31+G**, Onsager, $\epsilon=37.219$, $a_0=4.58$, File glycinesm6dielec.....	78
Deprotonated Glycine Salt 1 Starting Material Optimized Structure	80
(5) B3LYP/6-31+G**, Onsager, $\epsilon=37.219$, $a_0=4.52$, File glydeprotonsmdielec.....	80
(6) B3LYP/6-31+G**, Onsager, $\epsilon=37.219$, $a_0=4.52$, File glydeprotonsm2dielec.....	81
(7) B3LYP/6-31+G**, Onsager, $\epsilon=37.219$, $a_0=4.52$, File glydeprotonsm3dielec.....	82
(10) B3LYP/6-31+G**, Onsager, $\epsilon=37.219$, $a_0=4.52$, File glydeprotonsm6dielec.....	82
Rearranged Product 2 Optimized Structure	83
(5) B3LYP/6-31+G**, Onsager, $\epsilon=37.219$, $a_0=4.52$, File productoptdielec.....	83

(6) B3LYP/6-31+G**, Onsager, $\epsilon=37.219$, $a_0=4.52$, File productopt2dielec.....	84
(7) B3LYP/6-31+G**, Onsager, $\epsilon=37.219$, $a_0=4.52$, File productopt3dielec.....	85
(10) B3LYP/6-31+G**, Onsager, $\epsilon=37.219$, $a_0=4.52$, File productopt6dielec.....	86
G09 Calculations: Solution Phase Structures.....	87
Glycine Salt 1 Rearrangement Transition Structures	87
(5) B3LYP/6-31+G**, PCM, Solvent=n,n-DimethylFormamide File glycinetsg09.....	87
(6) B3LYP/6-31+G**, PCM, Solvent=n,n-DimethylFormamide File glycinets2g09.....	89
(10) B3LYP/6-31+G**, PCM, Solvent=n,n-DimethylFormamide File glycinets6g09.....	89
Glycine Salt v Starting Material Optimized Structure.....	90
(5) B3LYP/6-31+G**, PCM, Solvent=n,n-DimethylFormamide File glycinesmg09.....	90
(6) B3LYP/6-31+G**, PCM, Solvent=n,n-DimethylFormamide File glycinesm2g09.....	91
(10) B3LYP/6-31+G**, PCM, Solvent=n,n-DimethylFormamide File glycinesm6g09.....	91
Deprotonated Glycine Salt 1 Starting Material Optimized Structure	92
(5) B3LYP/6-31+G**, PCM, Solvent=n,n-DimethylFormamide File glydeprotonsmg09.....	92
(6) B3LYP/6-31+G**, PCM, Solvent=n,n-DimethylFormamide File glydeprotonsm2g09.....	94
(10) B3LYP/6-31+G**, PCM, Solvent=n,n-DimethylFormamide File glydeprotonsm6g09.....	94
Rearranged Product 2 Optimized Structure	95
(5) B3LYP/6-31+G**, PCM, Solvent=n,n-DimethylFormamide File productoptg09.....	95
(6) B3LYP/6-31+G**, PCM, Solvent=n,n-DimethylFormamide File productopt2g09.....	98
(10) B3LYP/6-31+G**, PCM, Solvent=n,n-DimethylFormamide File productopt6g09.....	97
VITA.....	98

Terms:

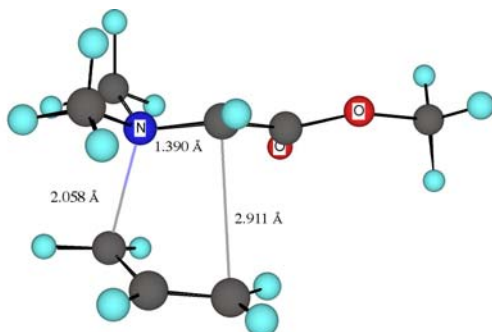
B3: Becke 3-parameter exchange model
 LYP: Lee-Yang-Parr gradient-corrected functionals
 RB: Restricted Becke
 HF: Hartree-Fock

Theoretical Structures from Chapter III

G03 Calculations: Gas Phase Structures

Glycine Salt **1** Rearrangement Transition Structures

Structure 5, B3LYP/6-31+G**, File glycinetsgp



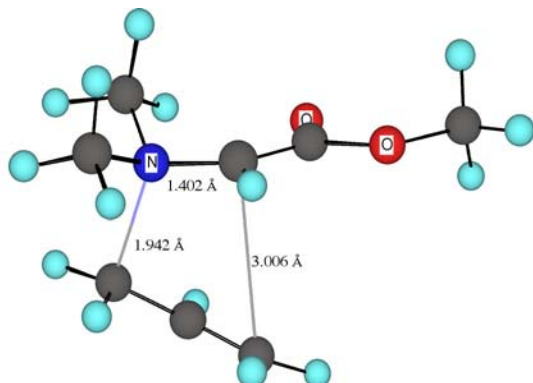
E(RB+HF-LYP) = -519.019890402

Zero-point correction= 0.222957 (Hartree/Particle)
 Thermal correction to Energy= 0.235738
 Thermal correction to Enthalpy= 0.236683
 Thermal correction to Gibbs Free Energy= 0.184608
 Sum of electronic and zero-point Energies= -518.796933
 Sum of electronic and thermal Energies= -518.784152
 Sum of electronic and thermal Enthalpies= -518.783208
 Sum of electronic and thermal Free Energies= -518.835282

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	147.928	47.021	109.600

C,0,2.0443095252,-0.8730486436,-2.3846942404
 O,0,2.7439675141,0.3731372091,-2.4709197435
 C,0,2.8301512156,0.9192810732,-3.7295078633
 C,0,3.5126932344,2.1708125866,-3.7021883315
 N,0,3.8098772809,2.8855607096,-4.8572923237
 C,0,4.679094253,4.0464596138,-4.57148554
 O,0,2.3420834881,0.3490560037,-4.7142384962
 C,0,4.3136127002,2.1141507299,-6.0223362889
 C,0,2.1346631484,3.7670219491,-5.6637222005
 C,0,1.5045358882,4.2959078683,-4.5069271327
 C,0,0.9130676086,3.4766081837,-3.5924259111
 H,0,2.0696136889,-1.1476348144,-1.3291982629
 H,0,1.0099169798,-0.7679096518,-2.724921045
 H,0,2.5354623621,-1.641421454,-2.9887709737
 H,0,3.7511394382,2.6301533254,-2.7552042853
 H,0,5.3224403406,1.7473246768,-5.8021313387
 H,0,3.6486478895,1.2721480916,-6.2023653966
 H,0,4.343651437,2.772808995,-6.8935083329
 H,0,5.6505129596,3.7003600582,-4.2010702034
 H,0,4.8208278725,4.6281736205,-5.4838434197
 H,0,4.2042284379,4.669836544,-3.8124174792
 H,0,2.5531351341,4.4443307197,-6.4043621286
 H,0,1.7649641431,2.8246605353,-6.0568177092
 H,0,1.6724140343,5.3422436714,-4.2541181221
 H,0,0.6770317315,2.4463906361,-3.8342582227
 H,0,0.5622116941,3.8510487626,-2.6353150083

Structure 6, B3LYP/6-31+G**, File glycinets2gp



E(RB+HF-LYP) = -519.016247196

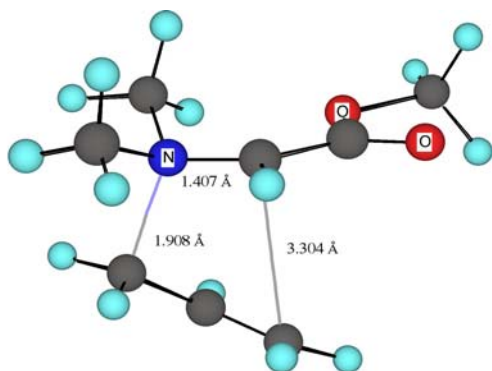
Zero-point correction= 0.222904 (Hartree/Particle)
 Thermal correction to Energy= 0.235758
 Thermal correction to Enthalpy= 0.236702
 Thermal correction to Gibbs Free Energy= 0.183862
 Sum of electronic and zero-point Energies= -518.793343
 Sum of electronic and thermal Energies= -518.780490
 Sum of electronic and thermal Enthalpies= -518.779545
 Sum of electronic and thermal Free Energies= -518.832385

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	147.940	46.965	111.211

C,0,1.6671848631,-0.1891409476,-2.2382030013
 C,0,1.4394735469,-0.2765955968,-0.9061291227
 C,0,0.2128326445,-0.8212355128,-0.4010610975
 N,0,0.3663998462,-2.7404193091,-0.6552161913
 C,0,1.083676221,-3.1056942302,-1.8028776416
 C,0,2.500985054,-3.2300075396,-1.8448365465
 O,0,2.913356094,-3.6001458499,-3.1103991486
 C,0,4.3247892869,-3.7577343242,-3.2732862138
 C,0,-1.0575939036,-3.1490458207,-0.7544510258
 C,0,0.932498638,-3.2111610036,0.643720131
 O,0,3.3192193788,-3.0789825094,-0.9282651821
 H,0,4.4662586904,-4.0591460842,-4.3126205809
 H,0,4.8517410159,-2.818589999,-3.0770150357
 H,0,4.7176004878,-4.5248262298,-2.5993780972
 H,0,2.2631022137,-0.122454463,-0.2127376487
 H,0,2.6410151298,0.0801906086,-2.634658215
 H,0,0.8693860818,-0.3348580075,-2.9605168839
 H,0,-1.6213972635,-2.7013258042,0.0671198536
 H,0,-1.4674120034,-2.8055624775,-1.7053570609
 H,0,-1.1286008668,-4.2391111648,-0.7040524462
 H,0,0.2799444219,-2.8695574906,1.4497816646
 H,0,0.9744229047,-4.3042218347,0.633252811
 H,0,1.9417269211,-2.8242379059,0.7542013247

H,0,-0.6655268809,-0.6754109272,-1.0264699933
 H,0,0.0056402938,-0.7324735649,0.6630775363
 H,0,0.5166771841,-3.1686620114,-2.7199981882

Structure 7 B3LYP/6-31+G, File glycinets3gp**



E(RB+HF-LYP) = -519.010009924

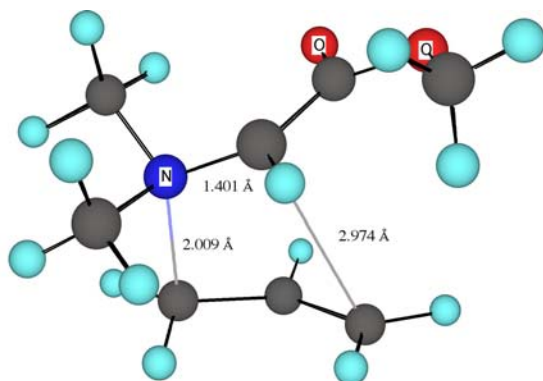
Zero-point correction= 0.223049 (Hartree/Particle)
 Thermal correction to Energy= 0.235838
 Thermal correction to Enthalpy= 0.236782
 Thermal correction to Gibbs Free Energy= 0.184383
 Sum of electronic and zero-point Energies= -518.786961
 Sum of electronic and thermal Energies= -518.774172
 Sum of electronic and thermal Enthalpies= -518.773228
 Sum of electronic and thermal Free Energies= -518.825627

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	147.990	46.935	110.282

C,0,2.3658964602,-1.2656907111,-1.9020957364
 C,0,1.8941721249,-1.1411413024,-0.6401424044
 C,0,0.4926475418,-0.9423259004,-0.3871561111
 N,0,-0.3341879932,-2.636932091,-0.6760631135
 C,0,-0.1785314098,-3.3223064224,0.6395011481
 C,0,0.1377812118,-3.3224428738,-1.8111292193
 C,0,1.2053483495,-4.2606351713,-1.9379229467
 O,0,1.5207658226,-4.7921425634,-3.0045781271
 C,0,-1.7599760299,-2.2471737832,-0.8548475673
 O,0,1.8676865867,-4.5946862989,-0.765456619
 C,0,2.9200076159,-5.554655865,-0.9191779635
 H,0,3.3155677732,-5.7179872788,0.0852216837
 H,0,2.5394487971,-6.4908057473,-1.336384646
 H,0,3.7046243,-5.1729937138,-1.578937049
 H,0,2.5438538343,-1.377767022,0.200246743
 H,0,3.3895009401,-1.5656146645,-2.1035475644
 H,0,1.7493193953,-1.0310856821,-2.7640109008
 H,0,-2.0515985606,-1.5606285836,-0.0564895427

H,0,-1.8795814299,-1.7536223425,-1.8197928889
 H,0,-2.3868668094,-3.1421181782,-0.8284012093
 H,0,-0.6621472806,-2.7121152143,1.4050158703
 H,0,-0.6528386722,-4.3056095696,0.5865797014
 H,0,0.8762395283,-3.4511561544,0.8596015518
 H,0,-0.0518516645,-0.3975045013,-1.1558551026
 H,0,0.1881353962,-0.6737021155,0.6229722503
 H,0,-0.3120328279,-3.0157062493,-2.7445592368

Structure 8 B3LYP/6-31+G, File glycinets4gp**



E(RB+HF-LYP) = -519.006477034

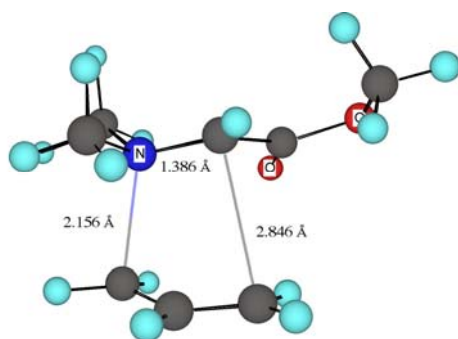
Zero-point correction= 0.223032 (Hartree/Particle)
 Thermal correction to Energy= 0.235624
 Thermal correction to Enthalpy= 0.236568
 Thermal correction to Gibbs Free Energy= 0.184798
 Sum of electronic and zero-point Energies= -518.783445
 Sum of electronic and thermal Energies= -518.770853
 Sum of electronic and thermal Enthalpies= -518.769909
 Sum of electronic and thermal Free Energies= -518.821679

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	147.856	46.901	108.959

C,0,1.6436042229,-0.0841222434,-2.1368679452
 C,0,1.5371382622,-0.2670742106,-0.7965734733
 C,0,0.3451235383,-0.7988790132,-0.2194986289
 N,0,0.3872529384,-2.743897533,-0.7190535135
 C,0,-1.045205617,-3.0213853763,-0.9805131175
 C,0,0.8032432516,-3.4046799753,0.5524217524
 C,0,1.1768432627,-3.0065619793,-1.845647904
 C,0,2.6024968386,-3.0700827373,-1.7722392677
 O,0,3.285758915,-2.9078073315,-0.7579384883
 O,0,3.2978696301,-3.3571656568,-2.9322999677
 C,0,2.6181829648,-3.6337194082,-4.1515850038
 H,0,3.3957080685,-3.8878321349,-4.8744535396
 H,0,1.9314259161,-4.4828914413,-4.0489625901

