Spring 5-31-2011

Thermochemistry and bond energies of acetohydrazide, amides and cyclic alkyl ethers

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Recommended Citation

Charaya, Sumit, "Thermochemistry and bond energies of acetohydrazide, amides and cyclic alkyl ethers" (2011). *Theses*. 88.
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ABSTRACT

THERMOCHEMISTRY AND BOND ENERGIES OF ACETOHYDRAZIDE, AMIDES AND CYCLIC ALKYL ETHERS

by
Sumit Charaya

Structure, thermochemical properties, bond energies and internal rotation potentials of Acetic Acid Hydrazide ($CH_3CONHNH_2$), Acetamide (CH_3CONH_2) and N-methyl Acetamide ($CH_3CONHCH_3$) and their radicals corresponding to loss of hydrogen atom have been studied. Gas phase standard enthalpies of formation and bond energies were calculated using the DFT methods B3LYP/6-31G(d,p), B3LYP/6-31G(2d,2p) and the composite CBS-QB3 methods employing a series of work reactions to further improve accuracy of the $\Delta H_f°(298K)$. Molecular structures, vibration frequencies and internal rotor potentials were calculated at DFT level. The enthalpies of the parent molecules CH_3-C=$ONHNH_2$, CH_3-C=ONH_2 and CH_3-C=$ONHCH_3$ are evaluated as -28.6, -58.1 and -56.5 kcalmol^{-1} respectively at B3LYP/6-31G(D,P), B3LYP/6-31G(2d,2p) and CBS-QB3 levels. Bond dissociation energies for H--CH_2C=$ONHNH_2$, CH_3-C=ON(--H)NH_2, CH_3-C=ONHNH--H, H--CH_2C=ONH_2, CH_3-C=ONH--H, H--CH_2-C=$ONHCH_3$, CH_3-C=ON(--H)CH_3 and CH_3-C=$ONHCH_2$—H are 99.9, 78.2, 81.9, 100.1, 111.5, 99.9, 104.2 and 93.7 kcal mol^{-1} respectively. The computed DFT and the Complete Basis Set enthalpy values are in close agreement with each other; and this accord is attributed to use of isodesmic work reactions for the analysis. The agreement also suggests this combination of B3LYP / work reaction approach is acceptable for larger molecules.

Cyclic ethers are a major initial product from the reactions or hydrocarbon radicals with triplet dioxygen ($^3O_2$) in low to moderate temperature oxidation and

combustion reaction systems and atmospheric chemistry of small hydrocarbons. Thermochemical properties, $\Delta H^\circ_{f\,(298)}$, S°_{298} and Cp° (T) ($10K<T<5000$ K) of eight target cyclic alkyl ethers were calculated using density functional methods. Density functional theory (DFT) calculations, based on the B3LYP method, were performed to determine thermochemistry and C—H Bond Dissociation Energies (BDE's) governing the thermochemical stabilization of the radicals of cyclic alkyl ethers. Enthalpies of formation of different cyclic alkyl ether (oxiranes, oxetanes and oxolanes) radicals are calculated using isodesmic reactions at the B3LYP/6-31G(d,p) and B3LYP/6-31G(2d,2p) level of theory. Knowledge of these properties allows combustion and atmospheric scientists to estimate reaction paths and kinetics for these intermediates.

THERMOCHEMISTRY AND BOND ENERGIES OF ACETOHYDRAZIDE, AMIDES AND CYCLIC ALKYL ETHERS

by
Sumit Charaya

A Thesis
Submitted to the Faculty of
New Jersey Institute of Technology
In Partial Fulfillment of the Requirements for the Degree of
Master of Science in Pharmaceutical Chemistry

Department of Chemistry and Environmental Science

May 2011

APPROVAL PAGE

THERMOCHEMISTRY AND BOND ENERGIES OF ACETOHYDRAZIDE, AMIDES AND CYCLIC ALKYL ETHERS

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This thesis is dedicated to my parents
for their unending love and encouragement

Never cut a tree down in the wintertime.
Never make a negative decision in the low time.
Never make your most important decisions when you are in your worst moods.
Wait. Be patient. The storm will pass. The spring will come.
Robert H. Schuller

Failure doesn’t mean you are a failure. It does mean you haven’t succeeded yet.
Failure doesn’t mean you have accomplished nothing. It does mean you have learned something.
Failure doesn’t mean you should give up. It does mean you must try harder.
Robert H. Schuller

When we are no longer able to change the situation, we are challenged to change ourselves.
Viktor Frankl

Success has been contagious to defined, is getting up **one more time** when you’ve been knocked down.
Life is hard, real hard, incredibly hard, you fail more often you win, no body is handing you anything, its upto you to overcome the difficult, the nasty, the mean, the unfair.
Gary Raser

ACKNOWLEDGMENT

I take this opportunity to express my deepest appreciation to Dr. Joseph W. Bozzelli, who not only served as my research supervisor, providing valuable and countless resources, insight, but also constantly gave me support, encouragement, and reassurance. I am grateful to Dr. Rubik Asatryan and Dr. Tamara Gund, who served as my committee members, for their inspirational and timely support, technical expertise, and acuity throughout the duration of the project. Special thanks are given to PhD Students Anjani Gunturu, Suarwee Snitsiriwat and Itsaso Auzmendi Murua for sharing their knowledge resources with me.

I would also like to thank Dr. Larry Lay for developing Vibir program and Mr. Chad Sheng for developing SMCPS program. Vibir was very useful in calculating the Internal Rotation contribution to Entropy and Heat Capacity and SMCPS was extremely useful in calculating the Translational, Vibrational, External Rotation contributions to Entropy and Heat capacity.

Last, but not least, I would like to express profound gratitude to my parents, siblings, and friends in India and in US for uncomplaining patience, perennial support, and enormous encouragement during my stay in USA. Special thanks to Kunal Joshi and Tarun Kumar who really helped me in my good and bad times. They both gave me moral support through out my studies and were always there when I was down and needed optimistic thoughts.

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ΔHrxn	Heat of Reaction
ΔH°_f	Heat of Formation
I	Moments of Inertia
S°298	Entropy at 298 K
Cp°(T)	Heat Capacity at Constant Temperature
PE	Potential Energy Curve

CHAPTER 1

THERMOCHEMISTRY, BOND ENERGIES AND INTERNAL ROTOR BARRIERS OF ACETIC ACID HYDRAZIDE, ACETAMIDE, N-METHYL ACETAMIDE (NMA) AND RADICALS

1.1 Objective

N-methyl acetamide (NMA) and other substituted amides are considered as model compounds for the peptide bonds in proteins[1]. Thermochemical and spectroscopic investigation of understanding their thermochemistry can provide information about secondary structure of proteins in the gas phase as well as in solution. There are no studies that we are aware of, which have targeted the thermochemical properties and bond energies of these molecules.

The structure, internal rotor potentials, bond energies and determined thermochemical properties ($\Delta H°_f$, S° and Cp° (T)) on the Acetohydrazide and Amides molecules are determined. Structure and thermochemical parameters (S° and Cp° (T)) are determined using Density Functional B3LYP/6-31G (d,p), B3LYP/6-31G (2d,2p) and composite CBS-QB3 ab initio computational chemistry calculations. Enthalpies of formation for stable species are calculated using the total energies at B3LYP/6-31G (d,p), B3LYP/6-31G (2d,2p), and CBS-QB3 levels with work reactions that are isodesmic in most cases. Contributions to S°298 and Cp° (T) of each species are calculated from the parameters determined using the B3LYP structures, frequencies, plus symmetry spin degeneracy and number of optical isomers. In place of the torsion frequency values the internal rotor potentials are analyzed and their contributions to entropy and heat capacity are included. Recommended values derived from the most stable conformers of respective nitro- and nitrite isomers include: -28.6, -58.1 and -56.5 kcal mol^{-1}. Entropy and heat capacity values are also reported for the homologues: Acetohydrazide, Acetamide and N-Methyl Acetamide.

1.2 Background Information

Thermochemical analysis of internal rotor studies and spectroscopic investigations of *N*-methyl acetamide (NMA) and other substituted amides have been used to estimate these properties for the peptide bonds in proteins. A thorough understanding of their thermochemistry can provide information about secondary structure of proteins in the gas phase as well as inferences in solution and helpful information toward understanding kinetics. There are no studies that we are aware of that have targeted the thermochemical properties: enthalpy, entropy, heat capacities and bond energies of these molecules.

There are a number of reasons for interest in the structure and chemistry of these amide systems. These include: (i) clear understanding of the NMA structure is considered as the basis for understanding the geometric constraints imposed by the peptide linkages that determine, at least partly, the protein structure, (ii) detailed understanding of NMA spectroscopic features is assumed as the fundamental basis for spectroscopic methods to monitor protein structure and dynamics[10] Both of these properties are of interest and of future applications only if both structures and spectroscopic properties of NMA are monitored in the natural environment of the biological system(s)

There are a number of infrared (IR) and Raman experiments which have focused on the spectral region spanned by the three amide bands of NMA, particularly in the easily detectable IR amide I regime that overlaps with the CO stretch. In water (aq), the CO stretch responds to the presence of water molecules by forming hydrogen bonds, and the resulting frequency shift can be used to assess the dynamics of protein-solvent interactions[1-8]. Similarly, the amide II and amide III bands, which overlap with the NH in-plane wagging motion, can be used to describe the interaction between CO and HN, which are part of a protein backbone. The amide hydrogen can also form a hydrogen - bond with the solvent ($H_2O\cdots HN$), and the corresponding frequency shift provides further information on protein behavior in aqueous solution[9].

There are a limited number of studies on structure and thermochemical properties for these amides. The structural stability of acetohydrazide $CH_3–CO–NH–NH_2$ was investigated by DFT-B3LYP and ab initio MP2 calculations with 6-311+G** basis set. The C–N rotational barrier in the molecule was calculated to be about 26 kcal mol^{-1} that suggested the planar sp2 nature of the nitrogen atom of the central NH moiety with the two-fold barrier. The N atom of the terminal NH_2 group was predicted to prefer the pyramidal sp3 structure with an inversion barrier of 7 – 8 kcal mol^{-1}. The molecule was predicted to have a *trans*-*syn* (N–H bond is *trans* with respect to C=O bond and the NH_2 moiety is *syn* to C–N bond) conformation as the lowest energy structure. The vibrational frequencies were computed at B3LYP/6-311+G** level of theory and normal coordinate calculations was carried out for the *trans*-*syn* acetohydrazide. Complete vibrational assignments were made on the basis of normal coordinate analyses and experimental infrared and Raman data[11].

The study of amide C-N rotation barriers is important because amide C-N bonds make up protein backbones. The preferred amide conformations play an important role in enzyme structure and the barrier to rotation has an effect on the rigidity of the structure. The rigidity of an enzyme’s structure can affect its selectivity in binding substrates. Ab initio calculations by Jasien et al.[12] have been used to determine the gas-phase rotational barrier about the C-N bond in acetamide. Their results indicate that the inclusion of polarization functions in the basis sets leads to a substantial decrease (ca. 5 kcal mol^{-1}) in the calculated barrier height at the HF - SCF level. Electron correlation effects decrease the barrier by less than 1 kcal mol^{-1}, while the addition of zero point energy corrections changed the barrier height only slightly. Based upon the current (**DZ + d/SCF**) calculations, the 0 K rotational barrier for acetamide is predicted to be 12.5 kcal mol^{-1}.

An investigation of the photolysis of Acetamide was performed using light in the 250A° region of the spectrum, where the goal was to breakdown the molecule into CH_3 and $CONH_2$ radicals. The authors reported this was probably accompanied by a second process yielding CH_3CN and H_2O. Methyl radicals were observed to react with the parent acetamide and with the $CONH_2$ radical to give methane as a product and to recombine yielding ethane. The $CONH_2$ radicals were reported to decompose both spontaneously and thermally to give CO and NH_2 radicals. The subsequent reaction of the NH_2 radicals with acetamide gives ammonia. In a separate experiment with acetone as a photo methyl radical source, the activation energy for the abstraction of hydrogen by methyl radical was found to be 9.2 kcal mol^{-1}.[13]

The importance of reliable and accessible thermochemical data (enthalpies of formation, entropies and heat capacities) is universally accepted among scientists and engineers. This work provides thermochemical data for Acetic acid hydrazide, Acetamide and N-methyl Acetamide and their radicals corresponding to loss of hydrogen atoms through use of computational chemistry.

1.3 Computational Methods

The structure and thermochemical parameters of $CH_3CONHNH_2$, CH_3CONH_2 and $CH_3CONHCH_3$ are based on the density functional and composite ab initio levels using Gaussian 98 and Gaussian 03[14]. Computation levels include B3LYP/6-31G(d,p), B3LYP/6-31G(2d,2p)[15 16]. The CBS-QB3 method is utilized for improved energies and serves to check the DFT calculations.

Standard enthalpies of formation for stable species are calculated using the total energies at B3LYP/6-31G(d,p), B3LYP/6-31G(2d,2p), and CBS-QB3 levels with work reactions that are isodesmic in most cases. Isodesmic reactions conserve the number and type of bonds on both sides of an equation. The use of a work reaction with similar bonding on both sides of an equation results in a cancellation of calculation error and improves the accuracy for energy analysis[17]. The reported enthalpy values can be compared with the known enthalpies of several molecules in the system to serve as a calibration on the thermochemistry.

Contributions to S°298 and Cp° (T) of each species are calculated using the "SMCPS" (Statistical Mechanics for Heat Capacity and Entropy Cp and S) program which incorporates the frequencies, moments of inertia, mass, symmetry, number of optical isomers, from the Gaussian calculation. It also incorporates frequency corrections. Contributions from hindered internal rotors to S°298 and Cp° (T) are determined using “VIBIR” program. The hindered rotor corrections to the S°298 and Cp° (T) are obtained by adding the S and Cp values obtained by employing VIBIR program to those obtained from SMCPS.

To evaluate heats of formation of the titled systems we used both homodesmic and isodesmic work reactions, where the bonding environments are similar in products and reagents. A homodesmic reaction is a hypothetical reaction where the number and type of bonds (hybridization of corresponding atoms) are conserved on both sides of the reaction. An isodesmic reaction is one where the number of bonds of each type is conserved on each side of the work reaction.

1.4 Results and Discussion

The optimized geometries at the CBS-QB3 composite level of theory, *viz.,* B3LYP/6-31(d,p) calculations, for the target molecules and corresponding abbreviated nomenclature are presented in Figure 1.1

1.4.1 Structure of Acetohydrazide

The torsional potentials of CH_3-C=ONHNH_2 (vide infra) show that corresponding anti- and syn-isomers respective to H_8N_7---C_5O_6 dihedral angles [see Figure 1.1]. The *anti*-acetohydrazide has a near 4.86 kcal mol^{-1} lower energy than for the *syn* configuration with a 20.7 kcalmol^{-1} barrier. These isomerizations do not occur at standard temperature, and the isomers should be considered as different molecules in their thermochemistry and probably in their reactions.

1.4.2 Structure of N-Methyl Acetamide

The *syn*- n-methyl acetamide has a 2.5 kcal mol^{-1} lower energy than for the *anti*-configuration with barrier 21.7 kcalmol^{-1}. This is in contrast to the relative energies of the and anti conformers of **Acetohydrazide.** The internal rotation energies for these syn–anti isomerization are high typically greater than 13 kcal mol^{-1} (see below). These isomerizations do not occur at standard temperature, and the isomers should be considered as different molecules in their thermochemistry and probably in their reactions.

1.4.3 Structure of Acetamide

In Acetamide (CH_3CONH_2), the barrier between (O_9-C_5----N_7-H_8) is 18.6 kcal mol^{-1}. The dihedral angle between these atoms is 0. In CH_3CONH_2 the C=O bond is 1.22 A° and C—N is 1.37 A°. The C—C bond distance in CH_3CONH_2 is 1.52 A° which is against the 1.45 A° in the C•H_2CONH_2.

Mulliken charges for the parent molecules and their radicals are listed in Appendix B1.1-B1.3

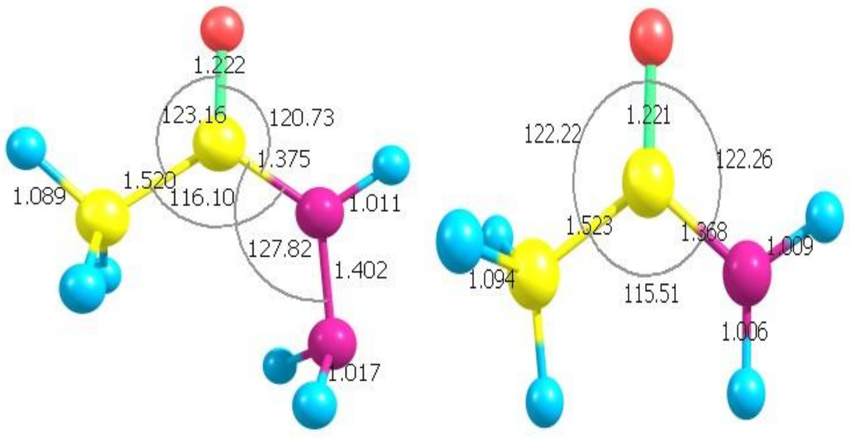
1.4.4 Enthalpies of Formation

Enthalpies of formation ($\Delta_f H^o_{298}$) are evaluated using calculated electronic energies, zero point vibration energy corrections (ZPVE) and thermal contributions (to 298 K) for each of species in the work reaction. [28, 29] Vibration frequencies are scaled by 0.9806 for CBS-QB3 level calculations.

Calculated reaction enthalpies, $\Delta_{rxn}H^\circ_{298}$, are used to find $\Delta_f H^o_{298}$ of the target molecules:

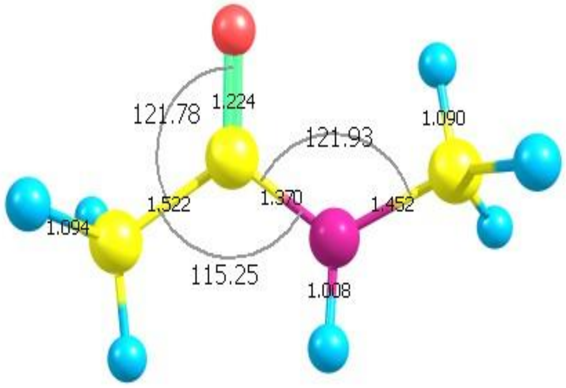
$$\Delta_{rxn}H^\circ_{298} = \Sigma\ H_f\ (\text{products}) - \Sigma\ H_f\ (\text{reactants}),$$

Where the two products and one reactant are the three reference molecules; we use the evaluated literature thermodynamic properties for the three reference species. The standard enthalpies of formation at 298.15 K for the reference species used in these reactions are summarized in Table 1.1



CH_3-C=ONHNH$_2$ *(cconn)*
Acetohydrazide

CH_3-C=ONH$_2$ *(ccon)*
Acetamide



CH_3-C=ONHCH$_3$ *(cconc)*
N-Methyl Acetamide

Figure 1.1 Geometry of the lowest energy conformers of the titled molecules and corresponding abbreviated nomenclatures.

Table 1.1 Standard Enthalpies of Formation at 298.15 K of Reference Species used in work reactions for enthalpy of formation.

Species	**$\Delta_fH^o_{298}$ kcal mol^{-1}**	**Ref.**
CH_3NH_2	-5.62	18
CH_3NHNH_2	22.6	18
CH_3CONH_2	-56.96 ± 0.19	18
CH_3CH_3	-20.04 ± 0.1	18
$CH_3CH_2CH_3$	-25.02 ± 0.12	18
$CH_3C{\cdot}H_2$	28.4 ± 0.5	18
NH_2CONH_2	-56.29 ± 0.29	18
CH_3COCH_3	-52.23 ± 0.14	18
CH_3CHO	-40 ± 0.35	18
$NH_2CH_2CO_2H$	-93.3 ± 1.1	18
CH_3CH_2OH	-56 ± 0.5	18
CH_3OH	-49. ± 3.	18
CH_3COOH	-103.5 ± 0.6	18
$CH_3CH_2NH_2$	-13.8	18
NH_2NH_2	22.79	18
$C{\cdot}H_2OH$	-2 ± 1.	18
$CH_3C{\cdot}HCH_3$	22.5 ± 0.5	18
NH_3	-10.98 ± 0.084	18
$NH_2N{\cdot}H$	52.74	18
$C{\cdot}H_2NH_2$	36.69	18
$CH_3C{\cdot}HOH$	-12.91	18
$CH_3N{\cdot}H$	44.84	18
$C{\cdot}H_2CHO$	3.55 ± 1.00	19
$N{\cdot}H_2$	44.5	20

As an example, the following equation is used to estimate $\Delta_fH^o_{298}$ for $CH_3CONHNH_2$

$$CH_3CONHNH_2 + CH_3NH_2 \rightarrow CH_3NHNH_2 + CH_3CONH_2$$

$\Delta_fH^o_{298}$ (kcal mol^{-1}): Target **-5.62** **22.6** **-56.96**

Since enthalpies of formation of the three reference compounds (values above in bold) are well established in the literature. The heat of reaction, $\Delta_{rxn}H^\circ_{298}$, is calculated and the enthalpy of formation of the target molecule $CH_3CONHNH_2$ is obtained as -28.49 kcal mol^{-1} from Hess's law.

The methods of isodesmic or homodesmic work reactions rely on the similarity of bonding environment in the reactants and products that leads to the cancellation of systematic errors in the ab initio and density functional theory calculations. The zero point energies are scaled by 0.9806 for B3LYP/6-31G(d,p) calculations as recommended by Scott et al[30]. The work reactions and the enthalpies obtained from three isodesmic reactions for parent are listed in Table 1.2. Comparing the values of the enthalpies of the parent molecules calculated by two DFT and the CBS-QB3 methods shows the values obtained by the DFT methods method are in close agreement with those obtained by CBS-QB3 calculations. We recommend the values obtained by the CBS-QB3 as it is a composite method and is known to have higher accuracy. The agreement of the DFT values suggests that use of B3LYP calculations with the 6-31G(d,p) and 6-31G(2d,2p) basis sets coupled with work reactions that result in cancelation of error provide reasonable results for these amide systems.

The recommended enthalpies of formation for the CH_3-C=ONHNH$_2$, CH_3-C=ONH$_2$ and CH_3-C=ONHCH$_3$ molecules obtained in this study are: -27.6 kcal mol^{-1}, -58.2 kcal mol^{-1} and -56.5 kcal mol^{-1} by the CBS-QB3 calculation.

The enthalpies of formation of the parent molecules, averaged over three work reactions for molecules CH_3-C=ONHNH$_2$, CH_3-C=ONH$_2$ and CH_3-C=ONHCH$_3$ were evaluated as -28.3, -58.5 and -56.5 kcal mol^{-1} respectively (values are average of B3LYP/6-31g(d,p), B3LYP/6-31g(2d,2p) and CBS-QB3 levels).

