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Computational investigations on S-nitrosothiols.

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Computational Investigations on S-nitrosothiols

by

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Abstract

Several computational investigations on the properties of S-nitrosothiols (RSNOs) and other interactions with the biochemically important Cu^+ ions are described.

In **Chapter 3**, the ability of conventional electron correlation (MP2 and QCISD) and DFT (B3LYP and B3P86) methods to provide accurate and reliable structures and homolytic S—N BDEs, for a range of RSNOs is considered. With a suitable large basis set, i.e., 6-311+G(2df,p) or larger, the different methods generally give optimized structures in close agreement with each other; the B3LYP method consistently overestimates r(S—N). The trends observed are due in part to the fact that the RS—NO bond does not possess considerable double-bond character as previously suggested, but rather is a long single S—N bond. For BDEs, B3P86/6-311+G(2df,p) consistently gives best agreement with higher accuracy methods. For all RSNOs, QCISD significantly underestimates BDEs, Of the methods considered, B3P86/6-311+G(2df,p) is found to perform the best for obtaining optimized structures and homolytic S—N BDEs of S-nitrosothiols.

In **Chapters 4** and **5**, the B3P86/6-311+G(2df,p) method has been used to investigate complexes formed upon interaction of Cu^+ with selected RSNOs. The most stable complexes are formed when Cu^+ coordinates to the RSNOs via S of the –SNO group, resulting in dramatic lengthening of r(S—N) and shortening of r(N—O). In contrast, when Cu^+ coordinates via N of the –SNO group, a shortening of r(S—N) and lengthening of r(N—O) is observed. These effects are tempered by the electron donating ability of other functional groups coordinated to the Cu^+ and on its coordination state.

In **Chapter 6**, the B3LYP/6-311G(d,p) method has been employed to investigate the structures and thermochemistry of complexes formed upon interaction of nitric oxide (NO) and its mono-ionic derivatives, with biologically relevant model aromatic

biomolecules. The three NO species are found to form quite distinct complexes. NO interacts very weakly via the π-system of the aromatics. In contrast, NO^+ forms much stronger interactions with the π-systems, resulting in the formation of quite stable sandwich complexes. NO^-, however, preferentially forms hydrogen bonds, thus interacting via the σ–framework and hence, does not form sandwich complexes.

Dedication

This work is dedicated to my family

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First of all, I would like to thank my supervisor, Dr. James W. Gauld for introducing me to the fascinating computational chemistry. His guidance and help throughout the years, and in particular his patience are greatly appreciated. Also, his optimism, even during some difficult moments, made me enjoy being part of his group.

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And if I forgot to acknowledge someone, I hope I will be forgiven.

Statement of Originality

I declare that the work reported in this thesis is my own and has not been submitted for any other degree.

Cristina Baciu

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List of Abbreviations and Symbols

Ar	Aromatic
BDE	Bond Dissociation Energy
B3LYP	DFT functional defined as the combination of the B3 exchange functional with the LYP correlation functional.
B3P86	DFT functional defined as the combination of the B3 exchange functional with the Perdew (P86) correlation functional.
CBS-4M	Complete Basis Set-4M
CBS-Q	Complete Basis Set-Q
CBS-QB3	Complete Basis Set-QB3
CT	Charge transfer
DFT	Density Functional Theory
GSNO	S-nitroso-L-gluthatione
G3	Gaussian-3 theory
HF	Hartree-Fock
MPn	nth-order Møller-Plesset
NO	Nitric oxide
Phe	Phenylalanine
QCISD	Quadratic configuration with Singles and Doubles
RSNO	S-nitrosothiol
Trp	Tryptophan
TS	Transition structure
Tyr	Tyrosine
ZPVE	Zero point vibrational energy

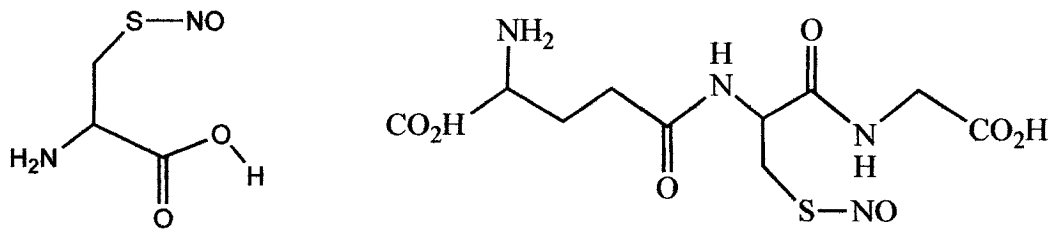
α	alpha
Å	Angstrom
β	beta
χ	chi
ε	epsilon
λ	lamda
μ	mu
ν	nu
π	pi
Ψ	Psi
φ	psi
ϕ	phi
ρ	rho
σ	sigma
τ	tau

Chapter 1

Introduction

S-nitrosothiols (RSNOs) are molecular species that contain an –SNO functional group. While they have been known for some time, it is only recently that there has been an increasing interest in their chemistry. This is due in large part to the fact that they have been found to form *in vivo* during nitric oxide (NO) metabolism.[1] Indeed, S-nitrosothiols are now recognized as biological carriers of nitric oxide (NO), an important signalling molecule,[2,3] and furthermore, to participate in many of the regulatory functions of NO itself.[4-8] In addition, the increasing interest in RSNOs has also been due to the fact that they been recognized as promising potential new therapeutics for a variety of deseases,[2,9] such as cardiovascular ailments.

It is thought that the predominant fraction of RSNOs found *in vivo* are formed by nitrosylation of cysteine and its derivatives, in particular S-nitroso-L-gluthathione (GSNO) (**Scheme 1.1**).



a **b**

Scheme 1.1 Schematic representation of: (a) S-nitroso-cysteine (CysSNO) and (b) S-nitroso-L-gluthathione (GSNO)

While the exact bio-synthetic pathways by which S-nitrosothiols may be formed remain unclear, it is known that reactive NO_x species can react with thiols to form RSNOs.[1,10,11] Similarly, the biochemical pathways by which RSNOs release NO, also remain unclear. However, it is known that the decomposition of RSNOs, hence the release of NO, can be catalyzed by bio-relevant metal ions.[10,12] Of the metal ions so far considered, the monocation Cu^+ has been found to be the most catalytically effective.[10] It has been proposed that Cu^+ coordinates with RSNOs via the S or N of the –SNO group, and other appropiate groups within the RSNOs, thus forming 'activated' complexes.[1,11, 13,14] While the exact structure and nature of such complexes, and their very existence is unknown, some structures have been proposed and are illustrated in **Figure 1.1**.

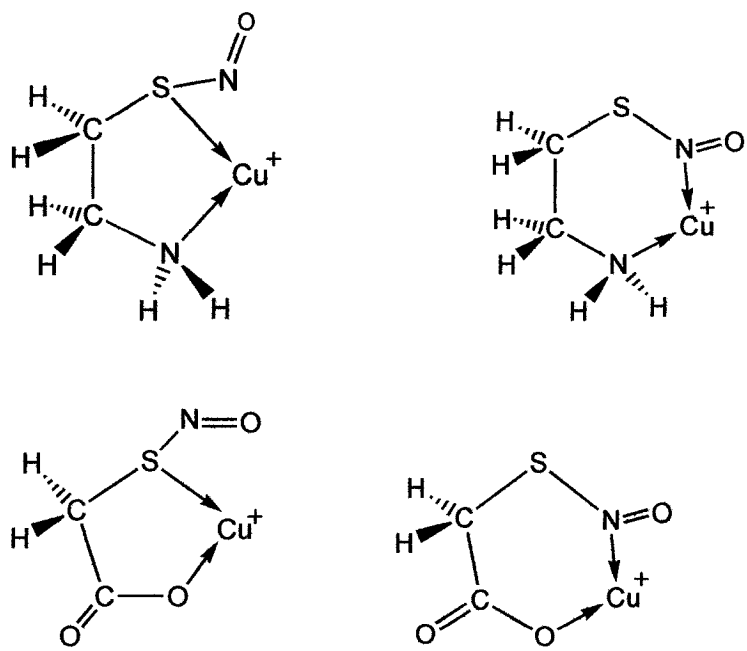


Figure 1.1 Ring complexes of Cu^+ with RSNOs as proposed in the literature (taken from ref.11).

In addition to simply being stores and transporters of NO, S-nitrosothiols exhibit their own biochemistry. For example, fibrinogen is a protein that plays an important role in blood clotting.[15] Fibrinogen is a long fibrous protein. It contains a region that appears to have a more random arrangement of residues. This region is known to be rich in aromatic amino acids residues. However, it has been found that GSNO can interact non-covalently with such regions, causing structural rearrangements.[15] The exact nature of this interaction and intriguing rearrangements, is unknown. This is all the more interesting, as NO^+ has recently been found to be able to form sandwich compounds with certain aromatic species.[16-18]

Despite the obvious insight into the chemistry provided by experimental investigations, such studies often encounter difficulties. This is due in large part due to the fact that S-nitrosothiols are generally unstable and reactive and are rapidly decomposed by metal ions, heat and light.[10-12]

Computational chemistry offers an attractive alternative, yet complementary approach to experimental studies of such species. Indeed, highly reactive or short-lived species are generally as amenable to such an approach as stable, long-lived species. However, such an approach has its own inherent difficulties, not the least of which is determining a level of theory that can provide accurate and reliable insight into such chemical species.

This thesis details the results of our computational investigations on various aspects of the properties and chemistry of S-nitrosothiols.

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Chapter 2

Theoretical Methods

2.1 Introduction

Rather than doing research experimentally, with the aid of computers, computational chemists study the properties of molecules, including transition structures, and other molecules that may be difficult to be investigated experimentally due to their instability or reactivity, intermediates and chemical reactions. Some basic types of calculations include: performing geometry optimization of molecules, computing the energy of a particular molecular structure and calculation of vibrational frequencies. The experimentalists use the computational results obtained about a specific chemical system, in order to gain greater understanding of that system.

The programs used in computational chemistry are based on many different quantum-chemical methods that solve the time-independent Schrödinger equation. The methods that do not include empirical or semi-empirical parameters in their equations are called *ab initio* methods. Such methods use only the values of the fundamental physical constants and a basic set of mathematical approximations.[1] The various types of *ab initio* methods used in this thesis, are described in this chapter.

2.2 The Schrödinger Equation

The time independent Schrödinger equation,[2] which is the basis of quantum chemistry, can be written as:

$$\hat{H}\Psi = E\Psi \qquad \textbf{(2.1)}$$

where $\hat{H}$ is the Hamiltonian operator, E is the energy of the system, and Ψ is the wavefunction of the system and which contains all the information needed to describe the system. The Hamiltonian operator can be written as a sum of kinetic ($\hat{T}$) and potential energy ($\hat{V}$) operators:

$$\hat{H} = \hat{T} + \hat{V} \qquad \textbf{(2.2)}$$

In atomic units, the Hamiltonian operator ($\hat{H}$) can be expressed as:

$$\hat{H} = -\sum_{i=1}^{N_E}\frac{1}{2}\nabla_i^2 - \sum_{A=1}^{N_N}\frac{1}{2M_A}\nabla_A^2 - \sum_{i=1}^{N_E}\sum_{A=1}^{N_N}\frac{Z_A}{r_{iA}} + \sum_{i=1}^{N_E}\sum_{j>i}^{N_E}\frac{1}{r_{ij}} + \sum_{A=1}^{N_N}\sum_{B>A}^{N_N}\frac{Z_A Z_B}{r_{AB}} \qquad \textbf{(2.3)}$$

where A and B refer to the nuclei and i and j refer to electrons, M_A is the ratio of the mass of nuclei A to the mass of an electron, Z_A is the atomic number of nucleus A, r_{ij} is the distance between particle i^{th} and j^{th} and ∇_i^2 and ∇_A^2 are Laplacian operators. The first and second terms are the kinetic energy of the nuclei and electrons; the third term is the coulomb attraction between the electrons and the nuclei; the fourth term represents the repulsion between electrons and fifth term is the repulsion between nuclei.

Due to the fact that the Schrödinger equation **2.1** is too difficult to be solved exactly, except for the hydrogen atom and hydrogen-like systems such as He^+ and Li^{2+}, some approximations must be made in order to solve this equation for larger systems.

2.3 The Born-Oppenheimer Approximation

One of these approximations is the Born-Oppenheimer approximation.[3] This is an assumption that the electronic motion and the nuclear motion can be separated in equation **2.1.** The resulting electronic Schrödinger equation may be written as:

$$\hat{H}_{el}\Psi_{el} = E_{el}\Psi_{el} \qquad \textbf{(2.4)}$$

In order to obtain **2.4**, following assumptions were made: (i) the nuclei are considered much heavier than the electrons and (ii) the electrons are moving so much faster than the nuclei, that the nuclei can be considered fixed.

The electronic Hamiltonian $\hat{H}_{el}$ is:

$$\hat{H}_{el} = -\sum_{i=1}^{N_E}\frac{1}{2}\nabla_i^2 - \sum_{i=1}^{N_E}\sum_{A=1}^{N_N}\frac{Z_A}{r_{iA}} + \sum_{i=1}^{N_E}\sum_{j>i}^{N_E}\frac{1}{r_{ij}} \qquad \textbf{(2.5)}$$

The symbols used are the same as in **2.3**.

For the ground-state of diatomic molecules, the error introduced by this approximation is small.

2.4 Orbital Approximation and Basis Set Expansion

2.4.1 Orbital Approximation

The orbital approximation simplifies the Schrödinger equation **2.4** by assuming that each electron is associated with a separate one-electron wavefunction or spin

orbital, χ. Hartree proposed that the wavefunction could be expressed simply as a product of spin orbitals, one for each electron.[4-6] The spin orbital χ_i is a product of the spatial, or molecular orbital of the i^{th} electron, $\varphi_i(x_i,y_i,z_i)$ and a spin function, α or β. The wavefunction, written as a product of spin orbitals, is:

$$\Psi_{product} = \chi_1(1)\,\chi_2(2)\ldots\,\chi_n(n) \tag{2.6}$$

where n is the n^{th} electron. The resulting wavefunction is known as the Hartree product. However, the Pauli Exclusion Principle states that the wavefunction for an n-electron system must be antisymmetric with respect to interchange of any two particles. Equation **2.6** does not satisfy this condition, therefore, $\Psi_{product}$ is not acceptable. The wavefunction may be written as a determinant of spin orbitals in order to satisfy the above conditions:

$$\Psi = (n!)^{-\frac{1}{2}} \begin{vmatrix} \chi_1(1) & \chi_2(1) & \cdots & \chi_n(n) \\ \chi_1(2) & \chi_2(2) & \cdots & \chi_n(n) \\ \vdots & \vdots & & \vdots \\ \chi_1(n-1) & \chi_2(n-1) & \cdots & \chi_n(n-1) \\ \chi_1(n) & \chi_2(n) & \cdots & \chi_n(n) \end{vmatrix} \tag{2.7}$$

This determinant of spin orbitals is called a Slater determinant,[7,8] and $(n!)^{-\frac{1}{2}}$ is a normalization constant which can be found by imposing that the wavefunction is normalized. That is:

$$\int \Psi^* \Psi d\tau = 1 \tag{2.8}$$

with Ψ^* being the complex conjugate of Ψ.

2.4.2 Basis Set Expansion

The spatial molecular orbitals, φ_i can be expended as a linear combination of basis functions, ϕ_μ, These basis functions are one-electron functions with unknown molecular orbital expansion coefficients, $c_{\mu i}$.

$$\varphi_i = \sum_{\mu=1}^{N} c_{\mu i}\phi_\mu \qquad \textbf{(2.9)}$$

The more basis functions used in **2.9**, the better the description of φ_i can be achieved. When the basis functions describe the atomic orbitals, equation **2.9** is known as a linear combination of atomic orbitals (LCAO).

2.5 The Variational Theorem and Hartree-Fock Theory

2.5.1 The Variational Theorem

The Variational Theorem[1] allows us to determine the coefficients $c_{\mu i}$. The theorem states that for a given approximate wavefunction, ϕ, the energy is greater than or equal to the true exact energy, E_1, as described by the following equation:

$$\frac{\int \phi^* \hat{H} \phi d\tau}{\int \phi^* \phi d\tau} \geq E_1 \qquad \textbf{(2.10)}$$

where $\hat{H}$ is the time independent Hamiltonian operator, E_1 is the lowest energy corresponding to the exact wavefunction and ϕ is any normalized well-behaved function. The function ϕ is called the trial variation function and the integral is called the variational integral.[1] One would expect that the lowest value for the integral, the better

approximation to E_1 can be obtained. However, it has been shown that a good approximation to E_1 can be achieved by using a poor function, ϕ.[1]

2.5.2 Hartree-Fock Theory

The variational theorem leads to the equations that describe the molecular orbital coefficients, $c_{\mu i}$. If ϕ is normalized, the Roothaan-Hall equations[9,10] are obtained:

$$\sum_{v=1}^{N} c_{\mu i}(F_{\mu v} - \varepsilon_i S_{\mu v}) = 0 \qquad \mu=1, 2,\ldots, N \qquad \textbf{(2.11)}$$

where $F_{\mu v}$ are elements of the Fock matrix that includes the energy of the electron in the electrostatic field of all the other electrons, ε_i is the orbital energy of molecular orbital φ_i and $S_{\mu v}$ is the overlap matrix and represents the overlap between basis functions. Because the Fock matrix is dependent on the coefficients $c_{\mu i}$, which are not known, only an iterative process can solve **2.11**. This process involves several steps: it starts with an initial guess of the $c_{\mu i}$ and the density matrix is formed and solved. A test for convergence follows. If there is no convergence, another iteration begins and the process continues until the convergence criteria is met and therefore, there is no further improvement in the $c_{\mu i}$, and ε_i. This was first described by Hartree[4-6] and Fock[11] and is known as the self-consistent field (SCF) theory or Hartree-Fock (HF) theory.

2.5.3 Restricted and Unrestricted Hartree-Fock Theory

The Hartree-Fock method described above is applicable only to closed-shell molecules, due to the fact that all electrons are assigned to molecular orbitals in pairs. This is known as the restricted Hartree-Fock (RHF) theory. A simple way to expand RHF

to open shell systems is to introduce separate spatial orbitals for electrons of different spin, α and β, leading to two sets of molecular orbital expansion coefficients:

$$\Psi_i^{\alpha} = \sum_{\mu=1}^{N} c_{\mu i}^{\alpha} \phi_{\mu} \qquad \Psi_i^{\beta} = \sum_{\mu=1}^{N} c_{\mu i}^{\beta} \phi_{\mu} \tag{2.12}$$

This is referred to as unrestricted Hartree-Fock (UHF) theory. Due to the variational principle, the UHF energy will be lower than or equal to the RHF energy. The molecular orbital coefficients, $c_{\mu i}^{\alpha}$ and $c_{\mu i}^{\beta}$ can be then obtained by solving the Pople-Nesbet equations:[12]

$$\sum_{\mu=1}^{N} c_{\mu i}^{\alpha} (F_{\mu\nu}^{\alpha} - \varepsilon_i^{\alpha} S_{\mu\nu}) = 0$$

$$\sum_{\mu=1}^{N} c_{\mu i}^{\beta} (F_{\mu\nu}^{\beta} - \varepsilon_i^{\beta} S_{\mu\nu}) = 0 \qquad \mu = 1, 2, \ldots, N \tag{2.13}$$

2.6 Electron Correlation Methods

As previously discussed, Hartree-Fock theory does not provide a proper treatment of the correlation of the motions of electrons, as it uses a single-determinant wavefunction and neglects the term $(r_{ij})^{-1}$ in the Hamiltonian (see **section 2.5**). Any method that attempts to treat properly this phenomena is known as an electron correlation method.[13] The more common correlation methods are described below.

2.6.1 Full Configuration Interaction

The full configuration interaction method (full CI) considers the Hartree-Fock wavefunction, Ψ_0, as being a linear combination of the Hartree-Fock determinant and all

possible substituted determinants,[13] to obtain what is known as the full configuration interaction wavefunction ($\Psi_{(\text{full CI})}$):

$$\Psi_{(\text{fullCI})} = a_0\Psi_0 + \sum a_i\Psi_i \qquad \textbf{(2.14)}$$

where a_i is the amplitude of configuration Ψ_i. Full CI is the most complete non-relativistic treatment of the molecular system.[13] When using a basis set of infinite size, the corresponding full CI wavefunction which contains an infinite number of configurations, gives the exact solution to the non-relativistic electronic Schrödinger equation, **2.4**. The full CI method is both variational and size-consistent. However, it is computationally expensive and hence, unpractical for large systems.

2.6.2 Limited Configuration Interaction

Configuration interaction methods take the approach of limiting the full CI methods by adding to the Hartree-Fock determinant a limited set of substitutions, thus truncating the CI expansion **2.14**. For example, if only double excitations are added, one can obtain what is known as Configuration Interaction, Doubles, CID.

$$\Psi_{\text{CID}} = a_0\Psi_0 + \sum_{i<j}^{\text{occ}}\sum\sum_{a<b}^{\text{virt}}\sum a_{ij}^{ab}\Psi_{ij}^{ab} \qquad \textbf{(2.15)}$$

The Configuration Interaction, Singles and Doubles, or CISD adds both single and double substitutions:

$$\Psi_{\text{CID}} = a_0\Psi_0 + \sum_{i}^{\text{occ}}\sum_{a}^{\text{virt}} a_i^a\Psi_i^a + \sum_{i<j}^{\text{occ}}\sum\sum_{a<b}^{\text{virt}}\sum a_{ij}^{ab}\Psi_{ij}^{ab} \qquad \textbf{(2.16)}$$

The CID and CISD methods are suitable for relatively large systems, with large number of electrons and basis functions. The CID and CISD methods are variational, being a full CI method. However, these methods are not size-consistent.

2.6.3 Quadratic Configuration Interaction

This method was developed by Pople and co-workers.[14] to ensure size consistency of CISD in the resulting total energy. This is known as Quadratic Configuration Interaction (QCI). The conventional equations of linear configuration interaction theory are modified by introducing new terms to the linear expansion **2.14**, which are quadratic in the configuration coefficients. It is applied in the truncated configuration space of single and double substitutions. The method, termed QCISD, leads to a set of quadratic equations. QCISD also accounts for some correlation effects to infinite order. The next level, QCISDT, which incorporates triple substitutions, is non-practical. A useful approximation for triple substitutions is to treat them as a perturbation of the solution already obtained at the singles-doubles level, resulting in the method denoted by QCISD(T) method.[14] The QCI methods are size-consistent, but not variational.

2.6.4 Møller-Plesset Perturbation Theory

An alternative approach to electron correlation is the Møller-Plesset perturbation theory.[15-18] This represents the perturbation treatment of atoms and molecules. The perturbation theory describes the total Hamiltonian of the systems, H_λ, as a sum of two parts: a Hartree-Fock part, H_0, and a perturbation, λV:

$$H_\lambda = H_0 + \lambda V \qquad \textbf{(2.17)}$$

The perturbation, λV, applied to H_0, is defined by:

$$\lambda V = \lambda(H - H_0) \tag{2.18}$$

where H is the exact Hamiltonian operator and λ is a dimensionless parameter. The perturbation, V, is obtained as a difference between the exact Hamiltonian operator and the Hartree-Fock Hamiltonian operator.

According to perturbation theory,[1] the full CI wavefunction, Ψ_λ, and the energy, E_λ, for a system described by the Hamiltonian H_λ can be expanded as Taylor series of λ:

$$\Psi_\lambda = \Psi^{(0)} + \lambda\Psi^{(1)} + \lambda^2\Psi^{(2)} + \ldots \tag{2.19}$$

$$E_\lambda = E^{(0)} + \lambda E^{(1)} + \lambda^2 E^{(2)} + \ldots \tag{2.20}$$

The Møller-Plesset first-order correction to the ground state energy corresponds to the Hartree-Fock energy:[1]

$$E_0^{(0)} + E_0^{(1)} = E_{HF} \tag{2.21}$$

MP2 represents truncation after second-order[1] and it contains contributions due to double excitations.[16,17] MP3 represents truncation after third-order[1] and also contains contributions only from double excitations.[16,17] However singles, doubles, triples and quadruples contribute to the MP4 energy correction, the triples being the most computationally demanding.[17,18] The MPn methods are size-consistent, but not variational.

2.7 Density Functional Theory

Unlike the methods described above, which are based on determining the wavefunction of the electronic Schrödinger equation **2.4**, Density Functional Theory (DFT) treats the electron correlation by using general functionals of the electron density, ρ.[13] A functional is defined as being a function of a function.[1]

The Hohenberg-Kohn Theorem,[19] states that the ground-state of the system can be defined by the electron density distribution ρ(x,y,z) which minimises the total energy. Furthermore, Hohenberg and Kohn proved that all other ground-state properties of the system can be determined from the ground state electron density. In 1965 it was shown by Kohn and Sham[20] that the exact ground-state electronic energy of a molecule with electron density ρ, can be calculated as a sum of several terms:

$$E_{Total}[\rho] = E^{T}[\rho] + E^{V}[\rho] + E^{J}[\rho] + E^{XC}[\rho] \qquad \textbf{(2.22)}$$

where E^T is the kinetic energy of a system of non-interacting electrons with the same electron density as the real system, E^V is the potential energy term due to nuclear-electron attraction, E^J is the electron-electron repulsion term and E^{XC} is the exchange-correlational term, due to the exchange and correlation terms and also due to the difference between the true kinetic energy of the system and of the ideal 'non-interacting' system.[13,21]

Kohn and Sham also showed that the exact ground-state electron density ρ can be calculated from the Kohn-sham orbitals, Ψ_i:

$$\rho = \sum_{i=1}^{n} |\Psi_i|^2 \qquad \textbf{(2.23)}$$

The Kohn-Sham orbitals are obtained by solving the one-electron equations:

$$\hat{F}_{KS}\Psi_i(1) = \varepsilon_{i,KS}\Psi i(1) \qquad \textbf{(2.24)}$$

where $\hat{F}_{KS}$ is the Kohn-Sham operator. An iterative process is used to solve **2.24**.[1] For closed-shell molecules, electrons are assigned to the Kohn-Sham orbitals in pairs, while for open-shell molecules, electrons of different spin, α or β, are assigned to two different sets of Kohn-Sham orbitals.[1,22]

Unfortunately, the correct exchange-correlational functional E^{XC} in **2.22** is unknown. Hence, several approximate functionals are used. A broad variety of functionals have been described. They can be either local functionals, depending only on electron spin density, or gradient-corrected, depending on the values of the electron spin densities and their gradients.[13]

Density Functional Theory methods are electron correlation methods and present the advantage that they are less expensive than the wavefunction-based electron correlation methods, as the effects of electron correlation are already in ρ. Hence, these methods are suitable for larger systems, e.g., biochemical systems. However, the major disadvantage of the DFT methods is that the functionals cannot be systematically improved.[1]

2.7.1 The B3P86 Functional

A widely used functional in this thesis is the hybrid DFT functional, B3P86. This is defined as a linear combination of Hartree-Fock, local and Becke[23] gradient-corrected

exchange terms and the correlation functional developed by Perdew.[24,25] Generally, a hybrid exchange-correlation functional can be expressed:

$$E_{hybrid}^{XC} = c_{HF}E_{HF}^{X} + c_{DFT}E_{DFT}^{XC} \quad \textbf{(2.25)}$$

where the c's are constants.[13]

In particular, the exchange-correlation energy of the B3P86 hybrid functional is:

$$E_{B3P86}^{XC} = E_{LDA}^{X} + c_0(E_{HF}^{X} - E_{LDA}^{X}) + c_X\Delta E_{B88}^{X} + E_{VWN3}^{C} + c_C(E_{P86}^{C} - E_{VWN3}^{C}) \quad \textbf{(2.26)}$$

where the c's are the constants determined by Becke,[13] E_{HF}^{X} and E_{LDA}^{X} are Hartree-Fock and Local Density Approximation (LDA) local exchange, ΔE_{B88}^{X} is Becke's gradient correction to LDA exchange, VWN3 is the Vosko, Wilk and Nusair local correlation functional[26] and P86 is the gradient-corrected correlation functional due to Perdew.[24,25]

2.7.2 The B3LYP Functional

Another hybrid functional used in this thesis is B3LYP. This is defined similarly to B3P86, but the P86 gradient-corrected correlation functional is replaced by Lee, Yang and Parr[27] correlation functional. The B3LYP exchange-correlation functional can be written as:

$$E_{B3LYP}^{XC} = E_{LDA}^{X} + c_0(E_{HF}^{X} - E_{LDA}^{X}) + c_X\Delta E_{B88}^{X} + E_{VWN3}^{C} + c_C(E_{LYP}^{C} - E_{VWN3}^{C}) \quad \textbf{(2.27)}$$

with the similar symbols as in **2.26**.

Both B3P86 and B3LYP functionals have been found to be quite successful, being used on a large scale when investigating, for example, biochemical systems.

2.8 Basis Sets

Each atom of a molecule is assigned a group of basis functions, χ_r, to approximate its orbitals. There are two main types of basis functions: Slater-type orbitals (STOs) and Gaussian-type functions (GTFs). STO orbitals contain an $e^{-\alpha r}$ expression and have a cusp at the nucleus, the GTFs instead contain a $e^{-\alpha r^2}$ factor and they do not have a cusp at the nucleus. However, they are much cheaper than STOs. In addition, an STO can be accurately approximated by a linear combination of GTFs, which are still cheaper. Usually, an atomic basis function is a linear combination of GTF's; this is called a contracted Gaussian basis function, described by equation **2.28**:[1]

$$\chi_r = \sum_u d_{ur} g_u \qquad \textbf{(2.28)}$$

where g_u's are normalized and known as primitive Gaussians, and d_u's are constants.

2.8.1 Split-Valence Basis Sets

Split-valence basis sets assign two or more basis functions per valence orbital and only one basis function for each inner-shell (core) orbital. Double-split-valence or double-zeta-valence basis sets have two basis functions per valence orbital, e.g., 6-31G. Triple-split-valence or triple-zeta-valence basis sets have three basis functions per valence orbital, e.g., 6-311G.[13] The notation 6-31G means that a set of 6 primitive Gaussians are used for the core orbitals and sets of three and one primitive Gaussians are used for each valence orbital.

2.8.2 Diffuse Functions

These are large *s*- and *p*- type functions which allow orbitals to occupy a larger region of space. Diffuse functions are denoted by a "+" sign, e.g., 6-31+G(d). This notation means that diffuse functions have been added to heavy atoms. It has been shown that diffuse functions have significant role for molecules with lone pairs, anions, etc.[13]

2.8.3 Polarization Basis Sets

Unlike the split valence basis sets which allow orbitals to change only shape, polarized functions permit both change in size and shape of orbitals. This is possible by adding basis functions of higher orbital angular momentum, e.g., *d*- and *f*-functions on all atoms other than hydrogen and helium, known as heavy atoms, and *p*- and *d*-functions to hydrogen and helium.

2.9 Notation

The commonly used notation to describe a method and level of theory is:

method 1 / basis set 1 // method 2 / basis set 2

For example, the notation:

QCISD/6-31+G(d)//HF/6-31G(d)

means that a single point calculation was performed using the Quadratic Configuration Interaction Singles and Doubles method (QCISD) in combination with the 6-31+G(d)

basis set, based on the geometry optimised at the Hartree-Fock (HF) level of theory using the 6-31G(d) basis set.

2.10 Compound Methods

The compound methods are characterized by the fact that they use the results obtained at relatively low levels of theory to approximate the result of a single, high-level computation. These methods have been developed in order to predict more accurately thermochemical properties of the molecules, e.g., atomization energy, electron affinity, ionization potential and proton affinity. Such properties are well predicted by high electron correlation methods. However, due to the increased computational cost, they are non-practical for larger systems. The compound methods attempt to correct this deficiency. The compound methods used in this thesis are described briefly below.

2.10.1 Gaussian-3 (G3) Theory Methods

These methods were developed for the molecules containing first and second-row atoms,[28] in order to correct deficiencies found in earlier compound method Gaussian-2.[29] For calculating the total energy of a given molecular species with G3 theory, several steps must be taken. An initial optimization of the structure is obtained at HF/6-31G(d) level. Zero point vibrational energies (ZPVE) are calculated at the same level and corrected by a factor of 0.8929.[30] The geometry is then optimized at MP2/6-31G(d) level. Using this geometry, a single-point energy calculation is carried out at the higher level of theory, i.e., MP4/6-31G(d). This 'base energy' is then corrected using several single points at MP2 and MP4 to approximate the total energy of the system that would be obtained at the much higher and considerable more expensive level of theory.

2.10.2 Complete Basis Set Methods (CBS)

These methods have been developed by Petersson and several collaborators to correct for the large errors in *ab initio* calculations due to basis set truncation.[31,32] Generally, CBS models include an optimization obtained using the Hartree-Fock method in combination with a very large basis set. Then, a base energy calculation with MP2 method in conjunction with a medium-size basis set is performed. Then, using several other single point calculations, it attempts to extrapolate to the total energy of the system that would be obtained if an infinitely sized basis set was used at the higher level. CBS methods used in this thesis are described below.

2.10.2.1 CBS-Q

With the CBS-Q model[32,33] the optimized geometry is obtained at MP2(FC)/6-31G(d) level. The correction for the ZPVE is calculated at HF/6-31G(d) level of theory. Then a base energy is computed using a large basis set MP2 calculation, i.e., MP2/6-311+G(3d2f,2df,2p) and the extrapolation is performed. Additional high-level single point calculations are also made, i.e., MP4(SDQ)/6-31+G(df,p) and QCISD(T)/6-31+G(d).

2.10.2.2 CBS-QB3

The CBS-QB3 model combines the general design of the CBS-Q energy calculation with B3LYP optimized geometries and frequencies.[34] Also, the QCISD(T) single point calculation in CBS-Q is replaced with CCSD(T) single point calculation. Compared to the CBS-Q method, the CBS-QB3 method provides a small improvement in

accuracy. Furthermore, due to the sometimes greater accuracy of B3LYP geometries relative to MP2, CBS-QB3 can be considered more reliable than the CBS-Q method.

2.10.2.3 CBS-4M

With the CBS-4M method,[35] the geometry optimization, as well as ZPVE calculations are done at the HF/3-21G(d) level of theory. The base energy is then calculated with the MP2 method using a large basis set. At the MP2/6-31+G(d) level, the CBS extrapolation is performed and a higher-level calculation follows, e.g., MP2(SDQ)/6-31+G(d,p). This method also includes the minimal population localization procedure[35] and improved empirical parameters.

2.11 Potential Energy Surfaces

The Potential Energy Surface (PES) gives a complete description of a chemical reaction. An example of a two-dimensional PES is given in **Figure 2.1**, which shows the energy level of reactants (A + B), intermediates (A···B) and (C···D), and products (C + D), and a maximum in between, the transition structure (TS). The energy difference between the reactants (A + B) and the intermediate (A···B) is the stabilization energy due to interaction, e.g., hydrogen bonding or electrostatic interactions. The energy difference between the TS and the intermediate (A···B) is called the activation energy.

2.12 Solvation Model

The influence of the solvent can be very important, as the characteristics of molecules can change in solution; some properties of the molecules differ substantially from the gas phase.

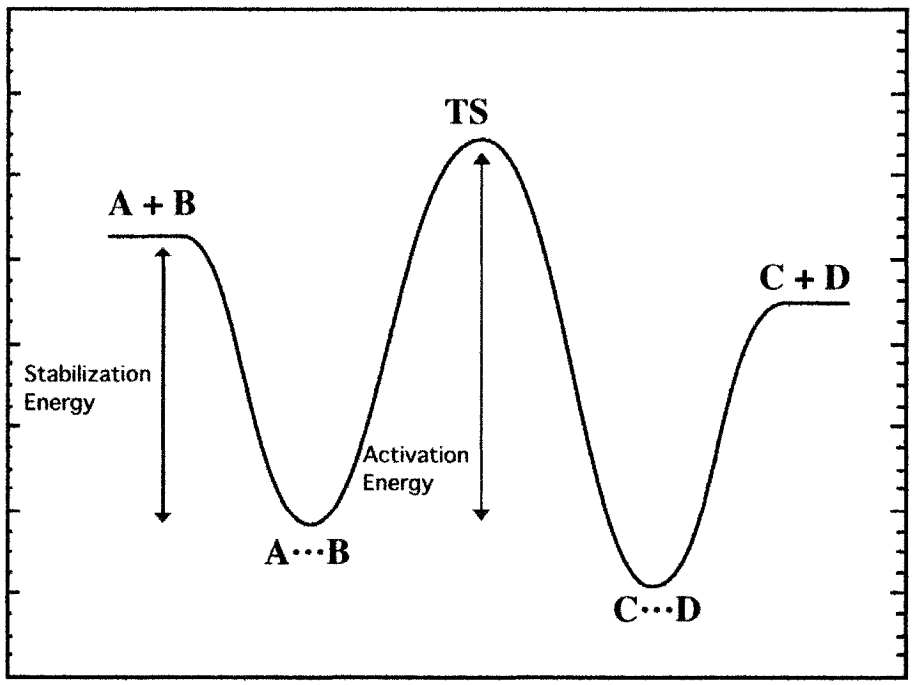

Figure 2.1 Schematic representation of potential energy surface

In this thesis we used the simplest Self-Consistent Reaction Field (SCRF) method, the Onsager model.[36] In this model, the solute is considered to sit inside a sphere with radius a_0 which occupies a space within the solvent. The solvent has a specified dielectric constant, ε, as shown in **Figure 2.2**. If a dipole moment is induced within the molecule, this in turn will induce a dipole in the solvent and the interaction between these dipole moments will lead to a stabilization of the molecule.[13]

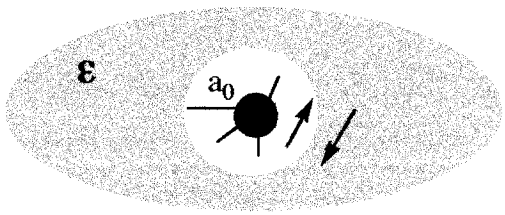

Figure 2.2 Schematic representation of the Onsager model

The Onsager model, without being the most accurate of the salvation models, it is fast and it provides a qualitatively good description of the solvent effect on the molecules. However, for the solvents with a dipole moment of zero, this model fails.

2.13 Technical Aspects and Units

All calculations were performed using the Gaussian 98 and Gaussian 03 suite of programs.[37,38] Versions used were:

(i) x86-Linux-G98 Revision A.11.1

(ii) x86-Linux-G03 Revision C.01

(iii) IBM-RS6000-G98 Revision A.7

(iv) MacOSX-G98 Revision A.11.

All of the energies reported in this thesis are expressed in kiloJoules per mole (kJ mol^{-1}) using the following conversion factors:

(i) 1 hartree = 2625.5 kJ mol^{-1}

2.14 Summary of Abbreviations Used

The abbreviations used more often in this thesis are:

HF	Hartree-Fock
MPn	nth-order Møller-Plesset
QCISD	Quadratic configuration with Singles and Doubles
G3	Gaussian-3 theory
CBS-4M	Complete Basis Set-4M
CBS-Q	Complete Basis Set-Q
CBS-QB3	Complete Basis Set-QB3

DFT	Density Functional Theory
B3LYP	DFT functional defined as the combination of the B3 exchange functional with the LYP correlation functional.
B3P86	DFT functional defined as the combination of the B3 exchange functional with the Perdew (P86) correlation functional.
ZPVE	Zero point vibrational energy

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Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*.; Gaussian, Inc.: Pittsburg, PA, 2003.

Chapter 3

An Assessment of Theoretical Methods For The Calculation of Accurate Structures and RS—NO Bond Dissociation Energies

3.1 Introduction

Since 1990, there has been increasing interest in S-nitrosothiols (RSNOs), species containing an –SNO functional group, due to the fact that they have been found to be formed *in vivo* as part of the metabolism of nitric oxide (NO),[1-3] an important biological messenger. In particular, they are thought to be a means of transporting and storing NO within the body.[1-6] Futhermore, they often show many of the same biological properties as NO including vasodilation of arteries, and inhibition of platelet aggregation.[5,7-11] Unfortunately, due in part to the fact that they are usually highly reactive, have short lifetimes, and are readily decomposed by heat, light or Cu^+ ions, experimental studies on RSNOs are often quite difficult.[12,13] As a result, our current level of understanding of many of the fundamental properties of this important class of compounds, and their chemistry, is unsatisfactory.

Computational chemistry would seem to offer an attractive alternative approach for investigations on RSNOs, particularly as studies of highly-reactive species are generally as straightforward as those of stable long-lived species. However, it can have its own inherent difficulties, not the least of which is determining a reliable and accurate level of theory for investigating chemical properties of interest, e.g., bond dissociation energies.

Recently, several theoretical studies on homolytic S—N bond dissociation energies (BDEs) of RSNOs have appeared in the literature.[4,14-17] In general, they have employed the common approach of performing large single-point or composite method, e.g., G3 or CBS calculations, based on optimized structures obtained at considerably lower levels of theory. More specifically, structures used in these studies have been obtained using the Hartree-Fock, MP2 or density functional theory (DFT) B3LYP method, in conjunction with a modest basis set, generally 6-31G(d) or smaller. Typically, such levels of theory provide reliable structures for well-behaved species. However, no previous theoretical investigations[4,14-17] have considered their reliability for S-nitrosothiols. Indeed, optimized structures of RSNOs obtained using such methods contain S—N bond lengths that vary considerably, from as short as 1.75 Å[16] to almost 2.05 Å.[16] This range and size is all the more remarkable considering it has been suggested that the RS—NO bond possesses considerable double-bond character.[15,16,18] Hence, it is unclear whether such variable optimized lengths are artefacts of the methods employed, or indicative of the nature of the RS—NO bond. In addition, such significant differences can potentially affect, for example, the reliability of calculated S—N BDEs based on such structures. Indeed, previously calculated S—N BDEs,[4,14-17] differ considerably from each other for some particular RSNOs by as much as 40 kJ mol^{-1}.[16] Furthermore, they also differ from the corresponding experimentally determined BDE by more than 30 kJ mol^{-1}.[16] Considering the potential utility of computational chemistry for studying such species, this is an unsatisfactory situation.

The aim of this chapter is to assess the ability of a range of commonly employed theoretical methods, in particular DFT methods, to obtain reliable structures and homolytic S—N BDEs of S-nitrosothiols. The methods considered are the conventional electron correlation methods MP2 and QCISD, and the DFT methods B3LYP and B3P86. A variety of model RSNOs: HSNO, CH_3SNO, C_2H_3SNO, C_2H_5SNO, C_6H_5SNO and

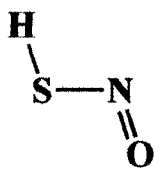
CysSNO (S-nitroso-cysteine), have been used. These were chosen to provide both various sized RSNOs, and a range of R groups used in previous experimental and theoretical studies, hence enabling greater comparison.

3.2 Computational Methods

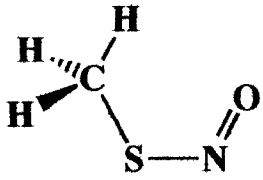
All geometry optimizations were performed with the Gaussian 98 and Gaussian 03 suite of programs (see **Chapter 2**). Optimized geometries were obtained using a variety of methods; the conventional electron-correlation methods MP2 and QCISD, and density functional theory methods. For the DFT methods, B3LYP and B3P86 were employed. All methods were used in combination with basis sets ranging from 6-31G(d) to 6-311++G(3df,3pd), depending on the size of molecule being investigated. Zero-point vibrational energy (ZPVE) corrections were also calculated at these levels of theory, and scaled by an appropriate factor.[19] For each RSNO, S—N homolytic bond dissociation energies were calculated using a variety of methods, each being corrected using appropriately scaled ZPVEs (see text). Restricted and unrestricted procedures were used for all closed- and open-shell species, respectively. All bond dissociation energies are in kJ mol^{-1} and bond lengths in Angstroms, unless otherwise noted. Optimized geometries obtained for species considered in chapter are given in the **Appendix A**.

3.3 Results and Discussion

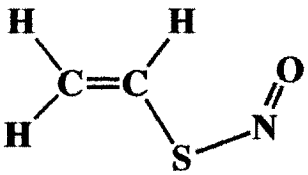
The S-nitrosothiols examined in this present study are shown schematically in **Figure 3.1**. In all cases, the most significant structural changes occur in the S—N and N—O bond lengths. Thus, the following discussion is limited to these parameters, unless otherwise noted.



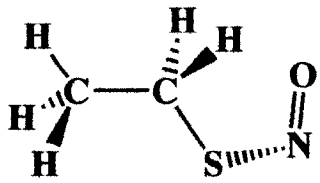
***trans*-HSNO**



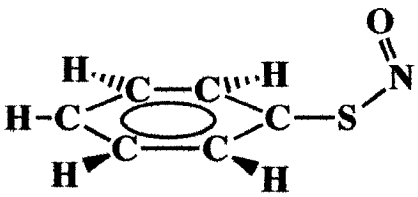
***cis*-CH_3SNO**



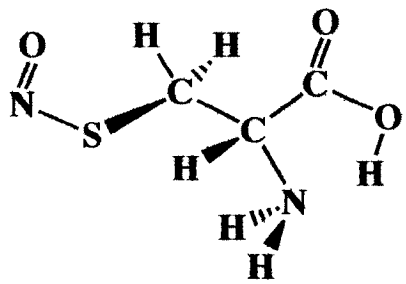
***cis*-C_2H_3SNO**



***cis*-C_2H_5SNO**



***cis*-C_6H_5SNO**



CysSNO

Figure 3.1 Schematic illustration of the structures of the S-nitrosothiols (RSNOs) considered in this chapter.

Optimized geometries: HSNO. HSNO, being the smallest S-nitrosothiol, was examined using the broadest range of methods and basis sets (**Table 3.1**). Unlike all other RSNOs presently considered, the lowest energy conformer of HSNO is *trans* (*anti*) with the *cis* (*syn*) conformer lying just a few kJ mol^{-1} higher in energy. Typically, primary and secondary RSNOs prefer a *syn*, and tertiary an *anti*, conformation.[20] For completeness, selected optimized parameters of both conformers are given in **Table 3.1**. As the trends observed are essentially the same for both, the following discussion is limited to the *trans* conformer, unless otherwise noted.

For the MP2 method with the smallest basis set used in this study, 6-31G(d), the *trans* and *cis* conformers have S—N bond lengths (r(S—N)) of 1.850 and 1.827 Å, respectively (**Table 3.1**). The inclusion of *p*-functions on hydrogen (6-31G(d) →6-31G(d,p)) has minimal affect. Improving the valence description from double- to triple-zeta (6-31G(d,p) →6-311G(d,p)), however, has a larger affect on the S—N bond, lengthening it by almost 0.04 Å to 1.891 Å. Further augmentation of the basis set by inclusion of diffuse functions on non-hydrogen atoms (6-311G(d,p) →6-311+G(d,p)) decreases r(S—N) by approximately 0.04 Å, while inclusion of a second set of *d*-functions (6-311G(d,p) →6-311G(2d,p)), has a similar-sized but opposite affect, i.e., r(S—N) increases by almost 0.04 Å. Inclusion of *f*-functions (6-311G(d,p) →6-311G(df,p)), however, dramatically shortens the S—N bond by more than 0.06 Å to 1.827 Å. Consequently, at the MP2/6-311+G(2df,p) level, in which these basis set enhancements are combined, the S—N bond (1.826 Å) is shorter relative to that obtained at the MP2/6-311G(d,p) level (1.891 Å), by about 0.06 Å. We note that the length is close to that obtained with the smaller 6-311G(df,p) basis set (1.827 Å). Improving the basis set to 6-311++G(3df,3pd), the largest used in this study, results in only a slight decrease in r(S—N) to 1.810 Å.

TABLE 3.1: Selected Optimized Parameters[a] for *trans*- and *cis*-HSNO

Method	Basis Set	r(S—N)		r(H—S)		r(N—O)	
		trans	*cis*	*trans*	*cis*	*trans*	*cis*
MP2	6-31G(d)	1.850	1.827	1.341	1.347	1.205	1.211
	6-31G(d,p)	1.853	1.832	1.331	1.338	1.204	1.209
	6-311G(d,p)	1.891	1.852	1.333	1.340	1.179	1.188
	6-311+G(d,p)	1.850	1.818	1.334	1.342	1.188	1.195
	6-311G(2d,p)	1.929	1.905	1.333	1.339	1.175	1.181
	6-311G(df,p)	1.827	1.794	1.335	1.344	1.186	1.193
	6-311+G(2df,p)	1.826	1.799	1.340	1.348	1.191	1.197
	6-311++G(3df,3pd)	1.810	1.785	1.333	1.341	1.191	1.197
QCISD	6-31G(d)	1.863	1.851	1.346	1.352	1.194	1.197
	6-31G(d,p)	1.864	1.853	1.334	1.339	1.193	1.197
	6-311G(d,p)	1.878	1.860	1.336	1.342	1.175	1.179
	6-311+G(d,p)	1.855	1.838	1.338	1.344	1.179	1.184
	6-311G(2d,p)	1.890	1.878	1.334	1.340	1.174	1.177
	6-311G(df,p)	1.834	1.814	1.338	1.345	1.176	1.180
	6-311+G(2df,p)	1.834	1.818	1.342	1.349	1.179	1.182
	6-311++G(3df,3pd)	1.820	1.804	1.347	1.342	1.179	1.182
B3LYP	6-31G(d)	1.913	1.901	1.349	1.355	1.175	1.178
	6-31G(d,p)	1.914	1.904	1.348	1.353	1.174	1.178
	6-311G(d,p)	1.942	1.928	1.347	1.353	1.160	1.164
	6-311+G(d,p)	1.910	1.894	1.347	1.354	1.166	1.170
	6-311G(2d,p)	1.922	1.909	1.342	1.348	1.163	1.166
	6-311G(df,p)	1.926	1.905	1.347	1.353	1.161	1.165
	6-311+G(2df,p)	1.874	1.857	1.344	1.351	1.169	1.172
	6-311++G(3df,3pd)	1.870	1.852	1.341	1.349	1.168	1.172
B3P86	6-31G(d)	1.881	1.867	1.345	1.352	1.174	1.178
	6-31G(d,p)	1.883	1.870	1.344	1.351	1.174	1.177
	6-311G(d,p)	1.903	1.884	1.344	1.351	1.161	1.165
	6-311+G(d,p)	1.878	1.860	1.345	1.353	1.165	1.169
	6-311G(2d,p)	1.882	1.867	1.340	1.346	1.164	1.167
	6-311G(df,p)	1.887	1.864	1.344	1.351	1.162	1.167
	6-311+G(2df,p)	1.843	1.824	1.342	1.350	1.168	1.173
	6-311++G(3df,3pd)	1.839	1.820	1.340	1.347	1.168	1.172

[a] Bond lengths are in Angstroms.

For the QCISD method, similar trends to those described for the MP2 method are observed (**Table 3.1**). However, the size of the changes observed for the r(S—N) are now more tempered. For example, including a second set of *d*-functions (6-311G(d,p) →6-311G(2d,p)) increases r(S—N) by just 0.012 Å, less than half that observed with the MP2 method. Furthermore, including diffuse or *f*-functions (6-311G(d,p) →6-311+G(d,p) or 6-311G(df,p)) decreases r(S—N) by about 0.02 and 0.04 Å, respectively, for both conformers. While these are non-negligible changes, they are smaller than observed for the MP2 method. At the QCISD/6-311++G(3df,3pd) level, the S—N bond length in *trans*-HSNO is 1.820 Å, close to that obtained using the smaller 6-311+G(2df,p) and 6-311G(df,p) basis sets (both 1.834 Å), see **Table 3.1**.

The DFT methods B3LYP and B3P86 exhibit similar basis set affects to each other, which differ from those observed for the conventional MP2 and QCISD methods. With the 6-31G(d) basis set, the B3LYP and B3P86 methods give optimized S—N bond lengths for *trans*-HSNO of 1.913 and 1.881 Å, respectively, longer than obtained at the corresponding MP2 and QCISD levels (**Table 3.1**). Increasing the basis set from 6-31G(d) to 6-311G(d,p) lengthens the S—N bond by 0.02-0.03 Å. The B3LYP method exhibits the largest increase, resulting in a quite long S—N bond length of 1.942 Å. Improving the 6-311G(d,p) basis set by including diffuse, a second set of *d*- or a set of *f*-functions, all result in modest decreases in the optimized values of r(S—N) by 0.016-0.032 Å. When each of these basis set enhancements are combined in the 6-311+G(2df,p) basis set, the B3LYP method still predicts a considerably longer S—N bond length (1.874 Å) than *any* of the other methods. In contrast, the B3P86 method now gives an S—N length of 1.843 Å, in reasonable agreement with the QCISD/6-311+G(2df,p) value of 1.834 Å (see **Table 3.1**). Improving the basis set to 6-311++G(3df,3pd) causes only minor decreases in r(S—N) of much less than 0.01 Å. At the B3LYP/6-311++G(3df,3pd) and B3P86/6-311++G(3df,3pd) levels, the S—N bond lengths of *trans*-HSNO are 1.870

and 1.839 Å, respectively. We note that while the agreement between the QCISD and B3P86 methods is slightly worse with this larger basis set, they still agree within 0.02 Å. Optimized H—S and N—O bond lengths are also included in **Table 3.1**. They are noticeably less sensitive to basis set changes than the S—N bond. Indeed, the largest single change observed for all methods occurs in the N—O bond upon going from 6-31G(d,p) to 6-311G(d,p), which shortens by 0.025 Å or less. It is interesting to note, however, that the DFT methods consistently predict slightly shorter N—O distances than the QCISD method, which are shorter than those obtained using the MP2 method, see **Table 3.1**.

An explanation for the trends noted above, i.e., sensitivity of r(S—N) to the basis set employed and the requirement for extensive basis sets, e.g., 6-311+G(2df,p), before convergence in its optimized length for a given method is achieved, is suggested by considering the pertinent bonds in $HSNH_2$, HNO and NO. Formally, $HSNH_2$ contains an S—N single-bond,[21,22a] HNO an N—O double-bond while NO has a bond order of 2.5.[22b] Selected optimized parameters of these species obtained using the 6-311+G(2df,p) basis set in conjunction with each method, are listed in **Table 3.2**. It can be seen that the optimized r(S—N) values for HSNO are all 0.10-0.15 Å greater than obtained for $HSNH_2$ at the same level of theory. Thus, the S—N bond in HSNO does not possess considerable double bond character as previously thought,[15,16,18] but instead is a long single-bond. An explanation for this bond character is suggested by considering the N—O length in HSNO, which is between that of r(N—O) in HNO and NO (*c.f.* **Table 3.1**). That is, the –NO moiety in HSNO retains significant multiple-bond character, less than that of NO but enhanced relative to HNO, consequently reducing its participation in the S—N bond, hence its lengthening. The sensitivity of long bonds to the method and basis set employed, i.e., the accuracy of the description of such longer-range interactions between moieties, has been noted previously.[23] Thus, the trends noted above are a direct

consequence of the long single-bond nature of the RS—NO bond. In addition, the above results suggest that the B3LYP method overestimates the length of such bonds, while the MP2 method is the most sensitive to the description of the orbitals involved, i.e., basis set. We note that a long single RS—NO bond may help explain the experimentally observed high-labililty of the NO moiety in RSNOs.

TABLE 3.2: Selected Optimized Parameters[a] For *trans*-$HSNH_2$, HNO and NO Obtained Using the 6-311+G(2df,p) Basis Set With Various Methods

	r(S—N)	r(N—O)	
Method	$HSNH_2$	HNO	NO
MP2	1.717	1.219	1.137
QCISD	1.721	1.204	1.152
B3LYP	1.724	1.198	1.146
B3P86	1.709	1.193	1.142

[a] Bond lengths are in Angstroms.

Optimized geometries: CH_3SNO. This next largest alkyl S-nitrosothiol was also examined with the broadest range of basis sets, to enable greater comparison with the prototypical RSNO, HSNO. The lowest energy conformer is *cis*, with one of the methyl hydrogens directed towards the oxygen (see **Figure 3.1**). Selected optimized parameters are listed in **Table 3.3**.

The same trends upon increasing the basis set for each method are observed as previously described for HSNO. For example, for the MP2 and QCISD methods,

inclusion of diffuse or *f*-functions (6-311G(d,p) →6-311+G(d,p) or 6-311G(df,p)) causes the S—N bond to shorten by 0.02-0.05 Å, while inclusion of *d*-functions lengthens it by 0.01-0.02 Å.

TABLE 3.3: Selected Optimized Parameters[a] for *cis*-CH_3SNO

Method	Basis Set	r(S—N)	r(C—S)	r(N—O)
MP2	6-31G(d)	1.811	1.795	1.214
	6-311G(d,p)	1.837	1.789	1.191
	6-311+G(d,p)	1.806	1.791	1.198
	6-311G(2d,p)	1.858	1.797	1.191
	6-311G(df,p)	1.783	1.783	1.196
	6-311+G(2df,p)	1.776	1.790	1.202
	6-311++G(3df,3pd)	1.761	1.784	1.203
QCISD	6-31G(d)	1.834	1.805	1.201
	6-311G(d,p)	1.846	1.801	1.183
	6-311+G(d,p)	1.828	1.804	1.186
	6-311G(2d,p)	1.852	1.809	1.183
	6-311G(df,p)	1.802	1.795	1.184
	6-311+G(2df,p)	1.799	1.801	1.187
B3LYP	6-31G(d)	1.867	1.813	1.187
	6-311G(d,p)	1.887	1.809	1.174
	6-311+G(d,p)	1.861	1.812	1.179
	6-311G(2d,p)	1.864	1.807	1.177
	6-311G(df,p)	1.865	1.808	1.175
	6-311+G(2df,p)	1.821	1.804	1.182
	6-311++G(3df,3pd)	1.814	1.799	1.182
B3P86	6-31G(d)	1.835	1.796	1.186
	6-311G(d,p)	1.848	1.792	1.175
	6-311+G(d,p)	1.829	1.795	1.178
	6-311G(2d,p)	1.827	1.790	1.178
	6-311G(df,p)	1.829	1.791	1.176
	6-311+G(2df,p)	1.793	1.787	1.182
	6-311++G(3df,3pd)	1.787	1.783	1.181

[a] Bond lengths are in Angstroms.

As for HSNO, the largest changes in r(S—N) for any basis set enhancement, occur for the MP2 method. In addition, for both of these methods, optimized r(S—N) values obtained using the 6-311G(df,p) and 6-311+G(2df,p) basis sets agree within 0.01 Å (see **Table 3.3**). For the MP2 method, increasing the basis set further to 6-311++G(3df,3pd) causes only a slight decrease in r(S—N). The B3LYP and B3P86 methods again exhibit a more tempered basis set dependence than the MP2 method. For example, improving the 6-311G(d,p) basis set by inclusion of diffuse, *d*- or *f*-functions all result in modest decreases in the optimized r(S—N) values of 0.02-0.03 Å (see **Table 3.3**). Similar to that noted for HSNO, of the two DFT methods, the largest changes in r(S—N) occur with the B3LYP method, which also consistently predicts longer S—N bonds, for a given basis set, than any of the other methods. Increasing the basis set to 6-311++G(3df,3pd) results in only minor shortenings of the S—N bonds. It should be noted that optimized S—N bond lengths obtained at the QCISD/6-311+G(2df,p) and B3P86/6-311+G(2df,p) levels are again in close agreement, being 1.799 and 1.793 Å, respectively.

The N—O bond, for all methods, is again quite insensitive to the basis set beyond 6-311G(d,p). The broadest variation occurs for the MP2 method, which also consistently predicts a slightly longer N—O bond than any of the methods. Indeed, the QCISD, B3LYP and B3P86 methods all give quite similar optimized N—O bond lengths of approximately 1.18 Å, while the MP2 method generally predicts a value close to 1.20 Å (see **Table 3.3**).

In CH_3SNO, for all methods in combination with the 6-311+G(2df,p) basis set or larger, the S—N bond is predicted to be significantly longer than in $HSNH_2$ while concomitantly, the N—O bond length lies midway between that of HNO and NO (*c.f.* **Table 3.2**). Thus, while the CH_3S—NO bond is shorter than that in HSNO (*c.f.* **Table**

3.1), it is still a lengthened S—N single-bond, again with considerable multiple-bond character in the –NO moiety.

Optimized geometries: CH_2CHSNO, CH_3CH_2SNO, C_6H_5SNO and CysSNO. Optimized S—N and N—O bond lengths for all four species are given in **Table 3.4**. Due to their larger size, a reduced range of basis sets and methods was used.

TABLE 3.4: Optimized S—N and N—O Bond Lengths[a] for *Cis* Conformers of CH_2CHSNO, CH_3CH_2SNO, C_6H_5SNO and CysSNO

		CH_2CHSNO		CH_3CH_2SNO		C_6H_5SNO		CysSNO	
Method	Basis Set	r(S—N)	r(N—O)	r(S—N)	r(N—O)	r(S—N)	r(N—O)	r(S—N)	r(N—O)
MP2	6-311G(d,p)	1.883	1.184	1.806	1.201	2.097	1.154	1.955	1.170
	6-311G(df,p)	1.800	1.194	1.762	1.204	1.900	1.174	1.791	1.197
	6-311+G(2df,p)	1.803	1.197	1.760	1.210	1.937	1.171	1.795	1.201
QCISD	6-311G(d,p)	1.866	1.180	1.833	1.187	1.906	1.173		
	6-311G(df,p)	1.816	1.181	1.792	1.188				
B3LYP	6-311G(d,p)	1.920	1.169	1.883	1.175	1.966	1.161	1.921	1.167
	6-311+G(2df,p)	1.856	1.176	1.817	1.184	1.887	1.169	1.855	1.174
B3P86	6-311G(d,p)	1.880	1.170	1.846	1.176	1.926	1.161	1.882	1.167
	6-311+G(2df,p)	1.825	1.176	1.792	1.183	1.854	1.169	1.825	1.174

[a] Bond lengths are in Angstroms.

In general, similar trends are observed as previously described for HSNO and CH_3SNO. For example, for the conventional MP2 and QCISD methods, inclusion of *f*-functions (6-311G(d,p) →6-311G(df,p)) significantly shortens the S—N bond with a concomitant, though less dramatic, lengthening of the N—O bond. In addition, increasing

the basis set further at the MP2 level to 6-311+G(2df,p), results in only quite minor changes in the optimized bond lengths. A notable exception to this occurs for C_6H_5SNO, where r(S—N) increases by almost 0.04 Å (see **Table 3.4**). However, the MP2 method appears to have considerable difficulty describing the interaction between the aromatic (C_6H_5S) system and the NO moiety, ultimately causing it to overestimate r(S—N). This is indicated by the fact that at the MP2/6-311G(d,p) level, the optimized S—N bond length is very long at 2.097 Å, while at the QCISD/6-311G(d,p) level it is 1.906 Å, 0.191 Å shorter. In comparison, at the same levels of theory, the corresponding differences obtained for the other RSNOs are all less than 0.03 Å (*c.f.* **Tables 3.1** and **3.3**). It should also be noted that the N—O bond length is 1.154 Å at the MP2/6-311G(d,p) level, markedly shorter than obtained for *any* other RSNO at *any* level of theory.

For the DFT methods, substantial decreases in the optimized r(S—N) values, with smaller concomitant increases in the r(N—O) values, also occur upon increasing the basis set from 6-311G(d,p) to 6-311+G(2df,p). In general, structures obtained at the B3P86/6-311+G(2df,p) level are again in better agreement with those obtained with the QCISD/6-311G(df,p) and MP2/6-311+G(2df,p) methods, than are those obtained at the B3LYP/6-311+G(2df,p) level, which again generally predicts longer S—N bonds than the other methods. The exception to this occurs for C_6H_5SNO, however, this is most likely due to overestimation of the C_6H_5S—NO bond length by the MP2 method, as noted above.

As for HSNO and CH_3SNO, comparison with the appropriate bond lengths of $HSNH_2$, HNO and NO, clearly illustrates the long single-bond nature of the RS—NO bond and multiple-bond character of the –NO group, in each of the above RSNOs (*c.f.* **Table 3.2**).

Homolytic S—N BDEs: HSNO and CH_3SNO. Calculated S—N BDEs of *trans*-HSNO and *cis*-CH_3SNO are listed in **Table 3.5**. Both exhibit very similar basis set dependencies. For all methods, improving the basis set from 6-311G(d,p) to 6-311+G(2df,p) increases the calculated BDEs.

TABLE 3.5: Calculated[a] Homolytic S—N BDEs of *trans*-HSNO and *cis*-CH_3SNO (kJ mol^{-1})

Method	HSNO	CH_3SNO
MP2/6-311G(d,p)	101.3	113.4
MP2/6-311+G(2df,p)	130.8	142.5
MP2/6-311++G(3df,3pd)	130.4	144.6
QCISD/6-311G(d,p)	65.0	75.9
QCISD/6-311+G(2df,p)	84.1	92.0
QCISD/6-311++G(3df,3pd)[b]	85.4	
B3LYP/6-311G(d,p)	109.1	112.8
B3LYP/6-311+G(2df,p)	116.8	121.0
B3LYP/6-311++G(3df,3pd)	116.8	121.7
B3P86/6-311G(d,p)	126.1	132.2
B3P86/6-311+G(2df,p)	135.5	142.2
B3P86/6-311++G(3df,3pd)	135.4	142.9
B3LYP/6-31G(d)[16]	120.9	123.8
B3LYP/6-311++G(2df,p)//B3LYP/6-31G(d)[16]	121.8	124.3
ROMP2/6-311++G(d,p)//B3LYP/6-31G(d)[16]	85.4	94.1
CBS-4M[16]	137.2	143.9
CBS-QB3[14]	122.2[a]	135.6
CBS-Q[16]	128.9	141.0
G3[16]	120.9	131.8

[a] From this thesis, unless otherwise noted. [b] ZPVE calculated at the QCISD/6-311G(d,p) level, scaled by 0.96.

The largest increases of approximately 30 and 20 kJ $mol^{-1}$are observed for the MP2 and QCISD methods, respectively, while those observed for the B3LYP and B3P86 methods are just 10 kJ mol^{-1} or less. Improving the basis set further, 6-311+G(2df,p) to 6-311++G(3df,3pd), results in only minor changes in the calculated BDEs. For a suitably large basis set, e.g., 6-311+G(2df,p) or larger, values obtained using the MP2 and B3P86 methods are in close agreement, agreeing within 5 kJ mol^{-1} (see **Table 3.5**). The corresponding values calculated using the B3LYP method are lower by 15-20 kJ mol^{-1}. Surprisingly, however, S—N BDEs calculated using the QCISD method with any basis set are significantly lower than obtained using any other method by 30-50 kJ mol^{-1}. Thus, while the QCISD method appears to provide reliable structures, it grossly underestimates the strength of the long single S—N bond.

Of the methods previously used to calculate S—N BDEs, the CBS-Q and G3 methods have the highest expected reliability and accuracy. We note that the CBS-QB3 method is of similar accuracy. In general, however, for the RSNOs in this present study it gives values that lie between those obtained with the G3 and CBS-Q methods. Thus, for simplicity, it is omitted from the following discussion, unless otherwise noted. From **Table 3.5** it can be seen that the G3 method predicts BDEs that are about 10 kJ mol^{-1} lower than obtained using the CBS-Q method. As a result, S—N BDEs obtained using the MP2 and B3P86 methods with the 6-311+G(2df,p) basis set or larger, are within 5 kJ mol^{-1} or less of those obtained using the CBS-Q method. However, BDEs obtained with the B3LYP method and 6-311+G(2df,p) basis set or larger, give the best agreement with those obtained using the G3 method, being just 10 kJ mol^{-1} or less lower. As the QCISD method underestimates the S—N BDE of HSNO and CH_3SNO, it gives poorest agreement with most of the previously calculated values, in particular those obtained using the CBS-Q and G3 methods, being approximately 35-50 kJ mol^{-1} too low.[14,16] We note that BDEs calculated at the QCISD/6-311+G(2df,p) level are close to those

obtained[16] using the mixed MP2/6-311++G(d,p)//B3LYP6-31G(d) method. However, these values are likely to be erroneously low, due in part to the fact that structures obtained with the B3LYP method possess considerably longer S—N bonds than obtained using the MP2 method (*c.f.* **Tables 3.1** and **3.3**).

Homolytic S—N BDEs: CH_2CHSNO, CH_3CH_2SNO, C_6H_5SNO and CysSNO. Calculated and experimental, where available, values for these RSNOs are listed in **Table 3.6**. In general, similar trends as previously describe for HSNO and CH_3SNO are observed. For instance, improving the basis set from 6-311G(d,p) to 6-311+G(2df,p) for any method increases the calculated S—N BDEs. The largest increases, approximately 25-30 kJ mol^{-1}, are again observed for the MP2 method while, in contrast, the DFT methods exhibit smaller increases of just 14.4 kJ mol^{-1} or less. In addition, the QCISD method again drastically underestimates RS—NO BDEs. For example, for CH_3CH_2SNO the BDE obtained at the QCISD/6-311G(d,p) level is 55.3 kJ mol^{-1} lower than obtained at the B3P86/6-311G(d,p) level, which is itself in good agreement with the previously calculated[16] G3 value (see **Table 3.6**).

Unlike HSNO and CH_3SNO, however, of all of the methods considered, the B3P86/6-311+G(2df,p) level gives closest agreement with values obtained at *both* the G3/G3(MP2) *and* CBS-Q levels, the differences being less than 10 and 5 kJ mol^{-1}, respectively. For the 6-311+G(2df,p) basis set, the B3LYP values are all approximately 20–25 kJ mol^{-1} less than the corresponding B3P86 values. Consequently, the B3LYP/6-311+G(2df,p) level no longer gives comparable agreement with the higher accuracy composite methods, as observed for HSNO and CH_3SNO. Indeed, values calculated at this level are lower than the corresponding G3/G3(MP2) and CBS-Q values by 11-26 kJ mol^{-1}, the difference increasing with increasing size of the RSNO (see **Table 3.6**). The B3P86/6-311+G(2df,p) and MP2/6-311+G(2df,p) S—N BDEs are now only in close

agreement for CH_3CH_2SNO and CysSNO, i.e., those containing saturated R groups. In contrast, for CH_2CHSNO and C_6H_5SNO, the MP2/6-311+G(2df,p) values are 28 and 105 kJ mol^{-1} higher, respectively, than the corresponding values obtained at the B3P86/6-311+G(2df,p) level.

