A Theoretical Study of Silylamides

Thesis

A Theoretical Study of Silylamides

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By

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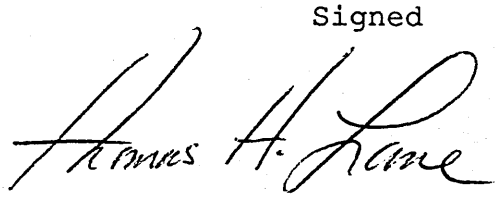
STATEMENT

The work embodied in this thesis was carried out by the author during the period January 1987 to May 1990 in the Department of Chemistry at the Open University and at the Dow Corning Corporation, under the supervision of Dr. A. R. Bassindale.

Signed



Thomas H. Lane

May 1990

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Thomas H. Lane

Abstract

Silylation is an important reaction in organosilicon and related chemistries. It involves the reversible exchange of an active hydrogen for a silyl group, generally trimethysilyl, which dramatically alters the physical and chemical characteristics of the original molecule. Among the various classes of silylating agents available, the silylamides are the most interesting. This class of silylating agent has demonstrated thermodynamic silylating power which spans over seven orders of magnitude. The structural complexity of these materials appears to be related to their reactivity and includes both tautomeric and rotameric species. The work presented here, explores this novel class of materials. The hindered rotation of silylamides, the 1,3-migration of silicon between nitrogen and oxygen in these materials, and some of their conformational effects on the silylation process are examined using both semiempirical quantum mechanical methods and *ab initio* techniques.

The computational data presented here, supports what is known about the rotational and tautomeric behaviour of silylamides and silylformamide. We have successfully calculated the torsional barrier for a series of materials and explained some of their unique electronic and chemical characteristics.

The activated 5-coordinate intermediate for the 1,3-migration of silicon between nitrogen and oxygen has been characterized and an estimated activation energy for the process given.

The reaction of N-silylformamide and O-silylformimide with water was studied. Those data suggest that the O-silylimidate tautomer is the preferred tautomeric species for the silylation of water. A calculated energy profile for each reaction is given and explained.

Several semiempirical molecular orbital methods were evaluated during this work and those findings are described and compared to *ab initio* results.

Conversions

	Multiply by:
atomic units to kcal mol^{-1}	627.54
kcal mol^{-1} to kJ mol^{-1}	4.184

A Theoretical Study of Silylamides

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Chapter One

Introduction and Background

Silylamides

1.0 Introduction and Background

1.1.1 Review of Silylamides

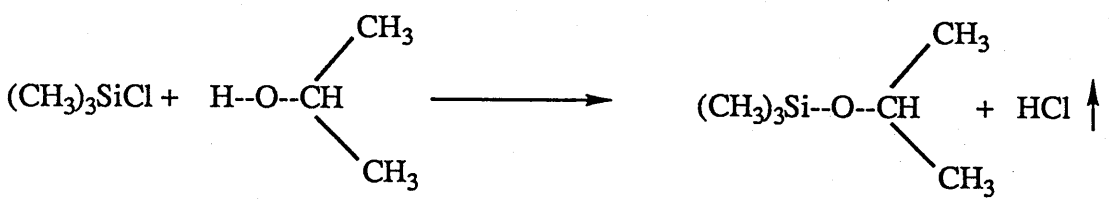
Silylating agents play an important role in the chromatographic sciences [1-4], synthetic organic chemistry [5-15], and in the drug industry [16-19]. In fact, over four million pounds of organosilicon compounds were used in Europe for the synthesis of pharmaceuticals [1] during 1977 alone.

The process of silylation involves the incorporation of a silyl group into an organic molecule in the place of an active hydrogen. The silyl group, generally trimethylsilyl, is substituted for an active hydrogen (H-O, H-N, H-S) which results in a decrease in molecular polarity. Consequently, hydrogen bonding interactions are markedly reduced and volatility generally enhanced. Such molecular modifications also result in increased lipophilicity and in some cases altered chemical reactivity. These reagents are often used for the derivatisation of organic molecules for gas chromatographic analysis. The four primary benefits of the derivatisation are to increase volatility, to increase thermal stability, to enhance detectability, and to improve separation.

A silylating agent is generally considered to be any silicon moiety directly attached to one of seven

heteroatoms, oxygen, nitrogen, sulphur, fluorine, chlorine, bromine, or iodine. An active hydrogen is defined as any hydrogen directly attached to one of the seven predefined heteroatoms. The remaining valencies in either the silicon or organic moiety are important in establishing the steric and electrostatic components of the reactants. Equation 1.1 shows an example of a typical silylation reaction. Note that all silylation reactions are reversible, but may be driven to completion through the use of Le Chatelier's principle.

Equation 1.1:



There are many commercially available silylating agents available today. The most common are given in Table 1.1.

Table 1.1:

Common Silylating Agents

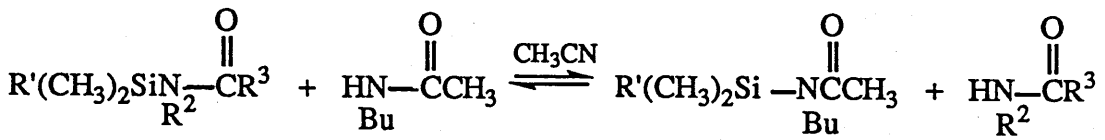
Chemical name	Formula
trimethylchlorosilane (TMCS)	$(CH_3)_3SiCl$
hexamethyldisilazane (HMDSz)	$((CH_3)_3Si)_2NH$
N-trimethylsilylimidazole (TSIM)	$(CH_3)_3SiNCH{=}N{-}CH{=}CH$ (|_____|)
N,O-bis(trimethylsilyl)acetamide (BSA)	$(CH_3)_3SiN{=}C(CH_3)OSi(CH_3)_3$
dimethyldichlorosilane (DMCS)	$(CH_3)_2SiCl_2$
chloromethyldimethylchlorosilane (CMDMS)	$ClCH_2(CH_3)_2SiCl$
N,N'-bis(trimethylsilyl)urea (BSU)	$((CH_3)_3SiN)_2CO$
N-trimethylsilyldiethylamine (TMSDEA)	$(CH_3)_3SiN(CH_2CH_3)_2$
N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA)	$(CH_3)_3SiN{=}C(CF_3)OSi(CH_3)_3$
N-methyl-N-trimethylsilyltrifluoroacetamide (MSTFA)	$(CH_3)_3SiN(CH_3)C(O)CF_3$
N-methyl-N-trimethylsilylacetamide (MMSTA)	$(CH_3)_3Si{-}N(CH_3)COCH_3$
t-butyldimethylchlorosilane	$t\text{-}C_4H_9(CH_3)_2SiCl$
t-butyldimethylsilylimidazole	$t\text{-}C_4H_9(CH_3)_2SiNCH{=}N{-}CH{=}CH$ (|_____|)

The area of silylation has been reviewed extensively over the last ten years [20-27,10]. The application of this technology has extended to the use of functional silylating agents for the modification of surfaces or for enhancing the molecular interactions between surfaces [28]. One of the most important and exciting classes of silylating agents is the N-substituted-trimethylsilylamides.

1.1.2 N-substituted-trimethylsilylamides

N-substituted-trimethylsilylamides are among the most and least powerful silyl donors. Their unusually broad range of reactivity makes them of special interest to study. Lane and Frye [38] studied these unique materials as a function of substituent at both the carbonyl carbon and at the nitrogen. The reaction scheme is shown in Equation 1.2.

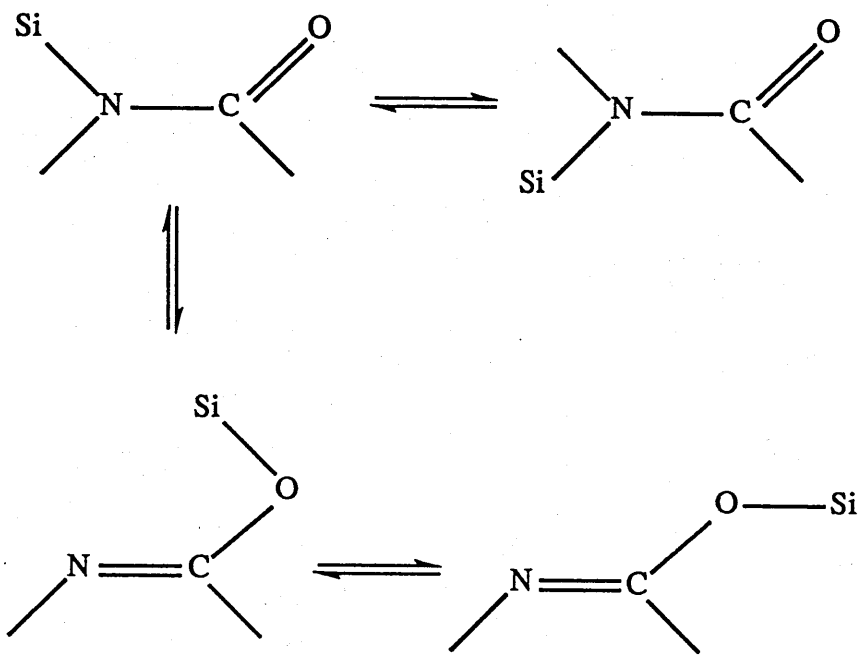
Equation 1.2:



The structural features of the silylamide were then correlated to the calculated equilibrium constant for the reaction. Lane and Frye reported several trends from these thermodynamic data and related them to the relative silylating ability of the various silylamides studied. The relative thermodynamic silylating ability of these materials increased with increasing steric bulk of the nitrogen substituent. For the acetamide series, a 1000 fold change in relative silylating ability was observed as the substituent was changed from methyl to t-butyl. Overall, changes in the nitrogen substituent resulted in relative silylating powers which differed by over seven powers of ten (10^7). Altering the steric bulk or electron donating ability of the carbonyl substituent also produced changes in the relative chemical stability of these silylamides. Although these changes were less dramatic, differences of over a factor of 100 in the relative silylating ability were noted for methyl substituted amides. The authors alluded to the possibility that these large differences in thermodynamic silylation ability might be related to the various tautomeric or topomeric differences available to this class of materials. It was this possible correlation between the structural complexity of silylamides and their relative thermodynamic and kinetic silylating ability or power which has captured our interest.

Silylamides can exist in either a N- or O-silyl tautomeric form with each having two possible rotameric structures. These two tautomeric pairs are generally illustrated in Equation 1.3.

Equation 1.3:



Bis-(trimethylsilyl)acetamide is known to exist only in the N,O-form rather than the N,N-bis-(trimethylsilyl)acetamide isomer [29] and believed to be one of the best silylation agents both in terms of kinetic and thermodymanic silylating ability [30]. Trimethylsilylacetanilides [31-33] are believed to consist of a dynamic mixture of N-silylamide and the O-silylated imidate tautomeric structures. Until recently, the N-alkyltrimethylsilylamides have been thought to be totally in the N-silylated form [34]. However, it has since been

demonstrated that the N-alkylsilylamides are in fact a mixture of tautomeric isomers [35-37]. Lane and Frye [38] have demonstrated using unambiguous examples that the thermodynamic silylating ability of amidosilanes does have structural dependence. For example, in the equilibrium that they studied, N,O-bis-trimethylsilylacetamide (BSA) was at least eight orders of ten more powerful than N-trimethylsilylpyrrolidinone. Larger ring systems like the trimethylsilyl-ε-caprolactam which are large enough to tautomerise were five orders of ten better silylating agents than the smaller, non-imidate, silylpyrrolidinone. The data of Lane and Frye seem to suggest that O-trimethysilylamides were better thermodynamic silylating agents than N-trimethylsilylamides. It was implied that for silylamides with intermediate thermodynamic silylating ability, they could be ranked based on their relative equilibrium concentration of the two tautomers. A higher ratio of the O-form would provide a stronger silylating agent. Their data seem to support this conclusion with the single exception of the trimethylsilyl derivative of 2-hydroxypyridine, a structure which is locked into the O-silylimidate form. This silylimidate was even less potent than N-trimethylsilylpyrrolidinone, the weakest of the silylamides studied. No additional experimental or theoretical work has been published which might have supported their supposition. It was, therefore, planned to study N-substituted trimethylsilylamides at the *ab initio* and semiempirical levels to help rationalise the steric and

electronic effects of silylamides on the topomeric distribution of this class of material and to determine how those parameters relate to silylating ability. Such calculations have not previously been reported in the literature.

1.2 Hindered Rotation

1.2.1 General Discussion

The hindered, intramolecular rotation of molecules has long been of interest to spectroscopists and theoreticians. The first citations concerning the free rotation of bonds within a molecule, by Van't Hoff, date back to the late 1800's. Bischoff provided the initial indications that rotation about a single bond was not always free, but could be restricted [39-41]. Subsequent work by Bischoff and others have helped to demonstrate that hindered rotation about a single bond can lead to conformations which are more stable than others. It is worth noting that even in simple molecules like ethane, thermodynamic and spectroscopic data for this molecule indicates that the rotation around the C-C bond is not free. In fact, the energy barrier for that specific rotation lies between 2.8 and 3.0 kcal mol^{-1}. A barrier of less than 0.6 kcal mol^{-1} would constitute free rotation at room temperature. Energies greater than this result in torsional vibration and, therefore, hindered rotation.

The general state of understanding of intramolecular rotations during the first half of this century is given by Mizushima in his excellent book, *Structure of Molecules and Internal Rotation* [42]. W. J. Orville-Thomas has expertly compiled, summarised, and presented much of the significant data concerning the physical and theoretical techniques in conformational analysis up to 1971 [43].

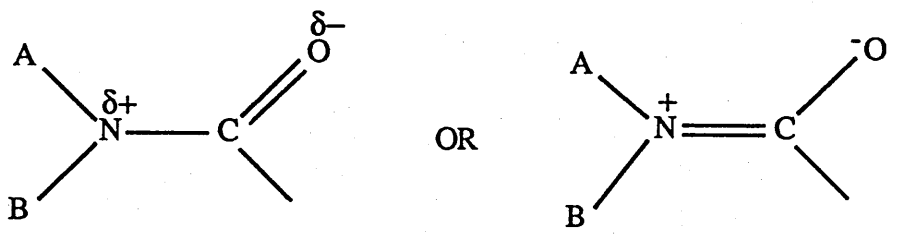
1.2.2 Hindered Rotation of Amides

NMR spectroscopy has been used to study the hindered rotation of amides [44-47] and to ascertain their preferred conformation in peptide structures [42]. NMR is especially well suited for studying this type of compound, with a high internal barrier to rotation. In the case of substituted amides or formamides, the 15-20 kcal mol^{-1} barrier to rotation about the nitrogen-carbonyl carbon bond or N-CO bond is attributed to conjugational resonance effects. This is illustrated in Figure 1.1 and has led to the use of the *cis-trans* nomenclature for these materials. The electronic structures of amides or formamides are characterised by a resonance interaction between the carbonyl 2p-pi electrons and the lone pair on nitrogen. This interaction tends to make nitrogen planar and the heavy atoms of the amide skeletal structure lie in a plane. Hence, one group on nitrogen will either be *cis* or *trans* to the carbonyl oxygen. Rotation about the nitrogen-carbonyl carbon bond or *cis-trans* isomerisation demands that the

resonance condition be broken. That is, that the lone pair on nitrogen must pass through a stage when it is no longer coupled to the carbonyl pi-system. This takes place when the substituents on nitrogen are orthogonal to the carbonyl plane, and this can be viewed as the transition state for isomerisation or rotation. Trimethylsilyl substituted amides and formamides have also been studied by NMR, but these materials are complicated by an additional isomerisation reaction. Namely, the 1,3-migration of a trimethylsilyl group which goes from nitrogen to oxygen via an intramolecular tautomerisation.

Figure 1.1:

Conjugational Resonance Effects in Simple Amides



1.3 Tautomerisation

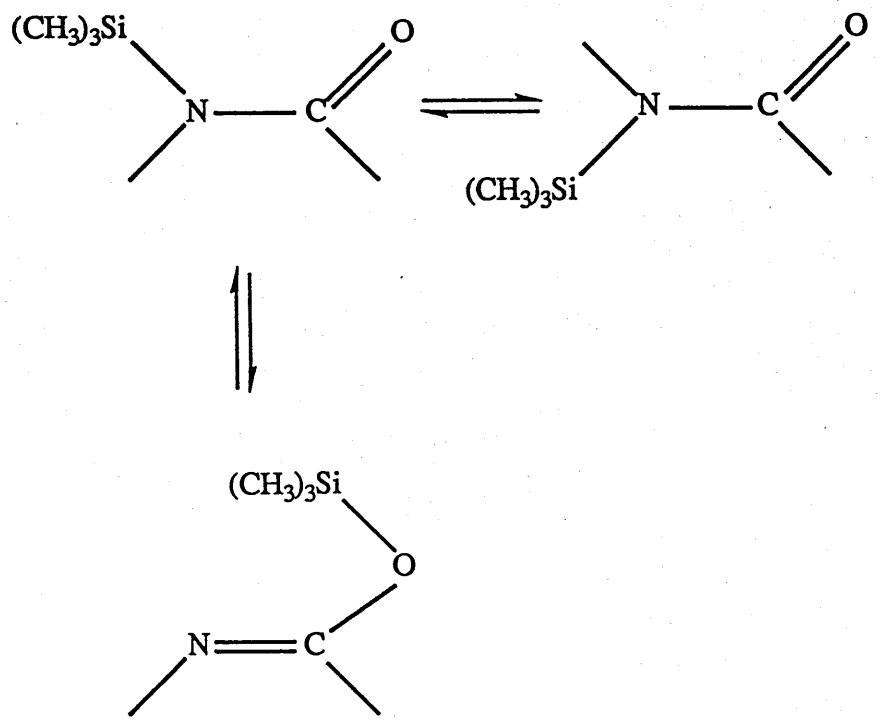
1.3.1 1,3 - Migration of Silicon From N to O

A complete review, up to 1980, of the 1,3-migration of silicon across an allylic framework is given by Bassindale and Brook [48]. Figure 1.2 summarises the various tautomeric and rotameric states possible in these silyl materials.

The tautomerisation is similar to the Chapman Rearrangement where N,N-diaryl amides are formed from the 1,3 migration of an aryl group from an aryl imidate. Experimental studies have shown that bis-(trimethylsilyl)acetamide exists only in its N,O-form rather than the N,N-bis-(trimethylsilyl)acetamide isomer [30,49].

Figure 1.2:

Rotameric and Tautomeric Scheme for Silylamides



Trimethylsilylacetanilides [31-33] are believed to consist of a dynamic mixture of rotameric and N,O-tautomeric structures. The distribution of tautomeric and rotameric forms appears to be strongly dependent on the nature of the substituents at the carbonyl carbon and at the nitrogen. For simple monosilylamides, the amount of the O-silyl imidate increases as the substituent at nitrogen becomes more electron withdrawing [36]. This effect has been rationalised by comparing the relative stabilities of the tautomers as a function of electron density at nitrogen. As electron density at nitrogen is increased, the pi-character of the C-N bond increases, favouring the N-tautomer. Reducing electron density at nitrogen, therefore, facilitates the formation of the strong Si-O bond in the O-tautomer. The dependence of tautomeric distribution on substitution at the carbonyl carbon is not trivial. For bis-silylamides, the imidate structures are preferred for all but the formamides. The N-alkyltrimethylsilylamides have been thought to be totally in the N-silylated form [34] and rotation about the C-N bond influenced by the size and electronic effects of the nitrogen substituent. The barriers of rotation about the C-N bond for simple amides decrease as the size of the group at nitrogen increases [50]. However, the size of the group at nitrogen has little effect on the barrier to rotation for formamides. As the electron withdrawing ability of the substituent at nitrogen increases, the barrier of rotation decreases. Yoder and Gardner

found that the steric parameters were the most important factor when attempting to correlate steric, inductive, and resonance parameters to the free energies of activation for rotation about the carbonyl-nitrogen bond for a series of acetamides and formamides [50]. However, it has since been demonstrated that some N-alkylsilylamides are in fact a mixture of rotameric and tautomeric isomers [35-37]. Bassindale corrected the structure of N-methyl-(trimethylsilyl)-trifluoroacetamide by showing that a highly electron withdrawing group, like trifluoromethyl, at the carbonyl carbon decreased the C-N pi-electron density and, therefore, favours the imidate form [37].

1.4 Thesis Statement

This thesis explores the hindered rotation of N-silyl-N-methylacetamide, N-trimethylsilyl-N-methylacetamide, dimethylacetamide and their tautomeric isomeric forms. It suggests the most appropriate semiempirical quantum mechanical method for the description of torsional behaviour and compares the results with the available experimental data. It also suggests how the structure of these silylamides is related to their thermodynamic silylating ability.

1.5 Summary

Silylation is an important class of reaction in organosilicon, organic, analytical, and related chemistries. It involves the reversible exchange of an active hydrogen for a silyl group, generally trimethysilyl, which dramatically alters the physical characteristics of the original molecule. Among the various types of silylating agents available, silylamides are the most interesting from both a reactivity and a structural standpoint. This class of silylating agent has demonstrated thermodynamic silylating power which spans over seven orders of magnitude. The structural complexity of these materials appears to be related to reactivity and includes both tautomeric and rotameric species. The rotameric structures arise from the restricted rotation about the amide bond (N-C(O)) while the tautomeric structures are the result of a 1,3 migration of silicon from nitrogen to oxygen. The distribution of tautomeric and rotameric forms appears to be strongly dependent on the nature of the substituents at the carbonyl carbon and at the nitrogen. For simple, monosilylamides, the amount of the O-silyl imidate increases as the substituent at nitrogen becomes more electron withdrawing or as the steric bulk of the substituent is very large. The dependence of tautomeric distribution on substitution at the carbonyl carbon is not trivial.

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Chapter Two

Introduction and Background

Computational Methods

2.0 Introduction and Background

2.1 Review of Computational Methods Related to Silicon

Computational chemistry is entering into a new era of utility and application for the experimental chemist. Software is being written with the user in mind, which in turn is having an impact on the rate of acceptance and willingness of the novice user to try these new tools. Large blocks of inexpensive computer time have also become available. Couple this with the increased costs of operating a wet experimental laboratory and there is little excuse not to apply these techniques to problems of interest before venturing into the laboratory.

The first obstacle generally encountered by the novice user is what method or level of calculation is most appropriate for their question. There are multiple levels of calculations available today ranging from molecular mechanics techniques, which treat the molecules as a collection of mass points connected by springs, to a collection of Molecular Orbital (MO) methods which are based on the linear combinations of atomic orbitals. Among these calculations, we can find methods which are considered to be completely rigorous, nonparameterised molecular orbital treatments derived from first principles, *ab initio;* to a collection of so-called semiempirical calculations which have made any number of simplifying assumptions in how a particular method treats atomic

orbital overlap and interaction. In the follow pages we will present a summary of each of the more useful methodologies used today. Y. Apeloig [1] has provided an expert review of the theoretical aspects of organosilicon chemistry and the use of calculational methodologies to study this branch of chemistry.

2.2 Force Field

2.2.1 Molecular Mechanics

Molecular mechanics (MM) is an extremely useful and rapid computational technique for determining optimised chemical structures, relative stabilities, heats of formation, strain energy, moments of inertia, dipole moment, and some limited spectroscopic data. However, MM techniques cannot be used to acquire vibrational information. The calculations can be carried out on platforms ranging from a personal computer (PC), to a mainframe with comparable result. The structural output can easily be transported to a larger computer for more sophisticated manipulations or calculations.

Force field or molecular mechanics calculations are based on a classical mechanics model of a molecular structure. The method's early history has been reviewed several times [2-3] and its application has been critically reviewed by many [4-8] and will therefore, not be reviewed in detail here. The method treats the molecule as a collection of

atoms governed by a set of classical mechanical potential functions. Alternatively, the molecule can be viewed as an array of balls (atoms) and springs (bonds) with adjustable force (spring) constants and lengths which then govern the three principle degrees of freedom in a molecule, bond stretching, angle bending, and torsional rotation. The principle is readily illustrated by considering the bond stretching term in a molecule. The potential at any given interatomic distance, r, is described by a harmonic oscillation curve. The energy minimum corresponds to the equilibrium bond length, r_o. The exact calculation for the r_o is complicated when derived from the Morse expression and an appropriate approximation can be made using the Hook's Law expression for simple harmonic motion

$$V=(k(r-r_o)^2)/2,$$

where V is the potential energy and k is a constant. This simple, easy to calculate approximation is valid for the majority of molecules. The exceptions are in those molecules which contain very long bonds which are generally caused by steric effects. In these molecules, the simple Hook's Law expression is no longer valid and an additional term proportional to $(r-r_o)^3$ is often added to the potential function. Caution must be exercised when using the cubic terms because at very long bond distances the forces becomes repulsive and molecules tend to fly apart if poor starting geometries are chosen. Allinger's MMP2 program includes the cubic term at a relatively late stage in the optimisation route so that this does not occur even if a poor starting geometry is used.

The remaining functions, angle bending and torsional rotation, are in principle the same as bond stretching. Energy increases as a given bond or torsional angle is deformed away from its optimum value. Simple potential functions are then calculated to give the desired constant or parameter.

Furthermore,the force field includes the van der Waals functions used to help account for steric interaction. These van der Waal or Hill potentials take the form of a 6/12 function. They have two terms, one proportional to the 6th power of the interatomic distance and the other dependant on the 12th power of the same distance. Other types of interaction may also have to be included in the force fields of polar molecules. The charges that build up on these groups and the dipole moments associated with them interact with each other to affect the energy of the molecule. Therefore, an electrostatic term or a dipole-dipole interaction term is often included in the force field.

Once the force field has been selected and its limitations understood, molecular mechanics can be exceedingly useful as a rapid method for calculating optimised molecular structures. In fact, since the method is parameterised it can be tuned to give outstanding results for very specific requests for information or for a specific class of molecules. Once an optimised geometry has been obtained it

can be used to calculate the moment of inertia and dipole moment. Limited spectroscopic data are also available from these calculations but, are not useful for vibrational information. The heat of formation and strain energy are also given as part of the calculation's output. An excellent "how-to" approach to molecular mechanics and some of the molecular orbital calculations is given in Tim Clark's handbook on computational chemistry [9].

The greatest limitation of the force field approximation is the lack of validated parameters for less traditional atom pairs. However, this has recently been addressed for most organosilicon materials. Grigoras and Lane have published a parameter set for Allinger's MM2 method [10] which were derived from *ab initio* computations and which give outstanding results even for the siloxane bond conformation [11-12].

2.2.2 Molecular Dynamics

Molecular dynamics is an important extension of molecular mechanics which should not be over looked. Unlike most molecular mechanics based techniques, molecular dynamics (MD) incorporates an explicit time and temperature dependence. Therefore, the atoms of the molecule move with time under the influence of the forces of those atoms which surround them. In addition to these forces, external forces such as sheer or tensile can be applied to the models in an MD simulation. The temperature is defined in

a MD study by the distribution of atomic velocities. By rescaling these velocities different amounts of kinetic energy, which is directly proportional to the temperature, can be imparted to the model. This applied kinetic energy is redistributed into its various vibrational, rotational, and translational modes making it possible to study the effects of applied stress and of thermal variations on test models. MD has been widely used to study the physical behaviour of many organic, inorganic, and biological systems. The sizes and complexity of those systems studied range from small atomic or molecular assemblies such as argon [13], water [14], or very large protein systems [15]. In material science, the method has been applied [16] to the study of such condensed phase properties as diffusion kinetics, melting behaviour, crystal growth, and crack propagation. Excellent reviews of the MD technique are found in the reference section [16-17]. The same parameters utilised in MM2 for silicon can be used in molecular dynamics.

2.3 Huckel Calculations

Huckel and the more recent Extended Huckel Theory (EHT) [18] type of calculations have limited utility in today's family of more advanced computational methods. However, this simple theory can provide information regarding ground state electronic configuration, reactivity, atomic charges, and spectroscopic properties. Additional information can be found in the bibliography [19-21]. These calculations

are rapid and because they are empirical in nature can be tuned by manipulating the adjustable parameters of the program to provide specific information on a single property of interest. The empirical parameters of Huckel theory are usually given the symbols of alpha and beta and represent the coulomb and resonance integrals respectively. In these calculations the overlap integrals are taken to be zero.

Despite the simple nature of Huckel calculations they have a number of unsatisfactory features. First, the values of the Huckel parameters, alpha and beta, are determined empirically by fitting theoretical calculations to experimental data or theoretical calculations to higher level calculations. As always, the optimum value for the adjustable parameters is a function of the experimental or calculational data under consideration. This can lead to a family of Huckel parameters. The disadvantage of this is that it results in a collection of programs each optimised for a specific physical property. Therefore, if a complete physical profile of a substance is required each of the programs must be run to generate the physical description.

The Huckel methodology is more reliable for non-polar molecules than for polar ones. This is true because of the neglect of electron repulsion in the calculation and because it is based on the assumption that alpha is independent of the charge on the atom, which of course is

not true in polar and non-uniform distributions of pi charge in unsaturated systems.

In heteroatomic or mixed atom systems, the number of empirical parameters required to complete a calculation often is large relative to the available experimental data. For example, if one takes the coulomb integrals directly from experimental atomic spectral data and uses them in a Huckel calculation, one generally ends up with unreasonably large bond polarities. This is due to the neglect of electron repulsion once again. Lastly, there are some molecular properties which cannot be fitted at all by Huckel theory. These include the energies and intensities of some electronic absorption bands. However, it was this shortcoming that prompted the initial development of the self consistent field theories on which many of the current calculational methods rely. The strength of the method is that with care, the calculation can be parameterised in such a way that for a family of compounds it does give reliable information of interest to the experimental chemist. In addition, larger molecules can be examined because only valence electrons are considered and some of the two electron integrals can be neglected. Therefore, the number of atomic orbitals that are considered in an empirical calculation is significantly less and the calculation substantially faster. Extended Huckel Theory calculations have been successfully used for organosilicon compounds and their use in bonding and structural analysis can be found in a review by Jones [22].

2.4 Self Consistent Field Methods

2.4.1 CNDO/2

The early semiempirical methods like CNDO (Complete Neglect of Differential Overlap) were developed by Pople and his group [23-25] and were intended to reproduce the results obtained from *ab initio* calculations. In general, the results were encouraging. Orbital energies and binding energies were generally more negative than those obtained from full SCF MO (Self-Consistent-Field Molecular-Orbital theory) but the differences in orbital energies were in good agreement. CNDO calculations have been used to calculate heats of formations and to perform structural geometry optimisations. Equilibrium bond lengths given by the method are considerably shorter than the observed values, although, the CNDO/2 version of the calculation gives better agreement with the observed bond lengths [26]. The CNDO method has been reviewed in detail in books by Pople [27], Murrell [19], and Dewar [28].

CNDO, like all of the other ZDO-SCF (Zero Differential Overlap) methods such as, NDDO (Neglect of Diatomic Differential Overlap), INDO (Intermediate Neglect of Differential Overlap), PNDO (Partial Neglect of Differential Overlap), and MINDO (Modified Intermediate Neglect of Differential Overlap) are based on the Born-Oppenheimer approximation of stationary nuclei. That is to

say, that the nuclei remain fixed on the time scale of electron movement. This, therefore, implies that the electronic wave function is not affected by nuclear motion. CNDO is the simplest of the SCF MO computational methods and assumes the atomic orbitals to be spherically symmetrical when evaluating electron repulsion integrals. The directionality of p-orbitals was included only via the one-electron resonance integral, the sizes of which depend on the orientations and distances of the orbitals and on a constant assigned to each type of bond. NDDO comes closest to the full SCF equations of Roothaan and, therefore, is more difficult to apply.

Although CNDO/2 has been parameterised [29] for use with the silicon atom, little has been done with this method in recent years. This is in part due to the availability of more powerful methodologies which give better answers in the approximately the same time. However, throughout the 1970's CNDO/2 was used to provide insight into organosilicon chemistry. One of its greatest uses was its application to the study, estimation, and prediction of Si29 chemical shift constants [30-33]. The method was heavily utilised for the prediction of binding energies in photoelectron spectroscopy, ESCA, and XPS studies of silicon compounds [34-40]. Still others applied this method for the structural investigation of silicon compounds in order to acquire information regarding charge distribution, dipole moments, ultraviolet transition energies, and ionisation energies [41-43]. The utility of

this method and EHT for the study of bonding and structure were described in Jones' 1974 annual review [22].

2.4.2 MINDO/#

As noted earlier, the goal of Pople and his coworkers in developing CNDO was to reproduce, as nearly as possible, the results of minimal basis set SCF MO *ab initio* calculations with a method that would require substantially less computer time. However, since these methods use approximations in the SCF calculation, one can only expect the results to be similar to, but less accurate than, minimal basis set *ab initio* SCF results. Therefore, these methods do well at providing molecular geometries and poorly at providing accurate binding energies. Dewar and his coworkers devised several semiempirical SCF MO theories which closely resemble CNDO and a modification of that technique, INDO. However, Dewar's aim was not to reproduce *ab initio* SCF wave functions, but to have a method which would give molecular binding energies with good chemical accuracy and that would be applicable to larger molecules without large investments in computer time. In 1967, Dewar and Klopman put forth PNDO, partial neglect of differential overlap [44]; in 1969, Baird and Dewar published MINDO/1 (modified INDO) [45]; and in 1970, Dewar and Haselbach produced MINDO/2 [46]. The parameters in these methods were chosen to have calculated molecular heats of formation to fit experimental data as nearly as possible. Although these methods work well for prediction of heats of

formation, they were relatively poor at providing molecular geometries. MINDO/2 provided better molecular information but gave large errors in dipole moments and in bond lengths to hydrogen atoms. Dewar's work culminated in the current method referred to as MINDO/3 [47] and represents a substantial improvement over the other methods. The method has been parameterised for some materials containing the following list of atoms: C, H, O, N, B, F, Cl, Si, P, and S. It is worth noting that MINDO/3 is not recommended for molecules which contain Si-H, Si-C, or Si-Si bond types. The method has been widely used to calculate properties of ground state organic molecules, even very large molecules, and to calculate potential-energy surfaces of some chemical reactions. However, the use of MINDO/3 has come under attack by advocates of *ab initio* SCF calculations [48-50].

One of the strong points of the method, MINDO/3, is its performance in carbocation calculations. It is the method of choice for systems which are too large for *ab initio* calculations and is generally preferable to minimal basis set *ab initio* calculations [51]. MINDO/3 has been successfully employed to predict mass spectrometric fragmentation [52-54]. However, there are a number of problem areas associated with the method which caused Dewar to develop an alternate method. Some of MINDO/3 weaknesses are: overestimation of the stability of organic triple bonds, the underestimation of the stability of aromatic compounds, the inability to describe rotational barriers in conjugated systems, its inability to describe hydrogen

bonding, and it seriously underestimates lone-pair repulsion. It has already been noted that the method is not recommended for material containing Si-C bonds [55]. However, Frenking suggests that the method not be used at all for compounds containing silicon, P, or S [56]. He states that a review of the literature [57] on MINDO/3 shows that several theoretical studies have been reported for molecules containing third row elements using false parameters, even after his publication warning against it [58]. He correctly states that the accuracy of MINDO/3 using its current parameters for Si, P, and S has not been tested and may yield studies without value.

2.4.3 MNDO

Because MINDO/3 did not meet Dewar's original goals and because of the number of serious deficiencies of the method, Dewar and his coworkers developed and introduced MNDO (Modified Neglect of Diatomic Overlap) in 1977 [59-61]. The real motivation for developing this method was that calculations such as MINDO/3, which are based on the INDO formalisation, cannot properly reproduce effects due to lone-pair repulsions. By basing MNDO on NDDO the authors hoped to avoid many of the weaknesses of MINDO/3. Like MINDO/3, MNDO is parameterised to reproduce gas phase heats of formations. The MNDO method has been parameterised for many common elements: H, Be, B, C, N, O, F, Si, P, S, I, Br, Al and Cl. One significant advantage of MNDO over MINDO/3 is that it needs only parameters

specific to each element, not to combinations of the elements. The results obtained from MNDO are substantially better for most calculations than those obtained from MINDO/3 with only a slight increase in computational time [62]. Despite the overall improvements which MNDO provides, it is generally not recommended for compounds containing silicon [63]; and we will, therefore, limit our discussion of the method. However, given the surprising conclusions of Verwoerd's work it is worth noting some of the possible causes for the substantial discrepancies between MNDO and MINDO/3. The better performance of MINDO/3 for compounds containing silicon is in part due to the fact that only silicon, hydrogen, and carbon compounds were used to parameterise the method, while MNDO included a broader class of materials including those compounds containing N and O. Some improvement can be made by adjusting the parameters in MNDO, but this will result in trade offs in some of the method's benefits. Better values can be obtained for compounds containing Si, N and O but only at the expense of those materials containing Si, C, and H.