H,0,2.0668325586,-2.75814611,-4.5182988494
 H,0,2.4313145199,-0.2134219912,-0.1812347666
 H,0,2.5861690131,0.1840805694,-2.6031681157
 H,0,0.7724969187,-0.1358228486,-2.7846611741
 H,0,-1.6432053919,-2.6609994497,-0.1410170279
 H,0,-1.3562644716,-2.5072220938,-1.8915082818
 H,0,-1.1966231453,-4.098404649,-1.1031404064
 H,0,0.1184979625,-3.0950089839,1.3444689037
 H,0,0.7490587871,-4.4900762531,0.4185832262
 H,0,1.8283145365,-3.1224379577,0.7770422749
 H,0,-0.5891199437,-0.5687551733,-0.7262821195
 H,0,0.2618610223,-0.8467526749,0.8627464703
 H,0,0.6496304416,-2.985493343,-2.7861314468

Structure 9 B3LYP/6-31+G, File glycinets5gp**



E(RB+HF-LYP) = -519.010522360

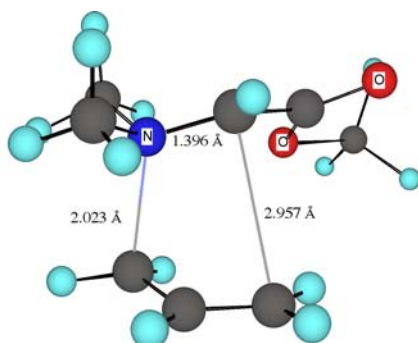
Zero-point correction= 0.223017 (Hartree/Particle)
 Thermal correction to Energy= 0.235578
 Thermal correction to Enthalpy= 0.236522
 Thermal correction to Gibbs Free Energy= 0.185253
 Sum of electronic and zero-point Energies= -518.787506
 Sum of electronic and thermal Energies= -518.774945
 Sum of electronic and thermal Enthalpies= -518.774000
 Sum of electronic and thermal Free Energies= -518.825270

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	147.827	46.978	107.905

C,0,2.0301310274,-0.8974085722,-2.3877929053
 H,0,2.5554975078,0.051499691,-2.4484912336
 H,0,1.6464550789,-1.3075770706,-3.3150154987
 C,0,2.0143783155,-1.6288594818,-1.2303432973
 H,0,2.4849852717,-1.2175373169,-0.3377568944
 C,0,1.1916401912,-2.7645167881,-1.0966251439
 H,0,0.8949183878,-3.3017709118,-1.9915184203
 H,0,1.1956164489,-3.3396207237,-0.1745739236
 N,0,-0.7288823103,-1.788998445,-1.0135006987

C,0,-0.753339991,-1.2768587992,0.3690766074
 H,0,-1.7204398659,-0.8037784761,0.5802884903
 H,0,0.0432063852,-0.5416512072,0.4954340984
 H,0,-0.5952050154,-2.1022078125,1.0652218154
 C,0,-1.636221424,-2.9493398522,-1.1801872581
 H,0,-2.665853234,-2.6395176313,-0.9629676483
 H,0,-1.5691049719,-3.3077917741,-2.2046774727
 H,0,-1.3352120969,-3.7311707139,-0.4790972693
 C,0,-0.7796100758,-0.7724258965,-1.9538996947
 H,0,-0.647826727,0.2277363859,-1.5742646238
 C,0,-0.8971533405,-1.0408118848,-3.3581472994
 O,0,-0.8616651285,-2.1585294598,-3.8764336318
 O,0,-1.0390655385,0.0283307154,-4.214507334
 C,0,-1.1409353367,1.3626582446,-3.7239411349
 H,0,-1.3040310705,1.9887212666,-4.6027378985
 H,0,-1.98854751,1.4770908268,-3.0379979024
 H,0,-0.2165659775,1.6813316875,-3.2260238276

Structure 10 B3LYP/6-31+G, File glycinets6gp**



E(RB+HF-LYP) = -519.013607840

Zero-point correction=	0.222881 (Hartree/Particle)
Thermal correction to Energy=	0.235685
Thermal correction to Enthalpy=	0.236629
Thermal correction to Gibbs Free Energy=	0.184451
Sum of electronic and zero-point Energies=	-518.790727
Sum of electronic and thermal Energies=	-518.777923
Sum of electronic and thermal Enthalpies=	-518.776978
Sum of electronic and thermal Free Energies=	-518.829157

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	147.895	47.128	109.819

C,0,2.4586657116,-1.329001609,-1.1417843833
 H,0,2.2996482316,-1.3523427634,-0.0623925949
 H,0,1.5111265754,-1.1682226028,-1.6627356567
 H,0,3.1465634578,-0.5228267239,-1.4101446446
 O,0,3.0163035617,-2.6086833614,-1.4766279901

C,0,3.3204223116,-2.7860908001,-2.819804949
 O,0,3.0777626067,-1.903257468,-3.6406220354
 C,0,3.8940504038,-4.0561308784,-3.1365461173
 H,0,3.9697520768,-4.2892342277,-4.1875907839
 N,0,4.2827607587,-5.0531043672,-2.2403242538
 C,0,5.0592523745,-4.6418173859,-1.04231819
 H,0,6.042041391,-4.2764326372,-1.3587171262
 H,0,5.1809696318,-5.5079874668,-0.3872723087
 H,0,4.5275105121,-3.8509783514,-0.5209812099
 C,0,4.9796207275,-6.152077008,-2.9499181149
 H,0,5.9051023412,-5.7731477989,-3.3963404947
 H,0,4.3282856146,-6.5350950791,-3.7361352858
 H,0,5.2107344088,-6.952250346,-2.2450565021
 C,0,2.7105256742,-6.0091368042,-1.398707241
 H,0,3.1739545737,-6.8451728847,-0.8794387388
 H,0,2.4568921724,-5.1648871056,-0.7647906281
 C,0,1.8723924884,-6.2703634212,-2.5200520614
 C,0,1.1978321197,-5.2702891401,-3.1495093596
 H,0,1.9304165514,-7.2500483627,-2.9928892491
 H,0,1.0733975486,-4.296176709,-2.690753556
 H,0,0.6862641743,-5.4343356974,-4.0931615244

Glycine Salt 1 Starting Material Optimized Structure

Structure 5 SM B3LYP/6-31+G**, File glycinesmgp

E(RB+HF-LYP) = -519.463605832

Zero-point correction= 0.240119 (Hartree/Particle)
 Thermal correction to Energy= 0.253164
 Thermal correction to Enthalpy= 0.254108
 Thermal correction to Gibbs Free Energy= 0.200539
 Sum of electronic and zero-point Energies= -519.223486
 Sum of electronic and thermal Energies= -519.210442
 Sum of electronic and thermal Enthalpies= -519.209498
 Sum of electronic and thermal Free Energies= -519.263067

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	158.863	47.509	112.747

C,0,2.1434525798,-0.935283082,-2.2746333443
 O,0,2.8477832494,0.3331040161,-2.4297119244
 C,0,2.8072864947,0.9051258822,-3.6249627488
 O,0,2.2395414365,0.4737959752,-4.6072623886
 C,0,3.5953456091,2.2146108251,-3.5561932637
 N,0,3.7141047015,2.9717104947,-4.8602527036
 C,0,4.4220440527,2.1393676937,-5.9073301822
 C,0,4.5481798397,4.2018750699,-4.5900392549
 C,0,1.4896624801,4.1881946059,-4.4715501569
 C,0,0.3093534252,3.7490070624,-4.0217433305
 C,0,2.3300605712,3.393932272,-5.4249201892

H,0,2.3097146936,-1.2205815686,-1.2384676207
 H,0,1.0815552723,-0.7923551513,-2.478634624
 H,0,2.562915459,-1.6732935406,-2.9594756264
 H,0,4.607599241,2.0050359493,-3.2018504133
 H,0,5.3943400356,1.8383202279,-5.5145021977
 H,0,3.8136274963,1.2671247008,-6.1351476718
 H,0,4.5582358551,2.7541533241,-6.7973984424
 H,0,5.5449027898,3.8909551144,-4.2751102444
 H,0,4.6161562227,4.7848523066,-5.5089799891
 H,0,4.081315278,4.7940456885,-3.8042674276
 H,0,2.5723571745,3.9706767594,-6.3225563767
 H,0,1.8372791334,2.467329572,-5.714865511
 H,0,1.8218387264,5.1920480617,-4.2146955081
 H,0,-0.080110963,2.769888843,-4.2903350482
 H,0,-0.317049572,4.3694151373,-3.3884901668
 H,0,3.1113717173,2.8725947604,-2.8315956448

Structure 6 SM B3LYP/6-31+G, File glycinesm2gp**

E(RB+HF-LYP) = -519.570066577

Zero-point correction= 0.239188 (Hartree/Particle)
 Thermal correction to Energy= 0.252196
 Thermal correction to Enthalpy= 0.253141
 Thermal correction to Gibbs Free Energy= 0.199987
 Sum of electronic and zero-point Energies= -519.330878
 Sum of electronic and thermal Energies= -519.317870
 Sum of electronic and thermal Enthalpies= -519.316926
 Sum of electronic and thermal Free Energies= -519.370079

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	158.256	47.528	111.871

C,0,1.9307579907,0.1578658964,-2.067640445
 C,0,1.6256408535,-0.5469113346,-0.9801210809
 C,0,0.2860993166,-1.1859383815,-0.8003152236
 N,0,0.2855994946,-2.7205846321,-0.6094058726
 C,0,0.8767910321,-3.0952428686,0.7330127798
 C,0,0.9607719418,-3.4249104097,-1.7682406264
 C,0,2.4890897594,-3.3367962913,-1.855337372
 O,0,3.2429838034,-3.1773427708,-0.9307872088
 C,0,-1.1600442764,-3.1615418094,-0.6128619389
 O,0,2.8333689362,-3.5526770443,-3.1173532601
 C,0,4.2592353329,-3.6451285774,-3.405067978
 H,0,4.3171326926,-3.8544949718,-4.4688949316
 H,0,4.742840448,-2.6996463262,-3.1641087995
 H,0,4.7009317282,-4.4514529525,-2.8212833613
 H,0,2.3282415631,-0.6055772625,-0.1560431524
 H,0,2.8776326359,0.6777322075,-2.1508406241
 H,0,1.2440023237,0.2608670457,-2.9023403214
 H,0,-1.6952282782,-2.6060948936,0.155138834
 H,0,-1.5956713006,-2.9592673751,-1.5899712268

H,0,-1.2054328756,-4.2273915271,-0.3962646327
H,0,0.2573436958,-2.6412035087,1.5048982907
H,0,0.8534825974,-4.1800174684,0.8282337528
H,0,1.9022088406,-2.7512140747,0.7908114298
H,0,-0.349209958,-0.9969359336,-1.6666579551
H,0,-0.2197554708,-0.8021735488,0.0890972347
H,0,0.5209340825,-3.0397649334,-2.687027029
H,0,0.7047330906,-4.4841432533,-1.6907442817

Structure 7 SM B3LYP/6-31+G, File glycinesm3gp**

E(RB+HF-LYP) = -519.456559684

Zero-point correction= 0.240035 (Hartree/Particle)
Thermal correction to Energy= 0.253136
Thermal correction to Enthalpy= 0.254080
Thermal correction to Gibbs Free Energy= 0.200192
Sum of electronic and zero-point Energies= -519.216525
Sum of electronic and thermal Energies= -519.203424
Sum of electronic and thermal Enthalpies= -519.202479
Sum of electronic and thermal Free Energies= -519.256368

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	158.845	47.594	113.418

C,0,1.9774414347,0.4350136938,-1.8061697652
C,0,1.4515765112,-0.2165518638,-0.7637459075
C,0,0.1753740841,-0.9973521499,-0.8529911034
N,0,0.322797931,-2.5301482166,-0.6404702783
C,0,-1.0649696433,-3.1248190197,-0.6932256985
C,0,0.936073916,-2.793555826,0.7151487849
C,0,1.1897283942,-3.0738836839,-1.760625885
C,0,1.5121038078,-4.5695036077,-1.8543708599
O,0,1.0074365328,-5.3396843944,-0.884390427
C,0,1.3222058547,-6.7661010091,-0.9757577837
O,0,2.1877984444,-4.951222828,-2.7776504652
H,0,0.8373068016,-7.2167107594,-0.1124932444
H,0,0.9244527912,-7.1676989937,-1.9082055252
H,0,2.4032374299,-6.903629731,-0.9397171209
H,0,1.9080117513,-0.114966349,0.2182265184
H,0,2.8653601685,1.0492351893,-1.6947366681
H,0,1.5327694462,0.3971894049,-2.7980877746
H,0,-1.6664321202,-2.6687932997,0.093698862
H,0,-1.5035561695,-2.9067654552,-1.6679193827
H,0,-0.9951600907,-4.1992244438,-0.5407959293
H,0,0.3512756671,-2.2600533824,1.4654485351
H,0,0.915685095,-3.8633371313,0.9066388807
H,0,1.9637864204,-2.4327139977,0.7159379711
H,0,-0.2947801142,-0.8782495741,-1.8317910431
H,0,-0.5365891502,-0.681873684,-0.0847853125
H,0,0.7069330608,-2.8003242339,-2.701982422
H,0,2.1419887451,-2.5422676535,-1.7175129557

Structure 10 SM B3LYP/6-31+G, File glycinesm6gp**

E(RB+HF-LYP) = -519.456430621

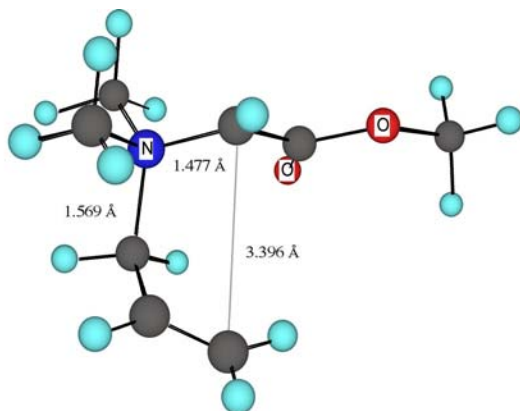
Zero-point correction= 0.239907 (Hartree/Particle)
 Thermal correction to Energy= 0.252154
 Thermal correction to Enthalpy= 0.253098
 Thermal correction to Gibbs Free Energy= 0.201820
 Sum of electronic and zero-point Energies= -519.216524
 Sum of electronic and thermal Energies= -519.204277
 Sum of electronic and thermal Enthalpies= -519.203333
 Sum of electronic and thermal Free Energies= -519.254610