1.4.5 Enthalpies of Formation Calculated by Atomization Reaction Method

Atomization reactions can also be used to determine the enthalpy of formation for a compound by considering the compound's decomposition to its balanced number of constituent atoms, C, H, N and O. Asatryan et al[38] developed an empirically corrected atomization method for gas phase molecules using the B3LYP/6-31G(d,p) and CBS-QB3 calculation and is presented in the Tables 1.3 and 1.7.

Comparison of values from the Asatryan's method determined from our calculated DFT energies to values from isodesmic reactions are listed in Table 1.3. For the parent compounds, the work reactions values of -28.97 kcal mol^{-1} for Acetohydrazide, -58.54 kcal mol^{-1} for Acetamide and -56.20 kcal mol^{-1} for N-Methyl Acetamide were 2.05 kcal mol^{-1}, 1.69 kcal mol^{-1} and 0.3 kcal mol^{-1} respectively lower than the Asatryan method of values of -26.92 kcal mol^{-1}, -56.85 kcal mol^{-1} and -55.9 kcal mol^{-1} for Acetohydrazide, Acetamide and N-Methyl Acetamide respectively.

Similarly comparison with the CBS-QB3 atomization values of the Asatryan's method and the calculated values from the isodesmic reactions are listed in Table 1.3 For the parent compounds, the work reactions values of -27.5 kcal mol^{-1} for Acetohydrazide, -58.2 kcal mol^{-1} for Acetamide and -56.5 kcal mol^{-1} for N-Methyl Acetamide were 1.81 kcal mol^{-1}, 1.87 kcal mol^{-1} and 2.5 kcal mol^{-1} respectively lower than the atomization values of -25.69 kcal mol^{-1}, -56.33 kcal mol^{-1} and -54.0 kcal mol^{-1} for Acetohydrazide, Acetamide and *N*-Methyl Acetamide respectively.

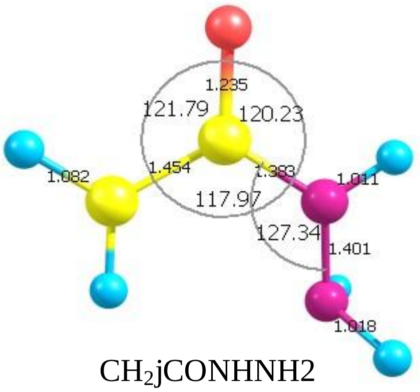
Table 1.2 Calculated Reaction Enthalpies at 298 K and Evaluated Enthalpies of Formation of Target Molecules[a]

Work Reactions							$\Delta_f H^o(298)$ kcal mol^{-1}		
							B3LYP		CBS-QB3
							6-31G(d,p)	6-31G(2d,2p)	
			$CH_3CONHNH_2$						
cconn	+	CH_3NH_2	--->	CH_3NHNH_2	+	CH_3CONH_2	-28.41	-29.55	-28.49
cconn	+	CH_3CH_2OH	--->	CH_3NHNH_2	+	$NH_2CH_2CO_2H$	-28.90	-28.55	-27.74
cconn	+	CH_3CHO	--->	NH_2CONH_2	+	CH_3COCH_3	-28.81	-28.76	-25.64
						Average	**-28.97**	**-29.21**	**-27.55**
			CH_3CONH_2						
ccon	+	CH_3CH_2OH	--->	CH_3COOH	+	$CH_3CH_2NH_2$	-58.45	-57.58	-59.08
ccon	+	CH_3CH_3	--->	CH_3COCH_3	+	CH_3NH_2	-59.48	-58.10	-56.93
ccon	+	CH_3NH_2	--->	CH_3NHNH_2	+	CH_3CHO	-58.50	-58.08	-59.45
						Average	**-58.81**	**-57.92**	**-58.48**
			$CH_3CONHCH_3$						
cconc	+	CH_3NH_2	--->	CH_3CONH_2	+	$CH_3CH_2NH_2$	-56.74	-56.40	-55.46
cconc	+	CH_3NH_2	--->	CH_3COCH_3	+	CH_3NHNH_2	-57.47	-56.51	-56.83
cconc	+	NH_2NH_2	--->	CH_3CONH_2	+	CH_3NHNH_2	-56.48	-56.29	-56.69
						Average	**-56.20**	**-56.93**	**-56.49**

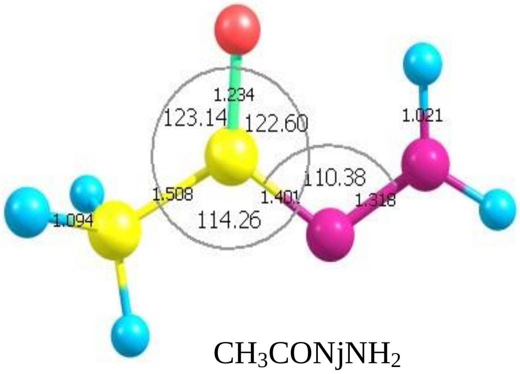
[a] Reaction enthalpies include thermal correction and zero-point energy.

Table 1.3 Formation Enthalpies of Acetohydrazide, Acetamide and N-Methyl Acetamide Calculated at Different Levels of Theory (Recommended Values are in **Bold)**

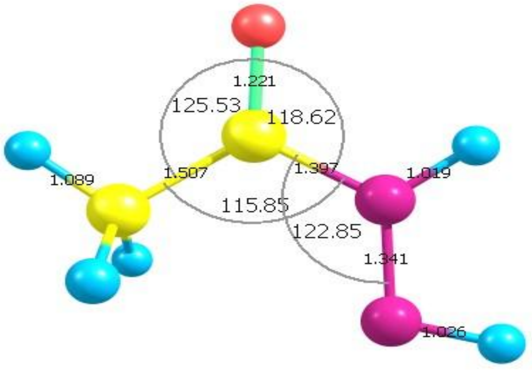
Species	**$\Delta_fH^o(298)$ (kcal mol^{-1})**			
	B3LYP/ 6-31G(d,p)	**CBS-QB3**	**Atomization**	**Literature**
$CH_3CONHNH_2$	-28.97	**-27.29**	-26.92	--
CH_3CONH_2	-58.54	**-58.21**	-56.85	-56.96 (NIST) [18] -57.0[31] -57.2[32]
$CH_3CONHCH_3$	-56.20	**-56.49**	-55.90	-59.3 (NIST) [18]



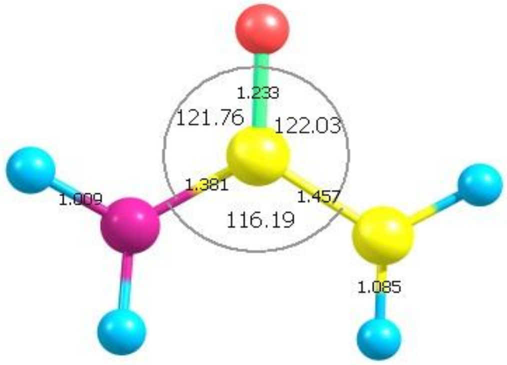
$CH_2jCONHNH2$
(cjconn)



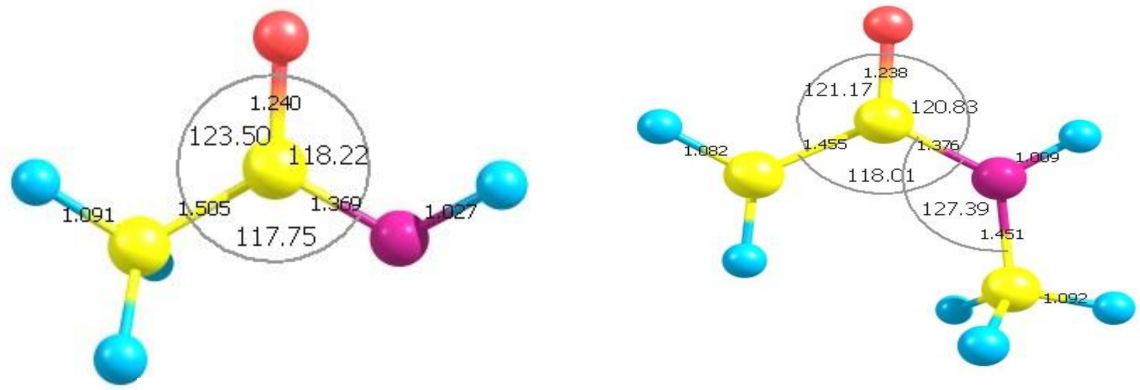
$CH_3CONjNH_2$
(cconjn)



$CH_3CONHNHj$
(cconnj)

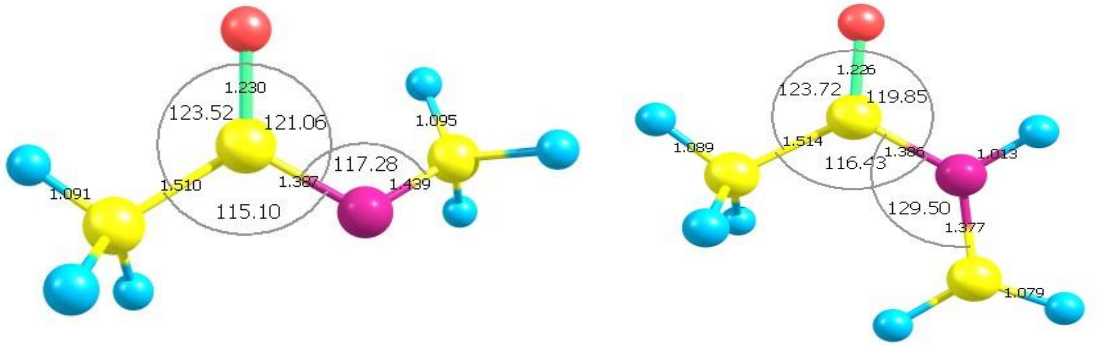


CH_2CONH_2
(cjcon)



CH_3CONHj
(cconj)

$CH_2CONHCH_3$
(cjconc)



$CH_3CONjCH_3$
(cconjc)

$CH_3CONHCH_2j$
(cconcj)

Figure 1.2 Illustrations of the lowest energy conformers of radicals corresponding to the loss of a hydrogen atom from parent molecules (see Table A1.2-A1.12, appendix B, for details) and nomenclature.

1.4.6 Bond Dissociation Energies

Bond energies are derived from $\Delta_rH^o_{298}$ of parent molecules and their radicals corresponding to the loss of hydrogen atoms. For the standard enthalpy of hydrogen atom at 298.15 K we used 52.103 kcal mol^{-1}. The resulted bond dissociation enthalpies computed from isodesmic enthalpies of formation are given in Table 1.6

CH_3-C=ONHNH$_2$ → C•H$_2$-C=ONHNH$_2$ + H•

-28.58 19.37 52.01 kcal mol^{-1}

ΔHrxn = [19.37 + 52.1] – [-28.58] = 100.05 kcal mol^{-1} = Bond Dissociation Enthalpy.

The largest difference in R—H bond energy for a given radical, considering the two DFT and the CBS-QB3 calculation methods and the four isodesmic reactions of each radical is less than 1.5 kcal mol^{-1}.

The bond dissociation energies for the C-H bonds in the methyl group adjacent to the carbonyl in CH_3-C=ONHNH$_2$ (100.2), CH_3-C(=O)NH$_2$ (100.1) and CH_3-C=ONHCH$_3$ (100.1) kcal mol^{-1} are in parenthesis. These compare, with the typical bond energy on a primary methyl site of a normal hydrocarbon of 101 kcal mol^{-1} and are ca. 1 kcal mol^{-1} lower. In contrast, they are ca. 4 kcal mol^{-1} higher than a typical primary methyl C—H bond on a ketone which is 96 kcal mol^{-1}. The C—H bond energy on the methyl group bonded to the amine to form the CH_3-C=ONHC•H$_2$ is 93.91 kcal mol^{-1}.

The N-H bond strengths for nitrogen atom adjacent to the carbonyl groups in CH_3-C=ONHNH$_2$ (78.6), CH3-C(=O)NH$_2$ (112.4), and CH_3-C=ONHCH$_3$ (105.4) kcal mol^{-1} are in the parenthesis. For comparison, the N—H bond in ammonia is 108 and the CH_3NH—H bond in methyl amine is 101.5 and the NH_2NH—H bond in hydrazine is 87 kcal mol^{-1}.

The C-H bond strength in the CH_3 group bonded to an amine in CH_3-C=ONHCH$_2$--H is 93.9 kcal mol^{-1} at the CBS-QB3 level. This compares with the C—H bond energy of H—CH$_2$-NH$_2$ which is 94.4 kcalmol^{-1}) in CH_3NH_2. This C—H bond in CH_3-C=ONHC•H$_2$ is several kcal mol^{-1}; lower than on the methyl groups bonded to C=O.

The N—H bond of the NH group in CH_3-C=O-NH-NH_2 is the weakest in this molecule at 78.8 kcal mol^{-1}, where the C—H bond in to form C•H_2-C=ONHNH_2 is 100.16 kcal mol^{-1}, which is significantly higher. The N—H bond energy for Acetohydrazide (CH_3-C=ON•NH_2) is markedly different at only 78.75 kcal mol^{-1}. In the N—H bond cleavage of CH_3-C=ON•NH_2, the electrons from the radical site re-arrange to form a partial double (Π) bond, from nitrogen to carbon. The N-H bond energy for CH_3-C=ON•CH_3 is 105.4 kcal mol^{-1} which is higher than the CH_3-C=ON•NH_2 (78.8 kcal mol^{-1})

The weakening of the N-H bonds in this hydrazide has been reported to be essentially independent of the nature of the β-substituent (H, RCO, CO_2Et, or PhSO_2) and the stabilizing effect on the radical is brought about entirely by the three-electron on N – NH_2 moiety[21].

The bond energies corresponding to C—H bond of Acetohydrazide, Acetamide and N-Methyl Acetamide compared with the C—H bond energies in Acetone, dimethyl ether and in oxamic acid are listed in Table 1.4.

The bond dissociation energies of N—H bond in Acetohydrazide and the two Amides are compared with methyl amine and hydrazine are listed in Table 1.5.

Table 1.4 C—H Bond Energies of Acetohydrazide, Acetamide and N-Methyl Acetamide compared to the C—H Bond Energies in Acetone, Dimethyl ether and Oxamic acid.

Bond	Bond dissociation energy, kcalmol^{-1}	Ref
(H---)CH_2COCH_3	94.4	33
(H---)CH_2CONO_2	95.9	34
(H---)CH_2OCH_3	96.1	35
(H---)$CH_2CONHNH_2$	100.2	This work
(H---)CH_2CONH_2	100.1	
(H---)$CH_2CONHCH_3$	100.1	

Table 1.5 N—H Bond Energies of Acetohydrazide, Acetamide and N-Methyl Acetamide compared to the N—H Bond Energies in Hydrazine and Methylamine.

Bond	Bond dissociation energy, kcalmol^{-1}	Ref
NH_2NH(---H)	87	36
CH_3NH(---H)	101.5	37
CH_3CON(---H)NH_2	78.8	This work
$CH_3CONHNH$(---H)	82.6	
CH_3CONH(---H)	112.4	
CH_3CON(---H)CH_3	105.4	

The carbonyl group shows a strong influence (positive - increase) on the N--H bond energies in CH_3CONH---H and in CH_3CON---HCH_3. Analysis of the charges on the carbon, nitrogen and oxygen atoms in these molecules can be found in the Mulliken charge values listed in Appendix B1.1-B1.3.

Table 1.6 Reaction Enthalpies at 298 K for Radicals, Calculated Enthalpies of Formation and Bond Energy[a]

Work Reactions Radicals Corresponding to H Atom Loss							**$\Delta_f H^o(298)$ kcal mol^{-1}**		
							B3LYP		**CBS-QB3**
							6-31G(d,p)	**6-31G(2d,2p)**	
$CH_3CONHNH_2$ system									
cjcocn									
cjconn	+	CH_3OH	--->	*cconn*	+	$C.H_2OH$	20.42	20.60	20.59
cjconn	+	CH_3NH_2	--->	*cconn*	+	$C.H_2NH_2$	18.72	18.69	19.33
cjconn	+	CH_3CHO	--->	*cconn*	+	$C.H_2CHO$	18.75	18.59	18.74
cjconn	+	$CH_3CH_2CH_3$	--->	*cconn*	+	$CH_3C.HCH_3$	19.60	19.19	19.23
						Average	**19.37**	**19.26**	**19.48**
						Bond Energy $H{-}{-}{-}CH_2CONHNH_2$	**100.04**	**99.94**	**100.16**
cconjn									
cconjn	+	CH_3NH_2	--->	*cconn*	+	$CH_3N.H$	0.26	0.52	0.05
cconjn	+	NH_2NH_2	--->	*cconn*	+	$N.HNH_2$	-2.44	-2.76	-2.73
cconjn	+	NH_3	--->	*cconn*	+	$N.H_2$	-2.84	-2.55	-2.46
cconjn	+	CH_3CH_2OH	--->	*cconn*	+	$CH_3C.HOH$	-4.08	-3.39	-2.55
						Average	**-2.27**	**-2.05**	**-1.93**
						Bond Energy $CH_3CON({-}{-}{-}H)NH_2$	**78.41**	**78.63**	**78.75**
cconnj									
cconnj	+	CH_3NH_2	--->	*cconn*	+	$CH_3N.H$	4.21	3.76	3.86
cconnj	+	NH_2NH_2	--->	*cconn*	+	$N.HNH_2$	1.51	0.47	1.07
cconnj	+	NH_3	--->	*cconn*	+	$N.H_2$	1.10	0.68	1.33
cconnj	+	CH_3CH_2OH	--->	*cconn*	+	$CH_3C.HOH$	-0.13	-0.15	1.25
						Average	**1.68**	**1.19**	**1.88**
						Bond Energy $CH_3CONHN({-}{-}{-}H)H$	**82.36**	**81.87**	**82.56**

Table 1.6 (Continued)

Work Reactions Radicals Corresponding to H Atom Loss							**$\Delta_f H^o(298)$ kcal mol^{-1}**		
							B3LYP		**CBS-QB3**
							6-31G(d,p)	**6-31G(2d,2p)**	
		CH_3CONH_2 system ***cjcon***							
cjcon	+	CH_3OH	--->	*ccon*	+	$C.H_2OH$	-8.43	-8.92	-9.07
cjcon	+	CH_3NH_2	--->	*ccon*	+	$C.H_2NH_2$	-10.12	-10.85	-10.320
cjcon	+	CH_3CHO	--->	*ccon*	+	$C.H_2CHO$	-10.10	-10.93	-10.391
cjcon	+	$CH_3CH_2CH_3$	--->	*ccon*	+	$CH_3C.HCH_3$	-9.27	-10.34	-10.42
						Average	**-9.48**	**-10.26**	**-10.18**
						Bond Energy H---CH_2CONH_2	**100.76**	**99.98**	**100.06**
		cconj							
cconj	+	CH_3NH_2	--->	*ccon*	+	$CH_3N.H$	4.46	3.51	4.16
cconj	+	NH_2NH_2	--->	*ccon*	+	$N.HNH_2$	1.76	0.23	1.37
cconj	+	NH_3	--->	*ccon*	+	$N.H_2$	1.36	0.44	1.64
cconj	+	CH_3CH_2OH	--->	*ccon*	+	$CH_3C.HOH$	0.12	-0.39	1.54
						Average	**1.97**	**0.95**	**2.18**
						Bond Energy CH_3CONH----H	**112.17**	**111.19**	**112.42**
		$CH_3CONHCH_3$ system ***cjcocc***							
cjconc	+	CH_3OH	--->	*cconc*	+	$C.H_2OH$	-7.51	-7.34	-7.42
cjconc	+	CH_3NH_2	--->	*cconc*	+	$C.H_2NH_2$	-9.20	-9.28	-8.68
cjconc	+	CH_3CHO	--->	*cconc*	+	$C.H_2CHO$	-9.18	-9.35	-9.26
cjconc	+	$CH_3CH_2CH_3$	--->	*cconc*	+	$CH_3C.HCH_3$	-8.35	-8.75	-8.78
						Average	**-8.56**	**-8.68**	**-8.54**
						Bond Energy H---$CH_2CONHCH_3$	**100.08**	**99.96**	**100.10**

Table 1.6 (Continued)

Work Reactions Radicals Corresponding to H Atom Loss							**$\Delta_fH^o(298)$ kcal mol^{-1}**		
							B3LYP		**CBS-QB3**
							6-31G(d,p)	**6-31G(2d,2p)**	
			cconjc						
cconj	+	CH_3NH_2	--->	*ccon*	+	$CH_3N.H$	-1.80	-1.91	-1.26
cconj	+	NH_2NH_2	--->	*ccon*	+	$N.HNH_2$	-4.50	-5.19	-4.05
cconj	+	NH_3	--->	*ccon*	+	$N.H_2$	-4.90	-4.98	-3.78
cconj	+	CH_3CH_2OH	--->	*ccon*	+	$CH_3C.HOH$	-6.14	-5.82	-3.87
						Average	**-4.34**	**-4.47**	**-3.24**
						Bond Energy $CH_3CON(---H)CH_3$	**104.30**	**104.17**	**105.40**
			cconcj						
cconcj	+	CH_3OH	--->	*cconc*	+	$C.H_2OH$	-13.69	-13.75	-13.61
cconcj	+	CH_3NH_2	--->	*cconc*	+	$C.H_2NH_2$	-15.38	-15.68	-14.87
cconcj	+	CH_3CHO	--->	*cconc*	+	$C.H_2CHO$	-15.36	-15.76	-15.46
cconcj	+	$CH_3CH_2CH_3$	--->	*cconc*	+	$CH_3C.HCH_3$	-14.53	-15.16	-14.97
						Average	**-14.74**	**-15.09**	**-14.73**
						Bond Energy $CH_3CONHC(---H)H_2$	**93.90**	**93.55**	**93.91**

[a] Reaction enthalpies include thermal correction and zero-point energy

Table 1.7 Summary of Formation Enthalpies (Δ_fH_{298}) and Bond Dissociation Energies (BDE) for Acetohydrazide, Acetamide and N-Methyl Acetamide and their Radicals[a] (in kcal mol^{-1}).