It is worth emphasising that MNDO works well for carbon containing materials, and there is a difference in the way MNDO treats carbon versus silicon. For the case of carbon, MNDO has two separately optimised beta parameters for use with s and p orbitals. Silicon uses a single common beta value. This would, of course, affect the differentiation between the s and p orbitals and contribute to the

discrepancies in results. Lastly, versions of MNDO before 1986 completely neglect 3d atomic orbitals which poses a substantial problem in the treatment of silicon versus carbon.

In 1986, Dewar and co-workers [64] published a revised MNDO parameter set for silicon. This new parameter set produces data which are in much better agreement with both experimental and high level *ab initio* calculations. The reader is also directed to the recent work of Stewart [65] who has developed new MNDO/AM1 type parameters for twelve elements, including silicon, using a new algorithm for optimising parameters for semiempirical methods.

Despite the general recommendation of not using the MNDO approximations for silicon compounds, Glidewell has obtained good results when the method is applied to silylcations [66-70], radicals [71], as well as for the study of silylcycloheptatrienes [72], and silylcyclopentadienes [73].

The method has also been used to evaluate the relative stabilities of CH_2N_2 versus H_2SiN_2. In this work, it was found that the results for the carbon example were in good agreement with experimental data but that the silicon compounds were found to be unstable with respect to decomposition to SiH_2 and N_2 [74]. Other workers have used this method to study the attack of a fluorine atom and a fluoride ion on methane and silane [75]. In this work,

attack of F atoms and fluoride ion on SiH_4 and methane were studied at both the *ab initio* and MNDO levels. Comparison of the two methods showed that MNDO gave satisfactory results in most cases. In the carbon example, abstraction occurred in preference to substitution. However, in the silicon examples, abstraction and substitution occurred with nearly equal ease.

2.4.4 AM1

In 1985, Dewar and his group published a new parametric quantum mechanical molecular model which was based on the NDDO approximation. The method is referred to as AM1, Austin Method 1 [76]. The intent of this new approximation was to overcome the many problems associated with MNDO without increasing computational time. The greatest weakness of MNDO was its failure to reproduce hydrogen bonds. In addition, the energies were too positive for crowded molecules and too negative for ones containing four-membered rings and the activation energies were too large [59]. All of these problems stemmed from a common cause, the tendency of MNDO to overestimate the repulsions between atoms at their van der Waals distance. After several failed attempts to correct this situation by modifying the core repulsion function, Dewar chose to use a brute force approach by modifying the existing function with additional Gaussian terms. This technique allowed them to find the optimum form of the function and provides the hope that it will later be replaced with an

approximation with fewer parameters. However, AM1 in its current form probably represents the best calculational technique that can be achieved using the NDDO approximation without specific allowance for the contributions of thermal energy. Given the relative newness of this approximation (AM1), little has been published with regard to its application to silicon chemistry. However, we have found the method to be in preference over other semiempirical techniques for the prediction of torsional barriers of rotation in various silylamides [77].

2.5 *Ab initio* Calculations

2.5.1 Introduction

Ab initio implies a rigorous, nonparameterised molecular orbital treatment from first principles. However, this is not entirely correct. The *ab initio* theory makes use of a number of simplifying assumptions but is still considered to be more complete than any of the other calculational methods. Because of this completeness, *ab initio* calculations are among the most expensive to run but are the most rich in information. *Ab initio* calculations have been used for a variety of applications ranging from the determination of inversion barriers in substituted amines to the study of hypervalent molecules. The book, *Ab initio Molecular Orbital Theory*, by W. J. Hehre, et al. is an excellent source of information on all aspects of the *ab initio* theory and its application [78]. Additional reviews

of the application of this methodology can be found in the reference section [79-85].

Ab initio techniques can be optimised for specific information by the careful selection and recognition of the various options available. For any given problem one must: choose not only the quantum mechanical model but also the wave function, Hartree-Fock or Moller-Plesset; choose the atomic orbitals or basis set to be employed; address the treatment of electron correlations; define the starting molecular geometry to be used for the calculation; determine if an established correlation between a calculated parameter and a desired physical or chemical property is known; and assess the various practical considerations of the calculations. Each of which can have a dramatic effect on the outcome of a calculation. For a discussion of the effects of Moller-Plesset corrections see the work of DeFrees and coworkers [86]. Basis set selection is one of the most critical considerations and provides the greatest flexibility in these calculations. In addition, polarisation and diffuse functions are often included in the basis set to obtain better computational results. The selection of basis sets will be discussed in a later section.

Ab initio theory, like the semiempirical calculations, makes use of the Born-Oppenheimer approximation [87]; the first step in simplifying a problem in quantum mechanics. This is achieved through the separation of the nuclear and

electronic motions. This is possible because the nuclear masses are much greater than those of the electrons. Therefore, we expect the nuclei to move much more slowly. As a consequence, the electrons in a molecule adjust their distribution to changing nuclear positions very rapidly. This makes it reasonable to suppose that electron distributions depends only on the instantaneous positions of the nuclei and not on their velocities. The electronic wave function is unaffected by nuclear motion. One of the greatest distinctions between *ab initio* methods and the semiempirical methods discussed earlier, is that the *ab initio* technique is an all-electron method whereas, the semiempirical techniques are limited to valence electrons.

The application of the *ab initio* technique to molecules containing silicon are many and varied. Luke and his colleagues recently conducted a theoretical survey of singly bonded silicon compounds [88] and unsaturated or multiply bonded and divalent silicon materials [89] comparing their structures and bond energies with their carbon analogs. In addition to this work, several other papers have been published which focus on structure and energy relationships, at the *ab initio* level, rather than the nature of bonding interactions [90-96,75]. This is not to suggest that the nature of the bonding in organosilicon compounds has been neglected. Gordon and his colleagues have studied silicon-phosphorus bonding [97], Baybutt the role of the d-functions in the silicon-nitrogen bond [98], Howell the role of d-orbitals in chlorosilanes [99], Zeeck,

the hyperconjugation in vinylsilanes [100] and several recent studies have shown that the silicon hydrogen bond is much more polar than had been previously thought [101-103]. However, bonds to silicon have long been considered to have a highly polar character [104], and this polarity to be important in controlling the chemistry about a silicon centre. The $S_N2(Si)$ process has often been compared to the analogous carbon centred process. However, in one example the reaction goes through a pentacoordinate intermediate (silicon) while in the carbon example the reaction proceeds through a pentacoordinate transition state [105-111]. The reader is directed to the work of Corriu [112-113], Deiters [114-115], and Bassindale [116] for a detailed review of the reaction mechanisms of nucleophilic attacks at silicon.

In addition to these fundamental studies, *ab initio* calculations have been used to give insight into a variety of topics related to silicon chemistry and understanding. Much has been done to understand the silicon-nitrogen bond. Lehn and coworker studied the nitrogen inversion barrier of silylamine [117], while Glidewell and Thomson evaluated the structure and acid-base properties of methyl and silyl amines [118] and Livant, et al. studied the more complicated tris(trimethylsilyl)amine, and related structures, both computationally and via laboratory experiments using photoelectron spectroscopic techniques [119]. The acidity of various substituted silanes has also been of extreme interest to computational and experimental chemists. Durmaz used *ab initio* techniques to study C-H

acidity of silylmethyl anion and methylsilane [120]. Ponec and coworker studied the basicity of a variety of carbofunctional organosilicon compounds to better understand the alpha silicon effect [121]. Others have tried to place substituted silanols in the absolute acidity scale through the utilisation of *ab initio* calculations [122]. Still others have evaluated the effects of silyl and methyl groups on acid-base reactions at oxygen, nitrogen and carbon [123]. The list of contributions that *ab initio* calculations have made is long but has been limited by the size of the molecule studied. Many of the greatest contributions have been on theoretical intermediates or high energy transit species. An excellent survey of unsaturated and divalent silicon compounds can be found in the work of Luke, et al. [89].

Much of the work done at the *ab initio* level makes use of simplifying assumptions or short cuts, but their contributions to silicon chemistry cannot be overlooked. Because of the expense associated with *ab initio* work, the calculations are often limited to very small molecules or assumptions are made that would allow a silyl group, H_3Si, to be used in place of a trimethylsilyl group for the sake of reducing the cost of the calculation. Where such assumptions cannot be made, primitive basis sets are often used to develop the initial insight and then semiempirical techniques are used to provide the final solution.

2.5.2 Basis Set Selection

Basis set selection is one of the most important elements in carrying out *ab initio* calculations. In selecting an atomic basis set, both the size of the expansion and the nature of the functions must be considered. For example, in a restricted Hartree-Fock treatment, the cost of the molecular orbital calculation is proportional to the fourth power of the total number of basis functions. One can readily see that size of the basis set determines the practically of the calculation. Therefore, selection of a basis set must be based on a compromise between the accuracy and efficiency. The reader is directed to two excellent books, *A Handbook of Computational Chemistry*, [124] by Clark and the other by Hehre, Radom, Schleyer, and Pople, *Ab initio Molecular Orbital Theory* [125], which discuss the various basis sets available in detail.

Most modern *ab initio* calculations use Gaussian type orbitals (GTO) basis sets. This type of basis set, in which each atomic orbital is made up of a number of probability functions, has substantial advantage over other types of basis functions for the evaluation of one and two electron integrals. They are computationally faster than equivalent Slater orbitals. Gaussian type orbital basis sets come in a wide variety of sizes and are considered the standard for high level calculations. The simplest of the the optional GTO basis sets is STO-xG. STO-xG is an abbreviation for Slater-Type-Orbitals simulated by x

Gaussian functions. STO-3G is the most popular and referred to as a minimal basis set. This means that it contains only as many orbitals as are necessary to accommodate the electrons of a neutral atom. Minimal basis sets of this type, STO-3G, are computationally fast and their performance has been extensively reviewed [126] and compared with MINDO/3 [48,50]. Even though STO-3G was found to outperform MINDO/3 and has served as the *ab initio* standard for several years it was replaced with a split-valence Gaussian basis set. The greatest disadvantage of any minimal basis set is its inability to expand or contract its orbitals to fit the molecular environment. The solution to this problem was the introduction of the split-valence or double zeta basis sets.

In these basis sets, the atomic orbitals are split into two parts, an inner compact orbital and a diffuse outer orbital. The coefficients of these two types of orbitals can be varied independently during the construction of the molecular orbitals. The size of the atomic orbital that contributes to the molecular orbital can be varied within the limits of the basis function. A split-valence basis set splits only the valence orbitals whereas the double zeta basis set also splits the core orbitals. A common split-valence basis set currently in use is 3-21G. This implies 3 primitive Gaussians for the core orbitals and a two/one split for the valence functions. The next step in improving a basis set is the addition of d-orbitals to all non-hydrogen atoms. For most organic or organosilicon

compounds these do not function as d-orbitals in the traditional sense of bonding formation. Rather their purpose is to polarise an orbital away from its normal distribution about the nucleus. This adjustment is important for small ring compounds and material made up of elements from the second row (Na - Ar). The most commonly used polarisation basis set is 6-31G*. This basis set has 6 primitive Gaussian functions for the core orbitals, a three/one split for the valence orbitals, and a single set of six d-functions attached to all non-hydrogen atoms (denoted by the asterisk).

One additional type of basis set is the diffuse augmented basis. It is intended for use in calculating anions or molecules that require very good descriptions of nonbonding electron pairs. These basis sets are obtained by adding a single set of very diffuse s and p-orbitals to non-hydrogen atoms in a standard basis set like 3-21G*. The diffuse augmented set would be referred to as 3-21+G*. The purpose of the diffuse function is to improve the basis set at large distances from the nucleus.

The basis set of choice for this computational study was the split-valence set described by Grigoras and Lane [127]. Their basis set is the result of a modification in the standard 3-21 set. In this modified basis set, which will be referred to as 3-21G*#, all non-hydrogen atoms have d-functions attached and the uncontracted polarisation function on silicon was altered. Such modifications of

standard basis sets are not uncommon, especially among those who study organosilicon compounds. Gordon [128] determined the value for the exponent of the d-function on silicon to be 0.395 by optimising the energy of silane as a function of the exponent at the 6-31G* level. Francl, et. al. [129] reported an average value of 0.45; Komornicki [130] used a value of 0.5; Goddard, Yoshioka, and Schaefer [131] a value of 0.6; and Oberhammer and Boggs [132] studied disiloxane using a value of 0.8. However, the best overall value for the d-function exponent is 0.3 as given by Grigoras and Lane. Not only did this modification provide accurate comparison between computations and experimental data, similar to what might be found at the 6-31G* level; but, it did so at the speed of a simple split valence basis set, 3-21G. The validity and utility of this basis set was recently illustrated in an article by Tachibana, et al. [133] who used this basis set to study siloxane bond formation in organosilane polymers.

2.6 Summary

Computational chemistry is entering into a new era of utility and application for the experimental chemist. However, the experimentalist turned paper chemist must be reminded that the same sound and logical principles which governed their experimental investigations must also be applied to their computations. In fact, even greater care must be taken to check and validate each calculation to insure its integrity. Unlike laboratory experiments, a

calculation always provides the user with an answer. The validity of the answer, however, is often dependent more upon the typing skills of the experimenter than their scientific prowess.

The first obstacle generally encountered by the novice user is, what method or level of calculation is most appropriate for their question. There are multiple levels of calculations available today ranging from molecular mechanic techniques to rigorous, nonparameterised molecular orbital treatments derived from first principles, *ab initio*. The following is a brief summary of the various methods available and their strengths and limitations.

2.6.1 Force Field Techniques

Strengths:

These methods are extremely useful and rapid computational techniques for determining optimised chemical structures, relative stabilities, heats of formation, strain energy, moments of inertia, dipole moment, and some limited spectroscopic data.

The calculations can be carried out on platforms ranging from a PC (personal computer) to a mainframe computer with comparable result.

Since the method is parameterised it can be tuned to give outstanding results for a very specific request for information or for a specific class of molecules.

Molecular dynamics is an important extension of molecular mechanics which should not be overlooked. Unlike most molecular mechanics based techniques, molecular dynamics (MD) incorporates an explicit time and temperature dependence. In addition to these forces, external forces such as sheer or tensile can be applied to the models in an MD simulation.

Limitations:

These methods cannot be used to acquire vibrational information.

Since the method is parameterised it can be tuned to give outstanding results for a very specific request for information or for a specific class of molecules.

The greatest limitation of the force field approximation is the lack of validated parameters for less traditional atom pairs.

2.6.2 Huckel Theory

Strengths:
This simple theory can provide information regarding ground state electronic configuration, reactivity, atomic charges and spectroscopic properties.

These calculations are rapid and because they are empirical in nature can be tuned by manipulating the adjustable parameters of the program to provide specific information on a single property of interest.

The Huckel methodology is more reliable for non-polar molecules than for polar ones.

The method can be parameterised in such a way, that for a family of compounds, it does give reliable information of interest to the experimental chemist.

Larger molecules can be examined because only valence electrons are considered and some of the two electron

integrals can be neglected. Therefore, the number of atomic orbitals that are considered in an empirical calculation is significantly less and the calculation substantially faster.

Limitations:

Method parameters are obtained empirically by fitting theoretical calculations to experimental data or theoretical calculations to higher level calculations. This can lead to a family of Huckel parameters. The disadvantage of this is one a collection of programs each optimised for a specific physical property. Therefore, if a complete physical profile of a substance is required each of the programs must be run to generate the physical description.

In heteroatomic or mixed atom systems, the number of empirical parameters required to complete a calculation often is large relative to the available experimental data.

There are some molecular properties which cannot be fitted at all by Huckel theory. These include the energies and intensities of some electronic absorption bands.

2.6.3 CNDO (Complete Neglect of Differential Overlap)

CNDO calculations have been used to calculate heats of formations and to perform structural geometry optimisations.

The method has been used to study, estimate, and make predictions of Si29 chemical shift constants.

The method was heavily utilised for the prediction of binding energies in photoelectron spectroscopy, ESCA and XPS studies of silicon compounds.

Others have successfully applied this method for the structural investigation of silicon compounds in order to acquire information regarding charge distribution, dipole moments, ultraviolet transition energies, and ionisation energies.

Limitations:
Equilibrium bond lengths given by the method are considerably shorter than the observed values.

CNDO/2 has been parameterised for use with the silicon atom; though, little has been done with this method in recent years.

2.6.4 PNDO, MINDO/X, and INDO

Strengths:

The parameters in these methods were chosen to provide calculated molecular heats of formation which would be in excellent correlation with experimental data.

Recent versions of the method have now been parameterised for some materials containing the following list of atoms: C, H, O, N, B, F, Cl, Si, P, and S.

The method has been widely used to calculate properties of ground state organic molecules, even very large molecules, and to calculate potential-energy surfaces of some chemical reactions.

One of the strong points of the method, MINDO/3, is its performance in carbocation calculations. It is the method of choice for systems which are too large for *ab initio* calculations and is generally preferable to minimal basis set *ab initio* calculations.

MINDO/3 has been successfully employed to predict mass spectrometric fragmentation.

Limitations:

Although these methods work well for heats of formation, they were relatively poor at providing molecular geometries.

MINDO/2 provided better molecular information but gave large errors in dipole moments and in bond lengths to hydrogen atoms.

MINDO/3 is not recommended for molecules which contain Si-H, Si-C, or Si-Si bond types.

There are a number of problem areas associated with the method which caused Dewar to develop an alternate method. For example, MINDO/3 overestimates of the stability of organic triple bonds, underestimates the stability of aromatic compounds, does not reasonably describe rotational barriers in conjugated systems, does not have the ability to describe hydrogen bonding, and it seriously underestimates lone-pair repulsion.

It has been suggested that the method not be used at all for compounds containing silicon, P, or S.

2.6.5 MNDO

Strengths:
MNDO is parameterised to reproduce gas phase heats of formations.

The MNDO method has been parameterised for many common elements: H, Be, B, C, N, O, F, Si, P, S, I, Br, Al and Cl. One significant advantage of MNDO over MINDO/3 is that it

needs only parameters specific to each element, not to combinations of the elements.

The results obtained from MNDO are substantially better for most calculations than those obtained from MINDO/3 with only a slight increase in computational time.

It is worth emphasising that MNDO works well for carbon-containing materials and that there is also a difference in the way MNDO treats carbon versus silicon.

The MNDO approximation has been successful for silicon-containing compounds. Good results have been obtained when the method was applied to silylcations, radicals, as well as for the study of silylcycloheptatrienes and silylcyclopentadienes.

Limitations:
Despite the overall improvements which MNDO provides, it is generally not recommended for compounds containing silicon.

The greatest weakness of MNDO was its failure to reproduce hydrogen bonds. In addition, the molecular energies were too positive for crowded molecules and too negative for ones containing four-membered rings. Also, the activation energies were too large. All of these problems stemmed from a common cause, the tendency of MNDO to overestimate the repulsions between atoms at their van der Waals distance.

2.6.6 AM1 (Austin Method 1)

Strengths:

The intent of this new approximation was to overcome the many problems associated with MNDO without increasing computational time.

AM1 in its current form probably represents the best calculational technique that can be achieved using the NDDO approximation without specific allowance for the contributions of thermal energy.

We have found the method to be in preference over other semiempirical techniques for the prediction of torsional barriers of rotation in various silylamides.

Limitations:

Given the relative newness of this approximation (AM1), little has been published with regard to its application to silicon chemistry.

2.6.7 *Ab initio*

Strengths:

Ab initio implies a rigorous, nonparameterised molecular orbital treatment from first principles and is considered to be more complete than any of the other calculational methods.

Ab initio techniques can be optimised for specific information by the careful selection and recognition of the various options available.

Basis set selection is one of the most critical considerations and provides the greatest flexibility in these calculations. In addition, polarisation and diffuse functions are often included in the basis set to obtain better computational results.

Limitations:

Ab initio calculations are the most expensive calculations to run.

2.7 References

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Chapter Three

Experimental Section

Computational Methods

3.0 Experimental Section

3.1 Computational Methods

The molecular orbital (MO) calculations in the present study were carried out with the Gaussian 82 [1] and Gaussian 86 programs [2] using the SCF method [3]. The general basis set option set was employed. All of the results which will be discussed here were obtained using a modified split valence 3-21G* basis set [4-5]. The polarisation function for silicon was modified as described by Grigoras and Lane [6]. AM1 and MNDO methods were used from the modeling package of MOPAC [7] without reparameterisation. CNDO/2 and EHT methods were obtained from QCPE and used as supplied [8].

Molecular surface areas were calculated using the method of Pearlman [9] and the atomic radius described by Bondi [10]. A hydration radius of zero was employed for all of our surface area calculations.

3.2 Hardware

All of the *ab initio* calculations described in this report were carried out on an IBM 3090-300E with a single vector processor. All other calculations were carried out on a VAX 11-750 with a floating point accelerator.

3.3 References

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Chapter Four

Rotational Behaviour of Silylamides

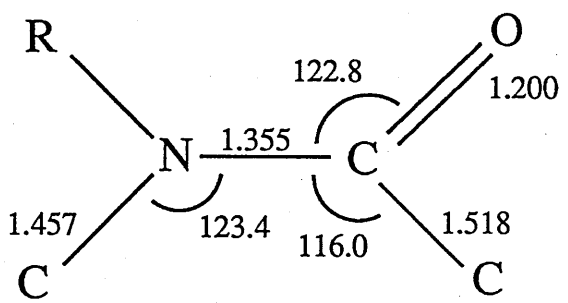
4.0 Discussion

4.1 Introduction

The conformational behaviour of amides are particularly important in the understanding of the chemistry of peptides, proteins, and other substances of life. Many of these structural features have been carefully studied and are summarised in Figure 4.1.

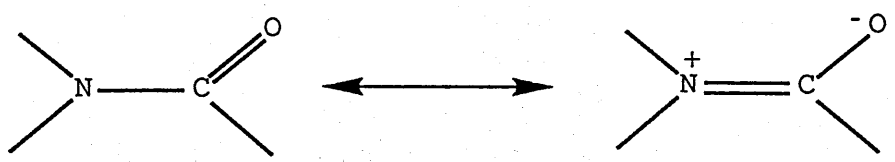
Figure 4.1:

Generalised Amide Structure



One of the more important features of the molecule is that the nitrogen, carbonyl carbon, oxygen, and substituent at the carbonyl carbon all lie in the same plane and results in what several refer to as the *cis-trans* nature of substituted amides. This coplanarity of the skeletal structure for this class of substance is readily explained on the basis of their electronic structure and is required if the dipolar structure is to have a significant effect on the physical properties of amides, Equation 4.1.

Equation 4.1:



Therefore, understanding the restricted rotation about the N-C(O) bond in amides is important in terms of understanding this class of material. As noted earlier, variable temperature NMR studies of several low molecular weight amides have provided insight into the barrier for the restricted rotation about the N-C(O) bond [1-5]. From these studies the barrier for rotation has been found to be on the order of 20 kcal mol^{-1}. This high barrier to rotation is due to the electronic structure of amides which is characterised by a resonance interaction between the carbonyl 2p-pi electrons and the nitrogen lone pair of electrons. This resonance interaction also accounts for the C-N bond in amides to be shorter and of a higher bond order than C-N bonds normally found in amines [6]. We began our study of silylamides by first approaching a simpler, symmetrical amide, dimethylacetamide.

4.2 Dimethylacetamide

We began our work with an *ab initio* level conformational study of dimethylacetamide. This work has shown that the C-N bond lengths in this compound, is indeed shorter than

those found in normal aliphatic amines. In amines, the bond length is 1.472Å which is considerably longer than the nitrogen-carbonyl bond length of 1.355Å found from our calculations. Even the N-methyl bond lengths, in dimethylacetamide, are slightly shorter than expected, 1.457Å, when compared to an amine. Rotation about the amide bond (N-C(O)) gave an *ab initio* maximum at 90 degrees with a barrier to rotation of 15.9 kcal mol^{-1} when an incomplete optimisation was used and the torsional rotation treated as a rigid rotor. That is to say that the valence geometry was not allowed to relax during the torsional scan of the bond. Only the torsional angle for nitrogen-carbon-carbon-oxygen was varied to simulate the torsional barrier. The difference between the initial rotational state which had a torsional angle (t) of zero degrees and the final state with t=180 degrees was over 4 kcal mol^{-1}. When the torsional scan was repeated with the skeletal geometry allowed to relax but the hydrogen positions fixed, the rotational barrier was determined to be 23.3 kcal mol^{-1} with a difference of 1.2 kcal mol^{-1} between the rotamers corresponding to t=0 and t=180 degrees. Only when we allowed the complete relaxation of the valence geometry and hydrogen position did we find the difference between the starting geometry, t=0, and the final geometry, t=180 degrees, to be zero. In that case, the rotational barrier was calculated to be 22.9 kcal mol^{-1}. This value is in reasonable agreement with the experimental value of 18.1 kcal mol^{-1} determined by Rogers [7-8]. We found that

semiempirical methods gave lower values for this restricted rotation. CNDO/2 gave a rotational barrier of 7.6 kcal mol^{-1}. AM1 and MNDO from the MOPAC package of software gave the same value for the rotation of 12.5 kcal mol^{-1}. Kumar and Murty [9] found the barrier to be 10.8 kcal mol^{-1} by Huckel molecular orbital methods which is similar to the PCILO value of 10.3 kcal mol^{-1} reported by Remko et al. [10].

Rotation about a methyl group on nitrogen (N-Me) showed a three-fold symmetry with equivalent minima at 0, 120, and 240 degrees. The energy barrier to this rotation was found to be 0.67 kcal mol^{-1} which is similar to those previously reported. Remko, Sekerka, and Frecer reported that the PCILO-calculated barrier was about 1.0 kcal mol^{-1}. They also calculated the rotational barrier of the methyl group bound to the carbonyl carbon (Me-C(O)). Our calculations, at the *ab initio* level, gave a value for this barrier of 2.5 kcal mol^{-1}. The PCILO-barrier was 2.6 kcal mol^{-1}. Table 4.1 summarised some of the structural information obtained from our calculations.

Table 4.1:

Ab initio Optimised Dimethylacetamide
Values for Bond Length and Bond Angles

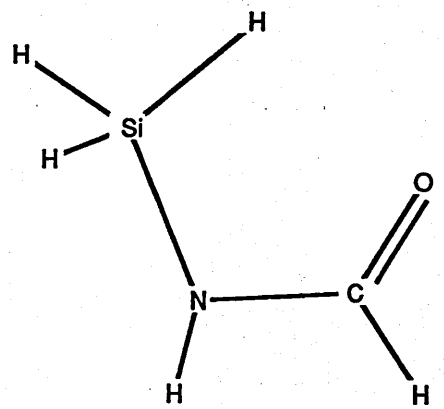
Bond Length (Å)		Bond Angle (degrees)	
N-C	1.4569	CNC	117.917
N-C(O)	1.3551	C-N-C(O)	123.387
C-O	1.2002	N-C-O	122.793
N-C	1.4547 *cis* to oxygen	N-C(O)-C	116.004
C-C(O)	1.5181	H-C-H	109.470
C-H	1.0901		

4.3 N-silylformamide

This simple silicon containing analog of N-methylformamide was used to further our understanding of substituted amides and in particular, silylamides. The structure was built, optimised, and studied at the *ab initio* level. The relevant structural data are given in Table 4.2. These studies have shown that the silyl group prefers to be *cis* to the carbonyl oxygen with a difference in energy between the *cis* and *trans* rotamers of 2.69 kcal mol^{-1}. The calculated barrier to rotation about the N-C(O) bond in this silylformamide was 21.0 kcal mol^{-1} in the forward direction and 18.3 kcal mol^{-1} in the backward direction, as indicated by Equation 4.2.

Table 4.2:

N-Silylformamide
Structural and Electronic Charge Data Based on *Ab Initio* Calculations at the 3-21G*(modified) level.

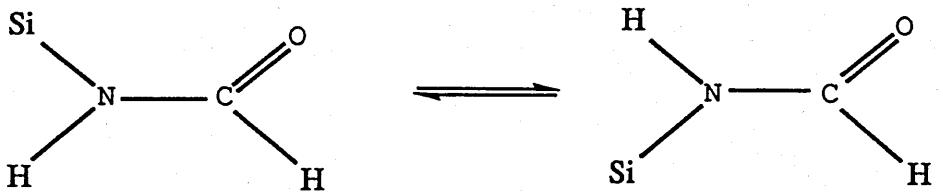


Bond Length (Å)		Bond Angle (degrees)	
Si-H	1.4831	N-Si-H	105.273
N-Si	1.7699	C-N-Si	119.055
C-N	1.3536	O-C-N	123.275
O-C	1.1937	H-C-N	114.082
H-C	1.0984	H-N-Si	123.503
H-N	1.0038	H-Si-N	111.156
H-Si	1.4782		
H-Si	1.4782		

Charges

ATM	CHR
SiH	-0.0705
Si	+0.5418
N	-0.9002
C	+0.6225
O	-0.6538
H	+0.2109
H	+0.3587
SiH	-0.0547
SiH	-0.0547

Equation 4.2:



The barrier to rotation can be seen graphically in Figure 4.2. It is obvious from this figure that the energy maximum for this torsional scan is at a torsional angle of 90 degrees. This corresponds to the complete uncoupling of the nitrogen lone pair from the carbonyl pi-system. This loss of electronic delocalisation or resonance interaction can also be see by the variation in net atomic charge at nitrogen, carbon, and oxygen. Figures 4.3, 4.4, and 4.5 represent these data graphically. The reader can see that as rotation begins about the N-C(O) bond the charge at nitrogen becomes less positive (or more negative) as does the charge at the carbonyl carbon. The charge at oxygen, on the other hand, becomes less negative (or more positive) reaching its maximum charge at a torsional angle of 90 degrees where there is complete uncoupling of the nitrogen lone pair from the pi-system. At a torsional angle of 90 degrees, the amide loses all of it dipolar nature. The same trends are observed if we look at the charge density between atoms. Figure 4.6 and 4.7 show these data.

Figure 4.2:

N-Silylformamide
Torsional Angle versus Energy

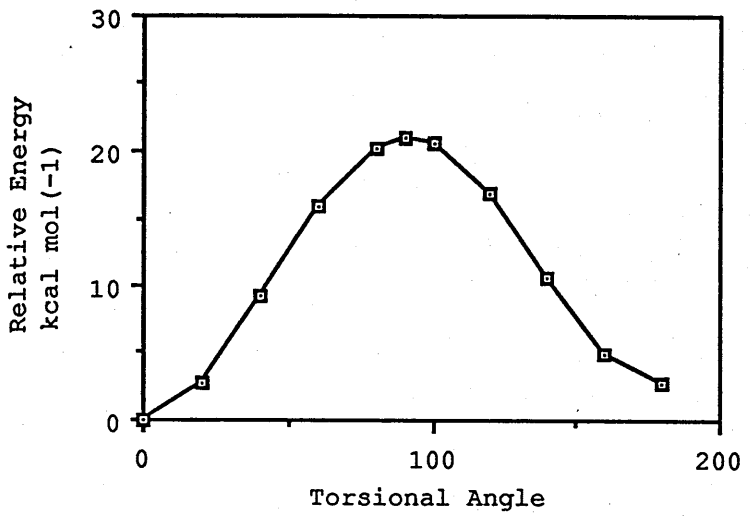


Figure 4.3:

N-Silylformamide

Si-N-C-O Torsional Angle versus Charge at Nitrogen

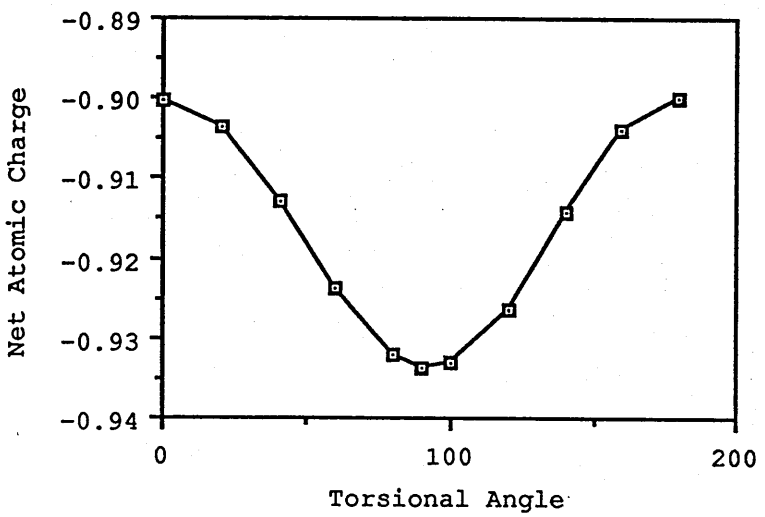


Figure 4.4:

N-Silylformamide

Si-N-C-O Torsional Angle versus Charge at Oxygen

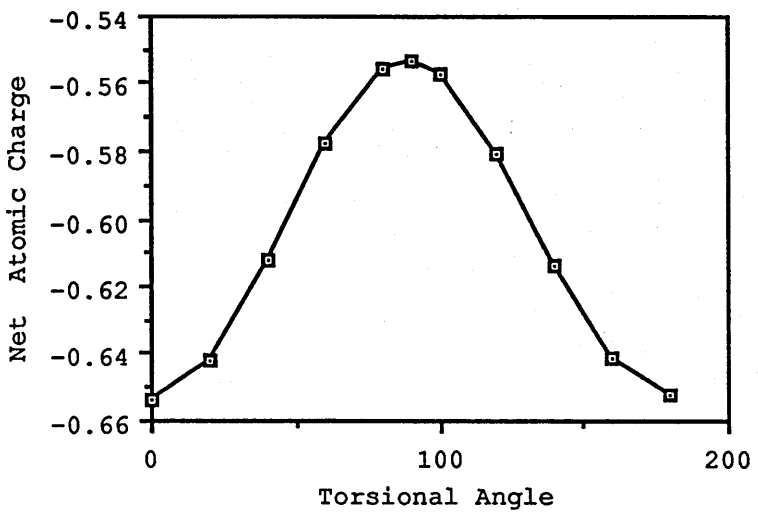


Figure 4.5:

N-Silylformamide

Si-N-C-O Torsional Angle versus Charge at Carbon

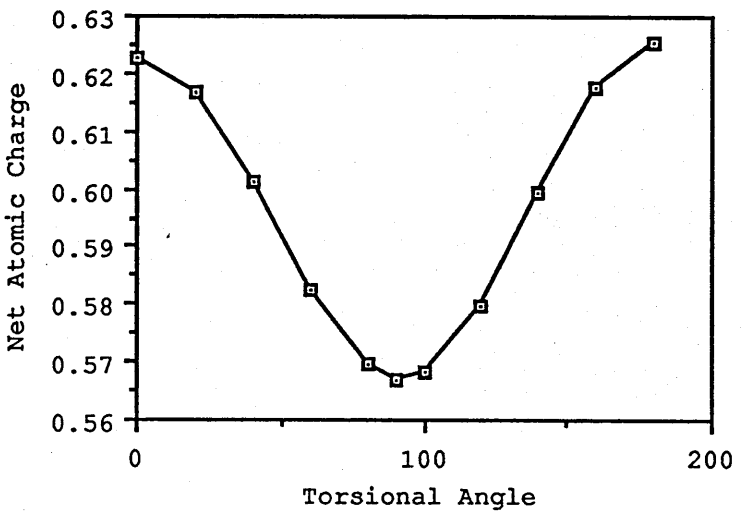


Figure 4.6:

N-silylformamide

Si-N-C-O Torsional Angle versus Charge Density Between Nitrogen and Carbon

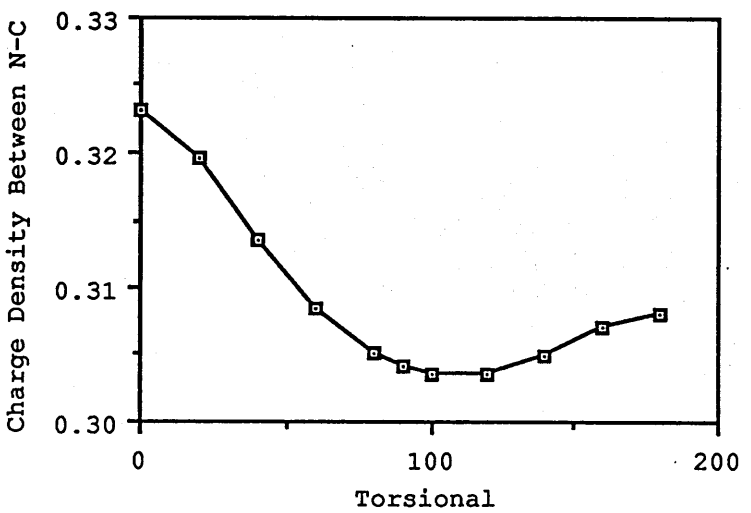
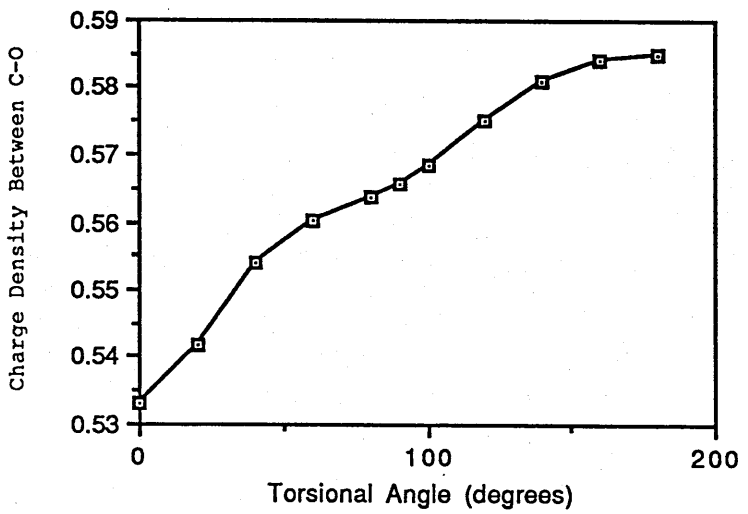


Figure 4.7:

N-silylformamide

Si-N-C-O Torsional Angle versus Charge Density Between Carbon and Oxygen



These studies have helped to demonstrate why it is important to do complete structural relaxation at each step during a torsional scan of these materials. As noted earlier, the resonance interaction of amides directly affects the apparent bond order in the molecule and therefore, there must be a direct relationship between bond order and internal rotation about a bond. Since bond length is a function of bond order, we can test our hypothesis by studying the bond length of the N-C(O) and C-O bonds as a function of the torsional angle, Si-N-C(O)-O or rotation about N-C(O). As seen in Figures 4.8 and 4.9 the bond length of the N-C(O) bond begins at a minimum of 1.3536Å, much shorter than a uncoupled N-C bond, and increases to a maximum of 1.414Å at the point where there are no resonance interactions. Conversely, we see a shortening of the C-O bond as the torsional angle is scanned. It reaches its minimum at 90 degrees, the point of complete uncoupling of resonance interactions. These data compare favourably with the AM1 calculated bond orders for this molecule. Figures 4.10 and 4.11 summarise these data for the torsional scan of the amide bond. In these examples the calculated bond order for N-C and C-O are presented as a function of the torsional angle. A torsional angle (tau) of zero corresponds to silicon *cis* to the carbonyl oxygen and a tau of 180 degrees is equal to the silicon *trans* to the carbonyl oxygen. The calculated bond order and equilibrium bond length plots reveal corroborating insight into the resonance stabilisation and restricted rotation of silylamides.