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	158.229	45.647	107.923

C,0,0.8293239988,-4.8656207724,-4.1758859607
 C,0,1.8107457968,-5.6193380035,-3.6694538821
 C,0,2.3985093142,-5.3779595351,-2.3115401205
 N,0,3.8871851788,-4.9424847223,-2.3267078931
 C,0,4.108320071,-3.6654235069,-3.1192684119
 C,0,3.5077180935,-2.3354867526,-2.6517817074
 O,0,2.6311782318,-2.413822366,-1.6433008754
 C,0,2.0454828897,-1.1447051426,-1.2099409121
 C,0,4.3620655219,-4.7872787539,-0.9007126261
 C,0,4.7205004316,-6.0200318614,-2.9838306922
 O,0,3.8359478119,-1.3242754221,-3.2210777006
 H,0,0.4303336912,-4.0042300226,-3.6455133887
 H,0,0.37665684,-5.1009572721,-5.1339350472
 H,0,2.1492372502,-6.4957950404,-4.2178165798
 H,0,2.3890418549,-6.2890689799,-1.7058066231
 H,0,1.8662758891,-4.5911592692,-1.7798737521
 H,0,5.4010987283,-4.4546577569,-0.9124277898
 H,0,3.7364654084,-4.0560074638,-0.3949419764
 H,0,4.2909815678,-5.7564616107,-0.4061340894
 H,0,5.7744121384,-5.7589393627,-2.884251077
 H,0,4.4559979421,-6.0923350875,-4.0376598294
 H,0,4.5245798746,-6.9677767074,-2.4812600552
 H,0,3.7320210407,-3.8449039983,-4.1287348925
 H,0,2.8359493689,-0.4759219564,-0.8679890182
 H,0,1.3722590667,-1.4085399458,-0.3971015927
 H,0,1.5052914174,-0.6897354083,-2.0406660942
 H,0,5.1874685813,-3.5119522794,-3.1854774121

Deprotonated Glycine Salt 1 Starting Material Optimized Structure

Structure 5 Int B3LYP/6-31+G**, File glydeprotonsmgp



E(RB+HF-LYP) = -519.029844334

Zero-point correction= 0.225306 (Hartree/Particle)
 Thermal correction to Energy= 0.238293
 Thermal correction to Enthalpy= 0.239237
 Thermal correction to Gibbs Free Energy= 0.186380
 Sum of electronic and zero-point Energies= -518.804538
 Sum of electronic and thermal Energies= -518.791551
 Sum of electronic and thermal Enthalpies= -518.790607
 Sum of electronic and thermal Free Energies= -518.843464

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	149.531	47.611	111.247

C,0,2.0963267025,-0.9379780431,-2.3916830212
 O,0,2.7294472976,0.3420620422,-2.4052250393
 C,0,2.9165213143,0.9014494235,-3.6591640307
 O,0,2.4685715613,0.3314709248,-4.6813506887
 C,0,3.626943214,2.1018099743,-3.6045531644
 N,0,3.7926763956,2.8777620104,-4.8505768016
 C,0,4.579759124,2.0848011652,-5.8684588652
 C,0,4.559687162,4.1208305249,-4.5328746328
 C,0,1.6113387674,4.2216682735,-4.7390168376
 C,0,0.7102595475,3.8256074698,-3.8328362442
 C,0,2.4366483158,3.2661863073,-5.5381490984
 H,0,2.0257349863,-1.2161867534,-1.3381988783
 H,0,1.0980273448,-0.8963472445,-2.8380875636
 H,0,2.6886611336,-1.6805899194,-2.9362328427
 H,0,3.8110238453,2.6437535854,-2.6914348558
 H,0,5.5501197838,1.8573510777,-5.4284568122

H,0,4.0307649948,1.1633260928,-6.0589216448
H,0,4.6938521225,2.6758762541,-6.7819442291
H,0,5.5224382473,3.8275830251,-4.1131645969
H,0,4.7012578498,4.7017224056,-5.4468357116
H,0,4.0027745616,4.7017161677,-3.7983086931
H,0,2.700759315,3.688857484,-6.5120816352
H,0,1.94295522,2.3025222687,-5.6738071003
H,0,1.7666155686,5.2856406168,-4.9121312311
H,0,0.525930653,2.7730407336,-3.6394269339
H,0,0.1302629716,4.5447061331,-3.2610048474

Structure 6 Int B3LYP/6-31+G, File glydeprotonsm2gp**

E(RB+HF-LYP) = -519.023999757

Zero-point correction= 0.224940 (Hartree/Particle)
Thermal correction to Energy= 0.238048
Thermal correction to Enthalpy= 0.238992
Thermal correction to Gibbs Free Energy= 0.185707
Sum of electronic and zero-point Energies= -518.799060
Sum of electronic and thermal Energies= -518.785952
Sum of electronic and thermal Enthalpies= -518.785008
Sum of electronic and thermal Free Energies= -518.838293

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	149.377	47.742	112.148

C,0,1.7860965126,0.3642808477,-1.9649805489
C,0,1.5235460737,-0.4216384399,-0.9180841431
C,0,0.225195749,-1.1483220854,-0.7736047421
N,0,0.3365338853,-2.6943381975,-0.6626584972
C,0,1.0318800928,-3.3386888497,-1.7990608641
C,0,2.4275108434,-3.3019310386,-1.9007552364
O,0,2.8527484933,-3.8236868957,-3.1155861759
C,0,4.267141157,-3.9199534802,-3.2793855311
C,0,-1.0720461294,-3.2128297705,-0.6431458408
C,0,0.9650285912,-3.0555343391,0.6635368135
O,0,3.2646019161,-2.9045383427,-1.0628505177
H,0,4.4169142043,-4.3349927743,-4.2783734346
H,0,4.746303489,-2.9388175157,-3.2035514454
H,0,4.7116328951,-4.5816578752,-2.5286038681
H,0,2.2555109177,-0.5289506541,-0.1235991442
H,0,2.7191990303,0.9141073226,-2.0362878908
H,0,1.0852934158,0.4747848549,-2.7890044148
H,0,-1.6203787846,-2.7503396047,0.1807864554
H,0,-1.5500978242,-2.9685158638,-1.5926992442
H,0,-1.0326034685,-4.2947313737,-0.5243440665
H,0,0.4189084279,-2.5469772903,1.4624415834
H,0,0.8948818395,-4.1376697128,0.7724240525
H,0,2.0151675281,-2.7722705847,0.6284846192
H,0,-0.4043110477,-0.9713406262,-1.6482456521
H,0,-0.3118112746,-0.8187580271,0.1253420438

H,0,0.3945534671,-3.5470996833,-2.6445703098

Structure 7 Int B3LYP/6-31+G, File glydeprotonsm3gp**

E(RB+HF-LYP) = -519.019856361

Zero-point correction= 0.225047 (Hartree/Particle)
 Thermal correction to Energy= 0.238152
 Thermal correction to Enthalpy= 0.239097
 Thermal correction to Gibbs Free Energy= 0.185875
 Sum of electronic and zero-point Energies= -518.794809
 Sum of electronic and thermal Energies= -518.781704
 Sum of electronic and thermal Enthalpies= -518.780760
 Sum of electronic and thermal Free Energies= -518.833981

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	149.443	47.862	112.014

C,0,1.8268910135,0.510458867,-1.8624313178
 C,0,1.4601059837,-0.2846442785,-0.8538584041
 C,0,0.1832875834,-1.0723800252,-0.8620971429
 N,0,0.3307383758,-2.5730348827,-0.6281388532
 C,0,0.9235102614,-2.8138396879,0.7460156465
 C,0,1.1540699656,-3.1371273847,-1.7324404035
 C,0,1.5059737974,-4.4899625043,-1.8390388036
 O,0,2.2689740501,-4.9843262751,-2.6754223783
 C,0,1.0718572557,-3.1405442235,-0.6344412247
 O,0,0.8833825797,-5.3329477303,-0.8848053236
 C,0,1.1971985598,-6.7226891351,-1.0206061268
 H,0,0.655659086,-7.2285770169,-0.2176615249
 H,0,0.8751258608,-7.1058767301,-1.9932648003
 H,0,2.2723327401,-6.8961368881,-0.920281666
 H,0,2.0666756482,-0.3163130655,0.0481842268
 H,0,2.7238956446,1.1189170269,-1.8040592093
 H,0,1.2481498371,0.5752344019,-2.7805966821
 H,0,-1.6496918839,-2.7020586624,0.1851151679
 H,0,-1.5193716265,-2.9035274509,-1.5986981676
 H,0,-0.9909674972,-4.2189918367,-0.5218172503
 H,0,0.3100037013,-2.3269210367,1.5108725606
 H,0,0.9514023355,-3.890804592,0.8984191068
 H,0,1.9384929874,-2.4232017539,0.7512269111
 H,0,-0.3156400307,-0.9736760315,-1.8283109846
 H,0,-0.4904698192,-0.7140069748,-0.0754945711
 H,0,1.7035111021,-2.4015721293,-2.2937777848

Structure 10 Int B3LYP/6-31+G, File glydeprotonsm6gp**

E(RB+HF-LYP) = -519.021499282

Zero-point correction= 0.225184 (Hartree/Particle)
 Thermal correction to Energy= 0.238174
 Thermal correction to Enthalpy= 0.239118

Thermal correction to Gibbs Free Energy= 0.186406
 Sum of electronic and zero-point Energies= -518.796315
 Sum of electronic and thermal Energies= -518.783326
 Sum of electronic and thermal Enthalpies= -518.782381
 Sum of electronic and thermal Free Energies= -518.835093

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	149.456	47.834	110.941

C,0,2.5376009103,-1.3253660022,-1.0387398202
 O,0,3.1306176126,-2.5723160585,-1.4177587859
 C,0,3.4706608326,-2.6759827551,-2.7869020099
 C,0,4.1164330955,-3.8733483917,-3.1317495042
 N,0,4.2802063758,-5.0253990798,-2.2168367032
 C,0,4.9799052497,-6.1096504158,-2.979328366
 O,0,3.198398182,-1.7437201908,-3.5506893953
 C,0,5.1464591879,-4.676476083,-1.029942955
 C,0,2.9347535854,-5.6028813646,-1.6445545853
 C,0,2.0512465708,-6.2072346265,-2.6877511413
 C,0,1.1728661704,-5.4983534055,-3.4064211109
 H,0,2.3406690395,-1.4048247214,0.0328733924
 H,0,1.605622521,-1.1492193017,-1.5831487628
 H,0,3.2167002976,-0.4914759363,-1.2380375193
 H,0,4.2215545871,-4.1192348007,-4.1759530098
 H,0,6.1004265401,-4.3179670527,-1.4147472642
 H,0,5.2849414067,-5.5643861235,-0.4059226269
 H,0,4.6540196959,-3.882359154,-0.4739885114
 H,0,5.9404603145,-5.7198173511,-3.316633827
 H,0,4.3723239197,-6.3817906085,-3.8413887908
 H,0,5.1223616218,-6.9751623985,-2.3285858341
 H,0,3.2142699611,-6.3416614671,-0.8873545225
 H,0,2.4748796094,-4.7417838932,-1.1613700397
 H,0,2.1519306428,-7.2765769689,-2.8665418536
 H,0,1.045034261,-4.4299163663,-3.260934322
 H,0,0.5583468087,-5.9696894826,-4.1683991311

Rearranged Product 2 Optimized Structure

Structure 5 Prod B3LYP/6-31+G**, File productoptgp

E(RB+HF-LYP) = -519.089430444

Zero-point correction= 0.224797 (Hartree/Particle)
 Thermal correction to Energy= 0.238216
 Thermal correction to Enthalpy= 0.239161
 Thermal correction to Gibbs Free Energy= 0.184216
 Sum of electronic and zero-point Energies= -518.864634
 Sum of electronic and thermal Energies= -518.851214
 Sum of electronic and thermal Enthalpies= -518.850270
 Sum of electronic and thermal Free Energies= -518.905215

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	149.483	47.055	115.641

C,0,2.9810145675,-0.5501971521,-1.8291829802
 O,0,2.9484539422,0.8279498254,-2.2539876513
 C,0,2.6820012714,1.0392223151,-3.5644266819
 O,0,2.4842114115,0.1376132892,-4.3559815231
 C,0,2.7188807407,2.5345612998,-3.921702991
 N,0,3.9304203207,2.9069532495,-4.6593316333
 C,0,4.1022783149,2.3095306302,-5.982023359
 C,0,5.1480427918,2.8186333313,-3.8605726609
 C,0,1.373199279,4.3647271424,-5.0658068663
 C,0,1.4201976085,2.9162897434,-4.6604190956
 C,0,0.9654180005,4.8105023425,-6.2570454215
 H,0,3.2034021435,-0.5200677453,-0.7630130736
 H,0,2.0141918556,-1.0259788901,-2.0098376554
 H,0,3.7561184371,-1.0969690836,-2.3712121462
 H,0,2.7552239932,3.0902818837,-2.9784744071
 H,0,4.3061829747,1.2262127804,-5.9540820148
 H,0,3.213570132,2.4752598156,-6.5934630729
 H,0,4.9426717261,2.8083850171,-6.4756450781
 H,0,5.4720930871,1.7815349894,-3.6534604505
 H,0,5.9615539426,3.3214712596,-4.393644848
 H,0,5.0027994145,3.3260854054,-2.9019879997
 H,0,0.9246486666,5.8719479463,-6.4833524011
 H,0,0.6571858511,4.1289857465,-7.0472375543
 H,0,1.6800550387,5.0851732747,-4.3070459556
 H,0,1.2654080751,2.2642010639,-5.5254260995
 H,0,0.5904524135,2.7054725198,-3.9695003792

Structure 6 Prod B3LYP/6-31+G, File productopt2gp**

E(RB+HF-LYP) = -519.086092530

Zero-point correction= 0.224926 (Hartree/Particle)
 Thermal correction to Energy= 0.238103
 Thermal correction to Enthalpy= 0.239047
 Thermal correction to Gibbs Free Energy= 0.184996
 Sum of electronic and zero-point Energies= -518.861166
 Sum of electronic and thermal Energies= -518.847989
 Sum of electronic and thermal Enthalpies= -518.847045
 Sum of electronic and thermal Free Energies= -518.901097

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	149.412	46.730	113.761

C,0,-0.0945067162,0.0480261675,-0.8378040638
 H,0,-0.4333512478,0.6530657508,-0.0020707412
 H,0,-0.7987524403,-0.0931351102,-1.6558573336
 C,0,1.1274583015,-0.4916483864,-0.8574097083
 H,0,1.7947525987,-0.3348511673,-0.0118295393

C,0,1.6754532628,-1.3094410602,-1.99864326
 H,0,0.869197012,-1.5946432142,-2.6823975139
 H,0,2.3693889756,-0.6996784426,-2.5932989117
 C,0,2.4627891763,-2.5808308635,-1.5681921521
 H,0,2.7275262647,-3.1232586328,-2.496796465
 N,0,1.7249333323,-3.4361755167,-0.6434757147
 C,0,0.4089467697,-3.8151602612,-1.1510038159
 H,0,-0.2292225131,-2.9380145099,-1.2699415182
 H,0,0.4567343714,-4.3560707151,-2.1175702558
 H,0,-0.0709045631,-4.4736701049,-0.42160566
 C,0,2.4891832436,-4.6253639233,-0.270542543
 H,0,1.9123200861,-5.2108853081,0.4509172155
 H,0,2.7163718944,-5.2761369474,-1.1381773853
 H,0,3.4268910635,-4.3396908791,0.2104798901
 C,0,3.784184038,-2.1098287697,-0.9495949079
 O,0,3.9824357322,-1.8413013701,0.2158277267
 O,0,4.724892107,-1.9660094636,-1.9133875926
 C,0,5.9907764231,-1.4285795069,-1.4823271664
 H,0,6.6069552441,-1.3836901294,-2.3798057478
 H,0,5.8563091297,-0.4318381512,-1.0550974101
 H,0,6.4456394537,-2.0809954849,-0.7333714257