TABLE 3.6: Comparison of Calculated[a] and Experimental Homolytic S—N BDEs of *cis*-CH_2CHSNO, *cis*-CH_3CH_2SNO, *cis*-C_6H_5SNO and *cis*-CysSNO (kJ mol^{-1})

Method	CH_2CHSNO	CH_3CH_2SNO	C_6H_5SNO	CysSNO
MP2/6-311G(d,p)	107.3	115.9	185.5	126.6
MP2/6-311+G(2df,p)	133.0	146.0	211.3	146.5[b]
QCISD/6-311G(d,p)[b]	53.5	75.9	70.1	
B3LYP/6-311G(d,p)	78.9	111.1	78.3	109.3
B3LYP/6-311+G(2df,p)	85.2	118.6	86.9	117.0
B3P86/6-311G(d,p)	97.1	131.2	95.9	126.9
B3P86/6-311+G(2df,p)	105.4	139.6	106.6	141.3
B3LYP/6-31G(d)[16]	84.3[a]	121.8	85.4	115.5[a]
B3LYP/6-31+G(d)[4]	82.6[a]	116.9[a]	84.5	123.5[a]
B3LYP/6-311++G(d,p)//B3LYP/6-31G(d)[16]	80.2[a]	128.9	88.3	119.6[a]
ROMP2/6-311++G(d,p)//B3LYP/6-31G(d)[16]	65.0[a]	101.3	77.0	102.2[a]
ROMP2/6-31G(2df,p)//ROMP2/6-31G(d)[17]				129.9
CBS-4M[16]	98.6[a]	143.9	115.9	147.0[a]
CBS-QB3[14]	97.5	133.9	103.9[a]	138.8[a]
CBS-Q[16]	101.8[a]	139.3	111.3	142.6[a]
G3[16]	96.6[a]	131.8	106.3	137.4[a,c]
Exptl.[4]			81.2	

[a] From this thesis, unless otherwise noted. [b] Scaled ZPVE obtained at the MP2/6-311G(d,p) level used. [c] Values calculated using the modified G3 method, G3(MP2) [Ref. 24].

This is due to high spin contamination of the underlying Hartree-Fock wavefunction for $CH_2CHS^{\bullet}$ and $C_6H_5S^{\bullet}$, with $<S^2>$ values of 0.94 and 1.20, respectively. Thus, erroneously high energies, and consequently S—N BDEs, are obtained. In contrast, spin contamination in all other $RS^{\bullet}$ radicals at the same level of theory was much lower, 0.75-0.78. We note that the QCISD method also experienced high spin contamination for these radicals. However, due in part to its explicit consideration of single and double excitations, it is less affected.

From **Tables 3.5** and **3.6** it can be seen that the B3P86/6-311+G(2df,p) BDEs of the saturated RSNOs (HSNO, CH_3SNO, CH_3CH_2SNO, CysSNO) are all within 10 kJ mol^{-1}. In contrast, the corresponding BDEs of the conjugated RSNOs CH_2CHSNO and C_6H_5SNO, while in close agreement with each other (see **Table 3.6**), are 29-37 kJ mol^{-1} lower. This is due to stabilization of the sulfur radical by the π-system of the adjacent R group.[25]

From **Table 3.6**, it can be seen that the various CBS and G3 style methods give homolytic S—N BDEs that are generally in reasonable agreement with each other, and furthermore are in reasonable agreement with those obtained at the B3P86/6-311+G(2df,p) method. This is despite the fact that they are all based upon different optimized structures. However, due to the 'elongated single-bond' nature of the RS—NO bond, it can be expected that the potential energy surface for homolytic dissociation is relatively flat. Hence, differences in optimized structures will not have as great an energetic consequence as is generally the case with more typical covalent single- and double-bonds, *as long as* an appropriate level of theory is chosen for obtaining the relative energies of interest, e.g., not QCISD or B3LYP.

The experimentally[4] determined S—N BDE of C_6H_5SNO is also listed in **Table 3.6**. It should be noted, however, that it was not directly measured but rather was estimated using a series of related thermochemical values. The present results suggest that it may be a lower estimate of the gas-phase S—N BDE of C_6H_5SNO.

3.4 Conclusions

The reliability and accuracy of the conventional electron correlation methods MP2 and QCISD, and the density functional theory methods B3LYP and B3P86, to obtain optimized structures and homolytic S—N BDEs of a range of S-nitrosothiols, has been investigated.

For all methods considered, optimized S—N bond lengths are found to be highly dependent on the basis set being employed. In particular, the MP2 method is found to be the most sensitive to the basis set being used, with the other methods exhibit more tempered affects. In general, to obtain convergence in the r(S—N) values of RSNO for a given method, the 6-311+G(2df,p) or larger basis set is required. For the conventional MP2 and QCISD methods, however, reliable structures can be obtained with the smaller, less computationally expensive, 6-311G(df,p) basis set. When suitably large basis sets are used, the MP2, QCISD and B3P86 methods generally give optimized structures that are close agreement with each other, particularly the QCISD and B3P86 methods. In contrast, the B3LYP method typically overestimates RS—NO bond lengths compared to the above methods. However, for N—O bond lengths, the MP2 method typically predicts longer RSN—O bonds than the other methods, which generally give lengths in good agreement with each other. In the case of C_6H_5SNO, the MP2 method fails to correctly predict the S—N bond length, with any of the basis sets used.

These observed basis set and method dependencies are found to be due to the fact that the S—N bond in RSNOs *does not* possess considerable double-bond character as previously suggested, but that it is in fact a long single S—N bond. Conversely, the –NO moiety within RSNOs is found to retain considerable multiple-bond character, between that of a formal N—O double-bond in HNO and the N—O bond (bond order 2.5) of isolated NO. Thus, of the methods considered, the DFT method B3LYP overestimates the distance of such long-bond interactions, while the MP2 method is most sensitive to the description of the molecular orbitals involved. In contrast, for obtaining optimized structures possessing such long-bonds, the DFT method B3P86 exhibits similar reliability and accuracy to that of the highest conventional electron correlation method used in this study, QCISD.

In general, to achieve convergence in the calculated homolytic RS—NO bond dissociation energy for a given method, the 6-311+G(2df,p) or larger basis set must be used. For all RSNOs considered in this present study, the QCISD method, regardless of the basis set employed, severely underestimates the strength of the RS—NO bond, predicting BDEs that are considerably lower than any other methods by as much as 55 kJ mol^{-1}. When the R group in the RSNO is not aromatic or conjugated, the MP2/6-311+G(2df,p) method gives values in reasonable agreement with those obtained using the B3P86/6-311+G(2df,p) and CBS-Q methods. When the R group is unsaturated or aromatic, however, it significantly overestimates BDEs due to spin contamination.

For the small S-nitrosothiols HSNO and CH_3SNO, S—N BDEs calculated at the B3LYP/6-311+G(2df,p) level give the best agreement of all methods with those calculated using the high accuracy G3 method. However, as the size of the RSNO increases, the B3LYP method increasingly underestimates the S—N BDEs, i.e., predicts values that become increasingly lower than the corresponding values obtained at the

G3/G3(MP2) and CBS-Q levels. In contrast, for small S-nitrosothiols, the B3P86/6-311+G(2df,p) method predicts BDEs in good agreement with those calculated using the CBS-Q method. However, as the size of the RSNO increases, it continues to give the best agreement with the CBS-Q calculated values and furthermore, now also gives the best agreement with those values obtained at the G3/G3(MP2) level. In addition, the absolute differences remain essentially constant as the size of the S-nitrosothiol increases.

Due to the elongated single-bond nature of the RS—NO bond, hence relatively flat potential energy surface for homolytic bond dissociation, reasonable homolytic S—N BDEs can be calculated using optimized structures with different (within reason) S—N bond lengths. This will hold as long as an appropriate method is chosen, e.g., G3, CBS or B3P86/6-311+G(2df,p) but not QCISD or B3LYP, for obtaining the necessary relative energies. Of course, the more accurate the structure used with, for example, the G3 method, the more reliable and accurate the calculated values will be.

Overall, the B3P86/6-311+G(2df,p) method represents the best compromise between computational cost and accuracy for obtaining reliable structures *and* homolytic S—N bond dissociation energies of S-nitrosothiols, particularly with increasing size of the RSNO.

It is noted that the structures and BDEs of RSNOs, in particular C_6H_5SNO, can also be thought of in terms of resonance structures, i.e., $[C_6H_5S]^+[NO]^- \leftrightarrow [C_6H_5SNO] \leftrightarrow [C_6H_5S]^-[NO]^+$. However, atomic charges from a Mulliken Population Analysis of C_6H_5SNO, suggest that contributions due to ionic structures are comparatively small; the –NO moiety exhibits atomic charges close to those calculated for isolated NO.

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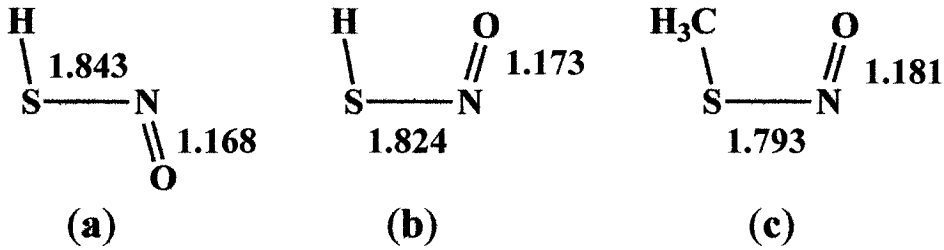
Chapter 4

Influence of Cu^+ on the RS—NO Bond Dissociation Energy of S-Nitrosothiols

4.1 Introduction

S-nitrosothiols (RSNOs) are of increasing interest as they are believed to be used within the body to store and transport the physiologically important species, nitric oxide (NO).[1-5] In addition, they have also shown potential as NO-releasing therapeutic agents for the treatment of a variety of diseases.[2] However, too much NO has also been proposed to play a key role in various diseases.[3,4] Thus, central to the biochemical function of RSNOs is an ability to regulate the release of NO. It is widely proposed that metal ions, in particular Cu^+, may play important roles in NO-release regulation.[2,6-9] Indeed, Cu^+ is known to catalyse decomposition of RSNOs. For example, their decomposition by the copper containing enzyme CuZn-superoxide dismutase has been observed.[10] In addition, it has been shown that Cu^{2+}-doped polymers can spontaneously generate NO from RSNOs, presumably via a Cu^+-intermediate.[11] Recently,[8] Toubin *et al.* investigated select RSNO···Cu^+ complexes theoretically and found that complexing Cu^+ at the S centre elongates the S—N bond, thus promoting decomposition. However, Cu^+ binding at N in the –SNO group has not been examined. In addition, despite increasing insight into NO release, factors that may instead aid in stabilizing RSNOs, an important part of NO-regulation, are not well understood. In this chapter, density functional theory (DFT) methods have been used to investigate the binding of Cu^+ to S versus N in RSNOs (R = H, CH_3; **Scheme 4.1**), in particular, with regard to the lability of NO group.



Scheme 4.1. Selected B3P86/6-311+G(2df,p) optimized (gas-phase) bond lengths (Å) of (a) *trans*-HSNO, (b) *cis*-HSNO and (c) *cis*-CH_3SNO.[12]

4.2 Computational Methods

Optimized geometries were obtained using the DFT method B3P86/6-311+G(2df,p), as implemented in the Gaussian 98 and 03 suite of programs (see **Chapter 2**). It has previously been shown that for RSNOs, this level of theory provides reliable structures and RS—NO bond dissociation energies (BDEs).[12] Harmonic vibrational frequencies and zero-point vibrational energies (ZPVEs) were also calculated at this level. Relative energies were calculated at the above level with inclusion of the appropriate ZPVE, vibrational and entropy corrections. Previously,[13] similar DFT-based approaches have been shown to give reliable relative $Cu^+\cdots X$ binding energies for a variety of ligands (X). This is found to also be the case for the DFT-method used in this study (See **Appendix B**). General solvent effects were included using the Onsager method (see **Chapter 2**), the solvent being water with a dielectric constant of 78.4.

4.3 Results and Disscussion

$[HSNO\cdots Cu]^+$: Schematic potential energy surfaces (PESs) for the reaction of Cu^+ with HSNO in gas- (blue) and aqueous-phases (red) are shown in **Figure 4.1**. In the gas-phase, the lowest energy complex is obtained when Cu^+ binds to the S centre to give the non-

planar complex **1**. Cu^+ is also found to bind to the N centre. However, unlike binding to S, when Cu^+ binds to N, the most stable complex formed is with *cis*-HSNO (**5**), which lies 46.3 kJ mol^{-1} higher in energy than **1**. The complex formed with *trans*-HSNO (**3**) lies 9.2 kJ mol^{-1} higher in energy than **5**. Both **3** and **5** are planar. Thus, the geometries of **1** and **3/5** indicate that Cu^+ interacts via the lone pairs of S and N, respectively. Complexes **1** and **3** are able to interconvert via transition structure (TS) **2**, with a barrier of 89.1 kJ mol^{-1}, while **3** and **5** can interconvert via TS **4** with a barrier of 51.8 kJ mol^{-1} relative to **3** (**Figure 4.1**). However, of particular interest is that homolytic cleavage of the S—N bond in **1** is predicted to require just 96.3 kJ mol^{-1}, while the analogous cleavage in **5**, assuming no rearrangement back to **1**, requires 185.1 kJ mol^{-1}, an increase of 88.8 kJ mol^{-1}.

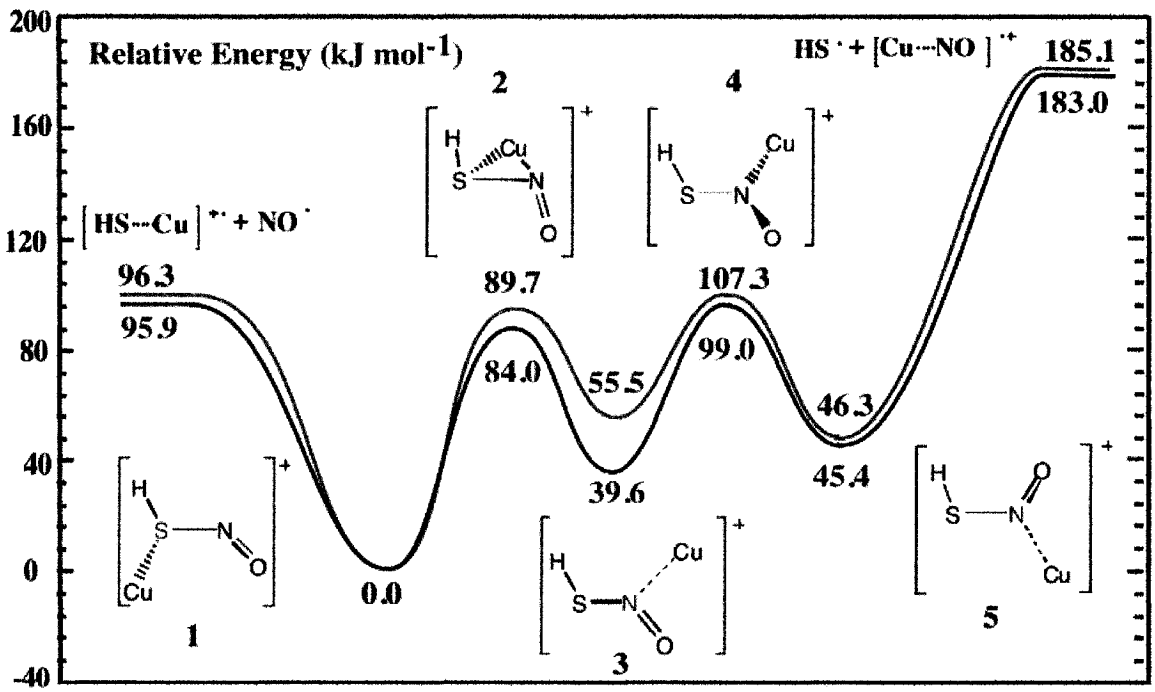


Figure 4.1. Schematic potential energy surfaces for reaction of Cu^+ with HSNO in the gas-phase (blue) and aqueous solution (red).

Insight into these observations is gained by examining the effects on the S—N and N—O bonds upon complexing Cu^+ with HSNO (**Table 4.1**). When Cu^+ binds at S to give **1**, the S—N bond lengthens dramatically to 2.227 Å while concomitantly, the N—O bond shortens considerably to just 1.108 Å (*c.f.* **Scheme 4.1**). That is, the –NO group increasingly resembles free NO, suggesting the promotion of HSNO degradation and NO release by Cu^+, as previously suggested.[8] In contrast, however, when Cu^+ binds at N to give **3** or **5**, the opposite effects are observed: the S—N bonds shorten significantly by almost 0.12 Å while the N—O bonds lengthen slightly by approximately 0.02 Å; that is HS—NO bonding is enhanced.

Table 4.1. Optimized S—N, N—O and Cu···X (X = S or N) Bond Lengths (Å) of the $[RSNO\cdots Cu]^+$ Complexes (R = H, CH_3).

	Species	r(S—N)	r(N—O)	r(Cu···X)
1	gas phase	2.227	1.108	2.163
	solution	2.236	1.107	2.164
3	gas phase	1.724	1.190	1.940
	solution	1.720	1.196	1.945
5	gas phase	1.709	1.191	1.940
	solution	1.707	1.194	1.941
6	gas phase	2.132	1.122	2.166
	solution	2.117	1.125	2.170
8	gas phase	1.691	1.200	1.930
	solution	1.689	1.202	1.933

The inclusion of solvation effects results in slight energetic and structural changes. The interconversion barriers, TS **2** and **4**, are reduced slightly by 6-8 kJ mol^{-1} (**Figure 4.1**; red line). Interestingly, the Cu···N bound complexes **3** and **5** are stabilized relative to

the Cu···S bound complex **1**, with the largest effect occurring for **3** which now lies just 39.6 kJ mol^{-1} higher in energy than **1**. Indeed, in solution, **3** is slightly more stable than **5** by 5.8 kJ mol^{-1}. Structurally (**Table 4.1**), the binding of Cu^+ to HSNO in solution has the same effects as observed in the gas-phase, although marginally enhanced. For example in solution, the S—N bond of **1** is lengthened to 2.236 Å, while in **3** and **5** the S—N bonds are marginally lengthend by < 0.005 Å (*c.f.* **Table 4.1**). We note that all complexes show marginally longer Cu^+···X distances in solution relative to the gas-phase.

$[CH_3SNO\cdots Cu]^+$: Schematic PESs for the reaction of Cu^+ with CH_3SNO in the gas-phase and solution are shown in **Figure 4.2**. Similar effects are observed upon solvation as noted for HSNO, hence the following discussion is limited to the solvated results, unless otherwise noted.

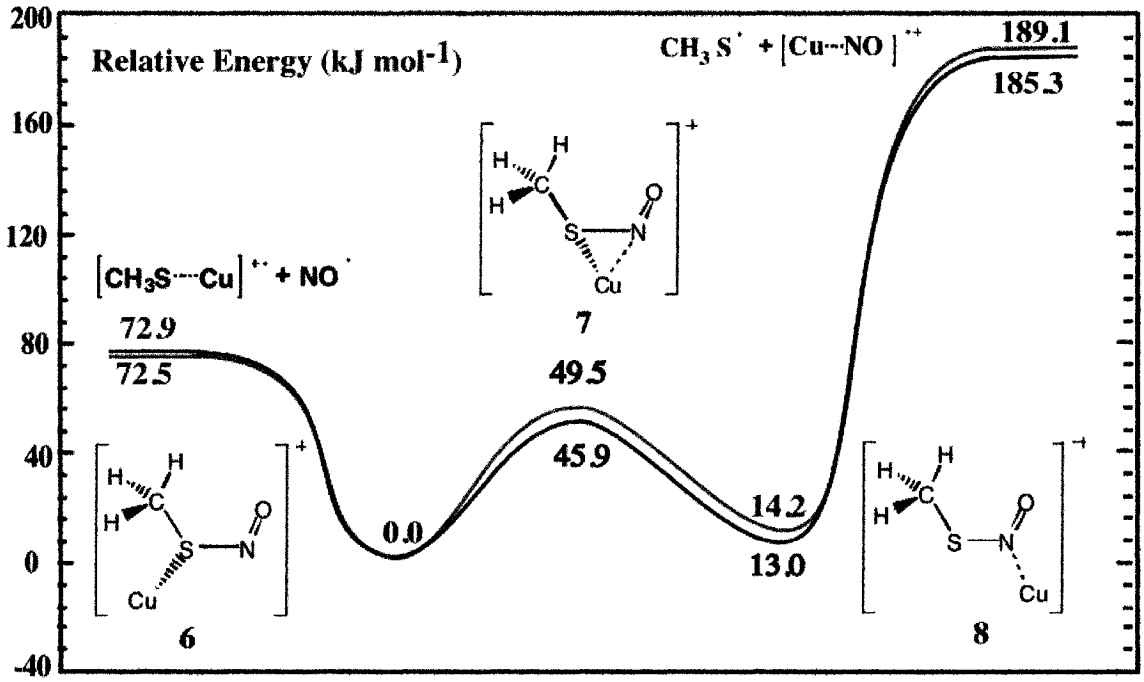


Figure 4.2. Schematic potential energy surfaces for reaction of Cu^+ with CH_3SNO in the gas-phase (blue) and aqueous solution (red).

As for HSNO, the lowest energy complex is again found when Cu^+ binds at S in CH_3SNO to give **6**. However, when Cu^+ binds at N it forms complex **8** lying higher in energy than **6** by just 13.0 kJ mol^{-1}. These complexes, both having the CH_3SNO moiety in the *cis* conformation, are able to interconvert via TS **7** at a cost of 45.9 kJ mol^{-1}. Direct homolytic cleavage of the S—N bond of **6** requires just 72.9 kJ mol^{-1}, while from **8** it requires 185.3 kJ mol^{-1}. Similar to HSNO, Cu^+ binding to the S centre again causes a dramatic lengthening of the S—N bond with concomitant shortening of the N—O bond (**Table 4.1**), although the effect in solution is again tempered marginally compared to the changes observed in the gas-phase. In comparison, Cu^+ binding to the N centre in CH_3SNO causes a considerable shortening of the S—N bond while the N—O bond is lengthened (see **Table 4.1**). Again, similar solvation effects are noted as previously described for HSNO.

4.4 Conclusions

The present results indicate that the interaction of Cu^+ at the S centre in RSNOs lengthens the S—N bond, thus enhancing NO loss as previously suggested.[10] Indeed, the lowest energy RS—NO bond cleavage occurs via Cu^+ bound to the S centre. Most significantly, however, it is found that the interaction of Cu^+ with the N centre of RSNOs has the opposite effect and in fact causes considerable shortening of the RS—NO bond. It is also found that the barrier for interconversion of Cu^+ bound from N to S is relatively modest. Hence, in order to stabilize the S—N bond for a period of time, the barrier to rearrangement must be enhanced either chemically or physically.

An example of how this may be achieved may come from rhodanese. Upon inhibition by nitrosylation of an active site cysteine, i.e., –SNO formation, it forms the remarkably stable S-nitrosorhodanese.[14] Significantly, due to constraints imposed by the

structure of the active site, the –SNO group is spatially close to a neighbouring arginine with which it can interact via its –NO moiety (see **Appendix B**). This results in effects similar to those described above for Cu^+ binding to the N centre and, furthermore, suggests that the effects detailed above may be a general consequence of cation-NO moiety interactions for RSNOs. Thus, these findings may also provide insight into how NO release from RSNOs may potentially be regulated, and how nitrosylated thiols within proteins may be stabilized.

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Chapter 5

Ring Complexes of S-nitrosothiols (RSNOs) with Cu^+: A Density Functional Study

5.1 Introduction

Due to the fact that metal ions have been found to play important roles in a diverse array of physiological processes, there is considerable interest in their roles and functions in biochemical systems.[1] Central to understanding these roles is elucidating their interactions with important biomolecules.

S-nitrosothiols (RSNOs), species with an –SNO functional group, are one such class of biomolecules. Within the body they store and transport nitric oxide (NO), an important biological messenger,[2] and furthermore, often take part in the same functions as NO.[3-8] Recently, they have shown potential as therapeutic NO-donors for the treatment of various diseases, e.g., cardiovascular disorders.[9] However, the biochemical mechanisms by which RSNOs may release NO remain unclear. It is known that certain metal ions such as Cu^+ and Fe^{2+} can catalyse the decomposition of RSNOs resulting in the release of NO,[10] Cu^+ being the most effective.[11] In addition, it has been reported that some copper-containing enzymes such as CuZn-superoxide dismutase can catalyse RSNO decomposition.[12,13] Hence, and due also in part to the high prevalence of copper within the body,[14] there is considerable interest in the interaction of Cu^+ with RSNOs.

Experimentally, large differences in the reactivity of RSNOs towards Cu^+ have been observed.[9] It has been suggested that this is due to the ability of some S-nitrosothiols to bind Cu^+ at the S or N centre in the –SNO group *and* an amino or carboxyl group within

the RSNO, leading to the formation of ring complexes.[9,15] These inner-shell complexes have also been proposed[10] as an activation step in the decomposition of RSNOs. However, due to the unstable nature and rapid decomposition of S-nitrosothiols by Cu^+, experimental studies on such complexes are difficult. Several experimental and theoretical studies have investigated the interaction of Cu^+ with various organic molecules.[16-20] In particular, Toubin *et al.*[16] have recently examined the complexation of Cu^+ with selected RSNOs and found that binding of Cu^+ to S lengthens the S—N bond, thus promoting release of NO. In contrast, it has also been shown[21] that binding of Cu^+ to the –SNO nitrogen can shorten the S—N bond. However, no systematic investigation on multiple binding interactions of metal ions with RSNOs has yet been performed. Thus, it remains unclear what may be the preferred modes for multiple interactions between these species and importantly, their effects upon the RS—NO bond and the resulting lability of the NO group.

Nitrosylated cysteine and derivatives thereof are thought to constitute a significant portion of the S-nitrosothiols formed *in vivo*, e.g., S-nitrosoglutathione. Hence, in this present chapter density functional theory methods are used to investigate ring structures formed upon interaction of Cu^+ with S-nitroso-cysteine (CysSNO) and the corresponding decarboxylated ($H_2NCH_2CH_2SNO$) and deaminated ($HOOCCH_2CH_2SNO$) derivatives. In addition, the effects of binding a water molecule to the resulting derivative complexes have also been considered.

5.2 Computational Methods

All calculations were performed using the Gaussian 98 and 03 suite of programs (see **Chapter 2**). The hybrid DFT method B3P86 was used in conjunction with the 6-311+G(2df,p) basis set. This level of theory has previously been shown to provide

reliable structures and RS—NO bond dissociation energies of S-nitrosothiols.[22] In addition, such hybrid DFT methods have been found to give reliable binding energies for model ligand-Cu^+ complexes.[17a,20] In particular, we have previously found[21] that the above method can provide reliable and accurate relative binding energies, for Cu^+ binding to appropriate model ligands such as H_2O, NH_3 and H_2S. Zero-point vibrational energy (ZPVE), enthalpy and entropy corrections were also calculated at the above level of theory. Relative enthalpies at 0 K were calculated for each $[Cu\cdots RSNO]^+$ complex by inclusion of the appropriate ZPVE. Gibbs free energies were calculated by including the appropriate vibrational and entropy effects at 298.15 K. Optimized structures of all species are listed in the **Appendix C**.

5.3 Results and Discussion

The most significant changes observed in the optimized structures of the S-nitrosothiols upon binding of Cu^+ occurred in the S—N and N—O bond lengths. Hence, the following discussion is limited to these parameters, and appropriate $Cu\cdots X$ (X = S, N, O) distances, unless noted.

Uncomplexed S-nitrosothiols: The lowest energy conformer with selected optimized bond lengths obtained for each isolated RSNO employed in this study, is shown in **Figure 5.1**. The formally single S—N bond of $HSNH_2$ has previously been found to be 1.709 Å long at the level of theory used in this chapter.[27] Thus, as observed for other RSNOs,[27] the S—N bonds in these isolated species are long S—N single bonds with the NO moiety retaining significant multi-bond character.

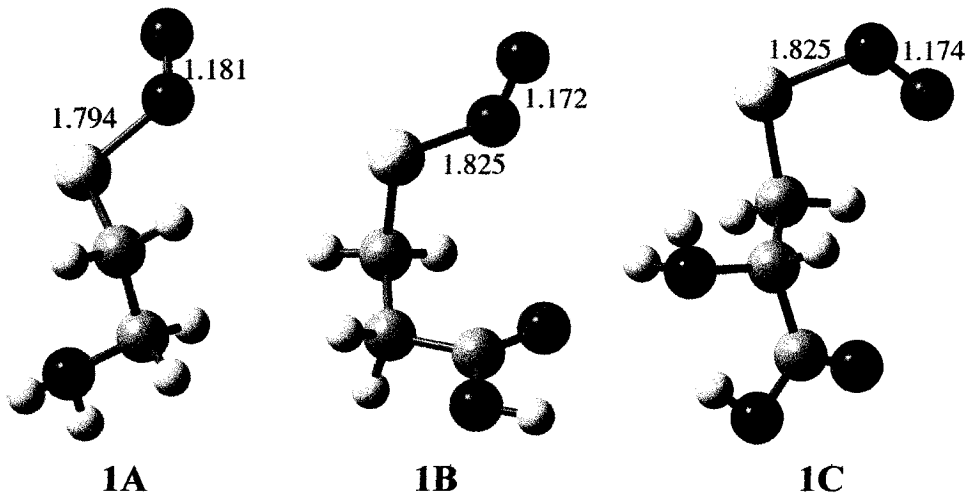


Figure 5.1. Schematic illustration of the lowest energy conformers of $H_2NCH_2CH_2SNO$ (**1A**), $HOOCCH_2CH_2SNO$ (**1B**) and CysSNO (**1C**) obtained at the B3P86/6-311+G(2df,p) level of theory, with selected bond lengths (Å).[22] [C (grey); N (blue); S (yellow); O (red); H (white)].

It has been suggested[10] that if the R–moiety of an RSNO contains polar functional groups, they may interact directly with the S or N centres in the –SNO moiety, thus stabilizing or destabilizing the S—N bond. For the RSNOs considered in this chapter, no conformers were located in which the $–NH_2$ or –COOH groups interacted directly with the –SNO group. We note that the S—N and N—O bond lengths of $H_2NCH_2CH_2SNO$ (**1A**), 1.794 and 1.181 Å respectively, are in close agreement with those previously[22] calculated at the same level of theory for the deaminated derivative CH_3CH_2SNO (1.792 Å and 1.183 Å, respectively). Similarly close agreement is also seen for the S—N bond lengths of $HOOCCH_2CH_2SNO$ (**1B**) and CysSNO (**1C**), (**Figure 5.1**). In addition, the amino N is over 3.1 Å from the S in **1A** and **1C** (**Appendix C**). Hence, incorporation of an $–NH_2$ into the R- species has negligible direct *or* indirect effect on the –SNO group. In contrast, when –COOH is incorporated such as going from CH_3CH_2SNO[27] to **1B** or

from **1A** to **1C**, the S—N bond elongates to 1.825 Å with a concomitant shortening of the N—O bond to approximately 1.17 Å, i.e., incorporation of an electron withdrawing –COOH group destabilizes the S—N bond. In **1B** and **1C** the –COOH group is at least 3.3 Å from the S (**Appendix C**), thus it is not due to direct interaction of the two groups.

The major focus of this present chapter was the structure and relative energies of ring complexes formed upon binding Cu^+ with RSNOs. Hence, only those complexes in which the Cu^+ ion is at least bidentately coordinated to the RSNO were considered. We note that no complexes were found in which Cu^+ was bidentately coordinated solely via the –SNO group, see **Figures 5.2 – 5.4**.

Ring complexes of Cu^+ with $H_2NCH_2CH_2SNO$ (**1A**): Optimized structures with selected bond lengths for complexes formed upon interaction of Cu^+ with **1A** are shown in **Figure 5.2**.

The lowest energy complex formed without water, lying 343.0 kJ mol^{-1} lower in energy than the separated reactants **1A** and Cu^+ (data not shown), is the 5-membered ring complex **2A** in which Cu^+ has bound to **1A** at both S and the $-NH_2$ nitrogen. Similar to previous observations,[16,21] binding of Cu^+ at S causes a dramatic lengthening of the S—N bond by 0.250 Å to 2.044 Å while the N—O bond shortens to just 1.130 Å. Indeed, the N—O bond is now between that of $NO^•$ (1.142 Å) and NO^+ (1.055 Å) at the same level of theory,[27] suggesting that the –NO moiety now has partial cationic charge. The alternative 6-membered ring complex **2B** formed when Cu^+ binds to both the –NO and $-NH_2$ nitrogens lies just 5.4 kJ mol^{-1} higher in energy than **2A** (**Table 5.1**). Now, however, the S—N bond is shortened by 0.033 Å to 1.761 Å while the N—O bond is lengthened slightly to 1.186 Å. That is, in contrast to binding to the S, Cu^+ binding via N of the –SNO group stabilizes the S—N bond. It has been suggested[10] that when Cu^+ binds to S in the –SNO group, σ-bonding to the metal ion via a lone pair on the S coupled with π-back

donation from the *d*-orbitals of Cu^+ causes a weakening of the S—N bond while when Cu^+ binds at the –NO nitrogen, σ-bond formation between the metal ion and N is coupled with electron density shift from lone pairs of the adjacent S towards the oxygen, strengthening the S—N bond while lengthening the N—O bond.

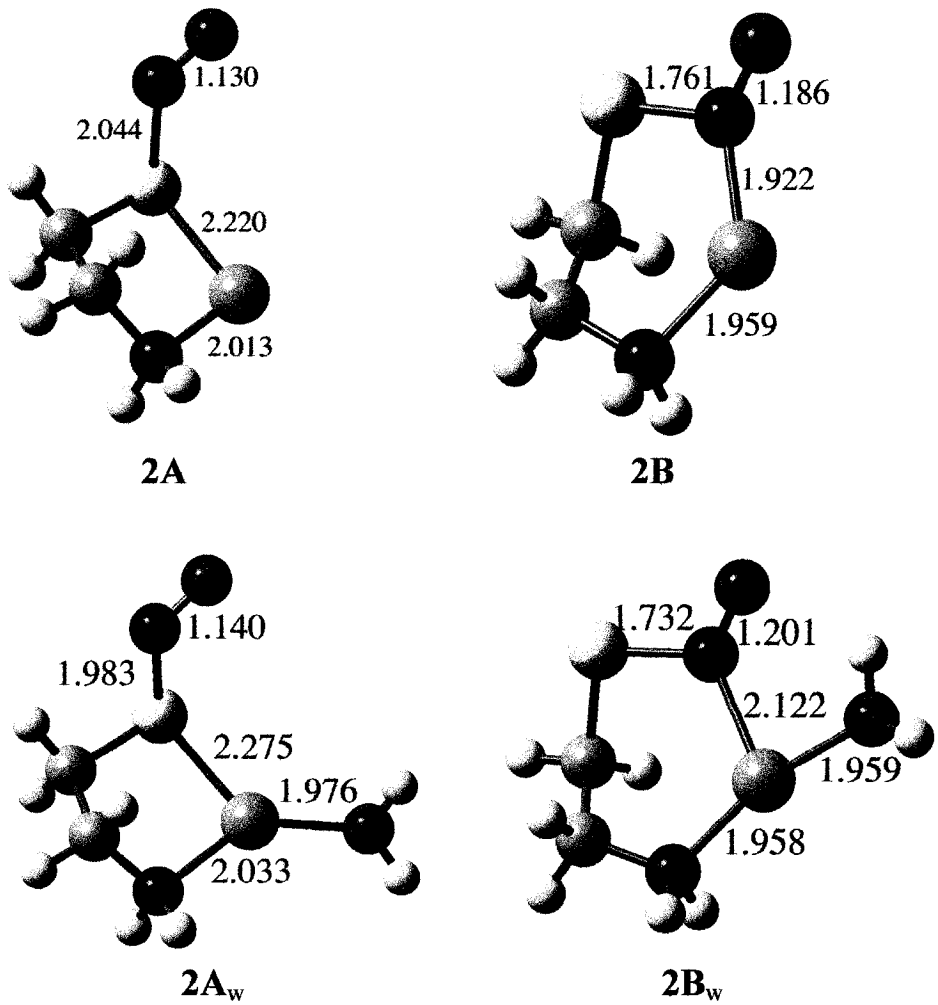


Figure 5.2. Ring complexes formed from $H_2NCH_2CH_2SNO$ and Cu^+, without (**2A** and **2B**) and with a single water molecule (**2A**$_w$ and **2B**$_w$) with selected bond lengths (Å) obtained at the B3P86/6-311+G(2df,p) level of theory. [Cu (orange); C (grey); N (blue); S (yellow); O (red); H (white)].

Table 5.1: Comparison Of B3P86/6-311+G(2df,p) Relative Enthalpies and Free Energies (kJ mol^{-1}) For All Complexes In Chapter 5.

Complex[a]	Relative Enthalpies (0 K)	Relative Free Energies (298.15 K)
2A	0.0	0.0
$2A_W$	–107.5	–106.2[b]
2B	5.4	9.3
$2B_W$	–93.5	–94.8[b]
$2A_{diss}$	9.0	11.0
3A	0.0	0.0
$3A_W$	–107.8	–106.3[b]
3B	3.4	7.5
$3B_W$	–100.2	–100.6[b]
$3A_{diss}$	8.2	10.9
$4A_S$	0.0	0.0
$4A_N$	14.1	17.2
$4A_{diss}$	10.0	11.1
$4B_S$	15.9	12.3
$4B_N$	18.8	19.6
$4B_{diss}$	21.6	20.1
$4C_S$	26.1	24.6
$4C_N$	33.0	35.7
$4C_{diss}$	24.6	25.1
4D	58.7	53.8

[a] Labels correspond to **Figures 5.1 – 5.5.** [b] Entropy correction not included.

The effects of binding a single H_2O to the Cu^+ centre in the above complexes, as might occur in solution, were also examined (**Figure 5.2**). Interaction of H_2O with the Cu^+ centre in **2A** leads to the formation of $\mathbf{2A_W}$, lying 107.5 kJ mol^{-1} lower in energy (**Table 5.1**). The effects noted above upon binding Cu^+ to **1A** are now slightly tempered. For example, the S—N bond in $\mathbf{2A_W}$ is now only 0.189 Å longer than in uncomplexed **1A**, while the N—O bond is now 1.140 Å. This is due to the fact that when H_2O ligates to the Cu^+ centre of **2A** the $Cu^+\cdots$S interaction is weakened, its length now being 2.275 Å. Interaction of H_2O with the Cu^+ centre in **2B** leads to the formation of $\mathbf{2B_W}$, lying 99.2 kJ mol^{-1} lower in energy. Similar to that observed in $\mathbf{2A_W}$, binding of H_2O to the Cu^+ centre weakens its interactions with the RSNO as illustrated by the increased $Cu^+\cdots$NO distance. However, rather than causing a lengthening of the S—N bond relative to **2B** as might be anticipated, the S—N bond shortens further by almost 0.03 Å to 1.732 Å. An explanation for this is found by considering the interactions of H_2O in $\mathbf{2B_W}$ compared to $\mathbf{2A_W}$. In $\mathbf{2B_W}$, unlike in $\mathbf{2A_W}$, the H_2O also forms a hydrogen bond with the oxygen in the –NO moiety (2.275 Å; **Appendix C**) resulting in an even longer N—O bond (1.201 Å) and, consequently, an even shorter S—N bond.

Ring complexes of Cu^+ with $HOOCCH_2CH_2SNO$ (**1B**): Previously[17b,c,19d] it has been shown that Cu^+ preferentially binds to the carbonyl (C=O) rather than the hydroxyl oxygen in –COOH containing biomolecules. Thus, in this present chapter, when Cu^+ interacts with the –COOH in **1B** or **1C**, only complexes in which Cu^+ binds via the C=O oxygen are considered. Optimized structures with selected bond lengths of the complexes formed upon Cu^+ binding to **1B** are shown in **Figure 5.3**.

When Cu^+ interacts with **1B**, the lowest energy complex formed is the 6-membered ring complex **3A**, lying 312.2 kJ mol^{-1} lower in energy than the separated reactants (data not shown), in which Cu^+ has bound to **1B** via both the C=O oxygen of the –COOH

group and the S. Thus, due in part to the reduced electron donating ability of the C=O oxygen relative to the $-NH_2$ nitrogen, Cu^+ binds less strongly to **1B** than **1A**.

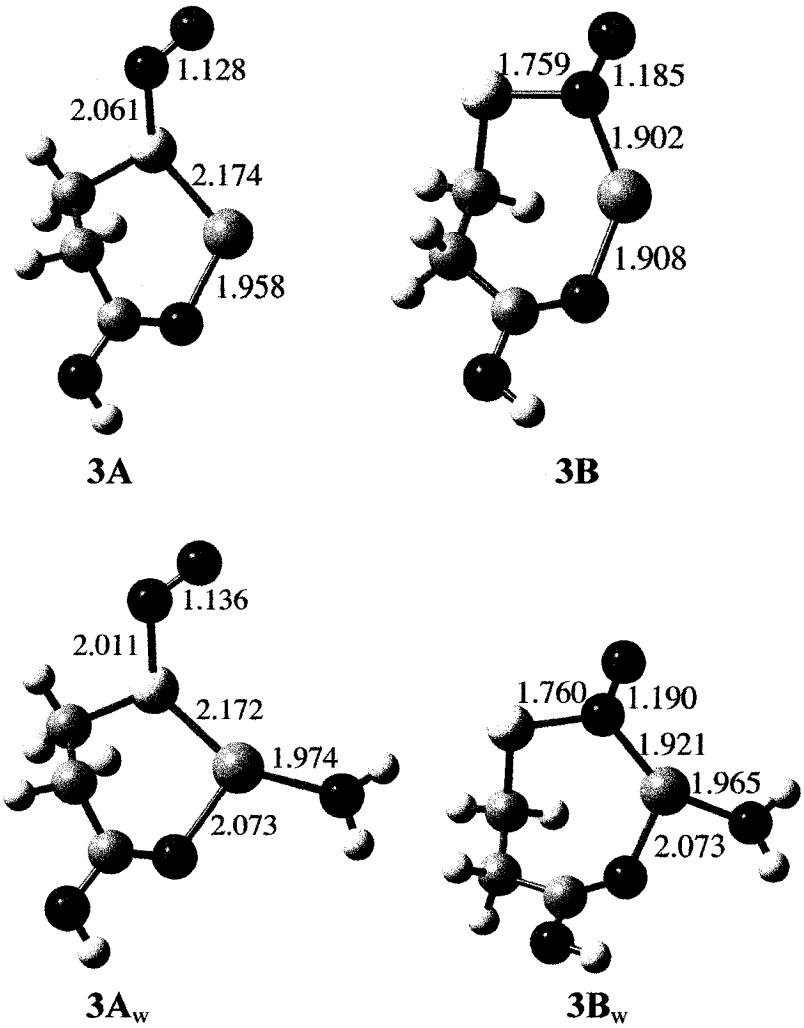


Figure 5.3. Ring complexes formed from $HOOCCH_2CH_2SNO$ and Cu^+, without (**3A** and **3B**) and with a single water molecule (**3A**$_w$ and **3B**$_w$) with selected bond lengths (Å) obtained at the B3P86/6-311+G(2df,p) level of theory. [Cu (orange); C (grey); N (blue); S (yellow); O (red); H (white)].

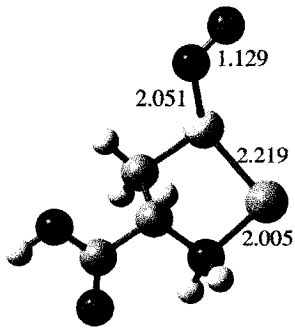
This lower donating ability results in a shorter $Cu^+\cdots S$ interaction in **3A** compared to **2A** by almost 0.05 Å. However, as observed for **2A**, the $Cu^+\cdots S$ interaction results in a considerable lengthening of the S—N bond (2.061 Å) with a significant shortening of the N—O bond (1.128 Å). Again, the short N—O bond indicates that the –NO moiety now has partial cationic charge. When Cu^+ binds to **1B** via the –SNO nitrogen rather than S, while still bound at the C=O oxygen, the 7-membered ring complex **3B** is formed lying higher in energy than **3A** by just 3.4 kJ mol^{-1} (**Table 5.1**). Similar to that noted for **2B**, the S—N bond is shortened significantly relative to the initial uncomplexed RSNO **1B** by almost 0.07 Å to 1.759 Å. In addition, the N—O bond has also lengthened marginally to 1.185 Å.

Interaction of H_2O with the Cu^+ centre of **3A** and **3B** results in the formation of $\mathbf{3A_W}$ and $\mathbf{3B_W}$, lying lower in energy than **3A** by 107.8 and 100.2 kJ mol^{-1}, respectively. Similar to that observed with the addition of H_2O to **2A** and **2B**, the difference in relative enthalpies between the complexes formed by Cu^+ coordination at S versus N in the –SNO moiety is increased slightly, with binding at S now preferred by 7.6 kJ mol^{-1} (**Table 5.1**). Structurally, slightly different effects are noted for $\mathbf{3A_W}$ and $\mathbf{3B_W}$ than for $\mathbf{2A_W}$ and $\mathbf{2B_W}$. In particular, the size of the changes in the S—N and N—O lengths upon binding of H_2O are less, as are the effects on the $Cu^+\cdots S$ and $Cu^+\cdots NO$ distances. Instead, the largest changes, 0.115 Å ($\mathbf{3A_W}$) and 0.165 Å ($\mathbf{3B_W}$), are now observed in the $Cu^+\cdots O{=}C$ distances. These differences are most likely due to the electron donating ability of H_2O being less than that of the –SNO moiety, but instead being competitive with the second group coordinating Cu^+, the C=O oxygen. Hence, the largest displacements are now observed in these distances.

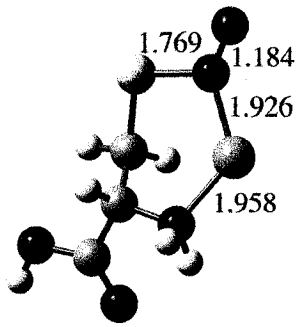
Ring complexes of Cu^+ with CysSNO (**1C**): Optimized structures with selected bond lengths of complexes formed upon interaction of Cu^+ with **1C** are shown in **Figure 5.4**.

$4A_S$

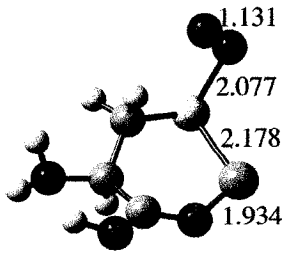
$4A_N$



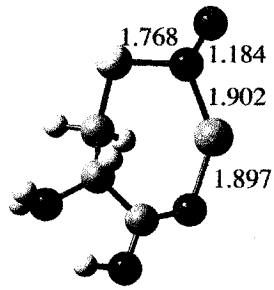
$4B_S$



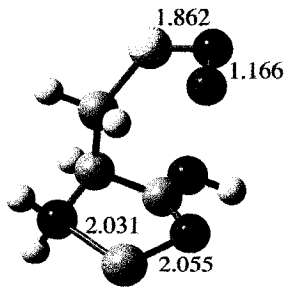
$4B_N$



$4C_S$



$4C_N$



4D

Figure 5.4. Ring complexes formed from CysSNO and Cu^+ with selected bond lengths (Å) obtained at the B3P86/6-311+G(2df,p) level of theory. [Cu (orange); C (grey); N (blue); S (yellow); O (red); H (white)].

Due to the size of the complexes, the addition of water was not considered. The lowest energy complex formed upon interaction of Cu^+ with **1C** is $\mathbf{4A_S}$, in which Cu^+ coordinates via the $-NH_2$ nitrogen, the –COOH carbonyl oxygen and the –SNO sulfur. It lies 345.5 kJ mol^{-1} lower in energy than the reactants Cu^+ and **1C**. This is similar to that noted for Cu^+ binding to **1A** (see above), suggesting a trade-off between forming an additional coordination bond between the RSNO and Cu^+, and increased strain from 'wrapping around' the Cu^+. Previously[16] $\mathbf{4B_S}$ was suggested to be the thermodynamically preferred complex at the lower B3LYP/6-31G(d) level, however, $\mathbf{4A_S}$ was not considered; the lowest energy complex at this level of theory is in fact also $\mathbf{4A_S}$.[23] As for complexes described above with Cu^+ bound at S, the S—N bond in $\mathbf{4A_S}$ has lengthened considerably relative to **1C** to 2.019 Å. This increase of 0.194 Å is not as large as observed for **2A** or **3A** due to the higher coordination state of the Cu^+, hence individual coordination bonds are longer and weaker. For example, the $Cu^+\cdots NH_2$ distance in **2A** is 2.013 Å while in $\mathbf{4A_S}$ it is 2.101 Å. The alternative complex $\mathbf{4A_N}$ with Cu^+ bound at the –NO nitrogen lies 14.1 kJ mol^{-1} higher in energy than $\mathbf{4A_S}$. Similar to such complexes described above, the S—N bond in $\mathbf{4A_N}$ (1.793 Å) is now shorter than in **1C** by 0.032 Å.

Four complexes were found in which Cu^+ bidentately coordinates with CysSNO via the –SNO group and with *either* the $-NH_2$ nitrogen or –COOH carbonyl oxygen, $\mathbf{4B_{S,N}}$ and $\mathbf{4C_{S,N}}$ respectively, all lying higher in energy than $\mathbf{4A_N}$ by 1.8 to 18.9 kJ mol^{-1}. Their relative enthalpies are ordered in accordance with the electron donating ability of the functional groups of CysSNO coordinating to the Cu^+. For example, complexes in which Cu^+ binds via the amino nitrogen, $\mathbf{4B_S}$ and $\mathbf{4B_N}$, are lower in energy than the analogous complexes in which it binds via the C=O oxygen, $\mathbf{4C_S}$ and $\mathbf{4C_N}$, respectively. Furthermore, complexes with Cu^+ bound at the –SNO sulfur, $\mathbf{4B_S}$ and $\mathbf{4C_S}$, are lower in energy than the corresponding complexes with Cu^+ bound at the –NO nitrogen, $\mathbf{4B_N}$ and $\mathbf{4C_N}$ (**Table 5.1**) by 2.9 and 6.9 kJ mol^{-1} respectively.

These bidenate complexes in which Cu^+ is bound via the –SNO moiety nicely illustrate the effects of the coordination state of the Cu^+ and the electron donating ability of the second coordinating group. This is particularly clear when Cu^+ binds at sulfur. For example, as one moves from $\mathbf{4A_S}$ to $\mathbf{4B_S}$ and $\mathbf{4C_S}$ the S—N bond is progressively, increasingly, elongated by 0.194 Å, 0.226 Å and 0.252 Å relative to the free ligand, respectively (**Figure 5.4**). It should be noted that the N—O length is only marginally affected. For Cu^+ binding at the –NO nitrogen, analogous effects for the S—N bond are observed on going from $\mathbf{4A_N}$ to $\mathbf{4B_N}$ and $\mathbf{4C_N}$, though considerably less dramatic. Again, the N—O bond is less sensitive to changes in the Cu^+ ligation. The $Cu^+\cdots S$ and $Cu^+\cdots NO$ distances also become increasingly shorter on going from **4A** to **4B** to **4C**; that is, lower the coordination state of the Cu^+ or weaker the electron donation by the non–SNO ligand, the stronger and hence larger the influence of Cu^+ on the S—N bond.

All of the above complexes involve Cu^+ and CysSNO coordinating via the –SNO moiety. In **4D**, however, the Cu^+ and CysSNO coordinate only via the $-NH_2$ nitrogen and the C=O oxygen of the –COOH, i.e., Cu^+ does not interact directly with the –SNO group. We note that while the oxygen of the –SNO group sits over the Cu^+, the distance between them is approximately 4.176 Å (**Appendix C**), hence any direct interaction is negligible. **4D** lies notably higher in energy than $\mathbf{4A_S}$ by 58.7 kJ mol^{-1} and is more than 25 kJ mol^{-1} higher in energy than any of the other bidentate complexes $\mathbf{4B_{S,N}}$ and $\mathbf{4C_{S,N}}$, in which Cu^+ coordinates via the –SNO moiety. Interestingly, however, despite no direct interaction between Cu^+ and the sulfur, similar effects as seen in the structures *with* a $Cu^+\cdots S$ bond are still observed, although they are less dramatic. For example, the S—N bond lengthens by 0.037 Å to 1.862 Å while the N—O bond shortens slightly to 1.166 Å (**Figure 5.4**) due to enhancement of the electron withdrawing nature of the –COOH group by coordination to Cu^+.

We note that for all of the complexes described in which the RSNO contains a –COOH group, other conformers are possible by rotation of the hydroxyl (–OH) group. However, these lie higher in energy as they are not stabilized by intramolecular hydrogen bonding within the –COOH group or between the –OH and $–NH_2$ group that occurs in each of the appropriate conformers described above (see **Figures 5.3** and **5.4**).

Relative enthalpies (0 K) versus Gibbs free energies (298.15 K): Gibbs free energies for each of the complexes were calculated, and are listed in **Table 5.1**. We note that these energies at this same level of theory have been shown to be in close agreement with experimentally measured Cu^+ binding energies for small model ligands appropriate to this present study, e.g., NH_3, H_2O, H_2S.[21] For any two corresponding complexes in which Cu^+ is bound to the S and N in the –SNO moiety, for example **2A** versus **2B**, inclusion of temperature and entropy effects to give Gibbs free energies results in the N bound complexes now being predicted to be even higher in energy relative to the S bound complex. This is due in part to the fact that the –NO bound complexes all involve the formation of larger rings. For example, **2A** and **2B** are 5- and 6-membered ring systems respectively. Importantly, however, the ordering of the relative free energies in general matches that obtained by comparing the relative enthalpies at 0 K (**Table 5.1**). The only exception occurs for the ordering of $\mathbf{4A_N}$ and $\mathbf{4B_S}$, with $\mathbf{4B_S}$ now lying slightly lower in energy by 4.9 kJ mol^{-1}. However, this does not alter the general findings of the present investigation.

'RS—NO Bond Dissociated' complexes: An alternative set of ring complexes of biochemical interest and of potential relevance to the role of Cu^+ in RSNO decomposition, are those in which the RS—NO bond has dissociated but the NO remains ligated to the Cu^+ centre, i.e., $[RS\cdots Cu\cdots NO]^+$. The optimized complexes corresponding to such an RS—NO cleavage in **2A**, **3S** and **4A/B/C**, i.e., $\mathbf{2A_{diss}}$, $\mathbf{3A_{diss}}$ and $\mathbf{4A/B/C_{diss}}$

respectively, are shown in **Figure 5.5** with relative enthalpies and free energies in **Table 5.1**.

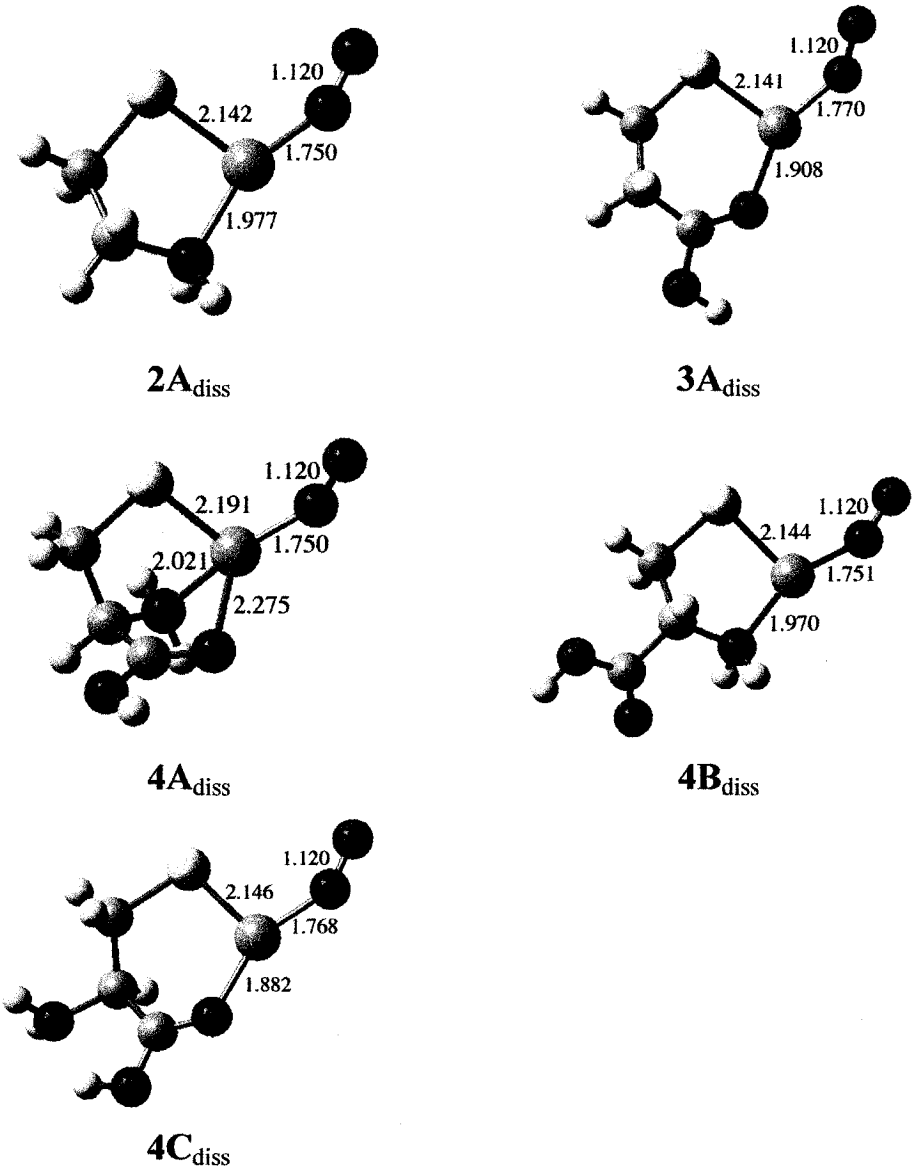


Figure 5.5 'RS—NO bond dissociated' complexes formed, with selected bond lengths (Å) obtained at the B3P86/6-311+G(2df,p) level, on cleaving the RS—NO bond of **2A**, **3A**, **4A**, **4B** and **4C** but with the NO remaining ligated to the Cu^+ centre. [Cu (orange); C (grey); N (blue); S (yellow); O (red); H (white)].

Structurally, in all such complexes the now separately Cu^+ ligated NO has a significantly shortened bond of 1.120 Å indicating increased NO^+ character, and a $Cu^+\cdots NO$ distance of 1.75-1.77 Å. The remaining Cu/RS interactions have all shortened slightly relative to their respective 'undissociated' parent complexes, except the $Cu^+\cdots O{=}C$ distance in $\mathbf{4A}_{diss}$. Energetically, **2/3** and $\mathbf{4A}_{diss}$ have free energies just 11 kJ mol^{-1} higher in energy than their respective 'undissociated' parent complexes **2/3** and **4A**. Indeed, despite the increased coordination of the Cu^+ centre, $\mathbf{2A}_{diss}$ and $\mathbf{3A}_{diss}$ lie higher in energy than either of **2A/B** or **3A/B** respectively. In contrast, $\mathbf{4A}_{diss}$ and $\mathbf{4C}_{diss}$, while being slightly higher in energy than $\mathbf{4A}_S$ and $\mathbf{4B}_S$ respectively, they are now calculated to lie 6.1 and 10.6 kJ mol^{-1} lower in energy than $\mathbf{4A}_N$ and $\mathbf{4C}_N$, respectively. In contrast, $\mathbf{4B}_{diss}$ is calculated to be just 0.5 kJ mol^{-1} higher in energy than $\mathbf{4B}_N$. Importantly, overall, such 'dissociated' complexes are energetically competitive with the parent $RSNO\cdots Cu^+$ complexes. We note that in $\mathbf{4A}_{diss}$ the Cu^+ centre is 4-coordinate in an approximate tetrahedral (**Appendix C**); the preferred coordination state and arrangement for a Cu(I) ion.[24] In contrast, $\mathbf{4B}_{diss}$ and $\mathbf{4C}_{diss}$ lie just 7.8 and 0.5 kJ mol^{-1} higher in energy than $\mathbf{4B}_S$ and $\mathbf{4C}_S$ respectively.

5.4 Conclusions

The DFT method B3P86/6-311+G(2df,p) has been employed in order to investigate various possible ring complexes that may form upon interaction of Cu^+ with nitrosylated cysteine (CysSNO) and its decarboxylated ($H_2NCH_2CH_2SNO$) and deaminated ($HOOCCH_2CH_2SNO$) derivatives. In addition, for complexes with $H_2NCH_2CH_2SNO$ and $HOOCCH_2CH_2SNO$ the effects of a H_2O molecule binding to the Cu^+ centre have been investigated.

The presence of an electron withdrawing functional group such as –COOH within the R– moiety of the RSNO is found to destabilize the RS—NO bond.

Importantly, the present results indicate that for the –SNO moiety, Cu^+ preferentially binds to the S rather than the N centre while no complexes were located in which Cu^+ coordinated via the oxygen. With respect to other functional groups within the S-nitrosothiol, Cu^+ preferentially binds to the most electron donating group. For example, the thermodynamically preferred bidentate complexes are those in which Cu^+ coordinates via the S and the $–NH_2$ nitrogen: **2A** is lower in energy than **3A** with respect to the separated reactants, **1A** + Cu^+ and **1B** + Cu^+, respectively. For CysSNO, the most stable complex, $\mathbf{4A_S}$, is formed by tridentate coordination with Cu^+ via the –SNO sulfur *and* both the $–NH_2$ nitrogen and carbonyl oxygen of the –COOH.

In all complexes in which Cu^+ coordinates via the S of the –SNO group, a weakening of the S—N bond and strengthening of the N—O bond is observed. In contrast, Cu^+ coordination via the N centre of the –SNO moiety has the opposite effects; stabilization of the S—N bond and a lengthening of the N—O bond. The effects of the interaction of the Cu^+ with the –SNO moiety for a given RSNO are tempered by the electron donating ability of the other groups simultaneously coordinated to the Cu^+ and on the coordination state of the Cu^+ ion. For example, $\mathbf{4C_S}$ in which Cu^+ is coordinated to the S centre and the carbonyl oxygen, has a longer S—N bond (2.077 Å) than $\mathbf{4B_S}$ (2.051 Å) in which Cu^+ is coordinated to the S centre and the amino nitrogen. In contrast, the tri-coordinate complex $\mathbf{4A_S}$ has a much shorter S—N bond (2.019 Å). Indeed, the further coordination of the Cu^+ centre by inclusion of a single H_2O weakens the $Cu^+\cdots$RSNO interactions and in general, tempering the effects of Cu^+ complexation. The only exception occurs for $\mathbf{2B_W}$ as Cu^+ bound H_2O enhances its effects by formation of a hydrogen bond between with the –NO oxygen.

The alternative $[RS\cdots Cu\cdots NO]^+$ ring complexes in which the RS—NO bond has broken but the RS remains at least bidentately coordinated to the Cu^+ and the NO group also remains complexed to the Cu^+ centre, are all found to lie only marginally higher in energy than their corresponding 'undissociated' parent complexes.

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Chapter 6

Interaction of Nitric Oxide and Its Ionic Species With Biomolecules in Gas Phase: A DFT Study

6.1 Introduction

Nitric oxide (NO) has been extensively studied in the past decade,[1-4] especially after the *in vivo* discovery of Nitric Oxide Synthases.[5] It is well known that NO is an important biological messenger[6] within the human body and it is believed that it plays a significant role in regulation of several physiological functions.[1,6-9] Experimental studies have shown that NO may potentially regulate the activity of particular enzymes.[5,8,10,11] Indeed, a variety of proteins essential in the human body are modified by NO (e.g., cyclooxygenase-2,[11] heme proteins,[12,13] guanylate cyclase[14,15]). Furthermore, it has been suggested that not only NO radical, but also, nitrosonium (NO^+) and nitroxide (NO^-) ions might be responsible for the diverse roles of NO observed.[16]

Also, S-nitrosothiols (RSNOs) have increasingly attracted the interest of scientists in recent years. This is due in part to the belief that RSNOs can perform similar biological roles as NO[8,9,17-20] and also to their potential therapeutic use as NO-releasing drugs.[5] It has been suggested that, for instance, GSNO, can interact with aromatic rich regions of proteins, causing structural changes.[21] However, the exact mechanism by which RSNOs may interact with such protein regions is unknown.

Recently, Rosokha and co-workers[22,23] investigated nitrosonium/arene and nitrosonium/diarene charge-transfer (CT) complexes with various aromatic donors. Generally, it was thought that only metal ions could form such complexes with aromatic

species.[24,26] Interestingly, Rosokha *et al.* were able to synthesize charge-transfer complexes of NO^+ with aromatic species.[22,29] However, their studies suggested that NO cannot form complexes with every type of organic arene compounds since some unstable complexes arise because an optimal placement of NO inside the ring sandwich cannot be achieved. Furthermore, the tendency to form complexes was also found to be related to the redox potentials of the arene donors. It has been suggested that CT interactions can play a significant role in biomolecular systems, for example via cation-π interactions of various metals with aromatic amino acids of proteins.[24-26] Such interactions are believed to induce partial covalent character in the electrostatic interactions that occur between two molecular systems with the effect of stabilizing or destabilizing the resulting complex.[27,28]

As a consequence of the above studies and due to the fact that NO containing compounds have been found to target aromatic rich regions of proteins, it remains unclear as to whether NO and its ionic species can form complexes with aromatic amino acids. Furthermore, if they can form complexes, whether or not such complexes are generally possible or only with certain aromatic amino acids and the exact nature of such complexes formed, is unknown. In this present chapter, density functional theory methods are used to gain a greater understanding of the ways in which NO and its ions may interact with aromatic rich regions of proteins.

6.2 Computational Methods

All geometry optimizations were performed with the Gaussian 98 and Gaussian 03 suite of programs (see **Chapter 2**). Optimized geometries were obtained at the DFT level of theory B3LYP/6-311G(d,p). ZPVE corrections were also calculated at this level of theory and scaled by an appropriate factor.[30] For each species formed upon complexation

of NO and its ions with various aromatic systems, the relative energies were also calculated and corrected by inclusion of the appropriate ZPVE. Atomic charges were calculated by using Mulliken charge analysis. Optimized geometries obtained for species considered in this present chapter are given in the **Appendix D**.

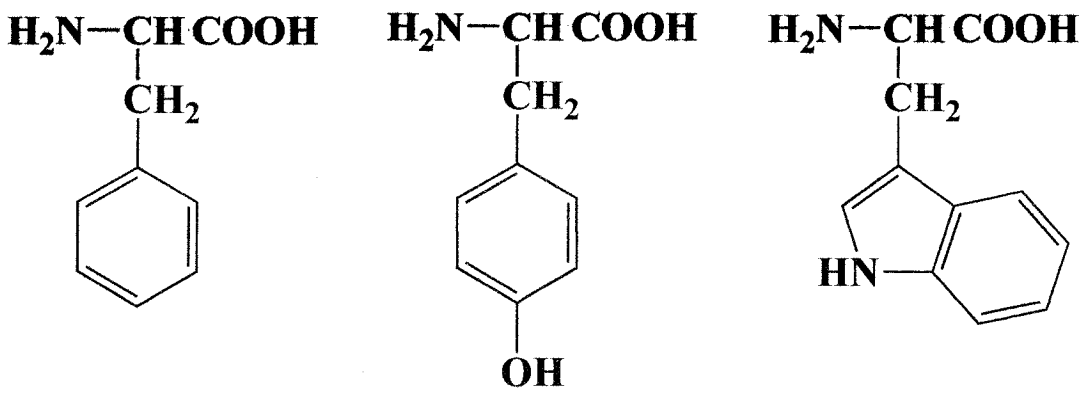
6.3 Results and Discussion

Optimized Structures of NO^+, $NO^\bullet$ and NO^-: The optimized structures of NO^+, $NO^\bullet$ and NO^-, obtained, are given in **Table 6.1**. At the B3LYP/6-311G(d,p) level of theory, NO^- is a triplet species, the singlet species lying higher in energy by 142.3 kJ mol^{-1} (data not shown).

Table 6.1. Optimized NO Bond Lengths (Å) for NO^+, $NO^\bullet$ and NO^-

NO^+	$NO^\bullet$	NO^-
1.060	1.148	1.273

We have systematically considered the structures of NO (and its ions) interacting with benzene, and model of the R groups ($R=CH_3$) of the amino acids phenylalanine (Phe), tyrosine (Tyr) and tryptophan (Trp), and the nucleobase guanine. Our modeled aromatic amino acids employed are shown schematically in **Figure 6.1**. Three sets of investigations were done: uncomplexed structures, single ring complexes and sandwich complexes. It should be noted that there are numerous possible complexes that can be formed by the interaction of two or three components. In order to simplify the following discussion, only the lowest energy structures found are described.