In addition to the major variations in the bond lengths of the N-C and C-O bonds, minor variations in nearly all bond lengths were observed during this torsional deformation.

Figure 4.8:

N-Silylformamide

Si-N-C-O Torsional Angle versus N-C Bond Length

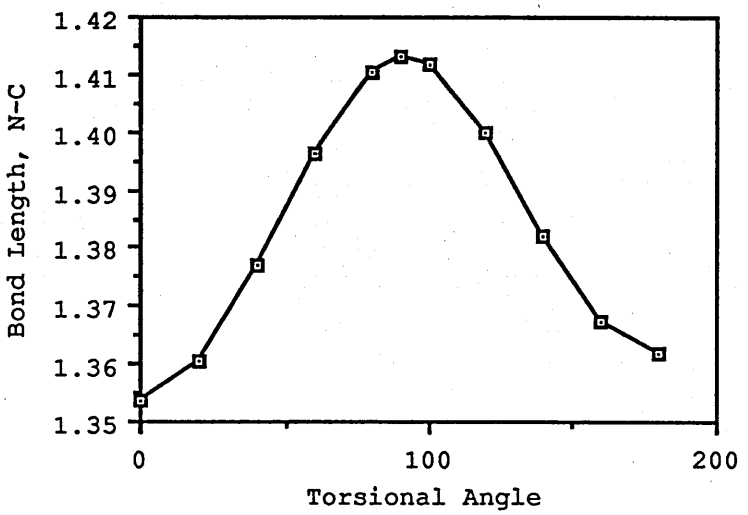


Figure 4.9:

N-Silylformamide

Si-N-C-O Torsional Angle versus C-O Bond Length

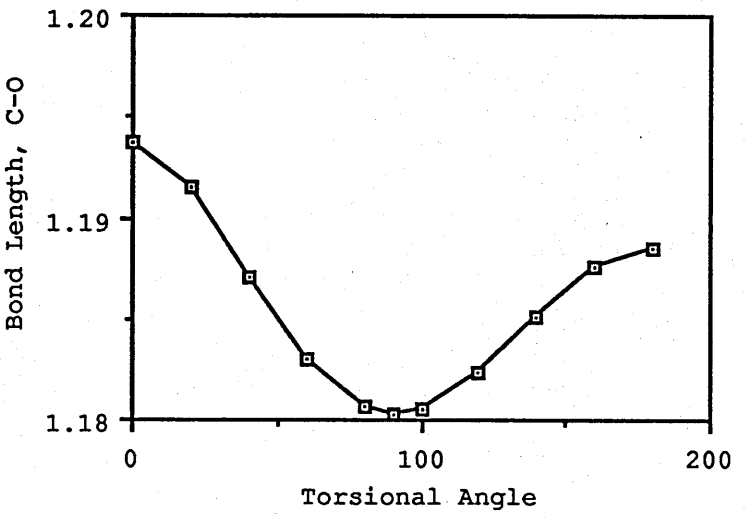


Figure 4.10:

Calculated Bond Order for N-C(O) in N-silylformamide

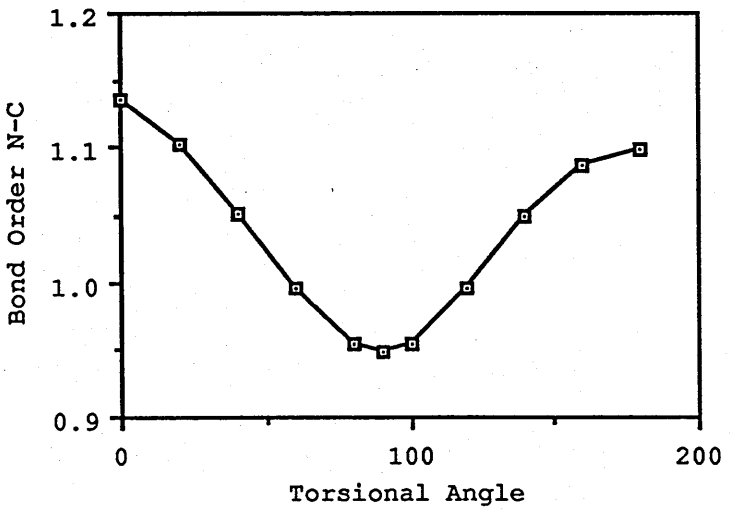
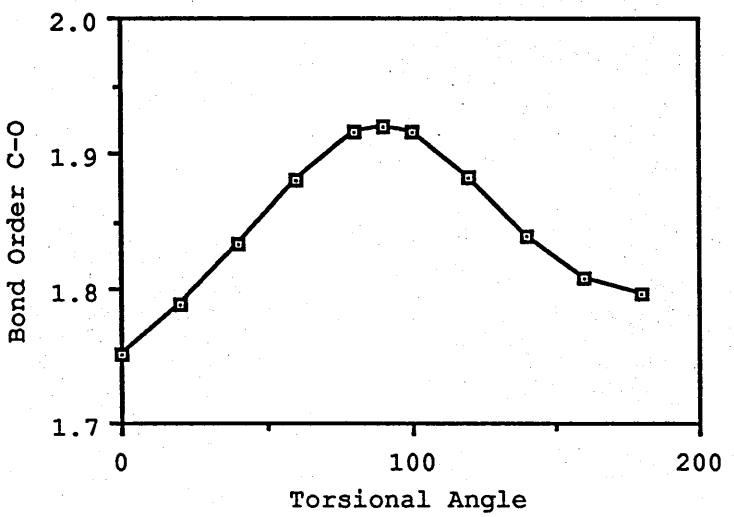


Figure 4.11:

Calculated Bond Order for C-O in N-silylformamide



Variations in other framework geometry were also noted. Among the most dramatic were the H-Si-N and H-N-Si bond angles. These data are represented in Figures 4.12 and 4.13. Less significant variations were observed for other angles.

Figure 4.12:

N-Silylformamide

Si-N-C-O Torsional Angle versus H-Si-N Bond Angle

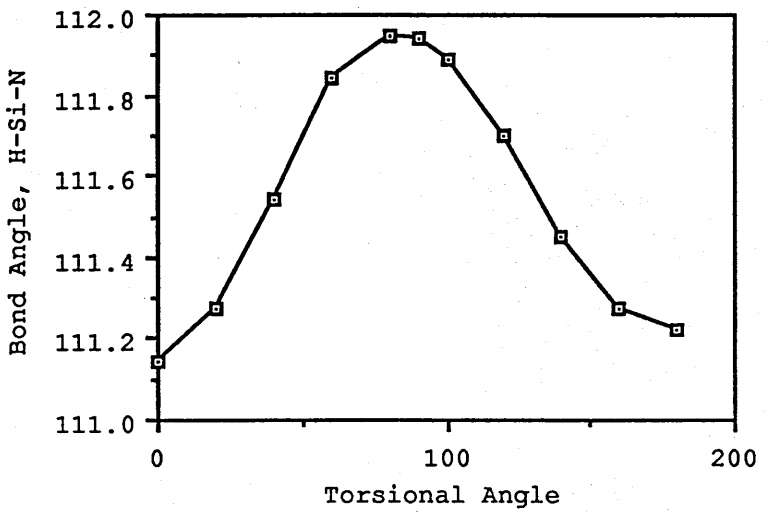
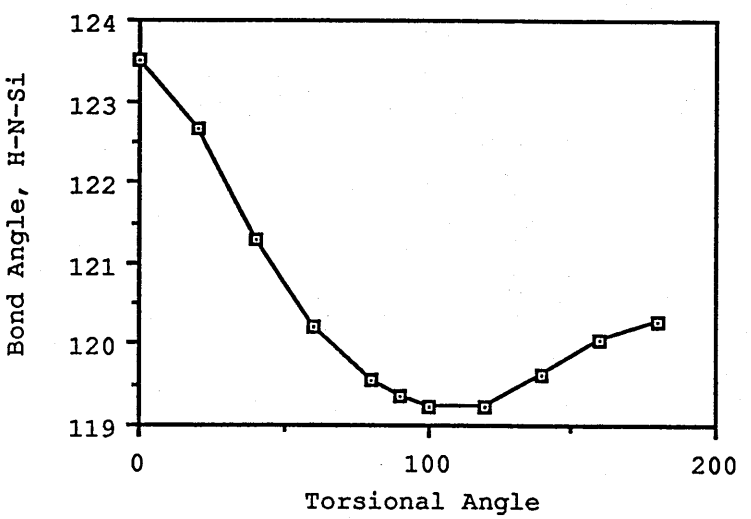


Figure 4.13:

N-Silylformamide

Si-N-C-O Torsional Angle versus H-N-Si Bond Angle



The study of the charge density between N-C and C-O as a function of torsional angle provides interesting insights into why the *cis* rotamer is thermodynamically preferred over the *trans* isomer. Figures 4.6, 4.7, 4.10, and 4.11 show what is occurring as the torsional angle about the N-C bond is varied from 0 to 180 degrees. The high charge density between nitrogen and the carbonyl carbon is lost as the torsional angle is varied from 0 to 90 degrees. The minimum charge density between these two atoms is obtained at a torsional angle of 90 degrees or when we have the complete decoupling of the lone pair of electrons on nitrogen from the pi orbitals of the carbonyl. More interestingly, as the torsional angle is varied from 90 to 180 degrees, the charge density between nitrogen and the carbonyl carbon does not completely recover, suggesting that the *cis* state is preferred over the *trans* through resonance stabilisation.

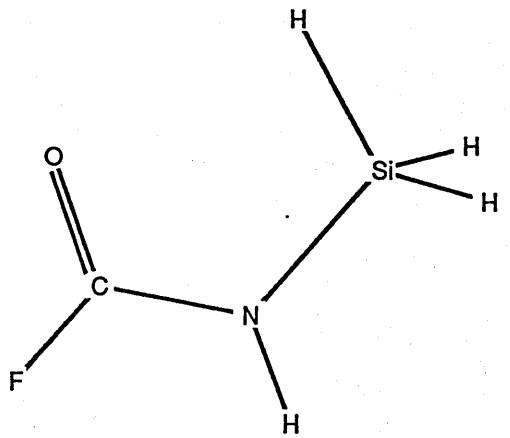
The charge density between the carbon and oxygen of the carbonyl shows a minimum at a torsional angle of zero, the silyl group *cis* to the oxygen, with an orderly increase in charge density as the angle is scanned to 180 degrees, the silyl group *trans* to oxygen. An increase in charge density between the carbon and oxygen of the carbonyl group is also consistent with the argument of loss of resonance stabilisation as the *cis* rotamer is converted to the *trans* species.

4.4 N-silylfluoroformamide

Replacing the hydrogen at the carbonyl carbon with an electron withdrawing group like fluorine, as in this molecule, has a tremendous effect on the preferred rotameric state of the molecule. In the case of this N-silylfluoroformamide, the preferred rotational conformation (by 0.75 kcal mol^{-1}) is with the silyl group *trans* to the carbonyl. This is in contrast to N-silylformamide where the *cis* structure is preferred by 2.69 kcal mol^{-1}. The rotational barrier about the N-C bond in N-silylfluoroformamide is only slightly higher than in the non-substituted case. The barrier to rotation is 21.6 kcal mol^{-1} (*trans* to *cis*) and 20.9 kcal mol^{-1} (*cis* to *trans*). This observed electron withdrawing effect on the rotational barrier about the N-C bond in formamides is consistent with what is known experimentally for more complex silylamides and silylformamides [11]. The *ab initio* optimised structure for *cis* and *trans*-N-silyltrifluoroformamide is given in Table 4.3 along with some other pertinent data.

Table 4.3:

N-silylfluoroformamide
Optimised Structural and Electronic Charge Data from *Ab initio* Calculations at the 3-21G*(modified) level.



Bond Length (Å)			Bond Angle (degrees)		
	Cis	*Trans*		*Cis*	*Trans*
Si-H	1.4807	1.4798	N-Si-H	105.110	105.110
N-Si	1.7708	1.7683	C-N-Si	119.608	124.120
C-N	1.3426	1.3443	O-C-N	126.361	129.708
O-C	1.1780	1.1719	F-C-N	111.670	108.744
F-C	1.3096	1.3245	H-N-Si	124.176	122.763
H-N	1.0038	1.0050	H-Si-N	110.562	110.886
H-Si	1.4771	1.4779			
H-Si	1.4771	1.4779			

Charges

	Cis
ATM	CHR
SiH	-0.0618
Si	+0.5551
N	-0.9506
C	+1.2194
O	-0.6803
F	-0.3582
NH	-0.3733
SiH	-0.0484
SiH	-0.0484

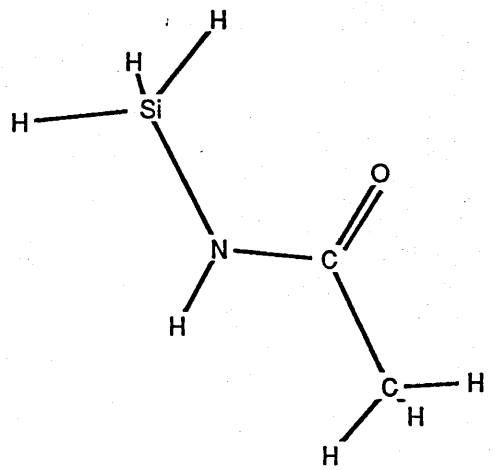
HF_{cis} = -555.0659837
HF_{trans} = -555.0671784

4.5 N-silylacetamide

N-silylacetamide was studied in much the same way as N-silylformamide. The energy difference between the two rotational states and the barrier to rotation about the N-C bond were calculated at the *ab initio* level using the modified 3-21 G*# basis set of Grigoras and Lane. From these calculations, it was found that the *cis* rotameric structure is more stable than the *trans* rotamer by 3.55 kcal mol^{-1}. The rotational barrier for this molecule was calculated to be 20.6 kcal mol^{-1} (*cis* to *trans*) and is nearly what we observed for N-silylformamide, 21.0 kcal mol^{-1}. Table 4.4 summarises some of the more important structural data for the cis rotamer.

Table 4.4:

Cis-N-silylacetamide
Structural Data and Electronic Charge Data Based on
Ab initio Calculations at the 3-21G*(modified) level.



Bond Length (Å)		Bond Angle (degrees)	
Si-H	1.4844	N-Si-H	105.295
N-Si	1.7662	C-N-Si	118.486
C-N	1.3617	O-C-N	120.745
O-C	1.1980	C-C-N	115.854
C-C	1.5128	H-N-Si	123.411
H-N	1.0033	H-Si-N	111.507
H-Si	1.4788	H-C-C	109.775
H-C	1.0889		

Charge	
ATM	CHR
SiH	-0.0748
Si	+0.5408
N	-0.9349
C	+0.9602
O	-0.7063
C	-0.7977
H	+0.3566
SiH	-0.0587
SiH	-0.0587
H	+0.2757
H	+0.2489
H	+0.2489

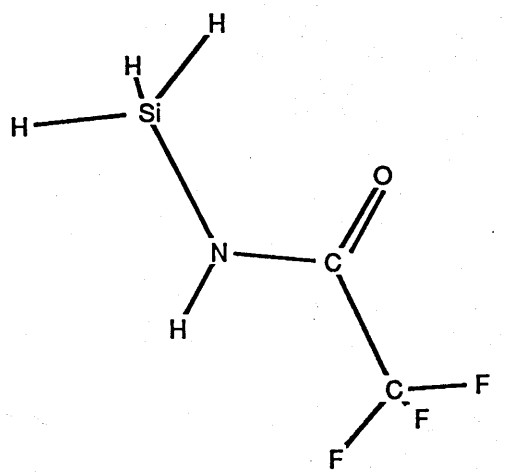
HF = -495.5370042

4.6 N-silylfluoroacetamide

As we substituted a trifluoromethyl group for the normal methyl group at the carbonyl carbon, we noted the destabilisation of the *cis* rotamer. In this case, the *cis* isomer was still the preferred structure but only by 1.34 kcal mol^{-1} as compared to the 3.55 kcal mol^{-1} in the unsubstituted example. In addition to the reduction in energy between the two rotameric states, we observed the expected lowering of the barrier to rotation about the N-C bond. In the trifluoromethyl example, the barrier to rotation was calculated to be 18.8 kcal mol^{-1} (*cis* to *trans*), down from 20.6 kcal mol^{-1}. Table 4.5 summarises the important structural data for N-silylfluoroacetamide.

Table 4.5:

Cis-N-silylfluoroacetamide
Structural and Electronic Charge Data Based on
Ab initio Calculations at the 3-21G*(modified) level.



Bond Length (Å)		Bond Angle (degrees)	
Si-H	1.4808	N-Si-H	105.054
N-Si	1.7750	C-N-Si	119.652
C-N	1.3464	O-C-N	124.798
O-C	1.1903	C-C-N	113.792
C-C	1.5270	H-N-Si	123.104
H-N	1.0042	H-Si-N	110.520
H-Si	1.4770	F-C-C	110.483
H-Si	1.4770		
F-C	1.3113		

Charge

ATM	CHR
SiH	-0.0603
Si	+0.5454
N	-0.9483
C	+0.8255
O	-0.6811
C	+1.1089
H	+0.3752
SiH	-0.0476
SiH	-0.0476
F	-0.3495
F	-0.3603
F	-0.3603

HF = -790.593386

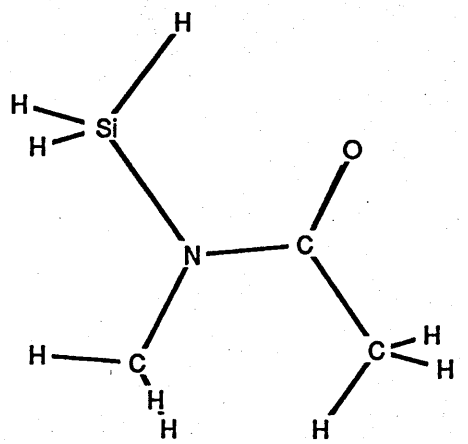
4.7 N-silyl-N-methylacetamide

Our *ab initio* calculations have taught us that for this yet unknown compound that the silicon atom prefers to be *trans* to the carbonyl oxygen by 1.57 kcal mol^{-1}. The *cis-trans* isomerisation barrier of the amide bond was calculated to be 15.9 kcal mol^{-1} (*cis* to *trans*) and 17.5 kcal mol^{-1}. (*trans* to *cis*) and has not been corroborated experimentally at this time. However, based on our understanding of the rotational process we would anticipate that this material would have a similar to slightly smaller barrier to rotation than dimethylacetamide. This difference would be due to the electron withdrawing ability and size of a silyl group relative to a methyl group. The silyl group should decrease the electron density at nitrogen and increase the resonance or hyperconjugation effects which control this restricted rotation, but the increased size of a silyl group relative to a methyl should reduce the barrier. A better comparison might be between N-silyl-N-methylacetamide and N-silylacetamide where we can evaluate only the effect of the size of the substituent at nitrogen. As the substituent at nitrogen is changed from hydrogen to methyl two differences occur. The first is the relative stabilities of the rotamers change. In the hydrogen example the *cis* rotamer is more stable relative to the rotamer where the silyl group is *trans* to the oxygen by 3.55 kcal mol^{-1}. In the case of the methyl substituent we see that the *trans* rotamer is preferred by 1.57 kcal mol^{-1}. The barrier to rotation about the N-C bond is reduced by

3.1 kcal mol^{-1} as the hydrogen at nitrogen is replaced by a methyl group. This observation is consistent with experimental observations that increasing the size of the substituent at nitrogen will reduce the N-C rotational barrier. Important structural data are summarised in Table 4.6.

Table 4.6:

N-methyl-N-silylacetamide
Structural and Electronic Charge Data Based on
Ab initio Calculations at the 3-21G*(modified) level.



Bond Length (Å)			Bond Angle (degrees)		
	Cis	*Trans*		*Cis*	*Trans*
N-Si	1.7731	1.7572	H-Si-N	113.087	110.719
H-Si	1.4710	1.4774	C-N-Si	121.171	130.675
C-N	1.3708	1.3734	O-C-N	121.869	121.103
O-C	1.1965	1.1959	C-N-Si	118.079	116.348
C-N	1.4634	1.4713	H-Si-N	108.431	109.861
H-Si	1.4857	1.4838	C-C-N	116.900	117.512
H-Si	1.4857	1.4838	H-C-N	110.580	110.144
C-C	1.5149	1.5144			
H-C	1.0887	1.0880			

	Charge	
	Cis	*Trans*
ATM	CHR	
Si	+0.5259	+0.5454
N	-0.8192	-0.8169
SiH	-0.0120	-0.0530
C	+0.9809	+0.9623
O	-0.7101	-0.7050
C	-0.5018	-0.5017
SiH	-0.0705	-0.0610
SiH	-0.0705	-0.0610
C	-0.8162	-0.8101
H	+0.2385	+0.2540
H	+0.2459	+0.9219
H	+0.2385	+0.2540
H	+0.2754	+0.2751
H	+0.2476	+0.2494
H	+0.2476	+0.2494

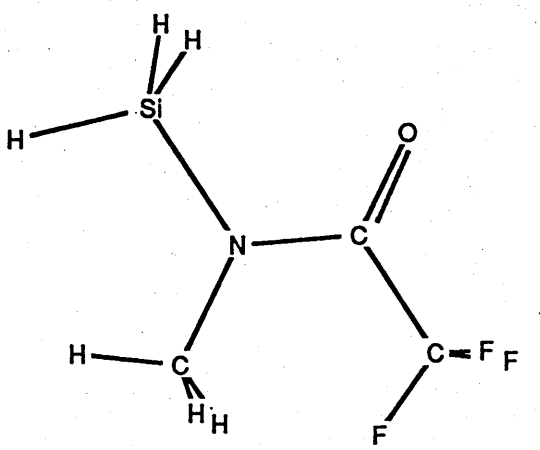
HF_{trans} = -534.3587138
HF_{cis} = -534.3561706

4.8 N-methyl-N-silylfluoroacetamide

N-methyl-N-silylfluoroacetamide was also studied to evaluate the effect of an electron withdrawing group at the carbonyl carbon. As in the other examples, we observed the shift in preference in the *trans* rotamer and a lowering in the barrier to N-C rotation. The *trans* rotamer is preferred to the *cis* isomer by 2.71 kcal mol^{-1} as compared to 1.57 kcal mol^{-1} in the methyl example. The restricted barrier to rotation about the nitrogen carbonyl carbon bond was calculated to be 14.6 kcal mol^{-1} (*trans* to *cis*) which is 2.9 kcal mol^{-1} lower than in the methyl case. The significant structural data are summarised in Table 4.7.

Table 4.7:

N-methyl-N-silylfluoroacetamide
Structural and Electronic Charge Data Based on
Ab initio Calculations at the 3-21G*(modified) level.



Bond Lengths			Bond Angle		
	Cis	*Trans*		*Cis*	*Trans*
N-Si	1.7813	1.7736	H-Si-N	111.922	112.570
H-Si	1.4704	1.4676	C-N-Si	120.862	131.676
C-N	1.3517	1.3506	O-C-N	125.161	124.896
O-C	1.1914	1.1904	C-N-Si	117.617	115.827
C-N	1.4716	1.4742	H-Si-N	107.965	107.901
H-Si	1.4829	1.481	C-C-N	117.503	116.181
H-Si	1.4829	1.481	H-C-N	110.464	110.118
C-C	1.5351	1.526	F-C-C	110.881	110.674
H-C	1.0853	1.0872			
F-C	1.3126	1.3128			

Charges

	Cis	*Trans*
ATM	CHR	CHR
Si	+0.5289	+0.5331
N	-0.8356	-0.8341
SiH	-0.0073	-0.0311
C	+0.8557	+0.8350
O	-0.6848	-0.6851
C	-0.5535	-0.5149
SiH	-0.0587	-0.0557
SiH	-0.0589	-0.0557
C	+1.1050	+1.1064
H	+0.2648	+0.2625
H	+0.2493	+0.2324
H	+0.2648	+0.2625
F	-0.3515	-0.3505
F	-0.3592	-0.3525
F	-0.3592	-0.3525

4.9 *Ab initio* Basis Set Study

In addition to these calculations, we also studied N-methyl-N-silylacetamide as a limited function of basis set since it is known that the calculated barriers of rotation about the amide bond are a function of basis set selection [12]. Tables 4.8 through 4.10 summarise the optimised structural information for the torsional angles about the N-C bond equal to zero (silyl group *cis* to oxygen), 90 and 180 degrees. Table 4.11 shows the effect of basis set on the rotational barrier, rotamer preference, and time required to carry out the optimisation at torsional angles of zero, 90, and 180 degrees. It is readily apparent that the modified basis set of Grigoras and Lane provide data which are comparable to those obtained from 6-31 G* and substantially reduced cost in terms of CPU minutes for the calculations.

Table 4.8:

Optimisation of N-methyl-N-silylacetamide at Si-N-C(O)-O tau=0, 90, and 180 as a Function of Basis Set

tau=0

Variable	3-21 G*#	3-21 G*	6-31 G*
	Bond Lengths (Å)		
Si-N	1.7731	1.7556	1.7686
Si-H	1.4710	1.4621	1.4606
N-C(O)	1.3708	1.3829	1.3747
C=O	1.1965	1.2165	1.1991
N-C	1.4634	1.4823	1.4624
Si-H	1.4857	1.4766	1.4762
Si-H	1.4857	1.4766	1.4762
C(O)-C	1.5149	1.5155	1.5143
C-H	1.0887	1.0818	1.0831
	Bond Angles (degrees)		
H-Si-N	113.087	112.671	112.721
Si-N-C(O)	121.171	122.299	121.662
N-C=O	121.869	121.625	121.731
Si-N-Me	118.079	117.265	117.275
H-Si-N	108.431	108.829	108.098
N-C(O)-C	116.900	116.704	117.540
H-C-N	110.580	110.368	110.668

Table 4.9:

Optimisation of N-methyl-N-silylacetamide at Si-N-C(O)-O tau=0, 90, and 180 as a Function of Basis Set

tau=90

Variable	3-21 G*#	3-21 G*	6-31 G*
	Bond Lengths (Å)		
R1 Si-N	1.7380	1.7231	1.7299
R2 Si-H	1.4833	1.4742	1.4735
R3 N-C(O)	1.4227	1.4302	1.4221
R4 C=O	1.1841	1.2044	1.1866
R5 N-C	1.4673	1.4905	1.4641
R6 Si-H	1.4870	1.4777	1.4776
R7 Si-H	1.4863	1.4770	1.4765
R8 C(O)-C	1.5153	1.5155	1.5141
R9 C-H	1.0897	1.0827	1.0841
	Bond Angles (degrees)		
A1 H-Si-N	107.348	107.391	107.068
A2 Si-N-C(O)	122.536	123.243	122.327
A3 N-C=O	122.586	122.493	122.008
A4 Si-N-Me	122.012	121.441	121.768
A5 H-Si-N	111.526	111.811	111.436
A6 N-C(O)-C	115.168	114.920	116.385
A7 H-C-N	110.474	110.216	110.574

Table 4.10:

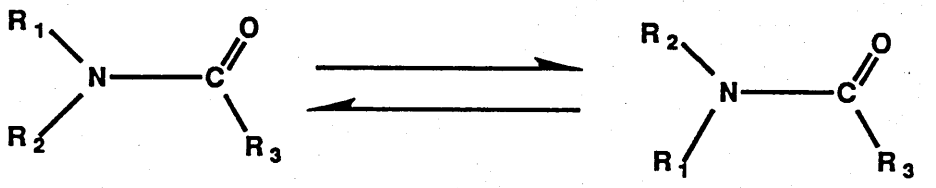
Optimisation of N-methyl-N-silylacetamide at Si-N-C(O)-O tau=0, 90, and 180 as a Function of Basis Set

tau=180

Variable	3-21 G*#	3-21 G*	6-31 G*
	Bond Lengths (Å)		
R1 Si-N	1.7572	1.7398	1.7524
R2 Si-H	1.4774	1.4688	1.4674
R3 N-C(O)	1.3734	1.3846	1.3763
R4 C=O	1.1959	1.2160	1.1985
R5 N-C	1.4713	1.4922	1.4677
R6 Si-H	1.4838	1.4743	1.4738
R7 Si-H	1.4838	1.4743	1.4738
R8 C(O)-C	1.5144	1.5153	1.5142
R9 C-H	1.0880	1.0811	1.0824
	Bond Angles (degrees)		
A1 H-Si-N	110.719	110.599	110.539
A2 Si-N-C(O)	130.675	131.094	130.425
A3 N-C=O	121.103	120.789	121.053
A4 Si-N-Me	116.348	115.918	115.630
A5 H-Si-N	109.861	110.234	109.617
A6 N-C(O)-C	117.512	117.326	118.030
A7 H-C-N	110.144	109.929	110.270

Table 4.11:

Effects of Basis Set Selection on Rotameric Preference and Restricted Barrier of Rotation in N-methyl-N-silylacetamide



Where R1= H_3Si, and R2=R3=methyl

Basis Set	delta E(*trans-cis*) (kcal/mol)	Barrier (F/R)	Time(minutes) (F)
3-21 G	-2.57	13.3/15.9	153
3-21 G*#	-1.57	15.9/17.3	315
6-31 G*	-1.76	14.6/16.3	1141

4.10 Optimisations and Approximations

An equally important observation when dealing with calculations of this magnitude is the optimisation procedure and the associated assumptions. All the calculations discussed to date have been fully optimised *ab initio* calculation conducted at the 3-21 G*# level, unless noted otherwise. For torsional scans, each step about a bond rotation has been optimised. As one can readily see, the magnitude of computational time required for larger molecules soon becomes prohibitive. However, there are many examples in the literature where rotational behaviour is studied using a rigid rotor approximation [13]. In these studies, all bond lengths and bond angles are held fixed during the rotation or scan of a bond. Often, the bond lengths and angles are experimental values or values derived from a full optimisation of the lowest energy conformer. As our study continued to expand in scope, it became important to re-evaluate the rigid rotor approximation. Three scenarios were evaluated. The first, which has already been described, is the full structural optimisation at each step about the torsional scan of the N-C bond. In this case we found the *trans* isomer (silyl group *trans* to the oxygen) to be the more stable rotamer by 1.60 kcal mol^{-1} for N-silyl-N-methylacetamide. The calculated barriers were 15.9 and 17.5 kcal mol^{-1} for the forward (*cis* to *trans*) and reverse rotations, respectively. The next scheme tried was the formal rigid rotor approximation. In this example, we

carried out a complete optimisation on the most stable rotamer, the *trans* isomer, by fixing all of the bond lengths and bond angles. The torsional scan was then allowed to occur without relaxing the valence structure. This resulted in a difference in energy between the *cis* and *trans* states of 7.41 kcal with the *trans* isomer remaining the most stable. The barriers to rotation about the N-C bond were calculated to be 10.8 and 18.2 kcal mol^{-1} for the *cis* to *trans* and *trans* to *cis* conversions, respectively. The last situation, where the *trans* isomer was optimised and the valence geometry fixed, differed from the rigid rotor model in that we allowed the hydrogen atoms to be relaxed at each torsional step. This provided a better estimate of the difference in energy between the two rotameric states, but resulted in a higher barrier to restricted rotation. The method successfully predicted that the *trans* rotamer would be the more stable, by 3.98 kcal mol^{-1} nearly 2.4 kcal mol^{-1}, higher than predicted values from a complete optimisation. The estimated barrier to rotation was calculated as 15.5 kcal mol^{-1}, *cis* to *trans* and 19.5 kcal mol^{-1}, *trans* to *cis*. Although each of these last two scenarios provides reasonable information with regard to restricted rotation, it is still recommended to use complete optimisation whenever possible. These data are summarised in Table 4.12.

Table 4.12:

Torsional barrier for N-methyl-N-silylacetamide

from tau=0 ===> tau=90 ====> tau=180

3-21 G*# *Ab initio*

Situation	delta E (kcal mol^{-1})	Barrier (kcal mol^{-1})
optimised structures, including transition tau=0,90, and 180	-1.57	15.9/17.5
backbone optimisation (tau=180), fixed hydrogens, rigid rotor rotation.	-7.41	10.8/18.2
backbone optimisation (tau=180), relaxed hydrogens.	-3.99	15.5/19.5

silicon *trans* to the carbonyl oxygen (tau=180) most stable in each case.