Molecules, Radicals and Selected Bonds	**$\Delta_fH^o_{298}$** (in **bold**) and **BDE** (*in italic)*		**CBS-QB3**	**Atomization**	
	B3LYP				
	6-31G(d,p)	**6-31G(2d,2p)**		**B3LYP/6-31G(d,p)**	**CBS-QB3**
$CH_3CONHNH_2$	**-28.97**	**-29.21**	**-27.55**	-26.92	-25.69
cjconn	**19.37**	**19.26**	**19.48**	17.95	21.24
(H---)$CH_2CONHNH_2$	*100.04*	*99.94*	*100.16*		
cconjn	**-2.27**	**-2.05**	**-1.93**	-4.98	0.35
CH_3CON(---H)NH_2	*78.41*	*78.63*	*78.75*		
cconnj	**1.68**	**1.19**	**1.88**	-1.03	4.16
CH_3CONHN(---H)H	*82.36*	*81.87*	*82.56*		
CH_3CONH_2	**-58.54**	**-57.65**	**-58.21**	-56.85	-56.32
cjcon	**-9.48**	**-10.26**	**-10.18**	-11.26	-9.49
(H---)CH_2CONH_2	*100.76*	*99.98*	*100.06*		
cconj	**1.97**	**0.95**	**2.18**	-1.15	3.49
CH_3CON(---H)H	*112.17*	*111.19*	*112.42*		
$CH_3CONHCH_3$	**-56.20**	**-56.93**	**-56.49**	-55.90	-54.00
cjconc	**-8.56**	**-8.68**	**-8.54**	-10.99	-7.12
(H---)$CH_2CONHCH_3$	*100.08*	*99.96*	*100.10*		
cconjc	**-4.34**	**-4.47**	**-3.24**	-8.06	-1.19
CH_3CON(---H)CH_3	*104.30*	*104.17*	*105.40*		
cconcj	**-14.74**	**-15.09**	**-14.73**	-17.17	-13.31
CH_3CONHC(---H)H_2	*93.90*	*93.55*	*93.91*		

[a] Radicals are represented by abbreviated formulas, for simplicity; j represents a radical site.

1.4.7 Internal Rotation Potentials

Energy profiles for internal rotations about the C—C=O, O=C—N, N—C and N—N bonds in the Acetohydrazide, Acetamide and N-Methyl Acetamide were calculated in order to determine the lowest energy configurations, energies of the rotational conformers, and to identify the interconversion barriers between isomers. Torsional potentials were used to evaluate contributions to the entropy and heat capacity values when there were low barriers (less than 3.5 kcal mol^{-1}) and internal rotation occurred.

The total energies as a function of the corresponding dihedral angles were computed at the B3LYP/6-31G(d,p) level of theory by scanning the torsion angles between 0° and 360° in steps of 15°, while all remaining coordinates were fully optimized. All potentials were rescanned when a lower energy conformer, relative to the initial low-energy conformer was found. The total energy of the corresponding most stable molecular conformer was arbitrarily set to zero and used as a reference point to plot the potential barriers. The resulting potential energy barriers for internal rotations in the stable nonradical and radical molecules are shown in Figs. 1.3.1 – 1.37. Dihedral angles obtained for the optimized lowest energy structures are shown in parenthesis.

The study of amide C—N rotation barriers is important for reasons other than finding the lowest energy conformer as the amide C—N bonds make up protein backbones. The preferred amide conformations play an important role in enzyme structure and the barrier to rotation has an effect on the rigidity of that structure. The rigidity of an enzyme's structure can affect its selectivity in binding substrates.

The CH_3-C=O-NH-NH_2 rotor is illustrated in Fig 1.3.1 for both the CH_3-C=O-N(-H)----NH_2 (H_{10}-N_9---N_7-H_8) and CH_3-C(=O)----NH-NH_2 (H_8-N_7----C_5-O_6) systems with barriers at 7.82 and 20.66 kcal mol^{-1} respectively. The CH_3-C(=O)----NH-CH_3 (H_8-N_7----C_5-O_6) rotor which shows a two fold symmetry with barrier at 21.7 kcal mol^{-1}.

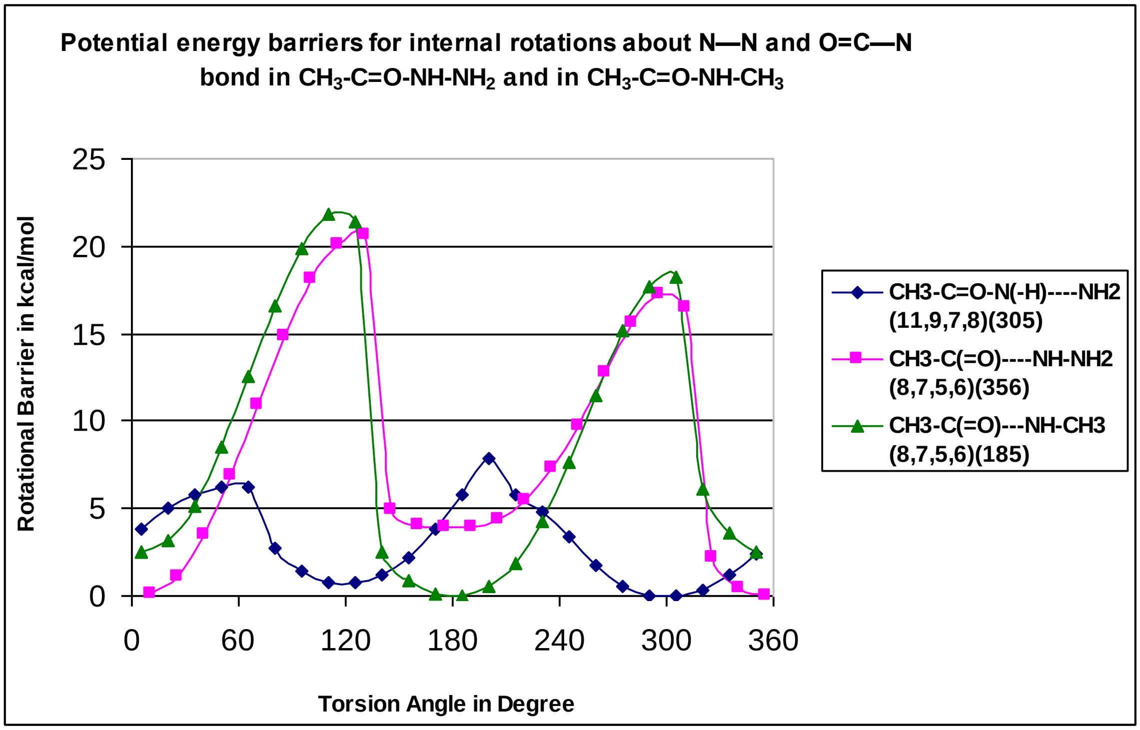


Figure 1.3.1 Potential energy barriers for internal rotations about N—N and O=C—N bond in CH_3-C=O-NH-NH_2 and in CH_3-C=O-NH-CH_3

The C—N rotor for the radical C•H$_2$-C(=O)---NH$_2$ (H$_7$-N$_6$---C$_4$-O$_5$ is 15.97 kcal mol^{-1}) and much higher to the value of its parent CH$_3$-C(=O)----NH$_2$ (H$_8$-N$_7$---C$_5$-O$_6$ = 18.66 kcal mol^{-1}). And according to Jasien et al.[12] based upon the current (**DZ + d/SCF**) calculations, the 0 K rotational barrier for acetamide between C—N bond is predicted to be 12.5 kcal mol^{-1}.

The two protons attached to N in Acetamide are inequivalent at low temperatures but become averaged by C—N rotation at higher temperatures. Typical bond rotation barriers for amides in solution are experimentally determined by NMR to be between 17 and 22 kcal/mol. However, the acetamide enolate, [CH$_2$CONH$_2$]$^-$, has a much lower barrier; according to recent NMR experiments, the enolate has free rotation at all accessible temperatures[22].

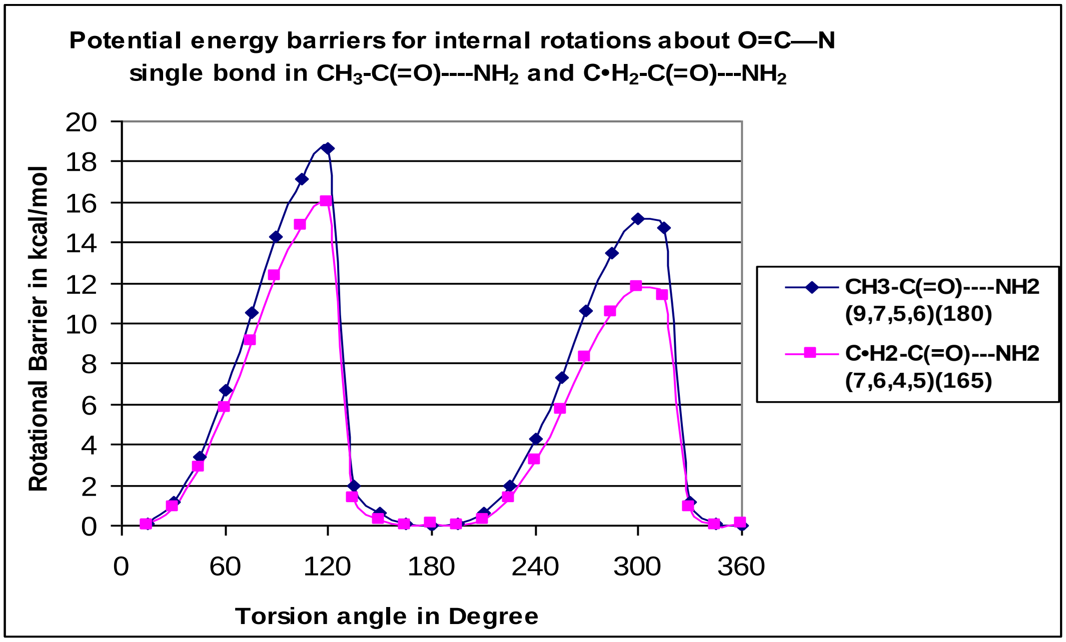


Figure 1.3.2 Potential energy barriers for internal rotations about O=C—N single bond in CH$_3$-C(=O)----NH$_2$ and C•H$_2$-C(=O)---NH$_2$

The C—C=O rotor for the CH_3----C(=O)-NH_2 (O_6-C_5---C_1-H_2) has very less barrier than O=C—N which shows three fold symmetry at 0.08 kcal mol^{-1}.

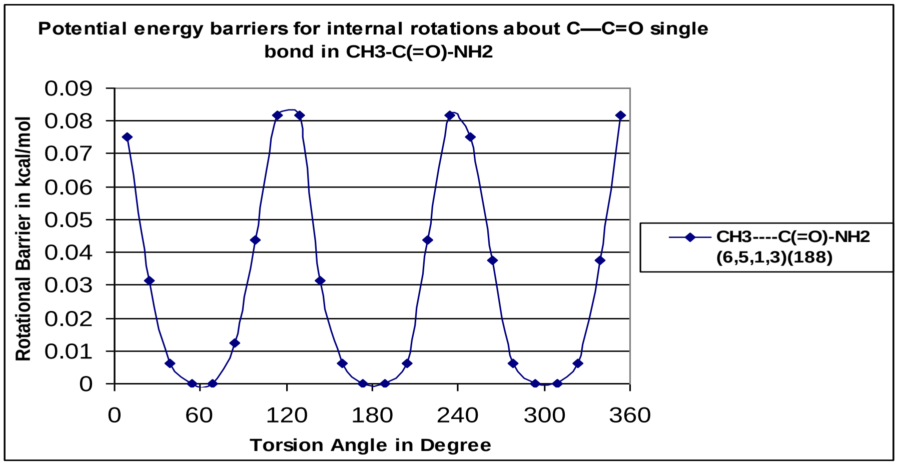


Figure 1.3.3 Potential energy barriers for internal rotations about C—C=O single bond in CH_3-C(=O)-NH_2

The CH_3-C=O-HN---CH_3 rotor is illustrated in Fig 1.3.4 which shows a three fold symmetry with barrier at 0.24 kcal mol^{-1}.

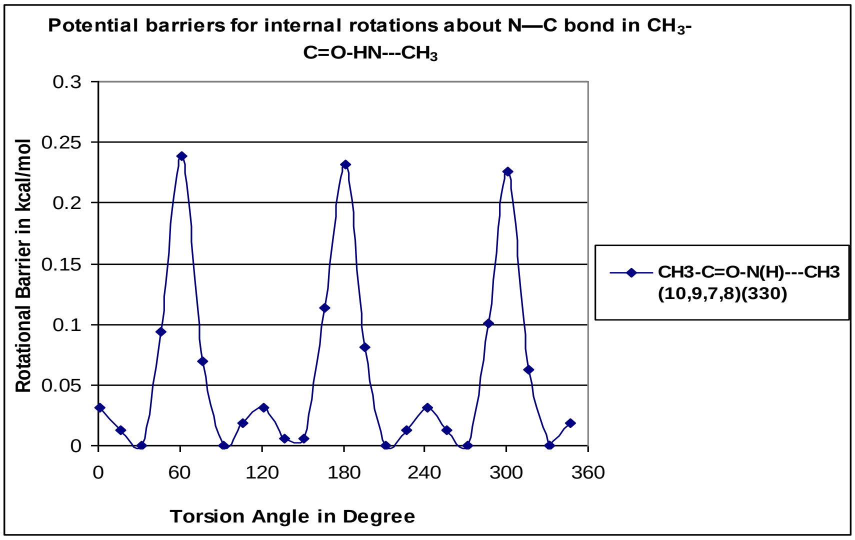


Figure 1.3.4 Potential barriers for internal rotations about N—C bond in CH_3-C=O-HN---CH_3

Potential barriers for internal rotations about N•---N bond in radical CH_3-C=ON•----NH_2 which shows a two fold symmetry with barrier at 14.6 kcal mol^{-1}.

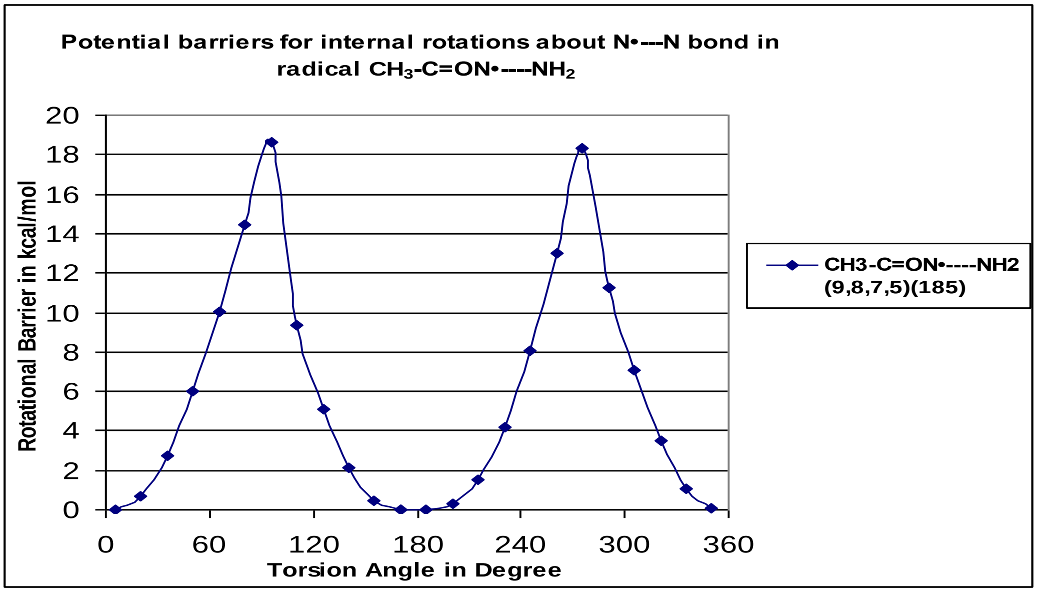


Figure 1.3.5 **Potential barriers for internal rotations about N•---N bond in radical CH_3-C=ON•----NH_2**

The C•H_2-C(=O)NH_2 rotor is illustrated in Fig 1.3.6 for both the C•H_2-C(=O)---NH_2 (H_7-N_6---C_4-O_5) and C•H_2---C(=O)NH_2 (O_5-C_4----C_1-H_2) systems with great difference in barriers at 16.0 and 6.6 kcal mol^{-1} respectively but with same two fold symmetry.

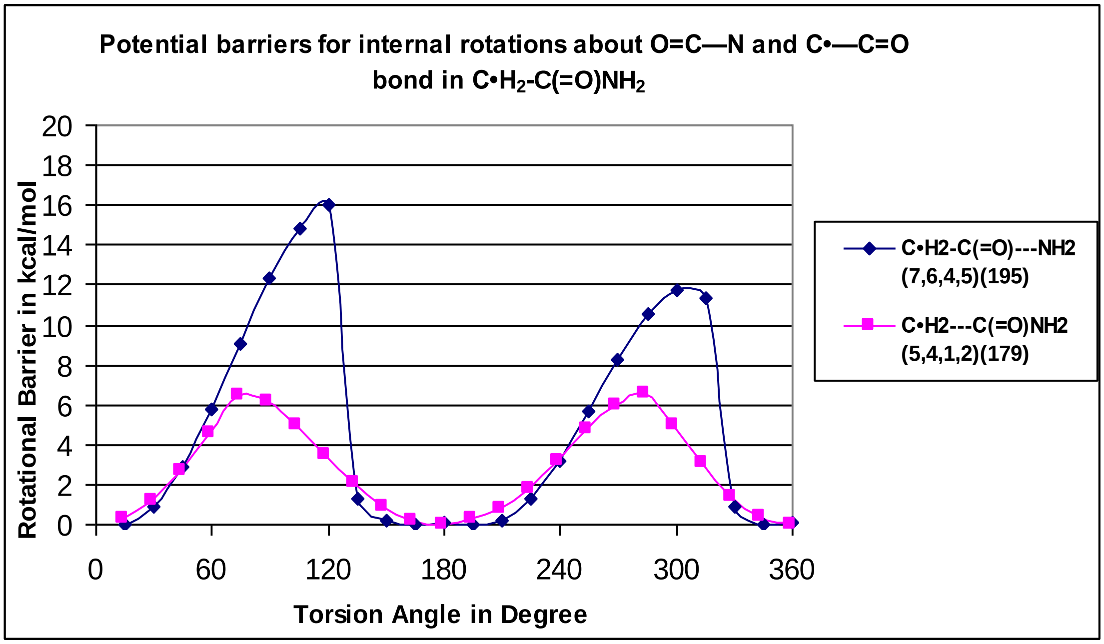


Figure 1.3.6 Potential barriers for internal rotations about O=C—N and C•—C=O bond in C•H_2-C(=O)NH_2

The CH_3-C(=O)N•---CH_3 (H_9-C_8----N_7-C_5) and CH_3-C(=O)N---C•H_2 (H_{10}-C_9----N_7-H_8) rotor is illustrated in Fig 1.3.7 and there is significant difference in their internal rotor barriers. CH_3-C(=O)N•---CH_3 shows three fold symmetry extremely low at 0.7 kcal mol^{-1} and CH_3-C(=O)N---C•H_2 shows two fold symmetry at 8.7 kcal mol^{-1} barrier.

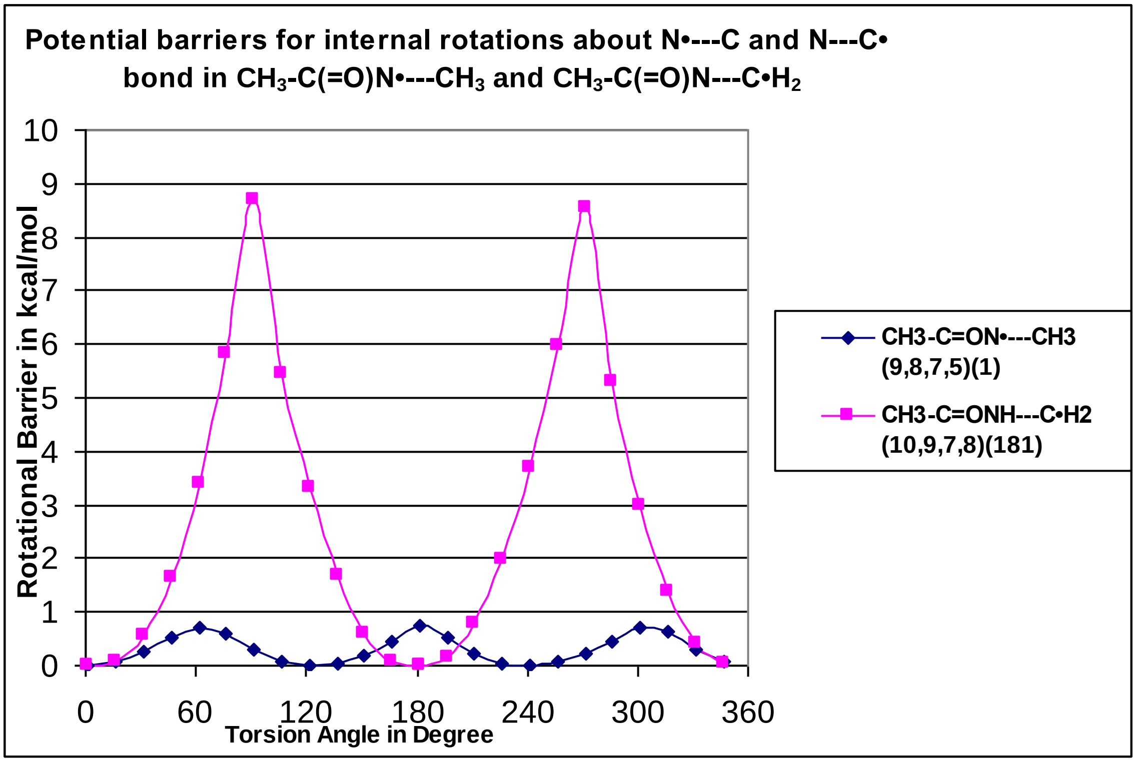


Figure 1.3.7 **Potential barriers for internal rotations about N•---C and N---C• bond in CH_3-C(=O)N•---CH_3 and CH_3-C(=O)N---C•H_2**

1.4.8 Entropy and Heat Capacity Data

The entropy and heat capacity data for the parent molecules and their radicals as a function of temperature were determined from the optimized structures, moments of inertia, vibrational frequencies, symmetries, the known mass of the molecules and internal rotor contributions when barriers were low. The calculations use standard formulas from statistical mechanics for the contributions of translation, external rotation and vibrations[23, 24]. Contributions to the entropy and the heat capacity from translation, vibrations and external rotation are calculated using the “SMCPS “program. This program utilizes the rigid-harmonic oscillator approximation from the optimized structures obtained at B3LYP/6-31G (d, p) level. The number of optical isomers and the spin degeneracy of unpaired electrons are also incorporated for calculation of *S*°298.

Contributions from hindered internal rotors to S°298 and Cp° (T) are determined using “VIBIR” program. This program utilizes the method of Pitzer and Gwinn[25, 26] the potential barriers, foldness and moments of inertia from the internal rotor analysis. The moments of inertia were calculated. The rotors with a barrier value greater than 3.5 kcal mol^{-1} were treated as torsion vibrations. The internal rotor data was combined with the S° (T) and Cp° (T) data from frequency, mass, moment of inertia; symmetry and electronic degeneracy from our statistical mechanics program SMCPS [27].