Structure 7 Prod B3LYP/6-31+G, File productopt3gp**

E(RB+HF-LYP) = -519.088956058

Zero-point correction= 0.224896 (Hartree/Particle)
 Thermal correction to Energy= 0.238292
 Thermal correction to Enthalpy= 0.239236
 Thermal correction to Gibbs Free Energy= 0.184293
 Sum of electronic and zero-point Energies= -518.864060
 Sum of electronic and thermal Energies= -518.850664
 Sum of electronic and thermal Enthalpies= -518.849720
 Sum of electronic and thermal Free Energies= -518.904663

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	149.530	47.027	115.637

C,0,2.0888564107,-1.2511133937,-1.3346345395
 C,0,0.8939044856,-0.7697710936,-0.9783519797
 C,0,0.1708322336,0.3403084682,-1.6919073649
 C,0,-0.1992048699,1.5043143281,-0.74786495
 C,0,-0.7094461602,2.7536686215,-1.485662465
 O,0,-1.3781105871,2.4642602426,-2.6249469437
 N,0,-1.1221381797,1.0873698351,0.3210454534
 C,0,-2.4952708417,0.8101215393,-0.0939045061
 C,0,-1.0825554189,1.9412589956,1.5070224357
 O,0,-0.5801080186,3.8870765594,-1.0635837102
 H,0,0.383381079,-1.1864890568,-0.1117472527
 H,0,-0.7384716484,-0.0467345046,-2.1668519183
 H,0,0.7950008112,0.7313326357,-2.5035820656
 H,0,-1.6418832919,1.4518886302,2.3115237321

H,0,-0.0473848626,2.0658147534,1.8377024837
 H,0,-1.513508125,2.9437457482,1.344025376
 H,0,-3.0120493446,0.2975911294,0.7238423373
 H,0,-3.0738519801,1.7193990419,-0.3403215861
 H,0,-2.5114927388,0.1514568328,-0.9649015897
 H,0,2.6334548989,-0.8574469323,-2.1907662711
 H,0,2.5627337003,-2.0591471128,-0.7845978987
 H,0,0.714169538,1.8358099655,-0.2441412284
 C,0,-1.9314049319,3.5898944797,-3.3366502579
 H,0,-2.4086303374,3.1679736877,-4.2206466446
 H,0,-2.6616561712,4.112632625,-2.7145173962
 H,0,-1.138355649,4.2861219748,-3.6192372498

Structure 10 Prod B3LYP/6-31+G, File productopt6gp**

E(RB+HF-LYP) = -519.085743514

Zero-point correction= 0.225141 (Hartree/Particle)
 Thermal correction to Energy= 0.238257
 Thermal correction to Enthalpy= 0.239201
 Thermal correction to Gibbs Free Energy= 0.185439
 Sum of electronic and zero-point Energies= -518.860603
 Sum of electronic and thermal Energies= -518.847487
 Sum of electronic and thermal Enthalpies= -518.846543
 Sum of electronic and thermal Free Energies= -518.900304

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	149.508	46.621	113.151

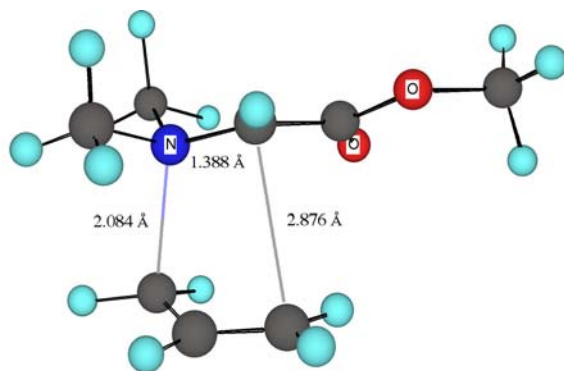
C,0,2.4925174939,-1.7806368871,-0.5036817525
 O,0,3.1050555386,-2.9120426732,-1.153209618
 C,0,3.4001901903,-2.750115633,-2.4540172009
 C,0,3.950917855,-4.0107772137,-3.1302934848
 N,0,4.7402388886,-4.8563588027,-2.2310343391
 C,0,5.1722029266,-6.1073663324,-2.8519565685
 O,0,3.1939238102,-1.719845597,-3.0665930506
 C,0,5.9014024473,-4.1358045047,-1.7075918829
 C,0,0.425934952,-5.1347872733,-2.8920143038
 C,0,1.7470923021,-5.318322868,-2.8123131418
 C,0,2.7440205986,-4.7426823093,-3.7832681665
 H,0,2.3372027542,-2.0911865182,0.5290834623
 H,0,1.5405236155,-1.5387439296,-0.9819093877
 H,0,3.1502869693,-0.9094064931,-0.5523279813
 H,0,4.5734373355,-3.6281479412,-3.9617997723
 H,0,6.606194313,-3.8290323549,-2.5048144529
 H,0,6.4391797044,-4.7789696377,-1.005029197
 H,0,5.5836353165,-3.2439128597,-1.1638360201
 H,0,5.7608032736,-5.9520488723,-3.7779088344
 H,0,4.3205970353,-6.7486739596,-3.088321405
 H,0,5.8023477665,-6.6501518298,-2.1418958129
 H,0,-0.254235321,-5.5890928328,-2.1772513427
 H,0,-0.0210338763,-4.5252730545,-3.6748383536

H,0,2.1546699034,-5.9226441647,-2.0036445063
 H,0,2.2505016581,-4.0299344834,-4.4522327154
 H,0,3.1419515488,-5.5375729743,-4.4255761713

G03 Calculations: Solution Phase Structures

Glycine Salt 1 Rearrangement Transition Structures

(5) B3LYP/6-31+G**, Onsager, $\epsilon=37.219$, $a_0=4.71$, File glycinetsdielec



E(RB+HF-LYP) = -519.021527425

Zero-point correction= 0.222849 (Hartree/Particle)
 Thermal correction to Energy= 0.235645
 Thermal correction to Enthalpy= 0.236589
 Thermal correction to Gibbs Free Energy= 0.184467
 Sum of electronic and zero-point Energies= -518.798678
 Sum of electronic and thermal Energies= -518.785882
 Sum of electronic and thermal Enthalpies= -518.784938
 Sum of electronic and thermal Free Energies= -518.837060

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	147.870	47.057	109.700

C,0,2.0496246032,-0.8621081873,-2.3656079406
 O,0,2.7352277692,0.3869953971,-2.4605292526
 C,0,2.8218019245,0.921380218,-3.7294165094
 C,0,3.4948296784,2.1766047636,-3.7084766566
 N,0,3.8119366512,2.8854697458,-4.8591805182
 C,0,4.6917401267,4.0391949394,-4.5703256105
 O,0,2.3388488309,0.3302260036,-4.7047010191
 C,0,4.3048583408,2.1133486849,-6.0270897515
 C,0,2.127516902,3.801853158,-5.6745977901
 C,0,1.4992320483,4.2940973247,-4.5045835041
 C,0,0.9150652857,3.4441204627,-3.6111400252

H,0,2.0734205293,-1.1274351447,-1.3070784289
 H,0,1.0145894928,-0.7726778151,-2.7107130779
 H,0,2.5496529173,-1.6330542036,-2.9601513661
 H,0,3.737850702,2.6311157348,-2.7602704195
 H,0,5.3094693097,1.7328350275,-5.8102938615
 H,0,3.6303066821,1.2805357044,-6.2131883013
 H,0,4.3448908757,2.776256299,-6.8942080723
 H,0,5.6599473336,3.685012231,-4.1995014047
 H,0,4.8405545873,4.6203040304,-5.4814275089
 H,0,4.2221502629,4.6669479026,-3.8118508348
 H,0,2.5587268645,4.4968040115,-6.3904806549
 H,0,1.7682796002,2.8665719318,-6.0931209388
 H,0,1.6685350661,5.3314654646,-4.2191328834
 H,0,0.6754072961,2.4229761054,-3.8861700208
 H,0,0.5697893195,3.7886242099,-2.6407996481

(6) B3LYP/6-31+G, Onsager, $\epsilon=37.219$, $a_0=4.71$, File glycinets2dielec**
 E(RB+HF-LYP) = -519.018399642

Zero-point correction= 0.222739 (Hartree/Particle)
 Thermal correction to Energy= 0.235614
 Thermal correction to Enthalpy= 0.236559
 Thermal correction to Gibbs Free Energy= 0.183738
 Sum of electronic and zero-point Energies= -518.795661
 Sum of electronic and thermal Energies= -518.782785
 Sum of electronic and thermal Enthalpies= -518.781841
 Sum of electronic and thermal Free Energies= -518.834662

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	147.850	47.045	111.171

C,0,1.6613643611,-0.2281364085,-2.2388211149
 C,0,1.4321144931,-0.2686086739,-0.9024054036
 C,0,0.206729452,-0.7905565547,-0.3851189263
 N,0,0.3688502369,-2.7436844088,-0.6538455605
 C,0,1.0952803234,-3.0839405485,-1.7990269533
 C,0,2.5094570722,-3.2217548475,-1.8402575469
 O,0,2.9173712288,-3.5877376891,-3.115410739
 C,0,4.323511692,-3.7528409809,-3.279536326
 C,0,-1.0559609296,-3.1489375345,-0.7649810048
 C,0,0.9287525279,-3.212395409,0.6461799082
 O,0,3.3378807854,-3.0889470946,-0.9296157809
 H,0,4.4633277823,-4.0511428424,-4.3208292269
 H,0,4.8591033199,-2.8181745125,-3.0801375044
 H,0,4.7149695694,-4.5250940455,-2.6095597216
 H,0,2.259127687,-0.1067311827,-0.2144721115
 H,0,2.6381383766,0.0181644888,-2.6434672478
 H,0,0.8594333162,-0.3747915331,-2.9558918652
 H,0,-1.623210016,-2.7092295854,0.0577307859
 H,0,-1.4615427836,-2.7948610364,-1.7136242835
 H,0,-1.1310704071,-4.2393757155,-0.7248990992

H,0,0.2699530902,-2.8751846083,1.4483743174
 H,0,0.9746466781,-4.3057029897,0.638204985
 H,0,1.9346816255,-2.8199639983,0.7662955631
 H,0,-0.6770572902,-0.6598835337,-1.0049122212
 H,0,0.009526502,-0.7109366721,0.6809977495
 H,0,0.5320203069,-3.1599620832,-2.7173456713

(7) B3LYP/6-31+G, Onsager, $\epsilon=37.219$, $a_0=4.71$, File glycinets3dielec**
 E(RB+HF-LYP) = -519.014229250

Zero-point correction= 0.222880 (Hartree/Particle)
 Thermal correction to Energy= 0.235684
 Thermal correction to Enthalpy= 0.236628
 Thermal correction to Gibbs Free Energy= 0.184176
 Sum of electronic and zero-point Energies= -518.791350
 Sum of electronic and thermal Energies= -518.778545
 Sum of electronic and thermal Enthalpies= -518.777601
 Sum of electronic and thermal Free Energies= -518.830053

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	147.894	47.018	110.396

C,0,2.3115051683,-1.286930338,-1.9390345159
 C,0,1.9007096506,-1.1407026539,-0.6544201514
 C,0,0.5255577535,-0.9083487468,-0.3443610535
 N,0,-0.3370515564,-2.6544703009,-0.6788546397
 C,0,-0.1996158691,-3.3411352057,0.6364864263
 C,0,0.1620192076,-3.3102945828,-1.8119614038
 C,0,1.2265022856,-4.2508732139,-1.9368223602
 O,0,1.5527188382,-4.7834946875,-3.0043536437
 C,0,-1.7525401871,-2.2403377827,-0.8739920667
 O,0,1.8788078433,-4.5875194885,-0.7614928846
 C,0,2.9282303123,-5.5472714821,-0.8982524093
 H,0,3.3076659051,-5.7118796865,0.1121751991
 H,0,2.5528865432,-6.4838348637,-1.3210832957
 H,0,3.7257386075,-5.1676915798,-1.5450743798
 H,0,2.5783729367,-1.400676071,0.1563652927
 H,0,3.3155633956,-1.6192195753,-2.1842229246
 H,0,1.6711411449,-1.0169319926,-2.7727562689
 H,0,-2.0459813494,-1.5617543679,-0.0707738638
 H,0,-1.851140299,-1.7293022927,-1.8323325959
 H,0,-2.3973285265,-3.1237571248,-0.8674631559
 H,0,-0.6997006208,-2.735802078,1.3941009172
 H,0,-0.669542847,-4.3269668908,0.5783096554
 H,0,0.85095118,-3.4620890743,0.8792427318
 H,0,-0.0538535703,-0.3596702471,-1.0828792515
 H,0,0.2492062243,-0.6856441989,0.6834418614
 H,0,-0.2894391712,-3.0119524738,-2.7474002193

(10) B3LYP/6-31+G, Onsager, $\epsilon=37.219$, $a_0=4.71$, File glycinets6dielec**
E(RB+HF-LYP) = -519.017001125

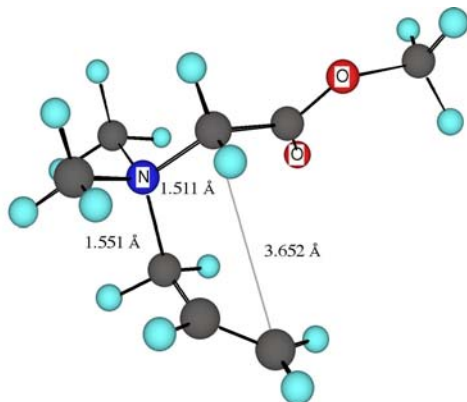
Zero-point correction= 0.222747 (Hartree/Particle)
 Thermal correction to Energy= 0.235572
 Thermal correction to Enthalpy= 0.236516
 Thermal correction to Gibbs Free Energy= 0.184333
 Sum of electronic and zero-point Energies= -518.794254
 Sum of electronic and thermal Energies= -518.781429
 Sum of electronic and thermal Enthalpies= -518.780485
 Sum of electronic and thermal Free Energies= -518.832669

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	147.824	47.199	109.829

C,0,2.4647046393,-1.3226897455,-1.1594472531
 H,0,2.3172812367,-1.3395234194,-0.0782648457
 H,0,1.5124762026,-1.1530930798,-1.6703922372
 H,0,3.1585785099,-0.5241312292,-1.4373362562
 O,0,3.0039711054,-2.6065306442,-1.4936775223
 C,0,3.2962700128,-2.800608695,-2.8348234457
 O,0,3.0439227401,-1.9245011074,-3.665092917
 C,0,3.8672104221,-4.0743468969,-3.1404544971
 H,0,3.9516043747,-4.3059265813,-4.1914482303
 N,0,4.2922706096,-5.0514342785,-2.2458163411
 C,0,5.0499917763,-4.6326310646,-1.0398577377
 H,0,6.0282190165,-4.2431973986,-1.3432706585
 H,0,5.1883064753,-5.5020074141,-0.3937401057
 H,0,4.4989426793,-3.861022506,-0.5105962048
 C,0,5.0006906842,-6.1475688884,-2.9470397392
 H,0,5.9252246507,-5.765538028,-3.3941833903
 H,0,4.3554150752,-6.5449286334,-3.7312889601
 H,0,5.2394345764,-6.9404250168,-2.2373697406
 C,0,2.6848638197,-6.0637384501,-1.3827737655
 H,0,3.1594613681,-6.9138520301,-0.8999085515
 H,0,2.4587045389,-5.2273879157,-0.7290691645
 C,0,1.8654135548,-6.2683334915,-2.5197626161
 C,0,1.2194003914,-5.2295935149,-3.1238791837
 H,0,1.9210639472,-7.2276401779,-3.0325198467
 H,0,1.0839467692,-4.2800864389,-2.619115216
 H,0,0.7248798237,-5.348353354,-4.0834865735