4.11 Semi-Empirical Approaches

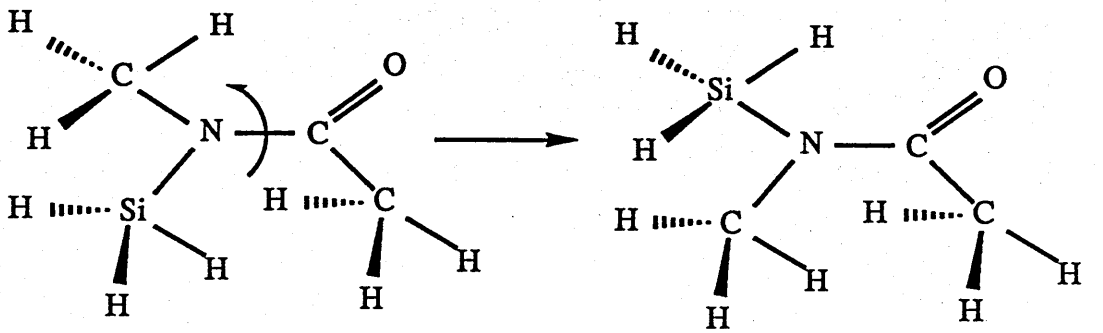
4.11.1 Rotational

As part of this general study of amides we felt it important to establish which of the semi-empirical methods would best mimic the observed *ab initio* results. Such information and knowledge of the relationships between the methods would then allow the study of larger amides or trimethylsilylamides. This would allow a computational method to contribute to the design of industrially important materials. We evaluated EHT, CNDO2, MNDO, and AM1. The difference in energy between the *cis* and *trans* forms of N-methyl-N- silylacetamide and the greatest barrier to rotation are given in Table 4.13. However, it must be noted that closeness to the *ab initio* values cannot be used as the sole criterion for recommending a semi-empirical method. Figures 4.14-4.17 show the torsional behaviour obtained by the various methods. It is obvious that EHT and MNDO methods are inappropriate for studying these barriers despite the fact that the energies given in the table appear to provide a good fit with *ab initio* results. We found that AM1 provided the best description of the torsional behaviour for silicon-containing amides relative to *ab initio* calculations. When these methods were applied to amides which did not contain silicon, both AM1 and MNDO provided excellent torsional barrier descriptions. As the table shows, AM1 underestimates the energy difference between the *cis* and *trans* isomers when

compared to *ab initio* results. In fact, in some examples, it failed to predict the preferred rotameric structure. For example, in the N-silylformamide examples we found that *ab initio* calculations predicted the *cis* rotameric structure to be preferred over the *trans* rotamer by 2.69 kcal mol^{-1}. The calculated barrier to rotation was 21.0 kcal mol^{-1}. Using the AM1 method, the calculations predicted the *trans* rotamer to be more stable than the *cis* form by 1.9-2.3 kcal mol^{-1} depending on how the calculations were run. When we used *ab initio* optimised bond lengths and bond angles as the input geometries for the AM1 torsional scanning of the N-C bond, we found the *trans* isomer to be preferred by 1.93 kcal mol^{-1}. When the calculations were repeated, this time using the *ab initio* values as the starting geometries for AM1 optimisation of each structure in the torsional scan, the *trans* rotamer was preferred by 2.3 kcal mol^{-1}. The maximum torsional barrier for each of these two scenarios were 12.12 and 12.66 kcal mol^{-1}, respectively. They are graphically represented in Figures 4.18 and 4.19. The AM1 values can be scaled to *ab initio*-like values by multiplying by a factor of 1.7. It is important to note, however, that this scalar is useful only for compounds containing silicon-nitrogen bonds. However, when these calculated barriers are scaled and compared to the reported *ab initio* barriers we find very good agreement among the calculated values. The *ab initio* barrier to rotation was found to be 21.0 kcal mol^{-1} and the scaled AM1 values 20.6 and 21.5 kcal mol^{-1}, respectively.

Table 4.13:

Torsional Barrier Using Rigid Rotor Approximation

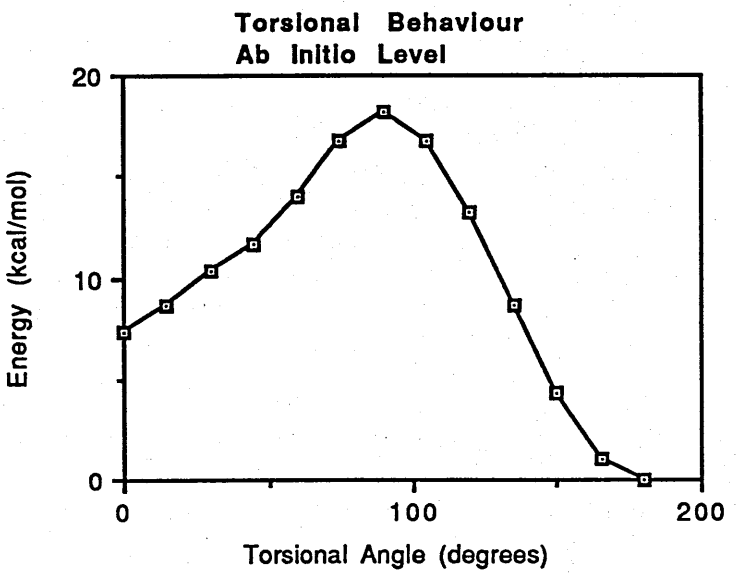


MOST STABLE

	ΔE	Barrier
Ab initio	7.41	18.2
AM1	4.30	10.7
MNDO	5.37	5.76
CND02	7.69	9.37
EHT	5.62	14.5

all energies are in kcal mol^{-1}

Figure 4.14:


Torsional Behaviour
Ab Initio Level
Energy (kcal/mol)
20
10
0
0
100
200
Torsional Angle (degrees)

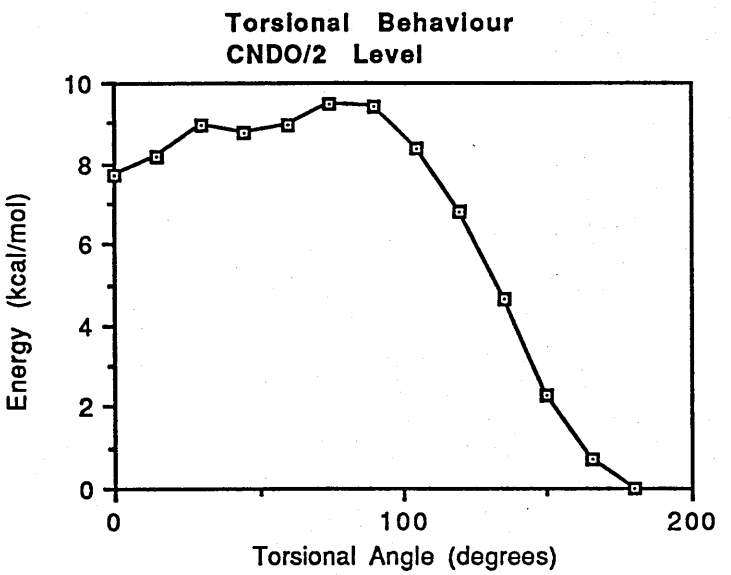
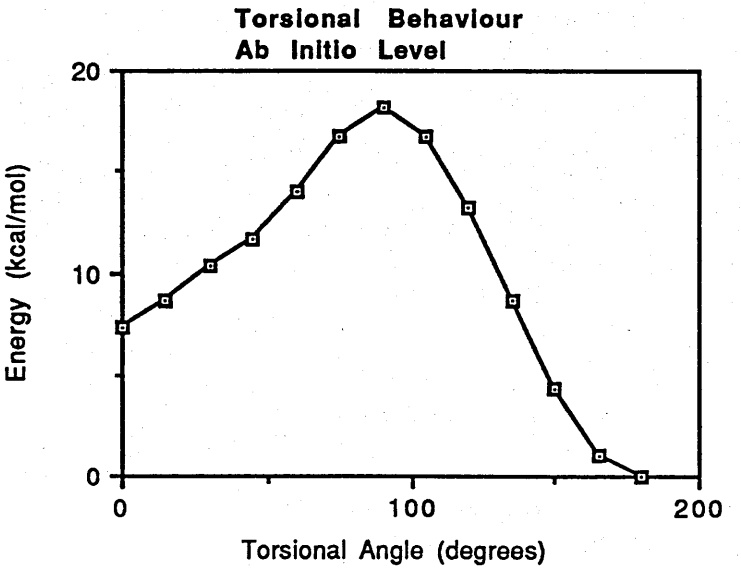

Torsional Behaviour
CNDO/2 Level
Energy (kcal/mol)
10
8
6
4
2
0
0
100
200
Torsional Angle (degrees)

Figure 4.15:


Torsional Behaviour
Ab Initio Level
Energy (kcal/mol)
20
10
0
0
100
200
Torsional Angle (degrees)

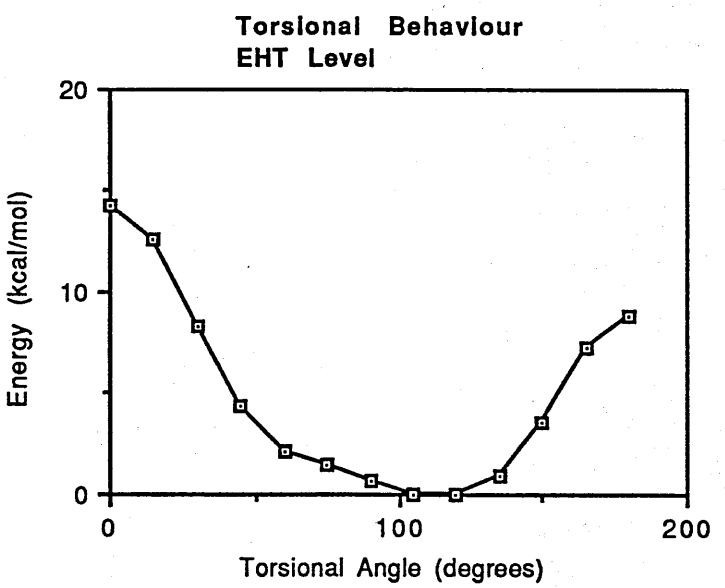
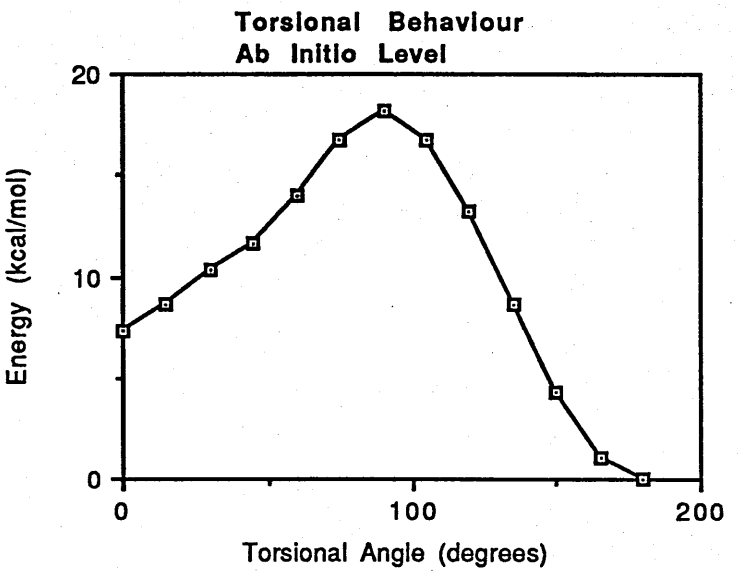

Torsional Behaviour
EHT Level
Energy (kcal/mol)
20
10
0
0
100
200
Torsional Angle (degrees)

Figure 4.16:


Torsional Behaviour
Ab Initio Level
Energy (kcal/mol)
20
10
0
0
100
200
Torsional Angle (degrees)

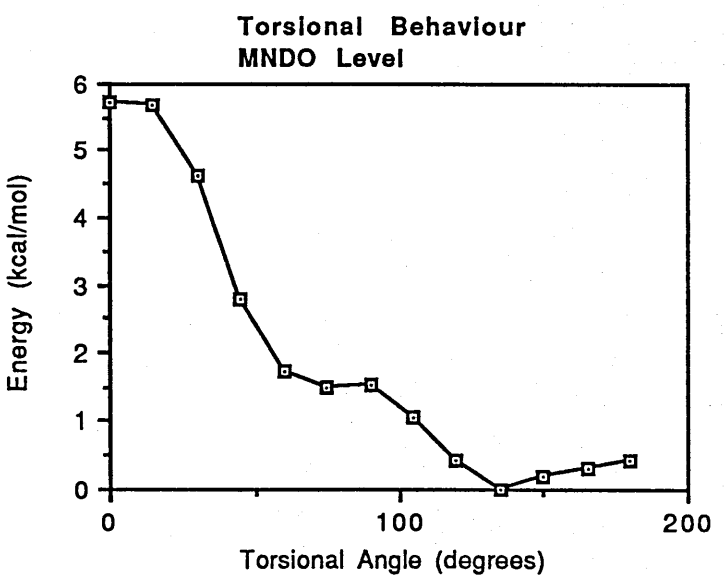

Torsional Behaviour
MNDO Level
Energy (kcal/mol)
6
5
4
3
2
1
0
0
100
200
Torsional Angle (degrees)

Figure 4.17:

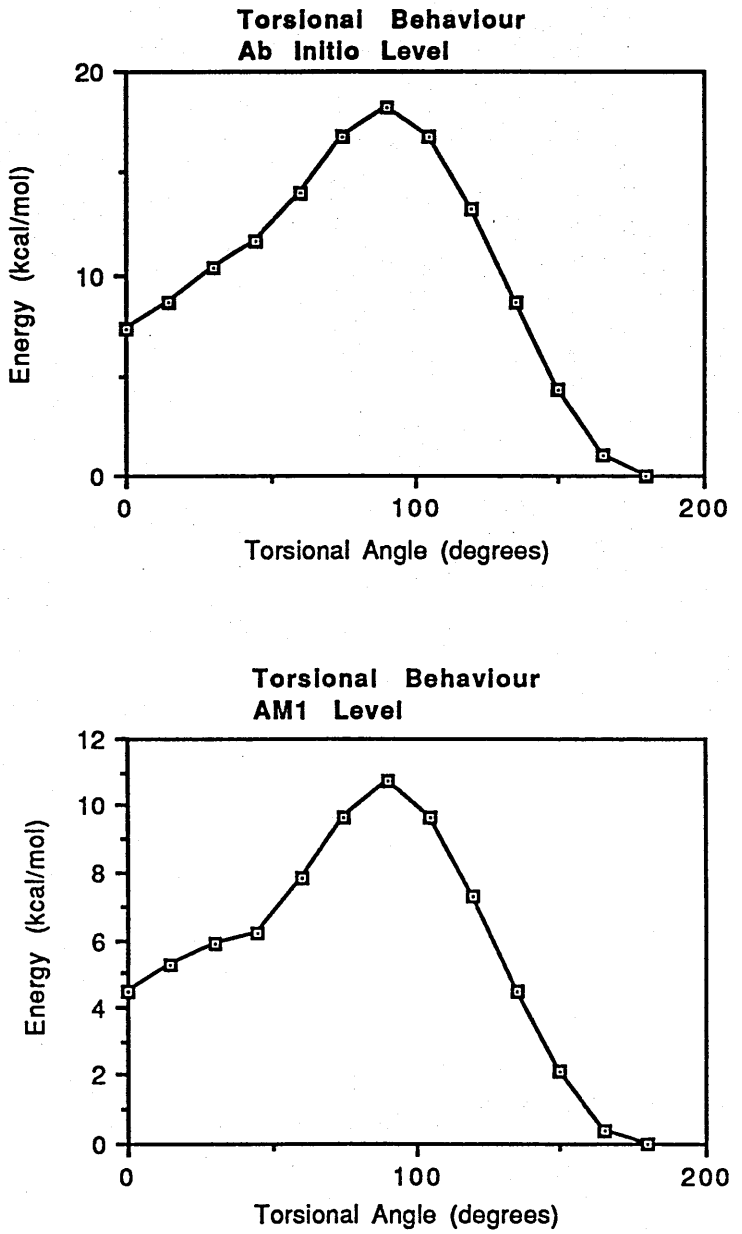

Torsional Behaviour
Ab Initio Level
Energy (kcal/mol)
20
10
0
0
100
200
Torsional Angle (degrees)
Torsional Behaviour
AM1 Level
Energy (kcal/mol)
12
10
8
6
4
2
0
0
100
200
Torsional Angle (degrees)

Figure 4.18:

Comparison of Delta E from *Ab Initio* and AM1 Calculations

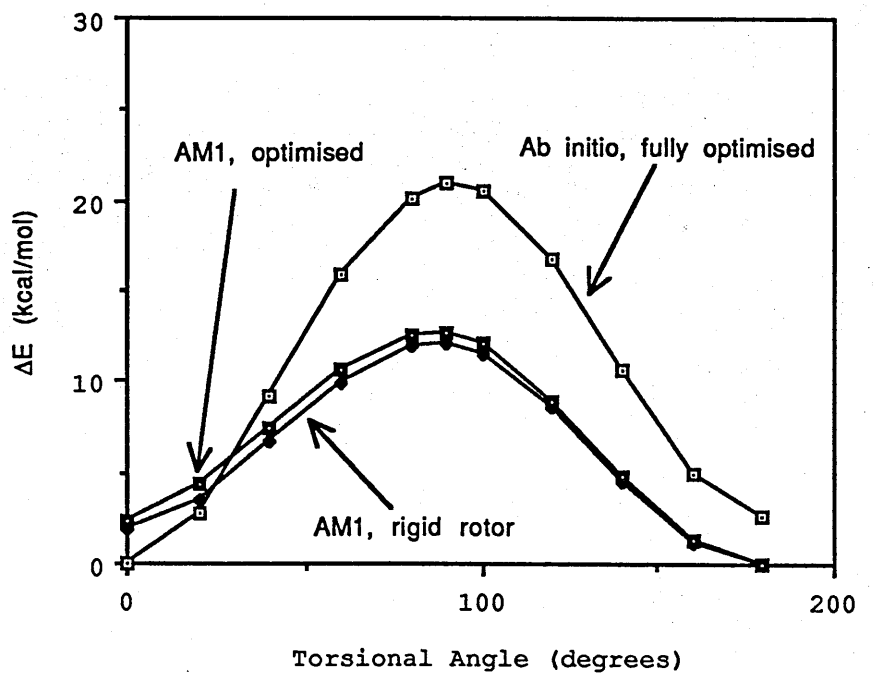
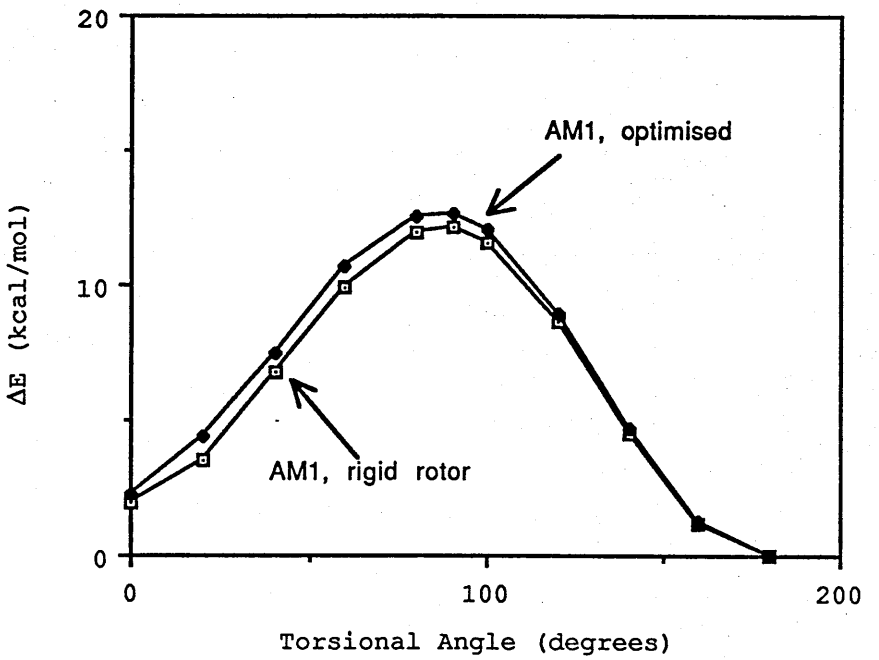


Figure 4.19:

Comparison of Delta Energy from AM1 Calculations



4.11.2 Tautomerisations

In addition to isomerisation or hindered rotation, silylamides have the ability to participate in a tautomerisation reaction. In this reaction, the silicon group migrates from the nitrogen to oxygen in an intramolecular 1,3-silyl migration, assuming that the silicon-containing group is *cis* to the carbonyl oxygen. This tautomerisation is outlined in Equation 4.3. The process will be discussed in substantially more detail in the next chapter. However, we did examine the relative stabilities of these two tautomeric states using both *ab initio* and AM1 techniques. Using N-methyl-N-silylacetamide as our model, *ab initio* calculations provided us with information which shows that the preferred structure for this example is the O-tautomer, by 2.57 kcal mol^{-1}. This is consistent with experimental studies of substituted trimethylsilylamides, which show that as electron withdrawing groups are placed on nitrogen there is a preference for the O-silyl form. AM1 calculations suggested that the O-silyl form was preferred by over 20 kcal mol^{-1}. The tendency of AM1 to underestimate the relative energies of Si-N compounds while overestimating the energies of Si-O materials complicates the calculations of the preferred tautomeric state. The latest release of AM1 (version 4.1) corrects for some of this but still should not be trusted for the comparison of relative stabilities of Si-N versus Si-O materials. Table 4.14

gives a comparison between *ab initio* values and AM1 values for four amides and their corresponding imidate structures.

Equation 4.3:

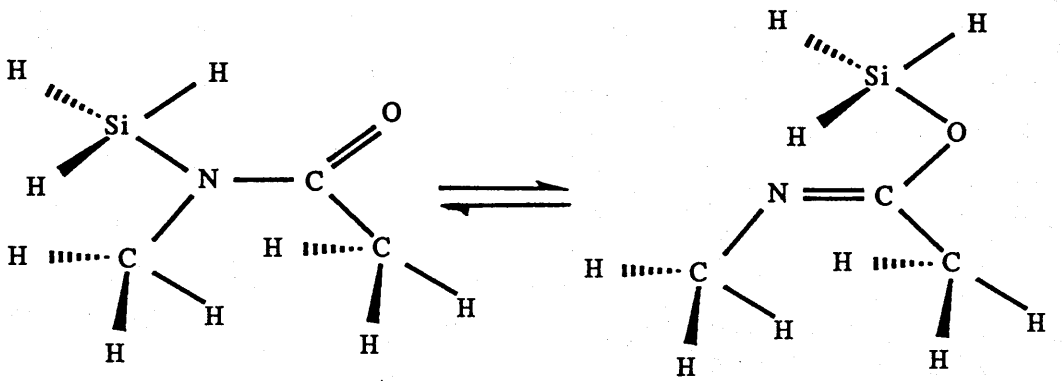
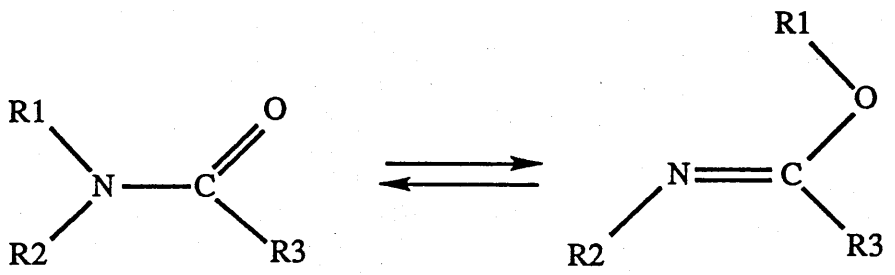


Table 4.14:

1-3 Migration of Silicon Across an Allylic FrameWork

Ab initio versus AM1 Calculations

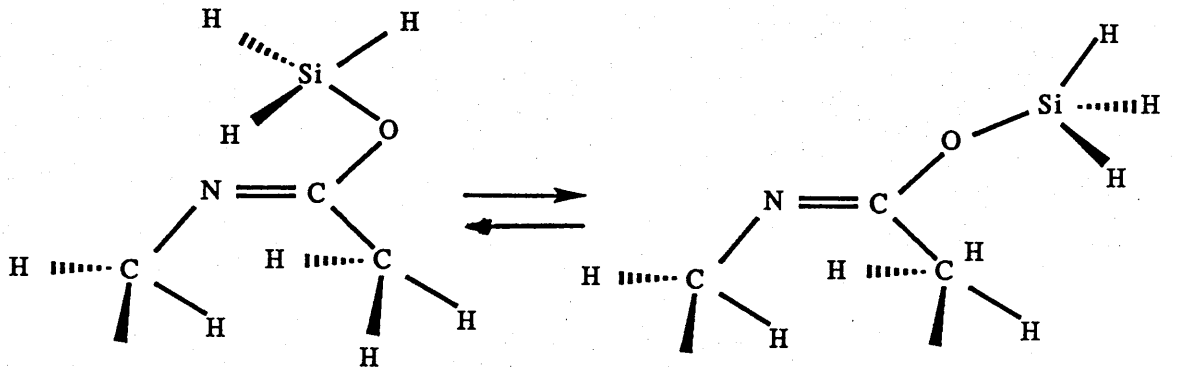


R1	R2	R3	*Ab initio* Delta E	AM1 Delta E
H3Si	H	H	+ 2.40	11.64
H3Si	H	F	+ 8.70	13.22
H3Si	H	CH3	+ 4.35	10.97
H3Si	H	CF3	+ 3.87	11.78

Delta E = $E_{product} - E_{reactant}$ (kcal mol^{-1})

The difference in energy between the two major rotameric states of the O-tautomer was calculated by *ab initio* methods to be 6.7 kcal mol^{-1} in favour of the syn isomer, Figure 4.20. AM1 and MNDO both overestimate this difference for materials containing silicon-oxygen bonds and afford values of 8.6 and 9.8 kcal mol^{-1}, respectively.

Figure 4.20:



4.12 N-methyl-N-trimethylsilylacetamide

4.12.1 AM1

The torsional and tautomeric behaviour was then studied using AM1 techniques from the geometry provided by *ab initio* results and total energies determined. The data generated from the study of the hindered rotation about the nitrogen carbonyl carbon bond are given in Table 4.15 and can be seen graphically in Figure 4.21. Equation 4.4 illustrates the process studied.

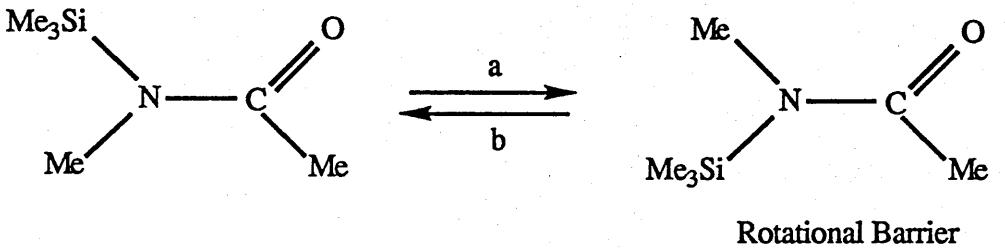
Table 4.15:

Hindered rotation about the nitrogen carbonyl carbon bond at the AM1 level of calculation.

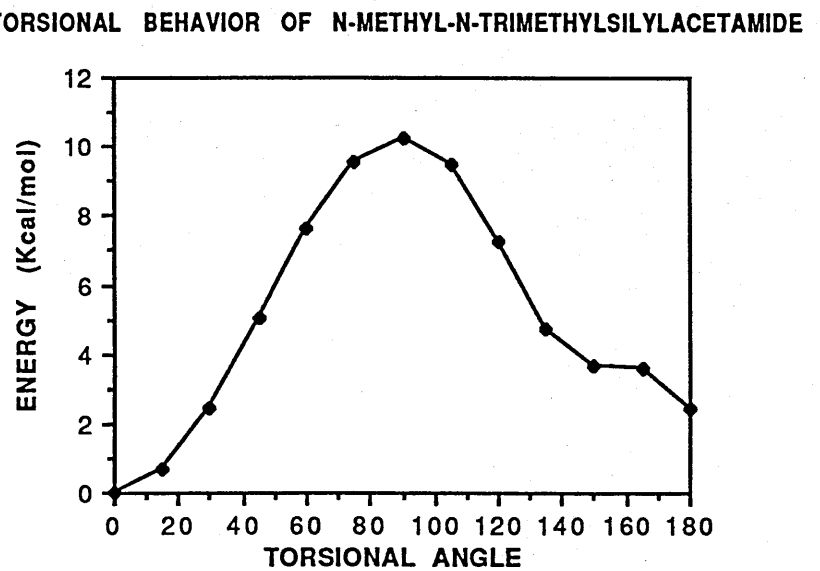
	AM1	SCALED AM1	EXP.
ΔE	2.46 kcal	4.18 kcal	+
F	7.81	13.5	14.4 kcal
R	10.3	17.8	15.8

where:
F is the foward reaction, *cis* to *trans*
R is the reverse reaction, *trans* to *cis*.
ΔE is the difference in energy between the *cis* and *trans* rotameric states.

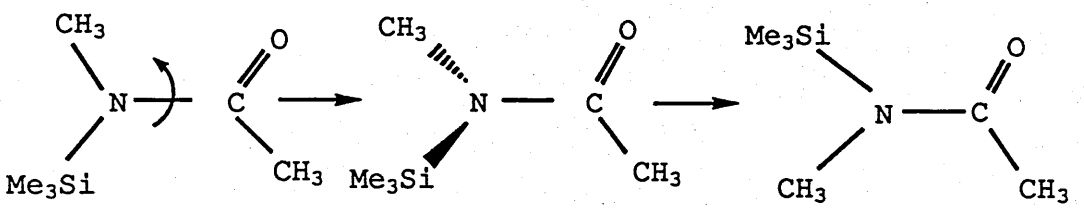
Figure 4.21:



Rotational Barrier



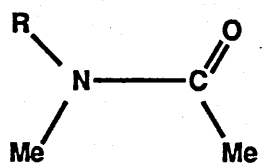
Equation 4.4:



These data show that the preferred rotameric conformation of N-methyl-N-trimethylsilylacetamide is one in which the silicon or trimethylsilyl group is *cis* to the carbonyl oxygen. The scaled difference between the two rotameric states is 4.2 kcal mol^{-1}. The total energy is large enough to suggest a rotameric preference for this *cis* configuration. The barriers for interconversion between rotameric states were calculated to be 13.5 kcal mol^{-1} (scaled) for the conversion of the least stable rotamer to the more stable and 17.8 kcal mol^{-1} (scaled) for the conversion of the more stable to the least. All of these data are in good agreement with the work of Komoriva and Yoder [14] who showed that the *cis* isomer of the molecule was, in fact, the preferred structure, via variable temperature NMR experiments. They also determined the free energies of activation for rotation and found them to be 14.4 and 15.8 kcal mol^{-1}. When the unscaled AM1 results for dimethylacetamide, N-methyl-N-silylacetamide, and N-methyl-N-trimethylsilylacetamide are compared, Table 4.16, we see a 3-4 kcal mol^{-1} lowering of the activation energy or barrier of rotation for the silylamide relative to dimethylacetamide. Substitution of a trimethylsilyl group for a methyl group in dimethylacetamide decreases the free energy by about 2-3 kcal mol^{-1}.

Table 4.16:

Unscaled AM1 Results for Various Substituted Acetamides



R	ΔE	F	B	average
Me	0	12.5	12.5	12.5
H3Si	4.30	10.7	6.40	8.55
Me3Si	2.46	10.3	7.81	9.06

Where:

All energies are given in (kcal mol^{-1})
F is the foward reaction, *cis* to *trans*
B is the reverse reaction, *trans* to *cis*.
ΔE is the difference in energy between the *cis* and *trans* rotameric states.

This is best explained by the greater size of the trimethylsilyl group relative to a methyl which should result in the destabilisation of the ground state and therefore, a reduction in rotational barrier [15]. A contributing effect might involve the electronic interactions between nitrogen and the polarisable silicon. Conjugation of silicon with nitrogen should lead to a reduction of (p-p)pi overlap between the carbon of the carbonyl and nitrogen, increasing the energy of the ground state. This leads to a reduction in energy at the transition state or a lowering of the rotational barrier. In the case of N-methyl-N-silylacetamide, the lowering of the average rotational barrier as compared to dimethylacetamide is best explained by the electron withdrawing ability of a silyl group relative to a methyl group. Electronically, the silyl group should decrease the carbonyl carbon-nitrogen pi density resulting in a higher ground state energy and a lower torsional barrier.

4.12.2 *Ab initio*

After generating these semi-empirical results we found ourselves in a position to repeat these calculations at the 3-21G*# *ab initio* level. Starting with the optimised skeletal values for N-methyl-N-silylacetamide (*trans*) we built and optimised the trimethylsilyl substituted structure. At this juncture, we applied the rigid rotor approximation and held the valence structure of the

molecule constant as the N-C bond was scanned. From this experiment we found that the *trans* rotamer, trimethylsilyl group *trans* to the oxygen, was the more stable structure by 5.33 kcal mol^{-1}. The calculated barrier to rotation was 19.4 kcal mol^{-1}. The barrier to hindered rotation obtained from this calculation was in reasonable agreement to the scaled value of 18 kcal mol^{-1} observed from AM1 calculations. However, the major difference between the *ab initio* and AM1 calculation was in the prediction of the more stable rotameric state. AM1 calculation demonstrated that the *cis* rotamer should be more stable by 4.2 kcal mol^{-1} (scaled) which is consistent with experimental findings. The rigid rotor approximation, *ab initio* calculation where we started from the *trans* rotamer, suggested that the *trans* isomer should be more stable by greater than 5.33 kcal mol^{-1}. The calculations were repeated, this time holding the valence geometry constant, but allowing the hydrogen positions to relax at each torsional step of the N-C scan. We used molecular mechanics to determine the positions of the hydrogens at each torsional step and then transported that information into the *ab initio* calculation. Combining molecular mechanics for hydrogen relaxation and *ab initio* calculations for final energy determinations we found that the *trans* rotamer was still preferred but this time by only 1.43 kcal mol^{-1}. This is a reduction of nearly 4 kcal mol^{-1} from the observed difference in the rigid rotor approximation model. The barrier to rotation about the N-C bond was determined to be 16.4 kcal mol^{-1}. However, the

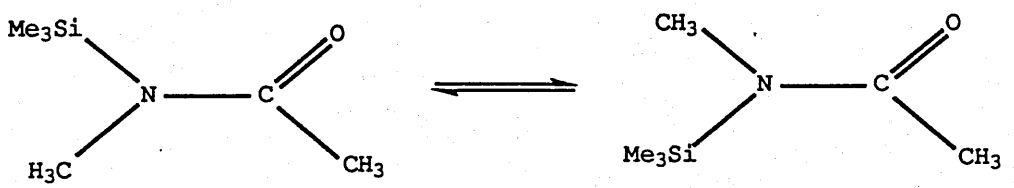
combination of calculations still failed to yield answers consistent with experimental findings. As a final step, we repeated this study using complete skeletal optimisation and hydrogen relaxation at the *ab initio* level. From these calculations we found that the data supported the *cis* rotamer to be the most stable topomeric form. The difference in energy between the *cis* and *trans* form of the molecule was determined to be 5.56 kcal mol^{-1} and supports the experimental finding of only a single rotamer form at ambient temperatures. The barrier to rotation was determined to be 19.3 kcal mol^{-1} for the *cis* to *trans* change and 13.6 for the *trans* to *cis* conversion. Table 4.17 summarises the results we found for the various assumptions made during the study of N-methyl-N-silylacetamide and N-methyl-N-trimethylsilylacetamide. The important structural information regarding this silylacetamide are given in Table 4.18.

Table 4.17:

Rotational Behaviour of Silylamides

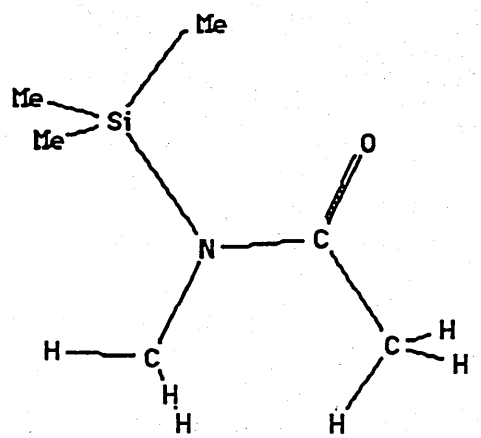
Comparison of Assumptions

Ab initio Calculations



Assumption	H3SiN(Me)C(O)Me		Me3SiN(Me)C(O)Me	
	delta E (kcal mol^{-1})	Barrier	delta E (kcal mol^{-1})	Barrier
Optimised frame - rigid rotor	- 7.41	10.8/18.2	- 5.33	14.1/19.4
Optimised frame - rigid rotor with relaxed hydrogens	- 3.99	15.5/19.5	- 1.43	15.0/16.4
Optimised	- 1.57	15.9/17.5	+ 5.56	19.3/13.6

Table 4.18:
Structural and Net Atomic Charge Data for
N-methyl-N-trimethylsilylacetamide
From *Ab initio* Calculations



Bond Length (Å)		Bond Angle (degrees)	
C-N	1.4662	C-N-C	120.107
C-N	1.3624	C-C-N	118.064
C-C	1.5166	H-C-C	109.470
H-C	1.0901	O-C-N	121.226
O-C	1.2035	Si-N-C	116.010
Si-N	1.7969	C-Si-N	109.471
C-Si	1.9100	H-C-N	109.471
H-C	1.0901	H-C-Si	109.471
H-C	1.0901		

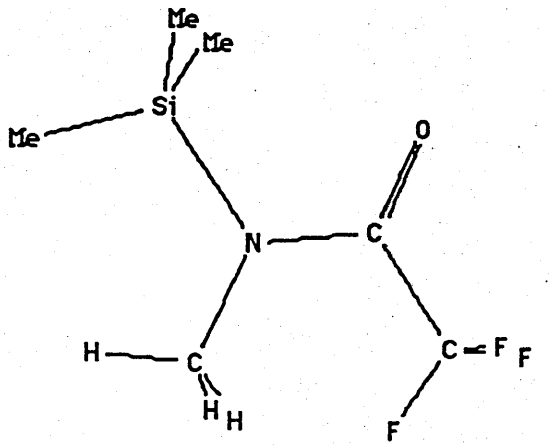
Charge	
ATM	CHR
N	-0.8043
C	-0.5142
C	+0.9649
C	-0.8084
H	+0.2733
H	+0.2467
H	+0.2462
O	-0.7239
Si	+1.4121
C	-1.0145
C	-1.0235
C	-1.0231
H	+0.2556
H	+0.2304
H	+0.2315
H	+0.2362
H	+0.2233
H	+0.2206
H	+0.2127
H	+0.2634
H	+0.2111
H	+0.2158
H	+0.2114
H	+0.2567

4.13 N-methyl-N-trimethylsilylfluoroacetamide

The effect of an electron withdrawing group at the carbonyl carbon was also evaluated. N-methyl-N-trimethylsilylfluoroacetamide (TMSTFA) as studied at the *ab initio* level, 3-21 G*#, utilising structural optimisation at each torsional step about the N-C bond so that these data could be readily compared to those data obtained for N-methyl-N-trimethylsilylacetamide. The important structural information regarding TMSTFA are given in Table 4.19. The data obtained for this example are consistent with other examples studied. There was a slight lowering of the difference in energy between the *cis* and *trans* rotamer, with the preferred structure being the *cis* isomer by approximately 5.5 kcal mol^{-1}. The calculated barrier to rotation was determined to be 19.5 kcal mol^{-1}, *cis* to *trans*, and 14.0 kcal *trans* to *cis*. The difference between the N-methyl-N-trimethylsilylacetamide and N-methyl-N-trimethylsilylfluoroacetamide in terms of their rotational behaviour is insignificant. However, their reactivity towards an active hydrogen is quite different. Given their similarities in rotational behaviour perhaps an explanation can be found in their tautomeric distribution or preference. The 1,3-migration of silicon across an allylic framework is the topic of the next chapter in this work and the possible connection between chemical reactivity and structure will continue there.