Table 1.8 Ideal Gas-phase Thermodynamic Property *vs.* Temperature $^{a, b}$

T(K)	$CH_3CONHNH_2$		CH_3CONH_2		$CH_3CONHCH_3$	
	Cp^{O} (T)	S^{O}(T) (6)	Cp^{O} (T)	S^{O}(T) (6)	Cp^{O} (T)	S^{O}(T) (9)
1	7.95	15.46	7.95	13.26	7.95	14.68
51	8.88	46.89	8.83	44.69	8.53	45.93
101	10.85	53.62	9.84	51.14	10.16	52.33
151	13.15	58.44	11.16	55.35	12.07	56.80
201	15.61	62.56	12.87	58.79	14.24	60.56
251	18.10	66.30	14.72	61.85	16.57	63.97
298	21.58	69.68	17.54	64.59	21.07	67.08
400	26.42	76.39	21.31	69.98	26.22	73.37
500	30.65	82.50	24.61	74.87	30.96	79.27
600	34.25	88.22	27.43	79.42	35.12	84.91
700	36.28	93.57	28.83	83.68	36.68	90.28
800	39.88	98.58	31.88	87.66	41.78	95.38
900	41.11	103.29	32.66	91.40	42.42	100.21
1000	44.05	107.72	35.21	94.92	46.74	104.79
1100	44.75	111.90	35.58	98.24	46.73	109.15
1200	46.24	115.85	36.77	101.38	48.48	113.29
1300	47.54	119.60	37.82	104.37	50.01	117.23
1400	48.69	123.17	38.75	107.20	51.34	120.98
1500	50.70	126.56	40.56	109.90	54.50	124.56
2000	53.24	141.38	42.45	121.71	56.54	140.26
2500	55.24	153.49	44.09	131.37	58.79	153.14
3000	56.46	163.67	45.09	139.51	60.13	163.98
3500	57.24	172.44	45.73	146.51	60.99	173.32
4000	57.76	180.11	46.16	152.64	61.57	181.50
4500	58.14	186.94	46.47	158.10	61.98	188.78
5000	58.41	193.08	46.70	163.00	62.28	195.32

Table 1.8 (Continued)

T(K)	***cjconn***		***cconjn***		***cconnj***	
	Cp^{O} (T)	**S^{O}(T) (4)**	**Cp^{O} (T)**	**S^{O}(T) (6)**	**Cp^{O} (T)**	**S^{O}(T) (3)**
1	7.95	17.47	7.95	16.52	7.95	18.04
51	9.56	49.62	8.90	47.94	8.20	49.18
101	11.60	56.80	10.98	54.73	9.84	55.31
151	14.39	62.01	13.16	59.59	12.07	59.70
201	17.27	66.54	15.37	63.67	14.49	63.50
251	20.00	70.68	17.57	67.33	16.91	66.99
298	22.46	74.40	21.53	70.59	20.28	70.15
400	27.09	81.67	25.64	76.99	24.79	76.43
500	30.85	88.12	29.27	82.76	28.66	82.15
600	33.91	94.02	32.37	88.12	31.92	87.47
700	36.42	99.43	33.74	93.11	33.63	92.44
800	38.53	104.43	37.22	97.76	36.95	97.08
900	40.34	109.07	37.97	102.11	37.92	101.43
1000	41.91	113.40	40.79	106.20	40.63	105.51
1100	43.28	117.46	41.12	110.04	41.11	109.35
1200	44.49	121.27	42.40	113.67	42.40	112.98
1300	45.55	124.87	43.51	117.11	43.52	116.42
1400	46.49	128.28	44.48	120.37	44.51	119.68
1500	47.32	131.52	46.40	123.46	46.37	122.78
2000	50.25	145.56	48.33	136.95	48.36	136.28
2500	51.93	156.97	50.01	147.93	50.04	147.26
3000	52.95	166.53	51.02	157.14	51.05	156.48
3500	53.61	174.75	51.67	165.06	51.70	164.40
4000	54.06	181.93	52.11	171.99	52.13	171.33
4500	54.38	188.32	52.42	178.14	52.44	177.49
5000	54.61	194.06	52.65	183.68	52.66	183.03

Table 1.8 (Continued)

T(K)	*cjcon*		*cconj*		*cjconc*		*Cconjc*		*cconcj*	
	Cp(T)	**S^{O}(T)(4)**	**Cp(T)**	**S^{O}(T)(3)**	**Cp(T)**	**S^{O}(T)(6)**	**Cp(T)**	**S^{O}(T)(9)**	**Cp(T)**	**S^{O}(T)(6)**
1	7.95	15.21	7.95	15.81	7.95	16.68	7.95	15.86	7.95	16.70
51	8.03	46.32	7.95	46.91	8.76	48.04	8.62	47.15	9.37	48.41
101	9.42	52.21	8.39	52.50	10.95	54.74	10.27	53.62	11.97	55.68
151	11.77	56.46	9.78	56.13	13.53	59.66	12.06	58.11	14.58	61.02
201	14.20	60.17	11.55	59.18	16.14	63.90	13.97	61.84	17.07	65.55
251	16.46	63.58	13.40	61.95	18.69	67.77	16.06	65.17	19.51	69.62
298	18.43	66.64	16.18	64.45	22.12	71.25	21.37	68.17	22.91	73.24
400	22.02	72.58	19.76	69.42	26.99	78.14	25.83	74.20	27.58	80.31
500	24.85	77.80	22.80	73.94	31.22	84.39	29.99	79.81	31.65	86.67
600	27.12	82.53	25.33	78.14	34.81	90.22	33.63	85.15	35.13	92.57
700	28.99	86.85	26.44	82.05	36.84	95.66	34.45	90.20	37.06	98.04
800	30.56	90.82	29.21	85.69	40.43	100.74	39.43	94.98	40.59	103.15
900	31.91	94.50	29.73	89.10	41.65	105.51	39.55	99.49	41.76	107.94
1000	33.09	97.92	32.04	92.30	44.58	110.00	43.74	103.76	44.65	112.43
1100	34.13	101.12	32.18	95.31	45.27	114.23	43.34	107.81	45.31	116.67
1200	35.04	104.13	33.17	98.15	46.73	118.23	44.86	111.64	46.75	120.67
1300	35.85	106.96	34.03	100.84	48.01	122.02	46.18	115.28	48.02	124.46
1400	36.57	109.65	34.78	103.39	49.14	125.61	47.33	118.74	49.14	128.06
1500	37.21	112.19	36.43	105.81	51.12	129.04	50.40	122.04	51.11	131.48
2000	39.48	123.23	37.72	116.34	53.55	143.97	51.76	136.46	53.53	146.41
2500	40.79	132.19	39.00	124.91	55.47	156.14	53.65	148.22	55.46	158.57
3000	41.60	139.70	39.76	132.09	56.63	166.36	54.77	158.11	56.62	168.79
3500	42.12	146.16	40.25	138.26	57.37	175.14	55.49	166.61	57.36	177.58
4000	42.47	151.80	40.58	143.65	57.87	182.84	55.97	174.05	57.86	185.27
4500	42.72	156.82	40.81	148.45	58.22	189.67	56.30	180.66	58.21	192.10
5000	42.90	161.33	40.98	152.75	58.48	195.82	56.55	186.61	58.47	198.25

[a] Thermodynamic properties are referred to standard state of an ideal gas at 1 atm. S°(T) and Cp° (T) are in cal mol^{-1} K^{-1}

[b] Symmetry numbers used for calculation of S°(T) are shown in color.

1.5 Conclusions

Thermochemical properties are presented for Acetic Acid Hydrazide, Acetamide, N-Methyl Acetamide and radicals that result from loss of H atoms from the carbons and the nitrogen atom. Enthalpies from all the work reactions and each of the calculation methods are in reasonable good agreement suggesting the B3LYP DFT calculations in conjunction with the work reactions used here, are acceptable methods for larger hydrazide and amides. C—H bond energy values for the radicals $C{\bullet}H_2\text{-}C{=}ONHNH_2$, $C{\bullet}H_2\text{-}C{=}ONH_2$ and $C{\bullet}H_2\text{-}C{=}ONHCH_3$ from the B3LYP/6-31G (d,p), B3LYP/6-31G (2d,2p) and CBS-QB3 levels of calculation are 100.0, 99.9, 100.2 and 100.8, 100.0, 100.1 and 100.1, 100.0, 100.1 kcal mol^{-1} respectively. The N—H bond in the Acetohydrazide is weak, at 78.8 kcal mol^{-1} but strong in N-Methyl Acetamide, is 105.4 kcal mol^{-1}. The N—HH bond energies for the formation of the radicals $CH_3\text{-}C{=}ONHN{\bullet}H$ and $CH_3\text{-}C{=}ON{\bullet}H$ from the parent molecules are also similar across the different B3LYP basis sets and CBS-QB3 level of calculations ($CH_3\text{-}C{=}ONHN{\bullet}H$ =82.4, 81.9, 82.6; $CH_3\text{-}C{=}ON{\bullet}H$ = 112.2, 111.2, 112.4 kcal mol^{-1}). The computed enthalpies of formation via isodesmic work reactions and bond dissociation energies for Acetohydrazide, Acetamide and N-Methyl Acetamide are in satisfactory agreement with the limited experimental data available.

CHAPTER 2

ENTHALPIES AND BOND DISSOCIATION ENERGIES OF CYCLIC ALKYL ETHERS: OXIRANES, OXETANES AND OXOLANES

2.1 Objective

Cyclic ethers are valuable and widely used starting reagents in organic synthesis and are often used as solvent. Three to six member ether rings are common product from the reactions or hydrocarbon radicals with triplet dioxygen ($^3O_2$) in low to moderate temperature oxidation and combustion reaction systems and in the atmospheric chemistry of small hydrocarbons. It is of value to determine the C—H bond energies on these ethers in order to understand their reactions.

Structures, enthalpy ($\Delta_f H^o_{298}$), entropy (S^o_{298}), heat capacity (C_p^o (T)) are determined for a series of cyclic alkyl ethers and their carbon centered radicals using the density functional B3LYP calculations. Enthalpies of formation ($\Delta_f H^o_{298}$) are determined at the B3LYP/6-31G(d,p) and B3LYP /6-31G(2d,2p) levels using several work reactions for each species. Entropy (S^o) and heat capacity (C_p^o (T)) values from vibration, translational, and external rotational contributions are calculated using the rigid-rotor-harmonic-oscillator approximation based on the vibration frequencies and structures obtained from the density functional studies. Calculated enthalpies of formation for a series of ten cyclic and substituted cyclic ethers are in good agreement with literature values and bond energies are reported secondary and tertiary carbon sites for 3 to 5 member ring cyclic ethers. Knowledge of these properties allows combustion and atmospheric scientists to estimate reaction paths and kinetics for these intermediates.

2.2 Background Information

Epoxides are also important compounds in the field of synthetic organic chemistry, and recent advances have provided the methodology to both synthesize and transform epoxides with high stereochemical and regiochemical selectivity. The importance of epoxides as synthetic intermediates has prompted the need for a better understanding of the mechanisms underlying these selectivities[40].

Epoxides and other cyclic ethers and lactones are formed in combustion (oxidation) of hydrocarbons at temperatures up to1200 K from hydrocarbon radical reactions with molecular oxygen. The initial reaction forms a peroxy radical with typically 25 to 38 kcal mol^{-1} of initial chemical activation energy. The energized or stabilized peroxy radical can undergo an intramolecular hydrogen atom transfer reaction forming an alkyl radical-hydroperoxide. The formed alkyl radical has a low reaction barrier for addition to the oxygen atom adjacent to the carbon (carbon-oxygen bond formation). This forms the cyclic ether and cleaves the weak (45 kcal mol^{-1}) RO--OH bond. Formation of the stronger C—O bond is exothermic and the accompanying generation of OH radical resulting in propagation and sometimes in generation of multi radical products, resulting in chain branching. This peroxy chemistry is critical to ignition in the developing HCCI (homogeneous charge compression ignition) engines, which have the significant advantage of low NOx emissions[39]. The thermochemistry of the cyclic ether intermediates formed in this oxidation process is important to understanding their further reactions in the combustion systems.

Experimental data of Jones et al[52] show that the vapor-phase oxidation of C_6-C_{16} hydrocarbons yields 11-25 wt % heterocyclic oxygenates as products. From *n*-hexane, this cyclic ether fraction contained 59% oxolanes (five-membered rings, also known as THF), 35% contained 68% oxolanes, 26% oxetanes, and 6% oxiranes. The moderate-temperature (580-600 K) oxidation of primary reference fuels *n*-heptane and isooctane (2,2,4-trimethylpentane) with air in a jet-stirred-flow reactor[53, 54] at pressures as high as 40 bar yielded, respectively, 10 and 60 mol % cyclic ethers together with aldehydes and olefins. The 2-methyl-5-ethyloxolane and 2,2,4,4-tetramethyloxolane were the most abundant cyclic ethers from *n*-heptane and isooctane, respectively.

Ethers are widely used as solvents and because of the ease with which they form peroxides, they are extremely hazardous. Relatively few experiments to determine the peroxide production of ethers following exposure to air have been reported[42, 43]. Therefore due to the paucity of data, it would be very useful to understand and be able to predict the autoxidative ability of ethers.

Peroxides and peroxide-forming substances are amongst the most common hazardous chemicals handled routinely in the laboratory. Peroxides are hazardous due to their extreme sensitivity to shock, heat, friction, and their action as strong oxidizing and reducing agents. In addition, many peroxides are more sensitive to shock than even TNT (trinitrotoluene) and they are highly flammable[41].

Agapito et al. studied Bond dissociation enthalpies on (tetrahydrofuran and 1,4-dioxane) and postulated that hyperconjugation and ring strain are the main factors that should be considered to understand their thermodynamic stabilisation. The C—H bond dissociation enthalpies of THF (leading to the β-furanyl) and 1,4-dioxane were 98.0 and 91.1 kcal mol^{-1} respectively at the CBS-Q level[35].

Hoshino et al. studied cyclopentyl - methyl ether and suggested that the instability of the cyclopentyl formed radical, relative to the parent molecule, is caused by the bond angle strain of the cyclopentyl ring. The bond dissociation energy of the C–H bond at the α-position of ether oxygen in cyclopentyl methyl ether (CPME) has been evaluated theoretically to be 94.0 kcal/mol by using an isodesmic reaction method[42].

Experimental BDEs of the C–H bond are available for a large number of organic compounds[45-48]. For ethers, values for only 14 compounds have been reported in the literature[48]. Examination of the trends in BDE of ethers requires access to a larger, more diverse database. Due to the lack of experimental values, theoretical methods have been adopted to evaluate BDEs. A number of quantum chemistry methods have been assessed to find the optimal compromise between computational speed and accuracy[49-51].

Thermochemical parameters are important in evaluating reaction paths and kinetic processes in the atmosphere and in combustion environments. These values also provide a base for estimation of equilibria and energies for simple dissociation and the formation of radical by hydrogen abstraction reactions.

2.3 Computational Methods

All calculations were performed using the Gaussian 03 program[14]. All structures were drawn using the GaussView application within Gaussian 03. Geometries, vibration frequencies, moments of inertia and internal rotor barriers for molecules and related radical species were optimized at the B3LYP/6-31G(d,p) and B3LYP/6-31G(2d,2p) level of theory[15, 16]. There is a general consensus that B3LYP methods provide excellent low-cost performance for structure optimizations[55]. The B3LYP/6-31G level of theory is one of the most reliable computational method for optimization geometries of small polar compounds[56] as well as being widely used for the calculation of radical species[57, 58].

Standard enthalpies of formation for stable species are calculated using the total energies at B3LYP/6-31G(d,p), B3LYP/6-31G(2d,2p) levels with work reactions that are isodesmic in most cases. Isodesmic reactions conserve the number and type of bonds on both sides of an equation. The use of a work reaction with similar bonding on both sides of an equation results in a cancellation of calculation error and improves the accuracy for energy analysis[17]. The reported enthalpy values can be compared with the known enthalpies of several molecules in the system to serve as a calibration on the thermochemistry.

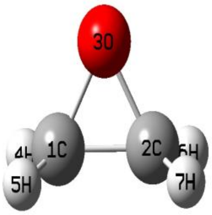
2.4 Result and Discussion

2.4.1 Enthalpies of Formation

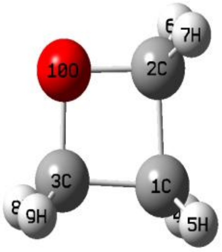
Enthalpies of formation ($\Delta H_f^o 298$) of the parent molecules have been determined using corresponding ΔHrxn (298) from the enthalpy of reaction in the isodesmic work reactions and calculated enthalpies of each species. The method of isodesmic reactions relies upon the similarity in bonding environment of the reactant and the products that leads to cancellation of systematic errors in the ab initio MO cancellation[49]. The structures of target molecules and an abbreviated nomenclature are presented in Scheme 1. The standard enthalpies of formation of the reference molecules at 298.15 K and the calculated $\Delta Hrxn^o 298$ are used to calculate the $\Delta_f Hrxn^o 298$ of the target molecule.

$$\Delta Hrxn^o 298 = \Sigma\ H_f \text{ products} - \Sigma\ H_f \text{ reactants}$$

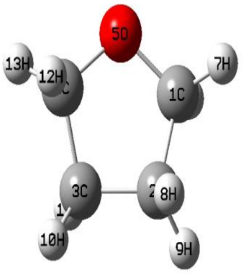
Where the two products and one reactant are the three reference molecules, we use the evaluated literature thermodynamic properties for the three reference species. The standard enthalpies of formation at 298.15 K of the reference species used in these reactions are summarized in Table 2.1



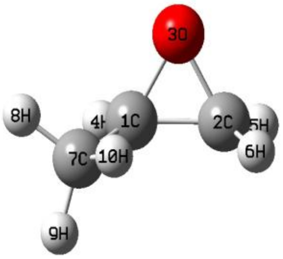
***Cy*occ,**
Oxirane



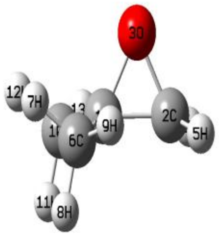
***Cy*occc,**
Oxetane



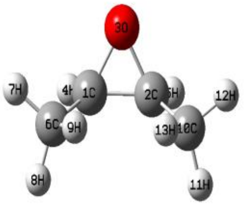
***Cy*occcc,**
Oxolane



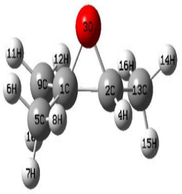
***Cy*oc[CH$_3$]c,**
2-methyl, oxirane



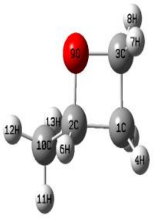
***Cy*oc[CH$_3$][CH$_3$]c,**
2-2, dimethyl
oxirane



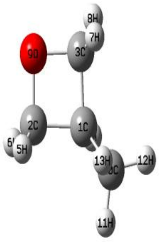
***Cy*oc[CH$_3$]c[CH$_3$],**
2-3, dimethyl
oxirane



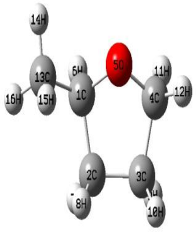
***Cy*oc[CH$_3$]**
[CH$_3$]c[CH$_3$],
2-2-3, trimethyl
oxirane



***Cy*oc[CH$_3$]cc,**
2-methyl, oxetane



***Cy*occ[CH$_3$]c,**
3-methyl, oxetane



***Cy*oc[CH$_3$]ccc,**
2-methyl, oxolane

Figure 2.1 Geometry of the lowest energy conformer of the parent molecules and abbreviated nomenclatures (see appendix C, Table C2.2-C2.11 for more details).

Table 2.1 The Standard Enthalpies of Formation at 298.15 K of Reference Species

Species	$\Delta_f H^\circ_{298}$ (kcal mol^{-1})	Source (Ref. No.)
CH_3OH	-49. ± 3.	18
$C{\cdot}H_2OH$	-2 ± 1.	18
$CH_3CH_2CH_3$	-25.02 ± 0.12	18
$CH_3C{\cdot}HCH_3$	22. ± 0.5	18
CH_3CHO	-40 ± 0.35	18
$C{\cdot}H_2CHO$	3.55 ± 1.00	19
$CH_3CH_2\ CH_2CH_3$	-25.02 ± 0.12	18
CH_3OCH_3	-43.99	18
$CH_3CH_2OCH_3$	-51.73	18
Cyclopropane	12.74	18
Cyclobutane	-30.03	18
Oxirane	-12.58 ± 0.15	18
Oxirane, 2-methyl-	-22.63 ± 0.15	18
Oxetane	-19.25 ± 0.15	18
Oxolane	-44.03 ± 0.17	18
Oxetane, 2-methyl-	-30.67	39
Oxetane, 3-methyl-	-27.21	39
Oxirane, 2-dimethyl-	-33.89	39
Oxolane, 2-methyl-	-54.58	39
Oxirane, 2,3-dimethyl-	-32.6	40
Oxirane, 2,3-trimethyl-	-42.11	40

As an example, the following equation is used to estimate $\Delta_f H^\circ_{298}$ for ***Cy***occ

$$(\text{Cyocc}) + (CH_3CH_2CH_3) \rightarrow (\text{Cyccc}) + (CH_3OCH_3)$$

$\Delta_f H^\circ_{298}$ (kcal mol^{-1}): Target -25.02 12.74 -43.99

The enthalpies of formation for oxirane, oxetane and oxolane (THF) for each of the reactions are shown in the Table 2.2 for the two levels of theory. There is good consistency with the B3LYP method for the $\Delta_f H^o 298$ values between the 6-31G (d,p) and 6-31G(2d,2p) basis sets, with all differences less than 1.3 kcal mol^{-1} for the oxirane, oxetane and oxolane and their corresponding radicals with or without alkyl substituent are even less than 0.72 kcal mol^{-1}.

The enthalpies of formation of the parent molecules, averaged over two work reactions for molecules Oxirane, Oxetane and Oxolane were evaluated as -12.6, -19.3 and -44.7 kcal mol^{-1} respectively (values are average of B3LYP/6-31G(d,p) and B3LYP/6-31G(2d,2p)). The enthalpy of formation of oxirane, oxetane and oxolanes agree with the literature values. A comparison of values of these parent compounds with literature is listed in Table 2.3 and shows very good agreement.

The three work reactions and calculated $\Delta_f H^o 298$ for use in determining the enthalpy of formation for each radical are shown in Table 2.4.