Glycine Salt 1 Starting Material Optimized Structure

(5) B3LYP/6-31+G**, Onsager, $\epsilon=37.219$, $a_0=4.58$, File glycinesmdielec



E(RB+HF-LYP) = -519.466070183

Zero-point correction= 0.240134 (Hartree/Particle)
 Thermal correction to Energy= 0.253166
 Thermal correction to Enthalpy= 0.254110
 Thermal correction to Gibbs Free Energy= 0.200676
 Sum of electronic and zero-point Energies= -519.225936
 Sum of electronic and thermal Energies= -519.212904
 Sum of electronic and thermal Enthalpies= -519.211960
 Sum of electronic and thermal Free Energies= -519.265394

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	158.864	47.491	112.461

C,0,2.1345842065,-0.9184583528,-2.2668261666
 O,0,2.8415443572,0.3421361277,-2.4245558797
 C,0,2.7976754247,0.9132303254,-3.6242570404
 O,0,2.2133736245,0.4773799031,-4.5948200284
 C,0,3.6006837282,2.2124951519,-3.563985943
 N,0,3.7176585864,2.9735640075,-4.8642712141
 C,0,4.4243775126,2.144055067,-5.9150733621
 C,0,4.5563919884,4.2038650815,-4.5904551752
 C,0,1.4870177951,4.17158871,-4.4609845301
 C,0,0.306264864,3.7201131945,-4.0254889226
 C,0,2.3354510775,3.3983659061,-5.4254059665
 H,0,2.3047373426,-1.2061110801,-1.2315637044
 H,0,1.0714508025,-0.7730118559,-2.4652812196
 H,0,2.5457399807,-1.6602883532,-2.9532308301
 H,0,4.6132562988,1.9899694496,-3.2182019256
 H,0,5.4001054377,1.8478072396,-5.5273766634
 H,0,3.818160678,1.2698960618,-6.1417299084
 H,0,4.5558280131,2.7596771399,-6.8052345303
 H,0,5.5516663128,3.8901341405,-4.2739467562

H,0,4.6289439852,4.7868030557,-5.508927215
 H,0,4.0893952374,4.796935919,-3.8054967909
 H,0,2.5758937288,3.9939711634,-6.3109426409
 H,0,1.8465940346,2.4758366226,-5.7339899794
 H,0,1.8152512038,5.1708278632,-4.1824707401
 H,0,-0.0774827385,2.744892022,-4.3158429333
 H,0,-0.3245979961,4.3274628067,-3.3840803289
 H,0,3.1328955136,2.8725136835,-2.8305306051

(6) B3LYP/6-31+G, Onsager, $\epsilon=37.219$, $a_0=4.58$, File glycinesm2dielec**
 E(RB+HF-LYP) = -519.461180009

Zero-point correction= 0.240086 (Hartree/Particle)
 Thermal correction to Energy= 0.253089
 Thermal correction to Enthalpy= 0.254033
 Thermal correction to Gibbs Free Energy= 0.200891
 Sum of electronic and zero-point Energies= -519.221094
 Sum of electronic and thermal Energies= -519.208091
 Sum of electronic and thermal Enthalpies= -519.207147
 Sum of electronic and thermal Free Energies= -519.260289

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	158.816	47.480	111.848

C,0,1.915002508,0.1437270812,-2.1179367808
 C,0,1.6081972823,-0.5470527283,-1.0158474858
 C,0,0.2676197243,-1.1873272069,-0.8261727187
 N,0,0.275387462,-2.7164031536,-0.5938980994
 C,0,0.8621930722,-3.0545562362,0.7618187116
 C,0,0.96302982,-3.4470755529,-1.7286020935
 C,0,2.4883431727,-3.3349830979,-1.8239859036
 O,0,3.2585571096,-3.1692562033,-0.9034885349
 C,0,-1.1731120619,-3.1689233245,-0.5942612875
 O,0,2.8359888072,-3.5468497294,-3.0933681546
 C,0,4.2584739056,-3.6223571924,-3.3752713747
 H,0,4.3223981701,-3.8337509439,-4.4406703926
 H,0,4.7324981972,-2.6693732695,-3.1341193203
 H,0,4.7110760376,-4.4229406955,-2.7876681213
 H,0,2.3098885329,-0.5877835116,-0.1872949986
 H,0,2.8607995551,0.6691589665,-2.2043350421
 H,0,1.2282344184,0.2327307625,-2.9564973956
 H,0,-1.7168153809,-2.5977038239,0.1583619762
 H,0,-1.6061261948,-2.992654392,-1.5793801333
 H,0,-1.2130183726,-4.2307889456,-0.3504730334
 H,0,0.2387853929,-2.5811571904,1.5208024119
 H,0,0.837673613,-4.1378719143,0.8862632079
 H,0,1.8888305024,-2.7073363365,0.8136120507
 H,0,-0.3658292582,-1.0238426665,-1.7011430937
 H,0,-0.24541865,-0.7804424218,0.050694689
 H,0,0.5144881952,-3.1020105266,-2.6612047478
 H,0,0.7252764396,-4.5094447466,-1.6152393352

(7) B3LYP/6-31+G, Onsager, $\epsilon=37.219$, $a_0=4.58$, File glycinesm3dielec**
 E(RB+HF-LYP) = -519.572131116

Zero-point correction= 0.238993 (Hartree/Particle)
 Thermal correction to Energy= 0.252136
 Thermal correction to Enthalpy= 0.253080
 Thermal correction to Gibbs Free Energy= 0.199141
 Sum of electronic and zero-point Energies= -519.333138
 Sum of electronic and thermal Energies= -519.319995
 Sum of electronic and thermal Enthalpies= -519.319051
 Sum of electronic and thermal Free Energies= -519.372990

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	158.218	47.698	113.524

C,0,1.9332143291,0.4665357787,-1.7575782157
 C,0,1.4145469626,-0.2067509031,-0.7321495221
 C,0,0.1473028109,-0.9966021236,-0.8389345521
 N,0,0.30441329,-2.5291779171,-0.6313137954
 C,0,-1.0786897485,-3.1310491193,-0.7047185082
 C,0,0.8991150507,-2.7919763555,0.7313273411
 C,0,1.1913124262,-3.0535292716,-1.7400732079
 C,0,1.5735022382,-4.5347038781,-1.8205894365
 O,0,1.0143218895,-5.3263705118,-0.9047768069
 C,0,1.3579894683,-6.742539674,-0.9782230164
 O,0,2.3262457149,-4.8902553343,-2.6861066457
 H,0,0.8165746975,-7.2076202873,-0.1595205294
 H,0,1.0398183518,-7.1458969762,-1.9382632099
 H,0,2.4332665143,-6.8647999095,-0.8580339619
 H,0,1.8593712734,-0.1087198892,0.2533598519
 H,0,2.8052514368,1.0968850902,-1.6305468764
 H,0,1.4913087436,0.440594473,-2.7490656297
 H,0,-1.6924241069,-2.6810284878,0.0737687443
 H,0,-1.5054797281,-2.9104636268,-1.6821645808
 H,0,-1.0066961181,-4.2034726019,-0.5538018799
 H,0,0.3020582801,-2.2641443598,1.4734529894
 H,0,0.8786826139,-3.8600073323,0.9223352142
 H,0,1.9229936344,-2.42542587,0.7485593568
 H,0,-0.3141275676,-0.8768674807,-1.8196821825
 H,0,-0.5732335879,-0.6886289598,-0.07856849
 H,0,0.7038459269,-2.8069148974,-2.684999431
 H,0,2.1224452038,-2.4889945751,-1.7006740195

(10) B3LYP/6-31+G, Onsager, $\epsilon=37.219$, $a_0=4.58$, File glycinesm6dielec**
 E(RB+HF-LYP) = -519.460297524

Zero-point correction= 0.239846 (Hartree/Particle)
 Thermal correction to Energy= 0.253066
 Thermal correction to Enthalpy= 0.254010
 Thermal correction to Gibbs Free Energy= 0.199077
 Sum of electronic and zero-point Energies= -519.220452

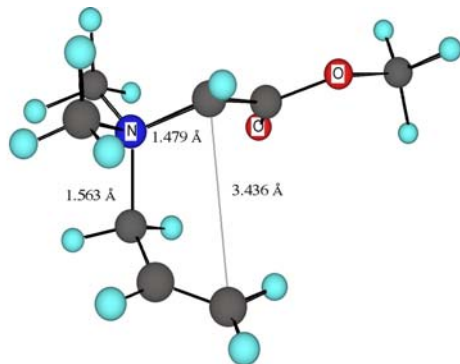
Sum of electronic and thermal Energies= -519.207232
 Sum of electronic and thermal Enthalpies= -519.206288
 Sum of electronic and thermal Free Energies= -519.261221

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	158.801	47.675	115.616

C,0,0.8203023641,-4.7358703833,-4.134772976
 C,0,1.8014216709,-5.5222726009,-3.6815273698
 C,0,2.3995307605,-5.3665247871,-2.314830239
 N,0,3.8951632736,-4.9651280066,-2.3145301743
 C,0,4.3593877117,-4.8236103442,-0.8804891733
 C,0,4.715576626,-6.0643460273,-2.9594041572
 C,0,4.1473788763,-3.6985603302,-3.1112856931
 C,0,3.424094011,-2.3929377079,-2.7680039542
 O,0,2.7493850606,-2.3882609617,-1.6128045543
 C,0,2.1045287745,-1.1313062849,-1.2519914882
 O,0,3.5193519425,-1.4547880028,-3.5236764303
 H,0,0.42573002,-3.9090759798,-3.5487662698
 H,0,0.3586406657,-4.9145198947,-5.1006500426
 H,0,2.1299733966,-6.3670358723,-4.2829009719
 H,0,2.3672073969,-6.307164522,-1.7573960435
 H,0,1.885331614,-4.5982014125,-1.7392347287
 H,0,5.4145278218,-4.5467708596,-0.8813306462
 H,0,3.7663699641,-4.0590572953,-0.3858404737
 H,0,4.234195355,-5.7853993951,-0.3823578329
 H,0,5.7720639908,-5.8050539348,-2.8845449459
 H,0,4.4318458813,-6.1649759059,-4.0057151272
 H,0,4.5273252573,-6.9973575397,-2.4276399078
 H,0,3.9052063832,-3.9149266087,-4.1521304096
 H,0,2.8574953351,-0.3474991473,-1.160646259
 H,0,1.6219611327,-1.3255004976,-0.2962966237
 H,0,1.3746838884,-0.8600672545,-2.0160709644
 H,0,5.2200298255,-3.4939074433,-3.0521785435

Deprotonated Glycine Salt 1 Starting Material Optimized Structure

(5) B3LYP/6-31+G**, Onsager, $\epsilon=37.219$, $a_0=4.52$, File glydeprotonsmdielec



E(RB+HF-LYP) = -519.034687960

Zero-point correction= 0.225191 (Hartree/Particle)
 Thermal correction to Energy= 0.238274
 Thermal correction to Enthalpy= 0.239218
 Thermal correction to Gibbs Free Energy= 0.185805
 Sum of electronic and zero-point Energies= -518.809497
 Sum of electronic and thermal Energies= -518.796414
 Sum of electronic and thermal Enthalpies= -518.795470
 Sum of electronic and thermal Free Energies= -518.848883

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	149.519	47.634	112.417

C,0,2.1236391472,-0.9518495375,-2.3754911864
 O,0,2.7522308082,0.32208419,-2.391338911
 C,0,2.917157654,0.8867905549,-3.6622557266
 O,0,2.457888681,0.2937886947,-4.6674419489
 C,0,3.6088828069,2.0905729015,-3.6113577476
 N,0,3.7861694996,2.8758344876,-4.8518129629
 C,0,4.5727701355,2.0885612659,-5.8746366087
 C,0,4.5609910761,4.1160429205,-4.5237566226
 C,0,1.6207011563,4.2419828871,-4.734481056
 C,0,0.6759440786,3.8624222075,-3.8680535866
 C,0,2.435898212,3.2728332842,-5.5310536199
 H,0,2.0628854804,-1.2354992899,-1.3208870928
 H,0,1.1188906042,-0.9150506392,-2.8113228041
 H,0,2.7073439712,-1.6977686846,-2.9282375651
 H,0,3.8306112744,2.6116128363,-2.6948772899
 H,0,5.5394827101,1.8496200009,-5.4327440499
 H,0,4.0187724231,1.174114335,-6.0823625392
 H,0,4.6991070364,2.6902829558,-6.778462827
 H,0,5.5264114255,3.8167646604,-4.1153109717
 H,0,4.6990088406,4.7059780682,-5.431602935

H,0,4.0108779558,4.691442902,-3.7803331789
 H,0,2.7000386565,3.6931295602,-6.5057414889
 H,0,1.9275057229,2.3173137592,-5.6672345254
 H,0,1.8131889685,5.3022248281,-4.888079966
 H,0,0.4548270118,2.8126954961,-3.6964264801
 H,0,0.0981326631,4.5927153552,-3.3086253089

(6) B3LYP/6-31+G, Onsager, $\epsilon=37.219$, $a_0=4.52$, File glydeprotonsm2dielec**
 E(RB+HF-LYP) = -519.029472672

Zero-point correction= 0.224856 (Hartree/Particle)
 Thermal correction to Energy= 0.238055
 Thermal correction to Enthalpy= 0.238999
 Thermal correction to Gibbs Free Energy= 0.185103
 Sum of electronic and zero-point Energies= -518.804617
 Sum of electronic and thermal Energies= -518.791417
 Sum of electronic and thermal Enthalpies= -518.790473
 Sum of electronic and thermal Free Energies= -518.844370

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	149.382	47.761	113.435

C,0,1.7563655619,0.4478014768,-1.8911750872
 C,0,1.5267940747,-0.4174861599,-0.9012242234
 C,0,0.2286555042,-1.1481046031,-0.7655046628
 N,0,0.3460960838,-2.6895086472,-0.667532865
 C,0,1.0476568894,-3.31228738,-1.8136078456
 C,0,2.4367028629,-3.3165046422,-1.9128205526
 O,0,2.844382185,-3.8577531628,-3.1434755777
 C,0,4.2494412924,-3.9637733999,-3.3152899471
 C,0,-1.0640217394,-3.2154032036,-0.6535968434
 C,0,0.9746378558,-3.0622017848,0.655311117
 O,0,3.3052492811,-2.9485462288,-1.0918128729
 H,0,4.3920537176,-4.3755434159,-4.3189016693
 H,0,4.7425961727,-2.9880127009,-3.2380143775
 H,0,4.6999392319,-4.632621162,-2.5717987186
 H,0,2.2794294293,-0.5768246272,-0.1352039914
 H,0,2.6814480183,1.0139119699,-1.9398041941
 H,0,1.028338145,0.6262994473,-2.6787609329
 H,0,-1.6126618769,-2.7655327621,0.1759230506
 H,0,-1.5446685982,-2.9595359254,-1.5983792815
 H,0,-1.021570701,-4.2982715183,-0.5459093923
 H,0,0.4245230347,-2.5665506744,1.4583056881
 H,0,0.9071293925,-4.1454198315,0.7539883404
 H,0,2.022792037,-2.773192351,0.6306907935
 H,0,-0.403759016,-0.9597805192,-1.6352909979
 H,0,-0.3074841355,-0.8272862463,0.136320122
 H,0,0.4073352969,-3.5482819474,-2.6488110783