Table 4.19:

Structural and Net Atomic Charge Data
for N-methyl-N-trimethylsilylfluoroacetamide
From *Ab initio* Calculations



Bond Length (Å)		Bond Angle (degrees)	
C-N	1.4662	C-N-C	120.107
C-N	1.3624	C-C-N	119.676
C-C	1.5279	F-C-C	110.761
F-C	1.3117	O-C-N	121.226
O-C	1.2035	Si-N-C	116.010
Si-N	1.7969	C-Si-N	109.471
C-Si	1.9100	H-C-N	109.471
H-C	1.0901	H-C-Si	109.471
H-C	1.0901	H-C-Si	109.471
H-C	1.0901	H-C-Si	109.471
H-C	1.0901		

Table 4.19 (continued):

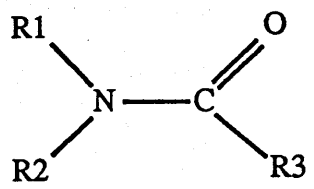
	Charge
ATM	CHR
N	-0.8144
C	-0.5581
C	+0.8245
C	+1.1153
F	-0.3508
F	-0.3566
F	-0.3573
O	-0.6981
Si	+1.4166
C	-1.0158
C	-1.0255
C	-1.0246
H	+0.2569
H	+0.2515
H	+0.2533
H	+0.2400
H	+0.2273
H	+0.2246
H	+0.2187
H	+0.2621
H	+0.2165
H	+0.2214
H	+0.2169
H	+0.2557

4.14 Rotational Summary

A complete summary of the data presented in this section is given in Tables 4.20 and 4.21.

Table 4.20:

Rotational Behaviour of Silylamides



#	R1	R2	R3	*Ab initio* delta E	Barrier (F/R).....
1	H3Si	H	H	+ 2.69	21.0/18.3
2	H3Si	H	F	- 0.750	20.9/21.6
3	H3Si	H	CH3	+ 3.55	20.6/17.1
4	H3Si	H	CF3	+ 1.34	18.8/17.5
5	H3Si	CH3	CH3	- 1.57	15.9/17.5
6	H3Si	CH3	CF3	- 2.71	11.89/14.6
7	Me3Si	CH3	CH3	+ 5.56	19.3/13.6+
8	Me3Si	CH3	CF3	+ 5.49	19.5/14.0
9	CH3	CH3	CH3	+ 0.0	22.9#
10	H	H	H	+ 0.0	15.3*

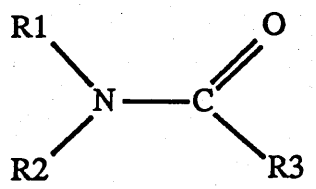
+ The experimental delta E and barrier to rotation are 1.4 kcal mol^{-1} and 15.8/14.4 kcal mol^{-1} respectively [14].

Experimental value for the rotational barrier in dimethylacetamide was found to be 18.1 kcal mol^{-1} [7,8,10].

* Dependent on basis set. Value from [12]. Experimental value for formamide's rotational barrier is 18-19 kcal mol^{-1} [16-18].

Table 4.21:

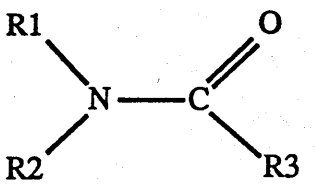
Ab initio Charges for Silylamides



R1	R2	R3	Atom	Amide
SiH3	H	H	Si	+0.5418
			N	-0.9002
			O	-0.6538
			C(O)	+0.6225
SiH3	H	F	Si	+0.5551
			N	-0.9506
			O	-0.6803
			C(O)	+1.2119
SiH3	H	CH3	Si	+0.5408
			O	-0.7063
			N	-0.9349
			C(O)	+0.9602
SiH3	H	CF3	Si	+0.5454
			N	-0.9483
			O	-0.6811
			C(O)	+0.8255

Table 4.21 (continued):

Ab initio Charges for Silylamides



R1	R2	R3	Atom	Amide
SiH3	CH3	CH3	Si	+0.5259
			N	-0.8192
			O	-0.7101
			C(O)	+0.9809
SiH3	CH3	CF3	Si	+0.5289
			N	-0.8356
			O	-0.6848
			C(O)	+0.8557
Me3Si	CH3	CH3	Si	+1.4121
			N	-0.8043
			O	-0.7239
			C(O)	+0.9649
Me3Si	CH3	CF3	Si	+1.4166
			N	-0.8144
			O	-0.6981
			C(O)	+0.8245

4.15 Summary

The conformational behaviour of amides is particularly important in the understanding of the chemistry of peptides, proteins, and other substances of life. The coplanarity of the skeletal structure for this class of material is important and has a significant effect on the physical and chemical properties of amides. The effect is readily explained on the basis of their electronic or resonance structure and serves as a basis for this work.

The restricted rotation barriers in silylated amides and formamide have been calculated to be on the order of 15-20 kcal mol^{-1} and therefore are in good agreement with what is known experimentally. The high barrier to rotation in these molecules is due to their electronic structure and is characterised by a resonance interaction between the carbonyl 2p-pi electrons and the nitrogen's lone pair of electrons. This resonance interaction also accounts for the C-N bond in amides to be shorter and of a higher bond order than C-N bonds normally found in amines.

Silylformamides have a higher rotational barrier than the corresponding silylamides or silylacetamides. The calculated barrier for rotation about the amide bond in N-methyl-N-trimethylsilylacetamide as well as the preferred rotameric form are both in agreement with NMR studies carried out by Yoder. The *cis* isomer, silicon *cis* to the carbonyl oxygen, is preferred to the *trans* rotamer by

approximately 5 kcal mol^{-1} with a calculated rotational barrier of 19 kcal mol^{-1}. Rotation about the C-N bond is influenced by the size and electronic effects of the nitrogen substituent. The barriers of rotation about the C-N bond for simple amides decrease as the size of the group at nitrogen increases. However, the size of the group at nitrogen has little effect on the barrier to rotation for formamides.

From these studies we have found that the silyl group, H3Si-, is not a reasonable substitute for the trimethylsilyl substitutent (TMS) in many calculational studies. The electronic behaviour of the silyl group is very much different from that of the larger and more electron donating TMS group. When N-methyl-N-silylacetamide was used to mimic N-methyl-N-trimethylsilylacetamide, we found that calculated barriers to rotation about the amide bond were lower than anticipated and that the preferred rotameric structure was in error.

The preferred calculational scheme for studying the rotational behaviour of silylamides is one in which complete structural relaxation is allowed. The rigid rotor approximations are not valid for the amides studied. This is due to the delocalisation and interaction of the lone pair of electrons on nitrogen with the pi system of the carbonyl. As the N-C(O) bond was scanned, the lone pair-pi interaction was disrupted allowing for the relaxation of

the N-C(O) bond to one with more single bond character. In a related fashion, the C-O bond order increases causing the C-O bond to shorten. This variance in bond order and structural geometry makes full structural relaxation mandatory for studying these molecules.

Among the semi-empirical methods studied, AM1 provided the best description of torsional behaviour in silylamides. However, the rotational barriers were underestimated. We found that the values for the rotational barriers could be scaled, by a factor of 1.7, to yield information which was in excellent agreement with *ab initio* results. This scaling factor is valid only for compounds containing Si-N bonds. For those structures with Si-O bonds, like those silyl-imidates studied in this work, we found that AM1 calculations overestimated the energies of these structures. AM1 calculations for N-methyl-N-silylacetamide suggested that the O-silyl form was preferred by over 20 kcal mol^{-1} (the difference in energy between the two tautomeric states by *ab initio* calculations was only 2.57 kcal mol^{-1}). The tendency of AM1 to underestimate the relative energies of Si-N compounds while overestimating the energies of Si-O materials complicates the calculations of the preferred tautomeric state. The latest release of AM1 (version 4.1) corrects for some of this, but still should not be trusted for the comparison of relative stabilities of Si-N versus Si-O materials.

4.16 References

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Chapter Five

1,3-Migration of Silicon Across an Allylic Framework

5.0 1,3-Migration of Silicon Across an Allylic Framework

5.1 Introduction

Although much has been published about the tautomerisation of silylamides, little has been done to study these complex molecular structures from a theoretical perspective. In fact, the only relevant information available to date is the work of Sygula [1] who studied the amide-iminol tautomerisation energies for formamide, 2-pyridone, and 4-pyridone via AM1 techniques, and Cieplak, et.al. [2] who studied both the gas phase and aqueous tautomeric behaviour of simple amides at the *ab initio* level. Although interesting, these papers provide only limited insight into the tautomerisation of silyl substituted amides, which are the focus of this study. Therefore, the experimental information and understanding of these materials must serve as our starting point. The first suggestion that silicon could readily migrate between nitrogen and oxygen was made in 1963, with particular reference to BSA (N,O-bis(trimethylsilyl)acetamide) [3]. In subsequent experiments by Pump and Rochow [4] using other bis(silyl)amides, they provided additional evidence that these materials were in rapid equilibrium between their N, N- and N,O-tautomeric states. They suggest that the process was not only rapid, but intramolecular in nature. Itoh, Katsuda, and Ishii extended this work by studying the bis(silyl)benzamides [5]. In this study they found that the rate of migration increased with increasing electron

release at the carbonyl carbon. The only known exception to the fact that bis(silyl)amides exist in the N, O-tautomeric form is bis(trimethylsilyl)formamide. This molecule appears to exist only in the N,N-tautomeric form [6].

Mono(silyl)amides, like trimethylsilylacetanilides, [7-9] are believed to consist of a dynamic mixture of rotameric and N,O-tautomeric structures. The distribution of tautomeric and rotameric forms appears to be strongly dependent on the nature of the substituents at the carbonyl carbon and at the nitrogen. For simple monosilylamides, the amount of the O-silyl imidate form increases as the substituent at nitrogen becomes more electron withdrawing [10]. This effect has been rationalised by comparing the relative stabilities of the tautomers as a function of electron density at nitrogen. As electron density at nitrogen is increased, the pi-character of the C-N bond increases, favouring the N-tautomer. Reducing electron density at nitrogen, therefore, facilitates the formation of the strong Si-O bond in the O-tautomer. The dependence of tautomeric distribution on substitution at the carbonyl carbon is not trivial. For bissilyamides, the imidate structures are preferred for all but the formamides. The N-alkyltrimethylsilylamides have been thought to be totally in the N-silylated form [11] and rotation about the C-N bond influenced by the size and electronic effects of the substituents at nitrogen. The barriers of rotation about the C-N bond for simple amides decrease as the size of the

group at nitrogen increases [12]. However, the size of the group at nitrogen has little effect on the barrier to rotation for formamides. N-Alkylsilylamides had generally been considered to exist only in the N-tautomeric form, however, it has since been demonstrated that some N-alkylsilylamides are in fact a mixture of rotameric and tautomeric isomers [10,13-14]. Bassindale corrected the structure of N-methyl(trimethylsilyl)trifluoroacetamide by showing that a highly electron withdrawing group, like trifluoromethyl, at the carbonyl carbon decreased the C-N pi-electron density and therefore favours the imidate form [10].

The stereochemistry at silicon for this 1,3-migration between nitrogen and oxygen is unknown. However, the process can be thought of as an internal nucleophilic displacement reaction and retention of configuration is to be expected. More regarding this process will be discussed in the next chapter.

5.2 Comparison of Computational Methods

Our initial calculations involved the comparison of MO results at the *ab initio* level against two semiempirical methods, namely AM1 and MNDO. Using N-methyl-N-silylacetamide as a model, we studied the relative stabilities of the N- and O-silyl tautomer by the three methods mentioned above. Equation 1.3 outlines the process being examined. *Ab initio* calculations provided us with

information to suggest that the O-silyl structure was preferred over the N-silyl form by 2.6 kcal mol^{-1}. This is consistent with what is known experimentally for N-substituted-trimethylsilylacetamides where electron withdrawing groups at the nitrogen show a preference for the O-silyl form. The difference between the two major rotameric states of the O-tautomer was calculated to be 6.7 kcal mol^{-1} in favour of the syn isomer. AM1 and MNDO both overestimated this value. AM1 overestimated the difference in the heat of formation by about 30%, giving a value of 8.6 kcal mol^{-1} for this difference between the two rotameric states of the O-silyl tautomer. MNDO calculations gave a value of 9.8 kcal mol^{-1}, an even higher over estimation of this energy difference. The fact that both AM1 and MNDO tend to overestimate the relative stabilities of Si-O compounds and grossly underestimate the relative energies of Si-N compounds makes these semiempirical methods of limited use in terms of studying the migration of silicon from nitrogen to oxygen.

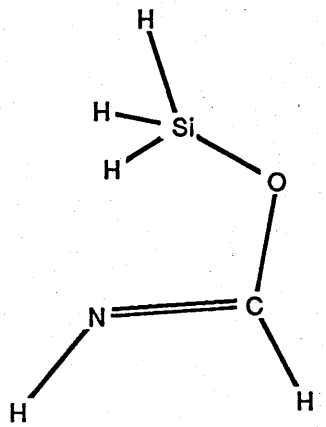
5.3 *Ab initio* Calculations

The family of structures studied in Chapter 4 were also evaluated here, in terms of tautomerisation. Table 5.9 summarises our findings. All the calculations reported in this table are *ab initio* at the 3-21 G *#(modified) level and the important structural features are summarised in Tables 5.1 through 5.8. Energy differences are reported as a function of structure and were calculated as the

difference in energy between the O-silyl form and the N-silyl form, or product minus reactant as illustrated in Table 5.9. Therefore, negative values suggest that the reaction will proceed as shown in Table 5.9. Positive values for delta energy indicated that the preferred structure is the N-silyl form.

Table 5.1:

O-silylformamide
Optimised Structural and Charge Data
From *Ab Initio* Calculation



Bond Length (Å)		Bond Angle (degrees)	
Si-H	1.4790	O-Si-H	104.288
O-Si	1.6891	C-O-Si	119.826
C-O	1.3356	N-C-O	122.079
N-C	1.2405	H-N-C	111.599
H-N	1.0104	H-C-O	111.284
H-C	1.0864	H-Si-O	111.222
H-Si	1.4787		
H-Si	1.4787		

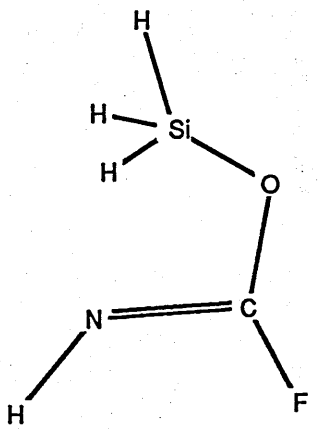
Charge

ATM	CHR
SiH	-0.0675
Si	+0.6441
O	-0.8209
C	+0.4760
N	-0.6630
H	+0.3172
H	+0.2385
SiH	-0.0622
SiH	-0.0622

HF = -456.6839457

Table 5.2:

O-silylfluoroformamide
Optimised Structural and Charge Data
From *Ab initio* Calculations



Bond Length (Å)		Bond Angle (degrees)	
Si-H	1.4767	O-Si-H	103.954
O-Si	1.6947	C-O-Si	119.674
C-O	1.311	N-C-O	124.689
N-C	1.2331	H-N-C	111.934
H-N	1.0094	F-C-O	110.295
F-C	1.3031	H-Si-O	110.341
H-Si	1.4762		

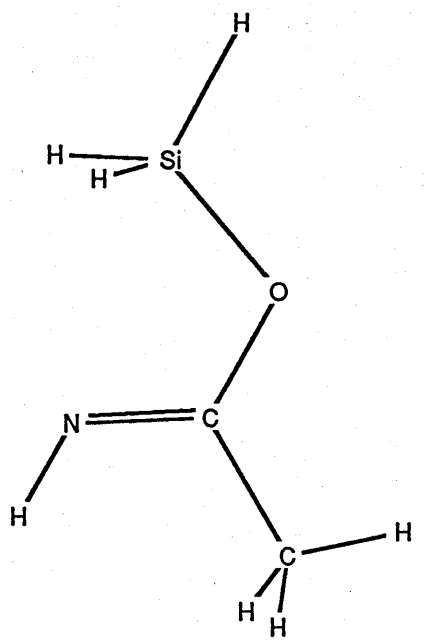
Charge

ATM	CHR
SiH	-0.0580
Si	+0.6518
O	-0.8424
C	+1.1067
N	-0.7403
H	+0.3254
F	-0.3409
SiH	-0.0512
SiH	-0.0512

HF = -555.0521249

Table 5.3:

O-silylacetamide
Optimised Structural Data and Charges
From *Ab initio* Calculations



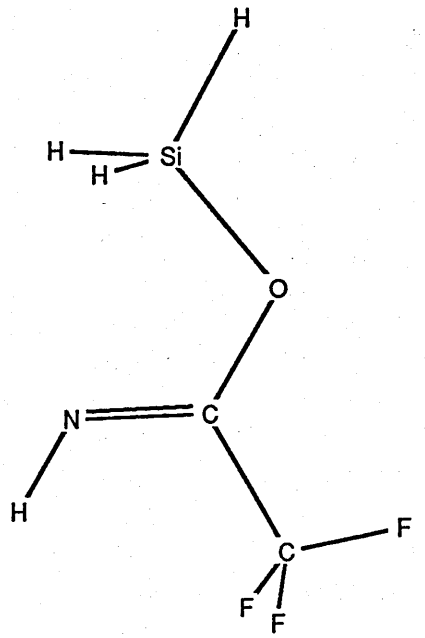
Bond Length (Å)		Bond Angle (degrees)	
Si-H	1.4801	O-Si-H	104.109
O-Si	1.6864	C-O-Si	119.343
C-O	1.3407	N-C-O	119.654
N-C	1.2445	H-N-C	112.000
H-N	1.0111	C-C-O	112.966
C-C	1.5104	H-Si-O	111.540
H-Si	1.4786	H-Si-O	111.540
H-Si	1.4786	H-C-C	110.032
H-C	1.0884		

Charge	
ATM	CHR
SiH	-0.0714
Si	+0.6400
O	-0.8584
C	+0.8406
N	-0.7202
H	+0.3075
C	-0.7929
SiH	-0.0640
SiH	-0.0640
H	+0.2701
H	+0.2563
H	+0.2563

HF = -495.5300676

Table 5.4:

O-silylfluoroacetamide
Optimised Structural Data and Charges
From *Ab initio* Calculations



Bond Length (Å)		Bond Angle (degrees)	
Si-H	1.4768	O-Si-H	104.061
O-Si	1.6931	C-O-Si	120.330
C-O	1.3249	N-C-O	123.381
N-C	1.2373	H-N-C	112.295
H-N	1.0114	C-C-O	112.828
C-C	1.5206	H-Si-O	110.495
H-Si	1.4772	F-C-C	110.736
F-C	1.3114		

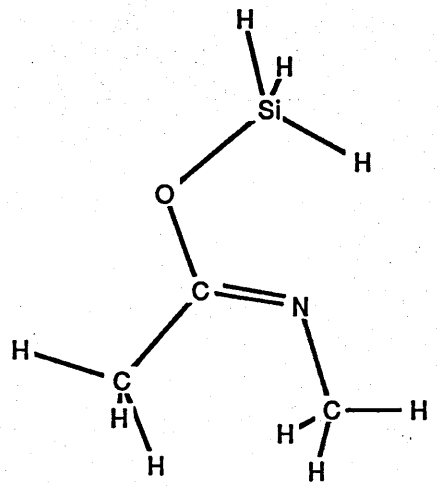
Charge

ATM	CHR
SiH	-0.0564
Si	+0.6404
O	-0.8566
C	+0.7008
N	-0.7034
H	+0.3300
C	+1.1218
SiH	-0.0538
SiH	-0.0538
F	-0.3548
F	-0.3570
F	-0.3570

HF = -790.5871178

Table 5.5:

N-methyl-O-silylacetamide
Optimised Structural Data and Charges
From *Ab initio* Calculations



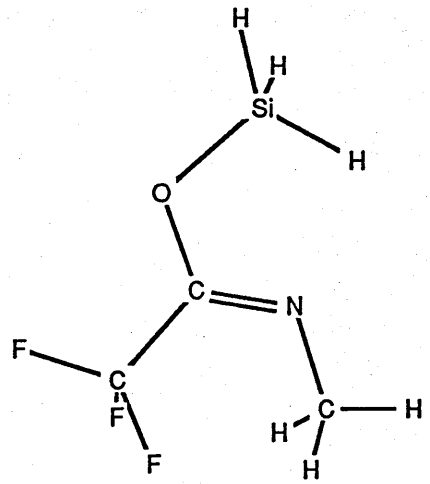
Bond Length (Å)		Bond Angle (degrees)	
N-C	1.4506	C-N-C	119.051
C-N	1.2416	O-C-N	119.516
O-C	1.3439	Si-O-C	119.326
Si-O	1.6836	C-C-N	127.822
C-C	1.5072	H-Si-O	109.236
H-Si	1.4802	H-Si-O	109.236
H-Si	1.4793	H-C-C	110.117
H-Si	1.4793	H-C-N	111.079
H-C	1.0885		
H-C	1.0910		

Charge	
ATM	CHR
C	-0.5227
N	-0.5880
C	+0.8875
O	-0.8728
Si	+0.6308
C	-0.7936
SiH	-0.0702
SiH	-0.0666
SiH	-0.0666
H	+0.2690
H	+0.2558
H	+0.2558
H	+0.2441
H	+0.2188
H	+0.2188

HF = -534.3602782

Table 5.6:

N-methyl-O-silylfluoroacetamide
Optimised Structural Data and Charges
From *Ab initio* Calculations



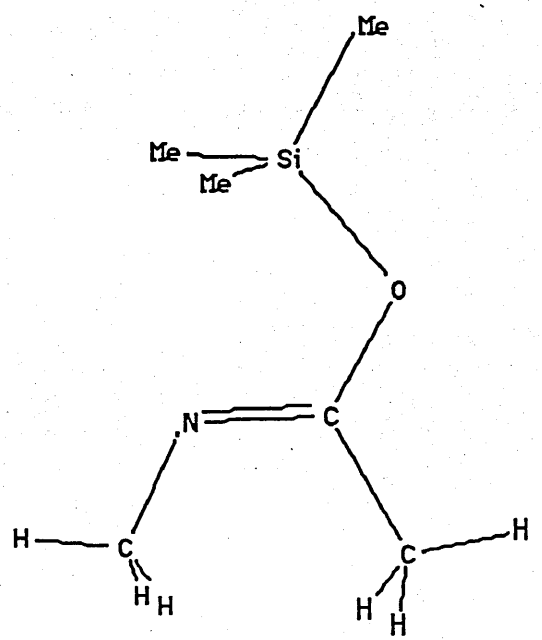
Bond Length (Å)		Bond Angle (degrees)	
N-C	1.4585	C-N-C	120.687
C-N	1.2332	O-C-N	122.797
O-C	1.3309	Si-O-C	120.032
Si-O	1.6895	C-C-N	125.648
C-C	1.5220	H-Si-O	108.613
H-Si	1.4772	F-C-C	110.970
H-Si	1.4780	H-C-N	110.371
F-C	1.3125		
H-C	1.0872		

	Charge
ATM	CHR
C	-0.5701
N	-0.5751
C	+0.7439
O	-0.8692
Si	+0.6328
C	+1.1302
SiH	-0.0574
SiH	-0.0582
SiH	-0.0582
F	-0.3561
F	-0.3564
F	-0.3564
H	+0.2534
H	+0.2485
H	+0.2485

HF = -829.4130089

Table 5.7:

N-methyl-O-trimethylsilylacetamide
Optimised Structural Data and Charges
From *Ab initio* Calculations



Bond Length (Å)		Bond Angle (degrees)	
O-C	1.3414	N-C-O	121.942
N-C	1.2401	C-N-C	118.326
C-N	1.4509	C-C-N	126.811
C-C	1.5118	H-C-C	110.236
H-C	1.0886	Si-O-C	135.548
Si-O	1.6835	C-Si-O	109.471
C-Si	1.9100	H-C-N	111.253
H-C	1.0916	H-C-Si	109.471
H-C	1.0901		

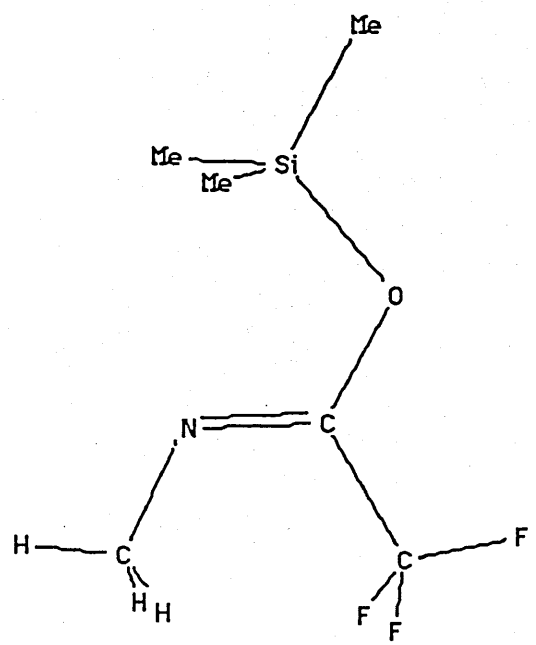
Table 5.7 (continued):

	Charge
ATM	CHR
C	+0.8733
O	-0.8728
N	-0.5772
C	-0.5223
C	-0.7959
H	+0.2631
H	+0.2510
H	+0.2509
Si	+1.4246
C	-0.9905
C	-1.0084
C	-1.0086
H	+0.2385
H	+0.2150
H	+0.2025
H	+0.2363
H	+0.2369
H	+0.2268
H	+0.2274
H	+0.2307
H	+0.2267
H	+0.2307
H	+0.2276

HF = -650.9070932

Table 5.8:

N-methyl-O-trimethylsilylfluoroacetamide
Optimised Structural Data and Charges
From *Ab initio* Calculations



Bond Length (Å)		Bond Angle (degrees)	
C-O	1.3414	N-C-O	121.942
C-N	1.2401	C-N-C	118.326
C-N	1.4509	C-C-N	126.846
C-C	1.5211	F-C-C	111.037
F-C	1.3127	Si-O-C	135.548
F-C	1.3127	C-Si-O	109.471
F-C	1.3127	H-C-N	111.253
Si-O	1.6835	H-C-Si	109.471
C-Si	1.9100	H-C-Si	109.471
C-Si	1.9100	H-C-Si	109.471
C-Si	1.9100		
H-C	1.0916		
H-C	1.0916		
H-C	1.0916		
H-C	1.0901		
H-C	1.0901		
H-C	1.0901		
H-C	1.0901		
H-C	1.0901		
H-C	1.0901		
H-C	1.0901		
H-C	1.0901		
H-C	1.0901		

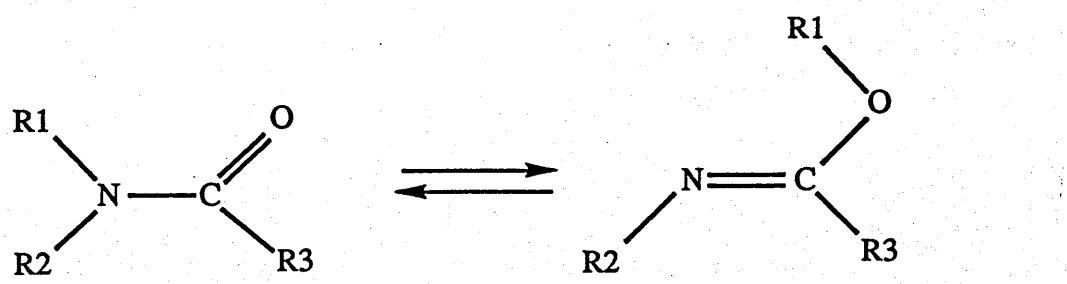
Table 5.8 (continued):

	Charge
ATM	CHR
C	+0.7215
O	-0.8723
N	-0.5531
C	-0.5708
C	+1.1246
F	-0.3563
F	-0.3563
F	-0.3569
Si	+1.4284
C	-0.9932
C	-1.0097
C	-1.0099
H	+0.2459
H	+0.2427
H	+0.2421
H	+0.2096
H	+0.2363
H	+0.2368
H	+0.2299
H	+0.2330
H	+0.2324
H	+0.2299
H	+0.2324
H	+0.2332

HF = -945.96728

Table 5.9:

1,3-Migration of Silicon Across an Allylic Frame Work
Ab initio Calculations



R1	R2	R3	Delta E (kcal mol^{-1})
H3Si	H	H	+ 2.40
H3Si	H	F	+ 8.70
H3Si	H	CH3	+ 4.35
H3Si	H	CF3	+ 3.87
H3Si	CH3	CH3	- 2.57
H3Si	CH3	CF3	- 2.11
Me3Si	CH3	CH3	+ 4.92
Me3Si	CH3	CF3	+ 4.06

Of the structures studied, only the N-methyl-N-silylacetamide and its fluoroacetamide counterpart had a negative delta energy between the two tautomeric states. That is to say, these two materials preferred to be in the O-silyl imidate form as opposed to the N-silyl amide structure.

5.4 Estimation of Gas Phase Equilibrium Constants for the 1,3-Migration of Silicon

From these gas phase calculations we can estimate the relative equilibrium constant for the process of the N-silyl tautomer being converted into the O-silyl species, see Equation 5.1.

Equation 5.1:

$$\Delta G = \Delta G^\circ + RT \ln K_{eq}$$

Where:

K_{eq} = [O-silyl]/[N-silyl] and

at Equilibrium $\Delta G = 0$

$$0 = \Delta G^\circ + RT \ln K_{eq}$$

$$\Delta G^\circ = -RT \ln K_{eq}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$\Delta G^\circ = \Delta H^\circ$$

For this approximation, we have made several simplifying assumptions. The first is that the Hartree-Fock energy which is derived from our *ab initio* calculations is directly related to the enthalpy, ΔH°, of the molecule, ignoring $P\Delta V$ contributions. The second is that the entropy

of the two tautomeric forms is not significantly different. The third assumption allows us to neglect the various conformational states given by the Boltzman approach. The final assumption is that there are no intermolecular interactions. The first assumption is reasonable given that the Hartee-Fock energy is based on a three component atomic Hamiltonian. This Hamiltonian is made up of a kinetic energy operator, the potential energy for the attraction between electrons and the nucleus, and the potential energy of the interelectronic repulsions which avoids counting the same interelectronic repulsion twice. When the Hartree-Fock equation is solved for a linear combination of atomic orbitals, an energy which describes the electronic cohesiveness of the molecule is generated in units of Hartrees or Atomic units. Atomic units are readily converted into the more recognised units of energy, kcal mol^{-1}, by multiplying Atomic units by a factor of 627.54. Converting kcals to kJ is achieved by multiplying the value in kcal by 4.184. Since we are interested in only the relative equilibrium constants for the materials in question, we did not strive to establish the direct relationship between Hartree-Fock energy and enthalpy. In fact, we are more interested in the differences between equilibrium constants which results in the cancellation of some errors.

The second assumption is based on the fact that the N- and O- isomeric forms of the silylamides being studied are tautomeric in nature and, therefore, the difference in

entropy between the two forms is zero or nearly so. This approximation is based on the fact that the entropy of a substance is related to its thermal energy and to its partition functions or, in other words, the sum of all rotational, vibrational, and translational energies in the molecule. Since these tautomeric structures have similar thermal energies and nearly identical partition functions, this assumption is reasonable.

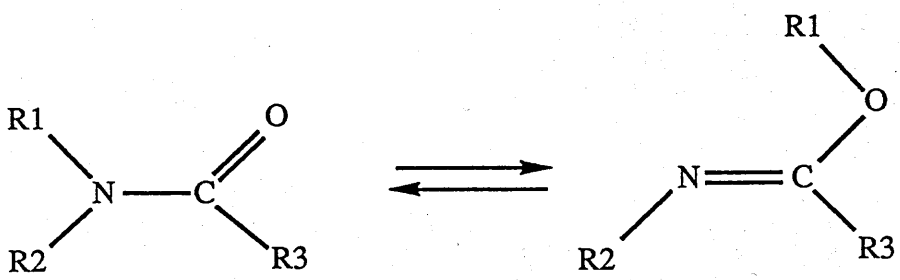
The last two assumptions are also reasonable given the nature of the these gas phase calculations. Intermolecular interactions are often ignored for unimolecular reactions and conformational variations need not be considered, given the high barrier to internal rotation about the amide bond, which was established in Chapter 4.

For the N-methyl-silylacetamide example, the estimated equilibrium constant is 74.5, indicating its strong preference for the O-silyl tautomer. In the N-silylacetamide case, the calculated equilibrium constant was 6.77×10^{-4} . The addition of a perfluoromethyl group in place to the methyl group at the carbonyl carbon increases the equilibrium constant by approximately a factor of eight, to 1.51×10^{-3} . The same shift in equilibrium constant was noted in the N-methyl-N-trimethylsilylacetamide versus N-methyl-N-trimethylsilylfluoroacetamide examples. When the methyl group at the carbonyl carbon was replaced with a perfluoromethyl group, the relative equilibrium position

shifted by about a factor of eight, in favour of the O-silyl tautomer. The estimated equilibrium constants for this case were 2.60×10^{-4} and 1.10×10^{-3}, respectively. Only the N-silylformamide and N-silylfluoroformamide yielded data which should be considered an exception to what has been observed in the acetamide examples. When an electron withdrawing group, fluoro, was substituted for the hydrogen at the carbonyl carbon, the equilibrium position shifted in favour of the N-silyl tautomer. The equilibrium constants were 1.78×10^{-2} for the N-silylformamide and 4.58×10^{-7} for the N-silylfluoroformamide example. These data are summarised in Table 5.10.

Table 5.10:

1,3-Migration of Silicon Across an Allylic Framework
Estimated Gas Phase Equilibrium Constants



R1	R2	R3	Estimated * Equilibrium Const
H3Si	H	H	1.78×10^{-2}
H3Si	H	F	4.58×10^{-7}
H3Si	H	CH3	6.77×10^{-4}
H3Si	H	CF3	1.51×10^{-3}
H3Si	CH3	CH3	74.5
H3Si	CH3	CF3	34.5
Me3Si	CH3	CH3	2.60×10^{-4}
Me3Si	CH3	CF3	1.10×10^{-3}

* calculated at 300° K

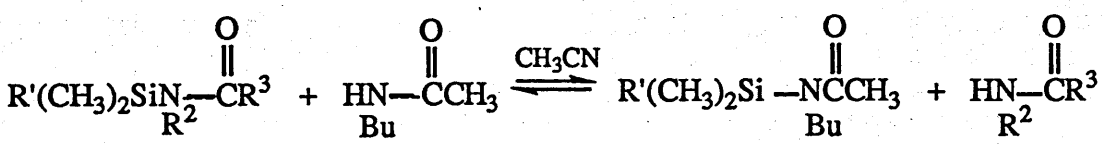
Although, these values are only estimates of what the equilibrium position might be in the liquid state, they are consistent with the suggestion that silylating power might be related to the relative proportion of O-silyl and N-silyl tautomer for a given trimethylsilylamide. For example, it is well known that N,O-bis-trimethylsilylacetamide is a powerful trimethylsilylating agent while bis-trimethylsilylformamide, which is entirely in the N,N-form, is a poor trimethylsilylating agent, as is the N-trimethylsilylacetamide.