Phe **Tyr** **Trp**

Figure 6.1. Computational model (in red) aromatic amino acids used in the present chapter. R= CH_3 (in black)

Interaction of NO• with a single aromatic biomolecule: We began our investigation by first considering the complexation of NO• with benzene, the simplest hydrocarbon aromatic system related to the standard aromatic amino acids tyrosine, phenylalanine and tryptophan. Due in part to the high symmetry of benzene (*point group* D_{6h}), the number of possible complexes with NO• and its ions is limited, enabling one to more easily find the possible minimum energy structures and their nature. Furthermore, it enables greater insight into the effects of adding functional groups to the aromatic ring on such species. The optimized N—O bond distances and the relative energies of complexes formed by interaction of NO• with one molecule of benzene, Phe, Tyr, Trp and guanine are given in **Table 6.2**. **Figure 6.2** illustrates the optimized structures of the species formed. When NO radical interacts with a single molecule of benzene, aromatic amino acids or guanine, they form a weak π-π interaction complex. The lowest structure in energy, [NO···Trp]• complex lies 4.3 kJ mol^{-1} lower than the separate reactants. These weak interactions are evident in the structure with the N—O bond length remaining essentially constant relative to the isolated NO• and the distance between N of NO moiety and the closest C of the

biomolecule structure being quite long, in a range from 3.025 Å ([NO···Trp]$^{\bullet}$) to 3.356 Å ([NO···benzene]$^{\bullet}$) (See **Figure 6.2**).

TABLE 6.2: Optimized N—O Bond Lengths (Å), Relative Energies (kJ mol^{-1}) and Charge Distribution (e^{-}) on NO$^{\bullet}$ of the [NO···Ar]$^{\bullet}$ Complexes

Species	r(N—O)	Relative En.	Charge distribution
[NO···C_6H_6]$^{\bullet}$	1.149	-1.7	0.0
[NO···Phe]$^{\bullet}$	1.149	-2.3	0.0
[NO···Tyr]$^{\bullet}$	1.150	-2.8	-0.02
[NO···Trp]$^{\bullet}$	1.153	-4.3	-0.04
[NO···guanine]$^{\bullet}$	1.150	-3.0	1.0

In order to evaluate the charge transfer that might occur from NO$^{\bullet}$ to biomolecule rings or vice versa, we have examined the Mulliken charge and spin density distribution on the complexes formed. In all the species, the atomic charge of NO moiety is virtually zero, as expected and there is no spin distribution on the aromatic species. These results suggest that a very little charge transfer has occurred from the aromatic molecules to the NO moiety, thus verifying that NO$^{\bullet}$ interacts weakly with biomolecules chosen in this study. Due to the very weak interaction of NO$^{\bullet}$ with one aromatic molecule, the formation of sandwich complexes seems highly unlikely, hence they were not being investigated.

Interaction of NO^+ with a single aromatic biomolecule: The N—O bond lengths and the relative energies of the species formed upon interaction of NO^+ with benzene, aromatic amino acids and guanine are shown in **Table 6.3**.

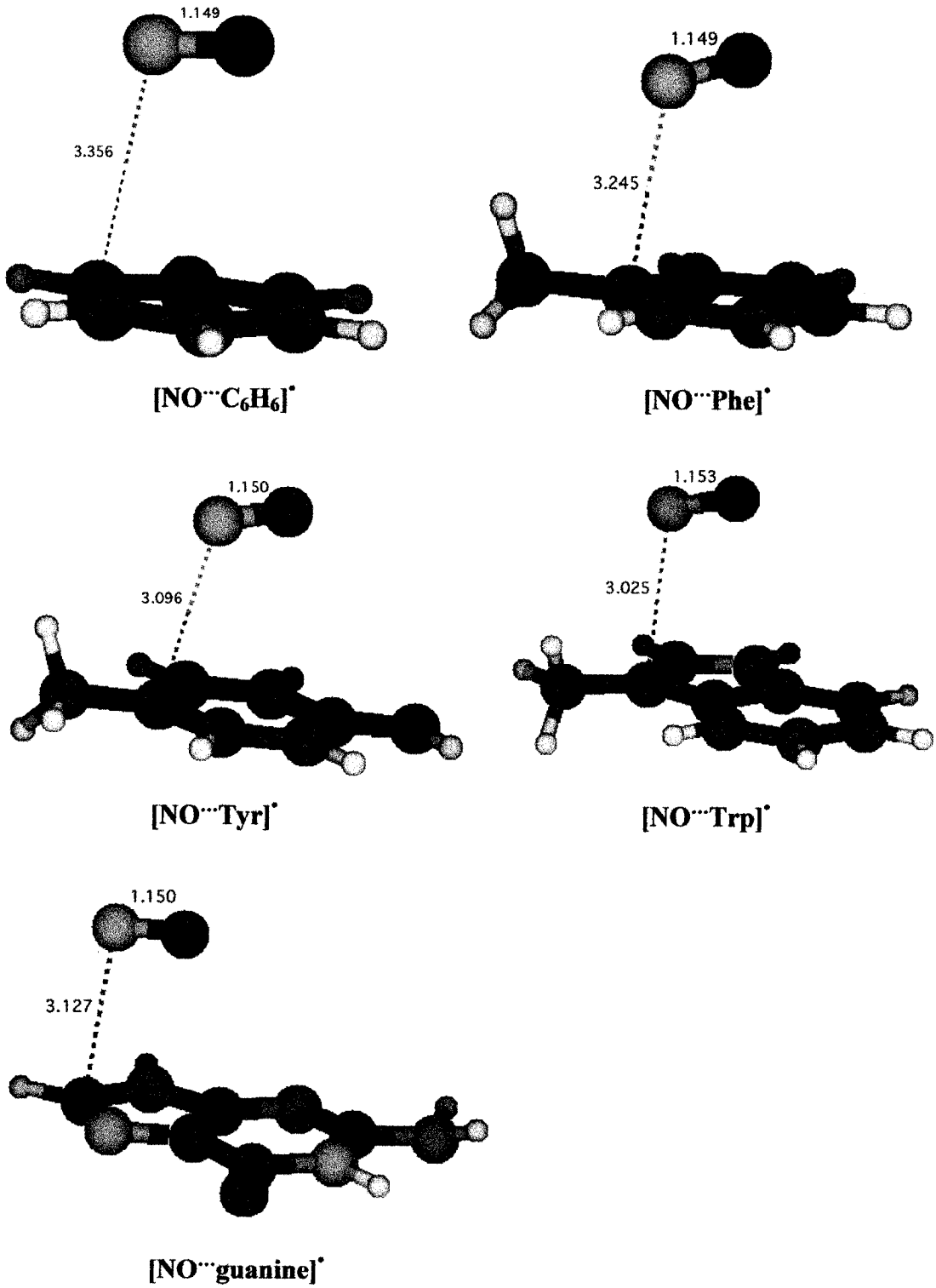


Figure 6.2. B3LYP/6-311G(d,p) optimized structures for $[NO\cdots Ar]^{\bullet}$ complexes [C (orange); N (blue); O (red); H (white)].

Graphical representation of the corresponding complexes is given in **Figure 6.3**. From **Table 6.3** it can be observed that when NO^+ interacts with a single biomolecule considered in this chapter, relatively stable complexes are formed. The NO^+ moiety lies at a maximum distance of 2.382 Å over the ring structures, i. e., $[NO\cdots Phe]^+$ complex, much closer than in the $NO^\bullet$ case (see **Figure 6.3**). These short distances indicate a relatively strong interaction between NO^+ and the biomolecule models.

TABLE 6.3: Optimized N—O Bond Lengths (Å), Relative Energies (kJ mol^{-1}) and Charge Distribution (e^-) on NO^+ of the $[NO\cdots Ar]^+$ Complexes

Species	r(N—O)	Relative En.	Charge distribution
$[NO\cdots C_6H_6]^+$	1.098	-177.6	0.49
$[NO\cdots Phe]^+$	1.101	-198.5	0.45
$[NO\cdots Tyr]^+$	1.110	-229.6	0.38
$[NO\cdots Trp]^+$	1.117	-267.3	0.34
$[NO\cdots guanine]^+$	1.117	-224.3	0.33

Indeed, the complexes formed upon interaction of NO^+ with one molecule of guanine or tryptophan, for example, lie 224.3 and 267.3 kJ mol^{-1} respectively, lower in energy than the individual reactants. As a consequence, a significant increase in N—O bond length is observed, e.g., from 1.060 Å to a maximum of 1.117 Å. By examining the Mulliken charge distribution on the cationic complexes formed, we note that the NO^+ moiety now has a charge of just 0.33–0.49, compared to +1 for the isolated NO^+. This suggests significant charge transfer from the NO^+ moiety to biomolecules, the largest charge transfer occurring for $[NO\cdots guanine]^+$ complex.

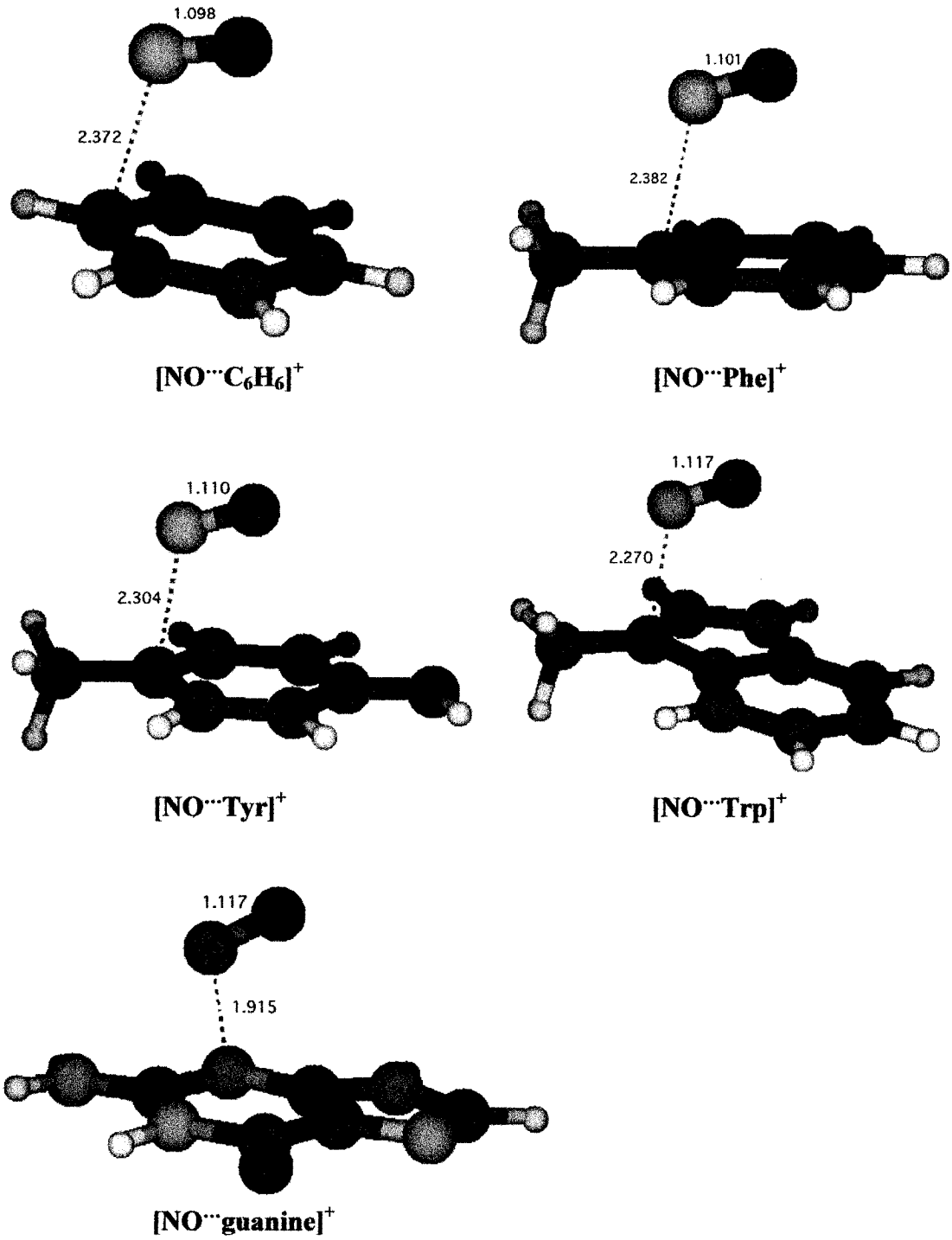


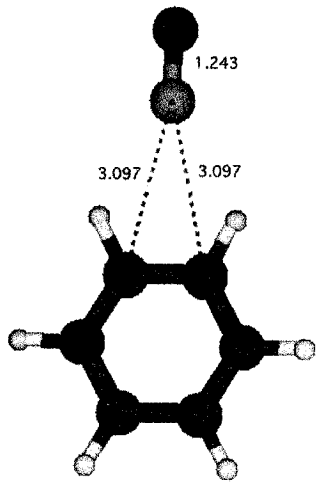
Figure 6.3. B3LYP/6-311G(d,p) optimized structures for $[NO\cdots Ar]^+$ complexes [C (orange); N (blue); O (red); H (white)].

Interaction of NO^- with a single aromatic biomolecule: NO^- in a triplet state forms complexes with aromatic amino acids and guanine in a different configuration than above described for $NO^•$ and NO^+. **Table 6.4** shows the optimized N—O bond lengths of the corresponding complexes, along with the relative energies. **Figure 6.4** shows the optimized geometries of the species formed upon complexation. As can be seen, instead of lying above the aromatic species, the NO^- moiety prefers mostly a planar configuration, relative to the positions of the rings. Unlike in the $NO^•$ and NO^+ cases, hydrogen bond interactions are preferred. For example, NO^- forms a hydrogen bond just 1.528 Å long with the hydroxyl moiety of tyrosine, suggesting a quite strong interaction. The strongest interaction, however, was found to occur between NO^- and guanine, as suggested by the two hydrogen bonds formed of lengths 1.890 and 1.677 Å (see **Figure 6.4**).

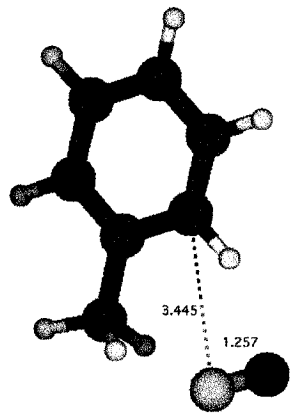
TABLE 6.4: Optimized N—O Bond Lengths (Å), Relative Energies (kJ mol^{-1}) and Charge Distribution (e$^-$) on NO^- of the $[NO^{\cdots}Ar]^-$ Complexes

Species	r(N—O)	Relative En.	Charge distribution
$[NO^{\cdots}C_6H_6]^-$	1.243	-209.9	-0.73
$[NO^{\cdots}Phe]^-$	1.257	-221.0	-0.75
$[NO^{\cdots}Tyr]^-$	1.252	-301.8	-0.73
$[NO^{\cdots}Trp]^-$	1.249	-287.4	-0.75
$[NO^{\cdots}guanine]^-$	1.281	-326.5	-0.77

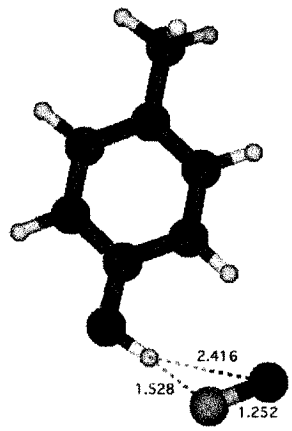
Interestingly, for guanine, the lowest energy complexes all involved hydrogen bond formation via the oxygen atom of the NO moiety. The relative energy for this species lies at 326.5 kJ mol^{-1}. In almost all cases, the interaction of NO^- with biomolecules considered in the present study results in shortening of the N—O bond lengths.



[NO···C_6H_6]$^-$



[NO···Phe]$^-$



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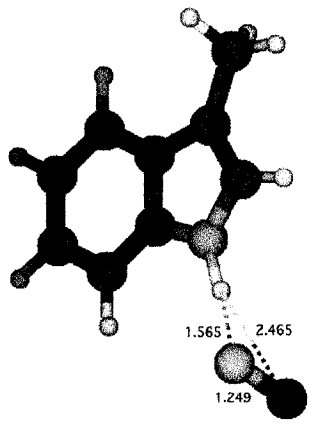
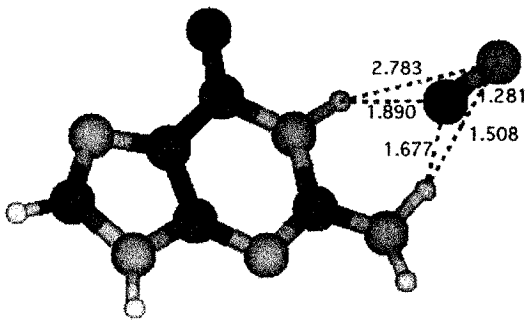


[NO···Trp]$^-$



[NO···guanine]$^-$

Figure 6.4. B3LYP/6-311G(d,p) optimized structures for [NO···Ar]$^-$ complexes [C (orange); N (blue); O (red); H (white)].

One exception is the complex formed with guanine, with r(N—O)=1.281 Å compared to 1.273 Å of the isolated NO^-, a slight increase. The relative binding energies of all the $[NO\cdots Ar]^-$ complexes are lower than that of the $[NO\cdots Ar]^+$ species, suggesting the formation of more stable complexes. An investigation of the charge distribution revealed a negative charge on the NO^- moiety of the anionic complexes formed, ranging from –0.73 (e.g., $[NO\cdots Tyr]^-$) to –0.77 ($[NO\cdots guanine]^-$). The spin is almost entirely distributed to the NO^- itself in all the complexes formed. The present results indicate a limited negative charge transfer occurring to the aromatic species from the NO^- moiety.

Several other possible configurations of the $[NO\cdots aromatic\ biomolecule]^-$ complexes have been investigated. For example, another three $[NO\cdots Tyr]^-$ species have been found, with NO^- moiety lying close to methyl group with either the oxygen or nitrogen of NO pointing toward it and on the side of the tyrosine ring. However, these complexes are 79.5-93.0 kJ mol^{-1} higher in energy than the $[NO\cdots Tyr]^-$ complex shown in **Figure 6.4**. For $[NO\cdots Trp]^-$ we noted other possible arrangements, with NO^- lying close to the six-member ring of Trp and to methyl group, with either nitrogen or oxygen of NO^- pointing toward Trp molecule. These complexes are 72.0-80.4 kJ mol^{-1} higher in energy than the corresponding species presented in **Figure 6.4**. Also, four other possible configurations have been found for $[NO\cdots guanine]^-$ complex: one in which NO^- lies between methyl group and the six-member ring of guanine and three other structures in which NO^- is close to the methyl group and the five-member ring of guanine. However, all these species are remarkable higher in energy, in a range from 503.9 to 554.0 kJ mol^{-1} compared to the $[NO\cdots guanine]^-$ complex shown in **Figure 6.4** (see **Appendix D**).

Complexes of NO^+ with two aromatic biomolecules: Optimized N—O bond distances and the relative energies of the complexes formed are given in **Table 6.5**. Graphical representation of the corresponding complexes is given in **Figure 6.5**. As described for

the complexes formed upon interaction of NO^+ with a single molecule of benzene, aromatic amino acids or guanine, an increase in N—O bond lengths has been noted for the corresponding species formed. Indeed, also in this case the N—O bonds show a slight increasing trend compared to the single ring complexes, except for the $[Trp\cdots NO\cdots Trp]^+$ structure.

TABLE 6.5: Optimized N—O Bond Lengths (Å), Relative Energies (kJ mol^{-1}) and Charge Distribution (e^-) on NO^+ of the $[NO\cdots(Ar)_2]^+$ Complexes

Species	r(N—O)	Relative En.	Charge distribution
$[NO\cdots(C_6H_6)_2]^+$	1.101	-236.5	0.43
$[NO\cdots(Phe)_2]^+$	1.105	-259.3	0.39
$[NO\cdots(Tyr)_2]^+$	1.114	-289.3	0.31
$[NO\cdots(Trp)_2]^+$	1.115	-321.4	0.31
$[NO\cdots(guanine)_2]^+$	1.120	-366.1	0.27

For instance, in $[Tyr\cdots NO\cdots Tyr]^+$ complex, r(N—O) =1.114 Å, compared to 1.110 Å in $[NO\cdots Tyr]^+$ species and to 1.060 Å in isolated NO^+. This is suggestive of enhanced charge transfer. Indeed, the Mulliken charge distribution shows 0.31 positive charge on NO, compared to the slightly higher value of 0.38 for the $[NO\cdots Tyr]^+$ species. For the sandwich structures formed by aromatic amino acids, Tyr and Trp, the two distances between N of the NO^+ moiety and the closest C atoms of the rings are essentially identical (see **Figure 6.5**). Hence, one assumes that NO^+ lies in the middle (equidistant) of the two rings and the charge distribution is equally shared. The NO^+ moiety donates an equal share of charge to both rings, this being supported by the calculated Mulliken charge distribution. A special case is represented by nitrosonium ion complexed with two molecules of guanine.

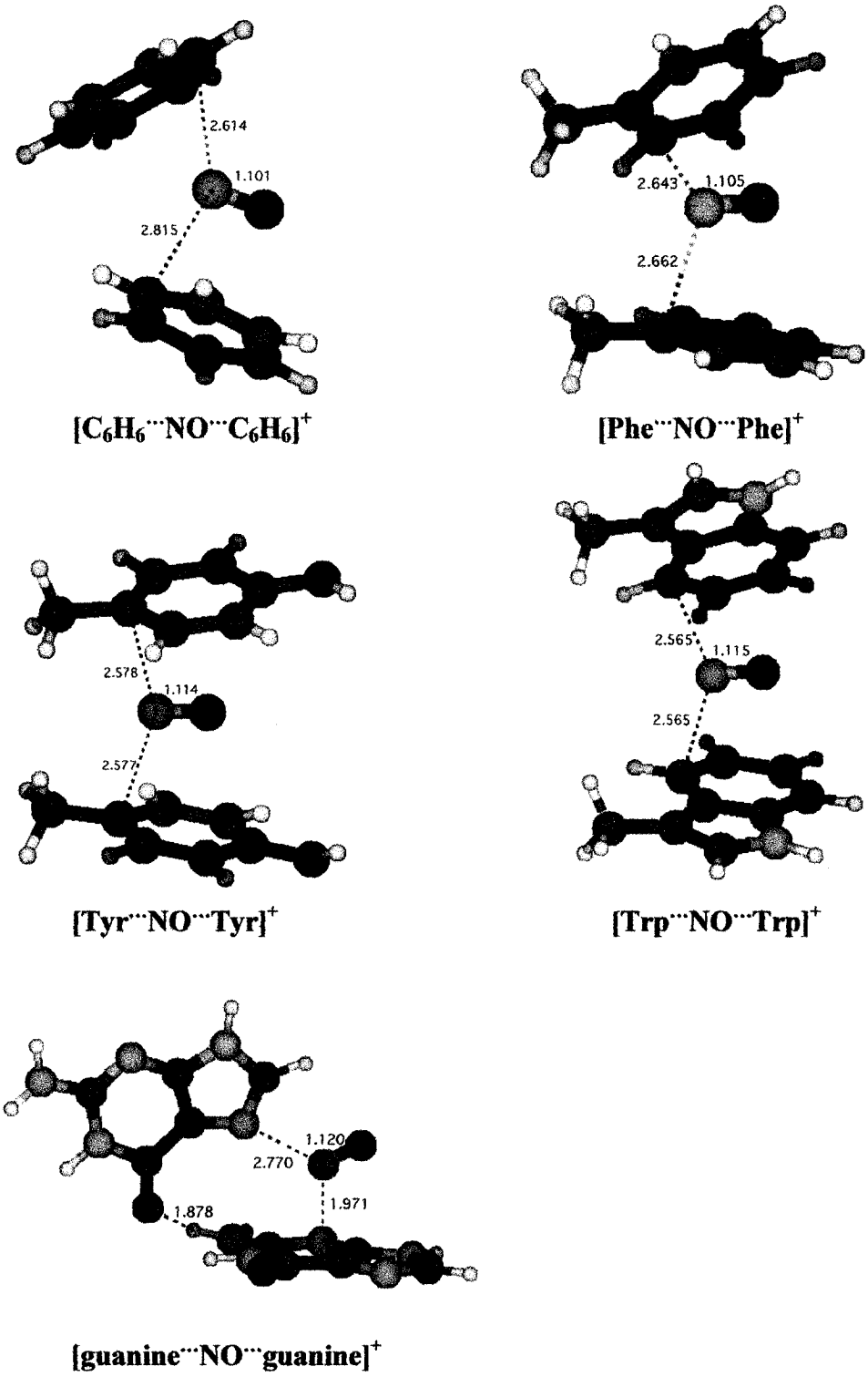


Figure 6.5. B3LYP/6-311G(d,p) optimized structures for $[NO\cdots(Ar)_2]^+$ complexes [C (orange); N (blue); O (red); H (white)].

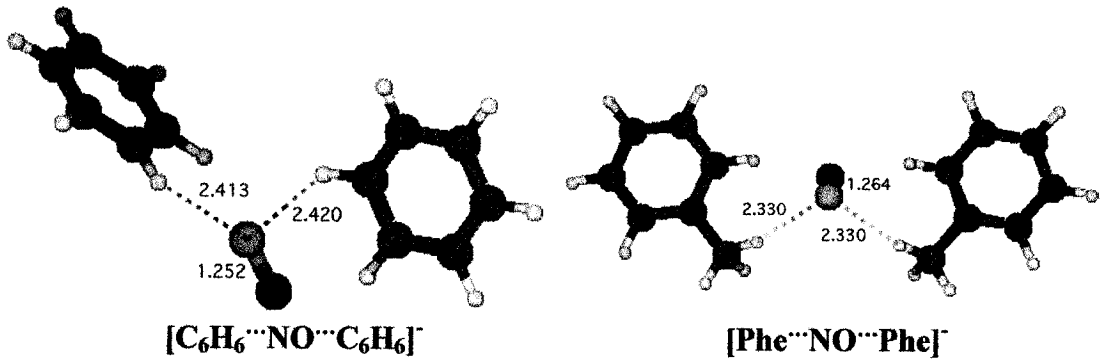
The NO^+ species is not sandwiched between the guanines, but is situated parallel with one guanine and at a bent orientation with the other one, at the closest distance of 1.971 Å and 2.770 Å to the aromatic species, respectively (**Figure 6.5**). The two-guanine molecules form a hydrogen bond of 1.878 Å. We did however, find a significant lengthening of the N—O bond, by 0.060 Å to 1.120 Å, compared to uncomplexed NO^+. Also, we note that the stability of the complex lies 366.1 kJ mol^{-1} lower in energy than the separated reactants, this being approximately 45.0-130.0 kJ mol^{-1} more stable compared to the sandwich complexes formed with the other biomolecules considered in the present chapter (**Table 6.5**).

Complexes of NO^- with two aromatic biomolecules: **Table 6.6** contains the optimized N—O bond lengths and the relative energies of the species formed upon interaction of nitroxide ion with two aromatic biomolecules.

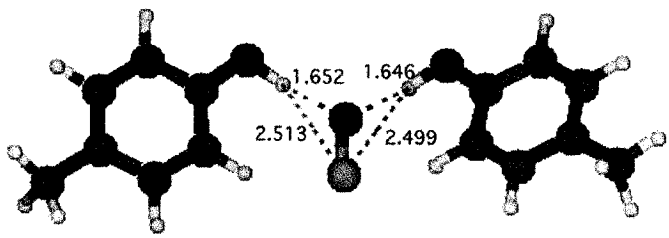
TABLE 6.6: Optimized N—O Bond Lengths (Å), Relative Energies (kJ mol^{-1}) and Charge Distribution (e^-) on NO^- of the $[NO^{\cdots}(Ar)_2]^-$ Complexes

Species	r(N—O)	Relative En.	Charge distribution
$[NO^{\cdots}(C_6H_6)_2]^-$	1.252	-252.5	-0.71
$[NO^{\cdots}(Phe)_2]^-$	1.264	-268.7	-0.69
$[NO^{\cdots}(Tyr)_2]^-$	1.277	-388.2	-0.70
$[NO^{\cdots}(Trp)_2]^-$	1.262	-258.4	-0.68
$[NO^{\cdots}(guanine)_2]^-$	1.262	-452.4	-0.68

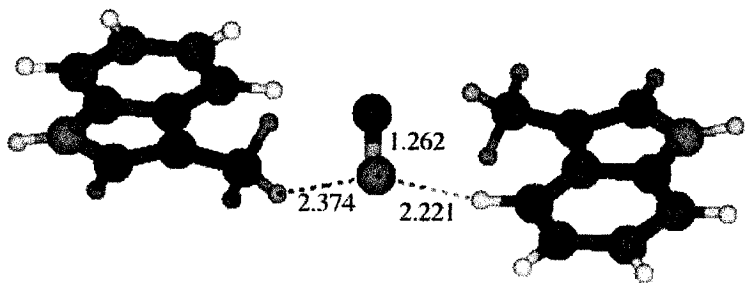
Unlike the complexes formed by nitrosonium ion with the same biomolecules, the species formed by NO^- are not sandwich structures.



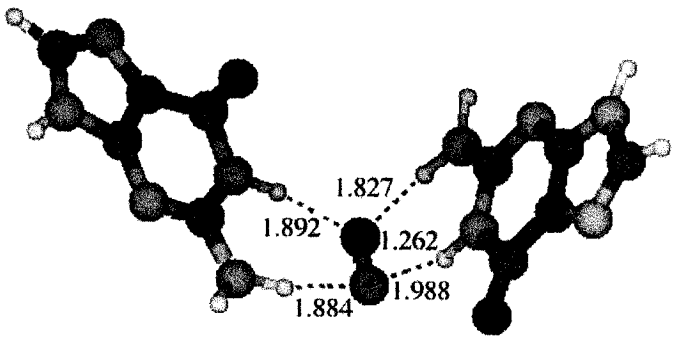
$[C_6H_6\cdots NO\cdots C_6H_6]^-$ **$[Phe\cdots NO\cdots Phe]^-$**



$[Tyr\cdots NO\cdots Tyr]^-$



$[Trp\cdots NO\cdots Trp]^-$



$[guanine\cdots NO\cdots guanine]^-$

Figure 6.6. B3LYP/6-311G(d,p) optimized structures for $[NO\cdots(Ar)_2]^-$ complexes [C (orange); N (blue); O (red); H (white)].

The NO^- moiety lies in between the two biomolecules, in a more planar orientation, at quite long distances from the aromatic rings (**Figure 6.6**). For example, in $[Phe\cdots NO\cdots Phe]^-$, the NO^- moiety is situated at a distance of 3.337 Å to the closest carbon atom of the rings. Also, the binding energies are stronger than the corresponding binding energies for $[NO\cdots(Ar)_2]^+$, (except for $[Trp\cdots NO\cdots Trp]^-$ complex), indicating the formation of more stable complexes. As discussed for $[NO\cdots Ar]^-$, a general decrease in the N—O bond lengths was observed, the exception being the $[Tyr\cdots NO\cdots Tyr]^-$ complex, for which a slight increase is noted. The most stable complex found is the $[guanine\cdots NO\cdots guanine]^-$ complex, this being 452.4 kJ mol^{-1} lower in energy than the separated reactants, and approximately 64-200 kJ mol^{-1} more stable than the other $[NO\cdots(aromatic\ biomolecule)_2]^-$ species formed (**Table 6.6**). The stability of the complex may be explained by the hydrogen bond interaction between NO^- and guanines. All of the results show a strong non-covalent interaction of nitroxide ion with two biomolecule species considered in this study. However, instead of forming sandwich complexes, it prefers to interact by complexing side-on via hydrogen bonds to the aromatic rings.

6.4 Conclusions

The interactions of nitric oxide and its ions, nitrosonium and nitroxide ions with one and/or two aromatic rings were investigated at the B3LYP/6-311G(d,p) level of theory. In the cases of the interaction with only one molecule aromatic ring, we found that, except for $NO^{\bullet}$, the ions, NO^+ and NO^- interact quite strongly with the aromatic biomolecules, forming relative stable complexes. The relative energies range from –177.6 to –267.3 kJ mol^{-1} and from –209.9 kJ mol^{-1} to –326.5 kJ mol^{-1}, respectively. As a result of these interactions, we noted a significant increase in the N—O bond lengths for $[NO\cdots Ar]^+$ complexes with 0.038-0.057 Å. The NO^+ moiety lies above the aromatic species, at a distance to the rings from 1.915 Å, ($[NO\cdots guanine]^+$) to 2.382 Å

($[NO\cdots Phe]^+$). These changes are generated by significant charge transfer from NO^+ to the biomolecules. When NO^+ interacts with two molecules of aromatic species, sandwich structures are formed, except for the $[guanine\cdots NO\cdots guanine]^+$ complex, in which NO^+ moiety prefers an arrangement parallel to one molecule and bent to the second one. The same changes in the calculated N—O bond lengths were noted, the magnitude of increase generally being enhanced relative to $[NO\cdots Ar]^+$ species.

In contrast, when nitrosonium ion interacts with the aromatic species considered, a general decrease in the N—O bond distances for $[NO\cdots Ar]^-$ species was observed, in a range from 0.016-0.030 Å. One exception was the $[NO\cdots guanine]^-$ complex, for which a slightly increase by 0.008 Å was observed. The $[NO\cdots Ar]^-$ complexes prefer more planar configurations, forming hydrogen bonds between NO^- and aromatic species that enhances the stability of the complexes formed as compared to the $[NO\cdots Ar]^+$ species. The interaction energy of NO^- with two aromatic rings is, as expected, even greater. Also in this case the configurations found do not look like sandwich structures, but a more planar configuration is preferred, NO^- interacting via hydrogen bonds to the aromatic rings.

As already mentioned, $NO^\bullet$ interacts very weakly with aromatic species, forming complexes that lie just few kJ mol^{-1} lower in energy compared to the separated reactants. These weak interactions are reflected in the N—O bond lengths which remain practically unchanged relative to the isolated $NO^\bullet$. These weak interactions of NO radical with aromatic biomolecules are suggestive for weak interactions with aromatic regions of proteins, so that all the structural changes that might occur within the proteins would be determined by the interaction of NO^+ or NO^- with the aromatic parts of proteins. Furthermore, the quite distinct complexes formed by NO+ and NO– with aromatic rings, may suggest a possible avenue for, for example, observing the form of 'NO' interacting

with the aromatic rich regions of proteins. Further investigations are currently in progress to more fully explore this possibility.

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Chapter 7

Conclusions

In this thesis S-nitrosothiols and the interactions of nitric oxide and its ions with aromatic biomolecules have been investigated. In addition, the ability of computational methods to reliably and accurately describe such species and their chemistry, has been examined.

In contrast to previous computational investigations[1-5] which simply chose to employ any commonly used method, this thesis showed that one must carefully choose a suitable method and basis set in order to obtain useful results. In particular, a systematic assessment of the ability of conventional electron correlation methods MP2, QCISD and DFT methods B3LYP and B3P86 to predict reliable structures and homolytic S—N bond dissociation energies of S-nitrosothiols was described in **Chapter 3**. Several model RSNOs were employed: HSNO, CH_3SNO, C_2H_3SNO, C_2H_5SNO, C_6H_5SNO and CysSNO. In general, with a suitable large basis set, i.e., 6-311+G(2df,p) or larger, the MP2, QCISD and B3P86 methods predict optimized geometries in good agreement with each other. In comparison, however, B3LYP systematically overestimates the length of the S—N bonds. The remarkable sensitivity of the optimized structures to method and basisi set is found to be due to the fact that, instead of possessing double-bond character, as previously believed,[3,4,6] the S—N bond is a long single-bond, while the –NO moiety retains considerable multiple-bond character.

For calculating accurate RS—NO bond dissociation energies, the same requirement for using the 6-311+G(2df,p) or larger basis sets is found. Furthermore, the QCISD method systematically underestimates, while the MP2 method overestimates

RS—NO BDEs, as evidenced by comparison with values calculated using the high level G3 and CBS-X (X=4M, Q, QB3).[2,4] The B3LYP method also underestimates RS—NO BDEs. Our results show that the consistently reliable and most accurate optimized structures and RS—NO BDEs for S-nitrosothiols are obtained at the B3P86/6-311+G(2df,p) level.

From this initial study in which a preferred method was determined and the nature of the RS—NO bond re-defined, we extended our studies to investigate the effects of binding of Cu^+ to S and to N in selected RSNOs: HSNO and CH_3SNO, in both gas phase and in solution (**Chapter 4**). Our results show that Cu^+ preferentially binds the S of the –SNO group, rather than the N centre. Binding at the S results in dramatic lengthening of the S—N bond, along with shortening of the N—O bond, enhancing release of NO. Remarkably, however, when Cu^+ binds via N centre of the –SNO moiety, opposite effects are observed, i.e., the S—N bond significantly shortens, with a concomitant lengthening of the N—O bond.

The above results lead to further detailed investigations on the interaction of Cu^+ with larger systems, in particular nitrosylated cysteine (CysSNO) and its decarboxilated and deaminated derivatives, $H_2NCH_2CH_2SNO$ and $HOOCCH_2CH_2SNO$, respectivelly (**Chapter 5**). For the latter two species, the addition of a water molecule to the corresponding Cu^+ complexes was also examined. The RSNOs were found to be able to form ring systems, with Cu^+ being bi- or tri-dentately coordinated to the RSNOs. Furthermore, we found that Cu^+ prefers to bind to the S of the –SNO group and to other distinct electron donating groups within the RSNO. No complexes were found in which Cu^+ was multiply co-ordinated to the –SNO group or via the O centre. For CysSNO, the most stable species was found to be the tridentately coordinated ring complex in which Cu^+ binds to the –SNO sulphur and to both the $–NH_2$ nitrogen and to the carbonyl oxygen

of the –COOH group. However, the higher the number of ligands simultaneously coordinated to the Cu^+ centre, the less its effects on the nature of the –SNO. For example, further coordination of the Cu^+ centre by addition of a single H_2O molecule generally determines more moderate effects of Cu^+ complexation.

In **Chapter 4** we also found that the stabilization of the S—N bond induced by Cu^+ binding to the N of RSNOs, could be analogue for the stabilization that can occur within the S-nitrosorhodanese active site, due to the interaction of the –SNO group with a neighbouring, positively charged arginine.

Following these investigations, the interaction of NO and its mono-ionic derivatives with one and/or two aromatic biomolecules, e.g., aromatic amino acids and nucleobasis, were considered (**Chapter 6**). The B3LYP/6-311G(d,p) method was employed. Our results show that while $NO^•$ interacts very weakly with aromatic species, NO^+ and NO^- interact quite strongly. Complexation involving NO^+ results in a significant increase in the N—O bond in the $[NO^{\cdots}Ar]^+$ complexes., i.e., the NO^+ moiety increasingly resembles $NO^•$ in character. This effect is explained by charge transfer occurring from the NO^+ moiety to the aromatic species, and this is enhanced when two aromatic rings are involved with the formation of sandwich complexes. In contrast, the interaction of NO^- with aromatic species results in a general decrease in the N—O bond length in the resulting $[NO^{\cdots}Ar]^-$ complexes, due to the charge transfer occurring from NO^- to the biomolecules considered. However, either the $[NO^{\cdots}Ar]^-$ or the $[NO^{\cdots}(Ar)_2]^-$ complexes are formed, the structure adopted is more planar, with the formation of hydrogen bonds between NO^- and the aromatic species. These hydrogen bonds determine an increase in the stability of the complexes formed compared to the $[NO^{\cdots}Ar]^+$ or to the $[NO^{\cdots}(Ar)_2]^+$ species. Overall, these results suggest that for all the structural changes that

might occur within the proteins upon their interaction with NO species, not $NO^{\bullet}$, but NO^{+} or NO^{-} could be responsible.

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Appendix A

Gaussian Archive Entries of all Optimized Geometries Obtained for all Species Considered in Chapter 3

A.1 Gaussian Archive Entries of all Optimized Geometries Obtained for S-nitrosothiols and Related Species Considered in Chapter 3

HSNO (trans) MP2/6-31G(d)

1\1\GINC-N10\Freq\RMP2-FC\6-31G(d)\H1N1O1S1\ROOT\14-Nov-2001\1\\#N GEO
M=ALLCHECK GUESS=TCHECK RMP2(FC)/6-31G(D) FREQ\\hsno-trans-mp2b1\\0,1\
S\N,1,r1\H,1,r2,2,a1\O,2,r3,1,a2,3,180.,0\\r1=1.84970837\r2=1.3406666\
r3=1.20470931\a1=90.6232652\a2=114.18190567\\Version=IBM-RS6000-G98Rev
A.7\State=1-A'\HF=-527.2879152\MP2=-527.7633975\RMSD=5.019e-10\RMSF=6.
207e-06\Dipole=0.4607176,0.,-0.2222846\PG=CS [SG(H1N1O1S1)]\\@

HSNO (trans) MP2/6-31G(d,p)

1\1\GINC-N03\Freq\RMP2-FC\6-31G(d,p)\H1N1O1S1\ROOT\06-Nov-2001\1\\#N G
EOM=ALLCHECK GUESS=TCHECK RMP2(FC)/6-31G(D,P) FREQ\\hsno-trans-mp2b3\\
0,1\S\N,1,r1\H,1,r2,2,a1\O,2,r3,1,a2,3,180.,0\\r1=1.85272922\r2=1.3314
956\r3=1.20400898\a1=90.39367585\a2=114.19273291\\Version=IBM-RS6000-G
98RevA.7\State=1-A'\HF=-527.2918625\MP2=-527.7742597\RMSD=6.968e-10\RM
SF=9.367e-06\Dipole=0.4286499,0.,-0.2073861\PG=CS [SG(H1N1O1S1)]\\@

HSNO (trans) MP2/6-311G(d,p)

1\1\GINC-SP\Freq\RMP2-FC\6-311G(d,p)\H1N1O1S1\ROOT\06-Nov-2001\1\\#N G
EOM=ALLCHECK GUESS=TCHECK RMP2(FC)/6-311G(D,P) FREQ\\hsno-trans-mp2b4\
\0,1\S\N,1,r1\H,1,r2,2,a1\O,2,r3,1,a2,3,180.,0\\r1=1.8910526\r2=1.3334
0264\r3=1.17921578\a1=89.38336347\a2=114.96388756\\Version=IBM-RS6000-
G98RevA.7\State=1-A'\HF=-527.3498177\MP2=-527.8632808\RMSD=1.573e-09\R
MSF=2.267e-06\Dipole=0.3677392,0.,-0.0426851\PG=CS [SG(H1N1O1S1)]\\@

HSNO (trans) MP2/6-311+G(d,p)

1\1\GINC-N09\Freq\RMP2-FC\6-311+G(d,p)\H1N1O1S1\ROOT\06-Nov-2001\1\\#N
GEOM=ALLCHECK GUESS=TCHECK RMP2(FC)/6-311+G(D,P) FREQ\\hsno-trans-mp2
b5\\0,1\S\N,1,r1\H,1,r2,2,a1\O,2,r3,1,a2,3,180.,0\\r1=1.85000763\r2=1.
33442738\r3=1.18779244\a1=89.79414476\a2=115.13792227\\Version=IBM-RS6
000-G98RevA.7\State=1-A'\HF=-527.3560027\MP2=-527.8727238\RMSD=1.052e-
09\RMSF=2.697e-05\Dipole=0.4123819,0.,-0.2303787\PG=CS [SG(H1N1O1S1)]
\\@

HSNO (trans) MP2/6-311G(2d,p)

1\1\GINC-N03\Freq\RMP2-FC\6-311G(2d,p)\H1N1O1S1\ROOT\07-Nov-2001\1\\#N
 GEOM=ALLCHECK GUESS=TCHECK RMP2(FC)/6-311G(2D,P) FREQ\\hsno-trans-mp2
b6\\0,1\S\N,1,r1\H,1,r2,2,a1\O,2,r3,1,a2,3,180.,0\\r1=1.92935224\r2=1.
33316595\r3=1.17473931\a1=88.90710992\a2=114.74830462\\Version=IBM-RS6

000-G98RevA.7\State=1-A'\HF=-527.3567445\MP2=-527.9098093\RMSD=5.670e-10\RMSF=5.093e-06\Dipole=0.3060992,0.,0.0971405\PG=CS [SG(H1N1O1S1)]\\@

HSNO (trans) MP2/6-311G(df,p)

1\1\GINC-N09\Freq\RMP2-FC\6-311G(df,p)\H1N1O1S1\ROOT\07-Nov-2001\1\\#N GEOM=ALLCHECK GUESS=TCHECK RMP2(FC)/6-311G(DF,P) FREQ\\hsno-trans-mp2b7\\0,1\S\N,1,r1\H,1,r2,2,a1\O,2,r3,1,a2,3,180.,0\\r1=1.82725895\r2=1.33481002\r3=1.18565781\a1=90.59168088\a2=114.70014221\\Version=IBM-RS6000-G98RevA.7\State=1-A'\HF=-527.3589647\MP2=-527.9277088\RMSD=1.432e-09\RMSF=5.479e-05\Dipole=0.4390473,0.,-0.2405341\PG=CS [SG(H1N1O1S1)]\\@

HSNO (trans) MP2/6-311+G(2df,p)

1\1\GINC-HAMMERHEAD4\Freq\RMP2-FC\6-311+G(2df,p)\H1N1O1S1\JGAULD\28-Oct-2002\1\\#N GEOM=ALLCHECK GUESS=TCHECK RMP2(FC)/6-311+G(2DF,P) FREQ\\hsno-trans-mp2b11\\0,1\S\N,1,r1\H,1,r2,2,a1\O,2,r3,1,a2,3,180.,0\\r1=1.8256114\r2=1.33964821\r3=1.19064021\a1=90.5221655\a2=114.60776485\\Version=DEC-AXP-Linux-G98RevA.11\State=1-A'\HF=-527.3735302\MP2=-527.9795241\RMSD=1.433e-09\RMSF=2.338e-05\Dipole=0.4272335,0.,-0.3069605\PG=CS [SG(H1N1O1S1)]\\@

HSNO (trans) MP2/6-311++G(3df,3pd)

1\1\GINC-N11\Freq\RMP2-FC\6-311++G(3df,3pd)\H1N1O1S1\ROOT\12-Nov-2001\1\\# MP2/6-311++G(3DF,3PD) GEOM=CHECK GUESS=READ FREQ=NORAMAN MAXDISK=3GB\\hsno-trans-mp2b9\\0,1\S\N,1,r1\H,1,r2,2,a1\O,2,r3,1,a2,3,180.,0\\r1=1.80996321\r2=1.33293131\r3=1.19135227\a1=90.69651356\a2=114.54146982\\Version=IBM-RS6000-G98RevA.7\State=1-A'\HF=-527.3779816\MP2=-527.9944511\RMSD=5.234e-10\RMSF=4.686e-05\Dipole=0.3884273,0.,-0.3457963\PG=CS [SG(H1N1O1S1)]\\@

HSNO (*cis*) MP2/6-31G(d)

1\1\GINC-N07\Freq\RMP2-FC\6-31G(d)\H1N1O1S1\ROOT\05-Nov-2001\1\\#N GEOM=ALLCHECK GUESS=TCHECK RMP2(FC)/6-31G(D) FREQ\\hsno-cis-b1\\0,1\S\N,1,r1\H,1,r2,2,a1\O,2,r3,1,a2,3,0.,0\\r1=1.82674121\r2=1.34734676\r3=1.21057364\a1=95.43812552\a2=114.97508914\\Version=IBM-RS6000-G98RevA.7\State=1-A'\HF=-527.2875018\MP2=-527.7623818\RMSD=3.158e-10\RMSF=3.702e-05\Dipole=0.3504824,0.,-0.3415741\PG=CS [SG(H1N1O1S1)]\\@

HSNO (*cis*) MP2/6-31G(d,p)

1\1\GINC-VLAD\Freq\RMP2-FC\6-31G(d,p)\H1N1O1S1\CRISTINA\27-Dec-2002\1\\#N GEOM=ALLCHECK GUESS=TCHECK RMP2(FC)/6-31G(D,P) FREQ\\hsno-cis-b3\\0,1\S\N,1,r1\H,1,r2,2,a1\O,2,r3,1,a2,3,0.,0\\r1=1.83163514\r2=1.33775783\r3=1.20949532\a1=95.1372627\a2=114.94785619\\Version=x86-Linux-G98RevA.11.1\State=1-A'\HF=-527.2913982\MP2=-527.7730682\RMSD=6.584e-10\RMSF=5.528e-05\Dipole=0.3283187,0.,-0.3172224\PG=CS [SG(H1N1O1S1)]\\@

HSNO (*cis*) MP2/6-311G(d,p)

1\1\GINC-N06\Freq\RMP2-FC\6-311G(d,p)\H1N1O1S1\ROOT\05-Nov-2001\1\\#N GEOM=ALLCHECK GUESS=TCHECK RMP2(FC)/6-311G(D,P) FREQ\\hsno-cis-b4\\0,1\S\N,1,r1\H,1,r2,2,a1\O,2,r3,1,a2,3,0.,0\\r1=1.85223694\r2=1.34015324\r3=1.18785991\a1=94.71178776\a2=115.42301132\\Version=IBM-RS6000-G98RevA.7\State=1-A'\HF=-527.3499315\MP2=-527.8619517\RMSD=1.866e-09\RMSF=8.295e-06\Dipole=0.3443087,0.,-0.2103386\PG=CS [SG(H1N1O1S1)]\\@

HSNO (*cis*) MP2/6-311+G(d,p)

1\1\GINC-N03\Freq\RMP2-F+C\6-311+G(d,p)\H1N1O1S1\ROOT\05-Nov-2001\1\\#N GEOM=ALLCHECK GUESS=TCHECK RMP2(FC)/6-311+G(D,P) FREQ\\hsno-cis-b5\\0 ,1\S\N,1,r1\H,1,r2,2,a1\O,2,r3,1,a2,3,0.,0\\r1=1.81829827\r2=1.3424811 \r3=1.1952292\a1=95.58278714\a2=116.04650155\\Version=IBM-RS6000-G98Re vA.7\State=1-A'\HF=-527.3555188\MP2=-527.8711457\RMSD=1.494e-09\RMSF=5 .345e-05\Dipole=0.3335576,0.,-0.3734912\PG=CS [SG(H1N1O1S1)]\\@

HSNO (*cis*) MP2/6-311G(2d,p)

1\1\GINC-N06\Freq\RMP2-FC\6-311G(2d,p)\H1N1O1S1\ROOT\05-Nov-2001\1\\#N GEOM=ALLCHECK GUESS=TCHECK RMP2(FC)/6-311G(2D,P) FREQ\\hsno-cis-b6\\0 ,1\S\N,1,r1\H,1,r2,2,a1\O,2,r3,1,a2,3,0.,0\\r1=1.90507249\r2=1.3391319 8\r3=1.18065617\a1=93.86005722\a2=115.02631418\\Version=IBM-RS6000-G98 RevA.7\State=1-A'\HF=-527.3564983\MP2=-527.9084459\RMSD=1.575e-09\RMSF =3.908e-05\Dipole=0.3414017,0.,-0.0188795\PG=CS [SG(H1N1O1S1)]\\@

HSNO (*cis*) MP2/6-311G(df,p)

1\1\GINC-N03\Freq\RMP2-FC\6-311G(df,p)\H1N1O1S1\ROOT\05-Nov-2001\1\\#N GEOM=ALLCHECK GUESS=TCHECK RMP2(FC)/6-311G(DF,P) FREQ\\hsno-cis-b7\\0 ,1\S\N,1,r1\H,1,r2,2,a1\O,2,r3,1,a2,3,0.,0\\r1=1.79379028\r2=1.3438641 3\r3=1.19321166\a1=95.80501776\a2=115.92985169\\Version=IBM-RS6000-G98 RevA.7\State=1-A'\HF=-527.3586689\MP2=-527.9268486\RMSD=1.033e-09\RMSF =1.412e-04\Dipole=0.3261894,0.,-0.3835413\PG=CS [SG(H1N1O1S1)]\\@

HSNO (*cis*) MP2/6-311+G(2df,p)

1\1\GINC-VLAD\Freq\RMP2-FC\6-311+G(2df,p)\H1N1O1S1\CRISTINA\04-Mar-200 2\1\\#N GEOM=ALLCHECK GUESS=TCHECK RMP2(FC)/6-311+G(2DF,P) FREQ\\hsno-cis-b10\\0,1\S\N,1,r1\H,1,r2,2,a1\O,2,r3,1,a2,3,0.,0\\r1=1.79879756\r2 =1.34791924\r3=1.19683987\a1=95.85023359\a2=116.02350576\\Version=x86-Linux-G98RevA.11.1\State=1-A'\HF=-527.3728307\MP2=-527.9782765\RMSD=1. 175e-09\RMSF=3.694e-05\Dipole=0.2904688,0.,-0.431441\PG=CS [SG(H1N1O1S1)]\\@

HSNO (*cis*) MP2/6-311++G(3df,3pd)

1\1\GINC-N03\Freq\RMP2-FC\6-311++G(3df,3pd)\H1N1O1S1\ROOT\13-Nov-2001\ 1\\#N GEOM=ALLCHECK GUESS=TCHECK RMP2(FC)/6-311++G(3DF,3PD) FREQ\\hsno -cis-b9\\0,1\S\N,1,r1\H,1,r2,2,a1\O,2,r3,1,a2,3,0.,0\\r1=1.78459521\r2 =1.34143362\r3=1.19682916\a1=95.91375879\a2=116.1557774\\Version=IBM-R S6000-G98RevA.7\State=1-A'\HF=-527.3771349\MP2=-527.9930389\RMSD=1.746 e-09\RMSF=3.736e-05\Dipole=0.2412505,0.,-0.4601211\PG=CS [SG(H1N1O1S1)] \\@

HSNO (*trans*) QCISD/6-31G(d)

1\1\GINC-CURIE\Freq\RQCISD-FC\6-31G(d)\H1N1O1S1\CRISTINA\16-May-2002\1 \\#N GEOM=ALLCHECK GUESS=TCHECK RQCISD(FC)/6-31G(D) FREQ\\hsno-trans-q cisdb1\\0,1\S\N,1,r1\H,1,r2,2,a1\O,2,r3,1,a2,3,180.,0\\r1=1.86288179\r 2=1.34637654\r3=1.19355475\a1=90.49640842\a2=114.14277021\\Version=x86 -Linux-G98RevA.11.1\State=1-A'\HF=-527.2889323\MP2=-527.763258\MP3=-52 7.7695037\MP4D=-527.7864024\MP4DQ=-527.7750977\MP4SDQ=-527.7844224\QCI SD=-527.7859703\RMSD=4.424e-10\RMSF=9.082e-05\Dipole=0.4753403,0.,-0.2 735404\PG=CS [SG(H1N1O1S1)]\\@

HSNO (*trans*) QCISD/6-31G(d,p)

1\1\GINC-VLAD\Freq\RQCISD-FC\6-31G(d,p)\H1N1O1S1\CRISTINA\17-May-2002\
1\\#N GEOM=ALLCHECK GUESS=TCHECK RQCISD(FC)/6-31G(D,P) FREQ\\hsno-tran
s-qcisdb2\\0,1\S\N,1,r1\H,1,r2,2,a1\O,2,r3,1,a2,3,180.,0\\r1=1.8643537
9\r2=1.33432126\r3=1.19327308\a1=90.38990053\a2=114.14473304\\Version=
x86-Linux-G98RevA.11.1\State=1-A'\HF=-527.2929966\MP2=-527.7741392\MP3
=-527.7805431\MP4D=-527.7973532\MP4DQ=-527.7857992\MP4SDQ=-527.7951162
\QCISD=-527.7965422\RMSD=6.865e-10\RMSF=8.730e-05\Dipole=0.4462084,0.,
-0.2655156\PG=CS [SG(H1N1O1S1)]\\@

HSNO (*trans*) QCISD/6-311G(d,p)

1\1\GINC-CURIE\Freq\RQCISD-FC\6-311G(d,p)\H1N1O1S1\CRISTINA\16-May-200
2\1\\#N GEOM=ALLCHECK GUESS=TCHECK RQCISD(FC)/6-311G(D,P) FREQ\\hsno-t
rans-qcisdb3\\0,1\S\N,1,r1\H,1,r2,2,a1\O,2,r3,1,a2,3,180.,0\\r1=1.8777
4751\r2=1.33636702\r3=1.17520708\a1=89.94952691\a2=114.51774726\\Versi
on=x86-Linux-G98RevA.11.1\State=1-A'\HF=-527.3512327\MP2=-527.8631962\
MP3=-527.8669753\MP4D=-527.8843672\MP4DQ=-527.871735\MP4SDQ=-527.88248
66\QCISD=-527.8834266\RMSD=1.201e-09\RMSF=1.307e-04\Dipole=0.4131941,0
.,-0.2021496\PG=CS [SG(H1N1O1S1)]\\@

HSNO (*trans*) QCISD/6-311+G(d,p)

1\1\GINC-VLAD\Freq\RQCISD-FC\6-311+G(d,p)\H1N1O1S1\CRISTINA\18-May-200
2\1\\#N GEOM=ALLCHECK GUESS=TCHECK RQCISD(FC)/6-311+G(D,P) FREQ\\hsno-
trans-qcisdb4\\0,1\S\N,1,r1\H,1,r2,2,a1\O,2,r3,1,a2,3,180.,0\\r1=1.855
35526\r2=1.33760807\r3=1.17927401\a1=90.02812211\a2=114.85635805\\Vers
ion=x86-Linux-G98RevA.11.1\State=1-A'\HF=-527.3570376\MP2=-527.8726272
\MP3=-527.8758395\MP4D=-527.893428\MP4DQ=-527.8806263\MP4SDQ=-527.8916
414\QCISD=-527.8927053\RMSD=7.603e-10\RMSF=9.549e-05\Dipole=0.4382648,
0.,-0.3057692\PG=CS [SG(H1N1O1S1)]\\@

HSNO (*trans*) QCISD/6-311G(2d,p)

1\1\GINC-VLAD\Freq\RQCISD-FC\6-311G(2d,p)\H1N1O1S1\CRISTINA\18-May-200
2\1\\#N GEOM=ALLCHECK GUESS=TCHECK RQCISD(FC)/6-311G(2D,P) FREQ\\hsno-
trans-qcisdb5\\0,1\S\N,1,r1\H,1,r2,2,a1\O,2,r3,1,a2,3,180.,0\\r1=1.889
53219\r2=1.33441737\r3=1.1744103\a1=90.10672254\a2=114.21367467\\Versi
on=x86-Linux-G98RevA.11.1\State=1-A'\HF=-527.359362\MP2=-527.9096353\M
P3=-527.913185\MP4D=-527.9318418\MP4DQ=-527.9161528\MP4SDQ=-527.927250
5\QCISD=-527.9278034\RMSD=1.575e-09\RMSF=1.499e-04\Dipole=0.3817376,0.
,-0.1558749\PG=CS [SG(H1N1O1S1)]\\@

HSNO (*trans*) QCISD/6-311G(df,p)

1\1\GINC-VLAD\Freq\RQCISD-FC\6-311G(df,p)\H1N1O1S1\CRISTINA\03-Jun-200
2\1\\#N GEOM=ALLCHECK GUESS=TCHECK RQCISD(FC)/6-311G(DF,P) FREQ\\hsno-
trans-qcisdb6\\0,1\S\N,1,r1\H,1,r2,2,a1\O,2,r3,1,a2,3,180.,0\\r1=1.834
26394\r2=1.33764469\r3=1.17596223\a1=90.83065105\a2=114.57704084\\Vers
ion=x86-Linux-G98RevA.11.1\State=1-A'\HF=-527.3599983\MP2=-527.9275934
\MP3=-527.9365554\MP4D=-527.9546649\MP4DQ=-527.939332\MP4SDQ=-527.9494
512\QCISD=-527.949919\RMSD=1.230e-09\RMSF=8.067e-05\Dipole=0.4610011,0
.,-0.2946441\PG=CS [SG(H1N1O1S1)]\\@

HSNO (*trans*) QCISD/6-311+G(2df,p)

1\1\GINC-CURIE\Freq\RQCISD-FC\6-311+G(2df,p)\H1N1O1S1\CRISTINA\29-May-
2002\1\\#N GEOM=ALLCHECK GUESS=TCHECK RQCISD(FC)/6-311+G(2DF,P) FREQ\\
hsno-trans-qcisdb7\\0,1\S\N,1,r1\H,1,r2,2,a1\O,2,r3,1,a2,3,180.,0\\r1=

1.83403465\r2=1.34181201\r3=1.17861436\a1=90.91456821\a2=114.48551033\
\Version=x86-Linux-G98RevA.11.1\State=1-A'\HF=-527.3748382\MP2=-527.97
93635\MP3=-527.9868337\MP4D=-528.0064593\MP4DQ=-527.9879394\MP4SDQ=-52
7.9985391\QCISD=-527.998744\RMSD=1.006e-09\RMSF=1.562e-04\Dipole=0.448
3874,0.,-0.3391851\PG=CS [SG(H1N1O1S1)]\\@

HSNO (*trans*) QCISD/6-311++G(3df,3pd)

1\1\GINC-POPLE\FOpt\RQCISD-FC\6-311++G(3df,3pd)\H1N1O1S1\JAMES\28-Dec-
2002\1\\# QCISD/6-311++G(3DF,3PD) FOPT=Z-MATRIX TEST\\hsno-trans-qcisd
b8\\0,1\S\N,1,r1\H,1,r2,2,a1\O,2,r3,1,a2,3,180.,0\\r1=1.8204254\r2=1.3
3466724\r3=1.17882474\a1=91.05431265\a2=114.45230637\\Version=x86-Linu
x-G98RevA.11.1\State=1-A'\HF=-527.3792728\MP2=-527.9942865\MP3=-528.00
15002\MP4D=-528.0211997\MP4DQ=-528.0020656\MP4SDQ=-528.0126663\QCISD=-
528.0129046\RMSD=1.853e-09\RMSF=1.501e-04\Dipole=0.409101,0.,-0.357434
6\PG=CS [SG(H1N1O1S1)]\\@

HSNO (*cis*) QCISD/6-31G(d)

1\1\GINC-VLAD\Freq\RQCISD-FC\6-31G(d)\H1N1O1S1\CRISTINA\21-Nov-2001\1\
\#N GEOM=ALLCHECK GUESS=TCHECK RQCISD(FC)/6-31G(D) FREQ\\hsno-cis-qcis
db1\\0,1\S\N,1,r1\H,1,r2,2,a1\O,2,r3,1,a2,3,0.,0\\r1=1.85080851\r2=1.3
5209504\r3=1.1967594\a1=94.89793832\a2=115.10266621\\Version=x86-Linux
-G98RevA.11.1\State=1-A'\HF=-527.2883806\MP2=-527.7621945\MP3=-527.768
2684\MP4D=-527.7850844\MP4DQ=-527.7739522\MP4SDQ=-527.7833467\QCISD=-5
27.7847621\RMSD=6.332e-10\RMSF=2.270e-04\Dipole=0.3040112,0.,-0.350308
7\PG=CS [SG(H1N1O1S1)]\\@

HSNO (*cis*) QCISD/6-31G(d,p)

1\1\GINC-VLAD\Freq\RQCISD-FC\6-31G(d,p)\H1N1O1S1\CRISTINA\21-Nov-2001\
1\\#N GEOM=ALLCHECK GUESS=TCHECK RQCISD(FC)/6-31G(D,P) FREQ\\hsno-cis-
qcisdb2\\0,1\S\N,1,r1\H,1,r2,2,a1\O,2,r3,1,a2,3,0.,0\\r1=1.85266222\r2
=1.3394444\r3=1.19666178\a1=94.75916924\a2=115.00762638\\Version=x86-L
inux-G98RevA.11.1\State=1-A'\HF=-527.2923685\MP2=-527.7729158\MP3=-527
.7791436\MP4D=-527.7958701\MP4DQ=-527.7844865\MP4SDQ=-527.7938724\QCIS
D=-527.7952033\RMSD=9.977e-10\RMSF=3.617e-05\Dipole=0.2808383,0.,-0.33
8005\PG=CS [SG(H1N1O1S1)]\\@

HSNO (*cis*) QCISD/6-311G(d,p)

1\1\GINC-VLAD\Freq\RQCISD-FC\6-311G(d,p)\H1N1O1S1\CRISTINA\21-Nov-2001
\1\\#N GEOM=ALLCHECK GUESS=TCHECK RQCISD(FC)/6-311G(D,P) FREQ\\hsno-ci
s-qcisdb3\\0,1\S\N,1,r1\H,1,r2,2,a1\O,2,r3,1,a2,3,0.,0\\r1=1.85987065\
r2=1.34216364\r3=1.17934251\a1=94.57154705\a2=115.3959855\\Version=x86
-Linux-G98RevA.11.1\State=1-A'\HF=-527.3507674\MP2=-527.8618747\MP3=-5
27.8655329\MP4D=-527.8828156\MP4DQ=-527.8704193\MP4SDQ=-527.88118\QCIS
D=-527.8820543\RMSD=8.242e-10\RMSF=3.473e-05\Dipole=0.2874551,0.,-0.28
41135\PG=CS [SG(H1N1O1S1)]\\@

HSNO (*cis*) QCISD/6-311+G(d,p)

1\1\GINC-VLAD\Freq\RQCISD-FC\6-311+G(d,p)\H1N1O1S1\CRISTINA\22-Nov-200
1\1\\#N GEOM=ALLCHECK GUESS=TCHECK RQCISD(FC)/6-311+G(D,P) FREQ\\hsno-
cis-qcisdb4\\0,1\S\N,1,r1\H,1,r2,2,a1\O,2,r3,1,a2,3,0.,0\\r1=1.8380885
5\r2=1.34416298\r3=1.18351387\a1=95.18602476\a2=115.94189442\\Version=
x86-Linux-G98RevA.11.1\State=1-A'\HF=-527.3562916\MP2=-527.8710167\MP3
=-527.8741354\MP4D=-527.8916304\MP4DQ=-527.8790496\MP4SDQ=-527.8900737
\QCISD=-527.8910455\RMSD=9.327e-10\RMSF=5.045e-05\Dipole=0.2826721,0.,

-0.388299\PG=CS [SG(H1N1O1S1)\\@

HSNO (*cis*) QCISD/6-311G(2d,p)

1\1\GINC-VLAD\Freq\RQCISD-FC\6-311G(2d,p)\H1N1O1S1\CRISTINA\21-Nov-200
1\1\\#N GEOM=ALLCHECK GUESS=TCHECK RQCISD(FC)/6-311G(2D,P) FREQ\\hsno-
cis-qcisdb3b5\\0,1\S\N,1,r1\H,1,r2,2,a1\O,2,r3,1,a2,3,0.,0\\r1=1.87822
843\r2=1.34040752\r3=1.17735603\a1=94.55398671\a2=115.24899243\\Versio
n=x86-Linux-G98RevA.11.1\State=1-A'\HF=-527.3585399\MP2=-527.9083297\M
P3=-527.9117826\MP4D=-527.9303932\MP4DQ=-527.9148821\MP4SDQ=-527.92601
34\QCISD=-527.9265068\RMSD=7.540e-10\RMSF=4.473e-05\Dipole=0.2708154,0
.,-0.2174752\PG=CS [SG(H1N1O1S1)\\@

HSNO (*cis*) QCISD/6-311G(df,p)

1\1\GINC-VLAD\Freq\RQCISD-FC\6-311G(df,p)\H1N1O1S1\CRISTINA\22-Nov-200
1\1\\#N GEOM=ALLCHECK GUESS=TCHECK RQCISD(FC)/6-311G(DF,P) FREQ\\hsno-
cis-qcisdb6\\0,1\S\N,1,r1\H,1,r2,2,a1\O,2,r3,1,a2,3,0.,0\\r1=1.8143850
1\r2=1.34459794\r3=1.18028525\a1=95.39965817\a2=115.86030797\\Version=
x86-Linux-G98RevA.11.1\State=1-A'\HF=-527.3596255\MP2=-527.9266783\MP3
=-527.9354234\MP4D=-527.9534367\MP4DQ=-527.9383171\MP4SDQ=-527.9484649
\QCISD=-527.9488396\RMSD=2.332e-09\RMSF=1.208e-04\Dipole=0.2834681,0.,
-0.384115\PG=CS [SG(H1N1O1S1)\\@

HSNO (*cis*) QCISD/6-311+G(2df,p)

1\1\GINC-VLAD\Freq\RQCISD-FC\6-311+G(2df,p)\H1N1O1S1\CRISTINA\05-Dec-2
001\1\\#N GEOM=ALLCHECK GUESS=TCHECK RQCISD(FC)/6-311+G(2DF,P) FREQ\\h
sno-cis-qcisdb7\\0,1\S\N,1,r1\H,1,r2,2,a1\O,2,r3,1,a2,3,0.,0\\r1=1.817
95439\r2=1.34896295\r3=1.1821886\a1=95.7139759\a2=116.06389262\\Versio
n=x86-Linux-G98RevA.11.1\State=1-A'\HF=-527.3740095\MP2=-527.9780816\M
P3=-527.9854555\MP4D=-528.0050247\MP4DQ=-527.986686\MP4SDQ=-527.997313
1\QCISD=-527.9974387\RMSD=1.771e-09\RMSF=2.594e-07\Dipole=0.2543516,0.
,-0.4199446\PG=CS [SG(H1N1O1S1)\\@

HSNO (*cis*) QCISD/6-311++G(3df,3pd)

1\1\GINC-POPLE\FOpt\RQCISD-FC\6-311++G(3df,3pd)\H1N1O1S1\JAMES\28-Dec-
2002\1\\# QCISD/6-311++G(3DF,3PD) FOPT=Z-MATRIX TEST\\hsno-cis-qcisdb8
\\0,1\S\N,1,r1\H,1,r2,2,a1\O,2,r3,1,a2,3,0.,0\\r1=1.80382261\r2=1.3423
0316\r3=1.18218823\a1=95.8369452\a2=116.12422612\\Version=x86-Linux-G9
8RevA.11.1\State=1-A'\HF=-527.3783559\MP2=-527.9928422\MP3=-527.999933
6\MP4D=-528.0195888\MP4DQ=-528.0006405\MP4SDQ=-528.0112817\QCISD=-528.
0114498\RMSD=1.589e-09\RMSF=1.274e-04\Dipole=0.2133146,0.,-0.4357152\P
G=CS [SG(H1N1O1S1)]\\@

HSNO (*trans*) B3LYP/6-31G(d)