(7) B3LYP/6-31+G, Onsager, $\epsilon=37.219$, $a_0=4.52$, File glydeprotonsm3dielec**
 E(RB+HF-LYP) = -519.029571002

Zero-point correction= 0.225145 (Hartree/Particle)
 Thermal correction to Energy= 0.238254
 Thermal correction to Enthalpy= 0.239198
 Thermal correction to Gibbs Free Energy= 0.185888
 Sum of electronic and zero-point Energies= -518.804426
 Sum of electronic and thermal Energies= -518.791317
 Sum of electronic and thermal Enthalpies= -518.790373
 Sum of electronic and thermal Free Energies= -518.843683

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	149.507	47.814	112.200

C,0,1.8302083494,0.5304424465,-1.8537901512
 C,0,1.4697986284,-0.2830219681,-0.8579580664
 C,0,0.196579786,-1.0749009998,-0.8792641474
 N,0,0.3412174203,-2.5792401462,-0.6335185858
 C,0,0.9268995885,-2.8039225567,0.7458151973
 C,0,1.1731455525,-3.159149587,-1.7247214046
 C,0,1.5002779109,-4.5085315839,-1.8491794592
 O,0,2.2354253503,-5.024545725,-2.7113563581
 C,0,-1.0661740955,-3.1375623397,-0.6366870306
 O,0,0.8990988199,-5.3470136669,-0.8753276476
 C,0,1.1942699165,-6.7334617501,-1.001689448
 H,0,0.6735865588,-7.2247001532,-0.1755884143
 H,0,0.8383647752,-7.1314450413,-1.9586215208
 H,0,2.2712623554,-6.9199568875,-0.9313722134
 H,0,2.0618378991,-0.3041838925,0.0537591563
 H,0,2.7066610989,1.1656407235,-1.7733318741
 H,0,1.2492444693,0.6074711476,-2.7697949112
 H,0,-1.6424070275,-2.6807372301,0.1720024561
 H,0,-1.5115524212,-2.909536571,-1.6041522451
 H,0,-0.9978086714,-4.2140271591,-0.5031532114
 H,0,0.3164759111,-2.2931511751,1.4953107086
 H,0,0.9388037561,-3.8767722381,0.9239009283
 H,0,1.9456927669,-2.423568123,0.7494284384
 H,0,-0.2967155395,-0.9798875224,-1.8486146254
 H,0,-0.4843559978,-0.7139938367,-0.1011949954
 H,0,1.6715458395,-2.4287941639,-2.3383095751

(10) B3LYP/6-31+G, Onsager, $\epsilon=37.219$, $a_0=4.52$, File glydeprotonsm6dielec**
 E(RB+HF-LYP) = -519.030135107

Zero-point correction= 0.225290 (Hartree/Particle)
 Thermal correction to Energy= 0.238332
 Thermal correction to Enthalpy= 0.239276
 Thermal correction to Gibbs Free Energy= 0.186155
 Sum of electronic and zero-point Energies= -518.804845
 Sum of electronic and thermal Energies= -518.791803

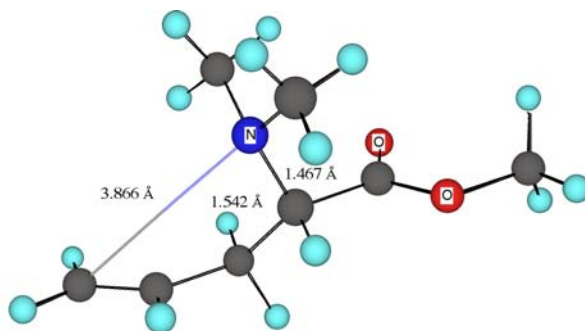
Sum of electronic and thermal Enthalpies= -518.790859
 Sum of electronic and thermal Free Energies= -518.843980

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	149.556	47.756	111.803

C,0,1.0753239842,-4.9229056452,-4.3427214639
 C,0,1.7529377156,-5.7695150024,-3.5610260962
 C,0,2.3618714605,-5.3721239411,-2.252353122
 N,0,3.8411367894,-4.8782978062,-2.3649147566
 C,0,4.6446332942,-5.9288041929,-3.0778470106
 C,0,4.0042302255,-3.6045244134,-3.1096773658
 C,0,3.4120455661,-2.3898061578,-2.7608503351
 O,0,3.4578199927,-1.3242176274,-3.4021605951
 C,0,4.3821952011,-4.7832147729,-0.9559626092
 O,0,2.7032405365,-2.4205058383,-1.5357972759
 C,0,2.1382535962,-1.1787512772,-1.125848343
 H,0,0.9385459746,-3.8807787939,-4.0681419333
 H,0,0.6381045075,-5.2523063712,-5.2810950329
 H,0,1.8653827688,-6.808108345,-3.8659340211
 H,0,2.3744177471,-6.2171960913,-1.5583274772
 H,0,1.8387763203,-4.5347487118,-1.793183841
 H,0,5.4227566992,-4.4685162345,-1.0250629094
 H,0,3.8041876611,-4.0358543127,-0.4184957442
 H,0,4.3043187627,-5.758852354,-0.4701098529
 H,0,5.6884744545,-5.6151498362,-3.0788443005
 H,0,4.2837001149,-6.0143343591,-4.1017018048
 H,0,4.5340481226,-6.8820735503,-2.5583338966
 H,0,4.4210658081,-3.7179324763,-4.0968589867
 H,0,2.9128149133,-0.4164201682,-0.9885390255
 H,0,1.6371419973,-1.379672312,-0.1757213987
 H,0,1.4162607861,-0.8071574086,-1.8606168017

Rearranged Product 2 Optimized Structure

(5) B3LYP/6-31+G**, Onsager, $\epsilon=37.219$, $a_0=4.52$, File productoptdielec



E(RB+HF-LYP) = -519.089960586

Zero-point correction= 0.224791 (Hartree/Particle)
 Thermal correction to Energy= 0.238204
 Thermal correction to Enthalpy= 0.239148
 Thermal correction to Gibbs Free Energy= 0.184255
 Sum of electronic and zero-point Energies= -518.865169
 Sum of electronic and thermal Energies= -518.851757
 Sum of electronic and thermal Enthalpies= -518.850812
 Sum of electronic and thermal Free Energies= -518.905705

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	149.475	47.065	115.532

C,0,3.0195767177,-0.5587695967,-1.8493310161
 O,0,2.9784771383,0.8206453959,-2.2731443863
 C,0,2.6546550724,1.039701552,-3.565841365
 O,0,2.4061304118,0.1461867509,-4.3537948729
 C,0,2.7012947141,2.5360098232,-3.9198796493
 N,0,3.918519259,2.9016901706,-4.6531686608
 C,0,4.1013685543,2.2806827729,-5.9627761666
 C,0,5.1318602098,2.83136711,-3.8438547639
 C,0,1.3783118493,4.3753873194,-5.0740383956
 C,0,1.4101627867,2.9276412085,-4.6657491031
 C,0,0.9781542269,4.8237743022,-6.2671343602
 H,0,3.2909637053,-0.5296426252,-0.7948634232
 H,0,2.0412967948,-1.0255391962,-1.9853508979
 H,0,3.7651997677,-1.1106662421,-2.4260960689
 H,0,2.7381922903,3.0903559773,-2.9761470592
 H,0,4.3097699622,1.1985691112,-5.9141940105
 H,0,3.2153239604,2.4301480553,-6.5828304933
 H,0,4.9433582221,2.7731103318,-6.4602896402
 H,0,5.4569932784,1.7997789207,-3.6159823532
 H,0,5.9467140462,3.3280575779,-4.3804466872
 H,0,4.9783264224,3.3551391753,-2.8957990834
 H,0,0.9493869184,5.8854050713,-6.4949005171
 H,0,0.666279961,4.1434058021,-7.0571151935
 H,0,1.690395442,5.0943208645,-4.3160908068
 H,0,1.2542365641,2.2748054407,-5.5300486428
 H,0,0.5747267246,2.7262159266,-3.978996383

(6) B3LYP/6-31+G, Onsager, $\epsilon=37.219$, $a_0=4.52$, File productopt2dielec**
 E(RB+HF-LYP) = -519.086815913

Zero-point correction= 0.224867 (Hartree/Particle)
 Thermal correction to Energy= 0.238077
 Thermal correction to Enthalpy= 0.239021
 Thermal correction to Gibbs Free Energy= 0.184813
 Sum of electronic and zero-point Energies= -518.861949
 Sum of electronic and thermal Energies= -518.848739
 Sum of electronic and thermal Enthalpies= -518.847795
 Sum of electronic and thermal Free Energies= -518.902003

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	149.396	46.769	114.090

C,0,-0.1099737695,0.0477482729,-0.8299552985
 H,0,-0.4511233542,0.6497809674,0.0073464641
 H,0,-0.812015136,-0.090967799,-1.650176577
 C,0,1.1135966741,-0.4888015249,-0.849556841
 H,0,1.7800195249,-0.3332516382,-0.0030454863
 C,0,1.6665269237,-1.2999395965,-1.992832881
 H,0,0.8630880137,-1.5856208092,-2.6795167558
 H,0,2.3577597693,-0.6838952386,-2.5841782511
 C,0,2.4591825539,-2.5688632167,-1.5660847335
 H,0,2.7242206335,-3.1085388298,-2.495148216
 N,0,1.7243596593,-3.429658868,-0.6416270563
 C,0,0.4159454063,-3.8222469156,-1.1605440088
 H,0,-0.2301000938,-2.9513225263,-1.283948917
 H,0,0.4768239896,-4.3607857159,-2.1268740675
 H,0,-0.0628028382,-4.4869771056,-0.4357830001
 C,0,2.4989576902,-4.6138652802,-0.2708904357
 H,0,1.9248109404,-5.2078344677,0.4461247728
 H,0,2.7359786824,-5.2589236435,-1.1392440053
 H,0,3.4324698632,-4.3209017952,0.2143565069
 C,0,3.7800381467,-2.095108233,-0.9480465036
 O,0,3.9686708311,-1.7968557975,0.2130554012
 O,0,4.7281504797,-1.9878938604,-1.9055313128
 C,0,6.0005331597,-1.4568394146,-1.4851964186
 H,0,6.6198566838,-1.4468074591,-2.3812757916
 H,0,5.8785538798,-0.4463183422,-1.0875520907
 H,0,6.4428726863,-2.0951171629,-0.7168504969

(7) B3LYP/6-31+G, Onsager, $\epsilon=37.219$, $a_0=4.52$, File productopt3dielec**

E(RB+HF-LYP) = -519.089337484

Zero-point correction=	0.224864 (Hartree/Particle)
Thermal correction to Energy=	0.238244
Thermal correction to Enthalpy=	0.239188
Thermal correction to Gibbs Free Energy=	0.184427
Sum of electronic and zero-point Energies=	-518.864473
Sum of electronic and thermal Energies=	-518.851093
Sum of electronic and thermal Enthalpies=	-518.850149
Sum of electronic and thermal Free Energies=	-518.904911

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	149.500	47.043	115.255

C,0,2.0972116997,-1.2394039194,-1.3419973751
 C,0,0.9038557079,-0.7630259154,-0.9736399636
 C,0,0.1622693882,0.3345687544,-1.6873465109
 C,0,-0.2059756183,1.5015483946,-0.7472168348
 C,0,-0.7220054405,2.7496595986,-1.4834955101

O,0,-1.3478563032,2.4630513282,-2.6450237075
 N,0,-1.1281441232,1.0848865598,0.3236681224
 C,0,-2.5071911626,0.8313419889,-0.0902253169
 C,0,-1.0744369562,1.9268417551,1.5172719421
 O,0,-0.6303355493,3.8788075708,-1.0377611767
 H,0,0.4065620709,-1.1771048615,-0.0980716168
 H,0,-0.7492559405,-0.0656557665,-2.1464930635
 H,0,0.7713763229,0.7234568213,-2.5112624917
 H,0,-1.6401314202,1.4375664507,2.3175201446
 H,0,-0.036675791,2.0320432924,1.8476581552
 H,0,-1.4904448035,2.9370626859,1.3644402978
 H,0,-3.0274405924,0.3107824892,0.7200361948
 H,0,-3.0749286877,1.7522027899,-0.3174268085
 H,0,-2.535223363,0.1886206917,-0.972497964
 H,0,2.6261652109,-0.8513856367,-2.2104317835
 H,0,2.5824437088,-2.0416630115,-0.793230955
 H,0,0.708162801,1.8341158005,-0.2449716168
 C,0,-1.9170017726,3.5829761165,-3.3550648518
 H,0,-2.376684979,3.157901212,-4.2464994871
 H,0,-2.663151439,4.0863711755,-2.7363181992
 H,0,-1.1343529684,4.2957716352,-3.6252756235

(10) B3LYP/6-31+G, Onsager, $\epsilon=37.219$, $a_0=4.52$, File productopt6dielec**
 E(RB+HF-LYP) = -519.086209304

Zero-point correction= 0.225090 (Hartree/Particle)
 Thermal correction to Energy= 0.238202
 Thermal correction to Enthalpy= 0.239147
 Thermal correction to Gibbs Free Energy= 0.185421
 Sum of electronic and zero-point Energies= -518.861119
 Sum of electronic and thermal Energies= -518.848007
 Sum of electronic and thermal Enthalpies= -518.847063
 Sum of electronic and thermal Free Energies= -518.900789

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	149.474	46.630	113.076

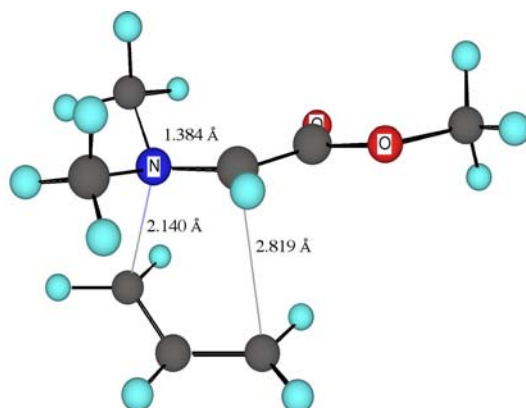
C,0,2.487779373,-1.7819295861,-0.5058834295
 O,0,3.1017892831,-2.9079264221,-1.161729972
 C,0,3.3963197536,-2.7433109156,-2.4610707631
 C,0,3.9527317417,-4.0017179147,-3.1371001045
 N,0,4.7352414621,-4.8483709583,-2.2351327498
 C,0,5.1656013089,-6.1029817345,-2.8506732632
 O,0,3.1853274825,-1.7125367801,-3.0732180904
 C,0,5.8958116773,-4.1316722175,-1.7050311321
 C,0,0.4249085842,-5.114275385,-2.9193328403
 C,0,1.7446302424,-5.3055511909,-2.8341085759
 C,0,2.7491362626,-4.7321723735,-3.7984721156
 H,0,2.3366627366,-2.0974042331,0.5259267021
 H,0,1.533325297,-1.5414692239,-0.9802297289
 H,0,3.1429447759,-0.9085173416,-0.5524104065