Trimethylsilylfluoroacetamide is also known to be a much better silylating agent than trimethylsilylacetamide. Our calculations would suggest that trimethylsilylfluoroacetamide has a higher proportion of the O-tautomer than does the trimethylsilylacetamide silylating agent. Lane and Frye suggested that the relative thermodynamic trimethylsilylating ability of a silylacetamide or silylformamide increased as the bulk of the substituent on nitrogen increased. They also suggested that the relative proportion of the O-tautomer increased under these same conditions. In their work, they recorded the infrared spectrum for a series of trimethylsilyl-amides and formamides. Based on what was known about silylimidates and silylamides, structural assignments were made for the N=C imidate and the C=O amide stretches. They then attempted to estimate the relative proportion of each of the two tautomeric states by determining the ratio of the imidate and amide frequencies. This ratio of

tautomeric species or an estimate of O-silyl tautomer could then be compared to the relative thermodynamic silylating ability of these materials. The relative thermodynamic silylating abilities of these materials were determined through the competitive trimethylsilylation of N-butylacetamide in acetonitrile. From this series of experiments, estimates of the effects of structure on silylating ability could be made and compared to the spectrophotometric data. Some of those data are given in Tables 5.11 and 5.12. Note that as the steric bulk increased at either the amide nitrogen or the carbonyl carbon, the relative thermodynamic silylating ability increased. The relative percent of O-silyl tautomer also increased under these conditions. Figure 5.1 shows the relationship between percent O-silyl imidate and the relative silylating ability for the series of silylating agents given in Table 5.11. The relationship between the thermodynamic silylating ability and the relative O-silyl imidate content in these materials is obvious. The comparison between the observed tautomeric distribution, as determined by infrared spectroscopy, and the relative equilibrium was never reported, because of their inability to corroborate the frequency assignments. However, as part of this study we were able to calculate the infrared spectra for several O- and N-silyl amides and imidates. These calculations were carried out at the *ab initio*, 3-21 G*(modified) level and the results are given in Table 5.13.

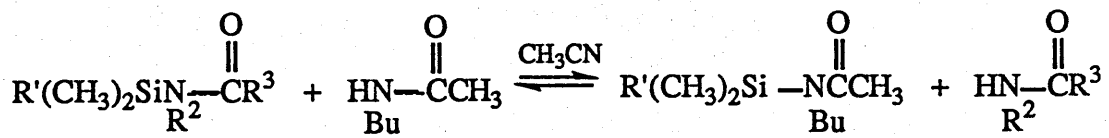
Table 5.11:

Experimental Equilibrium Constants and Approximate Percentage O-silyl Tautomer for Various Silylamides



Structure	K (equilibrium) Relative	apprx. % O-silyl
Me3SiN(t-butyl)C(O)Me	1.1 x10^{2}	95
N,O-bis (Me3Si)-NC(O)Me	2.2 x10^{1}	80
Me3SiN(n-butyl)C(O)Me	1.0	43
Me3SiN(Me)C(O)Me	3.0 x10^{-1}	15
Me3SiN(t-butyl)C(O)H	1.0 x10^{-1}	10
Me3SiN(Me)C(O)H	<4.2 x10^{-3}	0
Me3SiN(Me)C(O)t-butyl	5.0 x10^{-1}	30
Me3SiN(Me)C(O)Et	3.3 x10^{-1}	15
Me3SiN(Me)C(O)Me	3.0 x10^{-1}	15
Me3SiN(Me)C(O)H	<4.2 x10^{-3}	0
Me3SiN(t-butyl)C(O)Me	1.1 x10^{2}	95
Me3SiN(t-butyl)C(O)H	1.0 x10^{-1}	10

Figure 5.1:



Ln (Experimental Equilibrium Constants) vs Percent O-silyl Tautomer

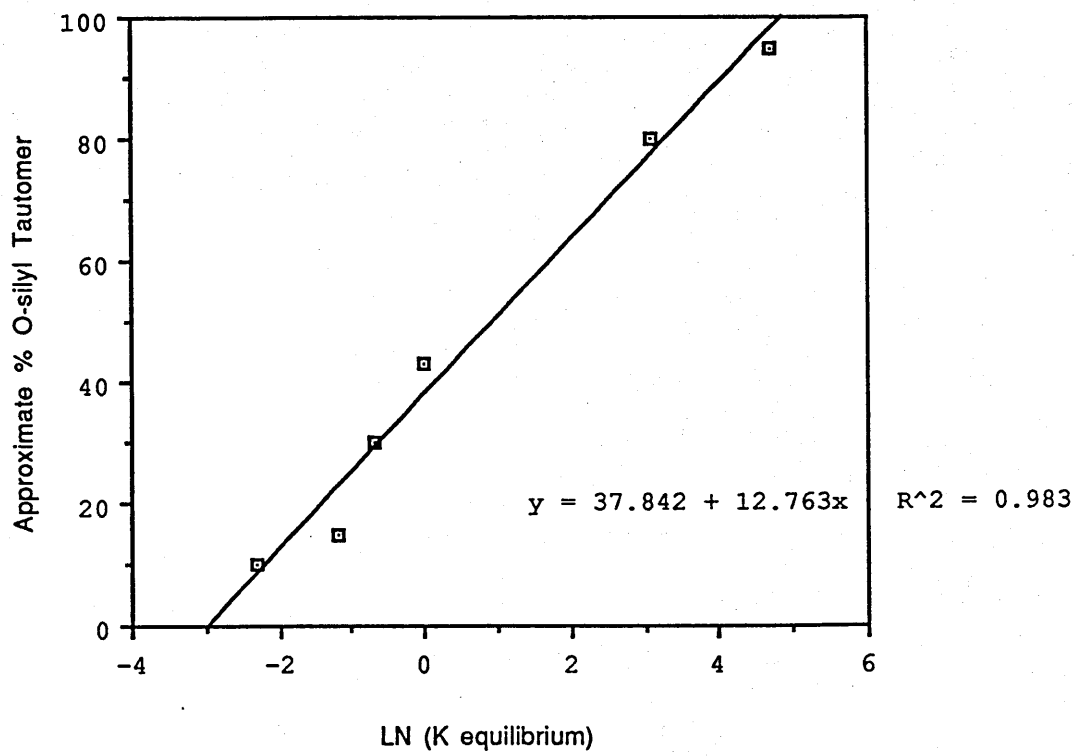


Table 5.12:

Experimentally Determined Frequencies for Various Silylamides

Structure	Frequency Measured	
	v C=N	v C=O
Me3SiN(t-butyl)C(O)Me	1685 cm^{-1}	-
N,O-bis (Me3Si)-NC(O)Me	1700	-
Me3SiN(n-butyl)C(O)Me	1680	1640
Me3SiN(Me)C(O)Me	1680	1650
Me3SiN(t-butyl)C(O)H	1660	1655
Me3SiN(Me)C(O)H		
Me3SiN(Me)C(O)t-butyl		
Me3SiN(Me)C(O)Et	1680	1650
Me3SiN(Me)C(O)Me	1680	1650
Me3SiN(Me)C(O)H		
Me3SiN(t-butyl)C(O)Me	1685	-
Me3SiN(t-butyl)C(O)H	1660	1655

Before looking at the *ab initio* frequency data obtained for our series of test molecules, it is important to consider some of the potential sources of error when comparing theoretical and experimental vibrational frequencies. In the laboratory and under the best of conditions, vibrational frequencies can be measured to within one wavenumber or less. However, the assignment of that frequency to a particular vibrational motion is more tenuous and errors are commonplace. Many assignments are made based on history or experience. Small molecules, with fewer than six atoms, pose a particular problem to the spectroscopist in that several of the rotational levels, other than the lowest, are significantly populated. This causes bands to broaden and resolution to be lost. Gross errors are possible in crowded regions of the spectrum corresponding to vibrational overlap. These errors can amount to 30-50 wavenumbers or more.

During the calculation of a vibrational spectrum, errors may arise from both uncertainties in the selected equilibrium geometry for the molecule in question, and from the inherent inaccuracies of the differentiation techniques required in the evaluation of the matrix of force constants. The evaluation of the force constant matrix can be achieved through the use of several differentiation techniques. However, the deviations for a given frequency are generally small as one moves from a strictly numerically derived force field to a hybrid numerical-analytical, to eventually a straight analytical approach.

The observed deviation from a numerically based approach to an analytical approach is on the order of 20 wavenumbers. Larger deviations are known, but are relatively infrequent and limited to large polyatomic systems. The selection of the proper equilibrium geometry is of greater concern when calculating vibrational spectra. It is essential that the structure in question be minimised using the same molecular orbital method that will be used to calculate the vibrational spectrum for the molecule. Frequency changes of over 60 cm^{-1} have been observed for variations in bond length of 0.005 Å. Similar effects have been noted for variation in bond angle of as small as 0.5 degrees.

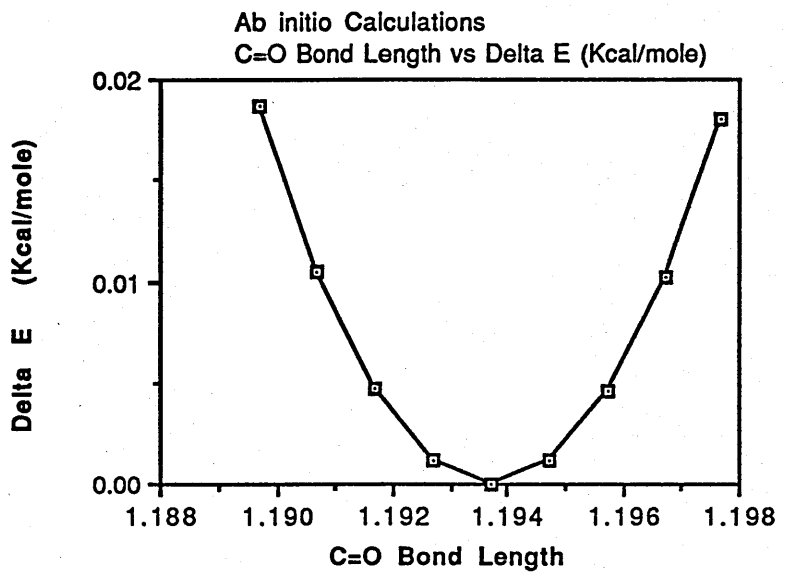
In order to illustrate the changes in vibrational frequencies that might be anticipated due to small errors in the exact choice of equilibrium geometry, we studied N-silylformamide at both the *ab initio* and AM1 levels. Figure 5.2 clearly shows how the carbonyl frequency shifts with small changes in the C-O bond length at the *ab initio* level. Note that in the accompanying graph, that the HF energy is near the minimum value through the bond length scan. As the C=O bond length was varied from 1.1897 to 1.1967 Å the HF energy varied by less than 0.02 kcal mol^{-1} from its minimum energy. However, as the C=O bond was scanned over the same range the position for the C=O stretching frequency varied by greater than 46 wavenumbers. Similar frequency shifts were noted when AM1 molecular orbital methods were employed. Figures 5.3 and 5.4 show the effects of small variations in the equilibrium

structure for N-silylformamide as determined by AM1. The first figure clearly illustrates the unpredictable shift in the carbonyl frequency as the C-O bond length was varied; the second figure shows the effect of Si-N bond length on the stretching frequency for the bond. Again, the minor variations in equilibrium geometry cause substantial and unpredictable shifts in frequency. It is important to note that the frequency shifts illustrated in the Figures 5.2, 5.3, and 5.4 are due to the anharmonicity of the potential function in the vicinity of the minimum. They occur irrespectively of the choice of differentiation technique employed. Care must be taken to ensure that only minimised structures are used. Even experimental geometries are not suitable replacements for theoretical structures. The uncertainties in measured equilibrium parameters are often on the order of 0.01 Å and one degree for bond lengths and angles, respectively.

When vibrational spectra for polyatomic molecules are calculated at the HF level, they are consistently larger than experimentally determined values, by 10-15%. This is due, in part, to the fact that HF is a closed shell molecular orbital method. That is to say, as bonds are stretched the electrons remained paired, with one atom causing the frequencies to be overestimated or shifted to higher frequencies. The calculated atomic charge is also a function of atomic position in space and, therefore, a contributor to the higher frequency shifts observed. The uncorrected frequencies given in the following tables must

be corrected by subtracting 13-15% of the given value to adjust the calculated value to better fit the experimentally measured frequency.

Figure 5.2:


Ab initio Calculations
C=O Bond Length vs Delta E (Kcal/mole)
0.02
0.01
0.00
Delta E (Kcal/mole)
1.188
1.190
1.192
1.194
1.196
1.198
C=O Bond Length

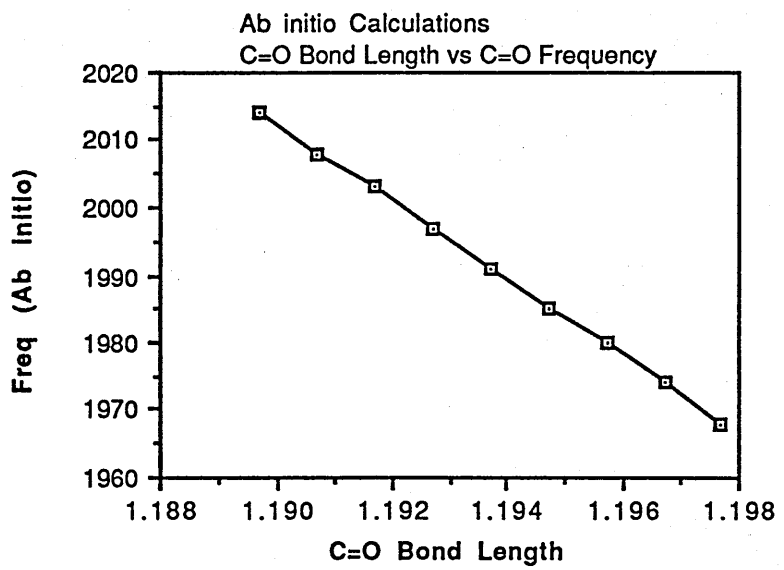

Ab initio Calculations
C=O Bond Length vs C=O Frequency
2020
2010
2000
1990
1980
1970
1960
Freq (Ab Initio)
1.188
1.190
1.192
1.194
1.196
1.198
C=O Bond Length

Figure 5.3:

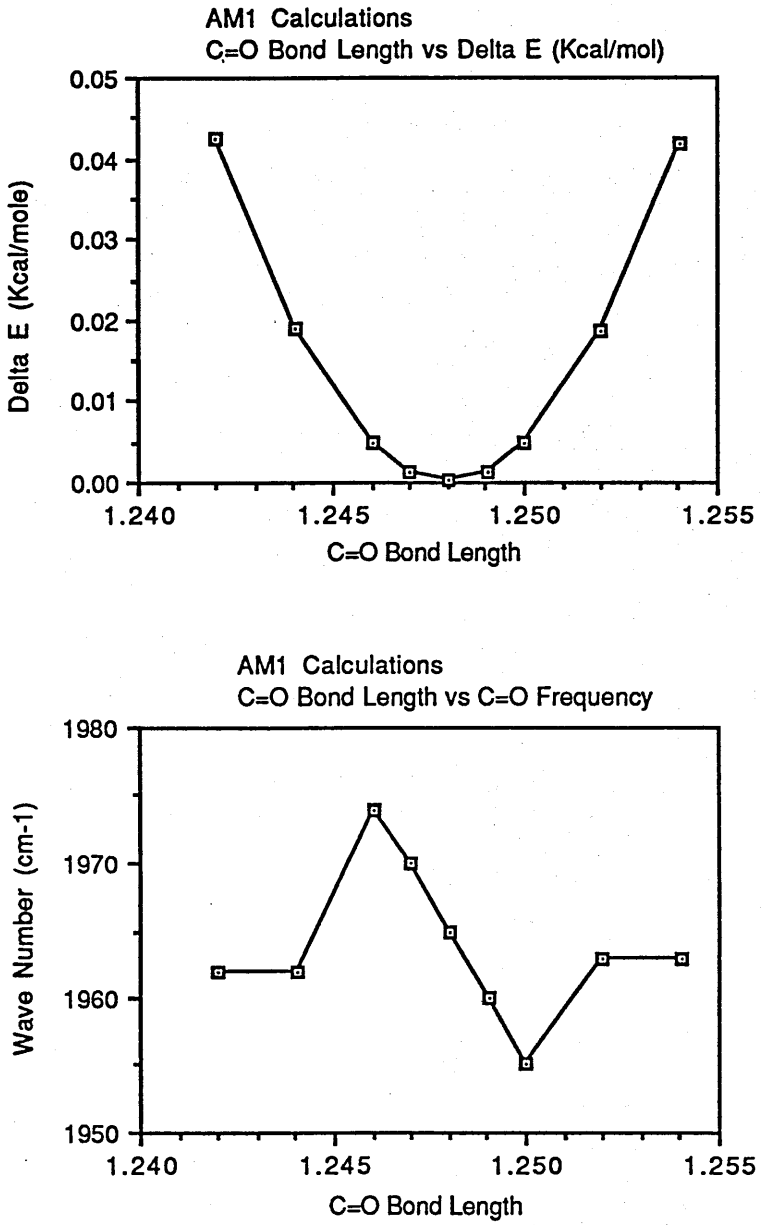
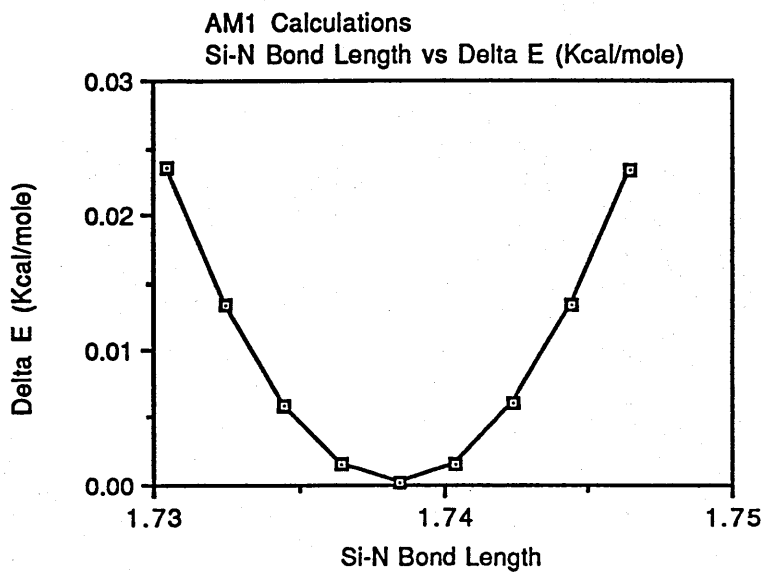

AM1 Calculations
C=O Bond Length vs Delta E (Kcal/mol)
Delta E (Kcal/mole)
0.05
0.04
0.03
0.02
0.01
0.00
1.240
1.245
1.250
1.255
C=O Bond Length
AM1 Calculations
C=O Bond Length vs C=O Frequency
Wave Number (cm-1)
1980
1970
1960
1950
1.240
1.245
1.250
1.255
C=O Bond Length

Figure 5.4:


AM1 Calculations
Si-N Bond Length vs Delta E (Kcal/mole)
Delta E (Kcal/mole)
0.03
0.02
0.01
0.00
1.73
1.74
1.75
Si-N Bond Length

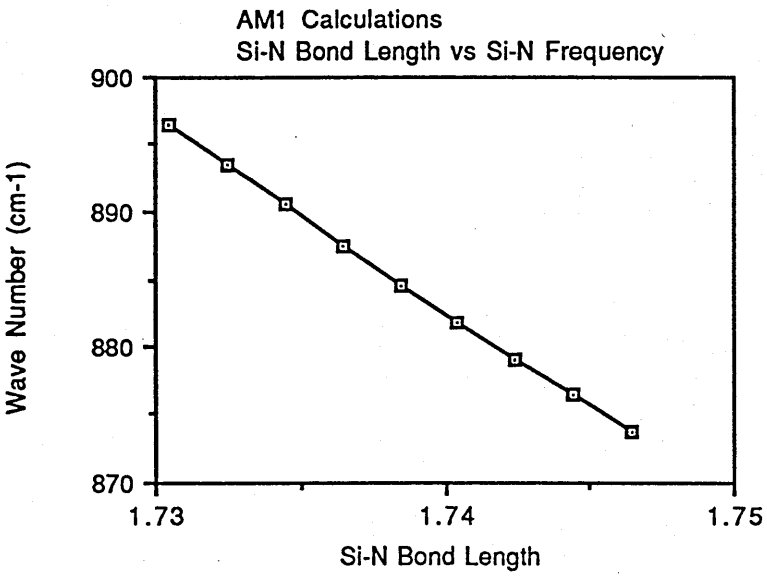

AM1 Calculations
Si-N Bond Length vs Si-N Frequency
Wave Number (cm-1)
900
890
880
870
1.73
1.74
1.75
Si-N Bond Length

Table 5.13 gives the uncorrected frequency shifts for the C=O and N=C in the silyl amides and imidates studied. These values are shown again in Table 5.14 where they are compared against both experimental and AM1 values. It is interesting to note in Table 5.13 that the N-silyl tautomer has a carbonyl absorption band which is at a higher frequency than the imidate C=N stretch in the O-silyl tautomer. However, as the molecular size of the system studied increased, the difference between the absorption position of the C=O and C=N bands decreased until they actually switched. That is to say, in the trimethylsilyl examples, we observed that the N-silyl tautomer was shifted to a low frequency position relative to the O-silyl imidate, C=N, stretch. This trend is not observed when AM1 is used to calculate the vibrational spectra of these materials. Table 5.15 summarises the AM1 calculations. Although AM1 techniques did provide reasonable estimates of the frequencies of interest, the method cannot be relied on to accurately predict tautomeric assignments of larger silylated amides.

Table 5.13:

Ab initio Frequency (uncorrected) Calculations for Various Silylamides and Silylimidates

			Ab Initio Frequency	
R1	R2	R3	C=O	N=C
H3Si	H	H	1991 cm^{-1}	1921 cm^{-1}
H3Si	H	F	2089	2002
H3Si	H	CH3	1990	1936
H3Si	H	CF3	2039	1980
H3Si	CH3	CH3	1985	1966
H3Si	CH3	CF3	1981	1969
Me3Si	CH3	CH3	1948	1964
Me3Si	CH3	CF3	1943	1969

Table 5.14:

Ab initio and AM1 Calculations of The Vibrational Spectra of Silylamides and Silylimidates Uncorrected Frequencies.

Substance	**Phase**	**Actual**	***Ab Initio***	**AM1**
Acetone	Gas	1725 cm^{-1}	1881 cm^{-1}	
SiH3-NH-C(H)=O	Gas			
(Amide)			1991	1965
(Imidate)			1921	1891
SiH3-NH-C(F)=O	Gas			
(Amide)			2089	2026
(Imidate)			2002	1931
SiH3-NH-C(Me)=O	Gas			
(Amide)			1990	1972
(Imidate)			1936	1923
SiH3-NH-C(CF3)=O	Gas			
(Amide)			2039	2036
(Imidate)			1980	1947
SiH3-N(Me)-C(Me)=O	Gas			
(Amide)			1985	1984
(Imidate)			1966	1932
SiH3-N(Me)-C(CF3)=O	Gas			
(Amide)			1981	2014
(Imidate)			1969	1956
Me3Si-N(Me)C(Me)=O				
(Amide)	Gas		1948	1971
(Imidate)	Gas		1964	1963
(Amide)	Liquid	1650	-	
(Imidate)	Liquid	1680	-	
Me3Si-N(Me)C(CF3)=O				
(Amide)	Gas	1704	1943	1999
(Imidate)			1969	1963
(Amide)	Liquid	1700	-	
(Imidate)	Liquid	1731	-	

Table 5.15:

AM1 Frequency (uncorrected) Calculations for Various Silylamides and Silylimidates

			AM1 Frequency	
R1	R2	R3	C=O	N=C
H3Si	H	H	1965cm^{-1}	1891cm^{-1}
H3Si	H	F	2026	1931
H3Si	H	CH3	1972	1923
H3Si	H	CF3	2036	1947
H3Si	CH3	CH3	1984	1932
H3Si	CH3	CF3	2014	1956
Me3Si	CH3	CH3	1971	1921
Me3Si	CH3	CF3	1999	1963

It is clear from the data presented in the various tables, that the infrared assignments for the N- and O-trimethylsilyl tautomeric species, made by Lane in his earlier work, were correct. The amide, C=O, frequency for N-methyl-N-trimethylsilylacetamide was calculated and corrected to be 1657 cm^{-1}, which is in excellent agreement with the experimental value of 1650 cm^{-1}. The imidate, N=C, frequency for the O-tautomer was calculated and corrected to be 1689 cm^{-1}, which is also in excellent agreement with the experimental value of 1680 cm^{-1}. The same observation was made for the two tautomers of trimethylsilyl-N-methylfluoroacetamide. The C=O absorption occurred at a lower frequency than the N=C of the O-silylimidate. These data and the earlier work of Lane, also support the suggestion that the thermodynamic silylating ability of a silylamide is related, at least in part, to the O-silylimidate tautomer.

5.5 Silylation

In order to better understand the relationship between the relative silylating ability of the two primary tautomeric forms of silylamides, N-silyl and O-silyl, we chose to briefly investigate the hypothesis put forth by Corriu [15, 16], which implies that the ability for silicon to undergo nucleophilic displacement is a function of the elastic nature of the silicon-leaving group bond. That is to say, using the Corriu model, that if the Si-O bond in a silylimidate were more elastic than the Si-N bond in a

silylamide, that the O-silyl tautomer would be the better silylating agent. To test this hypothesis we studied the N- and O- tautomers of N-methyl-N-trimethylsilylacetamide and N-methyl-N-trimethylsilylfluoroacetamide at the AM1 level. In these experiments, we varied the Si-N and Si-O bond lengths in predefined intervals from the equilibrium value. Figure 5.5 shows the results of those calculations for the N-methyl-N-trimethylsilylacetamide example. From this plot, it is apparent that there is no difference in the elastic nature of the Si-N and Si-O bonds in this tautomeric set of structures. The same observation was made for the N-methyl-N-trimethylsilylfluoroacetamide case. Figure 5.6 shows a comparison for the stretching of the Si-O bond for both N-methyl-O-trimethylsilylacetamide and N-methyl-O-trimethylsilylfluoroacetamide. Although the two curves do not superimpose upon one another, they are not different enough to justify a claim that N-methyl-O-trimethylsilylfluoroacetamide is a better silylating agent because of the slight increase in the elastic nature of the Si-O bond. In neither of the studies did we observe what might be considered support for Corriu's claim. In fact, from a computational sense, the assertion that the stretching coefficient for various Si-X bonds could be used to predict relative reactivity remains without support.

Figure 5.5:

Variance from Equilibrium Bond Lengths vs Relative Energy for Si-N and Si-O in N-Methyl-N-Trimethylsilylacetamide

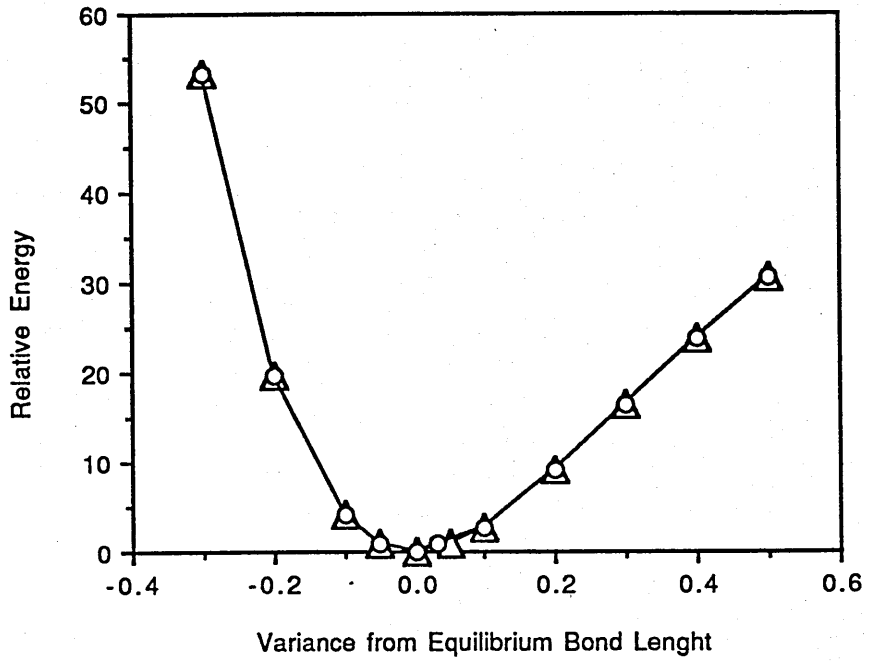
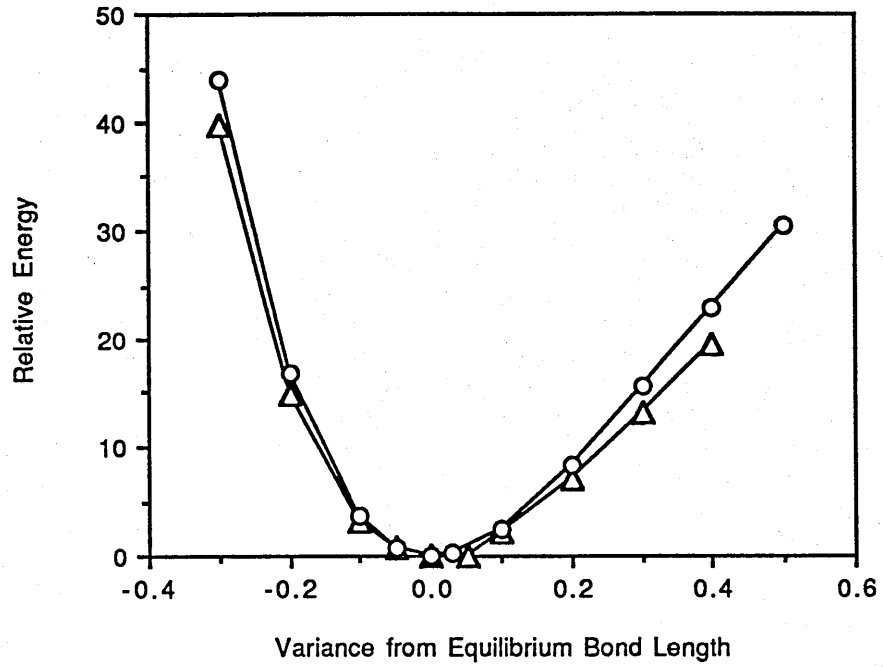


Figure 5.6:

Variance from Equilibrium Bond Lengths vs Relative Energy for Si-O in N-Methyl-N-Trimethylsilylacetamide, (°) and N-Methyl-N-Trimethylsilylfluoroacetamide, (Δ)



It has also been suggested that the relative electrophilicity of silicon could be used as a means of predicting thermodynamic silylating ability of silylamides. That is to say, that perhaps the relative charge on silicon for the two tautomeric forms could be used to gain additional insight into which of the two tautomers is responsible for silylation. However, a study of the charge distribution for both tautomeric species provides no additional insight into this question. Table 5.16 summarises the net atomic charges for Si, N, O, and C for the four most important cases which involve the trimethylsilyl substituted acetamides and fluoroacetamides. The charges represented in the table are from *ab initio* calculations. From these data it is apparent the silicon in the imidate form is indeed more electrophilic. However, the difference in charge at silicon between the two tautomeric states is very small and unlikely to account for the difference in observed silylating ability of these materials.

Table 5.16:

Ab initio Charges for

Trimethylsilylated Acetamides

Trimethylsilyl-N-methylacetamide

Charge at	Amide	Imidate
Si	1.412127	1.424552
O	-0.723876	-0.872823
N	-0.804265	-0.577159
C(O)	0.964858	0.873288

Me3Si-N(Me)-C(=O)CF3

Charge at	Amide	Imidate
Si	1.416633	1.428397
O	-0.698077	-0.872322
N	-0.814429	-0.553117
C(O)	0.824456	0.721465

Postulating that the relative silylating behaviour of the N- and O-tautomeric species might be related not to the relative charge at silicon, but rather the accessible area at silicon for nucleophilic attack, we calculated the surface areas for the N- and O-tautomeric species and the accessible area at silicon. Using the atomic radii suggested by Bondi [17] and the trimethylsilylated amides as a model, we calculated the accessible area at silicon for both N- and O-trimethylsilyl tautomers. We observed a small, but significant increase in accessible area at silicon for the O-silyl tautomer in both of the examples studied, N-,O-trimethylsilyl-N-methylacetamide and N-,O-trimethylsilyl-N-methylfluoroacetamide. The difference in both cases [O- and N- tautomers, area at silicon] was approximately 10 $Å^2$. Although interesting, this finding is not convincing enough to support the supposition that the O-silylamides are the better silylating agent when compared to the N-silyl form.

The question of which of the two tautomeric species is responsible for silylation, or which is the active silylating agent, was answered through the following study. In this study, we investigated the reaction of both N-silylformamide and O-silylformamide with water. The reaction schemes, I and II, are illustrated in Figures 5.7 and 5.8. For Scheme I, we first calculated at the *ab initio* level, the optimum or minimum energy structures for water, N-silylformamide, silanol, formimide and formamide. We also calculated the minimum energy structure for a

complex of water with N-silylformamide which is also shown in Scheme I. Once these calculations were completed, we were able to conduct an energy balance study in accordance with Hess' law. This law, Hess' Law of Constant Heat Summation, states that the amount of heat generated by a chemical reaction is the same whether the reaction takes place in one step or in several steps. It also goes on to state that all chemical reactions which start with the same original substances and end with the same final substances liberate the same amounts of heat regardless of the process by which the final state is reached. From this type of analysis we found that the first step in Scheme I is exothermic by 7.1 kcal mol^{-1}. However, the second step in this three step process is endothermic by 7.4 kcal mol^{-1}. The final step, which involves the tautomerisation of formimide to formamide, is exothermic by 13.8 kcal mol^{-1}. This conversion energy for formimide to formamide is in excellent agreement with the recent work of Sygula [18] who calculated the transformation to be 13.5 kcal mol^{-1} at the AM1 level of calculation.

The reaction of water with the O-silylformimide, as shown in Scheme II, is only a two step process. In this example, we minimised each of the structures and complexes, at the *ab initio* level, and conducted an energy survey. Again, we found that the formation of a complex of water with the silylating agent was exothermic. In this example, the formation of the complex was exothermic by 6.7 kcal mol^{-1}. The second step of the reaction was the collapse of the

complex to the expected products, silanol and formamide. This step was also exothermic by 9.20 kcal mol^{-1} making the overall process exothermic by 15.9 kcal mol^{-1}.

Energy diagrams for the two schemes are given in Figures 5.9 and 5.10. From these data, it is obvious that the O-silyl tautomer is a better thermodynamic silylating agent when compared to its N-silyl counterpart.

Tables 5.17 and 5.18 compare the important structural data for the N- and O-silyl tautomers with the corresponding tautomer/water complexes. From these data we can see that there is no significant (greater than 0.05 Å) variance in the bond lengths for the water complexed amide or imidate and the free structures. There are, however, some significant differences, greater than four degrees, between the water complex and free tautomer in terms of bond angles. For the uncomplexed N-silylformamide the observed Si-N-C(O) and Si-N-H bond angles were 119.06 and 123.50 degrees, respectively. In the water complex of the tautomer, the observed bond angles were 124.27 and 120.05 degrees, respectively. The broadening of the Si-N-C(O) bond angle at the expense of the Si-N-H bond angle is to be expected as the molecule of water positions itself for attack at silicon. Smaller variations were noted for the bond angle described by N-C-O which opened from 123.28 degrees in the uncomplexed state to 125.37 degrees in the water complexed state.