1\1\GINC-CURIE\Freq\RB3LYP\6-31G(d)\H1N1O1S1\CRISTINA\15-May-2002\1\\#
N GEOM=ALLCHECK GUESS=TCHECK RB3LYP/6-31G(D) FREQ\\hsno-tr-b3lypb1\\0,
1\S\N,1,r1\H,1,r2,2,a1\O,2,r3,1,a2,3,180.,0\\r1=1.91272254\r2=1.349046
09\r3=1.17481319\a1=89.89562344\a2=115.10747859\\Version=x86-Linux-G98
RevA.11.1\State=1-A'\HF=-528.6767138\RMSD=3.583e-09\RMSF=1.251e-05\Dip
ole=0.4243797,0.,-0.1175595\PG=CS [SG(H1N1O1S1)]\\@

HSNO (*trans*) B3LYP/6-31G(d,p)

1\1\GINC-VLAD\Freq\RB3LYP\6-31G(d,p)\H1N1O1S1\CRISTINA\17-May-2002\1\\
#N GEOM=ALLCHECK GUESS=TCHECK RB3LYP/6-31G(D,P) FREQ\\hsno-tr-b3lypb2\
\0,1\S\N,1,r1\H,1,r2,2,a1\O,2,r3,1,a2,3,180.,0\\r1=1.91450087\r2=1.347

58672\r3=1.17447752\a1=89.98761649\a2=115.0505165\\Version=x86-Linux-G
98RevA.11.1\State=1-A'\HF=-528.6797901\RMSD=2.313e-10\RMSF=7.973e-05\D
ipole=0.4194913,0.,-0.1146077\PG=CS [SG(H1N1O1S1)]\\@

HSNO (*trans*) B3LYP/6-311G(d,p)

1\1\GINC-CURIE\Freq\RB3LYP\6-311G(d,p)\H1N1O1S1\CRISTINA\15-May-2002\1
\\#N GEOM=ALLCHECK GUESS=TCHECK RB3LYP/6-311G(D,P) FREQ\\hsno-tr-b3lyp
b4\\0,1\S\N,1,r1\H,1,r2,2,a1\O,2,r3,1,a2,3,180.,0\\r1=1.94238368\r2=1.
34680773\r3=1.16043881\a1=89.4151167\a2=115.41891712\\Version=x86-Linu
x-G98RevA.11.1\State=1-A'\HF=-528.7445878\RMSD=3.303e-10\RMSF=1.029e-0
5\Dipole=0.3914815,0.,-0.0411295\PG=CS [SG(H1N1O1S1)]\\@

HSNO (*trans*) B3LYP/6-311+G(d,p)

1\1\GINC-VLAD\Freq\RB3LYP\6-311+G(d,p)\H1N1O1S1\CRISTINA\17-May-2002\1
\\#N GEOM=ALLCHECK GUESS=TCHECK RB3LYP/6-311+G(D,P) FREQ\\hsno-tr-b3ly
pb5\\0,1\S\N,1,r1\H,1,r2,2,a1\O,2,r3,1,a2,3,180.,0\\r1=1.90996309\r2=1
.34743923\r3=1.16576538\a1=89.6409109\a2=115.71010263\\Version=x86-Lin
ux-G98RevA.11.1\State=1-A'\HF=-528.7507571\RMSD=9.331e-09\RMSF=7.038e-
06\Dipole=0.4241687,0.,-0.1797958\PG=CS [SG(H1N1O1S1)]\\@

HSNO (*trans*) B3LYP/6-311G(2d,p)

1\1\GINC-VLAD\Freq\RB3LYP\6-311G(2d,p)\H1N1O1S1\CRISTINA\17-May-2002\1
\\#N GEOM=ALLCHECK GUESS=TCHECK RB3LYP/6-311G(2D,P) FREQ\\hsno-tr-b3ly
pb6\\0,1\S\N,1,r1\H,1,r2,2,a1\O,2,r3,1,a2,3,180.,0\\r1=1.92234701\r2=1
.34210547\r3=1.16281502\a1=89.85071755\a2=115.11948936\\Version=x86-Li
nux-G98RevA.11.1\State=1-A'\HF=-528.751223\RMSD=3.598e-09\RMSF=1.063e-
04\Dipole=0.3573826,0.,-0.0791839\PG=CS [SG(H1N1O1S1)]\\@

HSNO (*trans*) B3LYP/6-311G(df,p)

1\1\GINC-VLAD\Freq\RB3LYP\6-311G(df,p)\H1N1O1S1\CRISTINA\17-May-2002\1
\\#N GEOM=ALLCHECK GUESS=TCHECK RB3LYP/6-311G(DF,P) FREQ\\hsno-tr-b3ly
p7\\0,1\S\N,1,r1\H,1,r2,2,a1\O,2,r3,1,a2,3,180.,0\\r1=1.92551954\r2=1.
34659438\r3=1.16079383\a1=89.71379644\a2=115.45903853\\Version=x86-Lin
ux-G98RevA.11.1\State=1-A'\HF=-528.7493017\RMSD=3.335e-10\RMSF=4.014e-
05\Dipole=0.4076548,0.,-0.0743869\PG=CS [SG(H1N1O1S1)]\\@

HSNO (*trans*) B3LYP/6-311+G(2df,p)

1\1\GINC-CURIE\Freq\RB3LYP\6-311+G(2df,p)\H1N1O1S1\CRISTINA\16-May-200
2\1\\#N GEOM=ALLCHECK GUESS=TCHECK RB3LYP/6-311+G(2DF,P) FREQ\\hsno-tr
-b3lypb8\\0,1\S\N,1,r1\H,1,r2,2,a1\O,2,r3,1,a2,3,180.,0\\r1=1.87402428
\r2=1.34402703\r3=1.16858206\a1=90.30736856\a2=115.54585485\\Version=x
86-Linux-G98RevA.11.1\State=1-A'\HF=-528.7630673\RMSD=3.386e-09\RMSF=1
.001e-04\Dipole=0.4129517,0.,-0.2621395\PG=CS [SG(H1N1O1S1)]\\@

HSNO (*trans*) B3LYP/6-311++G(3df,3pd)

1\1\GINC-CURIE\Freq\RB3LYP\6-311++G(3df,3pd)\H1N1O1S1\CRISTINA\15-May-
2002\1\\#N GEOM=ALLCHECK GUESS=TCHECK RB3LYP/6-311++G(3DF,3PD) FREQ\\h
sno-tr-b3lypb9\\0,1\S\N,1,r1\H,1,r2,2,a1\O,2,r3,1,a2,3,180.,0\\r1=1.86
953405\r2=1.3412278\r3=1.1682494\a1=90.39739953\a2=115.45347056\\Versi
on=x86-Linux-G98RevA.11.1\State=1-A'\HF=-528.7665005\RMSD=3.341e-09\RM
SF=7.550e-05\Dipole=0.3758887,0.,-0.2632467\PG=CS [SG(H1N1O1S1)]\\@

HSNO (*cis*) B3LYP/6-31G(d)

1\1\GINC-N11\Freq\RB3LYP\6-31G(d)\H1N1O1S1\ROOT\09-Nov-2001\1\\#N GEOM

=ALLCHECK GUESS=TCHECK RB3LYP/6-31G(D) FREQ\\hsno-cis-b3lypb1\\0,1\S\N
,1,r1\H,1,r2,2,a1\O,2,r3,1,a2,3,0.,0\\r1=1.90111193\r2=1.35466781\r3=1
.1781682\a1=95.6507555\a2=115.71695486\\Version=IBM-RS6000-G98RevA.7\S
tate=1-A'\HF=-528.6753476\RMSD=8.476e-09\RMSF=3.881e-05\Dipole=0.34493
58,0.,-0.2003567\PG=CS [SG(H1N1O1S1)]\\@

HSNO (*cis*) B3LYP/6-31G(d,p)

1\1\GINC-N12\Freq\RB3LYP\6-31G(d,p)\H1N1O1S1\ROOT\07-Nov-2001\1\\#N GE
OM=ALLCHECK GUESS=TCHECK RB3LYP/6-31G(D,P) FREQ\\hsno-cis-b3lypb2\\0,1
\S\N,1,r1\H,1,r2,2,a1\O,2,r3,1,a2,3,0.,0\\r1=1.90430679\r2=1.3532067\r
3=1.17770997\a1=95.80649226\a2=115.79602733\\Version=IBM-RS6000-G98Rev
A.7\State=1-A'\HF=-528.678354\RMSD=1.675e-10\RMSF=4.774e-05\Dipole=0.3
446522,0.,-0.1930599\ \PG=CS [SG(H1N1O1S1)]\\@

HSNO (*cis*) B3LYP/6-311G(d,p)

1\1\GINC-N05\Freq\RB3LYP\6-311G(d,p)\H1N1O1S1\ROOT\07-Nov-2001\1\\#N G
EOM=ALLCHECK GUESS=TCHECK RB3LYP/6-311G(D,P) FREQ\\hsno-cis-b3lypb4\\0
,1\S\N,1,r1\H,1,r2,2,a1\O,2,r3,1,a2,3,0.,0\\r1=1.92782059\r2=1.3530116
9\r3=1.16422653\a1=95.53947713\a2=116.14718956\\Version=IBM-RS6000-G98
RevA.7\State=1-A'\HF=-528.7430311\RMSD=3.423e-09\RMSF=5.481e-05\Dipole
=0.3459997,0.,-0.1259898\PG=CS [SG(H1N1O1S1)]\\@

HSNO (*cis*) B3LYP/6-311+G(d,p)

1\1\GINC-N12\Freq\RB3LYP\6-311+G(d,p)\H1N1O1S1\ROOT\07-Nov-2001\1\\#N
GEOM=ALLCHECK GUESS=TCHECK RB3LYP/6-311+G(D,P) FREQ\\hsno-cis-b3lypb5\
\0,1\S\N,1,r1\H,1,r2,2,a1\O,2,r3,1,a2,3,0.,0\\r1=1.8944911\r2=1.354389
33\r3=1.16968113\a1=96.05212741\a2=116.67858906\\Version=IBM-RS6000-G9
8RevA.7\State=1-A'\HF=-528.7488065\RMSD=1.594e-09\RMSF=3.930e-05\Dipol
e=0.3359679,0.,-0.2679178\PG=CS [SG(H1N1O1S1)]\\@

HSNO (*cis*) B3LYP/6-311G(2d,p)

1\1\GINC-VLAD\Freq\RB3LYP\6-311G(2d,p)\H1N1O1S1\CRISTINA\02-Jan-2003\1
\\#N GEOM=ALLCHECK GUESS=TCHECK RB3LYP/6-311G(2D,P) FREQ\\hsno-cis-b3l
ypb6\\0,1\S\N,1,r1\H,1,r2,2,a1\O,2,r3,1,a2,3,0.,0\\r1=1.90930585\r2=1.
3481624\r3=1.16570076\a1=95.63381855\a2=116.15822077\\Version=x86-Linu
x-G98RevA.11.1\State=1-A'\HF=-528.7497396\RMSD=2.965e-09\RMSF=1.388e-0
4\Dipole=0.2885835,0.,-0.1504047\DipoleDeriv=0.1426566,0.,0.184925,0.,
-0.090354,0.,-0.1351927,0.,-1.1322705,0.4227015,0.,1.5056654,0.,-0.021
4524,0.,0.4850367,0.,2.1008998,-0.0343748,0.,-0.022994,0.,0.1211792,0.
,-0.100678,0.,0.0102526,-0.5309833,0.,-1.6675964,0.,-0.0093727,0.,-0.2
49166,0.,-0.9788819\Polar=28.1183351,0.,17.7099064,5.2994083,0.,51.313
3965\PG=CS [SG(H1N1O1S1)]\\@

HSNO (*cis*) B3LYP/6-311G(df,p)

1\1\GINC-N11\Freq\RB3LYP\6-311G(df,p)\H1N1O1S1\ROOT\09-Nov-2001\1\\#N
GEOM=ALLCHECK GUESS=TCHECK RB3LYP/6-311G(DF,P) FREQ\\hsno-cis-b3lypb7\
\0,1\S\N,1,r1\H,1,r2,2,a1\O,2,r3,1,a2,3,0.,0\\r1=1.90475792\r2=1.35343
393\r3=1.16531639\a1=96.01498306\a2=116.38997601\\Version=IBM-RS6000-G
98RevA.7\State=1-A'\HF=-528.7478991\RMSD=1.647e-09\RMSF=9.550e-05\Dipo
le=0.3331665,0.,-0.1761857\PG=CS [SG(H1N1O1S1)]\\@

HSNO (*cis*) B3LYP/6-311+G(2df,p)

1\1\GINC-N06\Freq\RB3LYP\6-311+G(2df,p)\H1N1O1S1\ROOT\09-Nov-2001\1\\#
N GEOM=ALLCHECK GUESS=TCHECK RB3LYP/6-311+G(2DF,P) FREQ\\hsno-cis-b3ly

pb8\\0,1\S\N,1,r1\H,1,r2,2,a1\O,2,r3,1,a2,3,0.,0\\r1=1.85671471\r2=1.3
5135021\r3=1.17237571\a1=96.54859416\a2=116.90321612\\Version=IBM-RS60
00-G98RevA.7\State=1-A'\HF=-528.7613943\RMSD=6.624e-09\RMSF=6.763e-05\
Dipole=0.264029,0.,-0.3519797\PG=CS [SG(H1N1O1S1)]\\@

HSNO (*cis*) B3LYP/6-311++G(3df,3pd)

1\1\GINC-KOHN\Freq\RB3LYP\6-311++G(3df,3pd)\H1N1O1S1\CRISTINA\03-Jan-2
003\1\\#N GEOM=ALLCHECK GUESS=TCHECK RB3LYP/6-311++G(3DF,3PD) FREQ\\hs
no-cis-b3lypb9\\0,1\S\N,1,r1\H,1,r2,2,a1\O,2,r3,1,a2,3,0.,0\\r1=1.8523
1402\r2=1.3485862\r3=1.17158071\a1=96.66004037\a2=116.97256859\\Versio
n=x86-Linux-G98RevA.11.1\State=1-A'\HF=-528.7647686\RMSD=1.742e-09\RMS
F=9.088e-05\Dipole=0.2311219,0.,-0.3500253\PG=CS [SG(H1N1O1S1)]\\@

HSNO (*trans*) B3P86/6-31G(d)

1\1\GINC-CURIE\Freq\RB3P86\6-31G(d)\H1N1O1S1\CRISTINA\16-May-2002\1\\#
N GEOM=ALLCHECK GUESS=TCHECK RB3P86/6-31G(D) FREQ\\hsno-tr-b3p86b1\\0,
1\S\N,1,r1\H,1,r2,2,a1\O,2,r3,1,a2,3,180.,0\\r1=1.88061915\r2=1.345076
06\r3=1.17407984\a1=89.89409707\a2=115.13145035\\Version=x86-Linux-G98
RevA.11.1\State=1-A'\HF=-529.2587983\RMSD=2.797e-10\RMSF=8.386e-05\Dip
ole=0.4497566,0.,-0.1826688\PG=CS [SG(H1N1O1S1)]\\@

HSNO (*trans*) B3P86/6-31G(d,p)

1\1\GINC-VLAD\Freq\RB3P86\6-31G(d,p)\H1N1O1S1\CRISTINA\17-May-2002\1\\
#N GEOM=ALLCHECK GUESS=TCHECK RB3P86/6-31G(D,P) FREQ\\hsno-tr-b3p86b2\
\0,1\S\N,1,r1\H,1,r2,2,a1\O,2,r3,1,a2,3,180.,0\\r1=1.88276125\r2=1.344
11666\r3=1.17383951\a1=89.98829818\a2=115.0540331\\Version=x86-Linux-G
98RevA.11.1\State=1-A'\HF=-529.2618548\RMSD=3.185e-10\RMSF=1.112e-04\D
ipole=0.4437784,0.,-0.1787854\PG=CS [SG(H1N1O1S1)]\\@

HSNO (*trans*) B3P86/6-311G(d,p)

1\1\GINC-CURIE\Freq\RB3P86\6-311G(d,p)\H1N1O1S1\CRISTINA\16-May-2002\1
\\#N GEOM=ALLCHECK GUESS=TCHECK RB3P86/6-311G(D,P) FREQ\\hsno-tr-b3p86
b4\\0,1\S\N,1,r1\H,1,r2,2,a1\O,2,r3,1,a2,3,180.,0\\r1=1.90266692\r2=1.
34404162\r3=1.1608014\a1=89.48376632\a2=115.54559701\\Version=x86-Linu
x-G98RevA.11.1\State=1-A'\HF=-529.3238144\RMSD=4.164e-09\RMSF=1.669e-0
4\Dipole=0.4233002,0.,-0.136473\PG=CS [SG(H1N1O1S1)]\\@

HSNO (*trans*) B3P86/6-311+G(d,p)

1\1\GINC-ANGSTROM\Freq\RB3P86\6-311+G(d,p)\H1N1O1S1\CRISTINA\28-May-20
02\1\\#N GEOM=ALLCHECK GUESS=TCHECK RB3P86/6-311+G(D,P) FREQ\\hsno-tr-
b3p86b5\\0,1\S\N,1,r1\H,1,r2,2,a1\O,2,r3,1,a2,3,180.,0\\r1=1.87819951\
r2=1.34525154\r3=1.16514147\a1=89.60525616\a2=115.75968413\\Version=x8
6-Linux-G98RevA.11.1\State=1-A'\HF=-529.3294029\RMSD=2.733e-09\RMSF=1.
480e-04\Dipole=0.4478677,0.,-0.2344226\PG=CS [SG(H1N1O1S1)]\\@

HSNO (*trans*) B3P86/6-311G(2d,p)

1\1\GINC-VLAD\Freq\RB3P86\6-311G(2d,p)\H1N1O1S1\CRISTINA\17-May-2002\1
\\#N GEOM=ALLCHECK GUESS=TCHECK RB3P86/6-311G(2D,P) FREQ\\hsno-tr-b3p8
6b6\\0,1\S\N,1,r1\H,1,r2,2,a1\O,2,r3,1,a2,3,180.,0\\r1=1.88155867\r2=1
.33994936\r3=1.16412976\a1=89.83765291\a2=115.13151909\\Version=x86-Li
nux-G98RevA.11.1\State=1-A'\HF=-529.331043\RMSD=1.771e-09\RMSF=4.798e-
05\Dipole=0.3900253,0.,-0.1774514\PG=CS [SG(H1N1O1S1)]\\@

HSNO (*trans*) B3P86/6-311G(df,p)

1\1\GINC-VLAD\Freq\RB3P86\6-311G(df,p)\H1N1O1S1\CRISTINA\17-May-2002\1

\\#N GEOM=ALLCHECK GUESS=TCHECK RB3P86/6-311G(DF,P) FREQ\\hsno-tr-b3p8
6b7\\0,1\S\N,1,r1\H,1,r2,2,a1\O,2,r3,1,a2,3,180.,0\\r1=1.88594833\r2=1
.34405034\r3=1.16167021\a1=89.757363\a2=115.57590503\\Version=x86-Linu
x-G98RevA.11.1\State=1-A'\HF=-529.3287346\RMSD=1.216e-09\RMSF=5.037e-0
5\Dipole=0.4404731,0.,-0.1711534\PG=CS [SG(H1N1O1S1)]\\@

HSNO (*trans*) B3P86/6-311+G(2df,p)

1\1\GINC-CURIE\Freq\RB3P86\6-311+G(2df,p)\H1N1O1S1\CRISTINA\16-May-200
2\1\\#N GEOM=ALLCHECK GUESS=TCHECK RB3P86/6-311+G(2DF,P) FREQ\\hsno-tr
-b3p86b8\\0,1\S\N,1,r1\H,1,r2,2,a1\O,2,r3,1,a2,3,180.,0\\r1=1.84331851
\r2=1.34208867\r3=1.16828172\a1=90.32795796\a2=115.53768485\\Version=x
86-Linux-G98RevA.11.1\State=1-A'\HF=-529.3424816\RMSD=4.329e-10\RMSF=1
.089e-04\Dipole=0.4355669,0.,-0.3146568\PG=CS [SG(H1N1O1S1)]\\@

HSNO (*trans*) B3P86/6-311++G(3df,3pd)

1\1\GINC-CURIE\Freq\RB3P86\6-311++G(3df,3pd)\H1N1O1S1\CRISTINA\16-May-
2002\1\\#N GEOM=ALLCHECK GUESS=TCHECK RB3P86/6-311++G(3DF,3PD) FREQ\\h
sno-tr-b3p86b9\\0,1\S\N,1,r1\H,1,r2,2,a1\O,2,r3,1,a2,3,180.,0\\r1=1.83
86791\r2=1.33966331\r3=1.16802133\a1=90.38101439\a2=115.49436523\\Vers
ion=x86-Linux-G98RevA.11.1\State=1-A'\HF=-529.3458914\RMSD=5.296e-09\R
MSF=1.413e-05\Dipole=0.3964696,0.,-0.3146657\PG=CS [SG(H1N1O1S1)]\\@

HSNO (*cis*) B3P86/6-31G(d)

1\1\GINC-N11\Freq\RB3P86\6-31G(d)\H1N1O1S1\ROOT\13-Nov-2001\1\\#N GEOM
=ALLCHECK GUESS=TCHECK RB3P86/6-31G(D) FREQ\\hsno-cis-b3p86b1\\0,1\S\N
,1,r1\H,1,r2,2,a1\O,2,r3,1,a2,3,0.,0\\r1=1.86654328\r2=1.35153051\r3=1
.17774297\a1=95.81209899\a2=115.77535197\\Version=IBM-RS6000-G98RevA.7
\State=1-A'\HF=-529.25741\RMSD=4.542e-09\RMSF=7.979e-05\Dipole=0.34632
15,0.,-0.2751678\PG=CS [SG(H1N1O1S1)]\\@

HSNO (*cis*) B3P86/6-31G(d,p)

1\1\GINC-SP\Freq\RB3P86\6-31G(d,p)\H1N1O1S1\ROOT\13-Nov-2001\1\\#N GEO
M=ALLCHECK GUESS=TCHECK RB3P86/6-31G(D,P) FREQ\\hsno-cis-b3p86b2\\0,1\
S\N,1,r1\H,1,r2,2,a1\O,2,r3,1,a2,3,0.,0\\r1=1.86960785\r2=1.35052277\r
3=1.17727572\a1=95.95466302\a2=115.85132724\\Version=IBM-RS6000-G98Rev
A.7\State=1-A'\HF=-529.2603953\RMSD=3.189e-10\RMSF=9.674e-05\Dipole=0.
3452578,0.,-0.2674356\PG=CS [SG(H1N1O1S1)]\\@

HSNO (*cis*) B3P86/6-311G(d,p)

1\1\GINC-SP\Freq\RB3P86\6-311G(d,p)\H1N1O1S1\ROOT\13-Nov-2001\1\\#N GE
OM=ALLCHECK GUESS=TCHECK RB3P86/6-311G(D,P) FREQ\\hsno-cis-b3p86b4\\0,
1\S\N,1,r1\H,1,r2,2,a1\O,2,r3,1,a2,3,0.,0\\r1=1.8844976\r2=1.35102755\
r3=1.16529495\a1=95.73487991\a2=116.21571601\\Version=IBM-RS6000-G98Re
vA.7\State=1-A'\HF=-529.3221932\RMSD=5.576e-10\RMSF=3.077e-05\Dipole=0
.3418239,0.,-0.2354427\PG=CS [SG(H1N1O1S1)]\\@

HSNO (*cis*) B3P86/6-311+G(d,p)

1\1\GINC-N11\Freq\RB3P86\6-311+G(d,p)\H1N1O1S1\ROOT\13-Nov-2001\1\\#N
GEOM=ALLCHECK GUESS=TCHECK RB3P86/6-311+G(D,P) FREQ\\hsno-cis-b3p86b5\
\0,1\S\N,1,r1\H,1,r2,2,a1\O,2,r3,1,a2,3,0.,0\\r1=1.85980186\r2=1.35256
329\r3=1.16942227\a1=96.12109986\a2=116.66266563\\Version=IBM-RS6000-G
98RevA.7\State=1-A'\HF=-529.3274645\RMSD=3.175e-09\RMSF=2.093e-05\Dipo
le=0.3370178,0.,-0.3339852\PG=CS [SG(H1N1O1S1)]\\@

HSNO (*cis*) B3P86/6-311G(2d,p)

1\1\GINC-SP\Freq\RB3P86\6-311G(2d,p)\H1N1O1S1\ROOT\13-Nov-2001\1\\#N G
EOM=ALLCHECK GUESS=TCHECK RB3P86/6-311G(2D,P) FREQ\\hsno-cis-b3p86b6\\
0,1\S\N,1,r1\H,1,r2,2,a1\O,2,r3,1,a2,3,0.,0\\r1=1.86717844\r2=1.346481
15\r3=1.16739804\a1=95.76643275\a2=116.19509177\\Version=IBM-RS6000-G9
8RevA.7\State=1-A'\HF=-529.3295155\RMSD=2.367e-09\RMSF=2.026e-05\Dipol
e=0.2800984,0.,-0.2563683\PG=CS [SG(H1N1O1S1)]\\@

HSNO (*cis*) B3P86/6-311G(df,p)

1\1\GINC-N06\Freq\RB3P86\6-311G(df,p)\H1N1O1S1\ROOT\13-Nov-2001\1\\#N
GEOM=ALLCHECK GUESS=TCHECK RB3P86/6-311G(DF,P) FREQ\\hsno-cis-b3p86b7\
\0,1\S\N,1,r1\H,1,r2,2,a1\O,2,r3,1,a2,3,0.,0\\r1=1.8637659\r2=1.351526
76\r3=1.16669694\a1=96.26312043\a2=116.48337187\\Version=IBM-RS6000-G9
8RevA.7\State=1-A'\HF=-529.3272987\RMSD=2.523e-09\RMSF=2.037e-05\Dipol
e=0.3293029,0.,-0.2815504\PG=CS [SG(H1N1O1S1)]\\@

HSNO (*cis*) B3P86/6-311+G(2df,p)

1\1\GINC-N11\Freq\RB3P86\6-311+G(2df,p)\H1N1O1S1\ROOT\13-Nov-2001\1\\#
N GEOM=ALLCHECK GUESS=TCHECK RB3P86/6-311+G(2DF,P) FREQ\\hsno-cis-b3p8
6b8\\0,1\S\N,1,r1\H,1,r2,2,a1\O,2,r3,1,a2,3,0.,0\\r1=1.82435246\r2=1.3
4986576\r3=1.17252279\a1=96.58843699\a2=116.8914727\\Version=IBM-RS600
0-G98RevA.7\State=1-A'\HF=-529.340845\RMSD=3.310e-09\RMSF=9.509e-06\Di
pole=0.2612776,0.,-0.4123947\PG=CS [SG(H1N1O1S1)]\\@

HSNO (*cis*) B3P86/6-311++G(3df,3pd)

1\1\GINC-SP\Freq\RB3P86\6-311++G(3df,3pd)\H1N1O1S1\ROOT\14-Nov-2001\1\
\#N GEOM=ALLCHECK GUESS=TCHECK RB3P86/6-311++G(3DF,3PD) FREQ\\hsno-cis
-b3p86b9\\0,1\S\N,1,r1\H,1,r2,2,a1\O,2,r3,1,a2,3,0.,0\\r1=1.81997411\r
2=1.34747318\r3=1.17178995\a1=96.68225284\a2=116.97181701\\Version=IBM
-RS6000-G98RevA.7\State=1-A'\HF=-529.3441831\RMSD=3.873e-09\RMSF=5.429
e-05\Dipole=0.2288488,0.,-0.4086414\PG=CS [SG(H1N1O1S1)]\\@

HSNO (*trans*) CBS-QB3

1\1\GINC-POPLE\Mixed\CBS-QB3\CBS-QB3\H1N1O1S1\CRISTINA\22-Jun-2003\0\\
CBS-QB3 OPT\\hsno-tr-cbsqb3\\0,1\S,-0.4688918051,-0.9422295332,0.\N,
0.0092005187,0.9274590638,0.\H,-1.7664337872,-0.600460808,0.\O,1.15053
73797,1.1479899865,0.\\Version=x86-Linux-G98RevA.11.1\State=1-A'\HF/Cb
sB3=-527.3722861\E2(CBS)/CbsB3=-0.6773944\CBS-Int/CbsB3=0.0216996\OIii
/CbsB3=4.704603\MP2/CbsB4=-527.8212797\MP4(SDQ)/CbsB4=-527.8445905\MP4
(SDQ)/6-31+G(d')=-527.803525\QCISD(T)/6-31+G(d')=-527.8244601\CBSQB3=-
528.0846571\FreqCoord=-0.8860770299,-1.7805556361,0.,0.0173864593,1.75
26434962,0.,-3.3380758348,-1.134706394,0.,2.1742003873,2.1693865122,0.
\PG=CS [SG(H1N1O1S1)]\\@

HS$^{\bullet}$ MP2/6-311G(d,p)

1\1\GINC-VLAD\Freq\UMP2-FC\6-311G(d,p)\H1S1(2)\CRISTINA\05-Feb-2002\1\
\#N GEOM=ALLCHECK GUESS=TCHECK UMP2(FC)/6-311G(D,P) FREQ\\HS-radical\\
0,2\H\S,1,r1\\r1=1.33801338\\Version=x86-Linux-G98RevA.11.1\HF=-398.09
28963\MP2=-398.2048236\PUHF=-398.0954163\PMP2-0=-398.206195\S2=0.75782
5\S2-1=0.750684\S2A=0.750014\RMSD=7.656e-10\RMSF=1.715e-05\Dipole=0.,0
.,-0.397149\DipoleDeriv=0.1570704,0.,0.,0.,0.1570703,0.,0.,0.,-0.07055
05,-0.1570704,0.,0.,0.,-0.1570703,0.,0.,0.,0.0705505\Polar=9.1926774,0
.,8.8955098,0.,0.,16.8728086\PG=C*V [C*(H1S1)]\NImag=0\\-0.00001174,0.
,-0.00001174,0.,0.,0.28920555,0.00001174,0.,0.,-0.00001174,0.,0.000011

74,0.,0.,-0.00001174,0.,0.,-0.28920555,0.,0.,0.28920555\\0.,0.,0.00002
970,0.,0.,-0.00002970\\\@

HS• MP2/6-311+G(2df,p)

1\1\GINC-VLAD\Freq\UMP2-FC\6-311+G(2df,p)\H1S1(2)\CRISTINA\05-Feb-2002
\1\\#N GEOM=ALLCHECK GUESS=TCHECK UMP2(FC)/6-311+G(2DF,P) FREQ\\HS-rad
ical\\0,2\H\S,1,r1\\r1=1.34124683\\Version=x86-Linux-G98RevA.11.1\HF=-
398.0986034\MP2=-398.2423742\PUHF=-398.1021648\PMP2-0=-398.2444795\S2=
0.763308\S2-1=0.752406\S2A=0.75004\RMSD=4.671e-10\RMSF=3.929e-05\Dipol
e=0.,0.,-0.3719122\DipoleDeriv=0.1467347,0.,0.,0.,0.1467347,0.,0.,0.,0
.0017033,-0.1467347,0.,0.,0.,-0.1467347,0.,0.,0.,-0.0017033\Polar=16.7
554001,0.,12.8623274,0.,0.,18.5007206\PG=C*V [C*(H1S1)]\NImag=0\\-0.00
002685,0.,-0.00002684,0.,0.,0.27861030,0.00002685,0.,0.,-0.00002685,0.
,0.00002684,0.,0.,-0.00002684,0.,0.,-0.27861030,0.,0.,0.27861030\\0.,0
.,0.00006805,0.,0.,-0.00006805\\\@

HS• MP2/6-311++G(3df,3pd)

1\1\GINC-KOHN\Freq\UMP2-FC\6-311++G(3df,3pd)\H1S1(2)\CRISTINA\07-Jan-2
003\1\\#N GEOM=ALLCHECK GUESS=TCHECK UMP2(FC)/6-311++G(3DF,3PD) FREQ\\
HS-radical\\0,2\H\S,1,r1\\r1=1.3355587\\Version=x86-Linux-G98RevA.11.1
\HF=-398.1003527\MP2=-398.2503152\PUHF=-398.1039483\PMP2-0=-398.252485
8\S2=0.763897\S2-1=0.75286\S2A=0.750045\RMSD=9.932e-10\RMSF=3.125e-05\
Dipole=0.,0.,-0.3020501\DipoleDeriv=0.1196789,0.,0.,0.,0.1196786,0.,0.
,0.,0.0059233,-0.1196789,0.,0.,0.,-0.1196786,0.,0.,0.,-0.0059233\Polar
=21.6654345,0.,17.534649,0.,0.,21.8157847\PG=C*V [C*(H1S1)]\NImag=0\\-
0.00002145,0.,-0.00002141,0.,0.,0.28537037,0.00002145,0.,0.,-0.0000214
5,0.,0.00002141,0.,0.,-0.00002141,0.,0.,-0.28537037,0.,0.,0.28537037\\
0.,0.,0.00005412,0.,0.,-0.00005412\\\@

HS• QCISD/6-311G(d,p)

1\1\GINC-VLAD\Freq\UQCISD-FC\6-311G(d,p)\H1S1(2)\CRISTINA\05-Feb-2002\
1\\#N GEOM=ALLCHECK GUESS=TCHECK UQCISD(FC)/6-311G(D,P) FREQ\\HS-radic
al\\0,2\H\S,1,r1\\r1=1.34309851\\Version=x86-Linux-G98RevA.11.1\HF=-39
8.0928642\MP2=-398.2048107\MP3=-398.2219453\MP4D=-398.2258876\MP4DQ=-3
98.2238825\PUHF=-398.0953853\PMP2-0=-398.206183\PMP3-0=-398.2226188\MP
4SDQ=-398.2245273\QCISD=-398.2252129\S2=0.757832\S2-1=0.750687\S2A=0.7
50014\RMSD=4.954e-10\RMSF=2.540e-06\Dipole=0.,0.,-0.3740982\DipoleDeri
v=0.1473932,0.,0.,0.,0.1473902,0.,0.,0.,-0.0999177,-0.1473932,0.,0.,0.
,-0.1473902,0.,0.,0.,0.0999175\PG=C*V [C*(H1S1)]\NImag=0\\-0.00000154,
0.,-0.00000248,0.,0.,0.27620139,0.00000154,0.,0.,-0.00000154,0.,0.0000
0248,0.,0.,-0.00000248,0.,0.,-0.27620139,0.,0.,0.27620138\\0.,0.,0.000
00440,0.,0.,-0.00000440\\\@

HS• QCISD/6-311+G(2df,p)

1\1\GINC-VLAD\Freq\UQCISD-FC\6-311+G(2df,p)\H1S1(2)\CRISTINA\05-Feb-20
02\1\\#N GEOM=ALLCHECK GUESS=TCHECK UQCISD(FC)/6-311+G(2DF,P) FREQ\\HS
-radical\\0,2\H\S,1,r1\\r1=1.34637764\\Version=x86-Linux-G98RevA.11.1\
HF=-398.0985414\MP2=-398.2423619\MP3=-398.2648264\MP4D=-398.2703687\MP
4DQ=-398.2666063\PUHF=-398.1021036\PMP2-0=-398.2444672\PMP3-0=-398.265
9078\MP4SDQ=-398.2672776\QCISD=-398.2676538\S2=0.763309\S2-1=0.752403\
S2A=0.750041\RMSD=5.255e-10\RMSF=1.045e-05\Dipole=0.,0.,-0.356572\Dipo
leDeriv=0.1401404,0.,0.,0.,0.1401419,0.,0.,0.,-0.0303085,-0.1401404,0.
,0.,0.,-0.1401419,0.,0.,0.,0.0303091\PG=C*V [C*(H1S1)]\NImag=0\\-0.000
00666,0.,-0.00000934,0.,0.,0.26714129,0.00000666,0.,0.,-0.00000666,0.,

0.00000934,0.,0.,-0.00000934,0.,0.,-0.26714129,0.,0.,0.26714130\\0.,0.
,0.00001810,0.,0.,-0.00001810\\\@

HS• QCISD/6-311++G(3df,3pd)

1\1\GINC-KOHN\Freq\UQCISD-FC\6-311++G(3df,3pd)\H1S1(2)\CRISTINA\07-Jan
-2003\1\\#N GEOM=ALLCHECK GUESS=TCHECK UQCISD(FC)/6-311++G(3DF,3PD) FR
EQ\\HS-radical\\0,2\H\S,1,r1\\r1=1.34007696\\Version=x86-Linux-G98RevA
.11.1\HF=-398.1003151\MP2=-398.2503054\MP3=-398.2726492\MP4D=-398.2782
695\MP4DQ=-398.274181\PUHF=-398.1039112\PMP2-0=-398.2524758\PMP3-0=-39
8.2737848\MP4SDQ=-398.2748977\QCISD=-398.2752455\S2=0.763896\S2-1=0.75
2857\S2A=0.750045\RMSD=3.509e-10\RMSF=9.075e-06\Dipole=0.,0.,-0.294443
5\DipoleDeriv=0.1162683,0.,0.,0.,0.1162759,0.,0.,0.,-0.019581,-0.11626
83,0.,0.,0.,-0.1162759,0.,0.,0.,0.0195835\PG=C*V [C*(H1S1)]\NImag=0\\-
0.00000587,0.,-0.00000811,0.,0.,0.27469946,0.00000587,0.,0.,-0.0000058
7,0.,0.00000811,0.,0.,-0.00000811,0.,0.,-0.27469940,0.,0.,0.27469934\\
0.,0.,0.00001572,0.,0.,-0.00001572\\\@

HS• B3LYP/6-311G(d,p)

1\1\GINC-VLAD\Freq\UB3LYP\6-311G(d,p)\H1S1(2)\CRISTINA\24-Jan-2002\1\\
#N GEOM=ALLCHECK GUESS=TCHECK UB3LYP/6-311G(D,P) FREQ\\HS-radical\\0,2
\H\S,1,r1\\r1=1.35321297\\Version=x86-Linux-G98RevA.11.1\HF=-398.77211
5\S2=0.752539\S2-1=0.\S2A=0.750002\RMSD=5.898e-10\RMSF=7.300e-06\Dipol
e=0.,0.,-0.4037617\DipoleDeriv=0.1578472,0.,0.,0.,0.1578821,0.,0.,0.,-
0.0713741,-0.1578472,0.,0.,0.,-0.1578821,0.,0.,0.,0.0713741\Polar=9.55
09954,0.,8.9917136,0.,0.,17.6489785\PG=C*V [C*(H1S1)]\NImag=0\\0.00015
339,0.,0.00013954,0.,0.,0.26194022,-0.00015339,0.,0.,0.00015339,0.,-0.
00013954,0.,0.,0.00013954,0.,0.,-0.26194022,0.,0.,0.26194022\\0.,0.,0.
00001264,0.,0.,-0.00001264\\\@

HS• B3LYP/6-311+G(2df,p)

1\1\GINC-VLAD\Freq\UB3LYP\6-311+G(2df,p)\H1S1(2)\CRISTINA\14-Feb-2002\
1\\#N GEOM=ALLCHECK GUESS=TCHECK UB3LYP/6-311+G(2DF,P) FREQ\\HS-radica
l\\0,2\H\S,1,r1\\r1=1.34879363\\Version=x86-Linux-G98RevA.11.1\HF=-398
.7758418\S2=0.753926\S2-1=0.\S2A=0.750006\RMSD=4.421e-10\RMSF=2.037e-0
5\Dipole=0.,0.,-0.3500201\DipoleDeriv=0.1373444,0.,0.,0.,0.1373256,0.,
0.,0.,-0.0327671,-0.1373444,0.,0.,0.,-0.1373256,0.,0.,0.,0.0327671\Pol
ar=17.9376362,0.,13.2570641,0.,0.,19.1889639\PG=C*V [C*(H1S1)]\NImag=0
\\0.00015179,0.,0.00014893,0.,0.,0.26132979,-0.00015179,0.,0.,0.000151
79,0.,-0.00014893,0.,0.,0.00014893,0.,0.,-0.26132979,0.,0.,0.26132979\
\0.,0.,0.00003529,0.,0.,-0.00003529\\\@

HS• B3LYP/6-311++G(3df,3pd)

1\1\GINC-KOHN\Freq\UB3LYP\6-311++G(3df,3pd)\H1S1(2)\CRISTINA\07-Jan-20
03\1\\#N GEOM=ALLCHECK GUESS=TCHECK UB3LYP/6-311++G(3DF,3PD) FREQ\\HS-
radical\\0,2\H\S,1,r1\\r1=1.34640803\\Version=x86-Linux-G98RevA.11.1\H
F=-398.7776836\S2=0.754\S2-1=0.\S2A=0.750006\RMSD=1.177e-10\RMSF=1.630
e-05\Dipole=0.,0.,-0.2935387\DipoleDeriv=0.1153533,0.,0.,0.,0.115342,0
.,0.,0.,-0.0148701,-0.1153533,0.,0.,0.,-0.115342,0.,0.,0.,0.0148701\Po
lar=22.6220649,0.,18.066855,0.,0.,22.528957\PG=C*V [C*(H1S1)]\NImag=0\
\0.00016744,0.,0.00016581,0.,0.,0.26477444,-0.00016744,0.,0.,0.0001674
4,0.,-0.00016581,0.,0.,0.00016581,0.,0.,-0.26477444,0.,0.,0.26477444\\
0.,0.,0.00002822,0.,0.,-0.00002822\\\@

HS• B3P86/6-311G(d,p)

1\1\GINC-VLAD\Freq\UB3P86\6-311G(d,p)\H1S1(2)\CRISTINA\05-Feb-2002\1\\
#N GEOM=ALLCHECK GUESS=TCHECK UB3P86/6-311G(D,P) FREQ\\HS-radical\\0,2
\H\S,1,r1\\r1=1.35050544\\Version=x86-Linux-G98RevA.11.1\HF=-399.08758
37\S2=0.752702\S2-1=0.\S2A=0.750002\RMSD=2.722e-09\RMSF=3.429e-06\Dipo
le=0.,0.,-0.4178394\DipoleDeriv=0.1637031,0.,0.,0.,0.1636835,0.,0.,0.,
-0.0555762,-0.1637031,0.,0.,0.,-0.1636835,0.,0.,0.,0.0555762\Polar=9.4
175228,0.,8.9748398,0.,0.,17.3874417\PG=C*V [C*(H1S1)]\NImag=0\\0.0001
6751,0.,0.00018731,0.,0.,0.26812404,-0.00016751,0.,0.,0.00016751,0.,-0
.00018731,0.,0.,0.00018731,0.,0.,-0.26812404,0.,0.,0.26812404\\0.,0.,-
0.00000594,0.,0.,0.00000594\\\@

HS• B3P86/6-311+G(2df,p)

1\1\GINC-VLAD\Freq\UB3P86\6-311+G(2df,p)\H1S1(2)\CRISTINA\05-Feb-2002\
1\\#N GEOM=ALLCHECK GUESS=TCHECK UB3P86/6-311+G(2DF,P) FREQ\\HS-radica
l\\0,2\H\S,1,r1\\r1=1.34647795\\Version=x86-Linux-G98RevA.11.1\HF=-399
.0917311\S2=0.7544\S2-1=0.\S2A=0.750007\RMSD=7.550e-10\RMSF=7.512e-06\
Dipole=0.,0.,-0.3603104\DipoleDeriv=0.1414592,0.,0.,0.,0.1414935,0.,0.
,0.,-0.0167038,-0.1414592,0.,0.,0.,-0.1414935,0.,0.,0.,0.0167038\Polar
=17.4656803,0.,13.057507,0.,0.,18.9568726\PG=C*V [C*(H1S1)]\NImag=0\\0
.00018487,0.,0.00021070,0.,0.,0.26731836,-0.00018487,0.,0.,0.00018487,
0.,-0.00021070,0.,0.,0.00021070,0.,0.,-0.26731836,0.,0.,0.26731836\\0.
,0.,0.00001301,0.,0.,-0.00001301\\\@

HS• B3P86/6-311++G(3df,3pd)

1\1\GINC-KOHN\Freq\UB3P86\6-311++G(3df,3pd)\H1S1(2)\CRISTINA\07-Jan-20
03\1\\#N GEOM=ALLCHECK GUESS=TCHECK UB3P86/6-311++G(3DF,3PD) FREQ\\HS-
radical\\0,2\H\S,1,r1\\r1=1.34451978\\Version=x86-Linux-G98RevA.11.1\H
F=-399.0935306\S2=0.754507\S2-1=0.\S2A=0.750007\RMSD=2.486e-09\RMSF=4.
930e-06\Dipole=0.,0.,-0.3012593\DipoleDeriv=0.1189938,0.,0.,0.,0.11853
04,0.,0.,0.,-0.0033197,-0.1189938,0.,0.,0.,-0.1185304,0.,0.,0.,0.00331
97\Polar=22.2242233,0.,17.9823671,0.,0.,22.3825851\PG=C*V [C*(H1S1)]\N
Imag=0\\0.00018997,0.,0.00022497,0.,0.,0.27013243,-0.00018997,0.,0.,0.
00018997,0.,-0.00022497,0.,0.,0.00022497,0.,0.,-0.27013243,0.,0.,0.270
13243\\0.,0.,0.00000854,0.,0.,-0.00000854\\\@

HS• CBS-QB3

1\1\GINC-POPLE\Mixed\CBS-QB3\CBS-QB3\H1S1(2)\CRISTINA\22-Jun-2003\0\\#
CBS-QB3 OPT\\HS-radical CBS-QB3\\0,2\H,0.,0.,-1.2686555409\S,0.,0.,0.
0792909713\\Version=x86-Linux-G98RevA.11.1\HF/CbsB3=-398.1000946\E2(CB
S)/CbsB3=-0.1699191\CBS-Int/CbsB3=0.0081001\OIii/CbsB3=1.5072272\MP2/C
bsB4=-398.1982089\MP4(SDQ)/CbsB4=-398.2211235\MP4(SDQ)/6-31+G(d')=-398
.1834509\QCISD(T)/6-31+G(d')=-398.1864145\CBSQB3=-398.2906431\FreqCoor
d=0.,0.,-2.3974113461,0.,0.,0.1498382091\PG=C*V [C*(H1S1)]\NImag=0\\0.
00015211,0.,0.00014366,0.,0.,0.26282032,-0.00015211,0.,0.,0.00015211,0
.,-0.00014366,0.,0.,0.00014366,0.,0.,-0.26282032,0.,0.,0.26282032\\0.,
0.,0.00005382,0.,0.,-0.00005382\\\@

CH_3SNO (*syn*) MP2/6-31G(d)

1\1\GINC-VLAD\Freq\RMP2-FC\6-31G(d)\C1H3N1O1S1\CRISTINA\24-Jul-2002\1\
\#N GEOM=ALLCHECK GUESS=TCHECK RMP2(FC)/6-31G(D) FREQ\\ch3sno-cis1-mp2
b1\\0,1\S\N,1,r1\C,1,r2,2,a1\H,3,r3,1,a2,2,0.,0\H,3,r4,1,a3,4,d1,0\H,3
,r4,1,a3,4,-d1,0\O,2,r5,1,a4,3,0.,0\\r1=1.81080784\r2=1.79512403\r3=1.
09717877\r4=1.09012661\r5=1.21421868\a1=102.08559749\a2=106.97064056\a

3=110.57587427\a4=116.7806694\d1=118.80649394\\Version=x86-Linux-G98Re
vA.11.1\State=1-A'\HF=-566.3262517\MP2=-566.9378076\RMSD=1.026e-09\RMS
F=8.251e-05\Dipole=0.5847706,0.,-0.5453383\PG=CS [SG(C1H1N1O1S1),X(H2)
]\\@

CH_3SNO (*syn*) MP2/6-311G(d,p)

1\1\GINC-VLAD\Freq\RMP2-FC\6-311G(d,p)\C1H3N1O1S1\CRISTINA\24-Jul-2002
\1\\#N GEOM=ALLCHECK GUESS=TCHECK RMP2(FC)/6-311G(D,P) FREQ\\ch3sno-ci
s1-mp2b2\\0,1\S\N,1,r1\C,1,r2,2,a1\H,3,r3,1,a2,2,0.,0\H,3,r4,1,a3,4,d1
,0\H,3,r4,1,a3,4,-d1,0\O,2,r5,1,a4,3,0.,0\\r1=1.83682362\r2=1.78918951
\r3=1.09834164\r4=1.08971365\r5=1.19135114\a1=101.35668567\a2=106.7536
4096\a3=110.8807652\a4=116.99605006\d1=118.46381169\\Version=x86-Linux
-G98RevA.11.1\State=1-A'\HF=-566.3943439\MP2=-567.0608855\RMSD=1.677e-
09\RMSF=1.014e-04\Dipole=0.5690059,0.,-0.4146638\PG=CS [SG(C1H1N1O1S1)
,X(H2)]\\@

CH_3SNO (*syn*) MP2/6-311+G(d,p)

1\1\GINC-VLAD\Freq\RMP2-FC\6-311+G(d,p)\C1H3N1O1S1\CRISTINA\24-Jul-200
2\1\\#N GEOM=ALLCHECK GUESS=TCHECK RMP2(FC)/6-311+G(D,P) FREQ\\ch3sno-
cis1-mp2b3\\0,1\S\N,1,r1\C,1,r2,2,a1\H,3,r3,1,a2,2,0.,0\H,3,r4,1,a3,4,
d1,0\H,3,r4,1,a3,4,-d1,0\O,2,r5,1,a4,3,0.,0\\r1=1.80575862\r2=1.791452
32\r3=1.09762834\r4=1.09004586\r5=1.19824964\a1=102.12565727\a2=107.46
981512\a3=110.58411234\a4=117.52184674\d1=118.74797115\\Version=x86-Li
nux-G98RevA.11.1\State=1-A'\HF=-566.400168\MP2=-567.0707002\RMSD=1.059
e-09\RMSF=1.358e-04\Dipole=0.5941903,0.,-0.5865713\PG=CS [SG(C1H1N1O1
S1),X(H2)]\\@

CH_3SNO (*syn*) MP2/6-311G(2d,p)

1\1\GINC-POPLE\FOpt\RMP2-FC\6-311G(2d,p)\C1H3N1O1S1\JAMES\27-Dec-2002\
1\\# MP2/6-311G(2D,P) GUESS=READ GEOM=CHECK FOPT=Z-MATRIX TEST\\input
from ch3sno-cis1-mp2b3\\0,1\S\N,1,r1\C,1,r2,2,a1\H,3,r3,1,a2,2,0.,0\H,
3,r4,1,a3,4,d1,0\H,3,r4,1,a3,4,-d1,0\O,2,r5,1,a4,3,0.,0\\r1=1.85762921
\r2=1.79677787\r3=1.09728628\r4=1.08777789\r5=1.19069859\a1=100.858007
78\a2=106.21460489\a3=110.7126519\a4=116.55693585\d1=118.48266203\\Ver
sion=x86-Linux-G98RevA.11.1\State=1-A'\HF=-566.4030292\MP2=-567.115338
9\RMSD=4.957e-09\RMSF=1.932e-05\Dipole=0.5633183,0.,-0.3454213\PG=CS [
SG(C1H1N1O1S1),X(H2)]\\@

CH_3SNO (*syn*) MP2/6-311G(df,p)

1\1\GINC-POPLE\FOpt\RMP2-FC\6-311G(df,p)\C1H3N1O1S1\JAMES\26-Dec-2002\
1\\# MP2/6-311G(DF,P) FOPT=Z-MATRIX TEST\\input from ch3sno-cis1-mp2b3
\\0,1\S\N,1,r1\C,1,r2,2,a1\H,3,r3,1,a2,2,0.,0\H,3,r4,1,a3,4,d1,0\H,3,r
4,1,a3,4,-d1,0\O,2,r5,1,a4,3,0.,0\\r1=1.78295725\r2=1.78290793\r3=1.09
784747\r4=1.08991038\r5=1.19597137\a1=102.44313788\a2=106.48198907\a3=
110.85829974\a4=117.73186345\d1=118.47827633\\Version=x86-Linux-G98Rev
A.11.1\State=1-A'\HF=-566.4043742\MP2=-567.1420862\RMSD=5.169e-09\RMSF
=1.070e-04\Dipole=0.5720075,0.,-0.5757168\PG=CS [SG(C1H1N1O1S1),X(H2)]
\\@

CH_3SNO (*syn*) MP2/6-311+G(2df,p)

1\1\GINC-CURIE\Freq\RMP2-FC\6-311+G(2df,p)\C1H3N1O1S1\CRISTINA\16-Aug-
2002\1\\#N GEOM=ALLCHECK GUESS=TCHECK RMP2(FC)/6-311+G(2DF,P) FREQ\\ch
3sno-cis1-mp2b4\\0,1\S\N,1,r1\C,1,r2,2,a1\H,3,r3,1,a2,2,0.,0\H,3,r4,1,
a3,4,d1,0\H,3,r4,1,a3,4,-d1,0\O,2,r5,1,a4,3,0.,0\\r1=1.77649181\r2=1.7

8959705\r3=1.09645111\r4=1.08854551\r5=1.20229974\a1=102.65209582\a2=1
06.65224791\a3=110.35803155\a4=117.65046485\d1=118.79569626\\Version=x
86-Linux-G98RevA.11.1\State=1-A'\HF=-566.4206045\MP2=-567.1996415\RMSD
=2.184e-09\RMSF=1.498e-04\Dipole=0.57249,0.,-0.6899416\PG=CS [SG(C1H1
N1O1S1), X(H2)]\\@

CH_3SNO (*syn*) MP2/6-311++G(3df,3pd)

1\1\GINC-POPLE\FOpt\RMP2-FC\6-311++G(3df,3pd)\C1H3N1O1S1\CRISTINA\20-J
un-2003\0\\# MP2/6-311++G(3DF,3PD) OPT\\ch3sno-cis1-mp2b6\\0,1\S,0.001
3721739,0.9260715577,0.\N,1.1977228128,-0.3655447852,0.\C,-1.544824144
6,0.0369981232,0.\H,-1.2893379228,-1.0260465983,0.\H,-2.115440306,0.27
43232637,0.8922304254\H,-2.115440306,0.2743232637,-0.8922304254\O,0.79
78936162,-1.500365012,0.\\Version=x86-Linux-G98RevA.11.1\State=1-A'\HF
=-566.425909\MP2=-567.2221033\RMSD=5.025e-09\RMSF=7.823e-05\Dipole=-0.
9010162,0.1534282,0.\PG=CS [SG(C1H1N1O1S1),X(H2)]\\@

CH_3SNO (*syn*) QCISD/6-31G(d)

1\1\GINC-KOHN\Freq\RQCISD-FC\6-31G(d)\C1H3N1O1S1\CRISTINA\29-Jul-2002\
1\\#N GEOM=ALLCHECK GUESS=TCHECK RQCISD(FC)/6-31G(D) FREQ\\ch3sno-cis1
-qcisdb1\\0,1\S\N,1,r1\C,1,r2,2,a1\H,3,r3,1,a2,2,0.,0\H,3,r4,1,a3,4,d1
,0\H,3,r4,1,a3,4,-d1,0\O,2,r5,1,a4,3,0.,0\\r1=1.83416626\r2=1.80534725
\r3=1.09738369\r4=1.09290307\r5=1.20108674\a1=101.80964073\a2=107.4133
8134\a3=110.32624543\a4=116.8979847\d1=119.06009196\\Version=x86-Linux
-G98RevA.11.1\State=1-A'\HF=-566.3273206\MP2=-566.9375722\MP3=-566.950
3805\MP4D=-566.9703395\MP4DQ=-566.9562826\MP4SDQ=-566.9678974\QCISD=-5
66.9700095\RMSD=2.111e-09\RMSF=4.241e-07\Dipole=0.5386554,0.,-0.566389
6\PG=CS [SG(C1H1N1O1S1),X(H2)]\\@

CH_3SNO (*syn*) QCISD/6-311G(d,p)

1\1\GINC-KOHN\Freq\RQCISD-FC\6-311G(d,p)\C1H3N1O1S1\CRISTINA\25-Jul-20
02\1\\#N GEOM=ALLCHECK GUESS=TCHECK RQCISD(FC)/6-311G(D,P) FREQ\\ch3sn
o-cis1-qcisdb2\\0,1\S\N,1,r1\C,1,r2,2,a1\H,3,r3,1,a2,2,0.,0\H,3,r4,1,a
3,4,d1,0\H,3,r4,1,a3,4,-d1,0\O,2,r5,1,a4,3,0.,0\\r1=1.84638124\r2=1.80
086958\r3=1.09688394\r4=1.09148273\r5=1.18316421\a1=101.46582368\a2=10
7.20825504\a3=110.50329278\a4=117.18042483\d1=118.81690795\\Version=x8
6-Linux-G98RevA.11.1\State=1-A'\HF=-566.3952745\MP2=-567.0607363\MP3=-
567.0724729\MP4D=-567.0934591\MP4DQ=-567.0772838\MP4SDQ=-567.0901802\Q
CISD=-567.0916052\RMSD=1.244e-09\RMSF=1.224e-04\Dipole=0.5196673,0.,-0
.4946614\PG=CS [SG(C1H1N1O1S1),X(H2)]\\@

CH_3SNO (*syn*) QCISD/6-311+G(d,p)

1\1\GINC-KOHN\Freq\RQCISD-FC\6-311+G(d,p)\C1H3N1O1S1\CRISTINA\26-Jul-2
002\1\\#N GEOM=ALLCHECK GUESS=TCHECK RQCISD(FC)/6-311+G(D,P) FREQ\\ch3
sno-cis1-qcisdb3\\0,1\S\N,1,r1\C,1,r2,2,a1\H,3,r3,1,a2,2,0.,0\H,3,r4,1
,a3,4,d1,0\H,3,r4,1,a3,4,-d1,0\O,2,r5,1,a4,3,0.,0\\r1=1.82751519\r2=1.
80398021\r3=1.09659992\r4=1.09175401\r5=1.1864979\a1=101.96707042\a2=1
07.83500078\a3=110.22249971\a4=117.56549215\d1=119.07596793\\Version=x
86-Linux-G98RevA.11.1\State=1-A'\HF=-566.4010442\MP2=-567.0704905\MP3=
-567.0818286\MP4D=-567.1030163\MP4DQ=-567.0865809\MP4SDQ=-567.099719\Q
CISD=-567.1012717\RMSD=1.602e-09\RMSF=5.272e-05\Dipole=0.545416,0.,-0.
6033974\PG=CS [SG(C1H1N1O1S1),X(H2)]\\@

CH_3SNO (*syn*) QCISD/6-311G(2d,p)

1\1\GINC-POPLE\FOpt\RQCISD-FC\6-311G(2d,p)\C1H3N1O1S1\JAMES\27-Dec-200

2\1\\# QCISD/6-311G(2D,P) GUESS=READ GEOM=CHECK FOPT=Z-MATRIX TEST\\in
put from ch3sno-cis1-mp2b3\\0,1\S\N,1,r1\C,1,r2,2,a1\H,3,r3,1,a2,2,0.,
0\H,3,r4,1,a3,4,d1,0\H,3,r4,1,a3,4,-d1,0\O,2,r5,1,a4,3,0.,0\\r1=1.8521
92\r2=1.80910356\r3=1.09495945\r4=1.08922211\r5=1.18322507\a1=101.4010
2469\a2=106.70491704\a3=110.31845817\a4=116.99725247\d1=118.85220331\\
Version=x86-Linux-G98RevA.11.1\State=1-A'\HF=-566.4046282\MP2=-567.115
1619\MP3=-567.1257799\MP4D=-567.14802\MP4DQ=-567.1283577\MP4SDQ=-567.1
418154\QCISD=-567.1428841\RMSD=3.872e-09\RMSF=6.234e-05\Dipole=0.51354
64,0.,-0.4687212\PG=CS [SG(C1H1N1O1S1),X(H2)]\\@

CH_3SNO (*syn*) QCISD/6-311G(df,p)

1\1\GINC-POPLE\FOpt\RQCISD-FC\6-311G(df,p)\C1H3N1O1S1\JAMES\27-Dec-200
2\1\\# QCISD/6-311G(DF,P) GEOM=CHECK GUESS=READ FOPT=Z-MATRIX TEST\\in
put from ch3sno-cis1-mp2dfp\\0,1\S\N,1,r1\C,1,r2,2,a1\H,3,r3,1,a2,2,0.
,0\H,3,r4,1,a3,4,d1,0\H,3,r4,1,a3,4,-d1,0\O,2,r5,1,a4,3,0.,0\\r1=1.802
19486\r2=1.79465216\r3=1.09642014\r4=1.09137477\r5=1.18383101\a1=102.2
8187018\a2=107.04465748\a3=110.4534852\a4=117.82558689\d1=118.84736311
\\Version=x86-Linux-G98RevA.11.1\State=1-A'\HF=-566.4055945\MP2=-567.1
418535\MP3=-567.1590552\MP4D=-567.1809748\MP4DQ=-567.1612486\MP4SDQ=-5
67.1735184\QCISD=-567.1742255\RMSD=4.733e-09\RMSF=1.323e-04\Dipole=0.5
317218,0.,-0.5884061\PG=CS [SG(C1H1N1O1S1),X(H2)]\\@

CH_3SNO (*syn*) QCISD/6-311+G(2df,p)

1\1\GINC-KOHN\FOpt\RQCISD-FC\6-311+G(2df,p)\C1H3N1O1S1\CRISTINA\17-Aug
-2002\1\\# QCISD/6-311+G(2DF,P) GEOM=CHECK GUESS=READ FOPT=(READFC,Z-M
ATRIX)\\ch3sno-cis1-qcisdb4\\0,1\S\N,1,r1\C,1,r2,2,a1\H,3,r3,1,a2,2,0.
,0\H,3,r4,1,a3,4,d1,0\H,3,r4,1,a3,4,-d1,0\O,2,r5,1,a4,3,0.,0\\r1=1.799
26171\r2=1.80055559\r3=1.0947965\r4=1.08990981\r5=1.18693664\a1=102.54
245264\a2=107.27805075\a3=110.10902869\a4=117.73995469\d1=119.09147622
\\Version=x86-Linux-G98RevA.11.1\State=1-A'\HF=-566.4220032\MP2=-567.1
993556\MP3=-567.2140905\MP4D=-567.237409\MP4DQ=-567.2141566\MP4SDQ=-56
7.2270797\QCISD=-567.2276244\RMSD=7.688e-09\RMSF=5.637e-05\Dipole=0.53
51551,0.,-0.6641836\PG=CS [SG(C1H1N1O1S1),X(H2)]\\@

CH_3SNO (*syn*) B3LYP/6-31G(d)

1\1\GINC-KOHN\Freq\RB3LYP\6-31G(d)\C1H3N1O1S1\CRISTINA\23-Jul-2002\1\\
#N GEOM=ALLCHECK GUESS=TCHECK RB3LYP/6-31G(D) FREQ\\ch3sno-cis1-b3lypb
1-1\\0,1\S\N,1,r1\C,1,r2,2,a1\H,3,r3,1,a2,2,0.,0\H,3,r4,1,a3,4,d1,0\H,
3,r4,1,a3,4,-d1,0\O,2,r5,1,a4,3,0.,0\\r1=1.86652117\r2=1.81262526\r3=1
.09856821\r4=1.09218243\r5=1.18707379\a1=101.55375898\a2=106.94737669\
a3=110.33053078\a4=116.62887151\d1=118.97452028\\Version=x86-Linux-G98
RevA.11.1\State=1-A'\HF=-567.998431\RMSD=2.239e-09\RMSF=6.777e-05\Dipo
le=0.5641991,0.,-0.5088687\PG=CS [SG(C1H1N1O1S1),X(H2)]\\@

CH_3SNO (*syn*) B3LYP/6-311G(d,p)

1\1\GINC-BOHR\Freq\RB3LYP\6-311G(d,p)\C1H3N1O1S1\CRISTINA\24-Jul-2002\
1\\#N GEOM=ALLCHECK GUESS=TCHECK RB3LYP/6-311G(D,P) FREQ\\ch3sno-cis1-
b3lypb2\\0,1\S\N,1,r1\C,1,r2,2,a1\H,3,r3,1,a2,2,0.,0\H,3,r4,1,a3,4,d1,
0\H,3,r4,1,a3,4,-d1,0\O,2,r5,1,a4,3,0.,0\\r1=1.886851\r2=1.8094092\r3=
1.09653727\r4=1.0892449\r5=1.17424225\a1=101.34558448\a2=106.93417222\
a3=110.30165254\a4=116.83094023\d1=118.86062529\\Version=x86-Linux-G98
RevA.11.1\State=1-A'\HF=-568.0736898\RMSD=6.418e-10\RMSF=5.332e-05\Dip
ole=0.5640512,0.,-0.4736957\PG=CS [SG(C1H1N1O1S1),X(H2)]\\@

CH_3SNO (*syn*) B3LYP/6-311+G(d,p)

1\1\GINC-BOHR\Freq\RB3LYP\6-311+G(d,p)\C1H3N1O1S1\CRISTINA\24-Jul-2002
\1\\#N GEOM=ALLCHECK GUESS=TCHECK RB3LYP/6-311+G(D,P) FREQ\\ch3sno-cis
1-b3lypb3\\0,1\S\N,1,r1\C,1,r2,2,a1\H,3,r3,1,a2,2,0.,0\H,3,r4,1,a3,4,d
1,0\H,3,r4,1,a3,4,-d1,0\O,2,r5,1,a4,3,0.,0\\r1=1.86057933\r2=1.8119540
3\r3=1.09579869\r4=1.08942163\r5=1.17884423\a1=101.9761375\a2=107.4991
5253\a3=110.004166\a4=117.29287582\d1=119.11967476\\Version=x86-Linux-
G98RevA.11.1\State=1-A'\HF=-568.0794918\RMSD=2.488e-09\RMSF=9.537e-05\
Dipole=0.5856775,0.,-0.6067394\PG=CS [SG(C1H1N1O1S1),X(H2)]\\@

CH_3SNO (*syn*) B3LYP/6-311G(2d,p)

1\1\GINC-POPLE\FOpt\RB3LYP\6-311G(2d,p)\C1H3N1O1S1\JAMES\27-Dec-2002\1
\\# B3LYP/6-311G(2D,P) GEOM=CHECK GUESS=READ FOPT=(READFC,Z-MATRIX) FR
EQ=NORAMAN TEST\\input from ch3sno-cis1-mp2b3\\0,1\S\N,1,r1\C,1,r2,2,a
1\H,3,r3,1,a2,2,0.,0\H,3,r4,1,a3,4,d1,0\H,3,r4,1,a3,4,-d1,0\O,2,r5,1,a
4,3,0.,0\\r1=1.86429419\r2=1.80661226\r3=1.09525858\r4=1.08824107\r5=1
.17687819\a1=101.80710598\a2=106.47162221\a3=110.24498378\a4=117.02048
525\d1=118.83167491\\Version=x86-Linux-G98RevA.11.1\State=1-A'\HF=-568
.0814624\RMSD=7.916e-09\RMSF=3.729e-05\Dipole=0.534377,0.,-0.5048684\P
G=CS [SG(C1H1N1O1S1),X(H2)]\\@

CH_3SNO (*syn*) B3LYP/6-311G(df,p)

1\1\GINC-POPLE\FOpt\RB3LYP\6-311G(df,p)\C1H3N1O1S1\JAMES\26-Dec-2002\1
\\# B3LYP/6-311G(DF,P) FOPT=Z-MATRIX FREQ=NORAMAN TEST\\input from ch3
sno-cis1-mp2b3\\0,1\S\N,1,r1\C,1,r2,2,a1\H,3,r3,1,a2,2,0.,0\H,3,r4,1,a
3,4,d1,0\H,3,r4,1,a3,4,-d1,0\O,2,r5,1,a4,3,0.,0\\r1=1.86518568\r2=1.80
807649\r3=1.09619532\r4=1.08905517\r5=1.17541415\a1=101.85520099\a2=10
6.87528621\a3=110.34345986\a4=117.20546548\d1=118.87465431\\Version=x8
6-Linux-G98RevA.11.1\State=1-A'\HF=-568.0799914\RMSD=7.153e-09\RMSF=2.
686e-05\Dipole=0.5567013,0.,-0.5193856\PG=CS [SG(C1H1N1O1S1),X(H2)]\\@

CH_3SNO (*syn*) B3LYP/6-311+G(2df,p)

1\1\GINC-BOHR\Freq\RB3LYP\6-311+G(2df,p)\C1H3N1O1S1\CRISTINA\24-Jul-20
02\1\\#N GEOM=ALLCHECK GUESS=TCHECK RB3LYP/6-311+G(2DF,P) FREQ\\ch3sno
-cis1-b3lypb4\\0,1\S\N,1,r1\C,1,r2,2,a1\H,3,r3,1,a2,2,0.,0\H,3,r4,1,a3
,4,d1,0\H,3,r4,1,a3,4,-d1,0\O,2,r5,1,a4,3,0.,0\\r1=1.82081619\r2=1.803
78075\r3=1.09450941\r4=1.08852669\r5=1.18214297\a1=102.8607049\a2=107.
11283193\a3=110.03767356\a4=117.79195968\d1=119.11071171\\Version=x86-
Linux-G98RevA.11.1\State=1-A'\HF=-568.0948552\RMSD=3.400e-09\RMSF=3.46
8e-05\Dipole=0.5417998,0.,-0.6921119\PG=CS [SG(C1H1N1O1S1),X(H2)]\\@

CH_3SNO (*syn*) B3LYP/6-311++G(3df,3pd)

1\1\GINC-KOHN\Freq\RB3LYP\6-311++G(3df,3pd)\C1H3N1O1S1\CRISTINA\20-Jun
-2003\0\\#N GEOM=ALLCHECK GUESS=TCHECK RB3LYP/6-311++G(3DF,3PD) FREQ\\
ch3sno-cis1-b3lypb6\\0,1\S,0.0005912995,0.9380729953,0.\N,1.217518813,
-0.4066367026,0.\C,-1.5698390027,0.0601712593,0.\H,-1.3398136043,-1.00
83126543,0.\H,-2.1382905245,0.3108695064,0.8917498615\H,-2.1382905245,
0.3108695064,-0.8917498615\O,0.8129170234,-1.5171456152,0.\\Version=x8
6-Linux-G98RevA.11.1\State=1-A'\HF=-568.0993097\RMSD=2.091e-09\RMSF=1.
162e-04\Dipole=-0.8598419,0.1547136,0.\PG=CS [SG(C1H1N1O1S1),X(H2)]\\@