H,0,4.5796617196,-3.616811329,-3.9648688546
 H,0,6.6060750541,-3.8279063576,-2.4986958639
 H,0,6.4273095247,-4.7762713747,-0.9995009265
 H,0,5.5784331137,-3.2385732749,-1.1629214305
 H,0,5.7580203225,-5.951808196,-3.7748429864
 H,0,4.3133333244,-6.7431699195,-3.087428288
 H,0,5.7914122546,-6.6452016312,-2.1368813542
 H,0,-0.2611422106,-5.5677898651,-2.2098068511
 H,0,-0.014451091,-4.4997370141,-3.7027907937
 H,0,2.1447698027,-5.9153135184,-2.0259927188
 H,0,2.2611885441,-4.0190442775,-4.4713366583
 H,0,3.1509366601,-5.5285639651,-4.4363628043

G09 Calculations: Solution Phase Structures

Glycine Salt 1 Rearrangement Transition Structures

(5) B3LYP/6-31+G**, PCM, Solvent=n,n-DimethylFormamide File glycinetsg09



E(RB3LYP) = -519.030461896

Zero-point correction= 0.222430 (Hartree/Particle)
 Thermal correction to Energy= 0.235289
 Thermal correction to Enthalpy= 0.236233
 Thermal correction to Gibbs Free Energy= 0.183974
 Sum of electronic and zero-point Energies= -518.808032
 Sum of electronic and thermal Energies= -518.795173
 Sum of electronic and thermal Enthalpies= -518.794229
 Sum of electronic and thermal Free Energies= -518.846488

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	147.646	47.281	109.988

C,0,2.0476510567,-0.8407403104,-2.3026811864
 O,0,2.7310208127,0.4131715152,-2.4448847656

C,0,2.8280507641,0.9119166699,-3.7261560083
 C,0,3.4650335389,2.1867478488,-3.724905834
 N,0,3.8206558858,2.8839346139,-4.865972667
 C,0,4.712214967,4.0272320428,-4.5680373699
 O,0,2.3871300251,0.2717237758,-4.6945147886
 C,0,4.2972616826,2.119310433,-6.0432499887
 C,0,2.1169626582,3.8744473635,-5.6992197342
 C,0,1.4876580643,4.2798007394,-4.5039010014
 C,0,0.9048984259,3.3661538213,-3.6676527796
 H,0,2.0715605224,-1.0658324375,-1.2361253173
 H,0,1.0122300634,-0.7638645071,-2.6460588278
 H,0,2.5545103763,-1.6304666701,-2.8637564433
 H,0,3.6913407653,2.6507027772,-2.776658122
 H,0,5.2883601357,1.7030153879,-5.8293946173
 H,0,3.6013199967,1.3122401785,-6.2558527697
 H,0,4.3645341237,2.7978287723,-6.8951871553
 H,0,5.6780323504,3.6602607755,-4.2031294264
 H,0,4.8640869524,4.6126546744,-5.4750442794
 H,0,4.2512680877,4.6543655618,-3.8041732751
 H,0,2.5807649839,4.6072054229,-6.353002532
 H,0,1.7828225199,2.9609905931,-6.1813019091
 H,0,1.6670953653,5.2904579057,-4.1395027803
 H,0,0.6497143448,2.3715876429,-4.0174576757
 H,0,0.5580755308,3.6426164093,-2.6762187455

(6) B3LYP/6-31+G, PCM, Solvent=n,n-DimethylFormamide File glycinets2g09**

E(RB3LYP) = -519.029228927

Zero-point correction= 0.222597 (Hartree/Particle)
 Thermal correction to Energy= 0.235405
 Thermal correction to Enthalpy= 0.236349
 Thermal correction to Gibbs Free Energy= 0.184030
 Sum of electronic and zero-point Energies= -518.806632
 Sum of electronic and thermal Energies= -518.793824
 Sum of electronic and thermal Enthalpies= -518.792880
 Sum of electronic and thermal Free Energies= -518.845199

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	147.719	47.120	110.115

C,0,1.6646225112,-0.2904658293,-2.2390273468
 C,0,1.3937924142,-0.2368358537,-0.9045727051
 C,0,0.1628660926,-0.7258261744,-0.3933679992
 N,0,0.3774319546,-2.7525042325,-0.6434514461
 C,0,1.1208787358,-3.0525286935,-1.7797241608
 C,0,2.5295543802,-3.2359787726,-1.8256722172
 O,0,2.9226306035,-3.5847772639,-3.1084147139
 C,0,4.3296649444,-3.7651605541,-3.3089600705
 C,0,-1.0413116214,-3.1724732519,-0.7678699265
 C,0,0.9305975468,-3.1746896314,0.6705803798
 O,0,3.3667659916,-3.1593138559,-0.9106730642

H,0,4.4428688019,-4.0349447061,-4.3597145832
 H,0,4.8787969936,-2.8420479366,-3.1000318166
 H,0,4.7213548777,-4.5649983231,-2.6742662511
 H,0,2.2024389182,-0.0310932714,-0.2054333651
 H,0,2.6522580529,-0.0674561726,-2.6315303005
 H,0,0.8776359534,-0.4662662045,-2.9659441738
 H,0,-1.6204797582,-2.7258963297,0.0417744639
 H,0,-1.438107362,-2.8359090369,-1.726117332
 H,0,-1.108291212,-4.2631894666,-0.7096080128
 H,0,0.2385010435,-2.8586957988,1.451667808
 H,0,1.0304638807,-4.2646703457,0.6875376426
 H,0,1.9076785264,-2.7244674684,0.8164348627
 H,0,-0.7104228343,-0.6639929718,-1.0364700281
 H,0,-0.0484895532,-0.6471558775,0.6692688841
 H,0,0.5637001178,-3.1190719772,-2.7027905277

(10) B3LYP/6-31+G, PCM, Solvent=n,n-DimethylFormamide File glycinets6g09**
 E(RB3LYP) = -519.027125741

Zero-point correction= 0.222446 (Hartree/Particle)
 Thermal correction to Energy= 0.235297
 Thermal correction to Enthalpy= 0.236241
 Thermal correction to Gibbs Free Energy= 0.183994
 Sum of electronic and zero-point Energies= -518.804680
 Sum of electronic and thermal Energies= -518.791829
 Sum of electronic and thermal Enthalpies= -518.790885
 Sum of electronic and thermal Free Energies= -518.843132

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	147.651	47.296	109.963

C,0,2.4719421222,-1.2895645714,-1.1934324898
 H,0,2.3483814669,-1.2912706862,-0.1103247096
 H,0,1.5072441878,-1.1321804541,-1.6820445521
 H,0,3.1629594455,-0.4977419294,-1.4932009523
 O,0,3.0059440967,-2.5846230552,-1.5187874031
 C,0,3.2785515491,-2.8202568244,-2.8427133059
 O,0,3.0294735082,-1.9616967253,-3.7059176082
 C,0,3.8349751529,-4.1024462747,-3.1354741118
 H,0,3.920885444,-4.3401167946,-4.1855943093
 N,0,4.2981370763,-5.059125223,-2.2453066851
 C,0,5.0259972772,-4.6291957359,-1.0265862579
 H,0,5.9938897656,-4.2017464912,-1.3119600805
 H,0,5.1882804963,-5.5038280271,-0.3944618081
 H,0,4.4442035154,-3.8870378975,-0.4886282257
 C,0,5.0337552427,-6.1405505657,-2.9426955493
 H,0,5.9574723588,-5.7415002801,-3.3762050151
 H,0,4.4073898266,-6.5481913053,-3.7366477693
 H,0,5.2765844059,-6.9297134649,-2.2311554963
 C,0,2.6700333229,-6.143090953,-1.383257763
 H,0,3.1694649296,-7.0124227558,-0.9656105476

H,0,2.4679842379,-5.337084547,-0.6850457186
 C,0,1.8583081545,-6.2683534831,-2.5301459781
 C,0,1.2245224835,-5.1824708879,-3.0709705017
 H,0,1.9247163509,-7.1851916007,-3.1143783927
 H,0,1.0747030609,-4.2764832571,-2.4941432633
 H,0,0.7364495217,-5.2332062092,-4.0399265056

Glycine Salt 1 Starting Material Optimized Structure

(5) B3LYP/6-31+G**, PCM, Solvent=n,n-DimethylFormamide File glycinesmg09

E(RB3LYP) = -519.537162910

Zero-point correction= 0.240131 (Hartree/Particle)
 Thermal correction to Energy= 0.253212
 Thermal correction to Enthalpy= 0.254156
 Thermal correction to Gibbs Free Energy= 0.200280
 Sum of electronic and zero-point Energies= -519.297032
 Sum of electronic and thermal Energies= -519.283951
 Sum of electronic and thermal Enthalpies= -519.283007
 Sum of electronic and thermal Free Energies= -519.336883

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	158.893	47.518	113.393

C,0,2.1534896449,-0.9414872192,-2.2643437961
 O,0,2.8407647356,0.3300924061,-2.4160514486
 C,0,2.8190434077,0.886548126,-3.624482364
 O,0,2.2770569689,0.4134890104,-4.6045784984
 C,0,3.5745546606,2.2094768622,-3.5563651044
 N,0,3.7058691113,2.9652990813,-4.8564904142
 C,0,4.4401622847,2.1453628067,-5.8944820138
 C,0,4.5258155736,4.2037589193,-4.5686015629
 C,0,1.4943148406,4.2036302368,-4.5166035797
 C,0,0.3069589592,3.7958297331,-4.0574246793
 C,0,2.3330362327,3.3715835379,-5.4397802911
 H,0,2.2892156868,-1.2117730953,-1.2195470349
 H,0,1.0955133981,-0.8201366629,-2.5008977653
 H,0,2.6053468462,-1.6863336113,-2.9208533498
 H,0,4.5821837373,2.0215467531,-3.1798460299
 H,0,5.4003756313,1.8401594447,-5.4795197767
 H,0,3.8384776321,1.2768105239,-6.1481962329
 H,0,4.5960061917,2.7721587955,-6.7713695591
 H,0,5.5270563339,3.8951516472,-4.2705919971
 H,0,4.573097761,4.8030420703,-5.477093175
 H,0,4.0589534765,4.7704892903,-3.7652834674
 H,0,2.5787321375,3.9187216804,-6.3533699709
 H,0,1.8342070456,2.4410485614,-5.7045865201
 H,0,1.8491166487,5.2032888818,-4.2778735622
 H,0,-0.0960280422,2.814700667,-4.2959428742
 H,0,-0.3059129184,4.4428356184,-3.4375127278

H,0,3.0654550142,2.860356935,-2.843284204

(6) B3LYP/6-31+G, PCM, Solvent=n,n-DimethylFormamide File glycinesm2g09**
E(RB3LYP) = -519.533323510

Zero-point correction= 0.240119 (Hartree/Particle)
Thermal correction to Energy= 0.253156
Thermal correction to Enthalpy= 0.254101
Thermal correction to Gibbs Free Energy= 0.200905
Sum of electronic and zero-point Energies= -519.293205
Sum of electronic and thermal Energies= -519.280167
Sum of electronic and thermal Enthalpies= -519.279223
Sum of electronic and thermal Free Energies= -519.332419

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	158.858	47.522	111.960

C,0,1.9668400681,0.0774849981,-2.1361906205
C,0,1.6174724358,-0.5657037681,-1.0177314988
C,0,0.2744275404,-1.2082277091,-0.8527239077
N,0,0.2888468929,-2.7323301473,-0.607360288
C,0,0.8710444944,-3.0563162635,0.7518494367
C,0,0.9790522993,-3.4679166536,-1.736114173
C,0,2.4995595376,-3.3509233193,-1.8327985632
O,0,3.2779302886,-3.2493661086,-0.9059841412
C,0,-1.1555037685,-3.1911842978,-0.61062103
O,0,2.8495089876,-3.4817309594,-3.1127180191
C,0,4.2725427105,-3.5343743677,-3.3975980849
H,0,4.3401759502,-3.680962424,-4.473337585
H,0,4.7417681991,-2.5945714929,-3.1028993807
H,0,4.7280683378,-4.3680959366,-2.8612069824
H,0,2.2873590613,-0.5712033855,-0.162256776
H,0,2.9191299465,0.5930318008,-2.2121674255
H,0,1.3122837835,0.1191620173,-3.0033509484
H,0,-1.7034330709,-2.6054266512,0.1261925701
H,0,-1.5776237613,-3.0364396725,-1.6029685268
H,0,-1.1875332448,-4.2473384424,-0.3466682369
H,0,0.2354007365,-2.5896094486,1.5033637191
H,0,0.8669120984,-4.1388046076,0.8782438106
H,0,1.8878616555,-2.6847519309,0.812110164
H,0,-0.3390854058,-1.05653076,-1.7424777772
H,0,-0.2548803538,-0.7964732742,0.0104793075
H,0,0.5286396913,-3.1300541463,-2.668788351
H,0,0.7500328897,-4.5302580491,-1.6153616917

(10) B3LYP/6-31+G, PCM, Solvent=n,n-DimethylFormamide File glycinesm6g09**
E(RB3LYP) = -519.534168792

Zero-point correction= 0.240188 (Hartree/Particle)
Thermal correction to Energy= 0.253313

Thermal correction to Enthalpy= 0.254258
 Thermal correction to Gibbs Free Energy= 0.199545
 Sum of electronic and zero-point Energies= -519.293981
 Sum of electronic and thermal Energies= -519.280855
 Sum of electronic and thermal Enthalpies= -519.279911
 Sum of electronic and thermal Free Energies= -519.334624

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	158.957	47.507	115.152

C,0,2.4594190925,-1.3322934793,-1.1552564146
 O,0,3.083950288,-2.5823612779,-1.564176769
 C,0,3.6244126779,-2.616993319,-2.7788508197
 C,0,4.2567985446,-3.945710338,-3.1861319682
 N,0,4.3544243163,-5.0880841121,-2.1947478836
 C,0,5.1070446831,-6.2040657358,-2.8880899033
 O,0,3.6349404167,-1.6929236405,-3.5666785338
 C,0,5.1470364552,-4.6905690448,-0.9700243226
 C,0,2.9697094498,-5.6032780565,-1.7407321828
 C,0,2.0802925762,-6.0516967696,-2.8618881348
 C,0,0.9100880131,-5.4650508246,-3.1329985952
 H,0,2.1002454451,-1.5156545913,-0.1452096276
 H,0,1.6335814464,-1.0991507741,-1.8280971725
 H,0,3.1992066175,-0.5313838971,-1.1685801401
 H,0,3.6950358903,-4.3119220057,-4.0474686466
 H,0,6.1143989281,-4.3077681102,-1.2946936626
 H,0,5.2854342072,-5.5786840087,-0.3548076789
 H,0,4.6000965782,-3.9294554219,-0.4209245992
 H,0,6.1188293745,-5.8600197839,-3.0981452054
 H,0,4.6023826395,-6.4607451929,-3.8171002209
 H,0,5.1358663645,-7.0648333352,-2.2211697309
 H,0,3.1974164506,-6.4294378759,-1.0626099851
 H,0,2.5162738542,-4.7937470017,-1.1724024494
 H,0,2.380448247,-6.9350029601,-3.4204709341
 H,0,0.559651051,-4.5968600716,-2.5804971557
 H,0,0.2588733137,-5.8485860411,-3.9122612558
 H,0,5.2722780788,-3.7241683307,-3.5195240078