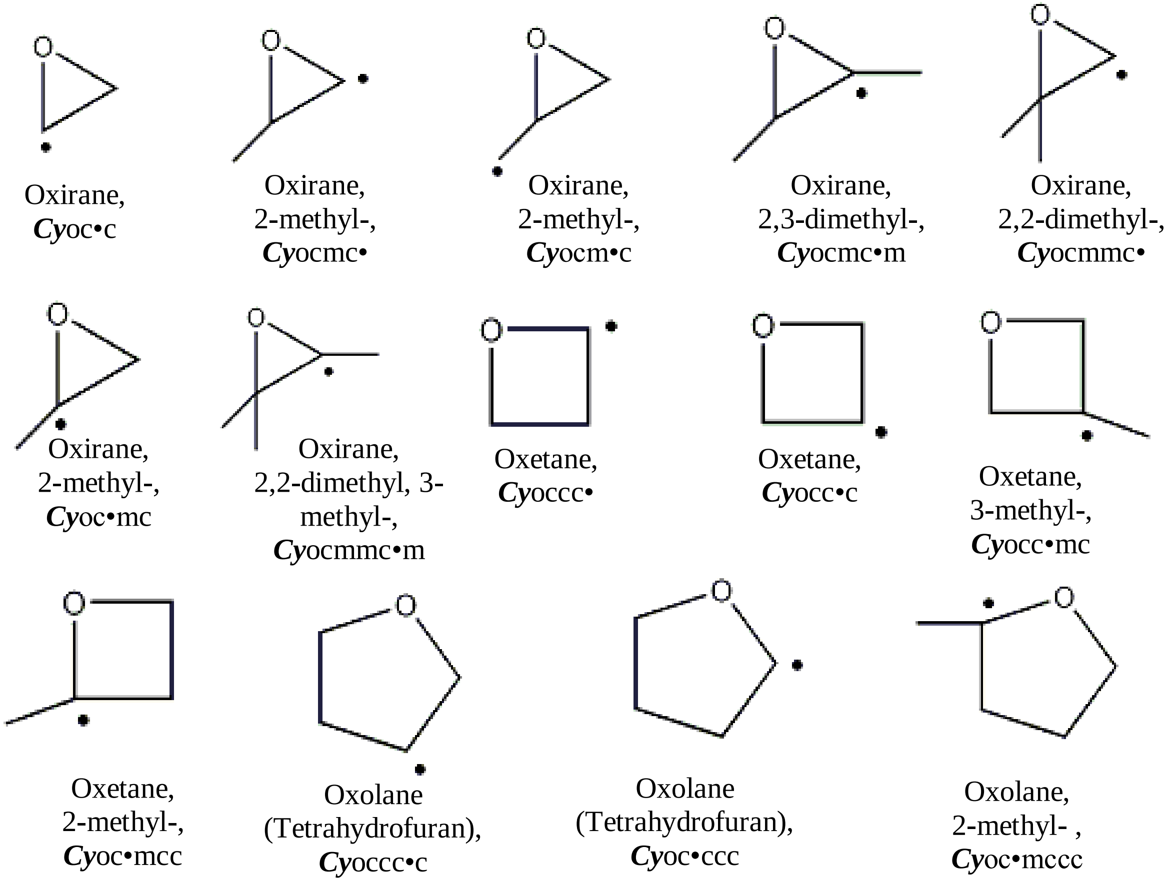
Table 2.2 Calculated Reaction Enthalpies at 298 K and Evaluated Enthalpies of Formation of Target Molecules[a]

Work Reactions							**$\Delta_f H^o$(298) kcal mol^{-1}**	
							B3LYP	
							6-31G(d,p)	**6-31G(2d,2p)**
				***Cy*(occ)**				
Cyocc)	+	ccc	--->	*Cy(ccc)*	+	coc	-12.76	-12.32
Cy(occ)	+	cccc	--->	*Cy(ccc)*	+	ccoc	-13.66	-11.71
						Average	**-13.21**	**-12.01**
				***Cy*(occc)**				
Cy(occc)	+	ccc	--->	*Cy(cccc)*	+	coc	-19.38	-19.13
Cy(occc)	+	cccc	--->	*Cy(cccc)*	+	ccoc	-20.28	-18.52
						Average	**-19.83**	**-18.82**
				***Cy*(occcc)**				
Cy(occcc)	+	ccc	--->	*Cy(ccccc)*	+	coc	-44.66	-44.68
Cy(occcc)	+	cccc	--->	*Cy(ccccc)*	+	ccoc	-45.56	-44.07
						Average	**-45.11**	**-44.37**

[a] Reaction enthalpies include thermal correction and zero-point energy.

Table 2.3 Comparison of Calculated Enthalpy of Formation of Parent Compounds with the Literature (Recommended Values are in Bold)

Species	Literature ($kcal mol^{-1}$)	This calculation ($kcal mol^{-1}$)
Oxirane, Cy(occ)	-12.58[18] -12.6[31] -12.61[32] -13.20[39]	**-12.61**
Oxetane, Cy(occc)	-19.25[18] -19.24[44] -19.65[39]	**-19.32**
Oxolane, Cy(occcc)	-44.03[18] -44.0[31] -44.58[39]	**-44.74**



m represents methyl group

Scheme 1. Target cyclic alkyl ethers with radical's sites and their structures and abbreviated nomenclature.

2.4.2 Bond Dissociation Energies

The relative stability of the radicals can be obtained by an examination of the BDE's of the C—H bonds. Stabilization of the radicals should be reflected in a lower BDE. Bond energies for the formation of radicals by loss of H atom reported at 298.15 K are calculated from the standard $\Delta_f H^o 298$ values of the parent molecules and of the radicals, obtained at B3LYP/6-31G(d,p) and B3LYP/6-31G(2d,2p) level. $\Delta_f H^o 298$ of 52.1 kcal mol^{-1} is used for H atom enthalpy.

Cy(occ)	→	***Cy***(oc•c)	+	H•	
-12.61		40.6		52.01	kcal mol^{-1}

$\Delta Hrxn = [40.6 + 52.1] – [-12.61] = 105.3$ kcal mol^{-1} = Bond energy

The recommended bond dissociation energies of oxirane,2-methyl (***Cy***oc•mc), oxitane, 2-methyl (***Cy***oc•mcc) and oxolane, 2-methyl (***Cy***oc•mccc) are 105.2 kcal mol^{-1}, 96.4 kcal mol^{-1} and 94.5 kcal mol^{-1}. The bond energies are decreasing as number central atoms in the ring increases, and this is due to strain in the rings.

Bond dissociation energies of secondary and tertiary carbon sites in three, four and five member rings (with or without alkyl substituent at different sites) are listed in Table 2.5.

Table 2.4 Reaction Enthalpies at 298 K for Radicals, Calculated Enthalpies of Formation and Bond Energy[a]

Work Reactions							**Δ_fH^o(298) kcal mol^{-1}**	
							B3LYP	
							6-31G(d,p)	**6-31G(2d,2p)**
			Cy(occ) **system**					
			Cy(oc•c)					
Cy(oc•c)	+	CH_3OH	--->	***Cy***(occ)	+	$C.H_2OH$	41.5	41.5
Cy(oc•c)	+	$CH_3C(=O)H$	--->	***Cy***(occ)	+	$C.H_2C(=O)H$	40.0	39.7
Cy(oc•c)	+	$CH_3CH_2CH_3$	--->	***Cy***(occ)	+	$CH_3C.HCH_3$	40.3	39.8
						Average	**40.6**	**40.3**
						Bond Energy ***Cy***(oc(---H)c)	*105.3*	*105.0*
			Cy(oc[CH_3]c) **system**					
			Cy(oc[C•H_2]c)					
Cy(oc[C•H_2]c)	+	CH_3OH	--->	***Cy***(oc[CH_3]c)	+	C•H_2OH	28.0	28.0
Cy(oc[C•H_2]c)	+	$CH_3C(=O)H$	--->	***Cy***(oc[CH_3]c)	+	C•H_2C(=O)H	26.5	26.1
Cy(oc[C•H_2]c)	+	$CH_3CH_2CH_3$	--->	***Cy***(oc[CH_3]c)	+	CH_3C•HCH_3	26.8	26.2
						Average	**27.1**	**26.7**
						Bond Energy ***Cy***(oc[C(---H)H_2]c)	*101.9*	*101.5*
			Cy(oc• [CH_3]c)					
Cy(oc•[CH_3]c)	+	CH_3OH	--->	***Cy***(oc[CH_3]c)	+	C•H_2OH	29.3	29.5
Cy(oc•[CH_3]c)	+	$CH_3C(=O)H$	--->	***Cy***(oc[CH_3]c)	+	C•H_2C(=O)H	27.8	27.7
Cy(oc•[CH_3]c)	+	$CH_3CH_2CH_3$	--->	***Cy***(oc[CH_3]c)	+	CH_3C•HCH_3	28.1	27.8
						Average	**28.4**	**28.3**
						Bond Energy ***Cy***(oc(---H)[CH_3]c)	*103.1*	*103.1*

Table 2.4 (Continued)

Work Reactions	$\Delta_f H^o(298)$ kcal mol^{-1}	
	B3LYP	
	6-31G(d,p)	**6-31G(2d,2p)**
Cy(oc [CH$_3$]c•)		
Cy(oc[CH$_3$]c•) + CH_3OH ---> ***Cy***(oc[CH$_3$]c) + C•H$_2$OH	31.1	31.1
Cy(oc[CH$_3$]c•) + $CH_3C(=O)H$ ---> ***Cy***(oc[CH$_3$]c) + C•H$_2$C(=O)H	29.6	29.3
Cy(oc[CH$_3$]c•) + $CH_3CH_2CH_3$ ---> ***Cy***(oc[CH$_3$]c) + CH$_3$C•HCH$_3$	30.0	29.4
Average	**30.2**	**30.0**
Bond Energy ***Cy***(oc [CH$_3$]c(---H))	*105.0*	*104.6*
Cy(occc) **system**		
Cy(occ•c)		
Cy(occ•c) + CH_3OH ---> ***Cy***(occc) + C•H$_2$OH	32.5	32.6
Cy(occ•c) + $CH_3C(=O)H$ ---> ***Cy***(occc) + C•H$_2$C(=O)H	30.9	30.8
Cy(occ•c) + $CH_3CH_2CH_3$ ---> ***Cy***(occc) + CH$_3$C•HCH$_3$	31.3	30.8
Average	**31.6**	**31.4**
Bond Energy ***Cy***(occ(---H)c)	*102.9*	*102.8*
Cy(occc•)		
Cy(occc•) + CH_3OH ---> ***Cy***(occc) + C•H$_2$OH	26.1	26.1
Cy(occc•) + $CH_3C(=O)H$ ---> ***Cy***(occc) + C•H$_2$C(=O)H	24.9	24.3
Cy(occc•) + $CH_3CH_2CH_3$ ---> ***Cy***(occc) + CH$_3$C•HCH$_3$	25.0	24.3
Average	**25.2**	**24.9**
Bond Energy ***Cy***(occc(---H))	*96.6*	*96.3*

Table 2.4 (Continued)

Work Reactions	**$\Delta_f H^o(298)$ kcal mol^{-1}**	
	B3LYP	
	6-31G(d,p)	**6-31G(2d,2p)**
Cy(oc[CH_3]cc) **system**		
Cy(oc•[CH_3]cc)		
Cy(oc• [CH_3]cc) + CH_3OH ---> ***Cy***(oc[CH_3]cc) + C•H_2OH	12.9	12.9
Cy(oc• [CH_3]cc) + $CH_3C(=O)H$ ---> ***Cy***(oc[CH_3]cc) + C•$H_2C(=O)H$	11.4	11.1
Cy(oc• [CH_3]cc) + $CH_3CH_2CH_3$ ---> ***Cy***(oc[CH_3]cc) + CH_3C•HCH_3	11.7	11.2
Average	**12.0**	**11.7**
Bond Energy ***Cy***(oc(---H)[CH_3]cc)	*94.8*	*94.9*
Cy(occ[CH_3]c) **system**		
Cy(occ• [CH_3]c)		
Cy(occ• [CH_3]c) + CH_3OH ---> ***Cy***(occ[CH_3]c) + C•H_2OH	20.9	20.9
Cy(occ• [CH_3]c) + $CH_3C(=O)H$ ---> ***Cy***(occ[CH_3]c) + C•$H_2C(=O)H$	19.3	19.1
Cy(occ• [CH_3]c) + $CH_3CH_2CH_3$ ---> ***Cy***(occ[CH_3]c) + CH_3C•HCH_3	19.8	19.1
Average	**20.0**	**19.7**
Bond Energy ***Cy***(occ(---H)[CH_3]c)	*99.3*	*99.0*

Table 2.4 (Continued)

Work Reactions							**$\Delta_f H^o(298)$ kcal mol^{-1}**	
							B3LYP	
							6-31G(d,p)	**6-31G(2d,2p)**
Cy(oc[CH_3]c[CH_3]) **system**								
Cy(oc[CH_3]c•[CH_3])								
Cy(oc[CH_3]c•[CH_3])	+	CH_3OH	--->	***Cy***(oc[CH_3]c[CH_3])	+	C•H_2OH	18.2	18.4
Cy(oc[CH_3]c•[CH_3])	+	CH_3C(=O)H	--->	***Cy***(oc[CH_3]c[CH_3])	+	C•H_2C(=O)H	16.7	16.5
Cy(oc[CH_3]c•[CH_3])	+	$CH_3CH_2CH_3$	--->	***Cy***(oc[CH_3]c[CH_3])	+	CH_3C•HCH_3	17.0	16.6
						Average	**17.3**	**17.2**
				Bond Energy ***Cy***(oc[CH_3]c(---H)[CH_3])			*102.0*	*101.9*
Cy(oc[CH_3][CH_3]c) **system**								
Cy(oc[CH_3] [CH_3]c•)								
Cy(oc[CH_3][CH_3]c•)	+	CH_3OH	--->	***Cy***(oc[CH_3][CH_3]c)	+	C•H_2OH	19.5	19.5
Cy(oc[CH_3][CH_3]c•)	+	CH_3C(=O)H	--->	***Cy***(oc[CH_3][CH_3]c)	+	C•H_2C(=O)H	18.0	17.6
Cy(oc[CH_3][CH_3]c•)	+	$CH_3CH_2CH_3$	--->	***Cy***(oc[CH_3][CH_3]c)	+	CH_3C•HCH_3	18.4	17.7
						Average	**18.6**	**18.2**
				Bond Energy ***Cy***(oc[CH_3] [CH_3]c(---H))			*104.6*	*104.2*

Table 2.4 (Continued)

Work Reactions	**$\Delta_f H^o(298)$ kcal mol^{-1}**	
	B3LYP	
	6-31G(d,p)	**6-31G(2d,2p)**
Cy(oc[CH_3][CH_3]c[CH_3]) **system**		
Cy(oc[CH_3][CH_3]c•[CH_3])		
Cy(oc[CH_3][CH_3]c•[CH_3]) + CH_3OH ---> ***Cy***(oc[CH_3][CH_3]c[CH_3]) + C•H_2OH	8.2	8.3
Cy(oc[CH_3][CH_3]c•[CH_3]) + $CH_3C(=O)H$ ---> ***Cy***(oc[CH_3][CH_3]c[CH_3]) + C•$H_2C(=O)H$	6.7	6.5
Cy(oc[CH_3][CH_3]c•[CH_3]) + $CH_3CH_2CH_3$ ---> ***Cy***(oc[CH_3][CH_3]c[CH_3]) + CH_3C•HCH_3	7.0	6.6
Average	**7.3**	**7.1**
Bond Energy ***Cy***(oc[CH_3][CH_3]c(---H)[CH_3])	*101.5*	*101.3*
Cy(occcc) **system**		
Cy(occc•c)		
Cy(occc•c) + CH_3OH ---> ***Cy***(occcc) + C•H_2OH	1.0	1.3
Cy(occc•c) + $CH_3C(=O)H$ ---> ***Cy***(occcc) + C•$H_2C(=O)H$	-0.5	-0.5
Cy(occc•c) + $CH_3CH_2CH_3$ ---> ***Cy***(occcc) + CH_3C•HCH_3	-0.2	-0.4
Average	**0.1**	**0.1**
Bond Energy ***Cy***(occc(---H)c)	*97.0*	*97.0*

Table 2.4 (Continued)

Work Reactions							**$\Delta_f H^o(298)$ kcal mol^{-1}**	
							B3LYP	
							6-31G(d,p)	**6-31G(2d,2p)**
Cy(occcc) **system**								
Cy(occcc•)								
Cy(occcc•)	+	CH_3OH	--->	***Cy***(occcc)	+	$C\bullet H_2OH$	-0.6	-0.6
Cy(occcc•)	+	$CH_3C(=O)H$	--->	***Cy***(occcc)	+	$C\bullet H_2C(=O)H$	-2.1	-2.5
Cy(occcc•)	+	$CH_3CH_2CH_3$	--->	***Cy***(occcc)	+	$CH_3C\bullet HCH_3$	-1.8	-2.4
						Average	**-1.5**	**-1.8**
						Bond Energy ***Cy***(occcc(---H))	*94.6*	*94.3*
Cy(oc[CH_3]ccc) **system**								
Cy(occc•c)								
Cy(oc•[CH_3]ccc)	+	CH_3OH	--->	***Cy***(o[CH_3]cccc)	+	$C\bullet H_2OH$	-12.8	-12.7
Cy(oc•[CH_3]ccc)	+	$CH_3C(=O)H$	--->	***Cy***(oc[CH_3]ccc)	+	$C\bullet H_2C(=O)H$	-13.6	-14.6
Cy(oc•[CH_3]ccc)	+	$CH_3CH_2CH_3$	--->	***Cy***(oc[CH_3]ccc)	+	$CH_3C\bullet HCH_3$	-13.3	-14.5
						Average	**-13.2**	**13.9**
						Bond Energy ***Cy***(occc(---H)c)	*93.5*	*92.7*

[a] Reaction enthalpies include thermal correction and zero-point energy

Table 2.5 Bond Dissociation Energies of Cyclic Alkyl Ethers with Nomenclature.

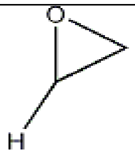
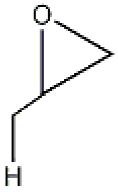
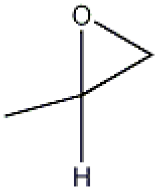
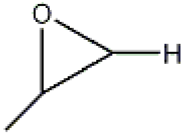
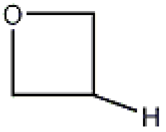
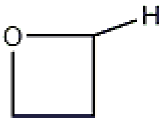
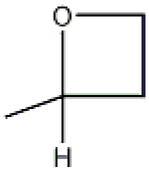
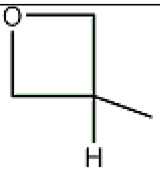
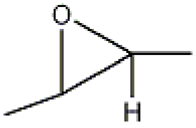
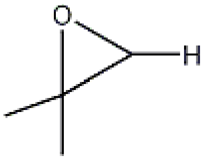
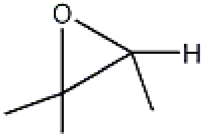
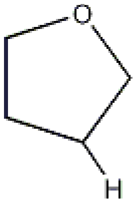
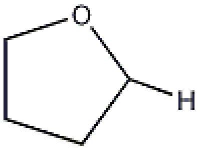
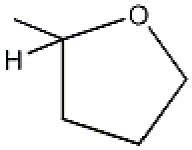
Ether	Bond	Optical Isomer	BDE (kcal mol^{-1})
Oxirane		**2**	**105.0**
Oxirane, 2-methyl-		**2**	**101.5**
Oxirane, 2-methyl-		**2**	**102.9**
Oxirane, 2-methyl-		**2**	**104.6**
Oxetane		**1**	**102.7**
Oxetane		**1**	**96.2**
Oxetane, 2-methyl-		**1**	**94.5**

Table 2.5 (Continued)

Ether	**Bond**	**Optical Isomer**	**BDE (kcal mol^{-1})**
Oxetane, 3-methyl-		**1**	**99.0**
Oxirane, 2,3-dimethyl-		**2**	**101.8**
Oxirane, 2,2-dimethyl-		**1**	**104.3**
Oxirane, 2,2-dimethyl, 3-methyl-		**2**	**101.3**
Oxolane		**1**	**96.8**
Oxolane		**1**	**94.3**
Oxolane, 2-methyl-		**2**	**92.9**

2.4.3 Entropy and Heat Capacity Data

The entropy and heat capacity data for the parent molecules as a function of temperature were determined from the optimized structures, moments of inertia, vibrational frequencies, symmetries, the known mass of the molecules and internal rotor contributions for all methyl rotors with barriers below 4 kcal mol^{-1}. The calculations use standard formulas from statistical mechanics for the contributions of translation, external rotation and vibrations[23, 24]. Contributions to the entropy and the heat capacity from translation, vibrations and external rotation are calculated using the “SMCPS “program. This program utilizes the rigid-harmonic oscillator approximation from the optimized structures obtained at B3LYP/6-31G (d,p) level. The number of optical isomers and the spin degeneracy of unpaired electrons are also incorporated for calculation of *S*°298.

Contributions from hindered internal rotors to S°298 and Cp° (T) are determined using “VIBIR” program. This program utilizes the method of Pitzer and Gwinn[25, 26] the potential barriers from the internal rotor analysis, foldness and the respective internal rotor moments of inertia. The rotors with a barrier value greater than 4.0 kcal mol^{-1} were treated as torsion vibrations. The internal rotor data was combined with the S° (T) and Cp° (T) data from frequency, mass, moment of inertia; symmetry and electronic degeneracy from our statistical mechanics program SMCPS [37] and is presented in Table 2.6.