CH_3SNO (*syn*) B3P86/6-31G(d)

1\1\GINC-BOHR\Freq\RB3P86\6-31G(d)\C1H3N1O1S1\CRISTINA\24-Jul-2002\1\\
#N GEOM=ALLCHECK GUESS=TCHECK RB3P86/6-31G(D) FREQ\\ch3sno-cis1-b3p86b

1\\0,1\S\N,1,r1\C,1,r2,2,a1\H,3,r3,1,a2,2,0.,0\H,3,r4,1,a3,4,d1,0\H,3,
r4,1,a3,4,-d1,0\O,2,r5,1,a4,3,0.,0\\r1=1.83534321\r2=1.79614977\r3=1.0
995873\r4=1.09176986\r5=1.18610219\a1=101.47715034\a2=106.62917243\a3=
110.57015347\a4=116.66929582\d1=118.83173542\\Version=x86-Linux-G98Rev
A.11.1\State=1-A'\HF=-568.7281554\RMSD=4.092e-09\RMSF=2.153e-05\Dipole
=0.5664917,0.,-0.5675812\PG=CS [SG(C1H1N1O1S1),X(H2)]\\@

CH_3SNO (*syn*) B3P86/6-311G(d,p)

1\1\GINC-BOHR\Freq\RB3P86\6-311G(d,p)\C1H3N1O1S1\CRISTINA\24-Jul-2002\
1\\#N GEOM=ALLCHECK GUESS=TCHECK RB3P86/6-311G(D,P) FREQ\\ch3sno-cis1-
b3p86b2\\0,1\S\N,1,r1\C,1,r2,2,a1\H,3,r3,1,a2,2,0.,0\H,3,r4,1,a3,4,d1,
0\H,3,r4,1,a3,4,-d1,0\O,2,r5,1,a4,3,0.,0\\r1=1.84828933\r2=1.79244543\
r3=1.09782743\r4=1.08925621\r5=1.17482708\a1=101.35892552\a2=106.58433
662\a3=110.53304716\a4=116.94174406\d1=118.71913007\\Version=x86-Linux
-G98RevA.11.1\State=1-A'\HF=-568.799703\RMSD=1.831e-09\RMSF=6.332e-05\
Dipole=0.5600236,0.,-0.5576873\PG=CS [SG(C1H1N1O1S1),X(H2)]\\@

CH_3SNO (*syn*) B3P86/6-311+G(d,p)

1\1\GINC-BOHR\Freq\RB3P86\6-311+G(d,p)\C1H3N1O1S1\CRISTINA\24-Jul-2002
\1\\#N GEOM=ALLCHECK GUESS=TCHECK RB3P86/6-311+G(D,P) FREQ\\ch3sno-cis
1-b3p86b3\\0,1\S\N,1,r1\C,1,r2,2,a1\H,3,r3,1,a2,2,0.,0\H,3,r4,1,a3,4,d
1,0\H,3,r4,1,a3,4,-d1,0\O,2,r5,1,a4,3,0.,0\\r1=1.82921846\r2=1.7950200
7\r3=1.09713402\r4=1.08943486\r5=1.17788507\a1=101.8168772\a2=107.1362
2587\a3=110.25040235\a4=117.30184509\d1=118.98116439\\Version=x86-Linu
x-G98RevA.11.1\State=1-A'\HF=-568.8049938\RMSD=8.062e-09\RMSF=2.547e-0
5\Dipole=0.5820204,0.,-0.6500088\PG=CS [SG(C1H1N1O1S1),X(H2)]\\@

CH_3SNO (*syn*) B3P86/6-311G(2d,p)

1\1\GINC-POPLE\FOpt\RB3P86\6-311G(2d,p)\C1H3N1O1S1\JAMES\27-Dec-2002\1
\\# B3P86/6-311G(2D,P) GEOM=CHECK GUESS=READ FOPT=(READFC,Z-MATRIX) FR
EQ=NORAMAN TEST\\input from ch3sno-cis1-mp2b3\\0,1\S\N,1,r1\C,1,r2,2,a
1\H,3,r3,1,a2,2,0.,0\H,3,r4,1,a3,4,d1,0\H,3,r4,1,a3,4,-d1,0\O,2,r5,1,a
4,3,0.,0\\r1=1.82691547\r2=1.7895408\r3=1.09670161\r4=1.08830144\r5=1.
17780742\a1=101.78354172\a2=106.01226781\a3=110.44725098\a4=117.112086
74\d1=118.68848381\\Version=x86-Linux-G98RevA.11.1\State=1-A'\HF=-568.
8083045\RMSD=3.205e-09\RMSF=4.360e-05\Dipole=0.5286953,0.,-0.5843099\P
G=CS [SG(C1H1N1O1S1),X(H2)]\\@

CH_3SNO (*syn*) B3P86/6-311G(df,p)

1\1\GINC-POPLE\FOpt\RB3P86\6-311G(df,p)\C1H3N1O1S1\JAMES\27-Dec-2002\1
\\# B3P86/6-311G(DF,P) GEOM=CHECK GUESS=READ FOPT=(READFC,Z-MATRIX) FR
EQ=NORAMAN TEST\\input from ch3sno-cis1-mp2b3\\0,1\S\N,1,r1\C,1,r2,2,a
1\H,3,r3,1,a2,2,0.,0\H,3,r4,1,a3,4,d1,0\H,3,r4,1,a3,4,-d1,0\O,2,r5,1,a
4,3,0.,0\\r1=1.82917675\r2=1.791476\r3=1.09752385\r4=1.08905183\r5=1.1
7598397\a1=101.81786279\a2=106.50976503\a3=110.56737853\a4=117.3129719
6\d1=118.73538803\\Version=x86-Linux-G98RevA.11.1\State=1-A'\HF=-568.8
062012\RMSD=4.295e-09\RMSF=2.390e-05\Dipole=0.5532747,0.,-0.5980327\PG
=CS [SG(C1H1N1O1S1),X(H2)]\\@

CH_3SNO (*syn*) B3P86/6-311+G(2df,p)

1\1\GINC-BOHR\Freq\RB3P86\6-311+G(2df,p)\C1H3N1O1S1\CRISTINA\25-Jul-20
02\1\\#N GEOM=ALLCHECK GUESS=TCHECK RB3P86/6-311+G(2DF,P) FREQ\\ch3sno
-cis1-b3p86b4\\0,1\S\N,1,r1\C,1,r2,2,a1\H,3,r3,1,a2,2,0.,0\H,3,r4,1,a3
,4,d1,0\H,3,r4,1,a3,4,-d1,0\O,2,r5,1,a4,3,0.,0\\r1=1.79277362\r2=1.786

95299\r3=1.09602061\r4=1.08858851\r5=1.18155804\a1=102.62351769\a2=106
.60521062\a3=110.27723872\a4=117.7715407\d1=118.94702587\\Version=x86-
Linux-G98RevA.11.1\State=1-A'\HF=-568.8212483\RMSD=2.493e-09\RMSF=3.55
0e-05\Dipole=0.5374785,0.,-0.7280654\PG=CS [SG(C1H1N1O1S1),X(H2)]\\@

CH_3SNO (*syn*) B3P86/6-311++G(3df,3pd)

1\1\GINC-KOHN\Freq\RB3P86\6-311++G(3df,3pd)\C1H3N1O1S1\CRISTINA\20-Jun
-2003\0\\#N GEOM=ALLCHECK GUESS=TCHECK RB3P86/6-311++G(3DF,3PD) FREQ\\
ch3sno-cis1-b3p86b6\\0,1\S,0.00059463,0.9306091906,0.\N,1.2030135338,-
0.3908969483,0.\C,-1.5491453955,0.0492700644,0.\H,-1.3011255397,-1.016
9992518,0.\H,-2.1215310018,0.2907965193,0.8920487544\H,-2.1215310018,0
.2907965193,-0.8920487544\O,0.8010563875,-1.501710323,0.\\Version=x86-
Linux-G98RevA.11.1\State=1-A'\HF=-568.8255926\RMSD=1.475e-09\RMSF=9.38
0e-05\Dipole=-0.8790929,0.1768271,0.\PG=CS [SG(C1H1N1O1S1),X(H2)]\\@

$CH_3S^\bullet$ MP2/6-311G(d,p)

1\1\GINC-VLAD\Freq\UMP2-FC\6-311G(d,p)\C1H3S1(2)\CRISTINA\13-Mar-2002\
1\\#N GEOM=ALLCHECK GUESS=TCHECK UMP2(FC)/6-311G(D,P) FREQ\\ch3s-radic
al\\0,2\S\C,1,r1\H,2,r3,1,a2\H,2,r2,1,a1,3,d1,0\H,2,r2,1,a1,3,-d1,0\\r
1=1.79473349\r2=1.09067624\r3=1.09587165\a1=111.89400137\a2=106.741641
72\d1=117.63550565\\Version=x86-Linux-G98RevA.11.1\State=2-A'\HF=-437.
1352406\MP2=-437.397613\PUHF=-437.1379041\PMP2-0=-437.3990898\S2=0.758
709\S2-1=0.750933\S2A=0.750028\RMSD=7.454e-10\RMSF=8.335e-05\Dipole=0.
0286769,0.,0.638728\ PG=CS [SG(C1H1S1),X(H2)]\\@

$CH_3S^\bullet$ MP2/6-311+G(2df,p)

1\1\GINC-VLAD\Freq\UMP2-FC\6-311+G(2df,p)\C1H3S1(2)\CRISTINA\13-Mar-20
02\1\\#N GEOM=ALLCHECK GUESS=TCHECK UMP2(FC)/6-311+G(2DF,P) FREQ\\ch3s
-radical\\0,2\S\C,1,r1\H,2,r3,1,a2\H,2,r2,1,a1,3,d1,0\H,2,r2,1,a1,3,-d
1,0\\r1=1.79385504\r2=1.08913523\r3=1.094703\a1=111.61485158\a2=106.50
683331\d1=117.71471403\\Version=x86-Linux-G98RevA.11.1\State=2-A'\HF=-
437.1442143\MP2=-437.4571457\PUHF=-437.1478823\PMP2-0=-437.459325\S2=0
.764012\S2-1=0.752607\S2A=0.750062\RMSD=7.930e-10\RMSF=9.758e-05\Dipol
e=0.0262348,0.,0.6523781\ PG=CS [SG(C1H1S1),X(H2)]\\@

$CH_3S^\bullet$ MP2/6-311++G(3df,3pd)

1\1\GINC-KOHN\FOpt\UMP2-FC\6-311++G(3df,3pd)\C1H3S1(2)\CRISTINA\21-Jun
-2003\0\\# MP2/6-311++G(3DF,3PD) OPT\\ch3s-rad-mp2b6\\0,2\S,0.00413666
63,-0.6879783439,0.\C,0.0046020127,1.1004933111,0.\H,-1.0427337907,1.4
078610522,0.\H,0.4744675273,1.498416292,0.8945836442\H,0.4744675273,1.
498416292,-0.8945836442\\Version=x86-Linux-G98RevA.11.1\State=2-A'\HF=
-437.1467187\MP2=-437.4719084\PUHF=-437.1504426\PMP2-0=-437.474169\S2=
0.764762\S2-1=0.753128\S2A=0.75007\RMSD=7.751e-09\RMSF=8.204e-05\Dipol
e=-0.0227025,0.6456866,0.\PG=CS [SG(C1H1S1),X(H2)]\\@

$CH_3S^\bullet$ QCISD/6-311G(d,p)

1\1\GINC-VLAD\Freq\UQCISD-FC\6-311G(d,p)\C1H3S1(2)\CRISTINA\13-Mar-200
2\1\\#N GEOM=ALLCHECK GUESS=TCHECK UQCISD(FC)/6-311G(D,P) FREQ\\ch3s-r
adical\\0,2\S\C,1,r1\H,2,r3,1,a2\H,2,r2,1,a1,3,d1,0\H,2,r2,1,a1,3,-d1,
0\\r1=1.80394178\r2=1.09265166\r3=1.09741941\a1=111.68451309\a2=106.90
295421\d1=117.81640817\\Version=x86-Linux-G98RevA.11.1\State=2-A'\HF=-
437.1352238\MP2=-437.3975736\MP3=-437.4252766\MP4D=-437.4327763\MP4DQ=
-437.4276858\PUHF=-437.1378862\PMP2-0=-437.3990506\PMP3-0=-437.4260203
\MP4SDQ=-437.4296044\QCISD=-437.4305668\S2=0.758711\S2-1=0.750939\S2A=

0.750029\RMSD=7.029e-10\RMSF=9.977e-05\Dipole=0.0257165,0.,0.6262192\
PG=CS [SG(C1H1S1),X(H2)]\\@

$CH_3S^\bullet$ QCISD/6-311+G(2df,p)

1\1\GINC-VLAD\Freq\UQCISD-FC\6-311+G(2df,p)\C1H3S1(2)\CRISTINA\22-Mar-
2002\1\\#N GEOM=ALLCHECK GUESS=TCHECK UQCISD(FC)/6-311+G(2DF,P) FREQ\\
ch3s-radical\\0,2\S\C,1,r1\H,2,r3,1,a2\H,2,r2,1,a1,3,d1,0\H,2,r2,1,a1,
3,-d1,0\\r1=1.8025633\r2=1.09074512\r3=1.09573797\a1=111.4431955\a2=10
6.63753551\d1=117.89020878\\Version=x86-Linux-G98RevA.11.1\State=2-A'\
HF=-437.1441884\MP2=-437.4571142\MP3=-437.4894203\MP4D=-437.4985478\MP
4DQ=-437.4906262\PUHF=-437.147855\PMP2-0=-437.4592916\PMP3-0=-437.4905
476\MP4SDQ=-437.4928449\QCISD=-437.4933186\S2=0.763996\S2-1=0.752597\S
2A=0.750062\RMSD=1.282e-09\RMSF=1.316e-07\Dipole=0.0238309,0.,0.644251
6\ PG=CS [SG(C1H1S1),X(H2)]\\@

$CH_3S^\bullet$ QCISD/6-311++G(3df,3pd)

1\1\GINC-KOHN\FOpt\UQCISD-FC\6-311++G(3df,3pd)\C1H3S1(2)\CRISTINA\26-J
un-2003\0\\# QCISD/6-311++G(3DF,3PD) OPT\\ch3s-rad-qcisdb6\\0,2\S,0.00
49402235,-0.6904437269,0.\C,0.0028173459,1.1044168021,0.\H,-1.04519812
82,1.4146821696,0.\H,0.4746252381,1.5029583239,0.8952583429\H,0.474625
2381,1.5029583239,-0.8952583429\\Version=x86-Linux-G98RevA.11.1\State=
2-A'\HF=-437.14671\MP2=-437.4718842\MP3=-437.5033422\MP4D=-437.5125785
\MP4DQ=-437.5041057\PUHF=-437.1504329\PMP2-0=-437.4741435\PMP3-0=-437.
504533\MP4SDQ=-437.5062703\QCISD=-437.5067551\S2=0.764749\S2-1=0.75312
\S2A=0.75007\RMSD=3.613e-09\RMSF=2.201e-04\Dipole=-0.0221391,0.6419601
,0.\PG=CS [SG(C1H1S1),X(H2)]\\@

$CH_3S^\bullet$ B3LYP/6-311G(d,p)

1\1\GINC-KOHN\Freq\UB3LYP\6-311G(d,p)\C1H3S1(2)\CRISTINA\14-Aug-2002\1
\\#N GEOM=ALLCHECK GUESS=TCHECK UB3LYP/6-311G(D,P) FREQ\\ch3s-radical\
\0,2\S\C,1,r1\H,2,r3,1,a2\H,2,r2,1,a1,3,d1,0\H,2,r2,1,a1,3,-d1,0\\r1=1
.80925244\r2=1.0905024\r3=1.09659113\a1=111.61399478\a2=106.53316645\d
1=117.53568459\\Version=x86-Linux-G98RevA.11.1\State=2-A'\HF=-438.0994
139\S2=0.752655\S2-1=0.\S2A=0.750004\RMSD=2.872e-09\RMSF=5.711e-05\Dip
ole=0.0342412,0.,0.7067245\ PG=CS [SG(C1H1S1),X(H2)]\\@

$CH_3S^\bullet$ B3LYP/6-311+G(2df,p)

1\1\GINC-VLAD\Freq\UB3LYP\6-311+G(2df,p)\C1H3S1(2)\CRISTINA\20-Mar-200
2\1\\#N GEOM=ALLCHECK GUESS=TCHECK UB3LYP/6-311+G(2DF,P) FREQ\\ch3s-ra
dical\\0,2\S\C,1,r1\H,2,r3,1,a2\H,2,r2,1,a1,3,d1,0\H,2,r2,1,a1,3,-d1,0
\\r1=1.80136556\r2=1.08974416\r3=1.09565656\a1=111.62560423\a2=106.435
5873\d1=117.57606965\\Version=x86-Linux-G98RevA.11.1\State=2-A'\HF=-43
8.1059025\S2=0.753951\S2-1=0.\S2A=0.750007\RMSD=1.465e-09\RMSF=4.719e-
07\Dipole=0.0296674,0.,0.6805717\ PG=CS [SG(C1H1S1),X(H2)]\\@

$CH_3S^\bullet$ B3LYP/6-311++G(3df,3pd)

1\1\GINC-KOHN\Freq\UB3LYP\6-311++G(3df,3pd)\C1H3S1(2)\CRISTINA\21-Jun-
2003\0\\#N GEOM=ALLCHECK GUESS=TCHECK UB3LYP/6-311++G(3DF,3PD) FREQ\\c
h3s-rad-b3lypb6\\0,2\S,0.0044617792,-0.6918912436,0.\C,0.0046673852,1.
1066183419,0.\H,-1.0447180093,1.4158618509,0.\H,0.4726626155,1.5073439
974,0.8967816065\H,0.4726626155,1.5073439974,-0.8967816065\\Version=x8
6-Linux-G98RevA.11.1\State=2-A'\HF=-438.1084727\S2=0.754063\S2-1=0.\S2
A=0.750008\RMSD=9.203e-10\RMSF=1.164e-04\Dipole=-0.0274846,0.6724261,0
.\ PG=CS [SG(C1H1S1),X(H2)]\\@

$CH_3S^\bullet$ B3P86/6-311G(d,p)

1\1\GINC-VLAD\Freq\UB3P86\6-311G(d,p)\C1H3S1(2)\CRISTINA\19-Mar-2002\1\\#N GEOM=ALLCHECK GUESS=TCHECK UB3P86/6-311G(D,P) FREQ\\ch3s-radical\\0,2\S\C,1,r1\H,2,r3,1,a2\H,2,r2,1,a1,3,d1,0\H,2,r2,1,a1,3,-d1,0\\r1=1.79388792\r2=1.09068332\r3=1.0966333\a1=111.85102775\a2=106.50044686\d1=117.38883836\\Version=x86-Linux-G98RevA.11.1\State=2-A'\HF=-438.5608172\S2=0.752761\S2-1=0.\S2A=0.750003\RMSD=6.165e-10\RMSF=3.916e-07\Dipole=0.03859,0.,0.7133672\ PG=CS [SG(C1H1S1),X(H2)]\\@

$CH_3S^\bullet$ B3P86/6-311+G(2df,p)

1\1\GINC-VLAD\Freq\UB3P86\6-311+G(2df,p)\C1H3S1(2)\CRISTINA\13-Mar-2002\1\\#N GEOM=ALLCHECK GUESS=TCHECK UB3P86/6-311+G(2DF,P) FREQ\\ch3s-radical\\0,2\S\C,1,r1\H,2,r3,1,a2\H,2,r2,1,a1,3,d1,0\H,2,r2,1,a1,3,-d1,0\\r1=1.78564607\r2=1.0899554\r3=1.09609901\a1=111.85749857\a2=106.46433505\d1=117.39994481\\Version=x86-Linux-G98RevA.11.1\State=2-A'\HF=-438.5677953\S2=0.754326\S2-1=0.\S2A=0.750008\RMSD=1.412e-09\RMSF=1.227e-04\Dipole=0.0333984,0.,0.6877774\ PG=CS [SG(C1H1S1),X(H2)]\\@

$CH_3S^\bullet$ B3P86/6-311++G(3df,3pd)

1\1\GINC-KOHN\Freq\UB3P86\6-311++G(3df,3pd)\C1H3S1(2)\CRISTINA\21-Jun-2003\0\\#N GEOM=ALLCHECK GUESS=TCHECK UB3P86/6-311++G(3DF,3PD) FREQ\\ch3s-rad-b3p86b6\\0,2\S,0.0045639922,-0.6867250306,0.\C,0.0052703889,1.0965594829,0.\H,-1.0446683421,1.405508091,0.\H,0.4700110671,1.5013677508,0.8971305833\H,0.4700110671,1.5013677508,-0.8971305833\\Version=x86-Linux-G98RevA.11.1\State=2-A'\HF=-438.5702115\S2=0.75448\S2-1=0.\S2A=0.750009\RMSD=1.322e-09\RMSF=6.317e-05\Dipole=-0.0306121,0.6804595,0.\PG=CS [SG(C1H1S1),X(H2)]\\@

CH_2CHSNO (*syn*) MP2/6-311G(d,p)

1\1\GINC-ANGSTROM\Freq\RMP2-FC\6-311G(d,p)\C2H3N1O1S1\CRISTINA\25-Apr-2002\1\\#N GEOM=ALLCHECK GUESS=TCHECK RMP2(FC)/6-311G(D,P) FREQ\\c2h3sno-cis-mp2b3\\0,1\O\N,1,r1\S,2,r2,1,a1\C,3,r3,2,a2,1,0.,0\C,4,r4,3,a3,2,180.,0\H,4,r5,3,a4,2,0.,0\H,5,r6,4,a5,3,180.,0\H,5,r7,4,a6,3,0.,0\\r1=1.18350091\r2=1.88324392\r3=1.74145207\r4=1.34189573\r5=1.09042359\r6=1.08443557\r7=1.08455432\a1=116.74629183\a2=100.31483219\a3=125.35891584\a4=113.27943654\a5=119.69499684\a6=122.43432406\\Version=x86-Linux-G98RevA.11.1\State=1-A'\HF=-604.2399129\MP2=-605.0331341\RMSD=9.720e-10\RMSF=3.157e-06\Dipole=0.3615151,0.,-0.2674758\PG=CS [SG(C2H3N1O1S1)]\\@

CH_2CHSNO (*syn*) MP2/6-311G(df,p)

1\1\GINC-POPLE\FOpt\RMP2-FC\6-311G(df,p)\C2H3N1O1S1\JAMES\28-Dec-2002\1\\# MP2/6-311G(DF,P) FOPT=(Z-MATRIX) TEST\\c2h3sno-cis\\0,1\O\N,1,r1\S,2,r2,1,a1\C,3,r3,2,a2,1,0.,0\C,4,r4,3,a3,2,180.,0\H,4,r5,3,a4,2,0.,0\H,5,r6,4,a5,3,180.,0\H,5,r7,4,a6,3,0.,0\\r1=1.19364586\r2=1.8002412\r3=1.73767244\r4=1.33677221\r5=1.08936698\r6=1.08443861\r7=1.08476722\a1=117.60597539\a2=102.21838439\a3=124.65560445\a4=113.29043651\a5=119.71528258\a6=122.44206057\\Version=x86-Linux-G98RevA.11.1\State=1-A'\HF=-604.2536833\MP2=-605.1281898\RMSD=8.290e-09\RMSF=5.733e-05\Dipole=0.6410454,0.,-0.1465412\PG=CS [SG(C2H3N1O1S1)]\\@

CH_2CHSNO (*syn*) MP2/6-311+G(2df,p)

1\1\GINC-CURIE\Freq\RMP2-FC\6-311+G(2df,p)\C2H3N1O1S1\CRISTINA\03-May-

2002\1\\#N GEOM=ALLCHECK GUESS=TCHECK RMP2(FC)/6-311+G(2DF,P) FREQ\\c2
h3sno-cis-mp2b2\\0,1\O\N,1,r1\S,2,r2,1,a1\C,3,r3,2,a2,1,0.,0\C,4,r4,3,
a3,2,180.,0\H,4,r5,3,a4,2,0.,0\H,5,r6,4,a5,3,180.,0\H,5,r7,4,a6,3,0.,0
\\r1=1.19730024\r2=1.80331235\r3=1.73873984\r4=1.33644019\r5=1.0885668
6\r6=1.08316249\r7=1.08332275\a1=117.24317723\a2=101.93768118\a3=124.2
2410992\a4=113.71512314\a5=119.74597565\a6=122.53480119\\Version=x86-L
inux-G98RevA.11.1\State=1-A'\HF=-604.2724991\MP2=-605.1938134\RMSD=1.2
86e-09\RMSF=1.246e-04\Dipole=0.7135603,0.,-0.1185584\PG=CS
[SG(C2H3N1O1S1)]
\\@

CH_2CHSNO (*syn*) QCISD/6-311G(d,p)

1\1\GINC-ANGSTROM\FOpt\RQCISD-FC\6-311G(d,p)\C2H3N1O1S1\CRISTINA\23-Ma
y-2002\1\\# QCISD/6-311G(D,P) GEOM=CHECK GUESS=READ FOPT=(READFC,Z-MAT
RIX)\\c2h3sno-cis-qcisdb3-1\\0,1\O\N,1,r1\S,2,r2,1,a1\C,3,r3,2,a2,1,0.
,0\C,4,r4,3,a3,2,180.,0\H,4,r5,3,a4,2,0.,0\H,5,r6,4,a5,3,180.,0\H,5,r7
,4,a6,3,0.,0\\r1=1.17994644\r2=1.86597052\r3=1.75735221\r4=1.3399038\r
5=1.08854707\r6=1.086054\r7=1.08645871\a1=117.08575896\a2=100.88290002
\a3=124.4824147\a4=113.49278758\a5=119.96129772\a6=122.59248579\\Versi
on=x86-Linux-G98RevA.11.1\State=1-A'\HF=-604.2417584\MP2=-605.0329486\
MP3=-605.0467593\MP4D=-605.0716276\MP4DQ=-605.0510488\MP4SDQ=-605.0660
144\QCISD=-605.0677567\RMSD=6.985e-09\RMSF=5.501e-06\Dipole=0.5143312,
0.,-0.157001\PG=CS [SG(C2H3N1O1S1)]\\@

CH_2CHSNO (*syn*) QCISD/6-311G(df,p)

1\1\GINC-POPLE\FOpt\RQCISD-FC\6-311G(df,p)\C2H3N1O1S1\JAMES\01-Jan-200
3\1\\# QCISD/6-311G(DF,P) FOPT=(Z-MATRIX) MAXDISK=5GB TEST\\c2h3sno-ci
s\\0,1\O\N,1,r1\S,2,r2,1,a1\C,3,r3,2,a2,1,0.,0\C,4,r4,3,a3,2,180.,0\H,
4,r5,3,a4,2,0.,0\H,5,r6,4,a5,3,180.,0\H,5,r7,4,a6,3,0.,0\\r1=1.1813134
\r2=1.81603756\r3=1.75079076\r4=1.33452285\r5=1.08823906\r6=1.08571704
\r7=1.0862668\a1=117.68593211\a2=101.92378301\a3=124.34961836\a4=113.4
8648191\a5=119.96278656\a6=122.59634431\\Version=x86-Linux-G98RevA.11.
1\State=1-A'\HF=-604.2550249\MP2=-605.1279502\MP3=-605.1475008\MP4D=-6
05.1733359\MP4DQ=-605.1485575\MP4SDQ=-605.1627618\QCISD=-605.163685\RM
SD=9.739e-09\RMSF=1.293e-04\Dipole=0.6353608,0.,-0.1138972\PG=CS [SG(C
2H3N1O1S1)]\\@

CH_2CHSNO (*syn*) B3LYP/6-31G(d)

1\1\GINC-ANGSTROM\Freq\RB3LYP\6-31G(d)\C2H3N1O1S1\CRISTINA\19-Jun-2003
\0\\#N GEOM=ALLCHECK GUESS=TCHECK RB3LYP/6-31G(D) FREQ\\c2h3sno-cis-b3
lypb6\\0,1\O,-1.768373077,-1.0197586912,0.\N,-1.7294022044,0.163218488
4,0.\S,-0.0076866544,0.9483529518,0.\C,1.0083826252,-0.4836966533,0.\C
,2.344656285,-0.4778375216,0.\H,0.4326563815,-1.4101151949,0.\H,2.8938
756056,-1.4151340512,0.\H,2.9310210678,0.4363471784,0.\\Version=x86-Li
nux-G98RevA.11.1\State=1-A'\HF=-606.0745964\RMSD=6.718e-10\RMSF=7.703e
-05\Dipole=0.5729037,-0.2151763,0.\PG=CS [SG(C2H3N1O1S1)]\\@

CH_2CHSNO (*syn*) B3LYP/6-31+G(d)

1\1\GINC-KOHN\Freq\RB3LYP\6-31+G(d)\C2H3N1O1S1\CRISTINA\21-Jun-2003\0\
\#N GEOM=ALLCHECK GUESS=TCHECK RB3LYP/6-31+G(D) FREQ\\c2h3sno-cis-b3ly
pb7\\0,1\O,-1.7821265776,-1.0076902565,0.\N,-1.7213307124,0.1772730229
,0.\S,-0.010013895,0.9375543022,0.\C,1.01196799,-0.4907224029,0.\C,2.3
513817952,-0.4743560816,0.\H,0.4491380985,-1.4251010828,0.\H,2.9057335

488,-1.4090532445,0.\H,2.9315795685,0.4443672908,0.\\Version=x86-Linux
-G98RevA.11.1\State=1-A'\HF=-606.0863521\RMSD=1.760e-09\RMSF=2.594e-05
\Dipole=0.7054039,-0.1669114,0.\PG=CS [SG(C2H3N1O1S1)]\\@

CH_2CHSNO (*syn*) B3LYP/6-311G(d,p)

1\1\GINC-VLAD\Freq\RB3LYP\6-311G(d,p)\C2H3N1O1S1\CRISTINA\24-Apr-2002\
1\\#N GEOM=ALLCHECK GUESS=TCHECK RB3LYP/6-311G(D,P) FREQ\\c2h3sno-cis-
b3lypb1-bis test\\0,1\O\N,1,r1\S,2,r2,1,a1\C,3,r3,2,a2,1,0.,0\C,4,r4,3
,a3,2,180.,0\H,4,r5,3,a4,2,0.,0\H,5,r6,4,a5,3,180.,0\H,5,r7,4,a6,3,0.,
0\\r1=1.1693912\r2=1.92031155\r3=1.75299239\r4=1.33242913\r5=1.0887444
7\r6=1.08388186\r7=1.08345908\a1=116.61935541\a2=100.48348419\a3=125.4
769037\a4=112.63067713\a5=119.99210608\a6=122.84906805\\Version=x86-Li
nux-G98RevA.11.1\State=1-A'\HF=-606.1601893\RMSD=4.206e-09\RMSF=1.015e
-04\Dipole=0.4962403,0.,-0.2059169\PG=CS [SG(C2H3N1O1S1)]\\@

CH_2CHSNO (*syn*) B3LYP/6-311+G(2df,p)

1\1\GINC-VLAD\Freq\RB3LYP\6-311+G(2df,p)\C2H3N1O1S1\CRISTINA\25-Apr-20
02\1\\#N GEOM=ALLCHECK GUESS=TCHECK RB3LYP/6-311+G(2DF,P) FREQ\\c2h3sn
o-cis-b3lypb2\\0,1\O\N,1,r1\S,2,r2,1,a1\C,3,r3,2,a2,1,0.,0\C,4,r4,3,a3
,2,180.,0\H,4,r5,3,a4,2,0.,0\H,5,r6,4,a5,3,180.,0\H,5,r7,4,a6,3,0.,0\\
r1=1.17624307\r2=1.85652797\r3=1.74427789\r4=1.33014516\r5=1.08752999\
r6=1.08309934\r7=1.08288363\a1=117.35917389\a2=101.82690002\a3=125.116
60121\a4=113.12179997\a5=120.10308885\a6=122.87274843\\Version=x86-Lin
ux-G98RevA.11.1\State=1-A'\HF=-606.1854074\RMSD=9.342e-09\RMSF=1.267e-
04\Dipole=0.68573,0.,-0.0953052\PG=CS [SG(C2H3N1O1S1)]\\@

CH_2CHSNO (*syn*) B3P86/6-311G(d,p)

1\1\GINC-KOHN\Freq\RB3P86\6-311G(d,p)\C2H3N1O1S1\CRISTINA\03-Jan-2003\
1\\#N GEOM=ALLCHECK GUESS=TCHECK RB3P86/6-311G(D,P) FREQ\\c2h3sno-cis-
b3p86b3\\0,1\O\N,1,r1\S,2,r2,1,a1\C,3,r3,2,a2,1,0.,0\C,4,r4,3,a3,2,180
.,0\H,4,r5,3,a4,2,0.,0\H,5,r6,4,a5,3,180.,0\H,5,r7,4,a6,3,0.,0\\r1=1.1
6985441\r2=1.88004127\r3=1.73989542\r4=1.33080049\r5=1.08998343\r6=1.0
8381407\r7=1.08354936\a1=116.71279694\a2=100.52231919\a3=125.47582457\
a4=112.43389317\a5=119.88948995\a6=122.78942873\\Version=x86-Linux-G98
RevA.11.1\State=1-A'\HF=-606.9902712\RMSD=1.800e-09\RMSF=4.035e-05\Dip
ole=0.5801558,0.,-0.1625648\PG=CS [SG(C2H3N1O1S1)]\\@

CH_2CHSNO (*syn*) B3P86/6-311+G(2df,p)

1\1\GINC-ANGSTROM\Freq\RB3P86\6-311+G(2df,p)\C2H3N1O1S1\CRISTINA\25-Ap
r-2002\1\\#N GEOM=ALLCHECK GUESS=TCHECK RB3P86/6-311+G(2DF,P) FREQ\\c2
h3sno-cis-b3p86b2\\0,1\O\N,1,r1\S,2,r2,1,a1\C,3,r3,2,a2,1,0.,0\C,4,r4,
3,a3,2,180.,0\H,4,r5,3,a4,2,0.,0\H,5,r6,4,a5,3,180.,0\H,5,r7,4,a6,3,0.
,0\\r1=1.17618977\r2=1.82458694\r3=1.73200892\r4=1.32823855\r5=1.08883
776\r6=1.08324098\r7=1.08310886\a1=117.34221603\a2=101.71998305\a3=125
.11042884\a4=112.84035735\a5=120.02396503\a6=122.77830071\\Version=x86
-Linux-G98RevA.11.1\State=1-A'\HF=-607.0154837\RMSD=1.861e-09\RMSF=8.8
93e-05\Dipole=0.7320827,0.,-0.0727204\PG=CS [SG(C2H3N1O1S1)]\\@

CH_2CHSNO (*syn*) CBS-4M

1\1\GINC-ANGSTROM\Mixed\CBS-4M\CBS-4M\C2H3N1O1S1\JAMES\30-Jul-2003\0\\
CBS-4M TEST\\c2h5sno-cis-cbsq\\0,1\C,2.3144076643,0.4214066988,-0.00
0004959\C,1.0021352808,0.503724168,-0.0000336934\S,-0.055133769,-0.902
602296,-0.000044942\N,-1.6335172665,-0.2021989675,-0.0000395935\O,-1.7
269771272,1.0091865634,0.0001556458\H,0.476642505,1.4365038643,-0.0000

373566\H,2.9145870641,1.3098899294,0.0000092422\H,2.8420909468,-0.5136
419941,0.0000110893\\Version=x86-Linux-G98RevA.11.1\HF/CbsB1=-604.2730
389\HF/CbsB2=-604.1798834\MP2/CbsB2=-604.9451651\E2(CBS)/CbsB2=-0.9767
032\CBS-Int/CbsB2=0.05486\OIii/CbsB2=8.4698205\MP2/6-31G=-604.507085\M
P4(SDQ)/6-31G=-604.5309893\CBS4M=-605.3474482\PG=CS [SG(C2H3N1O1S1)]\\@

CH_2CHSNO (*syn*) CBS-Q

1\1\GINC-POPLE\Mixed\CBS-Q\CBS-Q\C2H3N1O1S1\CRISTINA\26-Jun-2003\0\\#
CBS-Q OPT\\c2h5sno-cis-cbsq\\0,1\C,2.3504785762,0.4341324628,0.0064322
14\C,1.005019757,0.4586528788,0.005882477\S,-0.0274598212,-0.952220227
3,-0.0098149138\N,-1.7256205087,-0.1255058682,-0.0028757577\O,-1.73670
25979,1.0602056098,0.0092364626\H,0.4483796233,1.4006270947,0.01584752
02\H,2.909789814,1.3672282003,0.0168809622\H,2.9211620474,-0.492147508
,-0.0033394034\\Version=x86-Linux-G98RevA.11.1\HF/CbsB3=-604.2704522\M
P2/CbsB3=-605.2030293\E2(CBS)/CbsB3=-1.0279783\CBS-Int/CbsB3=0.0322458
\OIii/CbsB3=7.1632689\MP2/CbsB4=-604.9770879\MP4(SDQ)/CbsB4=-605.01406
11\MP4(SDQ)/6-31+G(d')=-604.9590155\QCISD(T)/6-31+G(d')=-604.995971\CB
SQ=-605.3287503\ PG=C01 [X(C2H3N1O1S1)]\\@

CH_2CHSNO (*syn*) G3

1\1\GINC-POPLE\Mixed\G3\G3\C2H3N1O1S1\CRISTINA\24-Jun-2003\0\\# G3 OPT
\\c2h3sno-cis-g3-1\\0,1\C,-0.5194934112,-0.0333231106,-2.3211961656\C,
-0.5153255649,0.0087143853,-0.983384285\S,0.9252230121,-0.0713886329,0
.0019654896\N,0.2366302484,0.0349481451,1.6829851818\O,-0.9687766087,0
.13091545,1.7734795755\H,-1.430745194,0.0979048203,-0.4006985643\H,-1.
4574676118,0.0220355304,-2.862316866\H,0.3873595981,-0.1220304881,-2.9
096825773\\Version=x86-Linux-G98RevA.11.1\MP2/6-31G(d)=-604.8978144\QC
ISD(T)/6-31G(d)=-604.9668789\MP4/6-31G(d)=-604.96802\MP2/6-31+G(d)=-60
4.9146231\MP4/6-31+G(d)=-604.985686\MP2/6-31G(2df,p)=-605.0842219\MP4/
6-31G(2df,p)=-605.1686177\MP2/GTLarge=-605.6807658\G3=-605.8055641\Fre
qCoord=-0.9686624592,0.307844405,-4.1294410202,-1.1796679573,-0.553162
5549,-1.8018429364,1.4847975054,-0.9924628749,0.163940741,0.641965019,
0.6168641298,2.9412431134,-1.3263309507,1.6051191214,2.9566954094,-2.9
626523416,-1.1366172149,-1.0281192728,-2.594831092,0.415261313,-5.3432
123691,0.8075983181,0.9136689199,-4.9062815429\PG=C01 [X(C2H3N1O1S1)]\

$CH_2CHS^{\bullet}$ MP2/6-311G(d,p)

1\1\GINC-VLAD\Freq\UMP2-FC\6-311G(d,p)\C2H3S1(2)\CRISTINA\08-Jan-2003\
1\\#N GEOM=ALLCHECK GUESS=TCHECK UMP2(FC)/6-311G(D,P) FREQ\\c2h3s-rad-
2-mp2 non-planar\\0,2\C\C,1,r1\H,2,r2,1,a1\H,2,r3,1,a2,3,d1,0\H,1,r4,2
,a3,3,d2,0\S,1,r5,2,a4,4,d3,0\\r1=1.34656016\r2=1.08552568\r3=1.084367
12\r4=1.08810633\r5=1.7029912\a1=121.10046747\a2=120.74624819\a3=119.0
5515065\a4=122.58242305\d1=179.99992348\d2=0.00005418\d3=0.00001916\\V
ersion=x86-Linux-G98RevA.11.1\HF=-474.9998968\MP2=-475.374148\PUHF=-47
5.0143787\PMP2-0=-475.3865077\S2=0.948421\S2-1=0.889246\S2A=0.755849\R
MSD=3.453e-10\RMSF=2.501e-07\Dipole=0.5969574,-.0000006,0.6941906\
PG=C01 [X(C2H3S1)]\\@

$CH_2CHS^{\bullet}$ MP2/6-311+G(2df,p)

1\1\GINC-VLAD\FOpt\UMP2-FC\6-311+G(2df,p)\C2H3S1(2)\CRISTINA\08-Jan-20
03\1\\# MP2/6-311+G(2DF,P) FOPT=Z-MATRIX\\c2h3s-rad-2-mp2 non-planar\\
0,2\C\C,1,r1\H,2,r2,1,a1\H,2,r3,1,a2,3,d1,0\H,1,r4,2,a3,3,d2,0\S,1,r5,
2,a4,4,d3,0\\r1=1.33674425\r2=1.08413164\r3=1.08282694\r4=1.0870274\r5
=1.70290659\a1=121.12361054\a2=120.71933542\a3=119.29984722\a4=122.236

44199\d1=179.96998251\d2=0.01737295\d3=0.00064685\\Version=x86-Linux-G
98RevA.11.1\HF=-475.0120545\MP2=-475.4549049\PUHF=-475.0265937\PMP2-0=
-475.4672258\S2=0.938784\S2-1=0.879919\S2A=0.75691\RMSD=6.821e-09\RMSF
=4.642e-05\Dipole=0.6108966,-0.0001574,0.6780151\PG=C01 [X(C2H3S1)]\\@

$CH_2CHS^\bullet$ QCISD/6-311G(d,p)

1\1\GINC-VLAD\FOpt\UQCISD-FC\6-311G(d,p)\C2H3S1(2)\CRISTINA\08-Jan-200
3\1\\# QCISD/6-311G(D,P) FOPT=Z-MATRIX\\c2h3s-rad-2-qcisd non-planar\\
0,2\C\C,1,r1\H,2,r2,1,a1\H,2,r3,1,a2,3,d1,0\H,1,r4,2,a3,3,d2,0\S,1,r5,
2,a4,4,d3,0\\r1=1.3693326\r2=1.08752859\r3=1.08644995\r4=1.08951263\r5
=1.70917195\a1=120.95558336\a2=120.80009583\a3=118.86297378\a4=122.986
6877\d1=179.89246136\d2=0.10248931\d3=-0.05578981\\Version=x86-Linux-G
98RevA.11.1\HF=-475.0002638\MP2=-475.3736007\MP3=-475.4059603\MP4D=-47
5.4161657\MP4DQ=-475.4080963\PUHF=-475.0157954\PMP2-0=-475.3869687\PMP
3-0=-475.4160392\MP4SDQ=-475.4132435\QCISD=-475.4199592\S2=0.972681\S2
-1=0.909459\S2A=0.757111\RMSD=5.307e-09\RMSF=4.704e-05\Dipole=0.539281
3,-0.0003193,0.5931466\PG=C01 [X(C2H3S1)]\\@

$CH_2CHS^\bullet$ B3LYP/6-31G(d)

1\1\GINC-ANGSTROM\Freq\UB3LYP\6-31G(d)\C2H3S1(2)\CRISTINA\20-Jun-2003\
0\\#N GEOM=ALLCHECK GUESS=TCHECK UB3LYP/6-31G(D) FREQ\\c2h3s-rad-2-b3l
ypb6\\0,2\C,-0.5004662726,0.510299484,0.0000907118\C,-1.6158079625,-0.
2811526978,0.0001840879\H,-2.6136080017,0.1522873282,0.0003975209\H,-1
.532041566,-1.3639417382,0.0001885412\H,-0.6315613036,1.5932204709,0.0
000756726\S,1.0921785176,-0.1097779236,-0.0001444083\\Version=x86-Linu
x-G98RevA.11.1\HF=-476.1508984\S2=0.774403\S2-1=0.\S2A=0.750106\RMSD=1
.265e-10\RMSF=1.050e-04\Dipole=-0.9746063,0.1284533,0.0001366\PG=C01
[X(C2H3S1)]\\@

$CH_2CHS^\bullet$ B3LYP/6-31+G(d)

1\1\GINC-KOHN\Freq\UB3LYP\6-31+G(d)\C2H3S1(2)\CRISTINA\21-Jun-2003\0\\
#N GEOM=ALLCHECK GUESS=TCHECK UB3LYP/6-31+G(D) FREQ\\c2h3s-rad-2-b3lyp
b7\\0,2\C,-0.5015725463,0.5092315162,0.0000833235\C,-1.6180392008,-0.2
83089901,0.0001758385\H,-2.6151831934,0.1526457916,0.0004075782\H,-1.5
353206799,-1.366562267,0.0001813737\H,-0.6319305971,1.5925338105,0.000
0698512\S,1.0937565596,-0.1084666892,-0.0001383609\\Version=x86-Linux-
G98RevA.11.1\HF=-476.1560842\S2=0.773798\S2-1=0.\S2A=0.750106\RMSD=2.1
12e-10\RMSF=9.618e-05\Dipole=-0.9594863,0.119989,0.0001359\PG=C01
[X(C2H3S1)]\\@

$CH_2CHS^\bullet$ B3LYP/6-311G(d,p)

1\1\GINC-HAMMERHEAD16\Freq\UB3LYP\6-311G(d,p)\C2H3S1(2)\JGAULD\08-Jan-
2003\1\\#N GEOM=ALLCHECK GUESS=TCHECK UB3LYP/6-311G(D,P) FREQ\\c2h3s-r
ad-2-b3lypb1 non-planar\\0,2\C\C,1,r1\H,2,r2,1,a1\H,2,r3,1,a2,3,d1,0\H
,1,r4,2,a3,3,d2,0\S,1,r5,2,a4,4,d3,0\\r1=1.36291121\r2=1.08541444\r3=1
.08379015\r4=1.08810272\r5=1.70802388\a1=120.97762649\a2=120.90374238\
a3=118.76255745\a4=123.48144934\d1=180.06610549\d2=-0.06559216\d3=0.01
198011\\Version=DEC-AXP-Linux-G98RevA.11\HF=-476.2000527\S2=0.772874\S
2-1=0.\S2A=0.750101\RMSD=1.680e-09\RMSF=4.091e-05\Dipole=0.6475055,0.0
004322,0.7192719\ PG=C01 [X(C2H3S1)]\\@

$CH_2CHS^\bullet$ B3LYP/6-311++G(d,p)

1\1\GINC-ANGSTROM\Freq\UB3LYP\6-311++G(d,p)\C2H3S1(2)\CRISTINA\22-Jun-
2003\0\\# B3LYP/6-311++G(D,P) SCF=TIGHT FREQ=NORAMAN\\c2h3s-rad-2-b3ly

pb8 single point using geom. from B3LYP/6-31G(d)\\0,2\C,-0.5009812258,
0.5097939355,0.0000907097\C,-1.6155232258,-0.2827840645,0.0001837097\H
,-2.6137602258,0.1496479355,0.0003977097\H,-1.5306632258,-1.3654880645
,0.0001887097\H,-0.6331702258,1.5925819355,0.0000757097\S,1.0922887742
,-0.1086750645,-0.0001442903\\Version=x86-Linux-G98RevA.11.1\HF=-476.2
016892\S2=0.77314\S2-1=0.\S2A=0.750103\RMSD=3.885e-09\RMSF=1.102e-03\D
ipole=-0.9331028,0.1192627,0.0001304\ PG=C01 [X(C2H3S1)]\\@

$CH_2CHS^\bullet$ B3LYP/6-311+G(2df,p)

1\1\GINC-VLAD\Freq\UB3LYP\6-311+G(2df,p)\C2H3S1(2)\CRISTINA\07-Jan-200
3\1\\#N GEOM=ALLCHECK GUESS=TCHECK UB3LYP/6-311+G(2DF,P) FREQ\\c2h3s-r
ad-2-b3lypb2 non-planar\\0,2\C\C,1,r1\H,2,r2,1,a1\H,2,r3,1,a2,3,d1,0\H
,1,r4,2,a3,3,d2,0\S,1,r5,2,a4,4,d3,0\\r1=1.35915532\r2=1.08464125\r3=1
.08304327\r4=1.08777036\r5=1.70131683\a1=121.06808189\a2=120.89548679\
a3=118.54050486\a4=123.49014357\d1=180.06626985\d2=-0.07132496\d3=0.01
835883\\Version=x86-Linux-G98RevA.11.1\HF=-476.2097876\S2=0.773333\S2-
1=0.\S2A=0.750136\RMSD=3.402e-10\RMSF=3.828e-05\Dipole=0.6241259,0.000
3982,0.6723698\ PG=C01 [X(C2H3S1)]\\@

$CH_2CHS^\bullet$ B3P86/6-311G(d,p)

1\1\GINC-VLAD\Freq\UB3P86\6-311G(d,p)\C2H3S1(2)\CRISTINA\08-Jan-2003\1
\\#N GEOM=ALLCHECK GUESS=TCHECK UB3P86/6-311G(D,P) FREQ\\c2h3s-rad-2-b
3p86b1 non-planar\\0,2\C\C,1,r1\H,2,r2,1,a1\H,2,r3,1,a2,3,d1,0\H,1,r4,
2,a3,3,d2,0\S,1,r5,2,a4,4,d3,0\\r1=1.36211289\r2=1.08544997\r3=1.08410
188\r4=1.08862329\r5=1.69681933\a1=121.01088476\a2=120.68846723\a3=118
.74372112\a4=123.26424307\d1=180.00084638\d2=-0.00096654\d3=-0.0005418
4\\Version=x86-Linux-G98RevA.11.1\HF=-476.7658876\S2=0.775561\S2-1=0.\
S2A=0.75012\RMSD=6.464e-10\RMSF=2.998e-05\Dipole=0.6426035,0.000011,0.
7200468\ PG=C01 [X(C2H3S1)]\\@

$CH_2CHS^\bullet$ B3P86/6-311+G(2df,p)

1\1\GINC-VLAD\Freq\UB3P86\6-311+G(2df,p)\C2H3S1(2)\CRISTINA\08-Jan-200
3\1\\#N GEOM=ALLCHECK GUESS=TCHECK UB3P86/6-311+G(2DF,P) FREQ\\c2h3s-r
ad-2-b3p86b2 non-planar\\0,2\C\C,1,r1\H,2,r2,1,a1\H,2,r3,1,a2,3,d1,0\H
,1,r4,2,a3,3,d2,0\S,1,r5,2,a4,4,d3,0\\r1=1.35824069\r2=1.08485754\r3=1
.08346681\r4=1.08831817\r5=1.69063114\a1=121.12552176\a2=120.64081317\
a3=118.57685497\a4=123.17972161\d1=180.00082605\d2=-0.00084464\d3=-0.0
0060184\\Version=x86-Linux-G98RevA.11.1\HF=-476.775703\S2=0.776327\S2-
1=0.\S2A=0.750168\RMSD=9.518e-10\RMSF=2.693e-05\Dipole=0.6266291,0.000
0108,0.6743144\ PG=C01 [X(C2H3S1)]\\@

$CH_2CHS^\bullet$ CBS-4M

1\1\GINC-ANGSTROM\Mixed\CBS-4M\CBS-4M\C2H3S1(2)\JAMES\30-Jul-2003\0\\#
 CBS-4M TEST\\c2h3s-rad CBS-4M\\0,2\C,-0.49893115,0.5077960029,0.00008
29646\C,-1.6121582893,-0.2846872768,0.0001768912\H,-2.5962358239,0.143
3558688,0.0003873392\H,-1.5302362362,-1.353747119,0.0002323542\H,-0.62
35731049,1.5744876841,0.0001171946\S,1.0885363625,-0.1064217994,-0.000
1435014\\Version=x86-Linux-G98RevA.11.1\HF/CbsB1=-475.0123946\HF/CbsB2
=-474.9658113\MP2/CbsB2=-475.328045\E2(CBS)/CbsB2=-0.4756603\CBS-Int/C
bsB2=0.0295818\OIii/CbsB2=4.7731748\MP2/6-31G=-475.1011158\MP4(SDQ)/6-
31G=-475.1301385\CBS4M=-475.5611217\ PG=C01 [X(C2H3S1)]\\@

$CH_2CHS^\bullet$ CBS-Q

1\1\GINC-POPLE\Mixed\CBS-Q\CBS-Q\C2H3S1(2)\CRISTINA\25-Jun-2003\0\\# C

BS-Q OPT\\c2h3s-rad CBS-Q\\0,2\C,-0.4992320707,0.5157629804,0.00007364
56\C,-1.5987566699,-0.2714800459,0.000221142\H,-2.6006038209,0.1551073
369,0.0003642395\H,-1.5081061393,-1.3553025599,0.0001965957\H,-0.62305
35339,1.6005965965,0.0001004779\S,1.0824809961,-0.1166311863,-0.000151
8774\\Version=x86-Linux-G98RevA.11.1\HF/CbsB3=-475.014625\MP2/CbsB3=-4
75.4645963\E2(CBS)/CbsB3=-0.5015008\CBS-Int/CbsB3=0.0181004\OIii/CbsB3
=3.9923712\MP2/CbsB4=-475.3529776\MP4(SDQ)/CbsB4=-475.3957379\MP4(SDQ)
/6-31+G(d')=-475.3443272\QCISD(T)/6-31+G(d')=-475.3646115\CBSQ=-475.54
39529\FreqCoord=-0.9383036759,0.9633591967,0.0001912228,-3.0536303346,
-0.5445726939,0.0004945851,-4.9202789454,0.2722956818,0.0006299336,-2.
8992761595,-2.5733559917,0.000349984,-1.1749731151,2.9895499646,0.0001
618633,2.0591332677,-0.2000755419,-0.0003285393\PG=C01 [X(C2H3S1)]\\@

$CH_2CHS^{\bullet}$ G3

1\1\GINC-POPLE\Mixed\G3\G3\C2H3S1(2)\CRISTINA\22-Jun-2003\0\\# G3 OPT\
\c2h3s-rad-G3\\0,2\C,-0.5004940606,0.5130042579,0.0000747034\C,-1.5945
287151,-0.2700921942,0.0002200904\H,-2.5931351777,0.1543601667,0.00036
22762\H,-1.5063980364,-1.3503455446,0.0001979839\H,-0.6237108996,1.593
9696285,0.000101557\S,1.080836298,-0.1159660395,-0.0001519112\\Version
=x86-Linux-G98RevA.11.1\MP2/6-31G(d)=-475.2956363\QCISD(T)/6-31G(d)=-4
75.3541846\MP4/6-31G(d)=-475.3456212\MP2/6-31+G(d)=-475.3027793\MP4/6-
31+G(d)=-475.3531114\MP2/6-31G(2df,p)=-475.4007317\MP4/6-31G(2df,p)=-4
75.4619332\MP2/GTLarge=-475.8503431\G3=-475.935067\FreqCoord=-0.941889
4197,0.9608245377,0.0001202932,-3.0510846348,-0.5437098186,0.000365927
,-4.912279973,0.2717220369,0.0007249605,-2.8990893018,-2.5671849495,0.
0004092157,-1.1771553848,2.9810761364,0.0002119939,2.0591480617,-0.199
2688462,-0.0002664682\PG=C01 [X(C2H3S1)]\\@

CH_3CH_2SNO (*syn*) MP2/6-311G(d,p)

1\1\GINC-BOHR\Freq\RMP2-FC\6-311G(d,p)\C2H5N1O1S1\CRISTINA\21-May-2002
\1\\#N GEOM=ALLCHECK GUESS=TCHECK RMP2(FC)/6-311G(D,P) FREQ\\c2h5sno-c
is1-mp2b1\\0,1\N\S,1,r1\C,2,r2,1,a1\C,3,r3,2,a2,1,d1,0\O,1,r4,2,a3,3,d
2,0\H,3,r5,2,a4,1,d3,0\H,3,r6,2,a5,1,d4,0\H,4,r7,3,a6,2,d5,0\H,4,r8,3,
a7,2,d6,0\H,4,r9,3,a8,2,d7,0\\r1=1.80558235\r2=1.79900969\r3=1.5261221
3\r4=1.20077694\r5=1.09548065\r6=1.09268471\r7=1.09434681\r8=1.0923596
5\r9=1.0922081\a1=100.64075655\a2=113.04185373\a3=116.31354968\a4=106.
68276872\a5=106.56544103\a6=110.27436726\a7=110.91126005\a8=110.531936
34\d1=84.35328341\d2=0.39946878\d3=-37.09605433\d4=-152.40864704\d5=18
0.74535584\d6=60.42194192\d7=-59.6627151\\Version=x86-Linux-G98RevA.11
.1\HF=-605.4407845\MP2=-606.2584769\RMSD=7.559e-10\RMSF=2.761e-06\Dipo
le=0.6096985,0.0437151,0.5541852\PG=C01 [X(C2H5N1O1S1)]\\@

CH_3CH_2SNO (*syn*) MP2/6-311G(df,p)

1\1\GINC-POPLE\FOpt\RMP2-FC\6-311G(df,p)\C2H5N1O1S1\JAMES\28-Dec-2002\
1\\# MP2/6-311G(DF,P) GEOM=CHECK GUESS=READ FOPT=Z-MATRIX TEST\\c2h5sn
o-cis1-mp2 starting point qcisd/6-311G(d,p)\\0,1\N\S,1,r1\C,2,r2,1,a1
\C,3,r3,2,a2,1,d1,0\O,1,r4,2,a3,3,d2,0\H,3,r5,2,a4,1,d3,0\H,3,r6,2,a5,
1,d4,0\H,4,r7,3,a6,2,d5,0\H,4,r8,3,a7,2,d6,0\H,4,r9,3,a8,2,d7,0\\r1=1.
76203573\r2=1.79212217\r3=1.52196284\r4=1.2041861\r5=1.09569293\r6=1.0
9323342\r7=1.09399935\r8=1.09229231\r9=1.09190399\a1=101.49548787\a2=1
12.91716856\a3=116.83301039\a4=106.64402406\a5=106.34513759\a6=110.216
07834\a7=110.89014973\a8=110.52137632\d1=82.81494564\d2=0.4340178\d3=-
38.64458739\d4=-154.10963051\d5=180.87795418\d6=60.60551524\d7=-59.570
5758\\Version=IBM-RS6000-G98RevA.7\HF=-605.4511723\MP2=-606.3535194\RM

SD=8.749e-09\RMSF=4.435e-05\Dipole=0.6177828,0.0488298,0.6759685\PG=C0
1 [X(C2H5N1O1S1)]\\@

CH_3CH_2SNO (*syn*) MP2/6-311+G(2df,p)

1\1\GINC-CURIE\Freq\RMP2-FC\6-311+G(2df,p)\C2H5N1O1S1\CRISTINA\08-Jun-
2002\1\\#N GEOM=ALLCHECK GUESS=TCHECK RMP2(FC)/6-311+G(2DF,P) FREQ\\c2
h5sno-cis1-mp2b2\\0,1\N\S,1,r1\C,2,r2,1,a1\C,3,r3,2,a2,1,d1,0\O,1,r4,2
,a3,3,d2,0\H,3,r5,2,a4,1,d3,0\H,3,r6,2,a5,1,d4,0\H,4,r7,3,a6,2,d5,0\H,
4,r8,3,a7,2,d6,0\H,4,r9,3,a8,2,d7,0\\r1=1.7597854\r2=1.79959793\r3=1.5
2088999\r4=1.2095294\r5=1.09441667\r6=1.09223466\r7=1.09256459\r8=1.09
071267\r9=1.09027022\a1=101.53841128\a2=112.90421717\a3=116.61459011\a
4=106.38546612\a5=105.83554768\a6=110.16975502\a7=110.98024913\a8=110.
84217716\d1=82.58074827\d2=0.46083725\d3=-39.73218112\d4=-154.5271021\
d5=180.6340708\d6=60.65735173\d7=-59.79893975\\Version=x86-Linux-G98Re
vA.11.1\HF=-605.4679959\MP2=-606.4158739\RMSD=1.036e-09\RMSF=3.861e-08
\Dipole=0.6302724,0.0576435,0.7805109\PG=C01 [X(C2H5N1O1S1)]\\@

CH_3CH_2SNO (*syn*) QCISD/6-311G(d,p)

1\1\GINC-POPLE\FOpt\RQCISD-FC\6-311G(d,p)\C2H5N1O1S1\JAMES\27-Dec-2002
\1\\# QCISD/6-311G(D,P) FOPT=Z-MATRIX TEST\\c2h5sno-cis1-mp2 starting
point mp2/6-311G(d,p)\\0,1\N\S,1,r1\C,2,r2,1,a1\C,3,r3,2,a2,1,d1,0\O,
1,r4,2,a3,3,d2,0\H,3,r5,2,a4,1,d3,0\H,3,r6,2,a5,1,d4,0\H,4,r7,3,a6,2,d
5,0\H,4,r8,3,a7,2,d6,0\H,4,r9,3,a8,2,d7,0\\r1=1.83333149\r2=1.80998826
\r3=1.52971719\r4=1.18711083\r5=1.09531645\r6=1.09401662\r7=1.09649645
\r8=1.09470019\r9=1.09433077\a1=100.42301119\a2=113.20288414\a3=116.31
01444\a4=106.91919646\a5=106.2292434\a6=110.17429806\a7=110.94035862\a
8=110.64122871\d1=84.65896435\d2=0.47776321\d3=-37.29061535\d4=-152.51
552397\d5=180.25658876\d6=60.04266071\d7=-60.1296725\\Version=IBM-RS60
00-G98RevA.7\HF=-605.4415599\MP2=-606.2582254\MP3=-606.2804934\MP4D=-6
06.3050729\MP4DQ=-606.2857181\MP4SDQ=-606.2993785\QCISD=-606.3010461\R
MSD=4.179e-09\RMSF=3.216e-05\Dipole=0.5683486,0.0419719,0.5518841\PG=C
01 [X(C2H5N1O1S1)]\\@

CH_3CH_2SNO (*syn*) QCISD/6-311G(df,p)

1\1\GINC-POPLE\FOpt\RQCISD-FC\6-311G(df,p)\C2H5N1O1S1\JAMES\07-Jan-200
3\1\\# QCISD/6-311G(DF,P) FOPT=(Z-MATRIX) MAXDISK=12GB TEST\\c2h5sno-c
is1-mp2b1 starting point qcisd/6-311G(d,p)\\0,1\N\S,1,r1\C,2,r2,1,a1\C
,3,r3,2,a2,1,d1,0\O,1,r4,2,a3,3,d2,0\H,3,r5,2,a4,1,d3,0\H,3,r6,2,a5,1,
d4,0\H,4,r7,3,a6,2,d5,0\H,4,r8,3,a7,2,d6,0\H,4,r9,3,a8,2,d7,0\\r1=1.79
1599\r2=1.80212099\r3=1.52514043\r4=1.1879225\r5=1.09541048\r6=1.09430
242\r7=1.09595445\r8=1.09443577\r9=1.09387174\a1=101.26577707\a2=113.1
9671889\a3=116.82643167\a4=106.91398122\a5=106.04241698\a6=110.1364061
1\a7=110.93976457\a8=110.66170098\d1=83.67046666\d2=0.41588285\d3=-38.
34322026\d4=-153.60374441\d5=180.37193591\d6=60.19532361\d7=-60.039442
71\\Version=x86-Linux-G98RevA.11.1\HF=-605.4525568\MP2=-606.353168\MP3
=-606.3812333\MP4D=-606.4069381\MP4DQ=-606.3834003\MP4SDQ=-606.3964026
\QCISD=-606.3971764\RMSD=5.265e-09\RMSF=1.303e-05\Dipole=0.5822574,0.0
46361,0.6396935\PG=C01 [X(C2H5N1O1S1)]\\@

CH_3CH_2SNO (*syn*) B3LYP/6-31+G(d)

1\1\GINC-ANGSTROM\Freq\RB3LYP\6-31+G(d)\C2H5N1O1S1\CRISTINA\22-Jun-200
3\0\\#N GEOM=ALLCHECK GUESS=TCHECK RB3LYP/6-31+G(D) FREQ\\c2h5sno-cis1
-b3lypb6-1\\0,1\N,1.6764927601,0.068967346,-0.2510000275\S,0.221061175
6,-1.0398003355,-0.0615541493\C,-1.0451496125,0.0780649625,0.634884120

9\C,-2.0600268979,0.5795022161,-0.3958017406\O,1.5432532131,1.20315720
05,0.092044758\H,-0.4922512341,0.9165125092,1.0789347546\H,-1.53180093
88,-0.4710173446,1.4473686683\H,-2.7875259372,1.2398170303,0.092822980
1\H,-2.6083752962,-0.2490445683,-0.8561692253\H,-1.5674413666,1.147105
6432,-1.1919429428\\Version=x86-Linux-G98RevA.11.1\HF=-607.3229559\RMS
D=1.985e-09\RMSF=6.360e-06.\PG=C01 [X(C2H5N1O1S1)]\\@

CH_3CH_2SNO (*syn*) B3LYP/6-311G(d,p)

1\1\GINC-VLAD\Freq\RB3LYP\6-311G(d,p)\C2H5N1O1S1\CRISTINA\10-May-2002\
1\\#N GEOM=ALLCHECK GUESS=TCHECK RB3LYP/6-311G(D,P) FREQ\\c2h5sno-cis1
-b3lypb1-2\\0,1\N\S,1,r1\C,2,r2,1,a1\C,3,r3,2,a2,1,d1,0\O,1,r4,2,a3,3,
d2,0\H,3,r5,2,a4,1,d3,0\H,3,r6,2,a5,1,d4,0\H,4,r7,3,a6,2,d5,0\H,4,r8,3
,a7,2,d6,0\H,4,r9,3,a8,2,d7,0\\r1=1.88303907\r2=1.82138261\r3=1.528406
66\r4=1.17545049\r5=1.09655506\r6=1.09124393\r7=1.09421798\r8=1.091938
36\r9=1.09185435\a1=101.62922596\a2=113.8613989\a3=116.83870142\a4=105
.02785528\a5=106.98825246\a6=109.89250673\a7=111.57577544\a8=111.02193
655\d1=105.8048652\d2=0.61656033\d3=-15.49344898\d4=-129.99323694\d5=1
80.29084106\d6=60.46390835\d7=-60.15613839\\Version=x86-Linux-G98RevA.
11.1\HF=-607.3989615\RMSD=1.696e-09\RMSF=1.646e-05\Dipole=0.624666,0.0
5587,0.521104\PG=C01 [X(C2H5N1O1S1)]\\@

CH_3CH_2SNO (*syn*) B3LYP/6-311+G(2df,p)

1\1\GINC-BOHR\Freq\RB3LYP\6-311+G(2df,p)\C2H5N1O1S1\CRISTINA\17-May-20
02\0\\# B3LYP/6-311+G(2DF,P) OPT=CALCALL\\c2h5sno-cis1-b3lypb2\\0,1\N,
-0.9332013003,-0.4250259091,-1.316645995\S,-0.9066810889,-0.2737109339
,0.4941556609\C,0.866859138,-0.1335347192,0.859665719\C,1.3524033311,1
.3024613523,1.0324262546\O,0.1072611569,-0.4125971267,-1.881411275\H,1
.3768039536,-0.6228668153,0.024479864\H,1.0397276807,-0.7315229803,1.7
554924739\H,2.4240972155,1.3093022771,1.2479911596\H,0.8382306468,1.80
15052196,1.8551975011\H,1.186782959,1.8853558202,0.12560875\\Version=x
86-Linux-G98RevA.11.1\HF=-607.4213039\RMSD=4.726e-09\RMSF=1.626e-05\Di
pole=0.6204103,0.1586437,0.7245197\PG=C01 [X(C2H5N1O1S1)]\\@

CH_3CH_2SNO (*syn*) B3P86/6-311G(d,p)

1\1\GINC-ANGSTROM\Freq\RB3P86\6-311G(d,p)\C2H5N1O1S1\CRISTINA\10-May-2
002\1\\#N GEOM=ALLCHECK GUESS=TCHECK RB3P86/6-311G(D,P) FREQ\\c2h5sno-
cis1-b3p86b1\\0,1\N\S,1,r1\C,2,r2,1,a1\C,3,r3,2,a2,1,d1,0\O,1,r4,2,a3,
3,d2,0\H,3,r5,2,a4,1,d3,0\H,3,r6,2,a5,1,d4,0\H,4,r7,3,a6,2,d5,0\H,4,r8
,3,a7,2,d6,0\H,4,r9,3,a8,2,d7,0\\r1=1.84605543\r2=1.80466672\r3=1.5209
1581\r4=1.17576601\r5=1.09801591\r6=1.09143657\r7=1.09366773\r8=1.0916
9257\r9=1.09159662\a1=101.62839758\a2=113.7344036\a3=116.94517594\a4=1
04.74228696\a5=107.24051562\a6=109.97984802\a7=111.6166826\a8=110.9891
5827\d1=106.19238681\d2=0.71163488\d3=-14.86341944\d4=-129.32844588\d5
=180.63661751\d6=60.76515555\d7=-59.82289847\\Version=x86-Linux-G98Rev
A.11.1\HF=-608.2710659\RMSD=6.611e-09\RMSF=1.597e-05\Dipole=0.6217933,
0.0605124,0.6000365\PG=C01 [X(C2H5N1O1S1)]\\@

CH_3CH_2SNO (*syn*) B3P86/6-311+G(2df,p)

1\1\GINC-ANGSTROM\Freq\RB3P86\6-311+G(2df,p)\C2H5N1O1S1\CRISTINA\30-Ju
l-2002\0\\#N GEOM=ALLCHECK GUESS=TCHECK RB3P86/6-311+G(2DF,P) FREQ\\c2
h5sno-cis1-b3p86b2\\0,1\N,1.6505261243,0.113591212,-0.1460606624\S,0.2
423989298,-0.9909718703,-0.232840951\C,-1.0548793377,-0.0433612937,0.5
768425989\C,-2.0246421787,0.6161321907,-0.3878958328\O,1.4944420171,1.
1596746954,0.3831138905\H,-0.5249378551,0.7057498272,1.1762470135\H,-1