Figure 5.7:

Silylation of water

Scheme I

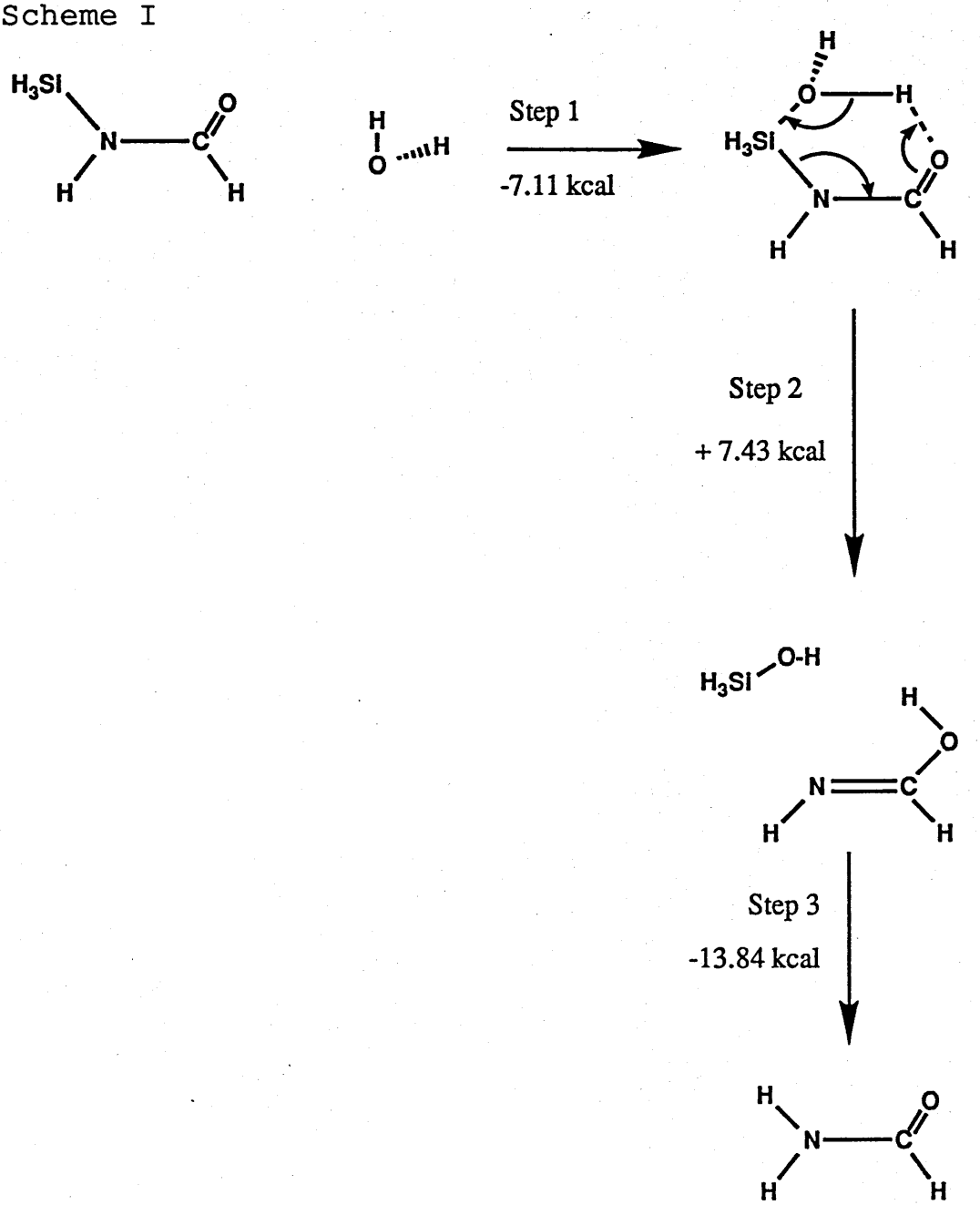


Figure 5.8:

Silylation of water

Scheme II

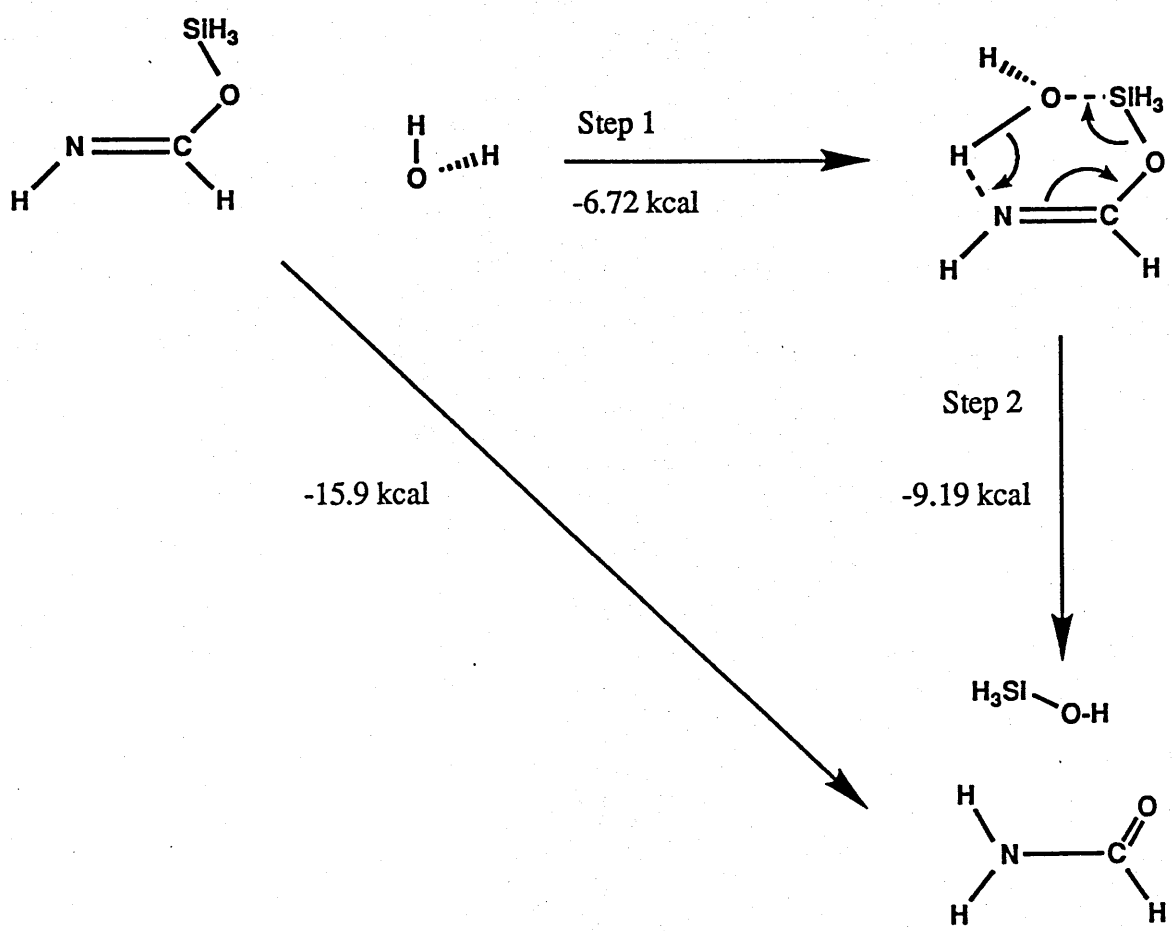


Figure 5.9:

Energy Diagram for Scheme I

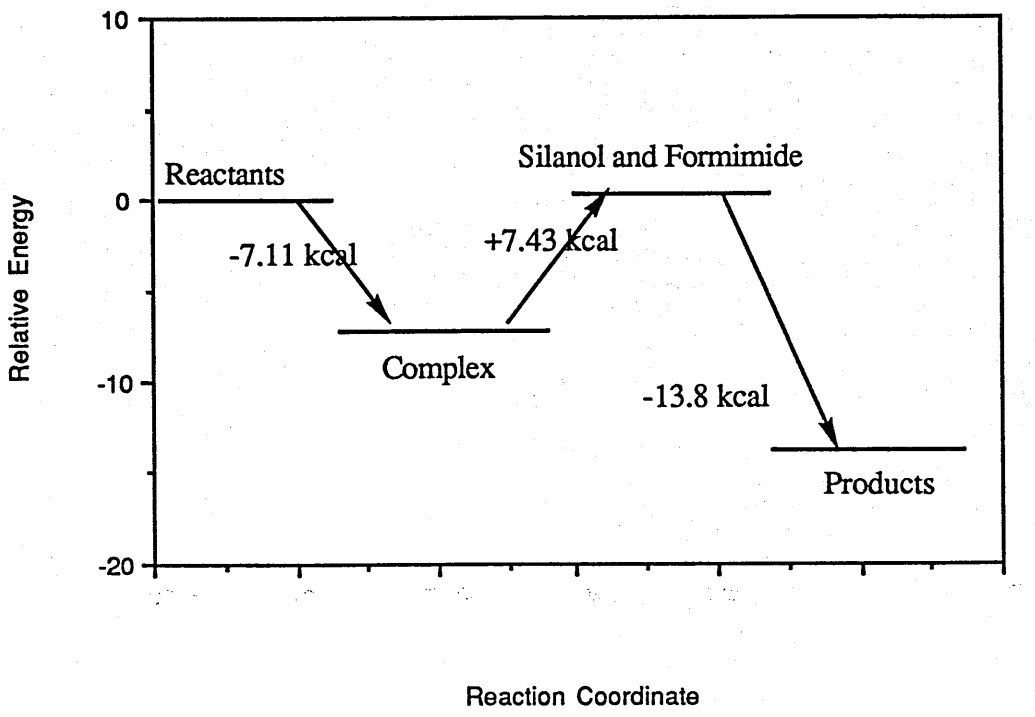


Figure 5.10:

Energy Diagram for Scheme II

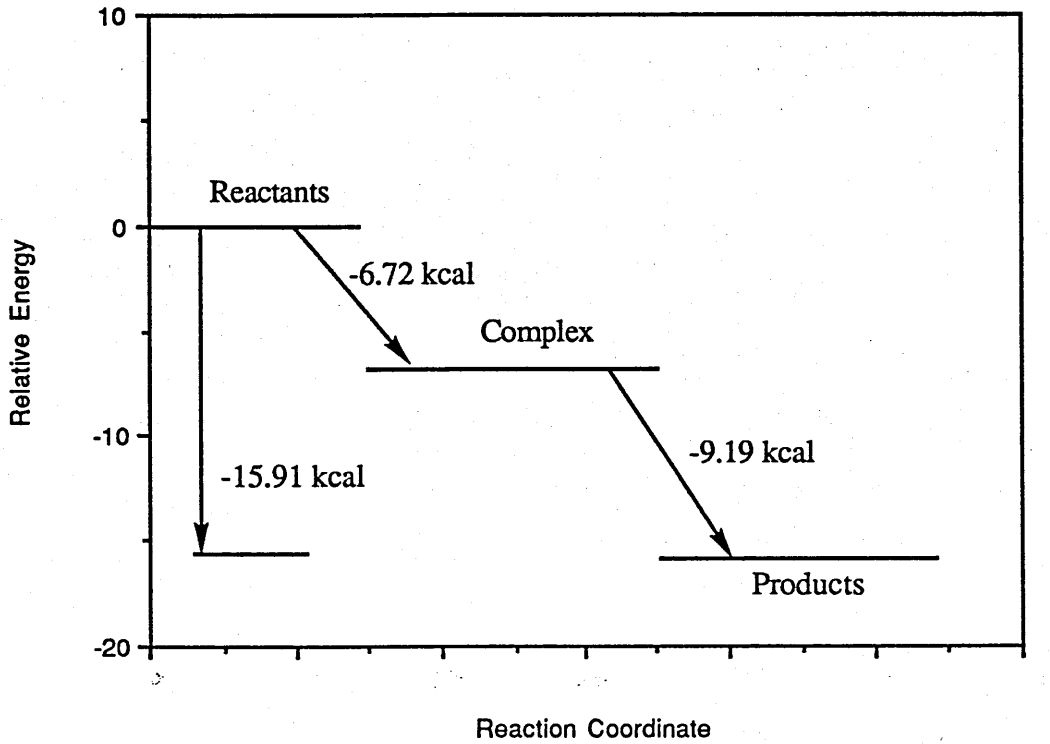
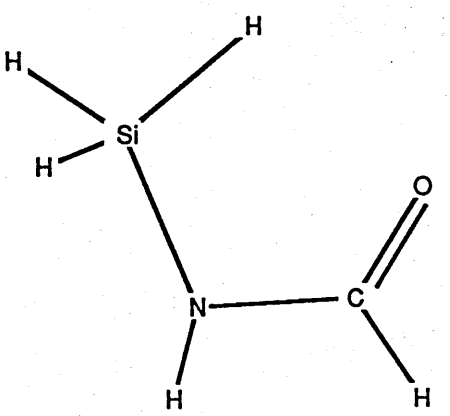
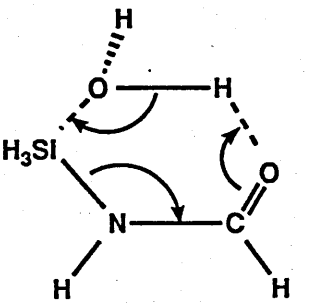


Table 5.17:

N-Silylformamide and N-silylformamide/water Complex Optimised Structural Data From *Ab Initio* Calculations





Bond Length (Å)

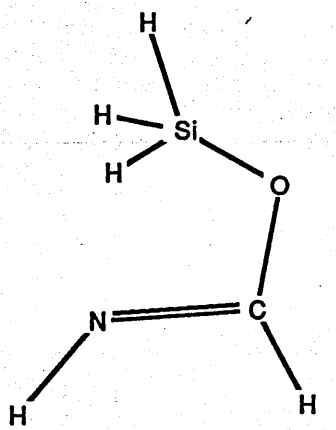
	Free Amide	Amide/Water Complex
Si-H	1.4831	1.4863
N-Si	1.7699	1.7830
C-N	1.3536	1.3447
O-C	1.1937	1.1987
H-C	1.0984	1.0974
H-N	1.0038	1.0068
H-Si	1.4782	1.4719
H-Si	1.4782	1.4719

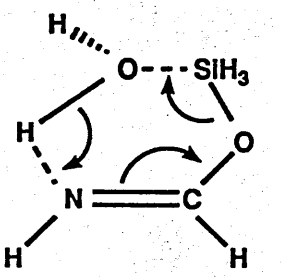
Bond Angle (degrees)

	Free Amide	Amide/Water Complex
N-Si-H	105.273.	102.462
C-N-Si	119.055	124.267
O-C-N	123.275	125.372
H-C-N	114.082	113.507
H-N-Si	123.502	120.047
H-Si-N	111.156	110.909

Table 5.18:

O-silylformamide and O-silylformimide/Water Complex
Optimised Structural Data From *Ab Initio* Calculations





Bond Length (Å)

	Free Imidate	Imidate/Water Complex
Si-H	1.4790	1.4818
O-Si	1.6891	1.6956
C-O	1.3356	1.3244
N-C	1.2405	1.2449
H-N	1.0104	1.0103
H-C	1.0864	1.0863
H-Si	1.4787	1.4731
H-Si	1.4787	1.4731

Bond Angle (degrees)

	Free Imidate	Imidate/Water Complex
O-Si-H	104.2875	102.6812
C-O-Si	119.8260	123.4764
N-C-O	122.0792	123.8259
H-N-C	111.5986	110.8939
H-C-O	111.2838	111.2055
H-Si-O	111.2220	105.2878

5.6 Summary

Although much has been published about the tautomerisation of silylamides, little has been done to study these complex molecular structures from a theoretical perspective. The focus of this study was to investigate this process at both the *ab initio* and AM1 calculational levels.

In our work to compare the utility of AM1, MDNO, and *ab initio* techniques for the study of the the 1,3-migration of silicon across this allylic system, we found that only the *ab initio* method provided answers which could be trusted. The fact that both AM1 and MNDO tend to overestimate the relative stabilities of Si-O compounds and grossly underestimate the relative energies of Si-N compounds makes these semiempirical methods of little use in terms of studying the migration of silicon from nitrogen to oxygen.

When our calculations were carried out at the *ab initio* level, we found that trimethylsilylamides and silylamides are a complicated and dynamic mixture of rotameric and N,O-tautomeric structures. The distribution of tautomeric and rotameric forms appears to be strongly dependent on the nature of the substituents at the carbonyl carbon and at the nitrogen. For simple monosilylamides, the amount of the O-silyl imidate increases as the substituent at nitrogen becomes more electron-withdrawing and more sterically cumbersome. The effect has been rationalised by comparing the relative stabilities of the tautomers as a

function of electron density at nitrogen. As electron density at nitrogen is increased, the pi-character of the C-N bond increases, favouring the N-tautomer. Reducing electron density at nitrogen, therefore, facilitates the formation of the strong Si-O bond in the O-tautomer. We found that trimethylsilyl-N-methylacetamide and trimethylsilyl-N-methylfluoroacetamide both prefer to be in the N-silyl form by approximately five and four kcal mol^{-1} respectively. However, our estimates of their relative equilibrium constants suggest that the silylfluoroacetamide should be about four times more likely to be in the O-silyl form in the gas phase. These finding are in good agreement with what is known experimentally about the trimethylsilyl derivatives of acetamides.

We were able to calculate the vibrational spectrum of all of the silylamides and silylimidates studied in this work at both the *ab initio* and AM1 level. From these calculations we have learned that the AM1 method provides a surprisingly good estimate of the *ab initio* calculated spectrum. However, both AM1 and *ab initio* methods calculate vibrational frequencies which are consistently larger than those obtained experimentally. The calculated frequency positions are overestimated by 10-15%. This is due, in part, to the fact that these methods are closed shell molecular orbital routines. That is to say, as bonds are stretched the electrons remained paired with one atom causing the frequencies to be overestimated or shifted to higher frequencies. The calculated atomic charge is also a

function of atomic position in space and, therefore, is a contributor to the higher frequency shifts observed.

Selection of the proper equilibrium geometry was also determined to be of critical importance when calculating vibrational spectra. It is essential that the structure in question be minimised using the same molecular orbital method that will be used to calculated the vibrational spectrum for the molecule. Frequency changes of over 50 cm^{-1} have been observed for small variations in bond length. Similar effects have been noted for variation in bond angle as small as 0.5 degrees. Yet, regardless of the limitations of a closed shell calculational method, it is clear from the data presented that the infrared assignments for the N- and O-trimethylsilyl tautomeric species, made by Lane in his earlier work, were correct. The data then support the suggestion that the thermodynamic silylating ability of a silylamide is related, at least in part, to the O-silylimidate tautomer.

In order to better understand the relationship between the relative silylating ability of the two primary tautomeric forms of silylamides, N-silyl and O-silyl, we investigated a hypothesis put forth by Corriu which suggests that the ability for silicon to undergo nucleophilic displacement is a function of the elastic nature of the silicon-leaving group bond. We did not find support for Corriu's claim. In fact, from a computational sense, the assertion that the

stretching coefficient for various Si-X bonds could be used to predict relative reactivity remains without support.

It had also been suggested that the relative electrophilicity of silicon could be used as a means of predicting thermodynamic silylating ability of silylamides. Suggesting that the relative charge on silicon for the two tautomeric forms could be used to gain additional insight into which of the two tautomers is responsible for silylation. However, a study of the charge distribution for both tautomeric species provided no additional insight into this question. Although, we did find that silicon in the imidate form is indeed more electrophilic, the difference in charge at silicon between the two tautomeric states is very small and unlikely to account for the difference in observed silylating ability of these materials.

The postulate that suggests that the relative silylating behaviour of the N- and O-tautomeric species might be related not to the relative charge at silicon, but rather the accessible area at silicon for nucleophilic attack was also evaluated. We observed a small, but significant increase in accessible area at silicon for the O-silyl tautomer in both of the examples studied. Although interesting, this finding is not convincing enough to support the supposition that the O-silylamides are the better silylating agent when compared to the N-silyl form.

However, the question of which of the two tautomeric species is responsible for silylation, or which is the better thermodynamic silylating agent, was answered. From our work, we found that the O-silyl tautomer is the better thermodynamic silylating agent.

When O-silylformimide was allowed to react with water, the model reaction, we found that a silylformimide/water complex exothermally formed and collapsed to yield silanol and formamide directly. The total driving force for the reaction was 16 kcal mol^{-1}. When N-silylformamide was allowed to react with water we observed a similar silylformamide/water complex form, exothermic by 7 kcal mol^{-1}, but its collapse to form silanol and formimide was endothermic by 7.4 kcal mol^{-1}. The final step of the reaction was the exothermic rearrangement of formimide to formamide. The energy released in this final step was 13.8 kcal mol^{-1}. Overall, the total energy released was 13.5 kcal mol^{-1}. Clearly, the O-silyl tautomer is the better thermodynamic silylating agent.

5.7 References

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Chapter Six

1,3 Migration of Silicon Across an Allylic Framework - Intermediate or Transition State?

6.0 1,3 Migration of Silicon Across an Allylic Framework - Intermediate or Transition State?

6.1 Introduction

The factors affecting the migration of silicon across an allylic framework and the relative thermodynamic silylating abilities of N- and O-tautomeric forms of silylamides were reviewed and discussed in Chapter 5. The primary focus of this chapter, is to discuss our findings as they relate to the 1,3-intramolecular migration of silicon between nitrogens in silylamidines, and between nitrogen and oxygen in silylamides. These studies have provided new insight into the question of intermediate versus a transition state for the migration and has given an estimate of the activation energy for the two processes.

6.1.1 Nucleophilic Substitution at Carbon

The exchange of silicon between nitrogen and oxygen is believed to be an internal nucleophilic displacement [1] which should occur with retention of configuration about the silicon. To a conventional organic chemist, the concept of a nucleophilic displacement reaction with retention of stereochemical configuration is an unusual one. In organic chemistry, a nucleophilic displacement at carbon will lead either to inversion of configuration about the carbon or racemisation. Nucleophilic substitution that follows first-order kinetics will also show racemisation and follow the reactivity sequence of $3^{\circ} > 2^{\circ} > 1^{\circ} > CH_3X$, in terms of the electrophile. Reactions that follow

second-order kinetics show complete stereochemical inversion and follow the reactivity sequence CH_3X > 1° > 2° > 3° for the electrophile. Figure 6.1 and 6.2 shows the two reaction schemes and how retention and racemisation occur in each case. These figures show a generalised representation of the two processes and support the suggested stereochemical configuration. However, some exceptions do exist. Both reactions are influenced by the electronic and steric characteristics of the electrophile and the attacking nucleophile. The polarity of the solvent also plays a role in these nucleophilic substitution reactions.

Figure 6.1

The S_N1 reaction: racemisation is the result of the front or backside attack of the nucleophilic reagent.

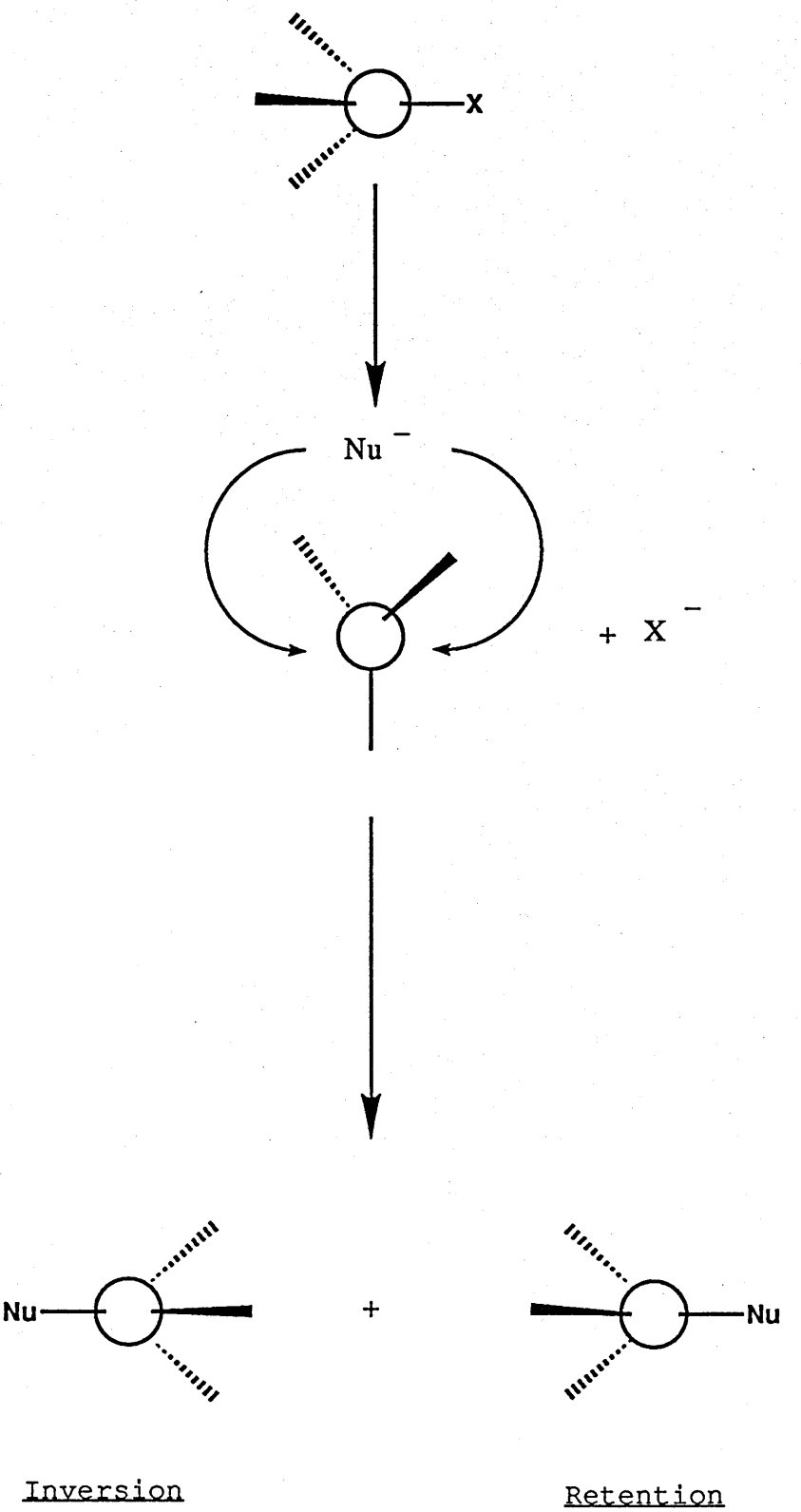
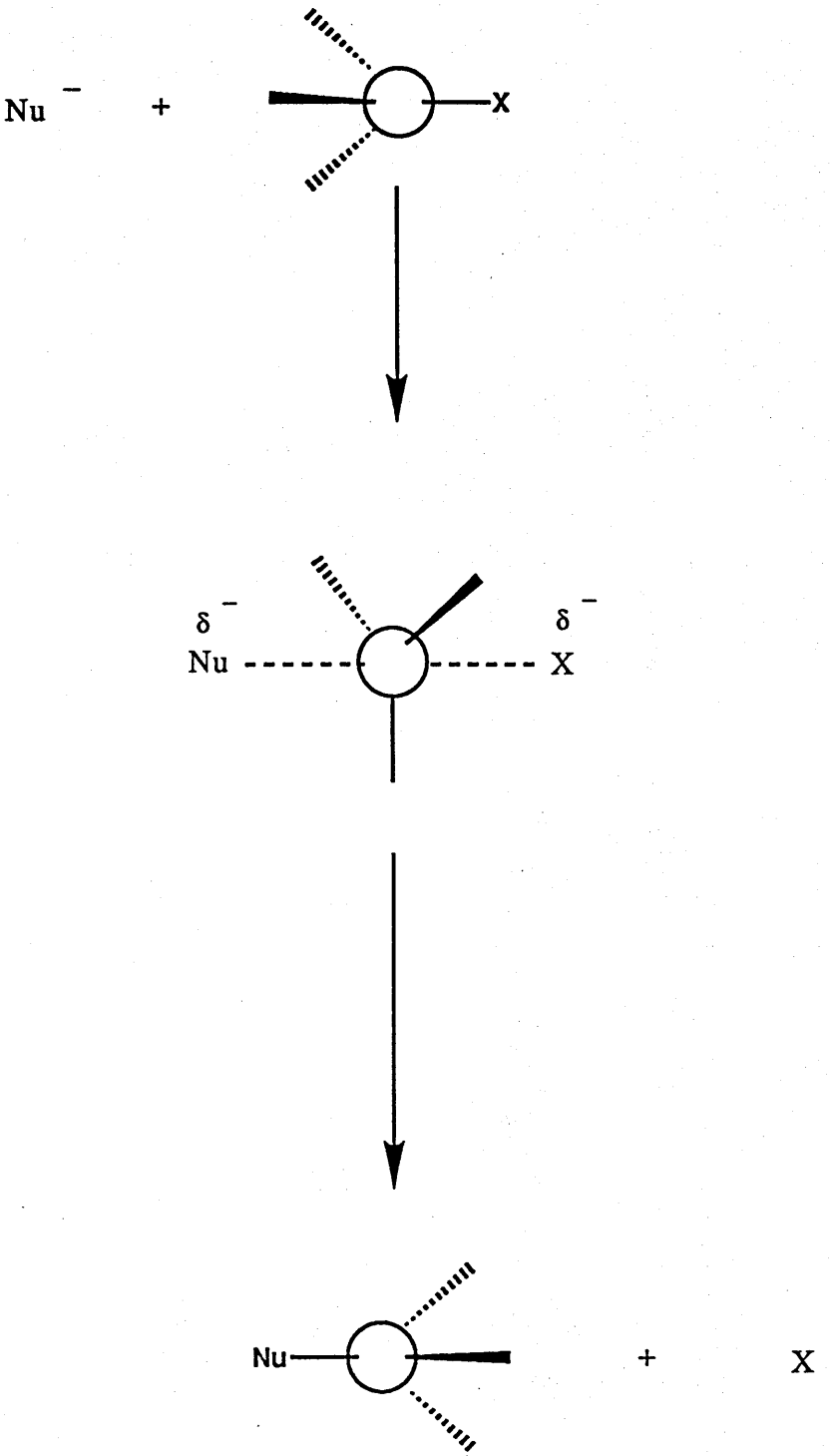


Figure 6.2

The S_N2 reaction: complete inversion of configuration.



6.1.2 Nucleophilic Substitution at Silicon

The mechanism of nucleophilic substitution at silicon has been reviewed on several occasions [2-7] with the most recent discussion of the topic by Bassindale and Taylor [8]. Silicon can undergo nucleophilic substitution with either inversion or with retention. Much of the discussion in this area has been centred on whether the 5-coordinate species exists as either an activated complex, as in the case of carbon chemistry, or as a stable intermediate. As in the carbon case, the stereochemical outcome of nucleophilic substitution at silicon depends upon the nature of the leaving group, the nucleophile, solvent, complexing agents, and whether or not silicon is part of a ring system. We will briefly examine nucleophilic substitution at silicon in terms of those conditions which promote substitution with inversion and with retention.

6.2 Nucleophilic Substitution at Silicon With Inversion of Configuration

6.2.1 General

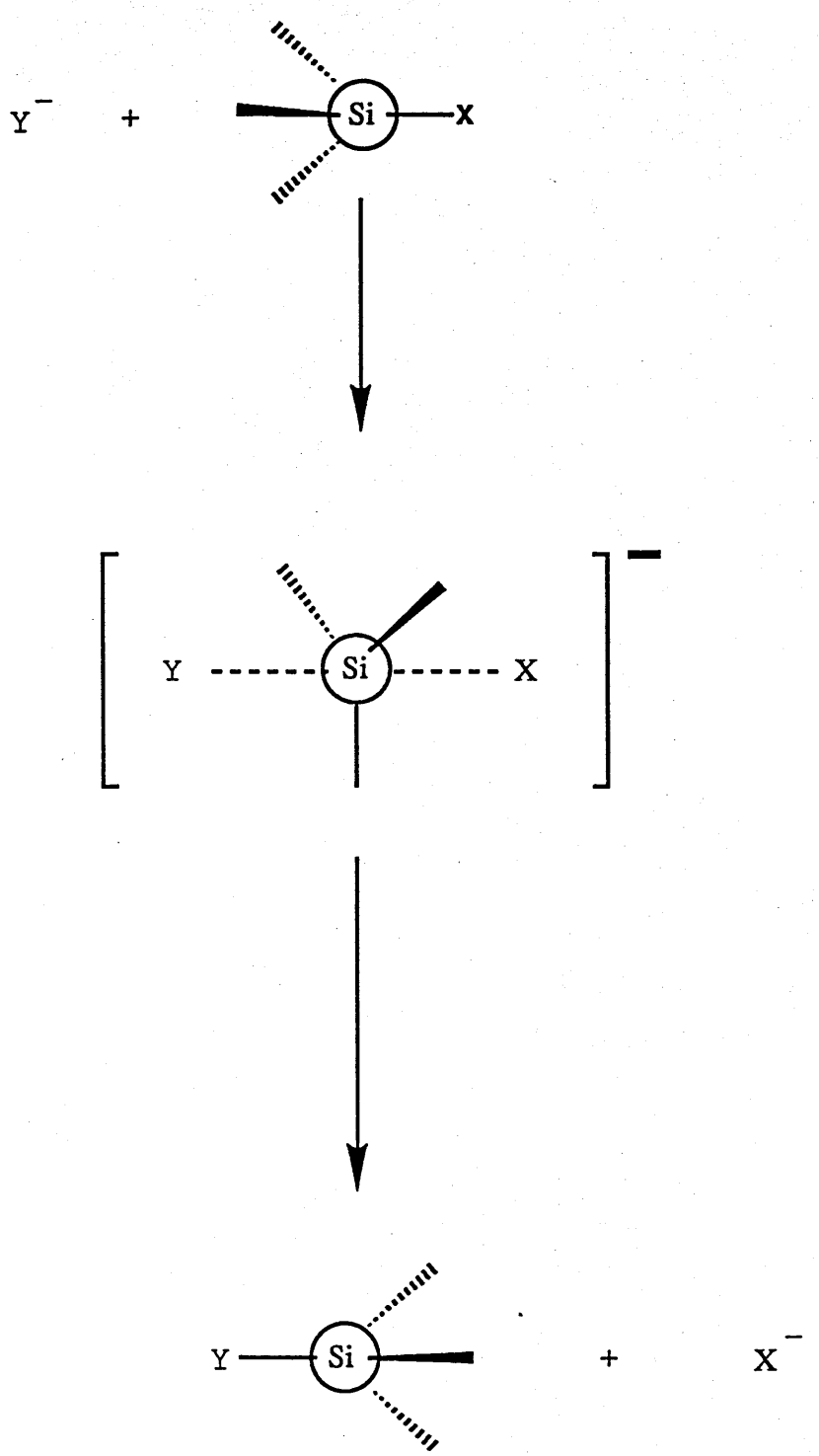
Nucleophilic substitution at silicon with inversion of configuration is most directly comparable to the second order nucleophilic displacement at carbon. For inversion to occur both the nucleophile and the leaving group must both be highly apicophilic, that is, must prefer to be in an apical position in the activated state. The accepted mechanism for inversion of configuration about silicon is

where the nucleophile attacks *trans* to the leaving group in the centre of a tetrahedral face. This gives rise to a trigonal bipyramidal activated state with both the entering and leaving groups in an axial position. The calculational work of Deiters and Holmes [13] supports this mechanism which is illustrated in Figure 6.3. Sommer [2] has observed that good leaving groups with low basicity, chlorine and bromine, tend to give inversion of configuration while poorer leaving groups with high basicity tend to result in retention of configuration. Corriu [6] has proposed an empirical relationship between the observed stereochemistry and the ability of leaving groups to be displaced. His relationship teaches that as the ability of a leaving group to be displaced varies in the order Br = Cl > SR = F > OMe > H the stereochemistry moves from one of inversion to one of retention. Deiters and Holmes [13] have calculated a similar order in leaving groups based on the concept of apicophilicity. Using Corriu's model, chlorine, which is easily displaced from silicon and highly apicophilic, will result in inversion of configuration about silicon, while the loss of hydrogen will result in retention of configuration. The mechanism for inversion does not violate the law of microscopic reversibility [9, 10] and the reverse reaction should occur by the reverse process. Although this type of mechanism is well established in carbon chemistry, the reaction proceeds through an activated intermediate in the case of silicon. Dewar and Healy have suggested that tetrahedral carbon is less reactive than silicon towards nucleophiles because it

is smaller and lacks valence shell d orbitals [11]. Bowie and his coworkers [12] concur with these assertions and suggest further that based on their calculations, five-coordinate silicon adducts are stable even when the nucleophile and attached groups are large, therefore, suggesting that the S_N2 mechanism for silicon never really resembles that of carbon, except to yield inversion under a set of well defined conditions.