Table 2.6 Ideal Gas-phase Thermodynamic Property *vs* Temperature[a, b]

T(K)	*Cyocc*		*Cyoccc*		*Cyocccc*		*Cyocmc*		*Cyocmmc*	
	Cp(T)	**S^{O}(T)(2)**	**Cp(T)**	**S^{O}(T)(1)**	**Cp(T)**	**S^{O}(T)(2)**	**Cp(T)**	**S^{O}(T)(3)**	**Cp(T)**	**S^{O}(T)(2)**
1	7.9	11.8	7.9	16.2	7.9	17.0	7.9	15.6	7.9	15.7
51	7.9	42.9	9.5	48.3	9.8	49.9	8.0	46.7	8.0	46.8
101	8.0	48.4	9.8	55.0	10.6	57.0	8.4	52.3	9.0	52.5
151	8.1	51.7	10.1	59.0	11.7	61.4	9.5	56.0	11.1	56.6
201	8.6	54.1	11.0	62.0	13.4	65.0	10.9	58.9	13.5	60.1
251	9.7	56.1	12.7	64.6	15.9	68.3	12.8	61.5	16.1	63.3
298	11.2	57.9	14.8	67.0	18.9	71.3	17.0	63.9	23.3	66.4
400	14.6	61.7	20.1	72.1	25.9	77.8	21.8	69.0	29.3	72.8
500	17.7	65.3	24.8	77.1	32.3	84.3	26.0	73.8	34.6	79.1
600	20.3	68.7	28.9	82.0	37.7	90.6	29.6	78.6	39.1	85.1
700	22.5	72.0	32.3	86.7	42.2	96.8	31.0	83.1	39.7	90.9
800	24.3	75.1	35.1	91.2	46.1	102.7	35.2	87.4	46.2	96.5
900	25.9	78.1	37.6	95.5	49.3	108.3	36.0	91.5	46.2	101.7
1000	27.2	80.9	39.6	99.5	52.1	113.6	39.3	95.4	51.5	106.7
1100	28.3	83.5	41.4	103.4	54.5	118.7	39.7	99.1	51.0	111.5
1200	29.3	86.0	42.9	107.1	56.5	123.5	41.1	102.6	53.0	116.0
1300	30.2	88.4	44.3	110.5	58.3	128.1	42.4	105.9	54.7	120.3
1400	30.9	90.7	45.4	113.9	59.8	132.5	43.5	109.1	56.2	124.4
1500	31.6	92.8	46.4	117.0	61.2	136.7	45.7	112.2	59.8	128.3
2000	33.9	102.3	49.8	130.9	65.8	154.9	47.9	125.5	61.9	145.5
2500	35.1	110.0	51.7	142.2	68.3	169.9	49.7	136.4	64.3	159.6
3000	35.8	116.4	52.8	151.8	69.8	182.5	50.8	145.5	65.8	171.5
3500	36.3	122.0	53.5	159.9	70.7	193.3	51.5	153.4	66.7	181.7
4000	36.6	126.9	54.0	167.1	71.3	202.8	52.0	160.3	67.4	190.6
4500	36.9	131.2	54.3	173.5	71.8	211.2	52.3	166.5	67.8	198.6
5000	37.0	135.1	54.6	179.2	72.1	218.8	52.6	172.0	68.1	205.8

Table 2.6 (Continued)

T(K)	*Cyocmcm*		*Cyocmmcm*		*Cyocmcc*		*Cyoccmc*		*Cyocmccc*	
	Cp(T)	S^{O}(T)(18)	Cp(T)	S^{O}(T)(27)	Cp(T)	S^{O}(T)(3)	Cp(T)	S^{O}(T)(3)	Cp(T)	S^{O}(T)(3)
1	7.9	14.5	7.9	14.0	7.9	17.7	7.9	16.4	7.9	19.5
51	8.0	45.6	8.1	45.1	8.1	48.8	8.1	47.5	8.3	50.6
101	9.2	51.4	10.0	51.2	9.3	54.8	9.4	53.5	10.4	57.0
151	11.1	55.5	13.0	55.8	11.0	58.8	11.2	57.7	12.7	61.6
201	13.3	59.0	16.0	59.9	13.0	62.3	13.1	61.1	15.4	65.7
251	15.9	62.2	19.3	63.8	15.6	65.4	15.6	64.3	18.8	69.4
298	22.6	65.2	28.7	67.5	20.6	68.4	20.6	67.2	24.7	73.0
400	28.3	71.6	35.5	75.2	27.4	74.8	27.2	73.6	33.2	80.8
500	33.6	77.7	41.9	82.7	33.4	81.1	33.2	79.8	40.8	88.6
600	38.2	83.7	47.4	90.1	38.5	87.2	38.3	86.0	47.2	96.2
700	39.5	89.5	48.2	97.1	40.9	93.2	40.8	91.9	50.8	103.6
800	45.6	95.0	56.4	103.8	46.3	98.9	46.2	97.6	57.1	110.7
900	46.1	100.2	56.3	110.2	47.7	104.3	47.7	103.0	59.4	117.5
1000	51.0	105.2	63.1	116.3	51.9	109.5	51.9	108.2	64.3	123.9
1100	50.9	109.9	62.3	122.1	52.8	114.4	52.7	113.1	65.8	130.0
1200	52.9	114.4	64.8	127.6	54.8	119.1	54.7	117.7	68.3	135.8
1300	54.6	118.7	66.9	132.9	56.5	123.5	56.5	122.2	70.5	141.4
1400	56.1	122.8	68.7	137.9	58.0	127.8	58.0	126.4	72.4	146.7
1500	59.6	126.8	73.6	142.7	60.6	131.8	60.6	130.5	75.3	151.7
2000	61.9	143.9	75.9	163.8	63.8	149.6	63.9	148.2	79.8	173.9
2500	64.3	158.0	79.0	181.1	66.3	164.1	66.3	162.8	82.9	192.1
3000	65.8	169.9	80.8	195.6	67.8	176.3	67.8	175.0	84.7	207.3
3500	66.7	180.1	81.9	208.2	68.7	186.9	68.7	185.5	85.9	220.5
4000	67.4	189.1	82.7	219.2	69.4	196.1	69.4	194.7	86.7	232.0
4500	67.8	197.0	83.3	228.9	69.8	204.3	69.8	202.9	87.2	242.3
5000	68.1	204.2	83.7	237.7	70.1	211.6	70.1	210.3	87.6	251.5

[a] Thermodynamic properties are referred to standard state of an ideal gas at 1 atm. S°(T) and Cp° (T) are in cal mol^{-1} K^{-1}

[b] Symmetry numbers used for calculation of S°(T) are shown in color.

2.5 Conclusions

Thermodynamic properties ($\Delta_f H^o_{298}$, S^o_{298}, and Cp^o (T), ($1 \leq T \leq 5000$ K)) for Cyclic alkyl ethers and corresponding radicals are reported. Standard enthalpies of formation,

$\Delta_f H^o_{298}$, were calculated using density functional theory and isodesmic reactions. The enthalpies of formation of the parent molecules, averaged over two work reactions for molecules Oxirane, Oxetane and Oxolane were evaluated as -12.61, -19.33 and -44.74 kcal mol^{-1} respectively. There is good consistency with the B3LYP method for the $\Delta_f H^o$298 values between the 6-31G (d,p) and 6-31G(2d,2p) basis sets, with all differences less than 1.3 kcal mol^{-1} for the oxirane, oxetane and oxolane and their corresponding radicals with or without alkyl substituent are even less than 0.72 kcal mol^{-1}. Enthalpies of formation, entropy, S°(T) and heat capacity, $C°_p(T)$, values are reported along with bond energies and corresponding thermochemical properties for radicals corresponding to loss of a hydrogen atom from the carbons sites. The recommended bond dissociation energies of ***Cy***oc•mc, ***Cy***oc•mcc and ***Cy***oc•mccc are 105.2 kcal mol^{-1}, 96.4 kcal mol^{-1} and 94.5 kcal mol^{-1}.

APPENDIX A

VIBRATION FREQUENCIES AND OPTIMIZED GEOMETRY OF ACETOHYDRAZIDE, ACETAMIDE AND N-METHYL ACETAMIDE AND THEIR RADICALS

Table A1.1 Calculated at CBS-QB3 composite, *viz.* B3LYP/6-31G(d,p) Level Vibration Frequencies

SYSTEM	Frequencies, cm^{-1}									
cconn	115.1	284.8	289.5	497.0	564.8	582.7	596.4	792.7	893.1	1014.3
	1051.2	1218.2	1320.7	1359.3	1410.5	1446.6	1479.8	1499.1	1695.3	1800.5
	3050.4	3111.4	3178.5	3471.1	3562.4	3618.4				
ccon	113.1	429.8	522.0	540.4	674.9	842.6	988.0	1058.8	1123.4	1351.9
	1412.7	1486.8	1505.1	1626.8	1810.7	3061.0	3138.6	3146.5	3609.0	3751.9
cconc	146.0	282.0	475.7	515.8	573.3	625.4	805.4	992.7	1053.6	1095.0
	1149.3	1200.2	1349.5	1410.7	1467.8	1475.4	1492.1	1500.1	1508.1	1534.4
	1797.9	3015.7	3050.7	3095.5	3113.0	3136.4	3177.6	3624.9		
cjconn	63.5	268.9	303.0	318.9	476.4	551.0	582.8	594.4	735.4	820.3
	923.9	992.3	1222.3	1317.0	1366.0	1432.5	1473.5	1671.9	1694.2	3183.3
	3302.2	3468.5	3562.4	3618.5						
cconjn	118.0	231.9	332.0	443.6	539.3	647.1	678.1	857.7	1020.7	1052.4
	1239.4	1268.5	1395.1	1411.5	1490.6	1491.6	1570.3	1694.8	3058.9	3123.1
	3165.2	3445.1	3711.4							
cconnj	198.9	291.9	435.6	494.3	598.3	601.4	681.8	818.5	1007.4	1055.2
	1240.3	1285.7	1368.8	1414.8	1473.8	1482.6	1551.9	1794.0	3069.4	3134.2
	3182.6	3427.8	3505.0							
cjcon	265.5	309.6	418.1	498.9	547.3	600.1	734.6	917.4	955.5	1119.4
	1353.3	1480.1	1619.5	1702.9	3168.7	3294.7	3597.5	3731.8		
conj	397.8	463.4	507.7	577.0	833.0	947.3	1030.6	1123.0	1309.4	1406.1
	1477.2	1485.3	1589.6	3060.8	3128.3	3169.4	3443.7	3103.9		
cjconc	126.3	278.7	285.1	448.5	476.4	564.4	594.7	735.2	858.1	991.7
	1103.1	1155.9	1207.0	1359.2	1447.2	1477.9	1492.0	1502.2	1535.8	1677.5
	3022.2	3072.2	3139.3	3182.1	3300.5	3646.7				
cconjc	136.3	285.6	402.7	526.1	615.1	783.9	974.3	1034.0	1043.4	1103.4
	1141.1	1285.7	1402.3	1415.9	1460.8	1478.8	1486.1	1500.0	1651.0	3003.5
	3057.7	3060.7	3110.5	3123.7	3167.9					
cconcj	89.9	207.1	284.8	293.6	481.6	545.6	580.6	717.1	806.5	983.2
	1049.7	1108.6	1253.3	1343.0	1409.5	1467.0	1486.6	1495.4	1524.1	1778.3
	3047.5	3108.5	3178.2	3224.3	3350.4	3597.9				

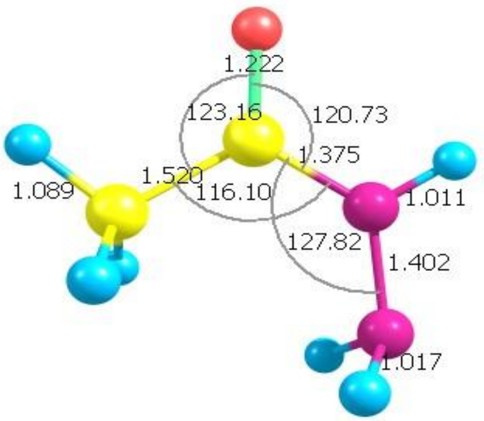


Table A1.2 Geometry Parameters of Acetohydrazide $CH_3CONHNH_2$ (*cconn*) Optimized at CBS-QB3 Composite, *viz.* B3LYP/6-31G(d,p) Level

Bond Distances, Angstrom (Ǻ)		Angle, degrees (°)		Dihedral Angle, degrees (°)	
R(1,2)	1.10	A(2,1,3)	109.18	D(2,1,5,6)	-120.04
R(1,3)	1.09	A(2,1,4)	107.47	D(2,1,5,7)	59.97
R(1,4)	1.10	A(2,1,5)	111.58	D(3,1,5,6)	-0.14
R(1,5)	1.52	A(3,1,4)	109.17	D(3,1,5,7)	179.87
R(5,6)	1.22	A(3,1,5)	107.85	D(4,1,5,6)	119.74
R(5,7)	1.37	A(4,1,5)	111.56	D(4,1,5,7)	-60.26
R(7,8)	1.01	A(1,5,6)	123.16	D(1,5,7,8)	179.95
R(7,9)	1.40	A(1,5,7)	116.10	D(1,5,7,9)	0.07
R(9,10)	1.02	A(6,5,7)	120.74	D(6,5,7,8)	-0.05
R(9,11)	1.02	A(5,7,8)	116.32	D(6,5,7,9)	-179.93
		A(5,7,9)	127.82	D(5,7,9,10)	-60.24
		A(8,7,9)	115.86	D(5,7,9,11)	60.06
		A(7,9,10)	110.55	D(8,7,9,10)	119.88
		A(7,9,11)	110.56	D(8,7,9,11)	-119.82
		A(10,9,11)	108.62		

Moments of Inertia (amu unit) for *cconn*: 203.34, 431.26 and 613.55

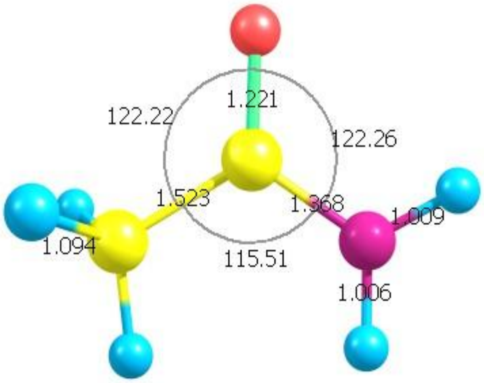


Table A1.3 Geometry Parameters of Acetamide CH_3CONH_2 (*ccon*) Optimized at CBS-QB3 Composite, *viz.* B3LYP/6-31G(d,p) Level

Bond Distances, Angstrom (Å)		Angle, degrees (°)		Dihedral Angle, degrees (°)	
R(1,2)	1.09	A(2,1,3)	109.13	D(2,1,5,6)	175.53
R(1,3)	1.09	A(2,1,4)	108.91	D(2,1,5,7)	-4.76
R(1,4)	1.09	A(2,1,5)	114.04	D(3,1,5,6)	53.63
R(1,5)	1.52	A(3,1,4)	107.34	D(3,1,5,7)	-126.65
R(5,6)	1.22	A(3,1,5)	108.55	D(4,1,5,6)	-62.80
R(5,7)	1.37	A(4,1,5)	108.65	D(4,1,5,7)	116.91
R(7,8)	1.01	A(1,5,6)	122.22	D(1,5,7,8)	-0.46
R(7,9)	1.01	A(1,5,7)	115.51	D(1,5,7,9)	-178.98
		A(6,5,7)	122.26	D(6,5,7,8)	179.26
		A(5,7,8)	122.94	D(6,5,7,9)	0.74
		A(5,7,9)	117.98		
		A(8,7,9)	119.06		

Moments of Inertia (amu unit) for *ccon*: 167.33, 195.81 and 351.97

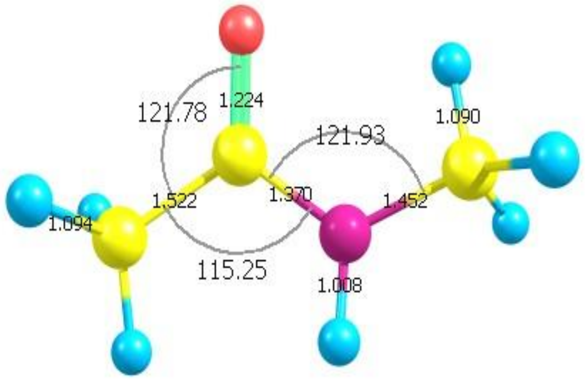


Table A1.4 Geometry Parameters of N-Methyl Acetamide CH$_3$CONHCH$_3$ (*cconc*) Optimized at CBS-QB3 Composite, *viz.* B3LYP/6-31G(d,p) Level

Bond Distances, Angstrom (Å)		Angle, degrees $(^{o})$		Dihedral Angle, degrees $(^{o})$	
R(1,2)	1.09	A(2,1,3)	109.13	D(2,1,5,6)	-1.79
R(1,3)	1.10	A(2,1,4)	109.34	D(2,1,5,7)	179.25
R(1,4)	1.10	A(2,1,5)	107.94	D(3,1,5,6)	117.92
R(1,5)	1.52	A(3,1,4)	107.52	D(3,1,5,7)	-61.03
R(5,6)	1.22	A(3,1,5)	111.26	D(4,1,5,6)	-121.97
R(5,7)	1.37	A(4,1,5)	111.62	D(4,1,5,7)	59.07
R(7,8)	1.01	A(1,5,6)	122.45	D(1,5,7,8)	-175.86
R(7,9)	1.45	A(1,5,7)	116.45	D(1,5,7,9)	-8.91
R(9,10)	1.09	A(6,5,7)	121.09	D(6,5,7,8)	5.17
R(9,11)	1.10	A(5,7,8)	113.16	D(6,5,7,9)	172.12
R(9,12)	1.09	A(5,7,9)	127.23	D(5,7,9,10)	166.53
		A(8,7,9)	118.37	D(5,7,9,11)	-73.40
		A(7,9,10)	108.86	D(5,7,9,12)	48.48
		A(7,9,11)	113.18	D(8,7,9,10)	-27.11
		A(7,9,12)	111.02	D(8,7,9,11)	92.95
		A(10,9,11)	107.97	D(8,7,9,12)	-145.16
		A(10,9,12)	107.42		
		A(11,9,12)	108.18		

Moments of Inertia (amu unit) for *cconc*: 206.50, 442.22 and 625.32

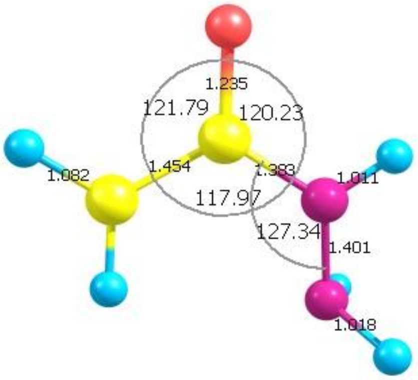


Table A1.5 Geometry Parameters of $CH_2CONHNH_2$ (*cjconn*) Optimized at CBS-QB3 Composite, *viz.* B3LYP/6-31G(d,p) Level

Bond Distances, Angstrom (Ǻ)		Angle, degrees (°)		Dihedral Angle, degrees (°)	
R(1,2)	1.08	A(2,1,3)	119.37	D(2,1,4,5)	2.15
R(1,3)	1.08	A(2,1,4)	116.91	D(2,1,4,6)	-179.14
R(1,4)	1.45	A(3,1,4)	123.69	D(3,1,4,5)	-176.00
R(4,5)	1.24	A(1,4,5)	121.79	D(3,1,4,6)	2.70
R(4,6)	1.38	A(1,4,6)	117.97	D(1,4,6,7)	174.90
R(6,7)	1.01	A(5,4,6)	120.23	D(1,4,6,8)	11.16
R(6,8)	1.40	A(4,6,7)	115.29	D(5,4,6,7)	-6.37
R(8,9)	1.02	A(4,6,8)	127.34	D(5,4,6,8)	-170.11
R(8,10)	1.02	A(7,6,8)	115.53	D(4,6,8,9)	-71.48
		A(6,8,9)	110.36	D(4,6,8,10)	49.53
		A(6,8,10)	111.03	D(7,6,8,9)	124.82
		A(9,8,10)	109.03	D(7,6,8,10)	-114.17

Moments of Inertia (amu unit) for *cjconn*: 181.76, 430.35 and 601.05

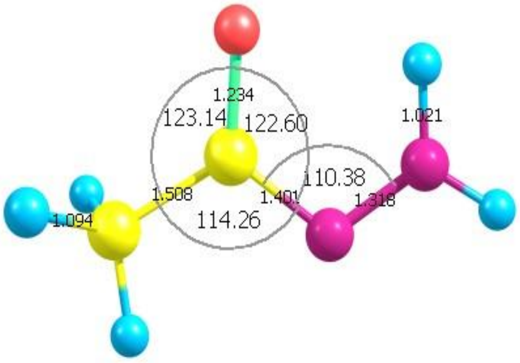


Table A1.6 Geometry Parameters of CH_3CONNH_2 (*cconjn*) Optimized at CBS-QB3 Composite, *viz.* B3LYP/6-31G(d,p) Level

Bond Distances, Angstrom (Å)		Angle, degrees (^{o})		Dihedral Angle, degrees (^{o})	
R(1,2)	1.09	A(2,1,3)	109.97	D(2,1,5,6)	-174.48
R(1,3)	1.09	A(2,1,4)	109.29	D(2,1,5,7)	5.83
R(1,4)	1.10	A(2,1,5)	111.46	D(3,1,5,6)	-52.59
R(1,5)	1.51	A(3,1,4)	107.15	D(3,1,5,7)	127.72
R(5,6)	1.23	A(3,1,5)	109.47	D(4,1,5,6)	64.54
R(5,7)	1.40	A(4,1,5)	109.39	D(4,1,5,7)	-115.15
R(7,8)	1.32	A(1,5,6)	123.14	D(1,5,7,8)	179.04
R(8,9)	1.02	A(1,5,7)	114.26	D(6,5,7,8)	-0.66
R(8,10)	1.01	A(6,5,7)	122.60	D(5,7,8,9)	1.26
		A(5,7,8)	110.38	D(5,7,8,10)	178.10
		A(7,8,9)	118.84		
		A(7,8,10)	117.82		
		A(9,8,10)	123.25		

Moments of Inertia (amu unit) for *cconjn*: 166.81, 422.29 and 577.92

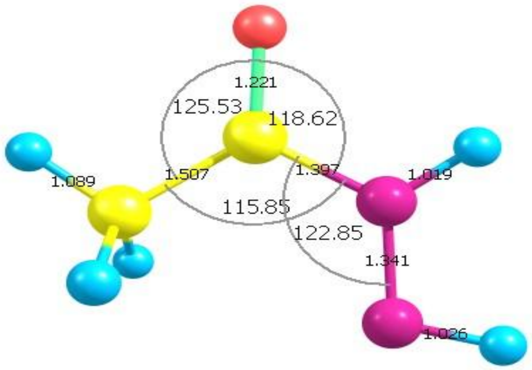


Table A1.7 Geometry Parameters of CH$_3$CONHNH (*cconnj*) Optimized at CBS-QB3 Composite, *viz.* B3LYP/6-31G(d,p) Level

Bond Distances, Angstrom (Å)		Angle, degrees (^{o})		Dihedral Angle, degrees (^{o})	
R(1,2)	1.09	A(2,1,3)	110.33	D(2,1,5,6)	-120.41
R(1,3)	1.09	A(2,1,4)	106.65	D(2,1,5,7)	59.55
R(1,4)	1.09	A(2,1,5)	110.52	D(3,1,5,6)	0.58
R(1,5)	1.51	A(3,1,4)	110.42	D(3,1,5,7)	-179.46
R(5,6)	1.22	A(3,1,5)	108.33	D(4,1,5,6)	121.72
R(5,7)	1.40	A(4,1,5)	110.60	D(4,1,5,7)	-58.32
R(7,8)	1.02	A(1,5,6)	125.53	D(1,5,7,8)	-179.98
R(7,9)	1.34	A(1,5,7)	115.85	D(1,5,7,9)	0.02
R(9,10)	1.03	A(6,5,7)	118.62	D(6,5,7,8)	-0.02
		A(5,7,8)	113.48	D(6,5,7,9)	179.98
		A(5,7,9)	122.85	D(5,7,9,10)	-179.98
		A(8,7,9)	123.67	D(8,7,9,10)	0.02
		A(7,9,10)	105.64		