.5599441247,-0.7261753022,1.2617750193\H,-2.7804390279,1.1768095159,0.
1675617591\H,-2.5380286648,-0.1213563025,-1.0064103725\H,-1.5071231131
,1.3113607568,-1.049885288\\Version=x86-Linux-G98RevA.11.1\HF=-608.293
5983\RMSD=5.675e-09\RMSF=5.530e-06\Dipole=-0.966584,-0.0369728,0.19605
99\PG=C01 [X(C2H5N1O1S1)]\\@

$CH_3CH_2S^\bullet$ MP2/6-311G(d,p)

1\1\GINC-CURIE\Freq\UMP2-FC\6-311G(d,p)\C2H5S1(2)\CRISTINA\08-May-2002
\1\\#N GEOM=ALLCHECK GUESS=TCHECK UMP2(FC)/6-311G(D,P) FREQ\\c2h5s-rad
-mp2b1\\0,2\S\C,1,r1\C,2,r2,1,a1\H,2,r3,1,a2,3,d1,0\H,2,r4,1,a3,3,d2,0
\H,3,r5,2,a4,1,d3,0\H,3,r6,2,a5,1,d4,0\H,3,r7,2,a6,1,d5,0\\r1=1.803266
82\r2=1.53452798\r3=1.09234686\r4=1.09233444\r5=1.09337015\r6=1.092514
46\r7=1.0925211\a1=109.17923436\a2=109.72645028\a3=109.74345468\a4=109
.5295259\a5=111.0390812\a6=111.04074138\d1=119.92934873\d2=-119.947761
63\d3=180.00984292\d4=60.34134938\d5=-60.32687989\\Version=x86-Linux-G
98RevA.11.1\HF=-476.1794286\MP2=-476.5940492\PUHF=-476.1821204\PMP2-0=
-476.5955482\S2=0.758949\S2-1=0.751002\S2A=0.750029\RMSD=2.216e-09\RMS
F=3.102e-05\Dipole=0.0760185,0.0001881,0.6972667\PG=C01 [X(C2H5S1)]\\@

$CH_3CH_2S^\bullet$ MP2/6-311+G(2df,p)

1\1\GINC-CURIE\Freq\UMP2-FC\6-311+G(2df,p)\C2H5S1(2)\CRISTINA\09-May-2
002\1\\#N GEOM=ALLCHECK GUESS=TCHECK UMP2(FC)/6-311+G(2DF,P) FREQ\\c2h
5s-rad-mp2b2\\0,2\S\C,1,r1\C,2,r2,1,a1\H,2,r3,1,a2,3,d1,0\H,2,r4,1,a3,
3,d2,0\H,3,r5,2,a4,1,d3,0\H,3,r6,2,a5,1,d4,0\H,3,r7,2,a6,1,d5,0\\r1=1.
80294611\r2=1.52890743\r3=1.09121317\r4=1.09120229\r5=1.09182155\r6=1.
09086148\r7=1.0908672\a1=108.79852309\a2=109.43431304\a3=109.44902419\
a4=109.58480358\a5=111.09818941\a6=111.09934455\d1=120.205363\d2=-120.
22033758\d3=180.01587707\d4=60.39665823\d5=-60.36984798\\Version=x86-L
inux-G98RevA.11.1\HF=-476.1899975\MP2=-476.6717883\PUHF=-476.1936679\P
MP2-0=-476.6739737\S2=0.764117\S2-1=0.752663\S2A=0.750064\RMSD=4.858e-
10\RMSF=4.067e-05\Dipole=0.0776484,0.0001422,0.7165418\PG=C01
[X(C2H5S1)]\\@

$CH_3CH_2S^\bullet$ QCISD/6-311G(d,p)

1\1\GINC-N02\FOpt\UQCISD-FC\6-311G(d,p)\C2H5S1(2)\JGAULD\28-Dec-2002\1
\\# QCISD/6-311G(D,P) FOPT=Z-MATRIX TEST\\c2h5s-cis1\\0,2\S\C,1,r2\C,2
,r3,1,a2\H,2,r5,1,a4,3,d3,0\H,2,r5,1,a4,3,-d3,0\H,3,r7,2,a6,1,180.,0\H
,3,r8,2,a7,1,d6,0\H,3,r8,2,a7,1,-d6,0\\r2=1.81293823\r3=1.53733286\r5=
1.09389841\r7=1.09570688\r8=1.09478914\a2=109.43657828\a4=109.53367932
\a6=109.58880765\a7=111.03370024\d3=120.11940787\d6=60.31394014\\Versi
on=IBM-RS6000-G98RevA.7\State=2-A'\HF=-476.1793932\MP2=-476.5939905\MP
3=-476.6320057\MP4D=-476.6432153\MP4DQ=-476.634875\PUHF=-476.1820829\P
MP2-0=-476.5954894\PMP3-0=-476.6327646\MP4SDQ=-476.6378485\QCISD=-476.
6390382\S2=0.758948\S2-1=0.751009\S2A=0.75003\RMSD=2.064e-09\RMSF=5.41
6e-05\Dipole=0.071755,0.,0.6859661\PG=CS [SG(C2H1S1),X(H4)]\\@

$CH_3CH_2S^\bullet$ B3LYP/6-31+G(d)

1\1\GINC-ANGSTROM\Freq\UB3LYP\6-31+G(d)\C2H5S1(2)\CRISTINA\20-Jun-2003
\0\\#N GEOM=ALLCHECK GUESS=TCHECK UB3LYP/6-31+G(D) FREQ\\c2h5s-rad-b3l
ypb6\\0,2\S,0.9423641063,-0.7554035353,-0.0732872619\C,-0.2766082762,0
.4360165908,0.5647704392\C,-1.3521973493,0.8733035963,-0.4288527278\H,
0.2980932025,1.2960363791,0.9380536723\H,-0.7205045376,-0.0251283422,1
.4589147787\H,-2.038265986,1.5891730225,0.0431347152\H,-1.938356834,0.
0162654638,-0.7772098227\H,-0.905957793,1.3541889191,-1.3058034216\\Ve

rsion=x86-Linux-G98RevA.11.1\HF=-477.3792623\S2=0.752716\S2-1=0.\S2A=0
.750004\RMSD=3.158e-10\RMSF=6.242e-06\Dipole=-0.5008317,0.4883981,0.25
94265\ PG=C01 [X(C2H5S1)]\\@

$CH_3CH_2S^\bullet$ B3LYP/6-311G(d,p)

1\1\GINC-CURIE\Freq\UB3LYP\6-311G(d,p)\C2H5S1(2)\CRISTINA\07-May-2002\
1\\#N GEOM=ALLCHECK GUESS=TCHECK UB3LYP/6-311G(D,P) FREQ\\c2h5s-rad-b3
lypb1\\0,2\S\C,1,r1\C,2,r2,1,a1\H,2,r3,1,a2,3,d1,0\H,2,r4,1,a3,3,d2,0\
H,3,r5,2,a4,1,d3,0\H,3,r6,2,a5,1,d4,0\H,3,r7,2,a6,1,d5,0\\r1=1.8168013
2\r2=1.52555517\r3=1.09645563\r4=1.09643877\r5=1.09493876\r6=1.0919982
6\r7=1.09199717\a1=115.64730055\a2=105.98382747\a3=106.00535399\a4=110
.37867301\a5=111.03864692\a6=111.04423961\d1=124.24898037\d2=-124.2886
9927\d3=179.95600723\d4=59.96544093\d5=-60.04597437\\Version=x86-Linux
-G98RevA.11.1\HF=-477.4258419\S2=0.752697\S2-1=0.\S2A=0.750004\RMSD=2.
735e-10\RMSF=1.262e-05\Dipole=0.0114313,0.0001276,0.7460641\PG=C01
[X(C2H5S1)]\\@

$CH_3CH_2S^\bullet$ B3LYP/6-311+G(2df,p)

1\1\GINC-CURIE\Freq\UB3LYP\6-311+G(2df,p)\C2H5S1(2)\CRISTINA\07-May-20
02\1\\#N GEOM=ALLCHECK GUESS=TCHECK UB3LYP/6-311+G(2DF,P) FREQ\\c2h5s-
rad-b3lypb2\\0,2\S\C,1,r1\C,2,r2,1,a1\H,2,r3,1,a2,3,d1,0\H,2,r4,1,a3,3
,d2,0\H,3,r5,2,a4,1,d3,0\H,3,r6,2,a5,1,d4,0\H,3,r7,2,a6,1,d5,0\\r1=1.8
0829347\r2=1.52303802\r3=1.09585743\r4=1.09585445\r5=1.09408663\r6=1.0
910948\r7=1.09108493\a1=115.72111444\a2=106.00970301\a3=106.01742604\a
4=110.45234187\a5=111.0198563\a6=111.02801199\d1=124.27565461\d2=-124.
30525805\d3=179.9367033\d4=59.91140227\d5=-60.02433287\\Version=x86-Li
nux-G98RevA.11.1\HF=-477.4335973\S2=0.753975\S2-1=0.\S2A=0.750008\RMSD
=2.491e-10\RMSF=8.941e-06\Dipole=0.0084166,0.000091,0.7210156\PG=C01
[X(C2H5S1)]\\@

$CH_3CH_2S^\bullet$ B3P86/6-311G(d,p)

1\1\GINC-CURIE\Freq\UB3P86\6-311G(d,p)\C2H5S1(2)\CRISTINA\08-May-2002\
1\\#N GEOM=ALLCHECK GUESS=TCHECK UB3P86/6-311G(D,P) FREQ\\c2h5s-rad-b3
p86b1\\0,2\S\C,1,r1\C,2,r2,1,a1\H,2,r3,1,a2,3,d1,0\H,2,r4,1,a3,3,d2,0\
H,3,r5,2,a4,1,d3,0\H,3,r6,2,a5,1,d4,0\H,3,r7,2,a6,1,d5,0\\r1=1.8010849
7\r2=1.51798776\r3=1.09689609\r4=1.09689593\r5=1.09444511\r6=1.0917697
1\r7=1.09176962\a1=115.61028174\a2=106.10013601\a3=106.10027309\a4=110
.55073415\a5=110.99715707\a6=110.99716942\d1=124.41319079\d2=-124.4133
2022\d3=179.99954376\d4=59.92876287\d5=-59.92966045\\Version=x86-Linux
-G98RevA.11.1\HF=-478.0334713\S2=0.752801\S2-1=0.\S2A=0.750004\RMSD=1.
229e-10\RMSF=2.075e-06\Dipole=0.0111009,0.0000006,0.7517327\PG=C01
[X(C2H5S1)]\\@

$CH_3CH_2S^\bullet$ B3P86/6-311+G(2df,p)

1\1\GINC-CURIE\Freq\UB3P86\6-311+G(2df,p)\C2H5S1(2)\CRISTINA\14-May-20
02\1\\#N GEOM=ALLCHECK GUESS=TCHECK UB3P86/6-311+G(2DF,P) FREQ\\c2h5s-
rad-b3p86b2\\0,2\S\C,1,r1\C,2,r2,1,a1\H,2,r3,1,a2,3,d1,0\H,2,r4,1,a3,3
,d2,0\H,3,r5,2,a4,1,d3,0\H,3,r6,2,a5,1,d4,0\H,3,r7,2,a6,1,d5,0\\r1=1.7
9314158\r2=1.51570845\r3=1.09632541\r4=1.09629378\r5=1.09367582\r6=1.0
9092108\r7=1.09092919\a1=115.6442882\a2=106.07348152\a3=106.10483913\a
4=110.61953582\a5=110.96046177\a6=110.96744858\d1=124.41208739\d2=-124
.44582828\d3=179.96457014\d4=59.85158892\d5=-59.92311209\\Version=x86-
Linux-G98RevA.11.1\HF=-478.0415693\S2=0.754349\S2-1=0.\S2A=0.750009\RM

SD=2.284e-10\RMSF=2.120e-05\Dipole=0.0081192,0.000113,0.7291131\ PG=C01
[X(C2H5S1)]\\@

C_6H_5SNO (*syn*) MP2/6-311G(d,p)

1\1\GINC-KOHN\Freq\RMP2-FC\6-311G(d,p)\C6H5N1O1S1\JAMES\02-Jul-2003\0\
\#N GEOM=ALLCHECK GUESS=TCHECK TEST RMP2(FC)/6-311G(D,P) FREQ\\c6h5sno
-cis-mp2b1: C6H5SNO Cs symmetry\\0,1\C,0.0139084592,0.,-0.5996611328\C
,-0.6390282351,1.212281775,-0.3044698135\C,-1.94873238,1.2098429217,0.
1818008492\C,-2.6009943354,0.,0.4446541246\C,-1.94873238,-1.2098429217
,0.1818008492\C,-0.6390282351,-1.212281775,-0.3044698135\H,-0.13064960
57,2.149115553,-0.5152266862\H,-2.4484131824,2.1527585118,0.3866998492
\H,-3.6184456236,0.,0.8250975419\H,-2.4484131824,-2.1527585118,0.38669
98492\H,-0.1306496057,-2.149115553,-0.5152266862\S,1.6893036456,0.,-1.
1011993709\N,2.3493959015,0.,0.8890312024\O,1.4846980249,0.,1.65374965
88\\Version=x86-Linux-G98RevA.11.1\State=1-A'\HF=-756.9277403\MP2=-758
.2720966\RMSD=3.322e-09\RMSF=1.687e-05\Dipole=-0.5810898,0.,0.7874799
\PG=CS [SG(C2H1N1O1S1),X(C4H4)]\\@

C_6H_5SNO (*syn*) MP2/6-311G(df,p)

1\1\GINC-KOHN\FOpt\RMP2-FC\6-311G(df,p)\C6H5N1O1S1\JAMES\03-Jul-2003\0
\\# MP2/6-311G(DF,P) GEOM=CHECK GUESS=READ OPT=RCFC TEST\\c6h5sno-cis-
mp2b2: C6H5SNO Cs symmetry\\0,1\C,-0.0128182824,0.,-0.5527381919\C,-0.
6653870593,1.2102270175,-0.2861954626\C,-1.9847331852,1.2069071106,0.1
583966173\C,-2.6413059775,0.,0.3971838508\C,-1.9847331852,-1.206907110
6,0.1583966173\C,-0.6653870593,-1.2102270175,-0.2861954626\H,-0.147477
766,2.146284052,-0.4760305514\H,-2.491472735,2.1490682928,0.3487667448
\H,-3.6700394186,0.,0.7465371483\H,-2.491472735,-2.1490682928,0.348766
7448\H,-0.147477766,-2.146284052,-0.4760305514\S,1.6758579827,0.,-1.00
96761223\N,2.4094991934,0.,0.7432064822\O,1.6242383546,0.,1.6159094046
\\Version=x86-Linux-G98RevA.11.1\State=1-A'\HF=-756.9551548\MP2=-758.4
227016\RMSD=9.034e-09\RMSF=8.776e-06\Dipole=-0.8181646,0.,0.263563\PG=
CS [SG(C2H1N1O1S1),X(C4H4)]\\@

C_6H_5SNO (*syn*) MP2/6-311+G(2df,p)

1\1\GINC-KOHN\FOpt\RMP2-FC\6-311+G(2df,p)\C6H5N1O1S1\JAMES\05-Jul-2003
\0\\# MP2/6-311+G(2DF,P) GEOM=CHECK GUESS=READ OPT=RCFC TEST\\c6h5sno-
cis-mp2b3: C6H5SNO Cs symmetry\\0,1\C,-0.0101975903,0.,-0.5353730632\C
,-0.6699977307,1.2108945433,-0.2947303859\C,-1.9831557159,1.206239725,
0.1641442599\C,-2.6413428551,0.,0.3945755719\C,-1.9831557159,-1.206239
725,0.1641442599\C,-0.6699977307,-1.2108945433,-0.2947303859\H,-0.1499
868685,2.1457766279,-0.4775090467\H,-2.4931123403,2.1467974258,0.34497
06087\H,-3.6651408747,0.,0.7534688231\H,-2.4931123403,-2.1467974258,0.
3449706087\H,-0.1499868685,-2.1457766279,-0.4775090467\S,1.6685565406,
0.,-1.0249120798\N,2.421335945,0.,0.7600889664\O,1.6315208824,0.,1.625
1746281\\Version=x86-Linux-G98RevA.11.1\State=1-A'\HF=-756.9779601\MP2
=-758.5168154\RMSD=4.456e-09\RMSF=5.523e-06\Dipole=-0.794787,0.,0.2938
853\PG=CS [SG(C2H1N1O1S1),X(C4H4)]\\@

C_6H_5SNO (*syn*) QCISD/6-311G(d,p)

1\1\GINC-KOHN\FOpt\RQCISD-FC\6-311G(d,p)\C6H5N1O1S1\JAMES\15-Jul-2003\
0\\# QCISD/6-311G(D,P) GEOM=CHECK OPT=RCFC MAXDISK=15500MB TEST\\c6h5s
no-cis-qb1: C6H5SNO Cs symmetry\\0,1\C,-0.0297699297,0.,-0.5114335004\
C,-0.6949622293,1.2135584279,-0.2765906075\C,-2.0251713811,1.212126537

3,0.1532850969\C,-2.6894410016,0.,0.3733877423\C,-2.0251713811,-1.2121
265373,0.1532850969\C,-0.6949622293,-1.2135584279,-0.2765906075\H,-0.1
729977246,2.1506224672,-0.4489518971\H,-2.5375503623,2.1547097113,0.32
64763783\H,-3.7233670765,0.,0.7083829852\H,-2.5375503623,-2.1547097113
,0.3264763783\H,-0.1729977246,-2.1506224672,-0.4489518971\S,1.66815531
5,0.,-1.0091560017\N,2.486557025,0.,0.7120435068\O,1.7506184936,0.,1.6
258375261\\Version=x86-Linux-G98RevA.11.1\State=1-A'\HF=-756.9391905\M
P2=-758.2707832\MP3=-758.287243\MP4D=-758.3270534\MP4DQ=-758.288178\MP
4SDQ=-758.3079204\QCISD=-758.3105479\RMSD=4.590e-09\RMSF=2.894e-06\Dip
ole=-0.8031322,0.,0.1017492\PG=CS [SG(C2H1N1O1S1),X(C4H4)]\\@

C_6H_5SNO (*syn*) B3LYP/6-311G(d,p)

1\1\GINC-KOHN\Freq\RB3LYP\6-311G(d,p)\C6H5N1O1S1\JAMES\03-Jul-2003\0\\
#N GEOM=ALLCHECK GUESS=TCHECK TEST RB3LYP/6-311G(D,P) FREQ\\c6h5sno-ci
s-b3lypb1: C6H5SNO Cs symmetry\\0,1\C,-0.0497696894,0.,-0.5118599755\C
,-0.7169584342,1.2109382453,-0.2839186732\C,-2.0403324786,1.2070475305
,0.1455902286\C,-2.7039089142,0.,0.3593976589\C,-2.0403324786,-1.20704
75305,0.1455902286\C,-0.7169584342,-1.2109382453,-0.2839186732\H,-0.19
69006962,2.145962705,-0.4529062051\H,-2.553021042,2.1471599273,0.31445
43687\H,-3.7352656313,0.,0.6931320223\H,-2.553021042,-2.1471599273,0.3
144543687\H,-0.1969006962,-2.145962705,-0.4529062051\S,1.6479963863,0.
,-1.0173412295\N,2.5391451887,0.,0.7355571765\O,1.8378391475,0.,1.6608
807903\\Version=x86-Linux-G98RevA.11.1\State=1-A'\HF=-759.8519028\RMSD
=3.174e-09\RMSF=2.213e-05\Dipole=-0.8507882,0.,0.1927961\PG=CS
[SG(C2H1N1O1S1),X(C4H4)]\\@

C_6H_5SNO (*syn*) B3LYP/6-311+G(2df,p)

1\1\GINC-KOHN\Freq\RB3LYP\6-311+G(2df,p)\C6H5N1O1S1\JAMES\04-Jul-2003\
0\\#N GEOM=ALLCHECK GUESS=TCHECK TEST RB3LYP/6-311+G(2DF,P) FREQ\\c6h5
sno-cis-b3lypb1: C6H5SNO Cs symmetry\\0,1\C,-0.0562420865,0.,-0.484878
4953\C,-0.725581602,1.2086492606,-0.2737320844\C,-2.0525964595,1.20469
28562,0.1346603031\C,-2.7170814402,0.,0.338820611\C,-2.0525964595,-1.2
046928562,0.1346603031\C,-0.725581602,-1.2086492606,-0.2737320844\H,-0
.2050045004,2.1440604749,-0.4358355533\H,-2.5679109534,2.1440028049,0.
294465973\H,-3.7525346502,0.,0.6570460668\H,-2.5679109534,-2.144002804
9,0.294465973\H,-0.2050045004,-2.1440604749,-0.4358355533\S,1.63859282
3,0.,-0.9795095554\N,2.5513843657,0.,0.6718135724\O,1.899908466,0.,1.6
425449567\\Version=x86-Linux-G98RevA.11.1\State=1-A'\HF=-759.8872553\R
MSD=1.736e-09\RMSF=6.052e-05\Dipole=-0.9581389,0.,-0.0318825\PG=CS
[SG(C2H1N1O1S1),X(C4H4)]\\@

C_6H_5SNO (*syn*) B3P86/6-311G(d,p)

1\1\GINC-KOHN\Freq\RB3P86\6-311G(d,p)\C6H5N1O1S1\JAMES\03-Jul-2003\0\\
#N GEOM=ALLCHECK GUESS=TCHECK TEST RB3P86/6-311G(D,P) FREQ\\c6h5sno-ci
s-b3p86b1: C6H5SNO Cs symmetry\\0,1\C,-0.0424439957,0.,-0.5082491609\C
,-0.7064462424,1.2083392564,-0.2812434976\C,-2.0267034077,1.2043925358
,0.1468190086\C,-2.6884210132,0.,0.3592768312\C,-2.0267034077,-1.20439
25358,0.1468190086\C,-0.7064462424,-1.2083392564,-0.2812434976\H,-0.18
4363889,2.1426569497,-0.4503374327\H,-2.5396935731,2.144407306,0.31567
12079\H,-3.7200071095,0.,0.6926106536\H,-2.5396935731,-2.144407306,0.3
156712079\H,-0.184363889,-2.1426569497,-0.4503374327\S,1.6455615164,0.
,-1.0036279241\N,2.5099731968,0.,0.7168776206\O,1.806538906,0.,1.64044
41352\\Version=x86-Linux-G98RevA.11.1\State=1-A'\HF=-761.1493026\RMSD=

5.150e-09\RMSF=2.033e-05\Dipole=-0.8820973,0.,0.1299495\PG=CS
[SG(C2H1N1O1S1),X(C4H4)]\\@

C_6H_5SNO (*syn*) B3P86/6-311+G(2df,p)

1\1\GINC-KOHN\Freq\RB3P86\6-311+G(2df,p)\C6H5N1O1S1\JAMES\05-Jul-2003\
0\\#N GEOM=ALLCHECK GUESS=TCHECK TEST RB3P86/6-311+G(2DF,P) FREQ\\c6h5
sno-cis-b3p86b1: C6H5SNO Cs symmetry\\0,1\C,-0.0484962761,0.,-0.484437
6105\C,-0.7138173009,1.2058857581,-0.2724707802\C,-2.0368621523,1.2020
071082,0.1370911204\C,-2.6991669732,0.,0.3412266882\C,-2.0368621523,-1
.2020071082,0.1370911204\C,-0.7138173009,-1.2058857581,-0.2724707802\H
,-0.1908376154,2.1404422142,-0.4354387112\H,-2.5520913091,2.1414071462
,0.2984215892\H,-3.7343918849,0.,0.661203645\H,-2.5520913091,-2.141407
1462,0.2984215892\H,-0.1908376154,-2.1404422142,-0.4354387112\S,1.6365
869863,0.,-0.9698232361\N,2.5202972408,0.,0.6596896627\O,1.8608637753,
0.,1.6244995238\\Version=x86-Linux-G98RevA.11.1\State=1-A'\HF=-761.184
233\RMSD=8.814e-10\RMSF=2.885e-05\Dipole=-0.9766145,0.,-0.0645969\
PG=CS [SG(C2H1N1O1S1),X(C4H4)]\\@

C_6H_5SNO (*syn*) CBS-QB3

1\1\GINC-BOHR\Mixed\CBS-QB3\CBS-QB3\C6H5N1O1S1\CRISTINA\01-Aug-2003\0\
\#CBS-QB3 OPT MAXDISK=25500MB TEST\\c6h5sno-cis-cbsqb3: C6H5SNO Cs sym
metry\\0,1\C,0.4991958611,-0.1102400833,0.\C,0.4888828611,0.5940029167
,1.211305\C,0.4888828611,1.9852809167,1.207293\C,0.4901708611,2.682189
9167,0.\C,0.4888828611,1.9852809167,-1.207293\C,0.4888828611,0.5940029
167,-1.211305\H,0.4875468611,0.0463559167,2.145741\H,0.4859068611,2.52
54989167,2.147127\H,0.4911718611,3.7661799167,0.\H,0.4859068611,2.5254
989167,-2.147127\H,0.4875468611,0.0463559167,-2.145741\S,0.4571508611,
-1.8770240833,0.\N,-1.4700561389,-2.1904480833,0.\O,-2.1414361389,-1.2
409340833,0.\\Version=x86-Linux-G98RevA.11.1\State=1-A'\HF/CbsB3=-756.
9826028\E2(CBS)/CbsB3=-1.6985617\CBS-Int/CbsB3=0.0515742\OIii/CbsB3=11
.5691123\MP2/CbsB4=-758.1795667\MP4(SDQ)/CbsB4=-758.2217459\MP4(SDQ)/6
-31+G(d')=-758.1517969\QCISD(T)/6-31+G(d')=-758.214555\CBSQB3=-758.704
8376\ PG=CS [SG(C2H1N1O1S1),X(C4H4)]\\@

$C_6H_5S^\bullet$ MP2/6-311G(d,p)

1\1\GINC-KOHN\Freq\UMP2-FC\6-311G(d,p)\C6H5S1(2)\JAMES\30-Jun-2003\0\\
MP2/6-311G(D,P) GEOM=CHECK GUESS=READ FREQ=NORAMAN MAXDISK=13650MB T
EST\\C6H5S radical\\0,2\C,0.5586410702,0.,0.\C,-0.1541819298,0.,1.2004
82\C,-1.5213539298,0.,1.199665\C,-2.2070929298,0.,0.\C,-1.5213539298,0
.,-1.199665\C,-0.1541819298,0.,-1.200482\H,0.3992410702,0.,2.13407\H,-
2.0673239298,0.,2.13751\H,-3.2928059298,0.,0.\H,-2.0673239298,0.,-2.13
751\H,0.3992410702,0.,-2.13407\S,2.2891320702,0.,0.\\Version=x86-Linux
-G98RevA.11.1\State=2-B1\HF=-627.6999634\MP2=-628.5836227\PUHF=-627.73
31724\PMP2-0=-628.613411\S2=1.243656\S2-1=1.116961\S2A=0.961575\RMSD=9
.165e-10\RMSF=9.191e-05\Dipole=-1.1998515,0.,0.\PG=C02V
[C2(H1C1C1S1),SGV(C4H4)]\\@

$C_6H_5S^\bullet$ MP2/6-311+G(2df,p)

1\1\GINC-KOHN\FOpt\UMP2-FC\6-311+G(2df,p)\C6H5S1(2)\JAMES\30-Jun-2003\
0\\# MP2/6-311+G(2DF,P) GUESS=READ OPT=RCFC GEOM=CHECK TEST\\C6H5S rad
ical\\0,2\C,0.5498724725,0.,0.\C,-0.1538540393,0.,1.1948364818\C,-1.51
48939933,0.,1.1935091705\C,-2.1959193646,0.,0.\C,-1.5148939933,0.,-1.1
935091705\C,-0.1538540393,0.,-1.1948364818\H,0.4004449363,0.,2.1263317
966\H,-2.0606853155,0.,2.129886233\H,-3.2802792858,0.,0.\H,-2.06068531

55,0.,-2.129886233\H,0.4004449363,0.,-2.1263317966\S,2.2813761118,0.,0
.\\Version=x86-Linux-G98RevA.11.1\State=2-B1\HF=-627.7230625\MP2=-628.
7514458\PUHF=-627.7539888\PMP2-0=-628.7789937\S2=1.198867\S2-1=1.07907
8\S2A=0.923784\RMSD=5.028e-09\RMSF=4.134e-05\Dipole=-1.1988823,0.,0.\P
G=C02V [C2(H1C1C1S1),SGV(C4H4)]\\@

$C_6H_5S^\bullet$ QCISD/6-311G(d,p)

1\1\GINC-KOHN\FOpt\UQCISD-FC\6-311G(d,p)\C6H5S1(2)\JAMES\01-Jul-2003\0
\\# QCISD/6-311G(D,P) GEOM=CHECK GUESS=READ OPT=RCFC TEST\\C6H5S radic
al\\0,2\C,0.5802209144,0.,0.\C,-0.1477465502,0.,1.2195461457\C,-1.5367
018279,0.,1.215419517\C,-2.2366193694,0.,0.\C,-1.5367018279,0.,-1.2154
19517\C,-0.1477465502,0.,-1.2195461457\H,0.404670868,0.,2.1547001733\H
,-2.0816326098,0.,2.155625823\H,-3.3234513874,0.,0.\H,-2.0816326098,0.
,-2.155625823\H,0.404670868,0.,-2.1547001733\S,2.3018216337,0.,0.\\Ver
sion=x86-Linux-G98RevA.11.1\State=2-B1\HF=-627.7023182\MP2=-628.581019
7\MP3=-628.6299875\MP4D=-628.6516003\MP4DQ=-628.6298715\PUHF=-627.7417
425\PMP2-0=-628.6167861\PMP3-0=-628.6592548\MP4SDQ=-628.6439276\QCISD=
-628.6587148\S2=1.343145\S2-1=1.199082\S2A=1.068883\RMSD=4.874e-09\RMS
F=8.597e-05\Dipole=-1.0684421,0.,0.\PG=C02V [C2(H1C1C1S1),SGV(C4H4)]\\
@

$C_6H_5S^\bullet$ B3LYP/6-311G(d,p)

1\1\GINC-KOHN\Freq\UB3LYP\6-311G(d,p)\C6H5S1(2)\JAMES\03-Jul-2003\0\\#
N GEOM=ALLCHECK GUESS=TCHECK TEST UB3LYP/6-311G(D,P) FREQ\\C6H5S radic
al\\0,2\C,0.5757928742,0.,0.\C,-0.1505475015,0.,1.2177260462\C,-1.5357
698343,0.,1.2125256714\C,-2.2328097328,0.,0.\C,-1.5357698343,0.,-1.212
5256714\C,-0.1505475015,0.,-1.2177260462\H,0.401698707,0.,2.149307014\
H,-2.0802574276,0.,2.1499109195\H,-3.31695532,0.,0.\H,-2.0802574276,0.
,-2.1499109195\H,0.401698707,0.,-2.149307014\S,2.3032488714,0.,0.\\Ver
sion=x86-Linux-G98RevA.11.1\State=2-B1\HF=-629.8926514\S2=0.766907\S2-
1=0.\S2A=0.750196\RMSD=5.168e-09\RMSF=1.879e-05\Dipole=-1.2933014,0.,0
.\ PG=C02V [C2(H1C1C1S1),SGV(C4H4)]\\@

$C_6H_5S^\bullet$ B3LYP/6-311+G(2df,p)

1\1\GINC-KOHN\Freq\UB3LYP\6-311+G(2df,p)\C6H5S1(2)\JAMES\03-Jul-2003\0
\\#N GEOM=ALLCHECK GUESS=TCHECK TEST UB3LYP/6-311+G(2DF,P) FREQ\\C6H5S
 radical\\0,2\C,0.5759089028,0.,0.\C,-0.1493811943,0.,1.2144662756\C,-
1.5317277734,0.,1.2095979135\C,-2.2274509629,0.,0.\C,-1.5317277734,0.,
-1.2095979135\C,-0.1493811943,0.,-1.2144662756\H,0.4019912601,0.,2.145
837586\H,-2.0756313765,0.,2.1464427141\H,-3.3108003398,0.,0.\H,-2.0756
313765,0.,-2.1464427141\H,0.4019912601,0.,-2.145837586\S,2.2962900342,
0.,0.\\Version=x86-Linux-G98RevA.11.1\State=2-B1\HF=-629.9129394\S2=0.
767446\S2-1=0.\S2A=0.750216\RMSD=6.952e-09\RMSF=1.049e-05\Dipole=-1.23
93009,0.,0.\ PG=C02V [C2(H1C1C1S1),SGV(C4H4)]\\@

$C_6H_5S^\bullet$ B3P86/6-311G(d,p)

1\1\GINC-KOHN\Freq\UB3P86\6-311G(d,p)\C6H5S1(2)\JAMES\04-Jul-2003\0\\#
N GEOM=ALLCHECK GUESS=TCHECK TEST UB3P86/6-311G(D,P) FREQ\\C6H5S radic
al\\0,2\C,0.5755971329,0.,0.\C,-0.1479934111,0.,1.2148562999\C,-1.5299
803062,0.,1.2098226698\C,-2.2248905487,0.,0.\C,-1.5299803062,0.,-1.209
8226698\C,-0.1479934111,0.,-1.2148562999\H,0.4065577139,0.,2.145571961
6\H,-2.0746555871,0.,2.1471861029\H,-3.3091591374,0.,0.\H,-2.074655587
1,0.,-2.1471861029\H,0.4065577139,0.,-2.1455719616\S,2.2922999991,0.,0
.\\Version=x86-Linux-G98RevA.11.1\State=2-B1\HF=-630.9260798\S2=0.7685

27\S2-1=0.\S2A=0.750236\RMSD=5.251e-09\RMSF=1.862e-05\Dipole=-1.273858
3,0.,0.\ PG=C02V [C2(H1C1C1S1),SGV(C4H4)]\\@

$C_6H_5S^\bullet$ B3P86/6-311+G(2df,p)

1\1\GINC-KOHN\Freq\UB3P86\6-311+G(2df,p)\C6H5S1(2)\JAMES\04-Jul-2003\0
\\#N GEOM=ALLCHECK GUESS=TCHECK TEST UB3P86/6-311+G(2DF,P) FREQ\\C6H5S
radical\\0,2\C,0.5753279681,0.,0.\C,-0.1468825378,0.,1.2117787009\C,-
1.5259482733,0.,1.2070448289\C,-2.2194337024,0.,0.\C,-1.5259482733,0.,
-1.2070448289\C,-0.1468825378,0.,-1.2117787009\H,0.4074130682,0.,2.142
1363929\H,-2.070279681,0.,2.1439560223\H,-3.303108407,0.,0.\H,-2.07027
9681,0.,-2.1439560223\H,0.4074130682,0.,-2.1421363929\S,2.2854653607,0
.,0.\\Version=x86-Linux-G98RevA.11.1\State=2-B1\HF=-630.9460489\S2=0.7
69354\S2-1=0.\S2A=0.750268\RMSD=4.555e-09\RMSF=1.059e-05\Dipole=-1.231
6278,0.,0.\ PG=C02V [C2(H1C1C1S1),SGV(C4H4)]\\@

$C_6H_5S^\bullet$ CBS-QB3

1\1\GINC-ANGSTROM\Mixed\CBS-QB3\CBS-QB3\C6H5S1(2)\CRISTINA\24-Jul-2003
\0\\# CBS-QB3 MAXDISK=550000MB TEST\\C6H5S-rad-cbsqb3\\0,2\C,0.,0.,0.5
764438338\C,0.,1.2176881272,-0.1493821908\C,0.,1.2124514688,-1.5342214
552\C,0.,0.,-2.2309945562\C,0.,-1.2124514688,-1.5342214552\C,0.,-1.217
6881272,-0.1493821908\H,0.,2.148691274,0.4034785305\H,0.,2.1495518698,
-2.0788512534\H,0.,0.,-3.3149992637\H,0.,-2.1495518698,-2.0788512534\H
,0.,-2.148691274,0.4034785305\S,0.,0.,2.2997682998\\Version=x86-Linux-
G98RevA.11.1\State=2-B1\HF/CbsB3=-627.729614\E2(CBS)/CbsB3=-1.1376418\
CBS-Int/CbsB3=0.0354434\OIii/CbsB3=8.1232163\MP2/CbsB4=-628.5263292\MP
4(SDQ)/CbsB4=-628.592679\MP4(SDQ)/6-31+G(d')=-628.5258297\QCISD(T)/6-3
1+G(d')=-628.5812117\CBSQB3=-628.916567\PG=C02V C2(H1C1C1S1),SGV(C4H4)]
\\@

CysSNO (*syn*) MP2/6-311G(d,p)

1\1\GINC-KOHN\Freq\RMP2-FC\6-311G(d,p)\C3H6N2O3S1\JAMES\19-Jul-2003\0\
\#N GEOM=ALLCHECK GUESS=TCHECK TEST RMP2(FC)/6-311G(D,P) FREQ\\cys-sno
-6-mp2b1\\0,1\S,1.8612542156,-0.9060870515,0.2014506951\C,0.3441200902
,-0.0723393078,0.6550623519\C,-0.800853792,-0.3540351228,-0.3135226306
\N,-1.2337324383,-1.7513144355,-0.4081109002\C,-2.0146163862,0.5305801
446,0.0286288323\O,-1.9039829456,1.6510514215,0.4639451616\O,-3.189528
0598,-0.0525039299,-0.2405503698\H,-2.9384536709,-0.9540524006,-0.5298
381802\N,2.8960650671,0.6608785244,-0.3420635558\O,2.3478007651,1.6897
480067,-0.2408379302\H,0.5462324421,1.009433352,0.6521488873\H,0.05945
35552,-0.3455688403,1.6761460156\H,-0.4888962171,-0.0413099516,-1.3177
848717\H,-1.1702399899,-2.1994038249,0.5024881399\H,-0.6307095195,-2.2
70252404,-1.0366161363\\Version=x86-Linux-G98RevA.11.1\HF=-848.1362677
\MP2=-849.6608366\RMSD=2.593e-09\RMSF=5.748e-07\Dipole=0.6623921,-1.19
23489,-0.2932493\PG=C01 [X(C3H6N2O3S1)]\\@

CysSNO (*syn*) MP2/6-311G(df,p)

1\1\GINC-KOHN\FOpt\RMP2-FC\6-311G(df,p)\C3H6N2O3S1\JAMES\20-Jul-2003\0
\\# MP2/6-311G(DF,P) GEOM=CHECK GUESS=READ OPT=RCFC MAXDISK=15500MB TE
ST\\cys-sno-6-mp2b1\\0,1\S,1.9151768486,-0.8101867903,0.4803304806\C,0
.3531223455,-0.0179309089,0.8420847872\C,-0.6937759085,-0.2601151429,-
0.2394526782\N,-1.0746347576,-1.6488219266,-0.4693472666\C,-1.95464766
57,0.5659533719,0.0675543974\O,-1.916300773,1.630964994,0.6252044259\O
,-3.0770764878,-0.0030163378,-0.372413817\H,-2.7829132277,-0.868740933
7,-0.7168635255\N,2.6602263146,0.4175906845,-0.5902491503\O,2.00806609

92,1.3966299459,-0.8110395291\H,0.5265840912,1.0589932242,0.9345364903
\H,0.0032616224,-0.3916600415,1.810234819\H,-0.3124387271,0.1395649144
,-1.1873921312\H,-1.1123976949,-2.1612502218,0.4064109894\H,-0.4097698
756,-2.1193723394,-1.0701670905\\Version=x86-Linux-G98RevA.11.1\HF=-84
8.1619707\MP2=-849.8373057\RMSD=4.472e-09\RMSF=7.109e-06\Dipole=0.4271
743,-1.5691165,-0.0982347\PG=C01 [X(C3H6N2O3S1)]\\@

CysSNO (*syn*) MP2/6-311+G(2df,p)

1\1\GINC-KOHN\FOpt\RMP2-FC\6-311+G(2df,p)\C3H6N2O3S1\JAMES\23-Jul-2003
\0\\# MP2/6-311+G(2DF,P) GEOM=CHECK GUESS=READ OPT=RCFC MAXDISK=15500M
B TEST\\cys-sno-6-mp2b3\\0,1\S,1.9186879404,-0.8088435836,0.4879443248
\C,0.3500367032,-0.0100936916,0.8435927687\C,-0.6944812537,-0.25256555
46,-0.2404731939\N,-1.0643757689,-1.6437528383,-0.4773428647\C,-1.9547
369683,0.5641686675,0.0718780762\O,-1.9240927704,1.6319928142,0.630075
8601\O,-3.0838459758,-0.0032823479,-0.3649805616\H,-2.8058991496,-0.87
28951482,-0.7286200363\N,2.6648084909,0.4076192964,-0.6002871231\O,2.0
069108267,1.3857638372,-0.8277638739\H,0.5312118484,1.0630174158,0.954
5815003\H,0.0067632531,-0.3933270915,1.8094062233\H,-0.3185130212,0.15
13983852,-1.187184737\H,-1.133415068,-2.1615237609,0.3957255365\H,-0.3
788714938,-2.1170886264,-1.0562450707\\Version=x86-Linux-G98RevA.11.1\
HF=-848.1898765\MP2=-849.9548136\RMSD=3.249e-09\RMSF=3.995e-05\Dipole=
0.4561477,-1.6174549,-0.047424\PG=C01 [X(C3H6N2O3S1)]\\@

CysSNO (*syn*) B3LYP/6-31G(d)

1\1\GINC-ANGSTROM\Freq\RB3LYP\6-31G(d)\C3H6N2O3S1\CRISTINA\19-Jun-2003
\0\\#N GEOM=ALLCHECK GUESS=TCHECK RB3LYP/6-31G(D) FREQ\\cys-sno-6-b6\\
0,1\S,1.8329892687,-0.9633258785,0.2520437642\C,0.3320717743,-0.015428
6909,0.6486961094\C,-0.8448482511,-0.3195904258,-0.2888698049\N,-1.349
2068988,-1.7004625616,-0.2879455905\C,-2.0205965829,0.6439446199,0.011
5310743\O,-1.860544659,1.7798702721,0.3902536384\O,-3.2243615236,0.104
5167102,-0.2240794944\H,-3.0421645319,-0.8345728423,-0.4769289849\N,2.
9737412854,0.4089892039,-0.3896653437\O,2.5265040342,1.5014085153,-0.3
893711833\H,0.5958911386,1.0475516018,0.5699889698\H,0.0638514505,-0.2
110628619,1.6924319205\H,-0.5365433309,-0.0965274346,-1.3182495492\H,-
1.3518512269,-2.0856187428,0.6563300768\H,-0.7612969609,-2.3061591605,
-0.8555640804\\Version=x86-Linux-G98RevA.11.1\HF=-851.2207495\RMSD=5.3
98e-09\RMSF=4.035e-05\Dipole=0.3401741,-1.6036542,-0.107353\ PG=C0
1[X(C3H6N2O3S1)]\\@

CysSNO (*syn*) B3LYP/6-31+G(d)

1\1\GINC-ANGSTROM\Freq\RB3LYP\6-31+G(d)\C3H6N2O3S1\CRISTINA\21-Jun-200
3\0\\#N GEOM=ALLCHECK GUESS=TCHECK RB3LYP/6-31+G(D) FREQ\\cys-sno-6-b7
\\0,1\S,1.8378466968,-0.9490116803,0.3191915219\C,0.3266594683,-0.0017
732578,0.6873744629\C,-0.8304054356,-0.3024690088,-0.279612922\N,-1.31
77709327,-1.6887540895,-0.3033437687\C,-2.019929499,0.6501376072,0.004
7134286\O,-1.8767572716,1.7951317367,0.3664679005\O,-3.2219431414,0.09
97470818,-0.2243152543\H,-3.0478184497,-0.8419127157,-0.4708374856\N,2
.9516275817,0.3630612934,-0.421175209\O,2.5095338721,1.4589330316,-0.4
936489932\H,0.5866196779,1.0630966956,0.6312082718\H,0.0380946751,-0.2
161012511,1.7225672891\H,-0.5050813725,-0.0611201995,-1.2996300193\H,-
1.3079823667,-2.1076685732,0.6261362642\H,-0.7509907309,-2.2781243438,
-0.9077548684\\Version=x86-Linux-G98RevA.11.1\HF=-851.2451938\RMSD=4.1
46e-09\ PG=C01[X(C3H6N2O3S1)]\\@

CysSNO (*syn*) B3LYP/6-311G(d,p)

1\1\GINC-VLAD\Freq\RB3LYP\6-311G(d,p)\C3H6N2O3S1\CRISTINA\15-Jan-2003\
0\\#N GEOM=ALLCHECK GUESS=TCHECK RB3LYP/6-311G(D,P) FREQ\\cys-sno-6 an
other config.\\0,1\S,-0.4301116581,0.5343288295,-1.9738089205\C,-0.371
0705325,0.6156318469,-0.1612164966\C,0.8316678052,-0.116330486,0.44650
9349\N,2.1604357389,0.4007159677,0.0946290473\C,0.6961207787,-0.171617
6279,1.9887349468\O,-0.3619675458,-0.2580215162,2.550459707\O,1.871999
6342,-0.1492748071,2.6265940847\H,2.5470270853,-0.0300940964,1.9237307
595\N,-1.9493672775,-0.6119986177,-2.2328328017\O,-2.4899883032,-0.983
3977855,-1.2675985992\H,-1.2960229591,0.1571547069,0.2065284693\H,-0.3
839439053,1.6664360255,0.1377664493\H,0.7993840004,-1.1619988392,0.122
2591544\H,2.1596500794,1.415126627,0.0368087918\H,2.4775544093,0.04254
33257,-0.7985329495\\Version=x86-Linux-G98RevA.11.1\HF=-851.386668\RMS
D=6.559e-09\RMSF=1.500e-05\Dipole=1.0319586,0.4389573,-1.1702445\PG=C0
1[X(C3H6N2O3S1)]\\@

CysSNO (*syn*) B3LYP/6-311+G(2df,p)

1\1\GINC-HAMMERHEAD3\Freq\RB3LYP\6-311+G(2df,p)\C3H6N2O3S1\JGAULD\23-J
an-2003\0\\#N GEOM=ALLCHECK GUESS=TCHECK RB3LYP/6-311+G(2DF,P) FREQ\\c
ys-sno-6 another config.\\0,1\S,-0.4788510706,0.5869257109,-1.94822003
98\C,-0.3949411635,0.643819896,-0.1401818805\C,0.8014205559,-0.1151088
784,0.4451427421\N,2.1288108627,0.3734043573,0.0638625696\C,0.68871266
97,-0.1710052228,1.9867973506\O,-0.3594843454,-0.2550789137,2.56431598
83\O,1.8690095029,-0.1571860682,2.6147829911\H,2.5482383828,-0.0467230
373,1.9151787623\N,-1.8582950112,-0.6176708607,-2.2420234645\O,-2.3817
892361,-1.0764877034,-1.2962157883\H,-1.32617297,0.2101254944,0.235542
9362\H,-0.3755871891,1.6940069257,0.1588243097\H,0.7397288669,-1.15933
45005,0.1235027982\H,2.157662999,1.3863959962,-0.0011352484\H,2.431096
3355,-0.0016300152,-0.8268814587\\Version=DEC-AXP-Linux-G98RevA.11\HF=
-851.4288042\RMSD=5.706e-09\RMSF=2.314e-06\Dipole=1.1472454,0.5768869,
-1.1949869\PG=C01 [X(C3H6N2O3S1)]\\@

CysSNO (*syn*) B3P86/6-311G(d,p)

1\1\GINC-VLAD\Freq\RB3P86\6-311G(d,p)\C3H6N2O3S1\CRISTINA\19-Jan-2003\
0\\#N GEOM=ALLCHECK GUESS=TCHECK RB3P86/6-311G(D,P) FREQ\\cys-sno-6 an
other config.\\0,1\S,-0.4321304993,0.5407234823,-1.9549585711\C,-0.379
1872093,0.6129224918,-0.1585235293\C,0.81549176,-0.1210952557,0.441201
748\N,2.1385256473,0.3876113881,0.0902602511\C,0.6852970682,-0.1738639
625,1.975641479\O,-0.3699016112,-0.2632323979,2.5388270727\O,1.8600522
19,-0.1431907458,2.5989900274\H,2.5188170539,-0.0194992828,1.878428422
2\N,-1.9052581137,-0.6000187875,-2.2182070778\O,-2.4455845576,-0.98255
0728,-1.2566467972\H,-1.3057152224,0.1491255888,0.2039731014\H,-0.3948
289499,1.6611806876,0.1502955513\H,0.7756028875,-1.1675702554,0.118752
6748\H,2.1381922715,1.40003556,0.0178006066\H,2.4630090992,0.016015113
9,-0.7935660413\\Version=x86-Linux-G98RevA.11.1\HF=-852.793202\RMSD=3.
221e-09\RMSF=2.148e-06\Dipole=1.1030403,0.4897668,-1.1992063\PG=C01 [X
(C3H6N2O3S1)]\\@

CysSNO (*syn*) B3P86/6-311+G(2df,p)

1\1\GINC-KOHN\Freq\RB3P86\6-311+G(2df,p)\C3H6N2O3S1\CRISTINA\21-Jan-20
03\0\\#N GEOM=ALLCHECK GUESS=TCHECK RB3P86/6-311+G(2DF,P) FREQ\\cys-sn
o-6 another config.\\0,1\S,-0.4653145675,0.572896799,-1.9324058267\C,-
0.3974165312,0.6252425054,-0.1405962726\C,0.7947381072,-0.1245894195,0
.442526699\N,2.1142844933,0.3655097613,0.0663502903\C,0.6824174162,-0.

1745193972,1.9763132369\O,-0.3639422842,-0.2713686176,2.5516639507\O,1
.8596346326,-0.1362759289,2.5923369621\H,2.5212481689,-0.0174306979,1.
8740104002\N,-1.8389960625,-0.590386098,-2.2309525595\O,-2.3779363509,
-1.0378118652,-1.2889708133\H,-1.3285015629,0.1765785126,0.2239858335\
H,-0.3929603875,1.6727677808,0.1695914109\H,0.7347108802,-1.1706005861
,0.124395968\H,2.1336335398,1.3764632349,-0.0178565608\H,2.4294014927,
-0.0231435108,-0.8131207164\\Version=x86-Linux-G98RevA.11.1\HF=-852.83
40515\RMSD=4.501e-09\RMSF=2.788e-06\Dipole=1.1884943,0.5989109,-1.2063
188\PG=C01 [X(C3H6N2O3S1)]\\@

CysSNO (*syn*) CBS-4M

1\1\GINC-ANGSTROM\Mixed\CBS-4M\CBS-4M\C3H6N2O3S1\JAMES\30-Jul-2003\0\\
CBS-4M MAXDISK=16900MB\\cys-sno-6\\0,1\S,1.9575943229,-0.7110606849,
0.5875913505\C,0.3484302598,0.055921365,0.8802297377\C,-0.6686028133,-
0.2045766656,-0.2394030927\N,-1.0045264204,-1.6073679585,-0.502236202\
C,-1.9640294922,0.5490694969,0.0854602072\O,-1.987738101,1.5625181788,
0.7277305586\O,-3.0571277673,-0.0193529898,-0.4390829134\H,-2.82334296
15,-0.8780421422,-0.8364249071\N,2.6305852872,0.3047690394,-0.63140266
63\O,1.9409427054,1.2322867929,-1.0169545262\H,0.4732009458,1.12029442
11,0.99957202\H,-0.0077544433,-0.3487293274,1.8198657838\H,-0.28370462
77,0.2219353465,-1.1556633077\H,-1.1314878363,-2.1606369967,0.32849641
12\H,-0.3942347337,-2.0657589427,-1.153101595\\Version=x86-Linux-G98Re
vA.11.1\HF/CbsB1=-848.1891867\HF/CbsB2=-848.0260443\MP2/CbsB2=-849.492
0385\E2(CBS)/CbsB2=-1.867916\CBS-Int/CbsB2=0.1002581\OIii/CbsB2=16.234
5321\MP2/6-31G=-848.6635192\MP4(SDQ)/6-31G=-848.6965832\CBS4M=-850.218
9326\ PG=C01 [X(C3H6N2O3S1)]\\@

CysSNO (*syn*) CBS-QB3

1\1\GINC-POPLE\Mixed\CBS-QB3\CBS-QB3\C3H6N2O3S1\JAMES\08-Aug-2003\0\\#
 CBS-QB3 MAXDISK=13650MB TEST\\cys-sno-6-cbsq\\0,1\S,1.8880793432,-0.8
670665275,0.2219628766\C,0.3308794189,-0.0571870384,0.6677824615\C,-0.
8162048508,-0.3539591882,-0.3067182999\N,-1.2370193797,-1.7565750407,-
0.4169647039\C,-2.0460832183,0.5234634199,0.0360129854\O,-1.9541528222
,1.634255321,0.483301511\O,-3.2139626665,-0.0646507126,-0.2480670964\H
,-2.9830342476,-0.9696758527,-0.5503912784\N,2.9254038276,0.627012176,
-0.3513337044\O,2.4067078558,1.6732196349,-0.2964976338\H,0.528083588,
1.0206523759,0.67766275\H,0.0684033061,-0.3521341307,1.6868434361\H,-0
.5091783633,-0.0329927513,-1.3077918907\H,-1.2054870463,-2.2256985924,
0.4836730588\H,-0.6470348994,-2.2766436618,-1.0556703726\\Version=x86-
Linux-G98RevA.11.1\HF/CbsB3=-848.191535\E2(CBS)/CbsB3=-1.9557647\CBS-I
nt/CbsB3=0.0575706\OIii/CbsB3=14.0259956\MP2/CbsB4=-849.5245189\MP4(SD
Q)/CbsB4=-849.5749923\MP4(SDQ)/6-31+G(d')=-849.4848677\QCISD(T)/6-31+G
(d')=-849.5385772\CBSQB3=-850.1695932\ PG=C01 [X(C3H6N2O3S1)]\\@

CysSNO (*syn*) CBS-Q

1\1\GINC-POPLE\Mixed\CBS-Q\CBS-Q\C3H6N2O3S1\JAMES\06-Aug-2003\0\\# CBS
-Q MAXDISK=13650MB TEST\\cys-sno-6-cbsq\\0,1\S,1.8716099282,-0.8898639
242,0.181806666\C,0.3447366712,-0.061252574,0.6449408404\C,-0.80820922
79,-0.361299272,-0.3151654395\N,-1.2342541095,-1.7617418652,-0.4041682
858\C,-2.0282230224,0.5143326244,0.0395478677\O,-1.9253904045,1.622810
1486,0.5128100893\O,-3.2029778958,-0.0542781832,-0.2639864067\H,-2.979
3971521,-0.9556899304,-0.5868898781\N,2.9135528946,0.6654771501,-0.341
3711547\O,2.3708961533,1.7017398088,-0.2303521283\H,0.5421424606,1.025
1007274,0.6411150131\H,0.0764446221,-0.3343692228,1.6745706413\H,-0.50

66384065,-0.0548492834,-1.3290587894\H,-1.2388822445,-2.1861544795,0.5
218713868\H,-0.5845689752,-2.295220882,-0.9754509929\\Version=x86-Linu
x-G98RevA.11.1\HF/CbsB3=-848.1860294\MP2/CbsB3=-849.9694962\E2(CBS)/Cb
sB3=-1.9650298\CBS-Int/CbsB3=0.0581819\OIii/CbsB3=14.0014829\MP2/CbsB4
=-849.5247968\MP4(SDQ)/CbsB4=-849.5745096\MP4(SDQ)/6-31+G(d')=-849.484
6552\QCISD(T)/6-31+G(d')=-849.5424016\CBSQ=-850.1679572\PG=C01
[X(C3H6N2O3S1)]\\@

CysSNO (*syn*) G3(MP2)

1\1\GINC-KOHN\Mixed\G3MP2\G3MP2\C3H6N2O3S1\JAMES\30-Jul-2003\0\\# G3MP
2 MAXDISK=16900MB\\cys-sno-6-g3\\0,1\S,1.9275415587,-0.8098542548,0.48
6734527\C,0.3541376092,-0.0124376771,0.8433438919\C,-0.6921152735,-0.2
549558939,-0.2402895283\N,-1.0684308214,-1.6479236953,-0.4831573573\C,
-1.9596770991,0.5522817738,0.0761679057\O,-1.937774449,1.6109236685,0.
6729409715\O,-3.0869404956,-0.0041708704,-0.3989926238\H,-2.8021997632
,-0.8716466627,-0.7829954778\N,2.6775362471,0.4270362523,-0.6049424472
\O,1.9969390638,1.408998669,-0.8255424624\H,0.5257678427,1.0630375178,
0.9467794589\H,0.0067764236,-0.3900328283,1.810591225\H,-0.3124111959,
0.1459760617,-1.1881227496\H,-1.1648834013,-2.1500678297,0.3999994047\
H,-0.3493171974,-2.1287270338,-1.0198863605\\Version=x86-Linux-G98RevA
.11.1\MP2/6-31G(d)=-849.3805017\QCISD(T)/6-31G(d)=-849.4812965\MP2/GTM
P2Large=-849.9721049\G3MP2=-850.2099242\ PG=C01 [X(C3H6N2O3S1)]\\@

CysS$^{\bullet}$ MP2/6-311G(d,p)

1\1\GINC-KOHN\FOpt\UMP2-FC\6-311G(d,p)\C3H6N1O2S1(2)\CRISTINA\21-Jun-2
003\0\\# MP2/6-311G(D,P) OPT\\cys-s-6-rad-mp2b1\\0,2\S,2.4356856223,-0
.704963596,0.1730910778\C,0.9633059997,0.2400857859,0.6090512891\C,-0.
1666486418,-0.0725186111,-0.381718821\N,-0.6399864664,-1.459747186,-0.
3981280568\C,-1.3600164244,0.8670410347,-0.0993806313\O,-1.2203768495,
2.0172742152,0.2357964464\O,-2.5450735694,0.2809621933,-0.2973668775\H
,-2.3073964402,-0.6475737942,-0.50799432\H,1.1561373303,1.3121454796,0
.574706926\H,0.6267054447,-0.0349022742,1.614710048\H,0.1675493367,0.1
82157379,-1.3950821832\H,-0.5132045506,-1.8865971428,0.5154750268\H,-0
.1170980633,-2.0211223344,-1.0595239164\\Version=x86-Linux-G98RevA.11.
1\HF=-718.8797302\MP2=-719.9950899\PUHF=-718.8824395\PMP2-0=-719.99660
12\S2=0.759034\S2-1=0.751029\S2A=0.750029\RMSD=6.014e-09\RMSF=3.580e-0
5\Dipole=0.4911537,-1.4023555,-0.1690359\PG=C01 [X(C3H6N1O2S1)]\\@

CysS$^{\bullet}$ MP2/6-311+G(2df,p)

1\1\GINC-CURIE\FOpt\UMP2-FC\6-311+G(2df,p)\C3H6N1O2S1(2)\JAMES\27-Jul-
2003\0\\# MP2/6-311+G(2DF,P) MAXDISK=15000MB OPT TEST\\cys-s-6-rad-mp2
b3\\0,2\S,-2.5599232442,-0.1664424689,-0.0742902784\C,-0.8773872523,-0
.6471944226,0.3182081056\C,0.1834752359,0.2339665486,-0.3269637216\N,0
.1522406937,1.6422740733,0.0556503009\C,1.5778150808,-0.3408619891,-0.
0551823407\O,1.7962917817,-1.5252881762,0.0094502897\O,2.5313047135,0.
588199396,0.0654801612\H,2.0553116012,1.4461512927,-0.0012938252\H,-0.
7495365694,-1.6886848016,0.0053189549\H,-0.7671208607,-0.6493018554,1.
4096684936\H,0.0570074216,0.190935169,-1.4145844888\H,-0.0628803478,1.
7466266078,1.0449931535\H,-0.5638845421,2.1426839964,-0.4608258076\\Ve
rsion=x86-Linux-G03RevB.03\State=2-A\HF=-718.9157257\MP2=-720.2138102\
PUHF=-718.919405\PMP2-0=-720.2160045\S2=0.7642\S2-1=0.752706\S2A=0.750
064\RMSD=1.613e-09\RMSF=5.456e-05\Dipole=-0.9829034,1.1357309,0.068879
2\PG=C01 [X(C3H6N1O2S1)]\\@

CysS• B3LYP/6-31G(d)

1\1\GINC-ANGSTROM\Freq\UB3LYP\6-31G(d)\C3H6N1O2S1(2)\CRISTINA\21-Jun-2
003\0\\#N GEOM=ALLCHECK GUESS=TCHECK UB3LYP/6-31G(D) FREQ\\cys-s-6-rad
-b6\\0,2\S,2.4889072287,-0.7383615823,0.1671873522\C,0.9870642647,0.20
80791846,0.5403000046\C,-0.2011576622,-0.0833532866,-0.3864220627\N,-0
.7094843323,-1.4614826567,-0.3800882897\C,-1.3675225294,0.886746033,-0
.084791609\O,-1.1975473384,2.0239932457,0.287994477\O,-2.5775190858,0.
3561365308,-0.3107787597\H,-2.4038291907,-0.5832079395,-0.5678244523\H
,1.237820955,1.275312933,0.5035789096\H,0.7225895275,0.0113827354,1.58
95293923\H,0.1051518014,0.134686857,-1.4175339807\H,-0.7265009516,-1.8
343514227,0.5694605074\H,-0.1011305206,-2.069529047,-0.9238337189\\Ver
sion=x86-Linux-G98RevA.11.1\HF=-721.2849384\S2=0.752541\S2-1=0.\S2A=0.
750003\RMSD=7.058e-10\RMSF=3.528e-06\Dipole=0.4239569,-1.3939443,-0.13
77191\ PG=C01 [X(C3H6N1O2S1)]\\@

CysS• B3LYP/6-31+G(d)

1\1\GINC-ANGSTROM\Freq\UB3LYP\6-31+G(d)\C3H6N1O2S1(2)\CRISTINA\21-Jun-
2003\0\\#N GEOM=ALLCHECK GUESS=TCHECK UB3LYP/6-31+G(D) FREQ\\cys-s-6-r
ad-b7\\0,2\S,2.4601918915,-0.7449454757,0.1741601391\C,0.9718433187,0.
2123182552,0.6086182013\C,-0.1803661814,-0.0942099355,-0.3763077853\N,
-0.7005590858,-1.4680940537,-0.3580728103\C,-1.3485264197,0.9002073252
,-0.1189856657\O,-1.1760915025,2.0694537425,0.1358933776\O,-2.56087207
01,0.3447944507,-0.2437353687\H,-2.3974857714,-0.6154964385,-0.4268747
86\H,1.1781375593,1.2838472696,0.5702732524\H,0.6539490404,-0.05233884
18,1.6249631327\H,0.1585335231,0.1213569485,-1.3977243226\H,-0.5887198
914,-1.8979331241,0.5591678359\H,-0.2255668476,-2.0675292426,-1.027070
2379\\Version=x86-Linux-G98RevA.11.1\HF=-721.3003806\S2=0.75277\S2-1=0
.\S2A=0.750004\RMSD=2.402e-10\RMSF=3.406e-06\Dipole=0.436328,-1.551399
3,-0.1251246\ PG=C01 [X(C3H6N1O2S1)]\\@

CysS• B3LYP/6-311G(d,p)

1\1\GINC-VLAD\Freq\UB3LYP\6-311G(d,p)\C3H6N1O2S1(2)\CRISTINA\16-Jan-20
03\0\\#N GEOM=ALLCHECK GUESS=TCHECK UB3LYP/6-311G(D,P) FREQ\\cys-s-rad
6\\0,2\S,-0.9855924382,0.3333876674,-2.3848075128\C,-0.8888786916,0.41
80189705,-0.5796622816\C,0.3108191884,-0.3072204207,0.040170023\N,1.63
74044607,0.2142294392,-0.3093038752\C,0.16974889,-0.363205271,1.579504
4125\O,-0.8917703292,-0.4548540637,2.1356540064\O,1.3414569369,-0.3362
693758,2.2247252784\H,2.0201406769,-0.2193830506,1.5250417023\H,-1.820
429044,0.0032418006,-0.1811289721\H,-0.8997128602,1.4769643732,-0.2936
452315\H,0.2834029673,-1.3525444477,-0.2854466359\H,1.6345032753,1.229
733389,-0.3527190142\H,1.9421135884,-0.1283929744,-1.2131617188\\Versi
on=x86-Linux-G98RevA.11.1\HF=-721.4148569\S2=0.75271\S2-1=0.\S2A=0.750
004\RMSD=2.752e-10\RMSF=5.682e-06\Dipole=0.8976883,0.367379,-1.1134221
\ PG=C01 [X(C3H6N1O2S1)]\\@

CysS• B3LYP/6-311+G(2df,p)

1\1\GINC-HAMMERHEAD13\Freq\UB3LYP\6-311+G(2df,p)\C3H6N1O2S1(2)\JGAULD\
19-Jan-2003\0\\#N GEOM=ALLCHECK GUESS=TCHECK UB3LYP/6-311+G(2DF,P) FRE
Q\\cys-s-rad6\\0,2\S,-0.950907348,0.3389522329,-2.359062088\C,-0.90584
75188,0.4709765095,-0.552814599\C,0.300884156,-0.2974230426,0.02139086
79\N,1.6225320245,0.2320683283,-0.3199575933\C,0.1542698388,-0.3933687
267,1.5635299069\O,-0.8942166447,-0.5912002545,2.1115083494\O,1.312748
1996,-0.2737586488,2.2151938382\H,1.9897907037,-0.0948361643,1.5242957
796\H,-1.8123473856,0.0561532561,-0.1169136884\H,-0.8237448058,1.52481

32472,-0.2719041044\H,0.2553894287,-1.3343066078,-0.3260048255\H,1.597
8444836,1.2345274729,-0.4777585244\H,2.0057696769,-0.195502444,-1.1532
726299\\Version=DEC-AXP-Linux-G98RevA.11\HF=-721.4401605\S2=0.753995\S
2-1=0.\S2A=0.750008\RMSD=3.624e-09\RMSF=1.127e-05\Dipole=0.9495555,0.4
330363,-1.1615009\ PG=C01 [X(C3H6N1O2S1)]\\@

CysS• B3P86/6-311G(d,p)

1\1\GINC-HAMMERHEAD4\Freq\UB3P86\6-311G(d,p)\C3H6N1O2S1(2)\JGAULD\18-J
an-2003\0\\#N GEOM=ALLCHECK GUESS=TCHECK UB3P86/6-311G(D,P) FREQ\\cys-
s-rad6\\0,2\S,-0.9676571354,0.3437534605,-2.3676638741\C,-0.8858609971
,0.4137922086,-0.5770131883\C,0.3049077354,-0.3109564263,0.0396534871\
N,1.6255314283,0.2058452092,-0.304840248\C,0.1644958165,-0.3662298484,
1.5703820557\O,-0.8956748179,-0.4669206525,2.1244358684\O,1.3325342902
,-0.3256413159,2.2053965287\H,1.9966603167,-0.2020485843,1.4898504916\
H,-1.8192760655,-0.0032539786,-0.182588778\H,-0.9019950242,1.470180960
2,-0.2793598631\H,0.273569058,-1.3569468011,-0.2853706166\H,1.61939253
13,1.2196512391,-0.362535184\H,1.9393122446,-0.1476945235,-1.200285632
2\\Version=DEC-AXP-Linux-G98RevA.11\HF=-722.5572713\S2=0.752816\S2-1=0
.\S2A=0.750004\RMSD=3.796e-10\RMSF=4.674e-05\Dipole=0.9015151,0.374480
5,-1.1489463\ PG=C01 [X(C3H6N1O2S1)]\\@

CysS• B3P86/6-311+G(2df,p)

1\1\GINC-FLEXOR\Freq\UB3P86\6-311+G(2df,p)\C3H6N1O2S1(2)\GAULD\22-Jan-
2003\0\\#N GEOM=ALLCHECK GUESS=TCHECK UB3P86/6-311+G(2DF,P) FREQ\\cys-
s-rad6\\0,2\S,-0.924593429,0.3498216027,-2.3396005241\C,-0.9063820853,
0.4666569692,-0.5477847922\C,0.2916077616,-0.3029212143,0.0193999214\N
,1.6076265101,0.223556443,-0.3154624888\C,0.1461449135,-0.3968210458,1
.5536992333\O,-0.8998885849,-0.6020650434,2.1001352987\O,1.3012371266,
-0.2619260735,2.1920411784\H,1.9599921882,-0.0766593145,1.4808187655\H
,-1.8131511576,0.0440698077,-0.1172959628\H,-0.8269318846,1.5171535505
,-0.2515984774\H,0.2410924113,-1.339780814,-0.3295237646\H,1.576942357
2,1.221407881,-0.495106923\H,2.0031535073,-0.2177911756,-1.1347458218\
\Version=SGI64-G98RevA.7\HF=-722.5813424\S2=0.75439\S2-1=0.\S2A=0.7500
09\RMSD=1.802e-09\RMSF=1.225e-05\Dipole=0.9540893,0.430554,-1.1784603\
PG=C01 [X(C3H6N1O2S1)]\\@

CysS• CBS-4M

1\1\GINC-ANGSTROM\Mixed\CBS-4M\CBS-4M\C3H6N1O2S1(2)\JAMES\31-Jul-2003\
0\\# CBS-4M\\cys-s-6-rad-cbs4m\\0,2\S,-2.5585406703,-0.1817351496,-0.0
845723626\C,-0.8672582637,-0.6883281957,0.3450211879\C,0.1680429978,0.
230780471,-0.3314469777\N,0.143504383,1.6393101117,0.0865673687\C,1.57
29695699,-0.3332048942,-0.0640979883\O,1.7998495059,-1.5093455863,0.01
16512273\O,2.5129104041,0.6124134944,0.0407155768\H,2.0891834796,1.491
9677718,0.0303020442\H,-0.6806890449,-1.6991720198,0.0219008981\H,-0.7
390596274,-0.6377918948,1.4184246749\H,0.0260854761,0.1995945534,-1.40
57981177\H,-0.0865692566,1.7640678242,1.0582513439\H,-0.4214360873,2.2
338978242,-0.4916863871\\Version=x86-Linux-G98RevA.11.1\HF/CbsB1=-718.
9112941\HF/CbsB2=-718.793297\MP2/CbsB2=-719.8679947\E2(CBS)/CbsB2=-1.3
786606\CBS-Int/CbsB2=0.0763137\OIii/CbsB2=12.5473347\MP2/6-31G=-719.25
30877\MP4(SDQ)/6-31G=-719.2891717\CBS4M=-720.414138\PG=C01
[X(C3H6N1O2S1)]\\@