Deprotonated Glycine Salt 1 Starting Material Optimized Structure

(5) B3LYP/6-31+G, PCM, Solvent=n,n-DimethylFormamide File glydeprotonsmg09**
 E(RB3LYP) = -519.047416758

Zero-point correction= 0.225075 (Hartree/Particle)
 Thermal correction to Energy= 0.238266
 Thermal correction to Enthalpy= 0.239210
 Thermal correction to Gibbs Free Energy= 0.185194
 Sum of electronic and zero-point Energies= -518.822342
 Sum of electronic and thermal Energies= -518.809151
 Sum of electronic and thermal Enthalpies= -518.808207

Sum of electronic and thermal Free Energies= -518.862223

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	149.514	47.781	113.687

C,0,2.1680807657,-0.9349891973,-2.2833868741
O,0,2.8281115627,0.3307905404,-2.3624357391
C,0,2.9508843895,0.8838109054,-3.6423853089
O,0,2.4544727899,0.2819670546,-4.630360816
C,0,3.6544060369,2.079011975,-3.6215566914
N,0,3.8073570757,2.8783591375,-4.8594925133
C,0,4.5537660197,2.0992901972,-5.9198412155
C,0,4.6189404975,4.1000523902,-4.5365804807
C,0,1.629659131,4.2079100757,-4.6181067034
C,0,0.4776939084,3.8289326502,-4.0559236451
C,0,2.453131903,3.3038599781,-5.482717371
H,0,2.1750031132,-1.2033508261,-1.2253239961
H,0,1.1353891401,-0.8733999971,-2.6405413676
H,0,2.6963633069,-1.7006189857,-2.8605586432
H,0,3.9216492521,2.5907457748,-2.7111400151
H,0,5.5310961656,1.841508356,-5.5143321695
H,0,3.9837631933,1.1976613865,-6.1339442594
H,0,4.6593996462,2.7172097784,-6.8136730991
H,0,5.5990427245,3.7751831833,-4.1886806768
H,0,4.7175671904,4.7091959494,-5.4355845056
H,0,4.1201694734,4.6634068927,-3.7498451504
H,0,2.7009022032,3.793876914,-6.4293686985
H,0,1.9371076715,2.3648520516,-5.6825645376
H,0,1.9719622941,5.2336278621,-4.4954754545
H,0,0.0948458651,2.8174978173,-4.167465121
H,0,-0.1214073196,4.5222501358,-3.4726409471

(6) B3LYP/6-31+G, PCM, Solvent=n,n-DimethylFormamide File glydeprotonsm2g09**
E(RB3LYP) = -519.043899320

Zero-point correction=	0.225171 (Hartree/Particle)
Thermal correction to Energy=	0.238270
Thermal correction to Enthalpy=	0.239214
Thermal correction to Gibbs Free Energy=	0.185645
Sum of electronic and zero-point Energies=	-518.818728
Sum of electronic and thermal Energies=	-518.805629
Sum of electronic and thermal Enthalpies=	-518.804685
Sum of electronic and thermal Free Energies=	-518.858255

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	149.517	47.670	112.747

C,0,1.7704868142,0.426204032,-1.8872786684
C,0,1.4382592971,-0.3456672273,-0.8483776029
C,0,0.1705775447,-1.1389521958,-0.8050564494

N,0,0.3549623387,-2.6700388549,-0.6627671639
 C,0,1.0817389265,-3.2792112121,-1.8004188025
 C,0,2.4682998949,-3.3149076983,-1.8989739996
 O,0,2.8543129367,-3.8057926459,-3.1580364104
 C,0,4.252853838,-4.0327344215,-3.3428530525
 C,0,-1.0337608033,-3.2582094705,-0.6464117923
 C,0,0.9869999989,-2.9845617497,0.6714210321
 O,0,3.3553903105,-3.0166847055,-1.0624889637
 H,0,4.3558956564,-4.4149042131,-4.360368467
 H,0,4.8297722031,-3.1087818702,-3.2373168177
 H,0,4.6378531862,-4.7722501101,-2.6328598307
 H,0,2.0718129047,-0.3645104585,0.0348439731
 H,0,2.6674064088,1.0383320522,-1.8720157181
 H,0,1.1549821482,0.4754558348,-2.7823554305
 H,0,-1.599720624,-2.8211177442,0.1770653856
 H,0,-1.5214011124,-3.0343357895,-1.5950895973
 H,0,-0.9436856647,-4.3360010235,-0.5216625226
 H,0,0.398843631,-2.5046277991,1.4551111428
 H,0,0.9766415633,-4.0671213127,0.7947616981
 H,0,2.0144104291,-2.6343856525,0.6631119585
 H,0,-0.3996687783,-1.0028754563,-1.7253952808
 H,0,-0.447900984,-0.8311637999,0.0452945416
 H,0,0.4520379357,-3.4615675079,-2.6582581616

(10) B3LYP/6-31+G, PCM, Solvent=n,n-DimethylFormamide File glydeprotonsm6g09**
 E(RB3LYP) = -519.043883469

Zero-point correction= 0.225120 (Hartree/Particle)
 Thermal correction to Energy= 0.238298
 Thermal correction to Enthalpy= 0.239243
 Thermal correction to Gibbs Free Energy= 0.185174
 Sum of electronic and zero-point Energies= -518.818763
 Sum of electronic and thermal Energies= -518.805585
 Sum of electronic and thermal Enthalpies= -518.804641
 Sum of electronic and thermal Free Energies= -518.858709

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	149.535	47.808	113.797

C,0,2.5004854509,-1.3180273861,-1.1595274816
 O,0,3.1150361372,-2.5619384397,-1.5140546968
 C,0,3.5752955518,-2.6768431468,-2.8302899019
 C,0,4.2054688996,-3.8776401706,-3.1347088876
 N,0,4.3251607398,-5.041347192,-2.2180048344
 C,0,5.0730882836,-6.1213641094,-2.9516081487
 O,0,3.4075072776,-1.7161140855,-3.6239114802
 C,0,5.1297295553,-4.7055790025,-0.9811843745
 C,0,2.9645813396,-5.606099123,-1.7364693893
 C,0,2.0683660154,-6.0831794307,-2.837770669
 C,0,0.8907491412,-5.516004328,-3.116346989
 H,0,2.221694729,-1.417971949,-0.1090865721

H,0,1.6083972927,-1.1289873204,-1.7633464886
 H,0,3.1957496291,-0.4822902283,-1.2805907173
 H,0,4.4735907945,-4.0928487748,-4.1566996452
 H,0,6.1101588557,-4.3627031245,-1.3084826826
 H,0,5.2227842332,-5.5982221498,-0.3591659314
 H,0,4.6155301115,-3.9134876007,-0.443404435
 H,0,6.0625352367,-5.7393416268,-3.2003761707
 H,0,4.5373809881,-6.3707604226,-3.8655133363
 H,0,5.1556843858,-6.9976031702,-2.3082733867
 H,0,3.2081297073,-6.4259934868,-1.0533165576
 H,0,2.501842465,-4.7954197012,-1.1757231913
 H,0,2.3761570556,-6.9709564544,-3.3864516252
 H,0,0.5394888394,-4.6374331068,-2.5809242568
 H,0,0.2380962843,-5.9184384696,-3.8855751502

Rearranged Product 2 Optimized Structure

(5) B3LYP/6-31+G, PCM, Solvent=n,n-DimethylFormamide File productoptg09**
 E(RB3LYP) = -519.097435780

Zero-point correction= 0.224596 (Hartree/Particle)
 Thermal correction to Energy= 0.237973
 Thermal correction to Enthalpy= 0.238917
 Thermal correction to Gibbs Free Energy= 0.184109
 Sum of electronic and zero-point Energies= -518.872840
 Sum of electronic and thermal Energies= -518.859463
 Sum of electronic and thermal Enthalpies= -518.858518
 Sum of electronic and thermal Free Energies= -518.913326

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	149.330	47.089	115.353

C,0,3.0425787406,-0.5360064263,-1.8337105834
 O,0,3.0020189838,0.8377910468,-2.2881996281
 C,0,2.6419407485,1.0428720276,-3.5690277475
 O,0,2.3576304003,0.1368308819,-4.3361249851
 C,0,2.6928794654,2.5323080072,-3.948346332
 N,0,3.9136481039,2.8795215049,-4.6904493421
 C,0,4.1085649547,2.206661761,-5.97486883
 C,0,5.1251131408,2.8370039598,-3.8716720376
 C,0,1.3323886873,4.3886171754,-5.0278079481
 C,0,1.3985995322,2.9238570207,-4.6900173857
 C,0,1.0079033644,4.885403623,-6.22591894
 H,0,3.3423718197,-0.4852187056,-0.7884005111
 H,0,2.055701526,-0.9931012619,-1.9293961365
 H,0,3.7709101561,-1.1042444231,-2.4155462846
 H,0,2.7355239857,3.0993089945,-3.0131469357
 H,0,4.3450844426,1.1336366497,-5.877257989
 H,0,3.2189920897,2.3051333951,-6.5999319981
 H,0,4.9404247102,2.6915122061,-6.4953359307

H,0,5.4397228575,1.8139373023,-3.5985424941
 H,0,5.9459458372,3.3010569533,-4.4273715034
 H,0,4.9709759769,3.4049089546,-2.9494562325
 H,0,0.9466054941,5.9563216421,-6.3986850935
 H,0,0.7910842102,4.2374108614,-7.0727893496
 H,0,1.5443648661,5.0767716469,-4.2082498367
 H,0,1.2647786551,2.3130060156,-5.5876402183
 H,0,0.563923251,2.6724811871,-4.0199697264

(6) B3LYP/6-31+G, PCM, Solvent=n,n-DimethylFormamide File productopt2g09**
 E(RB3LYP) = -519.084627831

Zero-point correction= 0.224904 (Hartree/Particle)
 Thermal correction to Energy= 0.237956
 Thermal correction to Enthalpy= 0.238900
 Thermal correction to Gibbs Free Energy= 0.185406
 Sum of electronic and zero-point Energies= -518.859724
 Sum of electronic and thermal Energies= -518.846672
 Sum of electronic and thermal Enthalpies= -518.845728
 Sum of electronic and thermal Free Energies= -518.899222

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	149.319	46.840	112.588

C,0,1.6366796561,-1.3267135131,-2.0472838687
 C,0,1.1593585746,-0.4455103829,-0.9224993564
 C,0,-0.0895303247,0.0172829689,-0.8055437519
 N,0,1.7199604844,-3.4298659258,-0.6375397797
 C,0,2.4869110721,-4.6388867158,-0.3160233169
 C,0,2.4333153029,-2.593982448,-1.6086700367
 C,0,3.7737719964,-2.1167344897,-1.0280625934
 O,0,3.9380173765,-1.8318011174,0.143549434
 C,0,0.3834437645,-3.8058404456,-1.1084888258
 O,0,4.8172530374,-1.9284678893,-1.8666731025
 C,0,4.8107217205,-2.316346025,-3.2606106963
 H,0,5.7885193941,-2.0175828235,-3.6364114755
 H,0,4.6939913292,-3.3973098053,-3.3619746537
 H,0,4.0323465031,-1.7915374957,-3.8175483625
 H,0,1.9043263381,-0.1564342192,-0.1830070408
 H,0,2.2946658269,-0.7420071201,-2.7041682384
 H,0,0.7936331745,-1.6361550015,-2.671750835
 H,0,-0.0706339489,-4.4719210497,-0.3700940795
 H,0,-0.2582850955,-2.928928146,-1.2029444901
 H,0,0.4057400489,-4.3367363738,-2.078747031
 H,0,1.9423826394,-5.2210145553,0.4322372908
 H,0,2.6502394072,-5.2827219544,-1.200407773
 H,0,3.458620861,-4.3754246571,0.1069527111
 H,0,-0.8681469354,-0.2462385671,-1.5187105461
 H,0,-0.3737860142,0.6794966022,0.0074062715
 H,0,2.6315788107,-3.1725498497,-2.5265948535

(10) B3LYP/6-31+G, PCM, Solvent=n,n-DimethylFormamide File productopt6g09**
 E(RB3LYP) = -519.094691052

Zero-point correction= 0.224996 (Hartree/Particle)
 Thermal correction to Energy= 0.238080
 Thermal correction to Enthalpy= 0.239024
 Thermal correction to Gibbs Free Energy= 0.185419
 Sum of electronic and zero-point Energies= -518.869695
 Sum of electronic and thermal Energies= -518.856611
 Sum of electronic and thermal Enthalpies= -518.855667
 Sum of electronic and thermal Free Energies= -518.909272

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	149.397	46.669	112.821

C,0,2.441390572,-1.7716528274,-0.5189075796
 O,0,3.0489564472,-2.9099189907,-1.1737616144
 C,0,3.367137291,-2.7589375587,-2.4640945494
 C,0,3.9458988755,-4.0156681844,-3.1220981534
 N,0,4.7437212392,-4.8306104426,-2.2001528003
 C,0,5.1989028276,-6.0884098882,-2.8011553316
 O,0,3.1644883319,-1.7298297361,-3.090318796
 C,0,5.9026780504,-4.0763702645,-1.709091931
 C,0,0.4486452748,-5.1644505483,-2.8921323662
 C,0,1.7661669234,-5.3895194064,-2.8470357453
 C,0,2.7656528122,-4.7782265837,-3.7924777215
 H,0,2.274532496,-2.0878847624,0.5093842998
 H,0,1.4955496185,-1.5190593286,-1.0021443947
 H,0,3.1148325601,-0.9129471814,-0.5529003434
 H,0,4.5732569868,-3.6322451348,-3.9484666213
 H,0,6.5919477461,-3.7874457403,-2.5243861354
 H,0,6.4570939865,-4.6902373957,-0.9940631908
 H,0,5.5802667592,-3.1697408028,-1.1921840129
 H,0,5.7795246057,-5.9345387397,-3.730055097
 H,0,4.3593999225,-6.7497622075,-3.0232788363
 H,0,5.8427391042,-6.603229016,-2.0832681707
 H,0,-0.2338675305,-5.6499893735,-2.2001057324
 H,0,0.0091402948,-4.4891996701,-3.6236827216
 H,0,2.1612570338,-6.0701537788,-2.0942419355
 H,0,2.2626461954,-4.0767305126,-4.4661419253
 H,0,3.197600576,-5.5567739247,-4.4315145937

VITA

Sean Christopher Collins received a Bachelor of Science degree in chemistry in May of 2007 from Schreiner University, Kerrville, Texas. He started his graduate studies at Texas A&M University in August 2007. Working under the direction of Dr. Daniel A. Singleton, he received his Master of Science in chemistry in August 2010.

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