Moments of Inertia (amu unit) for *cconnj*: 198.87, 399.58 and 587.38

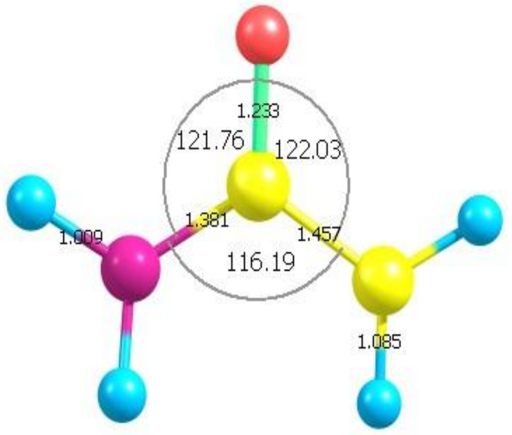


Table A1.8 Geometry Parameters of CH_2CONH_2 (*cjcon*) Optimized at CBS-QB3 Composite, *viz.* B3LYP/6-31G(d,p) Level

Bond Distances, Angstrom (Å)		Angle, degrees (^{o})		Dihedral Angle, degrees (^{o})	
R(1,2)	1.08	A(2,1,3)	119.35	D(2,1,4,5)	-1.26
R(1,3)	1.09	A(2,1,4)	117.67	D(2,1,4,6)	-179.52
R(1,4)	1.46	A(3,1,4)	122.98	D(3,1,4,5)	178.03
R(4,5)	1.23	A(1,4,5)	122.02	D(3,1,4,6)	-0.23
R(4,6)	1.38	A(1,4,6)	116.19	D(1,4,6,7)	-170.60
R(6,7)	1.01	A(5,4,6)	121.76	D(1,4,6,8)	-18.04
R(6,8)	1.01	A(4,6,7)	116.03	D(5,4,6,7)	11.15
		A(4,6,8)	121.00	D(5,4,6,8)	163.70
		A(7,6,8)	117.22		

Moments of Inertia (amu unit) for *cjcon*: 161.38, 176.80 and 337.65

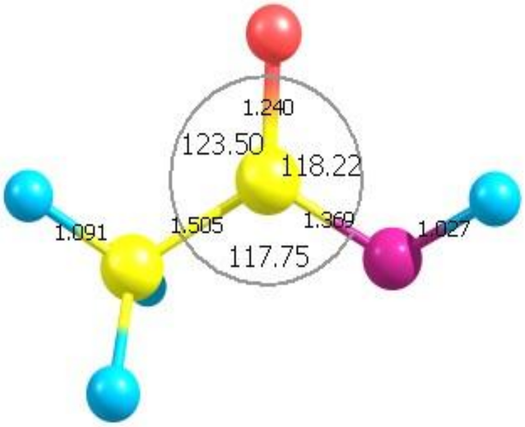


Table A1.9 Geometry Parameters of CH_3CONH (*cconj*) Optimized at CBS-QB3 Composite, *viz.* B3LYP/6-31G(d,p) Level

Bond Distances, Angstrom (Å)		Angle, degrees (°)		Dihedral Angle, degrees (°)	
R(1,2)	1.09	A(2,1,3)	110.27	D(2,1,5,6)	-139.05
R(1,3)	1.09	A(2,1,4)	107.40	D(2,1,5,7)	49.46
R(1,4)	1.09	A(2,1,5)	110.40	D(3,1,5,6)	-17.18
R(1,5)	1.51	A(3,1,4)	109.33	D(3,1,5,7)	171.34
R(5,6)	1.24	A(3,1,5)	109.95	D(4,1,5,6)	102.93
R(5,7)	1.37	A(4,1,5)	109.45	D(4,1,5,7)	-68.56
R(7,8)	1.03	A(1,5,6)	123.49	D(1,5,7,8)	-157.71
		A(1,5,7)	117.76	D(6,5,7,8)	30.34
		A(6,5,7)	118.22		
		A(5,7,8)	108.58		

Moments of Inertia (amu unit) for *cconj*: 149.55, 197.77 and 334.87

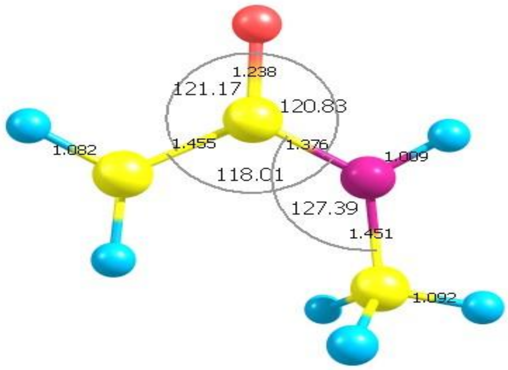


Table A1.10 Geometry Parameters of $CH_2CONHCH_3$ (*cjconc*) Optimized at CBS-QB3 Composite, *viz.* B3LYP/6-31G(d,p) Level

Bond Distances, Angstrom (Å)		Angle, degrees (°)		Dihedral Angle, degrees (°)	
R(1,2)	1.08	A(2,1,3)	119.24	D(2,1,4,5)	0.00
R(1,3)	1.08	A(2,1,4)	116.83	D(2,1,4,11)	0.00
R(1,4)	1.46	A(3,1,4)	123.93	D(3,1,4,5)	180.00
R(4,5)	1.38	A(1,4,5)	118.01	D(3,1,4,11)	180.01
R(4,11)	1.24	A(1,4,11)	121.17	D(1,4,5,6)	-0.01
R(5,6)	1.01	A(5,4,11)	120.83	D(1,4,5,7)	0.01
R(5,7)	1.45	A(4,5,6)	113.47	D(11,4,5,6)	-180.01
R(7,8)	1.09	A(4,5,7)	127.39	D(11,4,5,7)	-180.00
R(7,9)	1.10	A(6,5,7)	119.14	D(4,5,7,8)	-61.18
R(7,10)	1.10	A(5,7,8)	108.56	D(4,5,7,9)	61.19
		A(5,7,9)	112.26	D(4,5,7,10)	-0.02
		A(5,7,10)	112.26	D(6,5,7,8)	118.80
		A(8,7,9)	107.59	D(6,5,7,9)	-118.83
		A(8,7,10)	107.59	D(6,5,7,10)	
		A(9,7,10)	108.37		

Moments of Inertia (amu unit) for *cjconc*: 183.98, 441.11 and 613.69

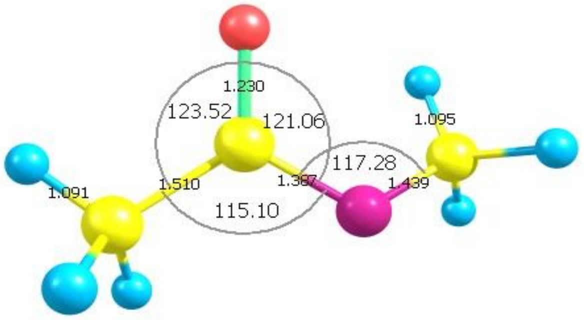


Table A1.11 Geometry Parameters of CH$_3$CONCH$_3$ (*cconjc*) Optimized at CBS-QB3 Composite, *viz.* B3LYP/6-31G(d,p) Level

Bond Distances, Angstrom (Å)		Angle, degrees (^{o})		Dihedral Angle, degrees (^{o})	
R(1,2)	1.09	A(2,1,3)	110.31	D(2,1,5,6)	16.57
R(1,3)	1.09	A(2,1,4)	109.30	D(2,1,5,7)	-169.84
R(1,4)	1.10	A(2,1,5)	109.63	D(3,1,5,6)	138.59
R(1,5)	1.51	A(3,1,4)	107.21	D(3,1,5,7)	-47.82
R(5,6)	1.23	A(3,1,5)	110.86	D(4,1,5,6)	-103.33
R(5,7)	1.39	A(4,1,5)	109.49	D(4,1,5,7)	70.26
R(7,8)	1.44	A(1,5,6)	123.52	D(1,5,7,8)	152.72
R(8,9)	1.10	A(1,5,7)	115.10	D(6,5,7,8)	-33.52
R(8,10)	1.10	A(6,5,7)	121.06	D(5,7,8,9)	123.35
R(8,11)	1.10	A(5,7,8)	117.28	D(5,7,8,10)	-122.19
		A(7,8,9)	109.30	D(5,7,8,11)	-0.08
		A(7,8,10)	107.64		
		A(7,8,11)	113.76		
		A(9,8,10)	105.79		
		A(9,8,11)	110.04		
		A(10,8,11)	109.97		

Moments of Inertia (amu unit) for *cconjc*: 179.33, 454.15 and 599.01

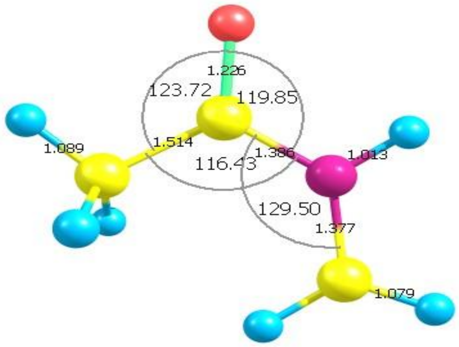


Table A1.12 Geometry Parameters of $CH_3CONHCH_2$ (*cconcj*) Optimized at CBS-QB3 Composite, *viz.* B3LYP/6-31G(d,p) Level

Bond Distances, Angstrom (Å)		Angle, degrees $(^{o})$		Dihedral Angle, degrees $(^{o})$	
R(1,2)	1.09	A(2,1,3)	109.35	D(2,1,5,6)	-0.15
R(1,3)	1.10	A(2,1,4)	109.31	D(2,1,5,7)	179.87
R(1,4)	1.10	A(2,1,5)	108.09	D(3,1,5,6)	-120.21
R(1,5)	1.51	A(3,1,4)	107.58	D(3,1,5,7)	59.81
R(5,6)	1.23	A(3,1,5)	111.23	D(4,1,5,6)	119.87
R(5,7)	1.39	A(4,1,5)	111.26	D(4,1,5,7)	-60.11
R(7,8)	1.01	A(1,5,6)	123.72	D(1,5,7,8)	-179.63
R(7,9)	1.38	A(1,5,7)	116.43	D(1,5,7,9)	-0.76
R(9,10)	1.08	A(6,5,7)	119.85	D(6,5,7,8)	0.40
R(9,11)	1.08	A(5,7,8)	112.07	D(6,5,7,9)	179.27
		A(5,7,9)	129.50	D(5,7,9,10)	178.03
		A(8,7,9)	118.42	D(5,7,9,11)	3.35
		A(7,9,10)	118.11	D(8,7,9,10)	-3.16
		A(7,9,11)	119.62	D(8,7,9,11)	-177.84
		A(10,9,11)	122.04		

Moments of Inertia (amu unit) for *cconcj*: 201.81, 413.51 and 604.04

APPENDIX B

MULLIKEN CHARGES OF ACETOHYDRAZIDE, ACETAMIDE, N-METHYL ACETAMIDE AND THEIR RADICALS

Table B1.1 Mulliken Atomic Charges for Acetohydrazide and its radicals

$CH_3CONHNH_2$		$C{\bullet}H_2CONHNH_2$		$CH_3CON{\bullet}NH_2$		$CH_3CONHN{\bullet}H$	
Atoms	**Charges**	**Atoms**	**Charges**	**Atoms**	**Charges**	**Atoms**	**Charges**
1 C	-0.402315	1 C	-0.234273	1 C	-0.377199	1 C	-0.375741
2 H	0.121192	2 H	0.143004	2 H	0.128190	2 H	0.147242
3 H	0.150336	3 H	0.099884	3 H	0.137384	3 H	0.136885
4 H	0.121365	4 C	0.570321	4 H	0.138721	4 H	0.147356
5 C	0.558623	5 O	-0.504403	5 C	0.510877	5 C	0.553199
6 O	-0.494651	6 N	-0.423541	6 O	-0.490789	6 O	-0.469507
7 N	-0.406385	7 H	0.278899	7 N	-0.300686	7 N	-0.340122
8 H	0.277625	8 N	-0.456181	8 N	-0.335637	8 H	0.271718
9 N	-0.451870	9 H	0.265755	9 H	0.292639	9 N	-0.317619
10 H	0.263059	10 H	0.260536	10 H	0.296499	10 H	0.246589
11 H	0.263020						

Table B1.2 Mulliken Atomic Charges for Acetamide and its radicals

CH_3CONH_2		$C{\bullet}H_2CONH_2$		$CH_3CON{\bullet}H$	
Atoms	**Charges**	**Atoms**	**Charges**	**Atoms**	**Charges**
1 C	-0.055334	1 C	-0.067481	1 C	-0.046469
2 H	-0.022534	2 H	0.018583	2 H	0.036769
3 H	0.019714	3 H	0.049910	3 H	0.025065
4 H	0.016401	4 C	0.914210	4 H	0.022283
5 C	1.077024	5 O	-0.665853	5 C	0.555443
6 O	-0.764450	6 N	-0.671122	6 O	-0.461093
7 N	-0.696651	7 H	0.208977	7 N	-0.342651
8 H	0.211890	8 H	0.212777	8 H	0.210653
9 H	0.213941				

Table B1.3 Mulliken Atomic Charges for N-Methyl Acetamide and its radicals

$CH_3CONHCH_3$		**$C{\bullet}H_2CONHCH_3$**		**$CH_3CON{\bullet}CH_3$**		**$CH_3CONHC{\bullet}H_2$**	
Atoms	**Charges**	**Atoms**	**Charges**	**Atoms**	**Charges**	**Atoms**	**Charges**
1 C	-0.360700	1 C	-0.234608	1 C	-0.067856	1 C	-0.401136
2 H	0.142160	2 H	0.137113	2 H	0.015848	2 H	0.146128
3 H	0.138604	3 H	0.110454	3 H	0.016119	3 H	0.132117
4 H	0.137617	4 C	0.562523	4 H	0.024339	4 H	0.131456
5 C	0.463021	5 N	-0.525521	5 C	0.802512	5 C	0.535968
6 O	-0.426924	6 H	0.268023	6 O	-0.573036	6 O	-0.488515
7 N	-0.531373	7 C	-0.171936	7 N	-0.443796	7 N	-0.442833
8 H	0.260401	8 H	0.122700	8 C	0.180754	8 H	0.277077
9 C	-0.180559	9 H	0.122862	9 H	0.014106	9 C	-0.129519
10 H	0.114890	10 H	0.122867	10 H	0.029614	10 H	0.116521
11 H	0.122017	11 O	-0.514477	11 H	0.001397	11 H	0.122736
12 H	0.120846						

APPENDIX C

VIBRATION FREQUENCIES AND OPTIMIZED GEOMETRY OF CYCLIC ALKYL ETHERS

Table C1.1 Calculated at CBS-QB3 composite, *viz.* B3LYP/6-31G(d,p) Level Vibration Frequencies

System	Frequencies, cm^{-1}							
Cyocc	816.9	860.1	900.6	1041.7	1145.1	1158.5	1170.2	1180.6
	1309.8	1520.0	1559.5	3091.4	3099.5	3173.5	3188.8	
Cyoccc	63.7	769.9	815.4	843.8	932.7	948.6	1046.4	1053.1
	1158.1	1166.9	1199.8	1239.7	1270.0	1317.5	1392.2	1506.4
	1531.3	1562.2	3018.1	3029.5	3062.9	3063.5	3088.9	3143.1
Cyocccc	39.7	256.6	581.5	675.8	847.7	886.7	911.0	921.1
	930.6	971.5	1035.5	1110.6	1178.8	1189.2	1198.2	1263.7
	1263.8	1323.2	1351.5	1374.5	1412.5	1501.8	1512.0	1538.6
	1552.9	2995.3	3001.4	3054.7	3057.2	3072.7	3073.7	3113.1
	3121.6							
Cyocmc	365.0	410.5	782.0	854.8	908.9	982.4	1042.4	1134.7
	1156.3	1167.2	1191.6	1300.0	1416.2	1453.8	1498.1	1512.3
	1548.7	3045.4	3087.5	3100.5	3112.4	3133.2	3173.7	
Cyocmmc	353.7	360.6	405.8	413.0	704.9	819.6	908.7	933.3
	959.5	1022.8	1079.0	1135.8	1152.0	1175.1	1290.0	1401.5
	1424.8	1434.8	1488.5	1500.9	1508.0	1520.2	1551.3	3041.5
	3046.8	3085.0	3106.0	3111.0	3134.6	3136.5	3169.1	
Cyocmcm	260.7	336.4	445.9	512.9	765.2	782.0	918.0	975.9
	1011.2	1037.0	1137.4	1139.1	1187.5	1191.1	1309.2	1394.4
	1430.8	1437.8	1480.3	1491.9	1502.7	1512.4	1536.1	3047.0
	3050.0	3079.3	3092.7	3109.7	3110.6	3142.3	3152.7	
Cyocmmcm	246.0	271.3	365.1	405.5	479.5	488.9	694.1	763.3
	894.1	946.8	971.8	993.3	1025.3	1102.7	1140.6	1158.4
	1188.4	1270.1	1360.5	1421.3	1424.2	1434.7	1474.5	1487.7
	1496.3	1497.9	1509.9	1519.3	1541.2	3041.5	3046.9	3049.6
	3077.0	3104.2	3108.5	3109.6	3133.6	3145.8	3156.7	

Table C1.1 (Continued)

Cyocmcc	237.0	332.5	434.5	712.1	805.8	879.6	888.2	946.4
	976.6	1030.4	1097.7	1128.1	1163.8	1193.4	1228.9	1265.2
	1299.7	1372.3	1395.7	1424.5	1495.8	1502.5	1511.5	1549.5
	3002.4	3020.9	3041.5	3065.6	3081.4	3115.1	3124.0	3138.5
Cyoccmc	230.8	321.2	402.0	705.2	871.6	898.4	912.1	940.9
	989.6	1040.3	1124.8	1145.0	1160.0	1165.0	1217.9	1287.8
	1315.5	1358.1	1409.7	1429.8	1509.8	1511.5	1527.5	1554.1
	3002.4	3013.7	3036.7	3056.4	3062.5	3078.6	3106.5	3110.1
Cyocmccc	191.1	242.1	319.1	471.8	595.8	670.4	807.0	844.5
	893.4	909.5	923.9	993.4	1026.7	1068.1	1129.1	1153.3
	1169.6	1228.6	1250.2	1272.9	1299.5	1320.2	1364.2	1394.7
	1406.0	1429.4	1498.2	1502.1	1513.4	1521.2	1536.8	2946.4
	2980.5	3049.6	3061.1	3075.3	3099.1	3108.0	3123.6	3125.7
	3130.6							

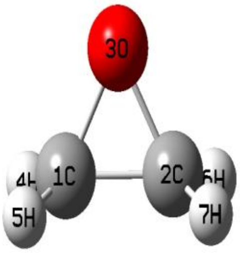


Table C1.2 Geometry Parameters of Oxirane, ***Cy****occ* Optimized at CBS-QB3 Composite, *viz.* B3LYP/6-31G(d,p) Level

Bond Distances, Angstrom (Å)		Angle, degrees (°)		Dihedral Angle, degrees (°)	
R(1,2)	1.47	A(2,1,4)	119.62	D(4,1,2,6)	-0.07
R(1,3)	1.43	A(2,1,5)	119.62	D(4,1,2,7)	-152.52
R(1,4)	1.09	A(3,1,4)	115.52	D(5,1,2,6)	152.52
R(1,5)	1.09	A(3,1,5)	115.52	D(5,1,2,7)	0.07
R(2,3)	1.43	A(4,1,5)	115.26		
R(2,6)	1.09	A(1,2,6)	119.67		
R(2,7)	1.09	A(1,2,7)	119.67		
		A(3,2,6)	115.56		
		A(3,2,7)	115.56		
		A(6,2,7)	115.12		

Moments of Inertia (amu unit) for ***Cy****occ*: 70.50, 81.79 and 127.92

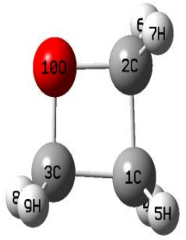


Table C1.3 Geometry Parameters of Oxetane, ***Cy***occc Optimized at CBS-QB3 Composite, *viz.* B3LYP/6-31G(d,p) Level

Bond Distances, Angstrom (Å)		Angle, degrees (^{o})		Dihedral Angle, degrees (^{o})	
R(1,2)	1.54	A(2,1,3)	84.50	D(3,1,2,6)	-115.55
R(1,3)	1.54	A(2,1,4)	115.43	D(3,1,2,7)	115.58
R(1,4)	1.09	A(2,1,5)	115.42	D(3,1,2,10)	0.01
R(1,5)	1.09	A(3,1,4)	115.43	D(4,1,2,6)	0.03
R(2,6)	1.10	A(3,1,5)	115.42	D(4,1,2,7)	-128.84
R(2,7)	1.10	A(4,1,5)	109.10	D(4,1,2,10)	115.59
R(2,10)	1.45	A(1,2,6)	115.73	D(5,1,2,6)	128.87
R(3,8)	1.10	A(1,2,7)	115.73	D(5,1,2,7)	0.00
R(3,9)	1.10	A(1,2,10)	91.94	D(5,1,2,10)	-115.57
R(3,10)	1.45	A(6,2,7)	108.71	D(2,1,3,8)	115.55
		A(6,2,10)	111.95	D(2,1,3,9)	-115.58
		A(7,2,10)	111.95	D(2,1,3,10)	-0.01
		A(1,3,8)	115.73	D(4,1,3,8)	-0.03
		A(1,3,9)	115.73	D(4,1,3,9)	128.84
		A(1,3,10)	91.94	D(4,1,3,10)	-115.59
		A(8,3,9)	108.71	D(5,1,3,8)	-128.87
		A(8,3,10)	111.95	D(5,1,3,9)	0.00
		A(9,3,10)	111.95	D(5,1,3,10)	115.57
		A(2,10,3)	91.62	D(1,2,10,3)	-0.01
				D(6,2,10,3)	118.80
				D(7,2,10,3)	-118.83
				D(1,3,10,2)	0.01
				D(8,3,10,2)	-118.80
				D(9,3,10,2)	118.83

Moments of Inertia (amu unit) for ***Cyoccc***: 149.65, 153.77 and 269.11

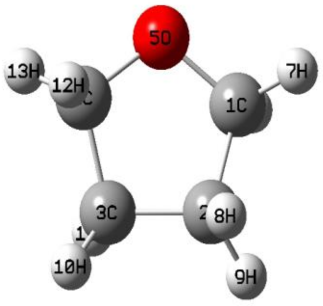


Table C1.4 Geometry Parameters of Oxolane ***Cy***occcc Optimized at CBS-QB3 Composite, *viz.* B3LYP/6-31G(d,p) Level