CysS• CBS-QB3

1\1\GINC-KOHN\Mixed\CBS-QB3\CBS-QB3\C3H6N1O2S1(2)\JAMES\03-Aug-2003\0\

\# CBS-QB3 MAXDISK=16900MB\\cys-s-6-rad-cbsqb3\\0,2\S,-2.5613571228,-0
.1981580579,-0.1228379376\C,-0.8816411619,-0.6615575346,0.3831396952\C
,0.1639163092,0.2530838443,-0.2919748825\N,0.1598028806,1.6637670307,0
.1090981234\C,1.5839092791,-0.3408004042,-0.0658104331\O,1.808088959,-
1.5198648157,-0.0504102702\O,2.5250715922,0.596840254,0.0720524406\H,2
.0397123643,1.4522961578,0.0611629714\H,-0.6640611412,-1.6892235265,0.
0969685552\H,-0.7920821085,-0.5640645438,1.469442868\H,0.0154608513,0.
2164449941,-1.3766698573\H,-0.1241698712,1.7703357457,1.0785566209\H,-
0.4741572632,2.2182119464,-0.4530046618\\Version=x86-Linux-G98RevA.11.
1\HF/CbsB3=-718.9165707\E2(CBS)/CbsB3=-1.4439131\CBS-Int/CbsB3=0.04400
97\OIii/CbsB3=10.8375697\MP2/CbsB4=-719.894474\MP4(SDQ)/CbsB4=-719.947
402\MP4(SDQ)/6-31+G(d')=-719.8609114\QCISD(T)/6-31+G(d')=-719.8960317\
CBSQB3=-720.3681823\ PG=C01 [X(C3H6N1O2S1)]\\@

CysS$^{\bullet}$ CBS-Q

1\1\GINC-KOHN\Mixed\CBS-Q\CBS-Q\C3H6N1O2S1(2)\JAMES\01-Aug-2003\0\\# C
BS-Q MAXDISK=16900MB\\cys-s-6-rad-g3\\0,2\S,-2.5445260043,-0.148403271
6,-0.1296684129\C,-0.8836696688,-0.6805940348,0.3538413004\C,0.1651297
663,0.2314262999,-0.3064258688\N,0.1478467545,1.6430029997,0.090562577
4\C,1.5753443313,-0.3480737946,-0.0425097376\O,1.7945483869,-1.5339123
063,0.0399233237\O,2.5256437375,0.5902807947,0.0459033732\H,2.04837209
25,1.4490692636,-0.0101560644\H,-0.6933166466,-1.7104736138,0.03639674
57\H,-0.7724469289,-0.6197392312,1.4455056745\H,0.0325772217,0.1961267
,-1.3991745753\H,-0.0853723519,1.7277774834,1.0782288148\H,-0.55468816
8,2.1631720153,-0.4260917707\\Version=x86-Linux-G98RevA.11.1\HF/CbsB3=
-718.9153162\MP2/CbsB3=-720.226229\E2(CBS)/CbsB3=-1.4477917\CBS-Int/Cb
sB3=0.0443292\OIii/CbsB3=10.8317597\MP2/CbsB4=-719.8948016\MP4(SDQ)/Cb
sB4=-719.9475748\MP4(SDQ)/6-31+G(d')=-719.8611434\QCISD(T)/6-31+G(d')=
-719.8978756\CBSQ=-720.366763\ PG=C01 [X(C3H6N1O2S1)]\\@

CysS$^{\bullet}$ G3(MP2)

1\1\GINC-KOHN\Mixed\G3MP2\G3MP2\C3H6N1O2S1(2)\JAMES\30-Jul-2003\0\\# G
3MP2 MAXDISK=16900MB\\cys-s-6-rad-g3\\0,2\S,-2.5389943106,-0.138901468
4,-0.1145584746\C,-0.8794645428,-0.6782295583,0.351353151\C,0.16453632
81,0.2253740086,-0.3128929346\N,0.1485112505,1.6357381321,0.0828571726
\C,1.5685703276,-0.3494778027,-0.049468709\O,1.7919130602,-1.541967257
8,0.0203417521\O,2.5210225253,0.5902357626,0.056314746\H,2.0327784545,
1.4524653569,0.0047683483\H,-0.6962096204,-1.7048679779,0.0336574702\H
,-0.7572529735,-0.6171912716,1.4377831084\H,0.0287584669,0.1883963433,
-1.4013823965\H,-0.097421377,1.7228180848,1.0692937279\H,-0.5516600954
,2.1584881099,-0.4383859033\\Version=x86-Linux-G98RevA.11.1\MP2/6-31G(
d)=-719.7712662\QCISD(T)/6-31G(d)=-719.8547106\MP2/GTMP2Large=-720.227
6324\G3MP2=-720.4043154\ PG=C01 [X(C3H6N1O2S1)]\\@

NO$^{\bullet}$ MP2/6-311G(d,p)

1\1\GINC-VLAD\Freq\UMP2-FC\6-311G(d,p)\N1O1(2)\CRISTINA\11-Feb-2002\1\
\#N GEOM=ALLCHECK GUESS=TCHECK UMP2(FC)/6-311G(D,P) FREQ\\no-radical\\
0,2\N\O,1,r1\\r1=1.13469236\\Version=x86-Linux-G98RevA.11.1\HF=-129.28
23271\MP2=-129.6194881\PUHF=-129.2876581\PMP2-0=-129.6235357\S2=0.7769
16\S2-1=0.763833\S2A=0.750429\RMSD=0.000e+00\RMSF=3.273e-06\Dipole=0.,
0.,0.0598048\DipoleDeriv=-0.0278907,0.,0.,0.,-0.0278907,0.,0.,0.,3.498
195,0.0278907,0.,0.,0.,0.0278907,0.,0.,0.,-3.498195\Polar=4.7002743,0.
,4.7217708,0.,0.,9.0244254\PG=C*V [C*(N1O1)]\NImag=0\\0.00000266,0.,0.
00000271,0.,0.,3.57790068,-0.00000266,0.,0.,0.00000266,0.,-0.00000271,

0.,0.,0.00000271,0.,0.,-3.57790068,0.,0.,3.57790068\\0.,0.,-0.00000567
,0.,0.,0.00000567\\\@

NO• MP2/6-311+G(2df,p)

1\1\GINC-VLAD\Freq\UMP2-FC\6-311+G(2df,p)\N1O1(2)\CRISTINA\11-Feb-2002
\1\\#N GEOM=ALLCHECK GUESS=TCHECK UMP2(FC)/6-311+G(2DF,P) FREQ\\no-rad
ical\\0,2\N\O,1,r1\\r1=1.13688317\\Version=x86-Linux-G98RevA.11.1\HF=-
129.2945461\MP2=-129.6869818\PUHF=-129.3002698\PMP2-0=-129.6911608\S2=
0.77554\S2-1=0.761609\S2A=0.750452\RMSD=0.000e+00\RMSF=1.018e-05\Dipol
e=0.,0.,0.0876702\DipoleDeriv=-0.0408071,0.,0.,0.,-0.0408071,0.,0.,0.,
2.8793336,0.0408071,0.,0.,0.,0.0408071,0.,0.,0.,-2.8793336\Polar=7.957
1501,0.,6.9447611,0.,0.,11.8336094\PG=C*V [C*(N1O1)]\\@

NO• MP2/6-311++G(3df,3pd)

1\1\GINC-CURIE\Freq\UMP2-FC\6-311++G(3df,3pd)\N1O1(2)\CRISTINA\24-Jul-
2003\0\\#N GEOM=ALLCHECK GUESS=TCHECK UMP2(FC)/6-311++G(3DF,3PD) FREQ\
\no-rad-mp9\\0,2\N,0.,0.,-0.6059691263\O,0.,0.,0.5302229855\\Version=x
86-Linux-G98RevA.11.1\HF=-129.2966591\MP2=-129.693935\PUHF=-129.302400
2\PMP2-0=-129.6981111\S2=0.77552\S2-1=0.761458\S2A=0.750457\RMSD=2.472
e-10\RMSF=5.054e-06\Dipole=0.,0.,0.0890506\DipoleDeriv=-0.0414749,0.,0
.,0.,-0.0414747,0.,0.,0.,2.6805528,0.0414749,0.,0.,0.,0.0414747,0.,0.,
0.,-2.6805528\Polar=8.3028152,0.,9.2970764,0.,0.,12.5903752\PG=C*V [C*
(N1O1)]\\@

NO• QCISD/6-311G(d,p)

1\1\GINC-VLAD\Freq\UQCISD-FC\6-311G(d,p)\N1O1(2)\CRISTINA\11-Feb-2002\
1\\#N GEOM=ALLCHECK GUESS=TCHECK UQCISD(FC)/6-311G(D,P) FREQ\\no-radic
al\\0,2\N\O,1,r1\\r1=1.15857078\\Version=x86-Linux-G98RevA.11.1\HF=-12
9.2794434\MP2=-129.6142179\MP3=-129.6109536\MP4D=-129.6212068\MP4DQ=-1
29.6156879\PUHF=-129.2883872\PMP2-0=-129.6218756\PMP3-0=-129.6163666\M
P4SDQ=-129.624336\QCISD=-129.6288087\S2=0.836442\S2-1=0.811262\S2A=0.7
51864\RMSD=0.000e+00\RMSF=2.506e-08\Dipole=0.,0.,0.0334827\DipoleDeriv
=-0.01529,0.,0.,0.,-0.0153054,0.,0.,0.,0.3530022,0.01529,0.,0.,0.,0.01
53054,0.,0.,0.,-0.353011\PG=C*V [C*(N1O1)] \\@

NO• QCISD/6-311+G(2df,p)

1\1\GINC-VLAD\Freq\UQCISD-FC\6-311+G(2df,p)\N1O1(2)\CRISTINA\11-Feb-20
02\1\\#N GEOM=ALLCHECK GUESS=TCHECK UQCISD(FC)/6-311+G(2DF,P) FREQ\\no
-radical\\0,2\N\O,1,r1\\r1=1.15203096\\Version=x86-Linux-G98RevA.11.1\
HF=-129.2926681\MP2=-129.6852771\MP3=-129.6816221\MP4D=-129.6930949\MP
4DQ=-129.6843519\PUHF=-129.299823\PMP2-0=-129.6910615\PMP3-0=-129.6855
128\MP4SDQ=-129.6925557\QCISD=-129.6943129\S2=0.798445\S2-1=0.779633\S
2A=0.751105\RMSD=0.000e+00\RMSF=3.997e-06\Dipole=0.,0.,0.0489263\Dipol
eDeriv=-0.0224818,0.,0.,0.,-0.022492,0.,0.,0.,0.3297965,0.0224818,0.,0
.,0.,0.022492,0.,0.,0.,-0.3297996\PG=C*V [C*(N1O1)]\\@

NO• QCISD/6-311++G(3df,3pd)

1\1\GINC-LOKI\Freq\UQCISD-FC\6-311++G(3df,3pd)\N1O1(2)\STUACC2\25-Dec-
2002\0\\#N GEOM=ALLCHECK GUESS=TCHECK UQCISD(FC)/6-311++G(3DF,3PD) FRE
Q\\no-rad-q9\\0,2\N,0.,0.,-0.6135602102\O,0.,0.,0.5368651839\\Version=
x86-Linux-G98RevA.11.1\HF=-129.2949095\MP2=-129.6924935\MP3=-129.68857
57\MP4D=-129.7001471\MP4DQ=-129.6910714\PUHF=-129.3019045\PMP2-0=-129.
6980966\PMP3-0=-129.6923131\MP4SDQ=-129.6992448\QCISD=-129.700831\S2=0
.795462\S2-1=0.777121\S2A=0.751043\RMSD=1.947e-10\RMSF=8.739e-06\Dipol

e=0.,0.,0.048426\DipoleDeriv=-0.0222647,0.,0.,0.,-0.0222635,0.,0.,0.,0
.3401501,0.0222647,0.,0.,0.,0.0222635,0.,0.,0.,-0.3401194\PG=C*V [C*(N
1O1)]\\@

NO• B3LYP/6-31G(d)

1\1\GINC-POPLE\Freq\UB3LYP\6-31G(d)\N1O1(2)\CRISTINA\22-Jun-2003\0\\#N
GEOM=ALLCHECK GUESS=TCHECK UB3LYP/6-31G(D) FREQ\\no-radical\\0,2\N,0.
,0.,-0.6179719599\O,0.,0.,0.5407254649\\Version=x86-Linux-G98RevA.11.1
\HF=-129.8881562\S2=0.752535\S2-1=0.\S2A=0.750004\RMSD=1.488e-10\RMSF=
1.141e-05\Dipole=0.,0.,0.034889\DipoleDeriv=-0.015922,0.,0.,0.,-0.0159
166,0.,0.,0.,0.4906893,0.015922,0.,0.,0.,0.0159166,0.,0.,0.,-0.4906893
\Polar=5.2321209,0.,5.5447883,0.,0.,12.0100053\PG=C*V [C*(N1O1)]\\@

NO• B3LYP/6-31+G(d)

1\1\GINC-POPLE\Freq\UB3LYP\6-31+G(d)\N1O1(2)\CRISTINA\22-Jun-2003\0\\#
N GEOM=ALLCHECK GUESS=TCHECK UB3LYP/6-31+G(D) FREQ\\no-radical\\0,2\N,
0.,0.,-0.6174182356\O,0.,0.,0.5402409561\\Version=x86-Linux-G98RevA.11
.1\HF=-129.8954772\S2=0.753016\S2-1=0.\S2A=0.750006\RMSD=2.393e-10\RMS
F=1.417e-05\Dipole=0.,0.,0.0344639\DipoleDeriv=-0.0157493,0.,0.,0.,-0.
0157377,0.,0.,0.,0.5777859,0.0157493,0.,0.,0.,0.0157377,0.,0.,0.,-0.57
77859\Polar=7.6765053,0.,6.8389016,0.,0.,14.5859332\PG=C*V[C*(N1O1)]
\\@

NO• B3LYP/6-311G(d,p)

1\1\GINC-VLAD\Freq\UB3LYP\6-311G(d,p)\N1O1(2)\CRISTINA\25-Jan-2002\1\\
#N GEOM=ALLCHECK GUESS=TCHECK UB3LYP/6-311G(D,P) FREQ\\no-radical\\0,2
\N\O,1,r1\\r1=1.14829055\\Version=x86-Linux-G98RevA.11.1\HF=-129.92670
22\S2=0.752536\S2-1=0.\S2A=0.750004\RMSD=3.787e-10\RMSF=3.060e-05\Dipo
le=0.,0.,0.0300296\DipoleDeriv=-0.0138257,0.,0.,0.,-0.0138179,0.,0.,0.
,0.5293828,0.0138257,0.,0.,0.,0.0138179,0.,0.,0.,-0.5293828\Polar=4.94
43477,0.,5.2338315,0.,0.,12.2602374\PG=C*V [C*(N1O1)] \\@

NO• B3LYP/6-311+G(2df,p)

1\1\GINC-VLAD\Freq\UB3LYP\6-311+G(2df,p)\N1O1(2)\CRISTINA\25-Jan-2002\
1\\#N GEOM=ALLCHECK GUESS=TCHECK UB3LYP/6-311+G(2DF,P) FREQ\\no-radica
l\\0,2\N\O,1,r1\\r1=1.14545466\\Version=x86-Linux-G98RevA.11.1\HF=-129
.9383168\S2=0.753249\S2-1=0.\S2A=0.750007\RMSD=3.539e-10\RMSF=4.396e-0
5\Dipole=0.,0.,0.0527456\DipoleDeriv=-0.0243402,0.,0.,0.,-0.0243511,0.
,0.,0.,0.5791436,0.0243402,0.,0.,0.,0.0243511,0.,0.,0.,-0.5791436\Pola
r=8.3706101,0.,7.4603756,0.,0.,14.4903684\PG=C*V [C*(N1O1)]\\@

NO• B3LYP/6-311++G(3df,3pd)

1\1\GINC-GAULD\Freq\UB3LYP\6-311++G(3df,3pd)\N1O1(2)\COMCHEM\23-Jul-20
03\0\\#N GEOM=ALLCHECK GUESS=TCHECK UB3LYP/6-311++G(3DF,3PD) FREQ\\no-
rad-b9\\0,2\N,0.,0.,-0.6104732471\O,0.,0.,0.5341640912\\Version=MacOSX
-G98RevA.11\HF=-129.9399026\S2=0.753333\S2-1=0.\S2A=0.750007\RMSD=4.49
7e-10\RMSF=9.427e-09\Dipole=0.,0.,0.0535594\DipoleDeriv=-0.0247557,0.,
0.,0.,-0.0247408,0.,0.,0.,0.5646388,0.0247557,0.,0.,0.,0.0247408,0.,0.
,0.,-0.5646388\Polar=9.6445337,0.,8.7363504,0.,0.,14.9038646\PG=C*V [C
*(N1O1)]\\@

NO• B3P86/6-311G(d,p)

1\1\GINC-VLAD\Freq\UB3P86\6-311G(d,p)\N1O1(2)\CRISTINA\06-Feb-2002\1\\

#N GEOM=ALLCHECK GUESS=TCHECK UB3P86/6-311G(D,P) FREQ\\no-radical\\0,2
\N\O,1,r1\\r1=1.14482427\\Version=x86-Linux-G98RevA.11.1\HF=-130.18386
65\S2=0.752407\S2-1=0.\S2A=0.750004\RMSD=3.263e-10\RMSF=3.171e-05\Dipo
le=0.,0.,0.0331156\DipoleDeriv=-0.0152487,0.,0.,0.,-0.0152888,0.,0.,0.
,0.5410266,0.0152487,0.,0.,0.,0.0152888,0.,0.,0.,-0.5410266\Polar=4.96
29793,0.,5.2409261,0.,0.,12.2726796\PG=C*V [C*(N1O1)]\\@

NO• B3P86/6-311+G(2df,p)

1\1\GINC-VLAD\Freq\UB3P86\6-311+G(2df,p)\N1O1(2)\CRISTINA\06-Feb-2002\
1\\#N GEOM=ALLCHECK GUESS=TCHECK UB3P86/6-311+G(2DF,P) FREQ\\no-radica
l\\0,2\N\O,1,r1\\r1=1.14227134\\Version=x86-Linux-G98RevA.11.1\HF=-130
.1945865\S2=0.753027\S2-1=0.\S2A=0.750006\RMSD=3.420e-10\RMSF=4.560e-0
5\Dipole=0.,0.,0.057608\DipoleDeriv=-0.0265874,0.,0.,0.,-0.0266651,0.,
0.,0.,0.5788353,0.0265874,0.,0.,0.,0.0266651,0.,0.,0.,-0.5788353\Polar
=8.1869882,0.,7.3531354,0.,0.,14.2549793\PG=C*V [C*(N1O1)]\\@

NO• B3P86/6-311++G(3df,3pd)

1\1\GINC-GAULD\Freq\UB3P86\6-311++G(3df,3pd)\N1O1(2)\COMCHEM\23-Jul-20
03\0\\#N GEOM=ALLCHECK GUESS=TCHECK UB3P86/6-311++G(3DF,3PD) FREQ\\no-
rad-p9\\0,2\N,0.,0.,-0.6088006339\O,0.,0.,0.5327005547\\Version=MacOSX
-G98RevA.11\HF=-130.1962373\S2=0.753127\S2-1=0.\S2A=0.750007\RMSD=1.72
8e-09\RMSF=1.556e-08\Dipole=0.,0.,0.05878\DipoleDeriv=-0.0271313,0.,0.
,0.,-0.0272184,0.,0.,0.,0.5646048,0.0271313,0.,0.,0.,0.0272184,0.,0.,0
.,-0.5646048\Polar=9.530247,0.,8.6774851,0.,0.,14.69794\PG=C*V [C*(N1O
1)]\\@

NO• CBS-4M

1\1\GINC-ANGSTROM\Mixed\CBS-4M\CBS-4M\N1O1(2)\JAMES\30-Jul-2003\0\\# C
BS-4M\\NO radical\\0,2\N,0.,0.,-0.6409656265\O,0.,0.,0.5608449232\\Ver
sion=x86-Linux-G98RevA.11.1\HF/CbsB1=-129.2835615\HF/CbsB2=-129.242832
3\MP2/CbsB2=-129.5486496\E2(CBS)/CbsB2=-0.3921784\CBS-Int/CbsB2=0.0189
686\OIii/CbsB2=3.2257068\MP2/6-31G=-129.3680396\MP4(SDQ)/6-31G=-129.38
19692\CBS4M=-129.7490871\FreqCoord=0.,0.,-1.2112494022,0.,0.,1.0598432
269\PG=C*V [C*(N1O1)]\\@

NO• CBS-QB3

1\1\GINC-ANGSTROM\Mixed\CBS-QB3\CBS-QB3\N1O1(2)\CRISTINA\21-Jun-2003\0
\\# CBS-QB3 OPT\\no-radical\\0,2\N,0.,0.,-0.6124216245\O,0.,0.,0.53586
89215\\Version=x86-Linux-G98RevA.11.1\HF/CbsB3=-129.2932021\E2(CBS)/Cb
sB3=-0.4325176\CBS-Int/CbsB3=0.0117369\OIii/CbsB3=2.9255206\MP2/CbsB4=
-129.5769221\MP4(SDQ)/CbsB4=-129.5862968\MP4(SDQ)/6-31+G(d')=-129.5862
968\QCISD(T)/6-31+G(d')=-129.5985189\CBSQB3=-129.7484162\FreqCoord=0.,
0.,-1.1573090598,0.,0.,1.0126454274\PG=C*V [C*(N1O1)]\\@

NO• CBS-Q

1\1\GINC-POPLE\Mixed\CBS-Q\CBS-Q\N1O1(2)\CRISTINA\25-Jun-2003\0\\# CBS
-Q OPT\\no-radical CBS-Q\\0,2\N,0.,0.,-0.6066302778\O,0.,0.,0.53080149
31\\Version=x86-Linux-G98RevA.11.1\HF/CbsB3=-129.2944925\MP2/CbsB3=-12
9.6869802\E2(CBS)/CbsB3=-0.4324671\CBS-Int/CbsB3=0.011774\OIii/CbsB3=2
.9357883\MP2/CbsB4=-129.5779031\MP4(SDQ)/CbsB4=-129.5866147\MP4(SDQ)/6
-31+G(d')=-129.5866147\QCISD(T)/6-31+G(d')=-129.5985539\CBSQ=-129.7470
172\FreqCoord=0.,0.,-1.12812785,0.,0.,0.9871118688\PG=C*V [C*(N1O1)]
\\@

NO• MP2(Full)/6-31G(d) (G3 and G3(MP2))

```
1\1\GINC-ANGSTROM\Mixed\G3MP2\G3MP2\N1O1(2)\JAMES\29-Jul-2003\0\\# G3M
P2\\NO radical\\0,2\N,0.,0.,-0.6094542873\O,0.,0.,0.5332725014\\Versio
n=x86-Linux-G98RevA.11.1\MP2/6-31G(d)=-129.5589\QCISD(T)/6-31G(d)=-129
.579153\MP2/GTMP2Large=-129.6867737\G3MP2=-129.753374\FreqCoord=0.,0.,
-1.135831001,0.,0.,0.9938521259\PG=C*V [C*(N1O1)]\\@
```

A.2 Gaussian Archive Entries of Optimized Geometries Obtained for $HSNH_2$, HNO and Additional NO Species Considered in Chapter 3

HS-NH_2 MP2/6-311+G(2df,p)

```
1\1\GINC-POPLE\Freq\RMP2-FC\6-311+G(2df,p)\H3N1S1\JAMES\29-Dec-2002\1\
\#N GEOM=ALLCHECK GUESS=TCHECK TEST RMP2(FC)/6-311+G(2DF,P) FREQ\\HSNH
2 (trans)\\0,1\S\N,1,r1\H,1,r2,2,a1\H,2,r3,1,a2,3,d1,0\H,2,r3,1,a2,3,-
d1,0\\r1=1.71659643\r2=1.34118931\r3=1.01274385\a1=97.02194807\a2=110.
59586534\d1=119.09506903\\Version=x86-Linux-G98RevA.11.1\State=1-A'\HF
=-453.7371485\MP2=-454.1220264\RMSD=6.462e-10\RMSF=1.035e-04\Dipole=-0
.1907585,0.,0.3498547\ PG=CS [SG(H1N1S1),X(H2)]\NImag=0\\@
```

HS-NH_2 QCISD/6-311+G(2df,p)

```
1\1\GINC-POPLE\FOpt\RQCISD-FC\6-311+G(2df,p)\H3N1S1\JAMES\09-Apr-2003\
1\\# QCISD/6-311+G(2DF,P) GEOM=CHECK GUESS=READ FOPT=(READFC,Z-MATRIX)
 TEST\\HSNH2 (trans)\\0,1\S\N,1,r1\H,1,r2,2,a1\H,2,r3,1,a2,3,d1,0\H,2,
r3,1,a2,3,-d1,0\\r1=1.72119114\r2=1.34482762\r3=1.01249103\a1=97.00927
175\a2=110.43615099\d1=119.38450685\\Version=x86-Linux-G98RevA.11.1\St
ate=1-A'\HF=-453.7370223\MP2=-454.1220125\MP3=-454.1473919\MP4D=-454.1
573555\MP4DQ=-454.1479789\MP4SDQ=-454.1506287\QCISD=-454.1506364\RMSD=
1.974e-09\RMSF=1.891e-05\Dipole=-0.2034312,0.,0.334422\PG=CS [SG(H1N1S
1),X(H2)]\\@
```

HS-NH_2 B3LYP/6-311+G(2df,p)

```
1\1\GINC-POPLE\Freq\RB3LYP\6-311+G(2df,p)\H3N1S1\JAMES\09-Apr-2003\1\\
#N GEOM=ALLCHECK GUESS=TCHECK TEST RB3LYP/6-311+G(2DF,P) FREQ\\HSNH2 (
trans)\\0,1\S\N,1,r1\H,1,r2,2,a1\H,2,r3,1,a2,3,d1,0\H,2,r3,1,a2,3,-d1,
0\\r1=1.7237094\r2=1.34908663\r3=1.01226808\a1=97.34769475\a2=110.9151
2504\d1=118.72329263\\Version=x86-Linux-G98RevA.11.1\State=1-A'\HF=-45
4.7839763\RMSD=4.450e-09\RMSF=1.059e-04\Dipole=-0.1954391,0.,0.3698415
\PG=CS [SG(H1N1S1),X(H2)]\\@
```

HS-NH_2 B3P86/6-311+G(2df,p)

```
1\1\GINC-POPLE\Freq\RB3P86\6-311+G(2df,p)\H3N1S1\JAMES\09-Apr-2003\1\\
#N GEOM=ALLCHECK GUESS=TCHECK TEST RB3P86/6-311+G(2DF,P) FREQ\\HSNH2 (
trans)\\0,1\S\N,1,r1\H,1,r2,2,a1\H,2,r3,1,a2,3,d1,0\H,2,r3,1,a2,3,-d1,
0\\r1=1.7089315\r2=1.34806409\r3=1.01112791\a1=97.49778106\a2=111.1191
8831\d1=118.48919504\\Version=x86-Linux-G98RevA.11.1\State=1-A'\HF=-45
5.26576\RMSD=9.554e-10\RMSF=8.881e-05\Dipole=-0.1848518,0.,0.3924401\
PG=CS [SG(H1N1S1),X(H2)]\\@
```

HNO MP2/6-311+G(2df,p)

1\1\GINC-CURIE\FOpt\RMP2-FC\6-311+G(2df,p)\H1N1O1\JAMES\17-Jul-2003\0\
\# MP2/6-311+G(2DF,P) OPT FREQ=NORAMAN TEST\\HNO\\0,1\N,-0.0750404746,
0.,-0.5877248486\O,-0.0495335921,0.,0.63101722\H,0.9215520587,0.,-0.93
406382\\Version=x86-Linux-G98RevA.11.1\State=1-A'\HF=-129.8312356\MP2=
-130.2640636\RMSD=5.388e-09\RMSF=2.442e-04\Dipole=0.5953916,0.,-0.3575
347\PG=CS [SG(H1N1O1)]\\@

HNO QCISD/6-311+G(2df,p)

1\1\GINC-CURIE\FOpt\RQCISD-FC\6-311+G(2df,p)\H1N1O1\JAMES\17-Jul-2003\
0\\# QCISD/6-311+G(2DF,P) OPT FREQ TEST\\HNO\\0,1\N,-0.0738714706,0.,-
0.5796884758\O,-0.0505600772,0.,0.6241372506\H,0.9215809121,0.,-0.9352
786742\\Version=x86-Linux-G98RevA.11.1\State=1-A'\HF=-129.8334807\MP2=
-130.2637893\MP3=-130.263342\MP4D=-130.2760585\MP4DQ=-130.2656135\MP4S
DQ=-130.2718376\QCISD=-130.2715447\RMSD=3.085e-09\RMSF=9.417e-05\Dipol
e=0.5785651,0.,-0.3841417\PG=CS [SG(H1N1O1)]\\@

HNO B3LYP/6-311+G(2df,p)

1\1\GINC-CURIE\FOpt\RB3LYP\6-311+G(2df,p)\H1N1O1\JAMES\17-Jul-2003\0\\
B3LYP/6-311+G(2DF,P) OPT FREQ=NORAMAN TEST\\HNO\\0,1\N,-0.0738595177
,0.,-0.576066905\O,-0.0511229615,0.,0.6215433567\H,0.9260003154,0.,-0.
9398785187\\Version=x86-Linux-G98RevA.11.1\State=1-A'\HF=-130.5219545\
RMSD=1.674e-09\RMSF=9.939e-05\Dipole=0.5646769,0.,-0.3719787\PG=CS [SG
(H1N1O1)]\\@

HNO B3P86/6-311+G(2df,p)

1\1\GINC-CURIE\FOpt\RB3P86\6-311+G(2df,p)\H1N1O1\JAMES\17-Jul-2003\0\\
B3P86/6-311+G(2DF,P) OPT FREQ=NORAMAN TEST\\HNO\\0,1\N,-0.1176100538
,0.,-0.5664077529\O,-0.0034776328,0.,0.6212533479\H,0.8510914392,0.,-1
.0051725129\\Version=x86-Linux-G98RevA.11.1\State=1-A'\HF=-130.7990504
\RMSD=2.118e-09\RMSF=7.441e-06\Dipole=0.532883,0.,-0.4081905\PG=CS [SG
(H1N1O1)]\\@

Appendix B

Gaussian Archive Entries of Optimized Geometries Obtained for all S-nitrosothiols, $[Cu^{\cdots}RSNO]^{+}$ Complexes and Related Species Considered in Chapter 4

HSNO (*trans*) (gas-phase)

1\1\GINC-CURIE\Freq\RB3P86\6-311+G(2df,p)\H1N1O1S1\CRISTINA\16-May-200
2\1\\#N GEOM=ALLCHECK GUESS=TCHECK RB3P86/6-311+G(2DF,P) FREQ\\hsno-tr
-b3p86b8\\0,1\S\N,1,r1\H,1,r2,2,a1\O,2,r3,1,a2,3,180.,0\\r1=1.84331851
\r2=1.34208867\r3=1.16828172\a1=90.32795796\a2=115.53768485\\Version=x
86-Linux-G98RevA.11.1\State=1-A'\HF=-529.3424816\RMSD=4.329e-10\RMSF=1
.089e-04\Dipole=0.4355669,0.,-0.3146568\PG=CS [SG(H1N1O1S1)]\\@

HSNO (*trans*) (solution)

1\1\GINC-FLEXOR\FOpt\RB3P86\6-311+G(2df,p)\H1N1O1S1\GAULD\07-Jun-2004\
0\\# B3P86/6-311+G(2DF,P) SCRF=DIPOLE OPT\\hsno-tr-b3p86b8-solv\\0,1\S
,-0.4577368114,-0.8864082692,0.\N,-0.0110969771,0.8638316316,0.\H,-1.7
661068196,-0.5827145225,0.\O,1.1459468301,1.0898031762,0.\\Version=SGI
64-G98RevA.7\State=1-A'\Dielectric=78.4\A0=3.1\HF=-529.3435907\RMSD=4.
685e-09\RMSF=7.096e-05\Dipole=-0.7294556,-0.4450569,0.\PG=CS [SG(H1N1O
1S1)]\\@

HSNO (*cis*) (gas-phase)

1\1\GINC-N11\Freq\RB3P86\6-311+G(2df,p)\H1N1O1S1\ROOT\13-Nov-2001\1\\#
N GEOM=ALLCHECK GUESS=TCHECK RB3P86/6-311+G(2DF,P) FREQ\\hsno-cis-b3p8
6b8\\0,1\S\N,1,r1\H,1,r2,2,a1\O,2,r3,1,a2,3,0.,0\\r1=1.82435246\r2=1.3
4986576\r3=1.17252279\a1=96.58843699\a2=116.8914727\\Version=IBM-RS600
0-G98RevA.7\State=1-A'\HF=-529.340845\RMSD=3.310e-09\RMSF=9.509e-06\Di
pole=0.2612776,0.,-0.4123947\PG=CS [SG(H1N1O1S1)]\\@

HSNO (*cis*) (solution)

1\1\GINC-FLEXOR\FOpt\RB3P86\6-311+G(2df,p)\H1N1O1S1\GAULD\07-Jun-2004\
0\\# B3P86/6-311+G(2DF,P) SCRF=DIPOLE OPT\\hsno-cis-b3p86-solv\\0,1\S,
-0.6147589227,-0.8128145664,0.\N,-0.0067353228,0.8789288978,0.\H,0.588
2189282,-1.4280455323,0.\O,1.1618838867,1.0350720387,0.\\Version=SGI64
-G98RevA.7\State=1-A'\Dielectric=78.4\A0=3.23\HF=-529.3415596\RMSD=9.5
17e-09\RMSF=5.434e-05\Dipole=0.0350328,-0.6829984,0.\PG=CS [SG(H1N1O1S
1)]\\@

$HS^{\bullet}$ (gas-phase)

1\1\GINC-VLAD\Freq\UB3P86\6-311+G(2df,p)\H1S1(2)\CRISTINA\05-Feb-2002\
1\\#N GEOM=ALLCHECK GUESS=TCHECK UB3P86/6-311+G(2DF,P) FREQ\\HS-radica
1\\0,2\H\S,1,r1\\r1=1.34647795\\Version=x86-Linux-G98RevA.11.1\HF=-399
.0917311\S2=0.7544\S2-1=0.\S2A=0.750007\RMSD=7.550e-10\RMSF=7.512e-06\
Dipole=0.,0.,-0.3603104\DipoleDeriv=0.1414592,0.,0.,0.,0.1414935,0.,0.

,0.,-0.0167038,-0.1414592,0.,0.,0.,-0.1414935,0.,0.,0.,0.0167038\Polar
=17.4656803,0.,13.057507,0.,0.,18.9568726\PG=C*V [C*(H1S1)]\NImag=0\\0
.00018487,0.,0.00021070,0.,0.,0.26731836,-0.00018487,0.,0.,0.00018487,
0.,-0.00021070,0.,0.,0.00021070,0.,0.,-0.26731836,0.,0.,0.26731836\\0.
,0.,0.00001301,0.,0.,-0.00001301\\\@

$HS^{\bullet}$ (solution)

1\1\GINC-VLAD\FOpt\UB3P86\6-311+G(2df,p)\H1S1(2)\CRISTINA\28-Oct-2003\
0\\# B3P86/6-311+G(2DF,P) SCRF=DIPOLE OPT\\HS-radical\\0,2\H,0.,0.,-1.
2672768526\S,0.,0.,0.0792048033\\Version=x86-Linux-G98RevA.11.1\Dielec
tric=78.4\A0=2.73\HF=-399.0922674\S2=0.754398\S2-1=0.\S2A=0.750007\RMS
D=5.911e-09\RMSF=6.788e-06\Dipole=0.,0.,-0.4166347\PG=C*V [C*(H1S1)]\\
@

CH_3SNO (*syn*) (gas-phase)

1\1\GINC-BOHR\Freq\RB3P86\6-311+G(2df,p)\C1H3N1O1S1\CRISTINA\25-Jul-20
02\1\\#N GEOM=ALLCHECK GUESS=TCHECK RB3P86/6-311+G(2DF,P) FREQ\\ch3sno
-cis1-b3p86b4\\0,1\S\N,1,r1\C,1,r2,2,a1\H,3,r3,1,a2,2,0.,0\H,3,r4,1,a3
,4,d1,0\H,3,r4,1,a3,4,-d1,0\O,2,r5,1,a4,3,0.,0\\r1=1.79277362\r2=1.786
95299\r3=1.09602061\r4=1.08858851\r5=1.18155804\a1=102.62351769\a2=106
.60521062\a3=110.27723872\a4=117.7715407\d1=118.94702587\\Version=x86-
Linux-G98RevA.11.1\State=1-A'\HF=-568.8212483\RMSD=2.493e-09\RMSF=3.55
0e-05\Dipole=0.5374785,0.,-0.7280654\PG=CS [SG(C1H1N1O1S1),X(H2)]\\@

CH_3SNO (*syn*) (solution)

1\1\GINC-FLEXOR\FOpt\RB3P86\6-311+G(2df,p)\C1H3N1O1S1\GAULD\07-Jun-200
4\0\\# B3P86/6-311+G(2DF,P) SCRF=DIPOLE OPT\\ch3sno-cis1-b3p86b4-solv\
\0,1\S,-0.0001505513,0.9227734275,0.\N,1.2023299671,-0.3778152037,0.\C
,-1.560011427,0.049828918,0.\H,-1.3238822255,-1.0193406071,0.\H,-2.128
9815301,0.3028516172,0.8927514705\H,-2.1289815301,0.3028516172,-0.8927
514705\O,0.8160016122,-1.5006255686,0.\\Version=SGI64-G98RevA.7\State=
1-A'\Dielectric=78.4\A0=3.72\HF=-568.8227125\RMSD=7.936e-09\RMSF=7.062
e-05\Dipole=-1.1073538,0.3012311,0.\PG=CS [SG(C1H1N1O1S1),X(H2)]\\@

$CH_3S^{\bullet}$ (gas-phase)

1\1\GINC-VLAD\Freq\UB3P86\6-311+G(2df,p)\C1H3S1(2)\CRISTINA\13-Mar-200
2\1\\#N GEOM=ALLCHECK GUESS=TCHECK UB3P86/6-311+G(2DF,P) FREQ\\ch3s-ra
dical\\0,2\S\C,1,r1\H,2,r3,1,a2\H,2,r2,1,a1,3,d1,0\H,2,r2,1,a1,3,-d1,0
\\r1=1.78564607\r2=1.0899554\r3=1.09609901\a1=111.85749857\a2=106.4643
3505\d1=117.39994481\\Version=x86-Linux-G98RevA.11.1\State=2-A'\HF=-43
8.5677953\S2=0.754326\S2-1=0.\S2A=0.750008\RMSD=1.412e-09\RMSF=1.227e-
04\Dipole=0.0333984,0.,0.6877774\ PG=CS [SG(C1H1S1),X(H2)]\\@

$CH_3S^{\bullet}$ (solution)

1\1\GINC-KOHN\FOpt\UB3P86\6-311+G(2df,p)\C1H3S1(2)\CRISTINA\24-Oct-200
3\0\\# B3P86/6-311+G(2DF,P) SCRF=DIPOLE OPT\\ch3s-rad-solv\\0,2\S,-0.0
189935325,0.,-0.687113542\C,0.0174581371,0.,1.0973948898\H,1.075033560
1,0.,1.3861492928\H,-0.4379429313,0.8988312653,1.51164902\H,-0.4379429
313,-0.8988312653,1.51164902\\Version=x86-Linux-G98RevA.11.1\State=2-A
'\Dielectric=78.4\A0=3.2\HF=-438.5690647\S2=0.754308\S2-1=0.\S2A=0.750
008\RMSD=3.802e-09\RMSF=1.533e-04\Dipole=0.0559366,0.,0.829826\PG=CS [
SG(C1H1S1),X(H2)]\\@

NO$^{\bullet}$ (gas-phase)

1\1\GINC-VLAD\Freq\UB3P86\6-311+G(2df,p)\N1O1(2)\CRISTINA\06-Feb-2002\
1\\#N GEOM=ALLCHECK GUESS=TCHECK UB3P86/6-311+G(2DF,P) FREQ\\no-radica
l\\0,2\N\O,1,r1\\r1=1.14227134\\Version=x86-Linux-G98RevA.11.1\HF=-130
.1945865\S2=0.753027\S2-1=0.\S2A=0.750006\RMSD=3.420e-10\RMSF=4.560e-0
5\Dipole=0.,0.,0.057608\DipoleDeriv=-0.0265874,0.,0.,0.,-0.0266651,0.,
0.,0.,0.5788353,0.0265874,0.,0.,0.,0.0266651,0.,0.,0.,-0.5788353\Polar
=8.1869882,0.,7.3531354,0.,0.,14.2549793\PG=C*V [C*(N1O1)]\\@

NO$^{\bullet}$ (solution)

1\1\GINC-KOHN\FOpt\UB3P86\6-311+G(2df,p)\N1O1(2)\CRISTINA\24-Oct-2003\
0\\# B3P86/6-311+G(2DF,P) SCRF=DIPOLE OPT\\no-rad-solv\\0,2\N,0.,0.,-0
.6091704062\O,0.,0.,0.5330241054\\Version=x86-Linux-G98RevA.11.1\Diele
ctric=78.4\A0=2.8\HF=-130.1945987\S2=0.753024\S2-1=0.\S2A=0.750006\RMS
D=8.058e-09\RMSF=2.812e-09\Dipole=0.,0.,0.0637055\PG=C*V [C*(N1O1)]\\@

[Cu···HSNO]$^{+}$: structure 1 (gas-phase)

1\1\GINC-VLAD\Freq\RB3P86\Gen\Cu1H1N1O1S1(1+)\CRISTINA\22-Oct-2003\0\\
#N GEOM=ALLCHECK GUESS=TCHECK RB3P86/CHKBAS FREQ\\1-hsno-tr-cu-p2 (ecp
on Cu)\\1,1\S,-0.6835408887,0.5228257045,0.5686253248\N,1.3200803483,
1.2167069735,1.22206585\H,-0.7400958448,-0.2253276279,1.6892664782\O,1
.7873421314,1.9819918558,0.5699886959\Cu,-0.4090534285,-1.1211299071,-
0.8241945584\\Version=x86-Linux-G98RevA.11.1\HF=-725.6680443\RMSD=8.28
0e-09\RMSF=2.491e-05\Dipole=0.4790743,-0.5375466,-0.148649\PG=C01[X(Cu
1H1N1O1S1)]\\@

[Cu···HSNO]$^{+}$: structure 1 (solution)

1\1\GINC-VLAD\FOpt\RB3P86\Gen\Cu1H1N1O1S1(1+)\CRISTINA\22-Oct-2003\0\\
B3P86/GEN PSEUDO=READ SCRF=DIPOLE OPT\\1-hsno-tr-cu-p2 (ecp on Cu) O
nsager model\\1,1\S,-0.6780359798,0.5351356333,0.5725557864\N,1.304158
309,1.2005767516,1.2152578064\H,-0.7358222727,-0.222372341,1.686866273
\O,1.7739345826,1.9749774104,0.5686487094\Cu,-0.4046960991,-1.12219497
71,-0.8242673509\\Version=x86-Linux-G98RevA.11.1\Dielectric=78.4\A0=3.
6\HF=-725.6704831\RMSD=8.669e-09\RMSF=6.680e-05\Dipole=0.3698273,-0.80
55312,-0.2815174\PG=C01 [X(Cu1H1N1O1S1)]\\@

[Cu···HSNO]$^{+}$: structure 3 (gas-phase)

1\1\GINC-VLAD\Freq\RB3P86\Gen\Cu1H1N1O1S1(1+)\CRISTINA\22-Oct-2003\0\\
#N GEOM=ALLCHECK GUESS=TCHECK RB3P86/CHKBAS FREQ\\hsno-tr-cu-p2 (ecp o
n Cu)\\1,1\S,-0.4098876877,0.4745084732,-1.8679594437\N,-0.6011728314,
0.1043825617,-0.1935893124\H,0.9301556507,0.334071528,-1.8334260216\O,
-1.7112756169,0.1145779289,0.2346446271\Cu,0.811257314,-0.3301209814,1
.0758188032\\Version=x86-Linux-G98RevA.11.1\State=1-A'\HF=-725.6518541
\RMSD=8.813e-09\RMSF=1.079e-05\Dipole=1.5343789,-0.2082448,0.2437289\P
G=CS [SG(Cu1H1N1O1S1)]\\@

[Cu···HSNO]$^{+}$: structure 3 (solution)

1\1\GINC-VLAD\FOpt\RB3P86\Gen\Cu1H1N1O1S1(1+)\CRISTINA\22-Oct-2003\0\\
B3P86/GEN PSEUDO=READ SCRF=DIPOLE OPT\\hsno-tr-cu-p2 (ecp on Cu) Ons
ager model\\1,1\S,-0.4143650072,0.4733979685,-1.8612756858\N,-0.617855
7732,0.1039619375,-0.1846838751\H,0.9277032062,0.3353369344,-1.8378293
214\O,-1.738830217,0.1201239103,0.2224934459\Cu,0.8254403123,-0.330980
3198,1.0734855122\\Version=x86-Linux-G98RevA.11.1\State=1-A'\Dielectri
c=78.4\A0=3.47\HF=-725.6604804\RMSD=6.863e-09\RMSF=2.415e-05\Dipole=1.

9235189,-0.2897138,0.4288737\PG=CS [SG(Cu1H1N1O1S1)]\\@

[Cu···HSNO]$^+$: structure 5 (gas-phase)

1\1\GINC-VLAD\Freq\RB3P86\Gen\Cu1H1N1O1S1(1+)\CRISTINA\01-Mar-2004\0\\
#N GEOM=ALLCHECK GUESS=TCHECK RB3P86/CHKBAS FREQ\\hsno-cis-cu-p2\\1,1\
S,1.7562355763,0.6687096533,0.\N,0.045356471,0.653544322,0.\H,1.885115
7762,2.0196710731,0.\O,-0.5774507654,1.6681010782,0.\Cu,-0.8856129025,
-1.0565049795,0.\\Version=x86-Linux-G98RevA.11.1\State=1-A'\HF=-725.65
55121\RMSD=7.761e-09\RMSF=1.513e-05\Dipole=0.091555,-0.8431674,0.\PG=C
S [SG(Cu1H1N1O1S1)]\\@

[Cu···HSNO]$^+$: structure 5 (solution)

1\1\GINC-VLAD\FOpt\RB3P86\Gen\Cu1H1N1O1S1(1+)\CRISTINA\14-Mar-2004\0\\
B3P86/GEN PSEUDO=READ SCRF=DIPOLE OPT\\hsno-cis-cu-p2-solv\\1,1\S,1.
7579838629,0.671701727,0.\N,0.0439534547,0.657425537,0.\H,1.8754696905
,2.0218082107,0.\O,-0.5685339307,1.6803055796,0.\Cu,-0.8883660081,-1.0
625330772,0.\\Version=x86-Linux-G98RevA.11.1\State=1-A'\Dielectric=78.
4\A0=3.54\HF=-725.6588004\RMSD=5.446e-09\RMSF=9.316e-05\Dipole=-0.0098
227,-1.1011157,0.\PG=CS [SG(Cu1H1N1O1S1)]\\@

[Cu···HSNO]$^+$: transition structure 2 (gas-phase)

1\1\GINC-POPLE\Freq\RB3P86\Gen\Cu1H1N1O1S1(1+)\CRISTINA\28-Oct-2003\0\
\#N GEOM=ALLCHECK GUESS=TCHECK RB3P86/CHKBAS FREQ\\hsno-tr-cu-b3p86 tr
ansition\\1,1\S,-0.6616234791,0.0697317192,-1.4673116346\Cu,-0.5764299
691,0.0569973478,0.6530548769\N,1.4551122638,0.0345064151,0.6856508883
\O,2.2278077833,-0.5535670376,0.1603321302\H,-0.7058033445,1.418360801
9,-1.543818538\\Version=x86-Linux-G98RevA.11.1\HF=-725.6334369\RMSD=3.
025e-09\RMSF=3.940e-05\Dipole=0.7381646,0.2100988,1.2166295\PG=C01[X(C
u1H1N1O1S1)]\\@

[Cu···HSNO]$^+$: transition structure 2 (solution)

1\1\GINC-VLAD\FTS\RB3P86\Gen\Cu1H1N1O1S1(1+)\CRISTINA\27-Oct-2003\0\\#
B3P86/GEN PSEUDO=READ SCRF=DIPOLE OPT=(TS,NOEIGEN)\\hsno-tr-cu-b3p86
transition Onsager model\\1,1\S,-0.6696448458,0.070968406,-1.471117577
8\Cu,-0.5894311674,0.0508540815,0.6566301468\N,1.4895035306,0.04761184
93,0.6783444613\O,2.2551174803,-0.5454172143,0.1605649517\H,-0.6596431
698,1.4197919084,-1.5373238549\\Version=x86-Linux-G98RevA.11.1\Dielect
ric=78.4\A0=3.8\HF=-725.6378227\RMSD=7.706e-09\RMSF=2.765e-05\Dipole=1
.0864893,0.1867728,1.5933766\PG=C01 [X(Cu1H1N1O1S1)]\\@

[Cu···HSNO]$^+$: transition structure 4 (gas-phase)

1\1\GINC-POPLE\Freq\RB3P86\Gen\Cu1H1N1O1S1(1+)\CRISTINA\25-Mar-2004\0\
\#N GEOM=ALLCHECK GUESS=TCHECK RB3P86/CHKBAS FREQ\\hsno-cu-n-transit (
cis)\\1,1\S,1.7761580632,0.6967472275,0.240194648\N,-0.0735095087,0.68
04049122,0.159751537\H,1.7192645664,0.4401776377,1.5656902311\O,-0.631
092159,1.6904826787,0.3147248184\Cu,-0.8473961981,-1.0301665204,-0.311
8918588\\Version=x86-Linux-G98RevA.11.1\HF=-725.6304694\RMSD=7.466e-09
\RMSF=1.456e-05\Dipole=-0.5108523,-1.2269676,0.0560719\PG=C01[X(Cu1H1N
1O1S1)]\\@

[Cu···HSNO]$^+$: transition structure 4 (solution)

1\1\GINC-POPLE\FTS\RB3P86\Gen\Cu1H1N1O1S1(1+)\CRISTINA\27-Mar-2004\0\\
B3P86/GEN PSEUDO=READ SCRF=DIPOLE OPT=(TS,NOEIGEN)\\hsno-cu-n-transi

t-solv (cis)\\1,1\S,1.7962725353,0.7066219474,0.245875701\N,-0.0610702
448,0.6760090434,0.1488390486\H,1.7258318973,0.4535090339,1.5707905643
\O,-0.6181508826,1.6831587668,0.3256075265\Cu,-0.8652928858,-1.0329928
838,-0.3155701839\\Version=x86-Linux-G98RevA.11.1\Dielectric=78.4\A0=4
.07\HF=-725.6346774\RMSD=7.762e-09\RMSF=9.981e-05\Dipole=-0.7025921,-1
.4215182,0.0185385\PG=C01 [X(Cu1H1N1O1S1)]\\@

[HS···Cu]$^+$ (gas-phase)

1\1\GINC-VLAD\Freq\UB3P86\Gen\Cu1H1S1(1+,2)\CRISTINA\23-Oct-2003\0\\#N
GEOM=ALLCHECK GUESS=TCHECK UB3P86/CHKBAS FREQ\\hs-cu-p2-ecp\\1,2\S,1.
1360255148,0.7110652524,-0.2083637421\H,1.0710351445,1.4035976001,0.95
50394316\Cu,-0.6637049442,-0.4407117807,0.0820269118\\Version=x86-Linu
x-G98RevA.11.1\State=2-A"\HF=-595.4165921\S2=0.754956\S2-1=0.\S2A=0.75
0016\RMSD=4.842e-09\RMSF=6.166e-05\Dipole=-0.4221919,-0.0694077,0.3834
449\PG=CS [SG(Cu1H1S1)] \\@

[HS···Cu]$^+$ (solution)

1\1\GINC-KOHN\FOpt\UB3P86\Gen\Cu1H1S1(1+,2)\CRISTINA\24-Oct-2003\0\\#
B3P86/GEN PSEUDO=READ SCRF=DIPOLE OPT\\hs-cu-p2-ecp-solv\\1,2\S,1.1373
385206,0.7093636472,-0.212567552\H,1.0625108034,1.3962073866,0.9533762
01\Cu,-0.6641354184,-0.439518129,0.0844036079\\Version=x86-Linux-G98Re
vA.11.1\State=2-A"\Dielectric=78.4\A0=3.24\HF=-595.4189751\S2=0.754904
\S2-1=0.\S2A=0.750016\RMSD=9.109e-09\RMSF=3.285e-05\Dipole=-0.5960839,
-0.1574562,0.4479964\PG=CS [SG(Cu1H1S1)]\\@

[ON···Cu]$^+$ (gas-phase)

1\1\GINC-VLAD\Freq\UB3P86\Gen\Cu1N1O1(1+,2)\CRISTINA\23-Oct-2003\0\\#N
GEOM=ALLCHECK GUESS=TCHECK UB3P86/CHKBAS FREQ\\no-cu-p2-ecp\\1,2\N,0.
5652362175,0.9956416211,0.\O,0.0911296927,2.0200257744,0.\Cu,-0.161575
5539,-0.7975757773,0.\\Version=x86-Linux-G98RevA.11.1\State=2-A'\HF=-3
26.4887518\S2=0.755194\S2-1=0.\S2A=0.750019\RMSD=7.509e-09\RMSF=7.369e
-05\Dipole=-0.1949521,-0.7362669,0.\PG=CS [SG(Cu1N1O1)]\\@

[ON···Cu]$^+$ (solution)

1\1\GINC-KOHN\FOpt\UB3P86\Gen\Cu1N1O1(1+,2)\CRISTINA\24-Oct-2003\0\\#
B3P86/GEN PSEUDO=READ SCRF=DIPOLE OPT\\no-cu-p2-ecp-solv\\1,2\N,0.5511
222507,0.9948692445,0.\O,0.0962026488,2.0312586822,0.\Cu,-0.1595681705
,-0.8004880748,0.\\Version=x86-Linux-G98RevA.11.1\State=2-A'\Dielectri
c=78.4\A0=3.49\HF=-326.4918671\S2=0.754736\S2-1=0.\S2A=0.750017\RMSD=6
.197e-09\RMSF=1.398e-04\Dipole=-0.2285969,-0.9301429,0.\PG=CS [SG(Cu1N
1O1)]\\@

[Cu···CH_3SNO]$^+$: structure 6 (gas-phase)

1\1\GINC-VLAD\Freq\RB3P86\Gen\C1H3Cu1N1O1S1(1+)\CRISTINA\23-Oct-2003\0
\\#N GEOM=ALLCHECK GUESS=TCHECK RB3P86/CHKBAS FREQ\\ch3sno-cu-s-ecp\\1
,1\S,0.1129757982,0.8876570744,-0.0722364312\N,0.276593149,0.219361188
7,1.9371720357\C,1.826027952,0.6407937205,-0.5576837981\H,1.8974867444
,0.1086170578,-1.5025159748\H,2.3360953581,0.0643809053,0.2232818929\H
,2.2916851037,1.6210127927,-0.6438287029\O,1.3336776968,-0.0149881236,
2.235774847\Cu,-1.0998145278,-0.7329968828,-0.8628087777\\Version=x86-
Linux-G98RevA.11.1\HF=-765.1502732\RMSD=6.645e-09\RMSF=9.273e-06\Dipol
e=-0.0589583,-0.7221847,-0.450868\PG=C01 [X(C1H3Cu1N1O1S1)]\\@

$[Cu{\cdots}CH_3SNO]^+$: structure 6 (solution)

1\1\GINC-VLAD\FOpt\RB3P86\Gen\C1H3Cu1N1O1S1(1+)\CRISTINA\27-Oct-2003\0
\\# B3P86/GEN PSEUDO=READ SCRF=DIPOLE OPT\\ch3sno-cu-s-ecp-vol\\1,1\S,
0.1184194738,0.8742680927,-0.0459200371\N,0.2805698982,0.2241566368,1.
9274776068\C,1.8279504727,0.6404565441,-0.5471566055\H,1.8904685404,0.
1107786044,-1.4944115747\H,2.3431515317,0.0599934034,0.2271105781\H,2.
2909278628,1.6213291395,-0.6359176445\O,1.3430383876,0.0020284953,2.23
8285122\Cu,-1.10673306,-0.7313260108,-0.8785429433\\Version=x86-Linux-
G98RevA.11.1\Dielectric=78.4\A0=3.84\HF=-765.1529998\RMSD=8.054e-09\RM
SF=1.670e-05\Dipole=-0.2293103,-0.8434764,-0.7840758\PG=C01 [X(C1H3Cu1
N1O1S1)]\\@

$[Cu{\cdots}CH_3SNO]^+$: structure 8 (gas-phase)

1\1\GINC-CURIE\Freq\RB3P86\Gen\C1H3Cu1N1O1S1(1+)\CRISTINA\17-Feb-2004\
0\\#N GEOM=ALLCHECK GUESS=READ SCRF=CHECK GENCHK RB3P86/CHKBAS FREQ\\c
h3sno-cu-n-nbo\\1,1\S,0.1776801378,1.484686965,-0.3062360261\N,0.17818
73803,-0.2076244674,-0.3071102708\C,1.0533205184,1.8548508078,-1.81542
34558\H,1.0863643807,2.943456683,-1.8723753536\H,0.5110846261,1.446776
8228,-2.6682250714\H,2.0627922752,1.4467768228,-1.7679141825\O,0.69394
66905,-0.824993318,-1.1960339488\Cu,-0.6766183374,-1.1264754759,1.1661
681119\\Version=x86-Linux-G03RevB.03\State=1-A'\HF=-765.1484166\RMSD=9
.727e-09\RMSF=1.290e-05\Dipole=-0.3854856,0.1373026,0.6643938\PG=CS[SG
(C1H1Cu1N1O1S1),X(H2)]\\@

$[Cu{\cdots}CH_3SNO]^+$: structure 8 (solution)

1\1\GINC-VLAD\FOpt\RB3P86\Gen\C1H3Cu1N1O1S1(1+)\CRISTINA\27-Oct-2003\0
\\# B3P86/GEN PSEUDO=READ SCRF=DIPOLE OPT\\ch3sno-cu-n-ecp-vol\\1,1\S,
0.3596222103,0.,-1.4888376146\N,0.3580304709,0.,0.2073607297\C,2.10837
60336,0.,-1.8439634953\H,2.1833300517,0.,-2.9315170533\H,2.5701592896,
-0.896137064,-1.4304108772\H,2.5701592896,0.896137064,-1.4304108772\O,
1.3919323201,0.,0.8170566121\Cu,-1.3575700708,0.,1.1272256417\\Version
=x86-Linux-G98RevA.11.1\State=1-A'\Dielectric=78.4\A0=3.66\HF=-765.151
3878\RMSD=8.412e-09\RMSF=8.795e-05\Dipole=-1.1032845,0.,0.0168181\PG=C
S [SG(C1H1Cu1N1O1S1),X(H2)]\\@

$[Cu{\cdots}CH_3SNO]^+$: transition structure 7 (gas-phase)

1\1\GINC-POPLE\Freq\RB3P86\Gen\C1H3Cu1N1O1S1(1+)\CRISTINA\23-Oct-2003\
0\\#P GEOM=ALLCHECK GUESS=TCHECK TEST RB3P86/CHKBAS FREQ\\ch3sno-cu tr
ansition structure (ECP on Cu)\\1,1\C,-1.0695175224,-0.5009050625,-2.1
618905473\S,-0.9292535557,-0.6782274511,-0.3893494455\Cu,1.0422759303,
-0.2159837215,1.0311144733\N,-0.3889561504,0.9498421294,0.1840956462\O
,-0.3666046686,1.8573481072,-0.5602035219\H,-0.631218666,0.4626548826,
-2.4380274727\H,-2.1234752301,-0.5288802578,-2.4345300585\H,-0.5306156
543,-1.3208568715,-2.6358691321\\Version=x86-Linux-G98RevA.11.1\HF=-76
5.1333193\RMSD=9.352e-09\RMSF=1.850e-05\Dipole=0.6428087,-0.8506466,-0
.0355968\PG=C01 [X(C1H3Cu1N1O1S1)]\\@

$[Cu{\cdots}CH_3SNO]^+$: transition structure 7 (solution)

1\1\GINC-POPLE\FTS\RB3P86\Gen\C1H3Cu1N1O1S1(1+)\CRISTINA\29-Oct-2003\0
\\#P B3P86/GEN PSEUDO=READ SCRF=DIPOLE OPT=(TS,NOEIGEN)\\ch3sno-cu tra
nsition structure (ECP on Cu)\\1,1\C,-1.0658333315,-0.497138784,-2.146
1790523\S,-0.9395079065,-0.6696719683,-0.3721019702\Cu,1.0671472306,-0
.2220206506,1.0071201095\N,-0.4209946737,0.9460587191,0.2023193961\O,-
0.4144259367,1.8633225486,-0.5412841118\H,-0.5845141005,0.4427903732,-

2.4289694868\H,-2.1171684799,-0.4903441062,-2.4285487341\H,-0.5560904042,-1.3452546257,-2.6042219957\\Version=x86-Linux-G98RevA.11.1\Dielectric=78.4\A0=3.44\HF=-765.1378903\RMSD=7.232e-09\RMSF=1.334e-05\Dipole=0.9154598,-1.1488441,0.081983\PG=C01 [X(C1H3Cu1N1O1S1)]\\@

$[CH_3S\cdots Cu]^+$ (gas-phase)

1\1\GINC-VLAD\Freq\UB3P86\Gen\C1H3Cu1S1(1+,2)\CRISTINA\23-Oct-2003\0\\#N GEOM=ALLCHECK GUESS=TCHECK UB3P86/CHKBAS FREQ\\ch3s-cu-p2\\1,2\S,0.6241050062,0.4621803609,0.7899553918\C,1.5246199652,1.4220638754,-0.4248077977\H,0.8295193193,2.0592858051,-0.9771175248\H,2.0125367349,0.7485769471,-1.1339472079\H,2.262324534,2.0245204103,0.1006925667\Cu,-0.8357855337,-0.7158500755,-0.2786230109\\Version=x86-Linux-G98RevA.11.1\HF=-634.9059452\S2=0.754869\S2-1=0.\S2A=0.750016\RMSD=1.692e-09\RMSF=1.448e-05\Dipole=-0.1698782,-0.067415,-0.6884143\PG=C01 [X(C1H3Cu1S1)]\\@

$[CH_3S\cdots Cu]^+$ (solution)

1\1\GINC-VLAD\FOpt\UB3P86\Gen\C1H3Cu1S1(1+,2)\CRISTINA\24-Oct-2003\0\\# B3P86/GEN PSEUDO=READ SCRF=DIPOLE OPT\\ch3s-cu-solv\\1,2\S,0.6281672512,0.4548163209,0.7984125681\C,1.5214117983,1.4184705899,-0.4199077855\H,0.8219656434,2.0497115542,-0.9737667888\H,2.0066287497,0.7453819629,-1.1316693371\H,2.2600494159,2.0255055045,0.0979931511\Cu,-0.8368203661,-0.7106373688,-0.2844038415\\Version=x86-Linux-G98RevA.11.1\Dielectric=78.4\A0=3.45\HF=-634.9083733\S2=0.754773\S2-1=0.\S2A=0.750015\RMSD=8.796e-09\RMSF=2.511e-05\Dipole=-0.3151871,-0.1709603,-0.8375688\PG=C01 [X(C1H3Cu1S1)]\\@

Appendix C

Gaussian Archive Entries of Optimized Geometries Obtained for all Species Considered in Chapter 5

1A

1\1\GINC-ANGSTROM\Freq\RB3P86\6-311+G(2df,p)\C2H6N2O1S1\CRISTINA\08-Se
p-2003\0\\#N GEOM=ALLCHECK GUESS=TCHECK RB3P86/6-311+G(2DF,P) FREQ\\no
Cu for 5ring-s-cu-p2\\0,1\C,0.6690444706,0.6769029898,0.5930628585\C,1
.8479831408,0.6596628771,-0.3592763375\N,2.5870605883,-0.5839060373,-0
.2321858341\S,-0.5208414141,-0.6383008825,0.265303759\N,-1.8680603684,
0.4767453303,-0.1348786597\O,-2.8988300665,-0.0261252192,-0.4160205098
\H,1.0057956413,0.5771650698,1.6276379084\H,0.1007904724,1.6085807813,
0.5106598484\H,2.4509243308,1.5616147347,-0.1688393232\H,1.4791400365,
0.7333455511,-1.3850325679\H,3.0927065263,-0.6292010772,0.6450515906\H
,3.2595789421,-0.698959438,-0.9794411896\\Version=x86-Linux-G98RevA.11
.1\HF=-663.803564\RMSD=5.413e-09\RMSF=1.820e-06\Dipole=1.5073425,0.533
0328,0.2186176\PG=C01[X(C2H6N2O1S1)]\\@

1B

1\1\GINC-N10\Freq\RB3P86\6-311+G(2df,p)\C3H5N1O3S1\CRISTINA\14-Jun-200
4\0\\#N GEOM=ALLCHECK GUESS=READ SCRF=CHECK GENCHK RB3P86/6-311+G(2DF,
P) FREQ\\6ring-n-wcu-co-1 (no Cu for 6ring-n-cu-co-1)\\0,1\C,0.0265308
854,1.303988383,0.4845471641\S,-1.3838176862,0.6678472737,-0.441808372
6\N,-1.9076980376,-0.5089969398,0.8516305207\O,-2.8430730745,-1.170001
0026,0.6053724489\C,1.3527635279,1.0741407894,-0.2157648964\C,1.790889
2189,-0.3643519284,-0.1864296405\H,-0.0022902299,0.7824736761,1.445820
902\H,-0.1313112374,2.3682194764,0.6580780156\H,2.1377157775,1.6463359
352,0.2930902458\H,1.3417635583,1.4291786118,-1.2475495409\O,1.4271520
294,-1.185818004,0.6097567747\O,2.6882019916,-0.6286820346,-1.15121353
65\H,2.9497420097,-1.5554406346,-1.0473605653\\Version=x86-Linux-G03Re
vB.03\State=1-A\HF=-797.3179797\RMSD=4.347e-09\RMSF=3.494e-05\Dipole=0
.981949,0.8460627,-0.2997519\PG=C01[X(C3H5N1O3S1)]\\@

1C

1\1\GINC-KOHN\Freq\RB3P86\6-311+G(2df,p)\C3H6N2O3S1\CRISTINA\21-Jan-20
03\0\\#N GEOM=ALLCHECK GUESS=TCHECK RB3P86/6-311+G(2DF,P) FREQ\\cys-sn
o-6 another config.\\0,1\S,-0.4653145675,0.572896799,-1.9324058267\C,-
0.3974165312,0.6252425054,-0.1405962726\C,0.7947381072,-0.1245894195,0
.442526699\N,2.1142844933,0.3655097613,0.0663502903\C,0.6824174162,-0.
1745193972,1.9763132369\O,-0.3639422842,-0.2713686176,2.5516639507\O,1
.8596346326,-0.1362759289,2.5923369621\H,2.5212481689,-0.0174306979,1.
8740104002\N,-1.8389960625,-0.590386098,-2.2309525595\O,-2.3779363509,
-1.0378118652,-1.2889708133\H,-1.3285015629,0.1765785126,0.2239858335\
H,-0.3929603875,1.6727677808,0.1695914109\H,0.7347108802,-1.1706005861
,0.124395968\H,2.1336335398,1.3764632349,-0.0178565608\H,2.4294014927,
-0.0231435108,-0.8131207164\\Version=x86-Linux-G98RevA.11.1\HF=-852.83
40515\RMSD=4.501e-09\RMSF=2.788e-06\Dipole=1.1884943,0.5989109,-1.2063
188\PG=C01[X(C3H6N2O3S1)]\\@

2A

1\1\GINC-ANGSTROM\Freq\RB3P86\6-311+G(2df,p)\C2H6Cu1N2O1S1(1+)\CRISTIN
A\06-Sep-2003\0\\#N GEOM=ALLCHECK GUESS=TCHECK RB3P86/6-311+G(2DF,P) F
REQ\\5ring-s-cu-p2\\1,1\C,-0.0118526453,1.5110845305,0.7366108915\C,0.
9805495905,1.672625546,-0.4073728923\N,2.015731382,0.6095766656,-0.420
9293152\Cu,0.9390424781,-1.0663178521,-0.1324338845\S,-0.8157320503,-0
.1223569066,0.8460298417\N,-2.3296459977,0.4221646899,-0.4151143355\O,
-3.0722759507,-0.3842643888,-0.6895974303\H,0.4588725608,1.6764201601,
1.7081394542\H,-0.8095405329,2.2513106587,0.6367002936\H,1.4410327933,
2.661915552,-0.331376302\H,0.4555232164,1.6262721662,-1.3625938399\H,2
.6864815087,0.7558828898,0.3309597879\H,2.5505396371,0.6587919528,-1.2
840672109\\Version=x86-Linux-G98RevA.11.1\HF=-2304.7299398\RMSD=9.231e
-09\RMSF=5.077e-06\Dipole=1.3143578,0.6217946,-0.4706932\PG=C01[X(C2H6
Cu1N2O1S1)]\\@