Figure 6.3

Nucleophilic Substitution at Silicon with Inversion of Configuration

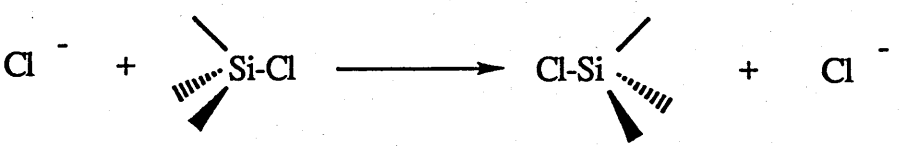


6.2.2 Reaction of Chloride Ion With Chlorosilane

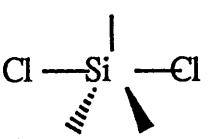
Our calculations of a simple system designed to give inversion were consistent with the collective insights discussed above. We evaluated the reaction of chloride ion with chlorosilane at the *ab initio* 3-21G*(modified) level. Figure 6.4 outlines the reaction studied and the important findings. We found that the reaction did occur with inversion of configuration as would be anticipated with an apicophilic leaving group like chloride and an unhindered apicophilic nucleophile like chloride ion. A symmetrical intermediate was found where all of the Si-H bonds had bond lengths of 1.46 Å and the two Si-Cl bonds were equal at bond lengths of 2.37 Å. A single transition state was observed. A frequency analysis of the intermediate state was consistent with a stable 5-coordinate intermediate. That is to say that we found no imaginary frequencies associated with bond breaking or making in the intermediate state. It is worth noting that the analogous carbon reaction occurs with inversion and passes through a single transition state [14].

Figure 6.4

Reaction of Chloride Ion With Chlorosilane



* No Transition State, Symetrical Intermediate



Si-H all 1.46 Å

Si-Cl 2.367 Å

* Corresponding Sn2 reaction for carbon has a T.S.

* Frequency analysis consistent with intermediate

6.3 Nucleophilic Substitution at Silicon With Retention of Configuration.

Retention of configuration requires nucleophilic attack from the same side as the leaving group. This can give rise to two different activated states. The first, is where the trigonal bipyramid arises from axial entry of the nucleophile and the leaving group occupies an equatorial position. This is the favoured route for phosphorus materials [15,16]. The second, is where attack occurs on the R1-X edge of the initial tetrahedron. This gives a trigonal bipyramid where the nucleophile occupies an equatorial site while the leaving group resides in an apical position. This path is generally not considered. Figure 6.5 shows the apical attack of a nucleophile on R1R2R3Si-X which is then followed by pseudorotation, Figure 6.6, to allow the leaving group to be lost from an axial site and the configuration is retained. We cannot have the simple loss of X from an equatorial position since this would violate the law of microscopic reversibility.

Figure 6.5

Nucleophilic Substitution at Silicon with Retention of Configuration.

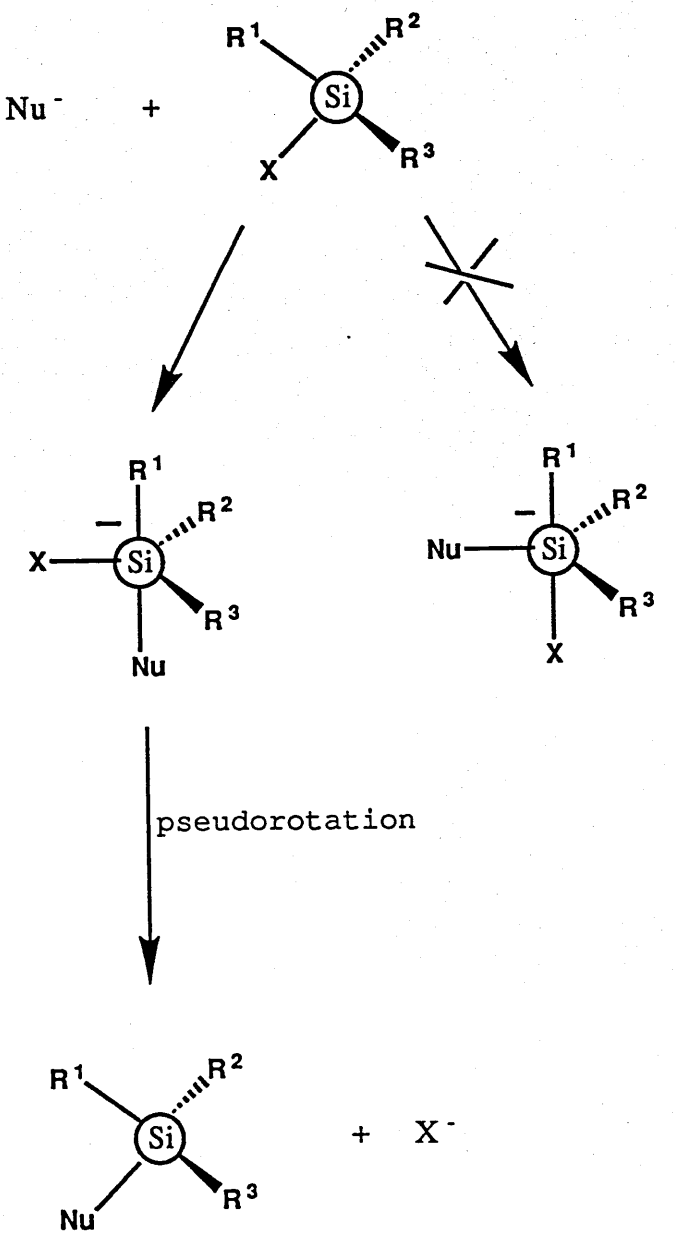
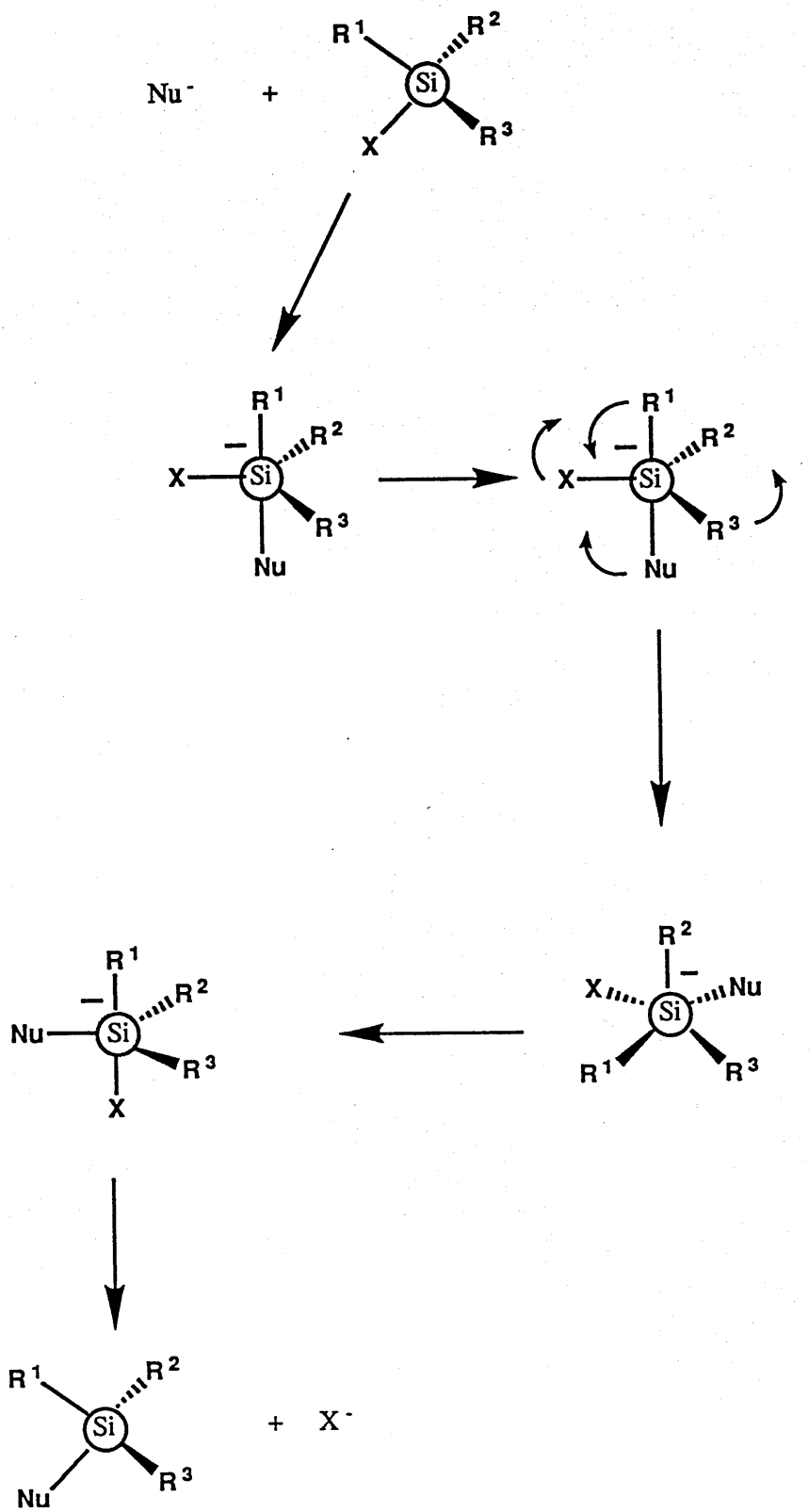


Figure 6.6

Nucleophilic Substitution at Silicon with Retention of Configuration - Pseudorotation.



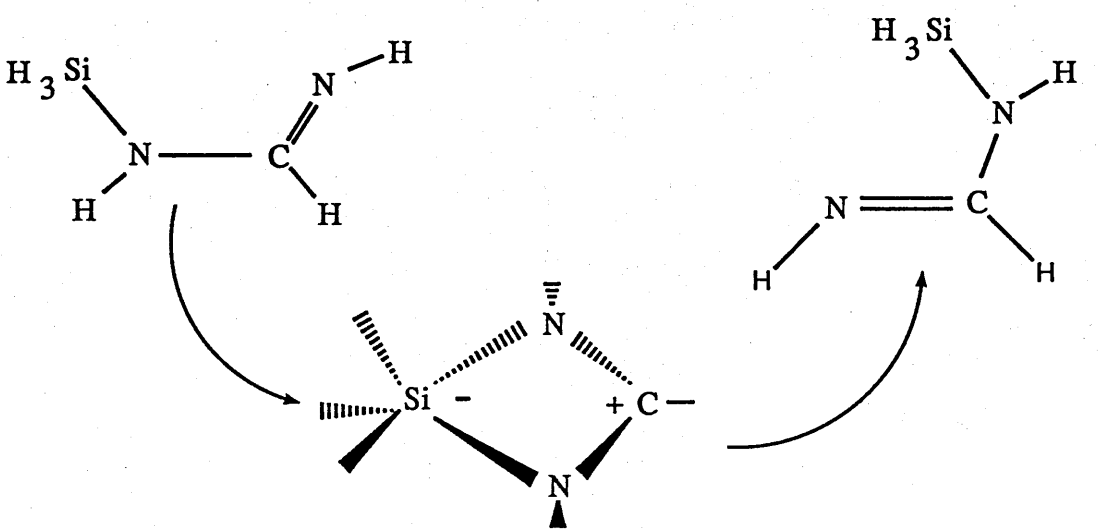
6.4 1,3 Migration of Silicon Between Nitrogen and Nitrogen

6.4.1 N-silylamidine, Evaluation of Tautomeric Reactants and Products

We began our study by first evaluating a less complex and symmetrical system, namely N-silylamidine. Figure 6.7 shows the system studied. The figure shows the intramolecular migration of the silyl group from one nitrogen to the other passing through an activated state, either a transition state or five-coordinate intermediate. We began by first comparing three *ab initio* basis sets against 6-31G* in order to find the best basis set for the study. We evaluated the following basis sets; 3-21G, 3-21G*, and 3-21G*(modified). Table 6.1 summarises and compares the results from that study.

Figure 6.7

Generalised Reaction Scheme for the 1,3 Migration of Silicon from Nitrogen to Nitrogen in N-silylamidine

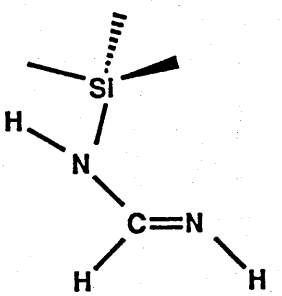


We found that 3-21G*(modified) gave values for the optimisation which were in excellent agreement with those obtained from 6-31G* calculations. It is worth noting that of the three basis sets compared, that only the 3-21G*(modified) and 6-31G* basis sets correctly gave the bond angle for H-N=C, of 112 degrees. Both 3-21G and 3-21G* overestimated this bond angle to be nearly 117 degrees. In order to determine if the 3-21G* basis function was capable of correctly predicting H-N-X bond angles in another system, we chose to examine ammonia as a model compound. Table 6.2 give the results from those calculations. From these calculations we found that the 3-21G* basis set overestimates the H-N-H bond angle and as a result, caution should be taken when dealing with hydrogens attached to atoms with a lone pair of electrons. The basis set, 3-21G*, overestimates the bond angle in this case by over five degrees.

Figure 6.8 summarizes the pertinent results of our structural optimisation study. N-silylamidine has only two relevant isomeric forms. They are represented as Structures I and II in the figure. The two structures differ only in the orientation of the silyl hydrogen. In Structure I, where the in-plane hydrogen on silicon is syn to the carbon, the N-C=N bond angle is 127 degrees and is substantially more open then in Structure II. The silicon hydrogen position in Structure II is such that the in-plane Si-H is anti to the carbon and the N-C=N bond angle was calculated to be 119 degrees by *ab initio* methods.

Table 6.1

Comparison of *Ab initio* Optimisation Calculations For N-Silylamidine



	3-21G*	3-21G*#	3-21G	6-31G*
		Bond Length (Å)		
C-H	1.0796	1.0905	1.0800	1.0840
N-C	1.3799	1.3679	1.3736	1.3677
N=C	1.2587	1.2506	1.2603	1.2564
N-H	0.9998	1.0019	0.9985	0.9955
=N-H	1.0074	1.0094	1.0073	1.0011
Si-N	1.7450	1.7598	1.7732	1.7543
Si-H (1)	1.4794	1.4880	1.4913	1.4776
Si-H	1.4698	1.4791	1.4806	1.4699
		Bond Angle (degrees)		
H-C-N	115.263	114.495	115.108	114.638
H-C=N	125.581	125.165	125.432	124.295
H-N-C	118.030	117.310	118.165	116.638
H-N=C	116.595	111.806	116.458	112.029
Si-N-C	119.247	119.802	119.266	122.319
H-Si-N(1)	103.868	104.139	103.735	103.837
H-Si-N	112.967	112.494	112.851	112.192

(1) Refers to the in plane hydrogen

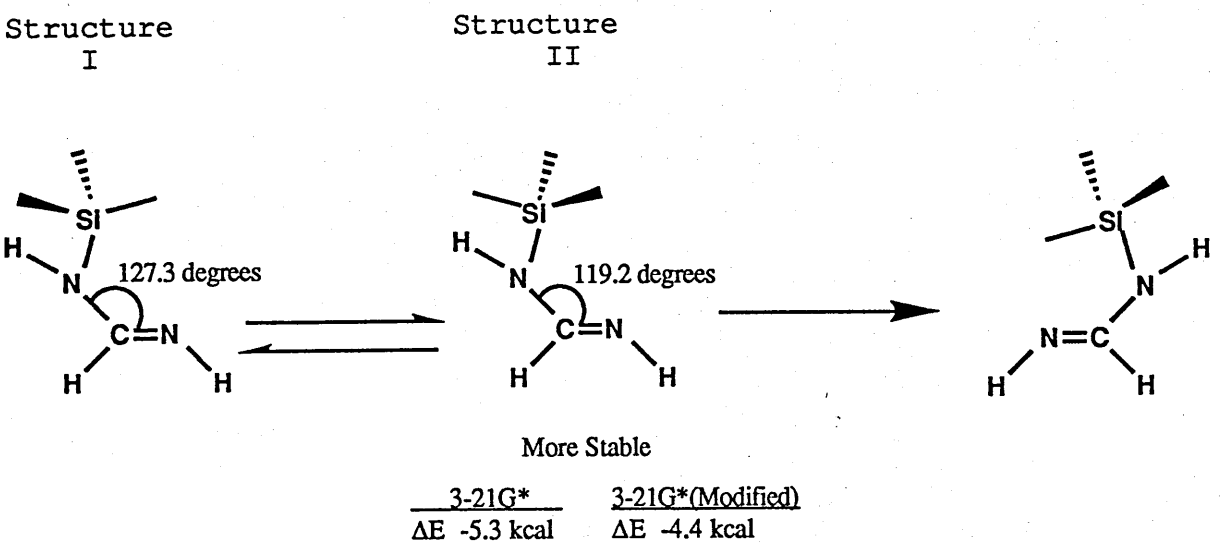
Table 6.2

Optimised Structure of Ammonia Based on *Ab initio* Calculations

	3-21G*	3-21G*#	6-31 G*
	Bond Length (Å)		
R1 (N-H)	1.0027	1.0126	1.0025
R2 (N-H)	1.0027	1.0126	1.0025
R3 (N-H)	1.0027	1.0126	1.0025
	Bond Angle (degrees)		
A1 (H-N-H)	112.402	105.603	107.177
A2 (H-N-H)	112.402	105.603	107.177
A3 (H-N-H)	112.402	105.603	107.177

Figure 6.8

Reaction Scheme for the 1,3-Migration of Silicon from Nitrogen to Nitrogen in N-silylamidine



More Stable

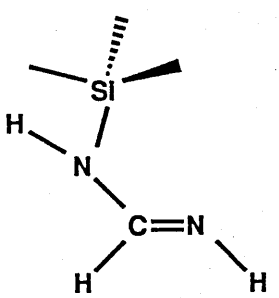
3-21G*	3-21G*(Modified)
ΔE -5.3 kcal	ΔE -4.4 kcal

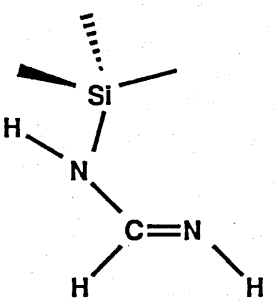
The barrier to rotation of the Si-N bond was not calculated, but the difference in energy between the two isomers was calculated at both the 3-21G* and 3-21G*(modified) levels to be about five kcal in favour of Structure II. Table 6.3 summarises and compares the results of our calculations for these two structures. Note again that the 3-21G* basis set overestimates the bond angle for a hydrogen attached to an atom containing a lone pair of electrons.

Once we had calculated the most stable structure and knew the difference in energy between the reactant (Structure II) and the product (Structure I) the main question could be addressed; does this migration occur through a single transition state or a 5-coordinate intermediate?

Table 6.3

Comparison of *Ab initio* Optimisation Calculations at the 3-21G* AND 3-21G*(modified) Level For N-Silylamidine





	3-21G*	3-21G*#	3-21G*	3-21G*#
		Bond Length (Å)		
C-H	1.0796	1.0905	1.0810	1.0914
N-C	1.3799	1.3679	1.3889	1.3754
N=C	1.2587	1.2506	1.2555	1.2479
N-H	0.9998	1.0019	1.0026	1.0041
=N-H	1.0074	1.0094	1.0087	1.0104
Si-N	1.7450	1.7598	1.7428	1.7590
Si-H (1)	1.4794	1.4880	1.4624	1.4715
Si-H	1.4698	1.4791	1.4784	1.4872
		Bond Angle (degrees)		
H-C-N	115.2631	114.4947	112.6042	112.1778
H-C=N	125.5808	125.1651	124.6295	124.4024
H-N-C	118.0303	117.3103	114.4450	114.1808
H-N=C	116.5950	111.8064	115.2217	110.3945
Si-N-C	119.2472	119.8020	127.2555	127.1308
H-Si-N(1)	103.8680	104.1393	112.0333	111.7286
H-Si-N	112.9673	112.4939	109.5540	109.3234

(1) Refers to the in-plane hydrogen

6.4.2 Transition State versus 5-coordinate Intermediate

In order to address the question of whether the intramolecular migration of silicon between nitrogens in silylamidine proceeds through a stable 5-coordinate intermediate or a transition state, we evaluated two retention models for the unimolecular/intramolecular nucleophilic displacement reaction. The inversion model of simultaneous axial attack, with loss of the leaving group from axial sites, was not considered given the constraints of the system (ring size). Retention of configuration requires nucleophilic attack from the same side as the leaving group. This can give rise to two different activated states. In the first, the trigonal bipyramid arises from axial entry of the nucleophile while the leaving group occupies an equatorial position. In the second, the attack occurs on the edge of the initial tetrahedron. This gives a trigonal bipyramid where both the nucleophile and the leaving group both occupy an equatorial site. Figure 6.9 illustrates the two possible activated states for retention with silylamidine. The figure also gives information regarding the approximate and relative activation energy for the two processes. It is clearly seen from this figure that edge attack, resulting in both nitrogens in an equatorial position, is not favoured. The enthalpy for this step was calculated to be 54 kcal mol^{-1} and 51 kcal mol^{-1} when 3-21G*(modified) and 3-21G* *ab initio* basis sets were used, respectively. The preferred route is axial attack to give

a 5-coordinate intermediate with the leaving group in an equatorial position. The calculated difference in energy between the intermediate and starting states for this process was 18 kcal mol^{-1} and 16 kcal mol^{-1}, respectively, when the two basis sets were employed. Tables 6.4 and 6.5 summarize the important structural information for the two 5-coordinate activated species. Calculated normal-mode vibrational analysis was used to evaluate each of the the proposed activated species. From this study, we determined that axial attack and axial departure, after pseudorotation, proceed through an intermediate as opposed to a saddle point or transition state. This technique of characterising structures and their relative energies through normal-mode vibrational analysis not only provides information about stable forms, but also about other stationary points on the potential surface. This corresponds to the ability to identify intermediates and transition structures. For example, an intermediate will have all real frequencies in its calculated vibrational spectrum. This can be readily distinguished from saddle point or a transition state which will have a single imaginary frequency which corresponds to bond making or breaking.

The 1,3 intramolecular migration of a silyl group from nitrogen to nitrogen in N-silylamidine proceeds through an intermediate, 5-coordinated activated silicon complex. The complex is the result of nucleophilic attack of nitrogen on silicon from an axial approach. The estimated activation

energy for the process is 18 kcal mol^{-1}. The barrier to pseudorotation was not calculated. However, there has been a substantial amount of work which would indicate that pseudorotation is to be expected at silicon. Martin [17] has shown that the barrier for pseudorotation for silicon is lower than that for phosphorus. Therefore, axial entry, pseudorotation and axial exit which is generally accepted for phosphorus is a viable mechanism. The barrier to pseudorotation is dependent on the number of electronegative groups present and values of much less than seven kcal $mole^{-1}$ have been observed for the process [8]. The calculated difference in energy between the two tautomeric structures, reactant and product, was determined to be 4.4 kcal $mole^{-1}$.

Although there are no published data regarding the migration of silicon between nitrogens in substituted amidines, there is some information concerning the migration of phosphorus in such a system. The work of Negrebetskii and coworkers [17] have experimentally determined the free energy of activation for the migration of several substituted phosphonium amidines. Their work gives the free energy of activation to be on the order of 16 kcal mol^{-1}. Our estimate of 18 kcal mol^{-1} for N-silylamidine is in good agreement with what little is known about these structures.

Figure 6.9

1,3-Migration of Silicon in Silylamidine

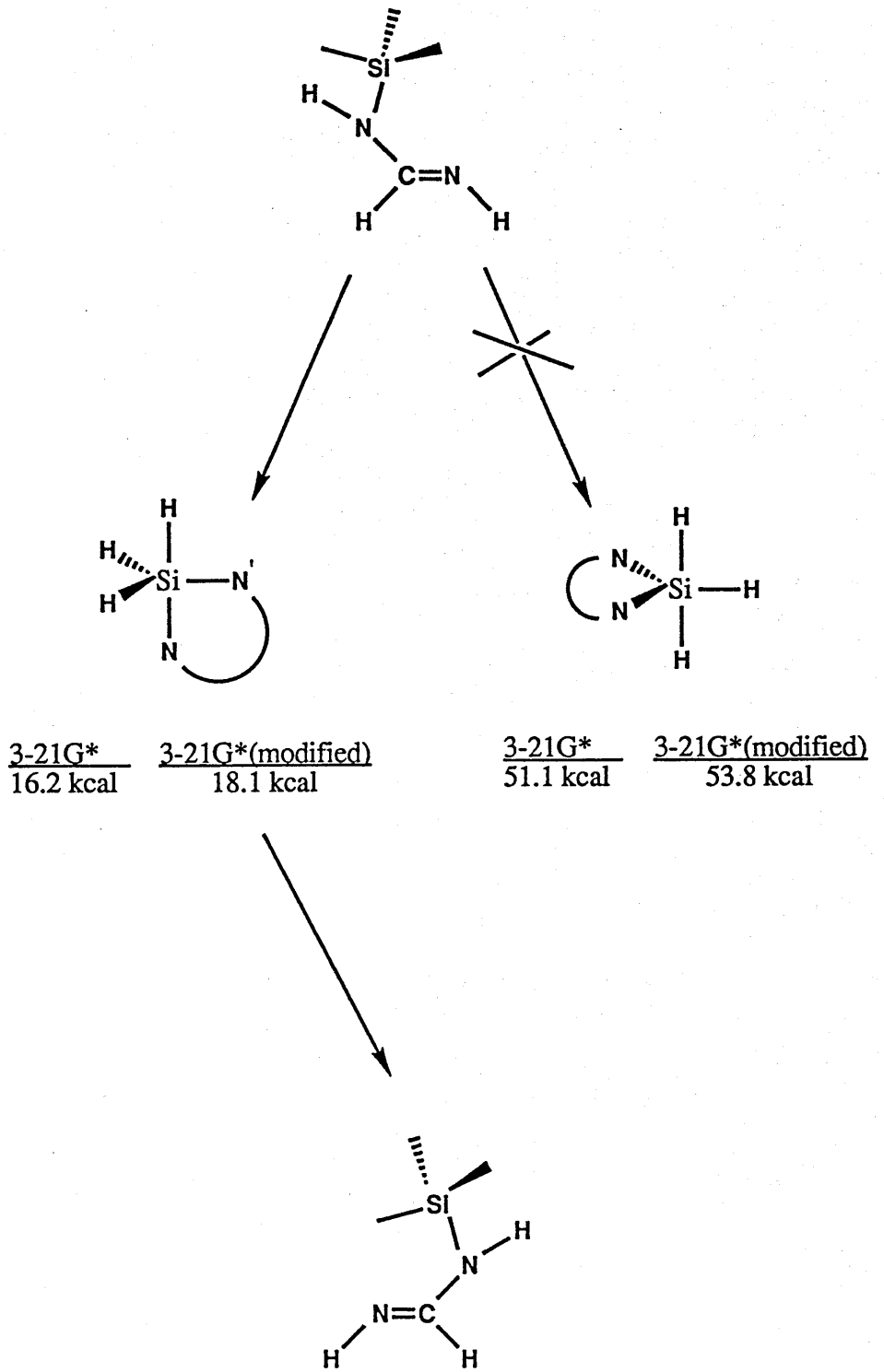
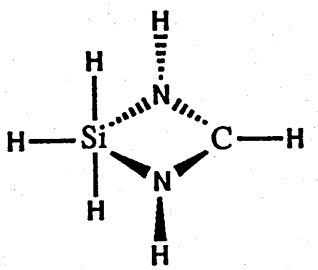


Table 6.4

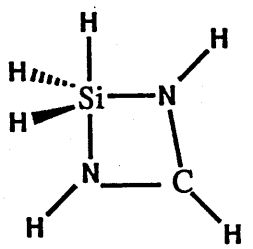
Structural Data for the equatorial, equatorial activated state for N-silylamidine. Calculations at the *Ab initio* 3-21G*(modified) Level.



	3-21G*	3-21G*#
	Bond Length (Å)	
C-H	1.0747	1.0867
C-N	1.3156	1.3029
N-H	0.9959	0.9998
Si-N		1.902
Si-H (A)	1.5116	1.5199
Si-H (E)	1.5255	1.5359
	Bond Angle (degrees)	
H-C-N	125.3899	124.5655
H-N-C	124.7632	122.3277
H-Si-H	90.00	90.00

Table 6.5

Structural Data for the axial, equatorial activated state for N-silylamidine. Calculations at the *Ab initio* 3-21G*(modified) Level.



	3-21G*	3-21G*#
	Bond Length (Å)	
C-H	1.0730	1.0848
C-N	1.3103	1.2981
N-H	0.9971	1.0011
Si-N		1.960
Si-H (A)	1.5047	1.5139
Si-H (E)	1.4831	1.4910
	Bond Angle (degrees)	
H-C-N	126.5407	125.7855
H-N-C	125.7094	123.3594

6.5 N-silylformamide: 1,3 Migration of Silicon Between Nitrogen and Oxygen

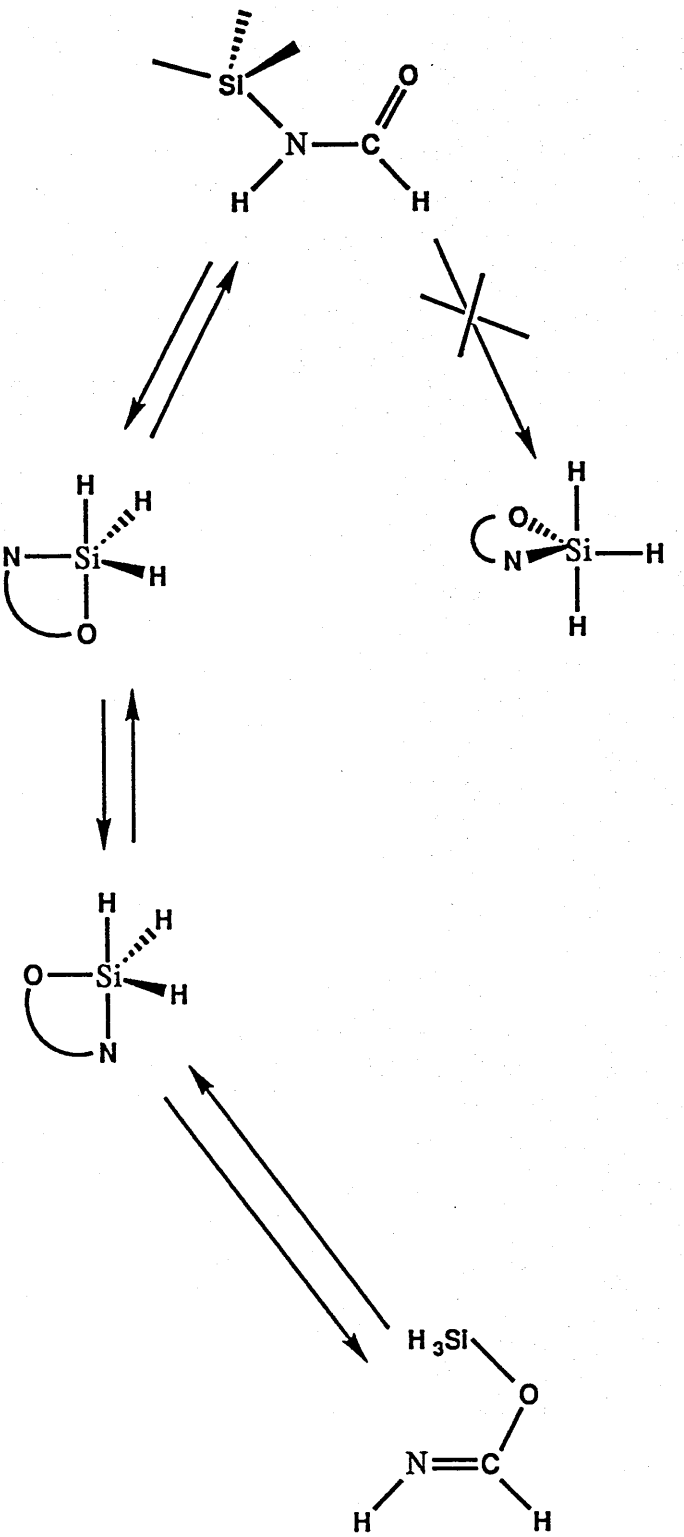
Much of the detail regarding the tautomerisation of silicon from nitrogen to oxygen in silylamides has already been discussed in Chapter 5 and will therefore, not be reviewed here. Figure 6.10 summarizes the process to be studied for N-silylformamide. The figure shows N-silylformamide undergoing an intramolecular nucleophile attack at silicon with retention of configuration. The pathway illustrated on the right hand side of the figure results from edge attack and yields an activated species where both the attacking and leaving groups are in an equatorial position. The estimated activation energy for this process is 56 kcal mol^{-1}. As before, axial attack followed by pseudorotation is the preferred pathway. The estimated activation energy for the preferred pathway was 26 kcal mol^{-1}. Pseudorotation gives the intermediate shown with nitrogen in a axial position, ready for departure. The reverse reaction, axial attack of nitrogen, gave an activation energy of 25 kcal mol^{-1}. Again, this must be followed by pseudorotation to give an activated species with oxygen in an axial position, before departure of the leaving group can occur. Both activated intermediates were studied by normal vibration calculations and their vibrational spectra contained no imaginary frequencies which could be associated with bond making or breaking. These data support that the activated complex formed in this migration is indeed an intermediate and not a transition state. The

difference in energy between the N- and O-silyl tautomer in this example was calculated to be 2.40 kcal mol^{-1} in favour of the N-tautomer.

From these calculations we can also conclude that the amide nitrogen is more apicophilic than the imidate oxygen by 1.2 kcal mol^{-1}. This is achieved by comparing the relative energies of the two activated intermediates.

Figure 6.10

1,3-Migration of N-silylformamide



6.6 N-silylfluoroformamide: 1,3-Migration of Silicon Between Nitrogen and Oxygen.

The 1,3-migration of silicon between nitrogen and oxygen in N-silylfluoroformamide was studied in much the same fashion as N-silylamidine and N-silylformamide, except that we did not consider the activated species where both the attacking and leaving group occupied an equatorial position. From these calculations we found that the activated species is an intermediate and the energy of activation for its formation is approximately 31 kcal mol^{-1}. The difference in energy between the two tautomeric structures is 8.7 kcal mol^{-1}. In this example, the introduction of a fluorine group in place of the hydrogen at the carbonyl causes both the activation energy for the tautomerization to increase as well as the difference in energy between the two structures to increase. It does not however, alter the preferred pathway.

6.7 N-silylacetamide: 1,3-Migration of Silicon Between Nitrogen and Oxygen

N-silylacetamide was the last structure to be studied. In this example we found that axial attack was preferred and yielded an intermediate structure which collapsed to the O-silyl tautomer after pseudorotation. The calculated activation energy was approximately 21 kcal mol^{-1}. The calculated difference in energy between the two tautomers was 4.4 kcal mol^{-1} in favour of the N-silyl tautomer. This

particular study is perhaps the most interesting since it did deal with a silylacetamide and not a formamide. The calculated barrier to tautomerisation is in good agreement with what is known from the literature. Fukui, Itoh, and Ishii [18] studied the migration of a trimethylsilyl group between nitrogen and oxygen in substituted benzamidosilanes. They found that the activation energy for the process that they studied was about 20 kcal mol^{-1} and was dependent on the electronic nature of the substitutent at the carbonyl carbon.

6.8 Summary

We have shown that the 1,3-migration of silicon across an allylic-like framework is an intramolecular nucleophilic substitution in which the stereochemical configuration about silicon is retained. The process involves the axial attack of a nucleophile to generate a 5-coordinate intermediate which undergoes pseudorotation to give a second intermediate with the leaving group in an axial position. The process is completed by loss of the leaving group to yield a tautomeric species. The process is reversible.

The migration of a silyl group in silylamidine was found to follow such a pathway. An estimated activation energy for the process was calculated to be 18 kcal mol^{-1}. A calculated normal-mode vibrational analysis of the activated species confirmed that the migration proceeds

through an intermediate as opposed to a saddle point or transition state.

The estimated activation energy for the migration of a silyl group between nitrogen and oxygen in N-silylformamide and in N-silylacetamide were calculated to be 26 and 21 kcal mol^{-1}, respectively. In each case, the tautomerisation was shown to proceed through an activated intermediate and not simply a transition state.

From these calculations we can also conclude that the amide nitrogen is more apicophilic than the imidate oxygen by 1.2 kcal mol^{-1}. This is achieved by comparing the relative energies of the two activated intermediates.

6.9 References

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