Bond Distances, Angstrom (Å)		Angle, degrees (^{o})		Dihedral Angle, degrees (^{o})	
R(1,2)	1.53	A(2,1,5)	106.42	D(5,1,2,3)	30.90
R(1,5)	1.43	A(2,1,6)	110.98	D(5,1,2,8)	-86.09
R(1,6)	1.10	A(2,1,7)	113.16	D(5,1,2,9)	152.87
R(1,7)	1.10	A(5,1,6)	109.51	D(6,1,2,3)	-88.17
R(2,3)	1.54	A(5,1,7)	108.82	D(6,1,2,8)	154.83
R(2,8)	1.10	A(6,1,7)	107.90	D(6,1,2,9)	33.80
R(2,9)	1.09	A(1,2,3)	101.53	D(7,1,2,3)	150.36
R(3,4)	1.53	A(1,2,8)	110.44	D(7,1,2,8)	33.37
R(3,10)	1.09	A(1,2,9)	112.84	D(7,1,2,9)	-87.67
R(3,11)	1.10	A(3,2,8)	110.30	D(2,1,5,4)	-12.15
R(4,5)	1.43	A(3,2,9)	113.61	D(6,1,5,4)	107.88
R(4,12)	1.10	A(8,2,9)	108.04	D(7,1,5,4)	-134.39
R(4,13)	1.10	A(2,3,4)	101.54	D(1,2,3,4)	-36.55
		A(2,3,10)	113.61	D(1,2,3,10)	-157.98
		A(2,3,11)	110.30	D(1,2,3,11)	80.55
		A(4,3,10)	112.84	D(8,2,3,4)	80.55
		A(4,3,11)	110.44	D(8,2,3,10)	-40.89
		A(10,3,11)	108.04	D(8,2,3,11)	-162.35
		A(3,4,5)	106.43	D(9,2,3,4)	-157.98
		A(3,4,12)	110.98	D(9,2,3,10)	80.58
		A(3,4,13)	113.15	D(9,2,3,11)	-40.88
		A(5,4,12)	109.50	D(2,3,4,5)	30.85
		A(5,4,13)	108.83	D(2,3,4,12)	-88.22
		A(12,4,13)	107.90	D(2,3,4,13)	150.32
		A(1,5,4)	109.98	D(10,3,4,5)	152.82

Table C1.4 (Continued)

Bond Distances, Angstrom (Å)	Angle, degrees (°)	Dihedral Angle, degrees (°)	
		D(10,3,4,12)	33.76
		D(10,3,4,13)	-87.71
		D(11,3,4,5)	-86.15
		D(11,3,4,12)	154.79
		D(11,3,4,13)	33.32
		D(3,4,5,1)	-12.06
		D(12,4,5,1)	107.98
		D(13,4,5,1)	-134.30

Moments of Inertia (amu unit) for ***Cy****occcc*: 251.02, 258.95 and 452.84

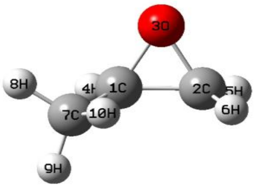


Table C1.5 Geometry Parameters of 2-methyl Oxirane ***Cy***ocmc Optimized at CBS-QB3 Composite, *viz.* B3LYP/6-31G(d,p) Level

Bond Distances, Angstrom (Å)		Angle, degrees (°)		Dihedral Angle, degrees (°)	
R(1,2)	1.47	A(2,1,4)	117.23	D(4,1,2,5)	-1.12
R(1,3)	1.44	A(2,1,7)	122.27	D(4,1,2,6)	-153.78
R(1,4)	1.09	A(3,1,4)	113.55	D(7,1,2,5)	152.70
R(1,7)	1.51	A(3,1,7)	116.50	D(7,1,2,6)	0.04
R(2,3)	1.43	A(4,1,7)	115.50	D(2,1,7,8)	144.49
R(2,5)	1.09	A(1,2,5)	120.13	D(2,1,7,9)	-95.88
R(2,6)	1.09	A(1,2,6)	119.36	D(2,1,7,10)	24.66
R(7,8)	1.10	A(3,2,5)	115.55	D(3,1,7,8)	75.81
R(7,9)	1.10	A(3,2,6)	115.40	D(3,1,7,9)	-164.56
R(7,10)	1.09	A(5,2,6)	115.06	D(3,1,7,10)	-44.01
		A(1,7,8)	110.67	D(4,1,7,8)	-61.27
		A(1,7,9)	110.76	D(4,1,7,9)	58.35
		A(1,7,10)	110.62	D(4,1,7,10)	178.90
		A(8,7,9)	107.90		
		A(8,7,10)	108.13		
		A(9,7,10)	108.66		

Moments of Inertia (amu unit) for ***Cy****ocmc*: 99.66, 272.15 and 305.14

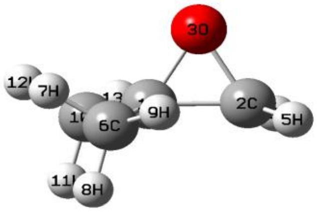


Table C1.6 Geometry Parameters of 2-2, dimethyl Oxirane ***Cy****ocmmc* Optimized at CBS-QB3 Composite, *viz.* B3LYP/6-31G(d,p) Level

Bond Distances, Angstrom (Å)		Angle, degrees (°)		Dihedral Angle, degrees (°)	
R(1,2)	1.47	A(2,1,6)	119.73	D(6,1,2,4)	153.98
R(1,3)	1.44	A(2,1,10)	119.72	D(6,1,2,5)	1.40
R(1,6)	1.51	A(3,1,6)	114.48	D(10,1,2,4)	-1.37
R(1,10)	1.51	A(3,1,10)	114.50	D(10,1,2,5)	-153.95
R(2,3)	1.43	A(6,1,10)	116.08	D(2,1,6,7)	145.45
R(2,4)	1.09	A(1,2,4)	119.83	D(2,1,6,8)	-95.07
R(2,5)	1.09	A(1,2,5)	119.83	D(2,1,6,9)	25.70
R(6,7)	1.10	A(3,2,4)	115.45	D(3,1,6,7)	78.57
R(6,8)	1.10	A(3,2,5)	115.46	D(3,1,6,8)	-161.96
R(6,9)	1.09	A(4,2,5)	114.87	D(3,1,6,9)	-41.19
R(10,11)	1.10	A(1,6,7)	110.38	D(10,1,6,7)	-58.33
R(10,12)	1.10	A(1,6,8)	110.94	D(10,1,6,8)	61.15
R(10,13)	1.09	A(1,6,9)	110.77	D(10,1,6,9)	-178.08
		A(7,6,8)	107.83	D(2,1,10,11)	94.92
		A(7,6,9)	108.15	D(2,1,10,12)	-145.61
		A(8,6,9)	108.66	D(2,1,10,13)	-25.85
		A(1,10,11)	110.93	D(3,1,10,11)	161.81
		A(1,10,12)	110.39	D(3,1,10,12)	-78.72
		A(1,10,13)	110.76	D(3,1,10,13)	41.04
		A(11,10,12)	107.84	D(6,1,10,11)	-61.31
		A(11,10,13)	108.67	D(6,1,10,12)	58.17
		A(12,10,13)	108.15	D(6,1,10,13)	177.93

Moments of Inertia (amu unit) for ***Cy****ocmmc*: 278.79, 327.71 and 462.50

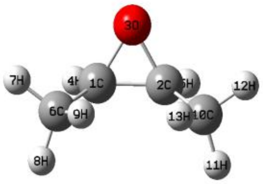


Table C1.7 Geometry Parameters of 2-3, dimethyl Oxirane ***Cy***ocmcm Optimized at CBS-QB3 Composite, *viz.* B3LYP/6-31G(d,p) Level

Bond Distances, Angstrom (Å)		Angle, degrees (°)		Dihedral Angle, degrees (°)	
R(1,2)	1.48	A(2,1,4)	116.21	D(4,1,2,5)	0.00
R(1,3)	1.44	A(2,1,6)	125.05	D(4,1,2,10)	-153.92
R(1,4)	1.09	A(3,1,4)	113.21	D(6,1,2,5)	153.92
R(1,6)	1.51	A(3,1,6)	117.32	D(6,1,2,10)	0.00
R(2,3)	1.44	A(4,1,6)	113.96	D(2,1,6,7)	144.19
R(2,5)	1.09	A(1,2,5)	116.20	D(2,1,6,8)	-96.96
R(2,10)	1.51	A(1,2,10)	125.05	D(2,1,6,9)	24.32
R(6,7)	1.10	A(3,2,5)	113.21	D(3,1,6,7)	74.25
R(6,8)	1.10	A(3,2,10)	117.33	D(3,1,6,8)	-166.90
R(6,9)	1.09	A(5,2,10)	113.96	D(3,1,6,9)	-45.61
R(10,11)	1.10	A(1,6,7)	109.99	D(4,1,6,7)	-61.38
R(10,12)	1.10	A(1,6,8)	110.46	D(4,1,6,8)	57.46
R(10,13)	1.09	A(1,6,9)	112.01	D(4,1,6,9)	178.75
		A(7,6,8)	107.78	D(1,2,10,11)	96.88
		A(7,6,9)	107.80	D(1,2,10,12)	-144.27
		A(8,6,9)	108.67	D(1,2,10,13)	-24.41
		A(2,10,11)	110.46	D(3,2,10,11)	166.80
		A(2,10,12)	109.99	D(3,2,10,12)	-74.34
		A(2,10,13)	112.00	D(3,2,10,13)	45.52
		A(11,10,12)	107.78	D(5,2,10,11)	-57.55
		A(11,10,13)	108.67	D(5,2,10,12)	61.30
		A(12,10,13)	107.81	D(5,2,10,13)	-178.84

Moments of Inertia (amu unit) for ***Cy****ocmcm*: 222.18, 412.35 and 526.27

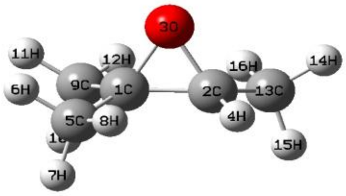


Table C1.8 Geometry Parameters of 2-2-3, trimethyl Oxirane ***Cy***ocmmcm Optimized at CBS-QB3 Composite, *viz.* B3LYP/6-31G(d,p) Level

Bond Distances, Angstrom (Å)		Angle, degrees (^{o})		Dihedral Angle, degrees (^{o})	
R(1,2)	1.48	A(2,1,5)	118.72	D(5,1,2,4)	0.58
R(1,3)	1.45	A(2,1,9)	122.35	D(5,1,2,13)	154.40
R(1,5)	1.52	A(3,1,5)	114.00	D(9,1,2,4)	-155.15
R(1,9)	1.51	A(3,1,9)	115.30	D(9,1,2,13)	-1.34
R(2,3)	1.44	A(5,1,9)	114.73	D(2,1,5,6)	143.91
R(2,4)	1.09	A(1,2,4)	115.76	D(2,1,5,7)	-96.61
R(2,13)	1.51	A(1,2,13)	125.92	D(2,1,5,8)	24.19
R(5,6)	1.10	A(3,2,4)	113.13	D(3,1,5,6)	77.50
R(5,7)	1.10	A(3,2,13)	117.41	D(3,1,5,7)	-163.02
R(5,8)	1.09	A(4,2,13)	113.55	D(3,1,5,8)	-42.22
R(9,10)	1.10	A(1,5,6)	110.37	D(9,1,5,6)	-58.56
R(9,11)	1.10	A(1,5,7)	111.01	D(9,1,5,7)	60.93
R(9,12)	1.09	A(1,5,8)	110.83	D(9,1,5,8)	-178.27
R(13,14)	1.10	A(6,5,7)	107.81	D(2,1,9,10)	95.06
R(13,15)	1.10	A(6,5,8)	108.09	D(2,1,9,11)	-146.11
R(13,16)	1.09	A(7,5,8)	108.62	D(2,1,9,12)	-26.41
		A(1,9,10)	110.77	D(3,1,9,10)	162.96
		A(1,9,11)	109.81	D(3,1,9,11)	-78.21
		A(1,9,12)	112.02	D(3,1,9,12)	41.49
		A(10,9,11)	107.70	D(5,1,9,10)	-61.56
		A(10,9,12)	108.64	D(5,1,9,11)	57.27
		A(11,9,12)	107.76	D(5,1,9,12)	176.96
		A(2,13,14)	109.90	D(1,2,13,14)	144.85
		A(2,13,15)	110.48	D(1,2,13,15)	-96.40
		A(2,13,16)	112.16	D(1,2,13,16)	24.97
		A(14,13,15)	107.74	D(3,2,13,14)	74.30

Table C1.8 (Continued)

Bond Distances, Angstrom (Ǻ)		Angle, degrees (°)		Dihedral Angle, degrees (°)	
		A(14,13,16)	107.79	D(3,2,13,15)	-166.96
		A(15,13,16)	108.65	D(3,2,13,16)	-45.59
				D(4,2,13,14)	-60.84
				D(4,2,13,15)	57.91
				D(4,2,13,16)	179.28

Moments of Inertia (amu unit) for ***Cy**ocmmcm*: 333.45, 622.87 and 741.69

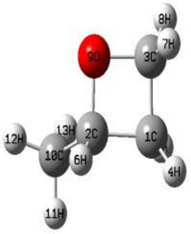


Table C1.9 Geometry Parameters of 2-methyl Oxetane ***Cy***ocmcc Optimized at CBS-QB3 Composite, *viz.* B3LYP/6-31G(d,p) Level

Bond Distances, Angstrom (Ǻ)		Angle, degrees (°)		Dihedral Angle, degrees (°)	
R(1,2)	1.55	A(2,1,3)	84.66	D(3,1,2,6)	-106.31
R(1,3)	1.54	A(2,1,4)	116.55	D(3,1,2,9)	6.22
R(1,4)	1.09	A(2,1,5)	113.69	D(3,1,2,10)	122.72
R(1,5)	1.09	A(3,1,4)	116.65	D(4,1,2,6)	10.88
R(2,6)	1.10	A(3,1,5)	114.37	D(4,1,2,9)	123.41
R(2,9)	1.45	A(4,1,5)	109.29	D(4,1,2,10)	-120.08
R(2,10)	1.52	A(1,2,6)	112.79	D(5,1,2,6)	139.39
R(3,7)	1.10	A(1,2,9)	91.24	D(5,1,2,9)	-108.08
R(3,8)	1.10	A(1,2,10)	118.75	D(5,1,2,10)	8.42
R(3,9)	1.45	A(6,2,9)	110.17	D(2,1,3,7)	108.90
R(10,11)	1.10	A(6,2,10)	110.10	D(2,1,3,8)	-122.17
R(10,12)	1.09	A(9,2,10)	112.38	D(2,1,3,9)	-6.26
R(10,13)	1.09	A(1,3,7)	114.69	D(4,1,3,7)	-8.19
		A(1,3,8)	116.85	D(4,1,3,8)	120.74
		A(1,3,9)	91.83	D(4,1,3,9)	-123.35
		A(7,3,8)	108.71	D(5,1,3,7)	-137.47

Table C1.9 (Continued)

Bond Distances, Angstrom (Å)	Angle, degrees (°)		Dihedral Angle, degrees (°)	
	A(7,3,9)	111.88	D(5,1,3,8)	-8.55
	A(8,3,9)	112.04	D(5,1,3,9)	107.36
	A(2,9,3)	91.54	D(1,2,9,3)	-6.60
	A(2,10,11)	110.55	D(6,2,9,3)	108.28
	A(2,10,12)	110.43	D(10,2,9,3)	-128.55
	A(2,10,13)	110.65	D(1,2,10,11)	73.60
	A(11,10,12)	108.18	D(1,2,10,12)	-166.72
	A(11,10,13)	108.72	D(1,2,10,13)	-46.90
	A(12,10,13)	108.24	D(6,2,10,11)	-58.56
			D(6,2,10,12)	61.11
			D(6,2,10,13)	-179.07
			D(9,2,10,11)	178.23
			D(9,2,10,12)	-62.09
			D(9,2,10,13)	57.73
			D(1,3,9,2)	6.63
			D(7,3,9,2)	-110.97
			D(8,3,9,2)	126.66

Moments of Inertia (amu unit) for ***Cy**ocmcc*: 182.27, 395.65 and 496.79

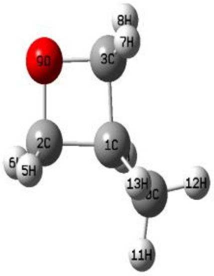


Table C1.10 Geometry Parameters of 3-methyl Oxetane ***Cy***occmc Optimized at CBS-QB3 Composite, *viz.* B3LYP/6-31G(d,p) Level

Bond Distances, Angstrom (Ǻ)		Angle, degrees (^{o})		Dihedral Angle, degrees (^{o})	
R(1,2)	1.55	A(2,1,3)	84.02	D(3,1,2,5)	-109.18
R(1,3)	1.55	A(2,1,4)	111.85	D(3,1,2,6)	122.04
R(1,4)	1.09	A(2,1,10)	118.31	D(3,1,2,9)	5.98
R(1,10)	1.52	A(3,1,4)	111.85	D(4,1,2,5)	139.66
R(2,5)	1.10	A(3,1,10)	118.31	D(4,1,2,6)	10.87
R(2,6)	1.10	A(4,1,10)	110.29	D(4,1,2,9)	-105.18
R(2,9)	1.45	A(1,2,5)	114.30	D(10,1,2,5)	9.84
R(3,7)	1.10	A(1,2,6)	116.94	D(10,1,2,6)	-118.94
R(3,8)	1.10	A(1,2,9)	91.96	D(10,1,2,9)	125.00
R(3,9)	1.45	A(5,2,6)	108.81	D(2,1,3,7)	109.18
R(10,11)	1.10	A(5,2,9)	111.91	D(2,1,3,8)	-122.04
R(10,12)	1.10	A(6,2,9)	112.07	D(2,1,3,9)	-5.98
R(10,13)	1.10	A(1,3,7)	114.30	D(4,1,3,7)	-139.66
		A(1,3,8)	116.94	D(4,1,3,8)	-10.87
		A(1,3,9)	91.96	D(4,1,3,9)	105.18
		A(7,3,8)	108.81	D(10,1,3,7)	-9.84
		A(7,3,9)	111.91	D(10,1,3,8)	118.94
		A(8,3,9)	112.07	D(10,1,3,9)	-125.00
		A(2,9,3)	91.39	D(2,1,10,11)	70.61
		A(1,10,11)	111.22	D(2,1,10,12)	-169.56
		A(1,10,12)	111.22	D(2,1,10,13)	-49.48
		A(1,10,13)	111.11	D(3,1,10,11)	169.56
		A(11,10,12)	107.54	D(3,1,10,12)	-70.61
		A(11,10,13)	107.80	D(3,1,10,13)	49.48
		A(12,10,13)	107.80	D(4,1,10,11)	-59.92
				D(4,1,10,12)	59.92
				D(4,1,10,13)	180.00

Table C1.10 (Continued)

Bond Distances, Angstrom (Å)		Angle, degrees (°)		Dihedral Angle, degrees (°)	
				D(1,2,9,3)	-6.37
				D(5,2,9,3)	110.86
				D(6,2,9,3)	-126.58
				D(1,3,9,2)	6.37
				D(7,3,9,2)	-110.86
				D(8,3,9,2)	126.58

Moments of Inertia (amu unit) for ***Cy**occmc*: 177.33, 419.23 and 516.90

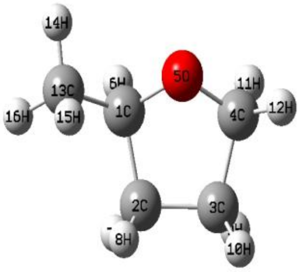


Table C1.11 Geometry Parameters of 2-methyl Oxolane ***Cy**ocmccc* Optimized at CBS-QB3 Composite, *viz.* B3LYP/6-31G(d,p) Level

Bond Distances, Angstrom (Å)		Angle, degrees (°)		Dihedral Angle, degrees (°)	
R(1,2)	1.54	A(2,1,5)	104.40	D(5,1,2,3)	-27.89
R(1,5)	1.43	A(2,1,6)	109.01	D(5,1,2,7)	-150.12
R(1,6)	1.11	A(2,1,13)	115.73	D(5,1,2,8)	90.47
R(1,13)	1.52	A(5,1,6)	108.93	D(6,1,2,3)	88.39
R(2,3)	1.55	A(5,1,13)	108.95	D(6,1,2,7)	-33.84
R(2,7)	1.09	A(6,1,13)	109.56	D(6,1,2,8)	-153.26
R(2,8)	1.10	A(1,2,3)	103.79	D(13,1,2,3)	-147.62
R(3,4)	1.55	A(1,2,7)	111.99	D(13,1,2,7)	90.15
R(3,9)	1.09	A(1,2,8)	109.69	D(13,1,2,8)	-29.27
R(3,10)	1.09	A(3,2,7)	113.02	D(2,1,5,4)	41.18
R(4,5)	1.42	A(3,2,8)	110.73	D(6,1,5,4)	-75.15
R(4,11)	1.10	A(7,2,8)	107.62	D(13,1,5,4)	165.37

Table C1.11 (Continued)

Bond Distances, Angstrom (Å)		Angle, degrees (^{o})		Dihedral Angle, degrees (^{o})	
R(4,12)	1.09	A(2,3,4)	103.31	D(2,1,13,14)	176.82
R(13,14)	1.09	A(2,3,9)	112.57	D(2,1,13,15)	56.97
R(13,15)	1.09	A(2,3,10)	110.98	D(2,1,13,16)	-63.11
R(13,16)	1.09	A(4,3,9)	111.40	D(5,1,13,14)	59.60
		A(4,3,10)	111.27	D(5,1,13,15)	-60.25
		A(9,3,10)	107.37	D(5,1,13,16)	179.68
		A(3,4,5)	106.15	D(6,1,13,14)	-59.47
		A(3,4,11)	110.43	D(6,1,13,15)	-179.33
		A(3,4,12)	113.91	D(6,1,13,16)	60.60
		A(5,4,11)	110.25	D(1,2,3,4)	5.76
		A(5,4,12)	107.90	D(1,2,3,9)	-114.53
		A(11,4,12)	108.16	D(1,2,3,10)	125.10
		A(1,5,4)	106.15	D(7,2,3,4)	127.31
		A(1,13,14)	110.72	D(7,2,3,9)	7.02
		A(1,13,15)	110.20	D(7,2,3,10)	-113.35
		A(1,13,16)	110.58	D(8,2,3,4)	-111.87
		A(14,13,15)	108.35	D(8,2,3,9)	127.84
		A(14,13,16)	108.33	D(8,2,3,10)	7.47
		A(15,13,16)	108.60	D(2,3,4,5)	18.33
				D(2,3,4,11)	-101.16
				D(2,3,4,12)	136.90
				D(9,3,4,5)	139.42
				D(9,3,4,11)	19.92
				D(9,3,4,12)	-102.01
				D(10,3,4,5)	-100.81
				D(10,3,4,11)	139.70
				D(10,3,4,12)	17.77
				D(3,4,5,1)	-37.62
				D(11,4,5,1)	81.99
				D(12,4,5,1)	-160.08

Moments of Inertia (amu unit) for *__Cy__ocmccc*: 275.48, 571.76 and 766.77

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