2B

1\1\GINC-BOHR\Freq\RB3P86\6-311+G(2df,p)\C2H6Cu1N2O1S1(1+)\CRISTINA\06
-Sep-2003\0\\#N GEOM=ALLCHECK GUESS=TCHECK RB3P86/6-311+G(2DF,P) FREQ\
\6ring-n-cu-p2\\1,1\C,0.5761420043,1.6216541087,0.4287674838\C,1.73542
81237,1.0927131454,-0.4114767086\N,2.0455130796,-0.3398509469,-0.12622
98981\Cu,0.3053945151,-1.1899842389,0.1694401213\N,-1.397214577,-0.307
4303314,0.0436143483\O,-2.4888144238,-0.7072361586,-0.191520643\S,-1.1
236601054,1.4168883645,-0.1867018426\H,0.6233318783,1.2758045399,1.465
0065942\H,0.6417269184,2.7132693839,0.4792107436\H,2.6174136885,1.7062
194764,-0.2110538543\H,1.5080843887,1.1818150692,-1.4739475176\H,2.631
2671049,-0.4064826655,0.704656992\H,2.6033018745,-0.7286420145,-0.8836
776528\\Version=x86-Linux-G98RevA.11.1\HF=-2304.7286489\RMSD=1.392e-09
\RMSF=3.395e-06\Dipole=2.3430377,0.3158764,0.1555717\PG=C01[X(C2H6Cu1N
2O1S1)]\\@

2A$_W$

1\1\GINC-CURIE\Freq\RB3P86\6-311+G(2df,p)\C2H8Cu1N2O2S1(1+)\CRISTINA\2
6-Aug-2003\0\\#N GEOM=ALLCHECK GUESS=READ SCRF=CHECK GENCHK RB3P86/6-3
11+G(2DF,P) FREQ\\h2o+5 memb. ring in a Cu(I) complex non-planar\\1,1\
C,-0.8867038144,1.7909150963,0.5599816431\S,-1.0467025926,-0.001391940
5,0.773930071\N,-2.5245264743,-0.1281548904,-0.5428682063\O,-2.9104566
739,-1.1745055334,-0.7797356935\C,0.1333551409,2.1789200991,-0.4939989
796\N,1.4270213737,1.4958890514,-0.2721751044\Cu,1.0506717622,-0.47901
92884,0.0320317361\O,1.9744310219,-2.2193671271,-0.121863754\H,-0.6353
575962,2.1992403519,1.541051447\H,-1.8747534182,2.172586813,0.29173047
51\H,0.255854455,3.2660295362,-0.4941689664\H,-0.2260139386,1.88537432
59,-1.4815201507\H,1.895124009,1.8919392057,0.5406279429\H,2.045523696
6,1.6753872702,-1.0584358672\H,2.9128792475,-2.3589206215,-0.282532115
7\H,1.5953368844,-3.0599754851,0.1536485278\\Version=x86-Linux-G03RevB
.03\State=1-A\HF=-2381.4101938\RMSD=2.435e-09\RMSF=1.296e-06\Dipole=1.
8318325,0.0777031,-0.2453916\PG=C01[X(C2H8Cu1N2O2S1)]\\@

2A$_{diss}$

1\1\GINC-N23\Freq\RB3P86\6-311+G(2df,p)\C2H6Cu1N2O1S1(1+)\CRISTINA\02-
Oct-2004\0\\#N GEOM=ALLCHECK GUESS=READ SCRF=CHECK GENCHK RB3P86/6-311
+G(2DF,P) FREQ\\2A-2\\1,1\C,-0.4873080483,2.1207444286,0.6686078475\S,
-1.2949650372,0.4823267864,0.6636027141\Cu,0.393749512,-0.5091829885,-
0.2055456783\N,1.4513279883,1.1364236379,-0.4923116902\C,0.4858465191,

2.2752268152,-0.4784501188\H,0.0005138115,2.2650758331,1.6354220421\H,
-1.2809600661,2.8656564413,0.5852838778\H,1.0255890889,3.2224459062,-0
.4029334501\H,-0.0478732043,2.2560955828,-1.429047013\H,2.1236364605,1
.2480780667,0.2667149255\H,2.0004756629,1.1565016482,-1.349259129\N,0.
0481853455,-2.224919127,-0.2316428305\O,-0.6260626459,-3.090141804,-0.
0045330921\\Version=IA32L-G03RevC.01\State=1-A\HF=-2304.7277894\RMSD=1
.496e-09\RMSF=1.600e-06\Dipole=1.529646,0.3937425,-0.5781438\PG=C01
[X(C2H6Cu1N2O1S1)]\\@

2B$_W$

1\1\GINC-LOKI\Freq\RB3P86\6-311+G(2df,p)\C2H8Cu1N2O2S1(1+)\STUACC2\13-
Dec-2002\0\\#N GEOM=ALLCHECK GUESS=TCHECK RB3P86/6-311+G(2DF,P) FREQ\\
h2o+6ring-n-cu-p2\\1,1\C,2.1529999339,-0.0803673465,0.4770238212\S,1.5
478993075,1.4569046962,-0.2570402432\N,-0.134328274,1.2693891804,0.110
1304753\O,-0.8625437801,2.1641760846,-0.2248851159\C,1.8941236013,-1.3
534293613,-0.3144331239\N,0.558916783,-1.9421874048,-0.0309915879\Cu,-
0.9433682737,-0.6923566392,0.0902151341\O,-2.7496775915,0.0583629376,0
.1435449023\H,1.7809375459,-0.1475021064,1.5020970137\H,3.2295288259,0
.0913696775,0.5490972396\H,2.6716381764,-2.0828500074,-0.0719813307\H,
1.9545824194,-1.1539921004,-1.3846676195\H,0.599303562,-2.4333662114,0
.8613259196\H,0.3685401832,-2.6664775467,-0.7205318971\H,-2.7855492062
,1.0178495501,0.0226917093\H,-3.5847802889,-0.3251082187,-0.1404207192
\\Version=x86-Linux-G98RevA.11.1\HF=-2381.406008\RMSD=8.273e-09\RMSF=1
.289e-06\Dipole=0.0069278,-1.8259904,0.0194898\PG=C01[X(C2H8Cu1N2O2S1)
]\\@

3A

1\1\GINC-FLEXOR\Freq\RB3P86\6-311+G(2df,p)\C3H5Cu1N1O3S1(1+)\GAULD\17-
Jun-2004\0\\#N GEOM=ALLCHECK GUESS=TCHECK RB3P86/6-311+G(2DF,P) FREQ\\
5ring-s-cu-co-2\\1,1\C,-0.3104778943,1.5053067181,0.6339164827\S,-1.07
75256447,-0.1037487335,1.0239505645\N,-2.805028591,0.3294765835,-0.013
2748492\O,-3.5624617691,-0.5019067438,-0.0969575503\C,0.546429167,1.62
85998068,-0.6305476673\C,1.8403247705,0.8627126758,-0.6440279654\Cu,0.
3671456113,-1.3689290725,0.0040386632\H,0.2476062105,1.7947310603,1.52
55483919\H,-1.1481542211,2.2017188584,0.5439523963\H,0.7793086719,2.68
44838035,-0.7747495789\H,-0.0240923872,1.2997375918,-1.5043837788\O,1.
9406927048,-0.3634567169,-0.5848307291\O,2.8985242775,1.6180741727,-0.
7628104092\H,3.7020214869,1.0705145397,-0.7970293441\\Version=SGI64-G9
8RevA.7\HF=-2438.2314326\RMSD=7.077e-09\RMSF=3.410e-06\Dipole=0.299973
4,0.4265946,-0.3561779\PG=C01[X(C3H5Cu1N1O3S1)]\\@

3A$_W$

1\1\GINC-N2\Freq\RB3P86\6-311+G(2df,p)\C3H7Cu1N1O4S1(1+)\CRISTINA\15-J
ul-2004\0\\#N GEOM=ALLCHECK GUESS=READ SCRF=CHECK GENCHK RB3P86/6-311+
G(2DF,P) FREQ\\optimization of w1-freq structure\\1,1\C,-0.1493837788,
-1.9951796084,0.4088572594\C,-1.2201575898,-1.6744124171,-0.6328204073
\C,-2.148281886,-0.5634203189,-0.2398216371\O,-3.3973876259,-0.9441073
044,-0.1032530598\S,1.0729376045,-0.7045965237,0.7751852402\Cu,0.17482
08283,1.1670354976,0.1355541792\O,-1.8087059678,0.5990980645,-0.063528
3097\N,2.433417623,-1.4681171735,-0.4943926544\O,3.3833049986,-0.86326
00156,-0.6424240788\H,-0.5932952622,-2.2796114149,1.3636712317\H,0.437
8280228,-2.8491100978,0.0603026194\H,-1.8078990774,-2.5751585867,-0.81
2774892\H,-0.7504898353,-1.3879320046,-1.577414354\H,-3.948688188,-0.1
820710097,0.1408001026\O,0.3080456861,3.0913829658,-0.2821230896\H,1.0

720274691,3.6517762856,-0.1148513355\H,-0.4553293829,3.6616063779,-0.4
196828177\\Version=IA32L-G03RevC.01\State=1-A\HF=-2514.911745\RMSD=7.3
17e-09\RMSF=7.667e-06\Dipole=-0.517119,1.0440921,-0.2837695\PG=C01[X(C
3H7Cu1N1O4S1)]\\@

$3A_{diss}$

1\1\GINC-N6\Freq\RB3P86\6-311+G(2df,p)\C3H5Cu1N1O3S1(1+)\CRISTINA\04-O
ct-2004\0\\#N GEOM=ALLCHECK GUESS=READ SCRF=CHECK GENCHK RB3P86/6-311+
G(2DF,P) FREQ\\3A-2\\1,1\C,-0.7446452135,1.9508296577,0.4924415298\C,0
.1851035853,2.2410789045,-0.6755263878\C,1.4361583412,1.4255198522,-0.
7022466928\O,2.483380019,2.0655425045,-1.1306814942\S,-1.6095583058,0.
3502349582,0.4697969123\Cu,0.0786304567,-0.9123082413,0.0968112567\O,1
.5277448307,0.23365551,-0.3779994612\H,-0.2330375763,2.0714191765,1.44
86989453\H,-1.553025282,2.6865215693,0.471564041\H,0.4743226407,3.2936
838439,-0.6788899937\H,-0.3256040545,2.054863005,-1.629010863\H,3.2574
193814,1.4774917688,-1.1700746791\N,-0.5622185225,-2.5347178603,0.3941
958131\O,-1.44507436,-3.1357411594,0.7319377207\\Version=IA32L-G03RevC
.01\State=1-A\HF=-2438.2289634\RMSD=2.014e-09\RMSF=5.312e-06\Dipole=0.
9013529,-0.0131494,-0.3128159\PG=C01 [X(C3H5Cu1N1O3S1)]\\@

3B

1\1\GINC-N8\Freq\RB3P86\6-311+G(2df,p)\C3H5Cu1N1O3S1(1+)\CRISTINA\12-J
un-2004\0\\#N GEOM=ALLCHECK GUESS=READ SCRF=CHECK GENCHK RB3P86/6-311+
G(2DF,P) FREQ\\6ring-n-cu-co-3\\1,1\C,0.0494153268,1.6397316748,0.3654
68284\S,-1.4403625789,1.4257945224,-0.6482700342\N,-1.8239202418,-0.\2
575566117,-0.3103989453\O,-2.8341821282,-0.6810140489,-0.7631323206\C,
1.4190801169,1.359416597,-0.2607799241\C,2.0996644711,0.0725822194,0.1
157304464\Cu,-0.3343116404,-1.1714673201,0.4405039206\H,-0.1036284827,
1.1152646617,1.31444908\H,-0.0104334397,2.7011019541,0.6188516855\H,2.
1122088613,2.1626259996,-0.0025253523\H,1.3697517031,1.370812308,-1.35
60016988\O,3.390881465,0.1282494549,-0.0464144368\O,1.5595146604,-0.95
83819515,0.5233619076\H,3.8017104167,-0.7282793023,0.1626917128\\Versi
on=x86-Linux-G03RevB.03\State=1-A\HF=-2438.2305954\RMSD=3.285e-09\RMSF
=8.562e-06\Dipole=1.458187,0.5324739,0.3756188\PG=C01[X(C3H5Cu1N1O3S1)
]\\@

$3B_W$

1\1\GINC-N5\Freq\RB3P86\6-311+G(2df,p)\C3H7Cu1N1O4S1(1+)\KGB\11-Jul-20
04\0\\#N GEOM=ALLCHECK GUESS=READ SCRF=CHECK GENCHK RB3P86/6-311+G(2DF
,P) FREQ\\h2o+6ring-n-cu-co-3\\1,1\C,0.1753687089,1.8776526648,0.56906
6736\C,1.6567020281,1.6710980062,0.311552202\C,2.073813223,0.266334355
6,-0.0043967606\O,1.4024028531,-0.7393801181,0.175163071\Cu,-0.6373975
489,-1.0435758246,0.38826469\N,-1.4503544494,0.2091012575,-0.820279161
6\O,-2.1996964818,-0.125929031,-1.6818671795\S,-0.8741458006,1.8697614
344,-0.8983499586\O,3.2978497927,0.2073910347,-0.4748697988\H,-0.23431
1191,1.1415582436,1.2719630117\H,0.0123553976,2.8551024591,1.025841333
4\H,2.2214376677,1.9568738324,1.2075968974\H,2.0250920197,2.3255623689
,-0.4812389929\H,3.5493125466,-0.7165162238,-0.6351518913\O,-0.8289646
519,-2.5261251317,1.6636457298\H,-1.6549408405,-2.9879722052,1.8411291
674\H,-0.1036385846,-3.1089655076,1.9118302903\\Version=IA32L-G03RevC.
01\State=1-A\HF=-2514.9091853\RMSD=2.226e-09\RMSF=6.502e-06\Dipole=0.8
573581,-0.921179,1.5643641PG=C01[X(C3H7Cu1N1O4S1)]\\@

$4A_S$

1\1\GINC-VLAD\Freq\RB3P86\6-311+G(2df,p)\C3H6Cu1N2O3S1(1+)\CRISTINA\13
-Nov-2003\0\\#N GEOM=ALLCHECK GUESS=TCHECK RB3P86/6-311+G(2DF,P) FREQ\
\cys-sno-cu-1b-p2 (Copper complexed with cys-sno-1-p2)\\1,1\C,-0.51769
41493,1.2309179366,-1.0507924182\S,-0.3678520381,1.3969835089,0.755395
0437\Cu,1.2699201942,-0.1595366878,0.820070246\N,1.7231108065,0.215226
4378,-1.1969686395\C,0.3398447514,0.1137915867,-1.6767853639\C,-0.1893
311087,-1.2418157827,-1.2418743004\O,-1.1205114338,-1.7098685585,2.039
4274544\N,-2.147265742,0.4983879085,1.0749087163\O,-2.4726061609,0.395
4036569,2.1567968671\H,2.1104469299,1.1320810375,-1.4022012625\H,2.322
4377443,-0.469863361,-1.650013367\H,-1.5758302425,1.0681058481,-1.2747
472206\H,-0.2374411856,2.1915243706,-1.4860652512\H,0.2521821041,0.194
0062683,-2.7643661971\H,-1.4568681529,-2.5560840151,-1.7000026491\O,0.
1950160159,-1.79773575,-0.2323481538\\Version=x86-Linux-G98RevA.11.1\H
F=-2493.7606114\RMSD=8.054e-09\RMSF=8.390e-06\Dipole=0.5683892,0.02502
09,-1.2226908\PG=C01[X(C3H6Cu1N2O3S1)]\\@

$4A_N$

1\1\GINC-FLEXOR\Freq\RB3P86\6-311+G(2df,p)\C3H6Cu1N2O3S1(1+)\GAULD\25-
Jun-2004\0\\# B3P86/6-311+G(2DF,P) GEOM=CHECK GUESS=READ OPT=(CALCALL,
NORAMAN)\\cys-sno-cu-1b-n (Copper complexed with cys-sno at N, N and O
))\\1,1\C,-0.7203536776,1.0827162689,-1.2823597607\C,0.0892784091,-0.1
584576552,-1.7094803528\C,-0.4333913447,-1.4104324167,-1.0232504849\O,
0.0627794212,-1.8368530644,-0.0029676006\Cu,1.2608842985,-0.0435772585
,0.6891967919\N,1.504839057,-0.0020710544,-1.3184798576\S,-1.540255202
1,1.1559797773,0.341808392\N,-0.1970350403,0.931508676,1.5071992773\O,
-0.4825076322,1.1259996917,2.6375989326\O,-1.4702948779,-1.9292822664,
-1.6339888967\H,1.881738968,0.8599859267,-1.7035047231\H,2.0684207019,
-0.7599899782,-1.6988784759\H,-1.5820309292,1.192137212,-1.9464638453\
H,-0.1120516972,1.9802839355,-1.4125997217\H,-0.0223526745,-0.27570896
65,-2.791629832\H,-1.8029295197,-2.6965794887,-1.1381964678\\Version=S
GI64-G98RevA.7\HF=-2493.7559453\RMSD=8.701e-09\RMSF=9.162e-06\Dipole=0
.6550742,-0.079966,-2.0597779\PG=C01[X(C3H6Cu1N2O3S1)]\\@

$4A_{diss}$

1\1\GINC-N10\Freq\RB3P86\6-311+G(2df,p)\C3H6Cu1N2O3S1(1+)\CRISTINA\04-
Oct-2004\0\\#N GEOM=ALLCHECK GUESS=READ SCRF=CHECK GENCHK RB3P86/6-311
+G(2DF,P) FREQ\\4As-2\\1,1\C,-1.07318648,1.2977599527,-1.2963015281\C,
-0.2227474617,0.1686455377,-1.8883739576\C,-0.7300296084,-1.1765518901
,-1.4091191393\O,-0.2521943316,-1.7269888435,-0.4359211961\Cu,0.769283
6893,0.0217337161,0.6006068525\N,1.1514602558,0.2960939247,-1.36500436
09\S,-0.9417586471,1.3890015091,0.5288342125\O,-1.7276689477,-1.641582
524,-2.1179341008\H,1.5188974478,1.2238027078,-1.564077431\H,1.7785527
419,-0.3780434588,-1.7987028719\H,-2.1213758668,1.1457789421,-1.556361
0969\H,-0.7547057509,2.2479827438,-1.7299689644\H,-0.2610801327,0.2096
807968,-2.980260013\H,-2.0489116414,-2.476329431,-1.7381762031\N,1.128
7307039,-0.1972522091,2.2991009816\O,0.8351106729,-0.0387021106,3.3679
417799\\Version=IA32L-G03RevC.01\State=1-A\HF=-2493.7580814\RMSD=3.443
e-09\RMSF=8.767e-06\Dipole=0.9785893,-0.3236754,-0.9783689\PG=C01
X(C3H6Cu1N2O3S1)] \\@

$4B_S$

1\1\GINC-N16\Freq\RB3P86\6-311+G(2df,p)\C3H6Cu1N2O3S1(1+)\CRISTINA\13-
Jun-2004\0\\#N GEOM=ALLCHECK GUESS=READ SCRF=CHECK GENCHK RB3P86/6-311

+G(2DF,P) FREQ\\cys-sno-co-3\\1,1\C,-0.3330908577,0.7018118707,0.87176
5798\S,-1.1479759358,-0.9236087457,0.8537841747\N,-2.7414164436,-0.236
032422,-0.238683364\O,-3.5096197849,-1.003828352,-0.5473789708\C,0.605
6415926,0.9902497354,-0.3121620643\N,1.5867442768,-0.0869377444,-0.540
7072984\Cu,0.5486098148,-1.7833920792,-0.2900731641\H,0.2075754188,0.7
525688624,1.8200310362\H,-1.1189568663,1.459447575,0.9031870029\C,1.34
71966619,2.2936306623,-0.027490375\H,0.0075603969,1.1105592454,-1.2174
990599\H,2.3623282844,0.0474472364,0.112684385\H,2.0051497473,0.030059
8559,-1.4607916401\O,2.5053303253,2.3221190139,0.2794701699\O,0.543951
2896,3.3432992333,-0.1346455744\H,1.0411995095,4.1499458471,0.07745272
65\\Version=x86-Linux-G03RevB.03\State=1-A\HF=-2493.7545233\RMSD=4.3\0
2e-09\RMSF=8.360e-06\Dipole=-0.0187207,-0.2926661,-0.6352185\PG=C01[X(
C3H6Cu1N2O3S1)]\\@

4B$_N$

1\1\GINC-N15\Freq\RB3P86\6-311+G(2df,p)\C3H6Cu1N2O3S1(1+)\CRISTINA\19-
Jun-2004\0\\#N GEOM=ALLCHECK GUESS=READ SCRF=CHECK GENCHK RB3P86/6-311
+G(2DF,P) FREQ\\cys-sno-6-co-1\\1,1\C,-0.4204578557,1.0375181475,-0.51
01680247\S,1.0780704721,1.7375535823,0.2342212606\N,2.1959448593,0.374
04916,0.0955256528\O,3.3204226608,0.5762506765,0.4077265565\C,-1.28624
17138,0.0877933467,0.3324308043\N,-0.774335734,-1.3050357185,0.3442364
507\Cu,1.1528037122,-1.2422063251,0.0043839077\H,-0.1653486457,0.59033
02345,-1.4755941029\H,-0.9953959259,1.9408051635,-0.7347553007\C,-2.70
03973379,0.0579978537,-0.2531478359\H,-1.3428056602,0.4622607588,1.356
3697378\H,-1.3198561029,-1.8171626061,-0.35972962\H,-1.0152923769,-1.7
484759775,1.2284043364\O,-3.1492505278,-0.9162461262,-0.7887547911\O,-
3.3145969031,1.2201712209,-0.1049721861\H,-4.2030207681,1.1710121921,-
0.4943895627\\Version=x86-Linux-G03RevB.03\State=1-A\HF=-2493.754124\R
MSD=3.835e-09\RMSF=6.042e-06\Dipole=-0.8368345,-0.3057009,0.1741831\PG
=C01[X(C3H6Cu1N2O3S1)]\\@

4B$_{diss}$

1\1\GINC-N26\Freq\RB3P86\6-311+G(2df,p)\C3H6Cu1N2O3S1(1+)\CRISTINA\04-
Oct-2004\0\\#N GEOM=ALLCHECK GUESS=READ SCRF=CHECK GENCHK RB3P86/6-311
+G(2DF,P) FREQ\\4Bs-2\\1,1\C,-0.7701177649,1.1972050331,0.8721673658\C
,0.1553402338,1.5024904123,-0.3012581965\C,0.9918310009,2.7379345062,0
.0034183768\O,0.2644069651,3.842208234,-0.0379257261\S,-1.5931712833,-
0.4191762845,0.6975784438\Cu,0.0805338838,-1.3147582936,-0.2992890656\
N,1.0770591563,0.3655826458,-0.5507212129\O,2.1594865853,2.670816734,0
.2742242881\H,-0.2219904159,1.2101132028,1.8173539592\H,-1.5531926327,
1.95463298,0.9292777754\H,-0.4422555306,1.6662151292,-1.1996700155\H,1
.8708960353,0.4778738054,0.0892564237\H,1.4901788156,0.465434339,-1.47
67999461\H,0.8210368621,4.6037216266,0.192496169\N,-0.2042964054,-3.03
87413863,-0.4081583629\O,-0.821527964,-3.945131036,-0.1822479133\\Vers
ion=IA32L-G03RevC.01\State=1-A\HF=-2493.7535983\RMSD=6.033e-09\RMSF=5.
596e-06\Dipole=0.4059338,-0.6683377,-0.725941\PG=C01 [X(C3H6Cu1N2O3S1)]
\\@

4C$_S$

1\1\GINC-CURIE\Freq\RB3P86\6-311+G(2df,p)\C3H6Cu1N2O3S1(1+)\CRISTINA\1
0-Sep-2003\0\\#N GEOM=ALLCHECK GUESS=READ SCRF=CHECK GENCHK RB3P86/6-3
11+G(2DF,P) FREQ\\cys-sno-cu-o-syn-p2\\1,1\C,0.1209266889,1.3752234374
,-0.3597118421\C,-1.3393755275,0.9234652146,-0.5763911764\C,-1.8338775
111,-0.204547628,0.3568321638\O,-1.2710191059,-1.2875162589,0.50535367

18\Cu,0.5097208081,-1.5801083289,-0.1888885596\S,1.4528221,0.256410196
2,-0.8823284079\N,-2.2673409273,2.0348326498,-0.4287074081\O,-2.944818
9577,0.0517047608,0.956415137\N,2.7546635064,0.5453801614,0.7102561849
\O,2.3990281436,1.2983799224,1.4758116885\H,0.2606965388,2.2913598377,
-0.9355197061\H,0.2988530596,1.6204504041,0.6972249481\H,-1.4351464693
,0.5187037861,-1.5887462386\H,-2.6283610597,2.3804848398,-1.3085379119
\H,-3.1934659626,0.9681387856,0.6352499086\H,-1.8924537368,2.814557530
1,0.099491465\\Version=x86-Linux-G03RevB.03\State=1-A\HF=-2493.7499641
\RMSD=5.419e-09\RMSF=1.236e-05\Dipole=0.0086354,1.4394133,-0.6216566\P
G=C01[X(C3H6Cu1N2O3S1)]\\@

4C$_N$

1\1\GINC-N2\Freq\RB3P86\6-311+G(2df,p)\C3H6Cu1N2O3S1(1+)\CRISTINA\16-J
ul-2004\0\\#N GEOM=ALLCHECK GUESS=READ SCRF=CHECK GENCHK RB3P86/6-311+
G(2DF,P) FREQ\\4cn-3\\1,1\C,0.3406938749,1.1533129054,0.8457143456\C,1
.4519712108,0.7622985971,-0.1604047466\C,1.8233987478,-0.7355917098,-0
.0752822848\O,0.998140119,-1.6494986334,-0.0222766648\Cu,-0.8559912765
,-1.2503583864,-0.0568913718\N,-2.0446191943,0.2320585328,-0.144989607
6\O,-3.1609362315,0.2943641658,-0.5347922733\S,-1.23386172,1.767378262
9,0.1880176601\O,3.0833641716,-0.9780884134,-0.1111514502\H,0.11827782
8,0.3572316279,1.5628305464\H,0.6805229509,2.0000276883,1.4479218491\H
,3.5117310467,-0.0730557875,-0.154991243\N,2.6858156159,1.517331934,-0
.0615752972\H,2.8586455061,1.9133744693,0.8552152667\H,2.7794878951,2.
2445948666,-0.758570134\H,1.0675668864,0.8800991588,-1.1792855109\\Ver
sion=IA32L-G03RevC.01\State=1-A\HF=-2493.7480189\RMSD=2.556e-09\RMSF=1
.871e-05\Dipole=1.126966,1.5026989,0.3485768\PG=C01[X(C3H6Cu1N2O3S1)]\
\@

4C$_{diss}$

1\1\GINC-N29\Freq\RB3P86\6-311+G(2df,p)\C3H6Cu1N2O3S1(1+)\CRISTINA\03-
Oct-2004\0\\#N GEOM=ALLCHECK GUESS=READ SCRF=CHECK GENCHK RB3P86/6-311
+G(2DF,P) FREQ\\4Cs-2\\1,1\C,0.1679932029,1.9236356862,-0.0929066106\S
,1.3853918632,0.7242671926,-0.7116349964\Cu,0.5444053791,-1.0926122524
,0.0620835357\O,-1.1363458189,-0.6490072822,0.7830568385\C,-1.75922626
38,0.4080224635,0.6218449052\O,-2.8822137476,0.5968697981,1.2070090113
\C,-1.3045199079,1.5600902602,-0.2851492561\N,-2.2311716472,2.65689160
38,-0.0440514751\H,0.366174774,2.8246353419,-0.679679749\H,0.381298194
,2.1589326474,0.9528912946\H,-1.4436908026,1.1945807273,-1.3088697259\
H,-2.5861279911,3.0762924294,-0.893896511\H,-3.1425009165,1.5287494241
,0.9116473655\H,-1.8416394231,3.3888165445,0.540414579\N,1.8109185646,
-2.2841505028,-0.2588995889\O,2.8471532852,-2.4521381462,-0.6499216784
\\Version=IA32L-G03RevC.01\State=1-A\HF=-2493.7512521\RMSD=3.479e-09\R
MSF=1.562e-05\Dipole=-0.1963511,0.81552,-0.4430903\PG=C01
[X(C3H6Cu1N2O3S1)]\\@

4D

1\1\GINC-LOKI\Freq\RB3P86\6-311+G(2df,p)\C3H6Cu1N2O3S1(1+)\STUACC2\02-
Dec-2002\0\\#N GEOM=ALLCHECK GUESS=TCHECK RB3P86/6-311+G(2DF,P) FREQ\\
cys-sno-cu-n-p2 larger basis set\\1,1\S,2.5662667821,0.2203694352,0.56
76657293\C,0.9336748846,-0.065676154,1.2336884147\C,-0.1552024774,0.96
32393947,0.8855686389\N,-1.4541514518,0.4312793396,1.3612515438\C,0.23
97486,1.168889941,-0.6202439248\O,-0.9252448752,0.4696932404,-1.351569
9913\O,0.5004945561,2.1513989006,-1.0494670769\N,2.70509218,-1.2302143
52,-0.5917628803\O,1.7887426285,-1.9486907461,-0.655826211\H,0.6329691

306,-1.053760181,0.8464495972\H,1.0084990397,-0.1346498794,2.321073623
6\H,0.0773257301,1.9238016218,1.3498524553\H,-2.0994328959,1.191535276
9,1.5676180628\H,-1.3214964495,-0.0688376283,2.2369833639\H,0.46064319
89,2.2121061213,-2.0194545583\Cu,-2.1627462994,-0.6821203951,-0.183129
9102\\Version=x86-Linux-G98RevA.11.1\HF=-2493.738258\RMSD=9.048e-10\RM
SF=8.352e-06\Dipole=-2.1445116,0.7258411,0.977241\PG=C01[X(C3H6Cu1N2O3
S1)]\\@

TS

1\1\GINC-N20\Freq\RB3P86\6-311+G(2df,p)\C2H6Cu1N2O1S1(1+)\CRISTINA\22-
Oct-2004\0\\#N GEOM=ALLCHECK GUESS=READ SCRF=CHECK GENCHK RB3P86/6-311
+G(2DF,P) FREQ\\2A-2-ts-1 (transition structure)\\1,1\C,-1.1265394482,
1.3604010444,-0.3509604355\C,-1.9930138472,0.1637829567,-0.7030108557\
N,-1.2056979864,-1.0294321075,-1.1224529976\Cu,0.397025104,-1.16122307
39,0.0097358692\S,-0.1271567164,1.1487030088,1.1668564948\H,-0.4698530
253,1.6652734722,-1.1702375971\H,-1.7660431705,2.2210167766,-0.1415316
578\H,-2.6809289622,0.4483798442,-1.5048832012\H,-2.5904675629,-0.1253
256563,0.1616245019\H,-0.9174725697,-0.9303250924,-2.0946757463\H,-1.8
008356688,-1.8552069841,-1.0988991407\N,1.4498178786,0.3993239052,0.30
82238354\O,2.2193576167,1.1422577564,-0.1350011749\\Version=IA32L-G03R
evC.01\State=1-A\HF=-2304.7090936\RMSD=2.290e-09\RMSF=1.194e-05\Dipole
=-1.3074404,-0.9180473,-1.1277052\PG=C01[X(C2H6Cu1N2O1S1)]\\@

Cu^+

1\1\GINC-GAULD\Freq\RB3P86\6-311+G(2df,p)\Cu1(1+)\COMCHEM\28-May-2003\
0\\#N GEOM=ALLCHECK GUESS=TCHECK RB3P86/6-311+G(2DF,P) FREQ\\Cu (I)\\1
,1\Cu,0.,0.,0.\\Version=MacOSX-G98RevA.11\HF=-1640.7926856\RMSD=7.714e
-09\RMSF=1.853e-24\Dipole=0.,0.,0.\DipoleDeriv=1.,0.,0.,0.,1.,0.,0.,0.
,1.\Polar=5.6873913,0.,5.6873915,0.,0.,5.6873915\PG=KH\NImag=0\\0.,0.,
0.,0.,0.,0.\\0.,0.,0.\\\@

H_2O

1\1\GINC-BOHR\Freq\RB3P86\6-311+G(2df,p)\H2O1\CRISTINA\12-Jun-2002\1\\
#N GEOM=ALLCHECK GUESS=TCHECK RB3P86/6-311+G(2DF,P) FREQ\\h2o b3b86b2\
\0,1\O\H,1,r1\H,1,r1,2,a1\\r1=0.96020756\a1=105.25708065\\Version=x86-
Linux-G98RevA.11.1\State=1-A1\HF=-76.6362307\RMSD=2.027e-10\RMSF=5.817
e-06\Dipole=0.652751,0.,0.4985508\PG=C02V [C2(O1),SGV(H2)]\\@

Appendix D

Gaussian Archive Entries of Optimized Geometries Obtained for all Species Considered in Chapter 6

$NO^{\bullet}$

```
1\1\GINC-VLAD\Freq\UB3LYP\6-311G(d,p)\N1O1(2)\CRISTINA\25-Jan-2002\1\\
#N GEOM=ALLCHECK GUESS=TCHECK UB3LYP/6-311G(D,P) FREQ\\no-radical\\0,2
\N\O,1,r1\\r1=1.14829055\\Version=x86-Linux-G98RevA.11.1\HF=-129.92670
22\S2=0.752536\S2-1=0.\S2A=0.750004\RMSD=3.787e-10\RMSF=3.060e-05\Dipo
le=0.,0.,0.0300296\DipoleDeriv=-0.0138257,0.,0.,0.,-0.0138179,0.,0.,0.
,0.5293828,0.0138257,0.,0.,0.,0.0138179,0.,0.,0.,-0.5293828\Polar=4.94
43477,0.,5.2338315,0.,0.,12.2602374\PG=C*V [C*(N1O1)]\NImag=0\\0.00011
309,0.,0.00006760,0.,0.,1.11740220,-0.00011309,0.,0.,0.00011309,0.,-0.
00006760,0.,0.,0.00006760,0.,0.,-1.11740220,0.,0.,1.11740220\\0.,0.,0.
00005300,0.,0.,-0.00005300\\\@
```

NO^{+}

```
1\1\GINC-VLAD\Freq\RB3LYP\6-311G(d,p)\N1O1(1+)\CRISTINA\25-Jan-2002\1\
\#N GEOM=ALLCHECK GUESS=TCHECK RB3LYP/6-311G(D,P) FREQ\\no-cation\\1,1
\N\O,1,r1\\r1=1.05969855\\Version=x86-Linux-G98RevA.11.1\State=1-SG\HF
=-129.5712762\RMSD=1.425e-09\RMSF=6.701e-08\Dipole=0.,0.,-0.173063\Dip
oleDeriv=0.553104,0.,0.,0.,0.553104,0.,0.,0.,0.9614926,0.446896,0.,0.,
0.,0.446896,0.,0.,0.,0.0385074\Polar=4.4381417,0.,4.4381417,0.,0.,9.03
08615\PG=C*V [C*(N1O1)]\NImag=0\\0.00005778,0.,0.00005778,0.,0.,1.7580
3915,-0.00005778,0.,0.,0.00005778,0.,-0.00005778,0.,0.,0.00005778,0.,0
.,-1.75803915,0.,0.,1.75803915\\0.,0.,-0.00000012,0.,0.,0.00000012\\\@
```

NO^{-}

```
1\1\GINC-VLAD\Freq\RB3LYP\6-311G(d,p)\N1O1(1-)\CRISTINA\25-Jan-2002\1\
\#N GEOM=ALLCHECK GUESS=TCHECK RB3LYP/6-311G(D,P) FREQ\\no-anion\\-1,1
\N\O,1,r1\\r1=1.26921107\\Version=x86-Linux-G98RevA.11.1\HF=-129.85618
66\RMSD=9.218e-10\RMSF=1.360e-04\Dipole=0.,0.,0.3604191\DipoleDeriv=-0
.6168919,0.,0.,0.,-0.6169215,0.,0.,0.,-0.0008739,-0.3831081,0.,0.,0.,-
0.3830785,0.,0.,0.,-0.9991261\Polar=4.7383852,0.,5.9032581,0.,0.,15.35
34978\PG=C*V [C*(N1O1)]\NImag=0\\0.00039867,0.,0.00019811,0.,0.,0.5959
1668,-0.00039867,0.,0.,0.00039867,0.,-0.00019811,0.,0.,0.00019811,0.,0
.,-0.59591668,0.,0.,0.59591668\\0.,0.,-0.00023552,0.,0.,0.00023552\\@
```

C_6H_6

```
1\1\GINC-ANGSTROM\Freq\RB3LYP\6-311G(d,p)\C6H6\CRISTINA\21-Apr-2003\0\
\#N GEOM=ALLCHECK GUESS=TCHECK RB3LYP/6-311G(D,P) FREQ\\benzene molecu
le\\0,1\C,1.3902177739,0.,0.\C,0.695108887,-1.203963909,0.\C,-0.695108
887,-1.203963909,0.\C,-1.3902177739,0.,0.\C,-0.695108887,1.203963909,0
.\C,0.695108887,1.203963909,0.\H,2.4750473956,0.,0.\H,1.2375236978,-2.
1434539202,0.\H,-1.2375236978,-2.1434539202,0.\H,-2.4750473956,0.,0.\H
,-1.2375236978,2.1434539202,0.\H,1.2375236978,2.1434539202,0.\\Version
=x86-Linux-G98RevA.11.1\State=1-A1G\HF=-233.0602923\RMSD=3.930e-10\RMS
F=2.138e-04\Dipole=0.,0.,0.\PG=D06H [3C2'(H1C1.C1H1)]\\@
```

Phe

1\1\GINC-KOHN\Freq\RB3LYP\6-311G(d,p)\C7H8\MARIAMA\13-Nov-2002\0\\#N G
EOM=ALLCHECK GUESS=TCHECK RB3LYP/6-311G(D,P) FREQ\\aromatic amino acid
R group phenylalanine ring structure (methyl group--- conformer 1)\\0
,1\C,1.6413065331,0.4369493799,-0.0045589151\C,0.9424560134,-0.7678907
608,0.0091957311\C,-0.456134508,-0.7900481429,0.0134607252\C,-1.136240
9129,0.4322454691,0.0091957311\C,-0.4422440034,1.639887843,-0.00455891
51\C,0.9508249665,1.6468771512,-0.0123769575\H,2.725882276,0.430336510
6,-0.005225269\H,1.4898841184,-1.7053299503,0.0190684376\C,-1.21123133
49,-2.0979142117,-0.0042503878\H,-2.221801118,0.4376125201,0.019068437
6\H,-0.9902587876,2.575851554,-0.005225269\H,1.4928957361,2.5857712653
,-0.020115423\H,-2.1793956821,-2.006401992,0.4936517662\H,-1.401729812
,-2.4278672529,-1.0315165168\H,-0.6478972542,-2.8906130216,0.493651766
2\\Version=x86-Linux-G98RevA.11.1\State=1-A'\HF=-271.6360528\RMSD=1.30
5e-09\RMSF=2.179e-07\Dipole=-0.0688516,-0.1192544,-0.0137373\PG=CS
[SG(C3H2),X(C4H6)]\\@

Tyr

1\1\GINC-KOHN\Freq\RB3LYP\6-311G(d,p)\C7H8O1\MARIAMA\08-Nov-2002\0\\#N
GEOM=ALLCHECK GUESS=TCHECK RB3LYP/6-311G(D,P) FREQ\\aromatic amino ac
id R group tyrosine ring structure (methyl group -- conformer 2)\\0,1\
C,1.4160810067,0.0409434443,0.0466089531\C,0.7206644948,-1.1598399855,
-0.002236202\C,-0.6790408172,-1.1989586065,-0.0504908339\C,-1.35884209
38,0.0195716192,-0.0514348041\C,-0.6768288081,1.2346415165,-0.00267083
33\C,0.7160568304,1.2492907393,0.0473791044\H,2.4986776227,0.064168988
8,0.0813277883\H,1.2798988397,-2.0903777743,-0.0045335994\C,-1.4194979
194,-2.5151020466,-0.0808141525\H,-2.4433590742,0.0272110449,-0.092403
1805\H,-1.2310432943,2.1692228461,-0.0069929476\O,1.4473581835,2.40493
78116,0.0944988639\H,0.8471022187,3.1573442276,0.0883132592\H,-2.46591
41447,-2.3752229992,-0.3606640364\H,-1.4036628416,-3.0056704681,0.8986
004182\H,-0.9721209551,-3.2094584423,-0.7976860042\\Version=x86-Linux-
G98RevA.11.1\HF=-346.8786543\RMSD=3.077e-09\RMSF=2.522e-06\Dipole=-0.4
928135,0.1667371,-0.0058948\PG=C01 [X(C7H8O1)]\\@

Trp

1\1\GINC-ANGSTROM\Freq\RB3LYP\6-311G(d,p)\C9H9N1\MARIAMA\19-Feb-2003\0
\\#N GEOM=ALLCHECK GUESS=TCHECK RB3LYP/6-311G(D,P) FREQ\\aromatic amin
o acid tryptophan molecule\\0,1\C,1.0840693301,1.2480893578,0.04654651
63\C,0.4279322936,0.0077182083,0.0069086436\C,-0.9928907157,-0.0154125
497,-0.0159763124\C,-1.7564143336,1.1540959113,-0.0003335339\C,-1.0777
423404,2.363946482,0.0389374287\C,0.3290858418,2.4111763599,0.06217249
74\H,2.1675281993,1.2967281452,0.0647300909\C,0.8819321158,-1.36038065
53,-0.0182931011\C,-0.244906047,-2.1373194752,-0.0543745631\N,-1.37571
8362,-1.3378428107,-0.0532555808\H,-2.8405092189,1.1211519506,-0.01815
71545\H,-1.6414402482,3.2899455283,0.0519661542\H,0.8255870073,3.37449
46811,0.0927519402\C,2.3034258191,-1.8321759989,-0.0070934753\H,2.8328
564737,-1.4947495852,0.8904848285\H,2.3571639501,-2.9230516216,-0.0320
261971\H,2.8605470486,-1.4531339699,-0.8706578624\H,-2.3233866478,-1.6
722441141,-0.0760524612\H,-0.3352698133,-3.2126671804,-0.0812148739\\V
ersion=x86-Linux-G98RevA.11.1\HF=-403.2368274\RMSD=4.835e-09\RMSF=3.98
2e-07\Dipole=-0.5033527,-0.6427407,-0.0231018\PG=C01 [X(C9H9N1)]\\@

Guanine

1\1\GINC-HAMMERHEAD8\Freq\RB3LYP\6-311G(d,p)\C5H5N5O1\JGAULD\07-Jan-20
03\0\\#N GEOM=ALLCHECK GUESS=TCHECK RB3LYP/6-311G(D,P) FREQ\\when npro
cl is different, how much difference on job running time\\0,1\N,-1.560
4058156,-0.0342511483,-0.3326985494\C,-1.4742614355,-0.0017142567,0.97
26527562\N,-0.2846165747,0.0258493538,1.6501660349\C,1.0347753472,0.02
88928004,1.0697887415\C,0.9225028066,-0.000739753,-0.3648319646\C,-0.3
469237335,-0.0196150075,-0.9379360677\O,2.0015861852,0.0610657162,1.79
84768713\N,-2.6230348985,0.0586429034,1.7260894537\H,-0.2790292666,0.1
11941502,2.6582026467\H,-3.4582245032,-0.1267458389,1.1907645283\H,-2.
6082548009,-0.3700624399,2.6391294456\N,1.9022478702,-0.0033302307,-1.
3371638103\C,1.2488116076,-0.0240095485,-2.4657502366\N,-0.1240923071,
-0.0352289056,-2.2880858927\H,-0.839755429,-0.049877725,-2.9977178621\
H,1.6924590441,-0.0324404446,-3.4498837558\\Version=DEC-AXP-Linux-G98R
evA.11\HF=-542.6979171\RMSD=5.123e-09\RMSF=5.523e-07\Dipole=-2.5212526
-0.3477484,-0.3122611\PG=C01 [X(C5H5N5O1)]\\@

[NO˙C_6H_6]$^{\bullet}$

1\1\GINC-LOKI\Freq\UB3LYP\6-311G(d,p)\C6H6N1O1(2)\STUACC2\02-Dec-2002\
0\\#N GEOM=ALLCHECK GUESS=TCHECK UB3LYP/6-311G(D,P) FREQ\\c6h6-no radi
cal\\0,2\O,2.4591555272,-0.6465118307,-0.0191129395\N,2.4726727438,0.5
022003728,-0.0031289108\C,-0.7457748598,1.3742028703,-0.3741232291\C,-
0.8638917578,0.3827075297,-1.3472761298\C,-0.9958818109,-0.9520207184,
-0.9691575414\C,-1.0132331529,-1.2952782332,0.3823715348\C,-0.90093507
14,-0.3037325848,1.3555536937\C,-0.7654530495,1.0309766182,0.977643394
\H,-0.6382730223,2.4122624998,-0.6680108998\H,-0.847922624,0.650122761
5,-2.3979493834\H,-1.0829259228,-1.7240831419,-1.7254551714\H,-1.11422
70977,-2.3340955308,0.6761606422\H,-0.9143074774,-0.5712177071,2.40624
39333\H,-0.6732790672,1.8025702629,1.7337464374\\Version=x86-Linux-G98
RevA.11.1\HF=-362.2364377\S2=0.752623\S2-1=0.\S2A=0.750005\RMSD=1.346e
-10\RMSF=7.456e-06\Dipole=-0.0816482,-0.0271397,-0.0004552\PG=C01[X(C6
H6N1O1)]\\@

[NO˙Phe]$^{\bullet}$

1\1\GINC-VLAD\Freq\UB3LYP\6-311G(d,p)\C7H8N1O1(2)\CRISTINA\21-Sep-2003
\0\\#N GEOM=ALLCHECK GUESS=TCHECK UB3LYP/6-311G(D,P) FREQ\\no-rad+phe-
2-b1\\0,2\C,-1.5858170992,0.8799142783,-0.4737555065\C,-1.5907536568,0
.8613278654,0.9198440522\C,-0.3824178127,0.7780970682,1.6076205644\C,0
.8187850838,0.7070816699,0.9055626446\C,0.8387412072,0.7219080125,-0.4
944647804\C,-0.3818615817,0.8146378016,-1.1711226336\C,2.1400039311,0.
6077053237,-1.2508699748\O,-0.696189519,-2.6259668953,0.0890853377\N,0
.4348193818,-2.4331539005,0.1491439576\H,-2.5270137659,0.9150019464,1.
4636343791\H,1.7552981844,0.640756103,1.4501463959\H,-0.3888950584,0.8
323765591,-2.2563405144\H,-0.3736745036,0.7669840911,2.6919874086\H,-2
.520794425,0.948687074,-1.0188671952\H,2.4127682521,-0.4434564738,-1.3
935288945\H,2.9593524992,1.0885736315,-0.7112079411\H,2.0686588657,1.0
668574171,-2.2394002384\\Version=x86-Linux-G98RevA.11.1\HF=-401.564338
9\PG=C01 [X(C7H8N1O1)]\\@

[NO˙Tyr]$^{\bullet}$

1\1\GINC-CURIE\Freq\UB3LYP\6-311G(d,p)\C7H8N1O2(2)\MARIAMA\03-Jan-2003
\0\\#N GEOM=ALLCHECK GUESS=TCHECK UB3LYP/6-311G(D,P) FREQ\\NO(nitric o
xide) attached to single tyrosine ring structure, nitric oxide facing
group. (methyl group -- conformer 1)\\0,2\O,-2.6257561323,-0.162373161

5,-0.380470934\N,-2.4604384363,-0.0654363891,0.7532669299\C,0.5543868675,1.2161346344,0.6213629059\C,0.6360522721,1.2348150538,-0.7699736601\C,0.7453805874,0.0378359574,-1.4765713368\C,0.7774984628,-1.172673052,-0.7784393921\C,0.6964453458,-1.1728128674,0.6064951422\C,0.578832147,0.0179323605,1.338231242\H,0.466839937,2.1563230951,1.1558456409\H,0.6129997302,2.1811306975,-1.3029610134\O,0.8307018883,-0.0173271516,-2.8392254811\H,0.7848726324,0.8758086805,-3.1954950986\H,0.8650584978,-2.095811171,-1.3384425287\H,0.7206273626,-2.121106268,1.1341047008\C,0.4764755266,-0.0049147326,2.8441992485\H,-0.4675069112,-0.453763027,3.1692993078\H,1.2869577796,-0.5885732372,3.2907661683\H,0.5232267231,1.0037443341,3.2597607369\\Version=x86-Linux-G98RevA.11.1\HF=-476.8071378\PG=C01 [X(C7H8N1O2)]\\@

[NO˙Trp]•

1\1\GINC-ANGSTROM\Freq\UB3LYP\6-311G(d,p)\C9H9N2O1(2)\MARIAMA\05-Mar-2003\0\\#N GEOM=ALLCHECK GUESS=TCHECK UB3LYP/6-311G(D,P) FREQ\\Nitroxide ion facing away from 5membered ring portion of tryptophan molecule\\0,2\C,1.2225503421,1.3628664203,-0.7210183235\C,0.3613094537,0.6627932441,0.1390839714\C,0.7243994828,-0.6449538562,0.5579406627\C,1.9113758238,-1.2555827799,0.1467476931\C,2.7412995421,-0.5371209681,-0.7015740478\C,2.4008711977,0.7596423214,-1.1321589524\H,0.9696891071,2.3620134107,-1.0586604904\C,-0.9070518962,0.973764465,0.7473462645\C,-1.252441877,-0.1236664908,1.4970547963\N,-0.2782909325,-1.0975465798,1.3897393689\H,2.1762079699,-2.2548082563,0.4748255171\H,3.6694626798,-0.9831770302,-1.040448347\H,3.0737987786,1.2901677809,-1.7961423022\C,-1.6901879618,2.2396611447,0.5902821661\H,-1.9739392013,2.4040366736,-0.4543162445\H,-2.6081817674,2.2111185693,1.1812442058\H,-1.1123469914,3.1122192632,0.9127458803\H,-0.3124235068,-2.0031009916,1.8252173287\N,-2.5683929435,-0.8072679321,-1.0472984043\O,-1.8623620281,-1.6426254754,-1.4109619855\H,-2.1293283556,-0.2881850366,2.1039182025\\Version=x86-Linux-G98RevA.11.1\HF=-533.1660472\S2=0.753096\S2-1=0.\S2A=0.750007\RMSD=2.447e-09\RMSF=2.126e-06\Dipole=-0.1924053,-0.4118572,0.6030621\PG=C01[X(C9H9N2O1)]\\@

[NO˙guanine]•

1\1\GINC-BOHR\Freq\UB3LYP\6-311G(d,p)\C5H5N6O2(2)\QINGHANG\25-Nov-2002\0\\#N GEOM=ALLCHECK GUESS=TCHECK UB3LYP/6-311G(D,P) FREQ\\one guanine with no0, from optimized guanine, increasing the r between n and x\\0,2\N,-0.83501076,-1.4213103003,-0.6965324173\C,-1.5593408737,-0.5269872922,-1.3205255489\N,-1.1946014309,0.786937283,-1.4456213849\C,0.0075936034,1.3966714196,-0.936608779\C,0.7943606267,0.4004068784,-0.2567172641\C,0.3173885582,-0.9086710577,-0.2016789258\O,0.2022090952,2.5756876928,-1.130851849\N,-2.7274829314,-0.9113358402,-1.9333160425\H,-1.7661120224,1.4206111842,-1.9891657726\H,-3.0265878258,-1.8395203989,-1.673815255\H,-3.4711868031,-0.232973389,-1.9974557365\N,2.009989111,0.5090429492,0.3837327729\C,2.264878665,-0.6954122982,0.8193018282\N,1.2727562027,-1.6023163977,0.488889761\H,1.2313559566,-2.5828950074,0.7188057263\H,3.1419519741,-0.9916083936,1.3740242703\N,0.6483295971,0.1490289942,3.3596257399\O,-0.3617795048,0.3818139682,2.8617930866\\Version=x86-Linux-G98RevA.11.1\HF=-672.6262947\S2=0.752806\S2-1=0.\S2A=0.750006\RMSD=4.512e-10\RMSF=3.499e-06\Dipole=-1.6366635,-2.005903,-0.1458643\PG=C01 [X(C5H5N6O2)]\\@

$[NO^{\cdot\cdot}C_6H_6]^+$

1\1\GINC-POPLE\Freq\RB3LYP\6-311G(d,p)\C6H6N1O1(1+)\CRISTINA\08-Aug-20
02\0\\#N GEOM=ALLCHECK GUESS=TCHECK RB3LYP/6-311G(D,P) FREQ\\test\\1,1
\O,-1.9716709793,0.,-0.5511829436\N,-1.8726549246,0.,0.5424694372\C,0.
3521331729,0.,1.3648588261\C,0.5550408076,-1.229564781,0.6929646631\C,
0.8460890757,-1.2239875836,-0.6612049633\C,0.95552922,0.,-1.3440010752
\C,0.8460890757,1.2239875836,-0.6612049633\C,0.5550408076,1.229564781,
0.6929646631\H,0.1350094945,0.,2.427019118\H,0.4688174122,-2.161150469
9,1.2395405618\H,0.9901705016,-2.1544373164,-1.1967248599\H,1.16943402
82,0.,-2.4067359363\H,0.9901705016,2.1544373164,-1.1967248599\H,0.4688
174122,2.1611504699,1.2395405618\\Version=x86-Linux-G98RevA.11.1\State
=1-A'\HF=-361.948983\RMSD=2.404e-09\RMSF=2.469e-05\Dipole=-0.8409352,0
.,0.046345\PG=CS [SG(C2H2N1O1),X(C4H4)]\\@

$[NO^{\cdot\cdot}Phe]^+$

1\1\GINC-CURIE\Freq\RB3LYP\6-311G(d,p)\C7H8N1O1(1+)\MARIAMA\26-Nov-200
2\0\\#N GEOM=ALLCHECK GUESS=TCHECK RB3LYP/6-311G(D,P) FREQ\\one phenyl
alanine ring structure associated with nitrosium ion trial #1\\1,1\O,-
2.0691840709,0.4190543615,-0.5994801662\N,-1.7958869867,-0.4747826176,
-0.0169649373\C,0.4936768799,-0.7909848382,0.5575627577\C,0.8249881618
,0.4066549361,-1.5413422586\C,0.6553232553,1.6253260808,-0.8649641714\
C,0.4770080278,1.6479608306,0.5275503286\C,0.7462970035,-0.7860916143,
-0.8430874398\C,0.3972976011,0.4587770685,1.2317447067\C,0.473544268,-
2.0761788819,1.3252950031\H,0.7018018731,2.557243894,-1.4162848122\H,1
.0083684348,0.4028600427,-2.609034316\H,0.3936384599,2.5956567238,1.04
57495465\H,0.8735031185,-1.7319623667,-1.3578985735\H,0.2570354241,0.4
668931017,2.3069877137\H,1.4952420494,-2.3177621499,1.642470098\H,-0.1
342564846,-2.0038075684,2.2288811692\H,0.1205374143,-2.9108597355,0.71
71715065\\Version=x86-Linux-G98RevA.11.1\HF=-401.2844648\RMSD=4.360e-0
9\RMSF=2.172e-06\Dipole=-0.7105591,0.0003855,-0.1196611\PG=C01
[X(C7H8N1O1)]\\@

$[NO^{\cdot\cdot}Tyr]^+$

1\1\GINC-CURIE\Freq\RB3LYP\6-311G(d,p)\C7H8N1O2(1+)\MARIAMA\29-Dec-200
2\0\\#N GEOM=ALLCHECK GUESS=TCHECK RB3LYP/6-311G(D,P) FREQ\\NO+ attach
ed to single tyrosine ring structure, nitrosonium ion facing hydroxyl
group. (methyl group -- conformer 1)\\1,1\O,-2.1652951413,-0.024417692
5,-0.2032705252\N,-1.8941479942,-0.0181526352,0.8726763173\C,0.4747111
193,1.2164654102,0.5738708319\C,0.5639833706,1.2384491721,-0.797633203
7\C,0.6030418879,0.018059832,-1.5149333708\C,0.5931314405,-1.217607413
7,-0.8196990021\C,0.5057583032,-1.2256261422,0.5489291253\C,0.37134551
04,-0.0127351737,1.2904681409\H,0.4547970729,2.1494597155,1.1261310929
\H,0.6187368195,2.1809415155,-1.3323057282\O,0.679413838,-0.046711082,
-2.8367354585\H,0.7177882676,0.8281411275,-3.2480540176\H,0.6716735412
,-2.1315607523,-1.3952852299\H,0.5104366208,-2.1692544311,1.0830635469
\C,0.381666236,-0.0276739627,2.7906473917\H,-0.1096893346,-0.916984861
,3.189703907\H,1.4169858661,-0.0403876837,3.1491971166\H,-0.0964696758
,0.8597536792,3.2089634816\\Version=x86-Linux-G98RevA.11.1\HF=-476.539
5525\RMSD=3.638e-09\RMSF=2.367e-06\Dipole=-0.4906948,0.5570559,0.07762
93\PG=C01 [X(C7H8N1O2)]\\@

$[NO^{\cdot\cdot}Trp]^+$

1\1\GINC-ANGSTROM\Freq\RB3LYP\6-311G(d,p)\C9H9N2O1(1+)\MARIAMA\04-Mar-
2003\0\\#N GEOM=ALLCHECK GUESS=TCHECK RB3LYP/6-311G(D,P) FREQ\\Nitroxi

de ion facing away from 5membered ring portion of tryptophan molecule\
\1,1\C,1.783404299,-0.5990782967,-0.2701514984\C,0.3967807658,-0.39598
45077,-0.3264443872\C,-0.1042487367,0.8801629367,-0.6706778641\C,0.716
7960984,1.9581797726,-0.9682112376\C,2.0899104139,1.7286724407,-0.9108
305053\C,2.6155385479,0.4712518505,-0.567793016\H,2.1966294617,-1.5676
024522,-0.0159270882\C,-0.7404973794,-1.2517540297,-0.0733534172\C,-1.
8863031622,-0.4641719769,-0.3554644262\N,-1.5080051022,0.7874980683,-0
.6529242101\H,0.3203384126,2.9296839428,-1.2365536579\H,2.7689816397,2
.5403660041,-1.1412877558\H,3.6897438065,0.3378195135,-0.5425473545\C,
-0.7275741661,-2.7208654737,0.1768691215\H,-0.0388562463,-2.9775308929
,0.9865794265\H,-1.7185144969,-3.0977737446,0.4328769088\H,-0.38478310
35,-3.2498986398,-0.7177985726\H,-2.1408082151,1.5405997327,-0.8888476
573\N,-1.106770779,-0.5125477433,2.0412509382\O,-1.0407077427,0.592045
0292,2.1914291627\H,-2.9264782324,-0.7551522659,-0.3298712631\\Version
=x86-Linux-G98RevA.11.1\HF=-532.9120032\RMSD=5.122e-09\RMSF=6.677e-07\
Dipole=-1.2889379,0.1078247,0.2921275\PG=C01 [X(C9H9N2O1)]\\@

[NO⁻guanine]⁺

1\1\GINC-BOHR\Freq\RB3LYP\6-311G(d,p)\C5H5N6O2(1+)\QINGHANG\12-Nov-200
2\0\\#N GEOM=ALLCHECK GUESS=TCHECK RB3LYP/6-311G(D,P) FREQ\\one guanin
e with no+, from optimized guanine\\1,1\N,-0.6124153413,-0.9936579553,
-0.1713427543\C,-1.653498186,-0.1752267781,0.1507668548\N,-1.444118537
3,1.0534211749,0.6508814205\C,-0.1456498974,1.7036312317,0.8974317452\
C,0.9274727897,0.7760593974,0.6018000761\C,0.6245567459,-0.4947838051,
0.1293416239\O,-0.1365109712,2.8237277859,1.3085485726\N,-2.8893939892
,-0.6294278814,-0.0648963823\H,-2.232275402,1.6266977895,0.9356595732\
H,-3.0316789927,-1.60230479,-0.2892185903\H,-3.705036007,-0.0492082145
,0.0610092132\N,2.2662012261,0.9047704403,0.8185433528\C,2.7806796264,
-0.2513743909,0.4790657368\N,1.8250192421,-1.1500036756,0.0534831101\H
,1.9806452907,-2.1186032519,-0.1887599761\H,3.8285650469,-0.5082974406
,0.5119767461\N,-0.8578343896,-1.4790630347,-2.007865023\O,0.129786735
7,-1.6537767233,-2.5001397293\\Version=x86-Linux-G98RevA.11.1\HF=-672.
3561315\RMSD=2.755e-09\RMSF=2.197e-06\Dipole=-2.0881268,-2.6851091,-1.
3261757\PG=C01 [X(C5H5N6O2)]\\@

[NO⁻C_6H_6]⁻

1\1\GINC-CURIE\Freq\UB3LYP\6-311G(d,p)\C6H6N1O1(1-,3)\JESSE\21-May-200
3\0\\#N GEOM=ALLCHECK GUESS=TCHECK UB3LYP/6-311G(D,P) FREQ\\single ben
zene ring structure associated with nitrosonium ion triplet.\\-1,3\O,0
.,0.,-4.184412928\N,0.,0.,-2.9415464539\C,0.6973182935,0.,0.0762599812
\C,-0.6973182935,0.,0.0762599812\C,1.3962447339,0.,1.2874684168\C,-1.3
962447339,0.,1.2874684168\C,0.6959423725,0.,2.5017279609\C,-0.69594237
25,0.,2.5017279609\H,1.1843673539,0.,-0.8937661763\H,-1.1843673539,0.,
-0.8937661763\H,2.4825374831,0.,1.2901735145\H,-2.4825374831,0.,1.2901
735145\H,1.2378631357,0.,3.4439188085\H,-1.2378631357,0.,3.4439188085\
\Version=x86-Linux-G98RevA.11.1\State=3-A2\HF=-362.2443133\S2=2.006943
\S2-1=0.\S2A=2.000026\RMSD=2.510e-09\RMSF=2.431e-04\Dipole=0.,0.,4.073
3988\PG=C02V [C2(N1O1),SGV(C6H6)]\\@

[NO⁻Phe]⁻

1\1\GINC-CURIE\Freq\UB3LYP\6-311G(d,p)\C7H8N1O1(1-,3)\JESSE\23-Jun-200
3\0\\#N GEOM=ALLCHECK GUESS=TCHECK UB3LYP/6-311G(D,P) FREQ\\NO- attach
ed to phenylalanine as a triplet.\\-1,3\O,-2.7731252108,1.6585313401,0
.2974923153\N,-3.0097963816,1.2659066437,-0.8728097232\C,1.5054702548,

1.1168404011,0.1580712269\C,0.2143572922,0.5905783631,0.1347310674\C,0
.0258135161,-0.8040912864,0.0630616487\C,1.1528050356,-1.6279888664,-0
.0038504453\C,2.4450017707,-1.0967122086,0.013494739\C,2.6244397242,0.
2845432933,0.0981071886\H,1.6383094547,2.1937484418,0.2156243686\H,-0.
6662135559,1.228135793,0.1901921088\C,-1.3729869394,-1.3572328075,0.05
60981367\H,1.0176492051,-2.7050363053,-0.0728621042\H,3.3050506057,-1.
7586839263,-0.038358834\H,3.6252338272,0.7071710541,0.11075843\H,-1.83
92765848,-1.2373247319,1.0406728843\H,-2.0122093163,-0.7734919217,-0.6
247383867\H,-1.3843712032,-2.4197369612,-0.209840298\\Version=x86-Linu
x-G98RevA.11.1\HF=-401.5767603\S2=2.008027\S2-1=0.\S2A=2.000034\RMSD=6
.602e-09\RMSF=1.678e-06\Dipole=3.3933198,-1.7063901,0.5380435\PG=C01
[X(C7H8N1O1)]\\@

[NO˙Tyr]⁻

1\1\GINC-BOHR\Freq\UB3LYP\6-311G(d,p)\C7H8N1O2(1-,3)\JESSE\10-Jul-2003
\0\\#N GEOM=ALLCHECK GUESS=TCHECK UB3LYP/6-311G(D,P) FREQ\\NO- attache
d to single tyrosine ring triplet.\\-1,3\C,-1.5047369286,-0.1135778967
,0.0210198087\C,-1.7192404185,0.3456315174,1.3280151451\C,-0.589402612
,0.7011491773,2.0697394434\C,0.6923903007,0.6079195488,1.5363079264\C,
0.9015601095,0.1488875481,0.221455561\C,-0.2358561722,-0.2158632031,-0
.5347878469\C,-3.1138825795,0.4723279205,1.8975213304\O,2.1440133471,0
.0752646746,-0.2446443472\H,-0.7124459119,1.058764285,3.0902814949\H,1
.5625874781,0.8833649469,2.1232705242\H,2.1835652694,-0.2831967342,-1.
2418708074\H,-0.0951471757,-0.5776430076,-1.5494744952\H,-2.3609513074
,-0.4037285471,-0.5849159871\H,-3.6542137149,1.3342490527,1.4838554882
\H,-3.7212288052,-0.4148037841,1.6851012542\H,-3.0870488453,0.59961818
79,2.9842046189\N,2.2921450724,-0.7949275608,-2.6775263953\O,1.2628463
166,-1.1141370681,-3.3157800943\\Version=x86-Linux-G98RevA.11.1\HF=-47
6.8494391\S2=2.00745\S2-1=0.\S2A=2.00003\RMSD=4.402e-09\RMSF=9.303e-07
\Dipole=-2.5136104,0.8946634,2.974498\PG=C01[X(C7H8N1O2)]\\@

[NO˙Tyr]⁻ (not in Figure 4)

1\1\GINC-BOHR\Freq\UB3LYP\6-311G(d,p)\C7H8N1O2(1-,3)\JESSE\05-Jul-2003
\0\\#N GEOM=ALLCHECK GUESS=TCHECK UB3LYP/6-311G(D,P) FREQ\\NO- attache
d to single tyrosine ring triplet.\\-1,3\C,-0.3997272794,-0.2425479846
,-1.8345827779\C,-0.8690644677,-0.0986534469,-0.5263024369\C,0.0671610
009,0.1324801904,0.4941013485\C,1.4248802481,0.2403829567,0.1868020493
\C,1.8722017362,0.1070101861,-1.1264087081\C,0.9584433246,-0.140260123
4,-2.1479320304\C,-2.3408881934,-0.1646880123,-0.1928331871\O,3.212144
0229,0.2035277036,-1.4617014492\H,-0.2840414304,0.2698153014,1.5206989
351\H,2.1420057497,0.4195636022,0.9869867014\H,3.6977777833,0.36719030
34,-0.6473064628\H,1.3170517621,-0.2505274534,-3.1655852425\H,-1.10834
84717,-0.4420997105,-2.6351257766\H,-2.8001373706,0.8288731397,-0.2706
969227\H,-2.8744877124,-0.8298851869,-0.8814859959\H,-2.4856337494,-0.
4981902094,0.8410495345\N,-1.5283392713,0.5524791409,3.227947011\O,-2.
1101252576,-0.5453322497,3.0290477753\\Version=x86-Linux-G98RevA.11.1\
HF=-476.8199259\S2=2.00789\S2-1=0.\S2A=2.000033\RMSD=8.619e-09\RMSF=1.
601e-06\Dipole=2.3156778,-0.0281296,-3.451676\PG=C01 [X(C7H8N1O2)]\\@

[NO˙Tyr]⁻ (not in Figure 4)

1\1\GINC-BOHR\Freq\UB3LYP\6-311G(d,p)\C7H8N1O2(1-,3)\JESSE\10-Jun-2003
\0\\#N GEOM=ALLCHECK GUESS=TCHECK UB3LYP/6-311G(D,P) FREQ\\NO- attache
d to single tyrosine ring triplet.\\-1,3\C,-1.5984834058,0.0281581169,
-0.0157659086\C,-1.6933584851,0.0492082132,1.3744167008\C,-0.544764678

1,0.0660770182,2.1763567303\C,0.7151567605,0.0596375656,1.5750782044\C
,0.8298762174,0.0401875783,0.1861334451\C,-0.3217727483,0.0257064975,-
0.6015212725\O,1.8737872746,0.0728902024,2.3296212693\C,-2.834862754,0
.0133587864,-0.8861010929\H,-2.6713227008,0.053246843,1.8502076543\H,-
0.6334155133,0.0831875168,3.2612578905\H,1.6166823148,0.0792136677,3.2
565061102\H,1.791929192,0.026440282,-0.315698668\H,-0.1725849228,-0.00
33092626,-1.6842509499\H,-2.9014805887,0.9188380157,-1.4994867636\H,-2
.8195800873,-0.8337410444,-1.5796248225\H,-3.7476550081,-0.0545018237,
-0.2856553481\N,1.2448913154,-0.1912354431,-3.3145698065\O,2.315268058
8,-0.150981296,-2.6612271814\\Version=x86-Linux-G98RevA.11.1\HF=-476.8
137344\S2=2.007577\S2-1=0.\S2A=2.000031\RMSD=1.705e-09\RMSF=4.349e-06\
Dipole=-2.4569796,0.2246482,4.189852\PG=C01[X(C7H8N1O2)]\\@

[NO˙˙Tyr]˙ (not in Figure 4)

1\1\GINC-BOHR\Freq\UB3LYP\6-311G(d,p)\C7H8N1O2(1-,3)\JESSE\14-Jun-2003
\0\\#N GEOM=ALLCHECK GUESS=TCHECK UB3LYP/6-311G(D,P) FREQ\\NO- attache
d to single tyrosine ring triplet.\\-1,3\C,-0.910301124,-1.3354671133,
-1.1963642988\C,-1.0170048771,-0.2851537573,-0.2802474757\C,0.15654752
69,0.3630643186,0.1325107791\C,1.3956991626,-0.0424377376,-0.374510697
3\C,1.4816501562,-1.0914317545,-1.287600712\C,0.325711226,-1.746701681
7,-1.705906079\C,-2.3545752938,0.1687043073,0.2603960834\O,2.692586464
,-1.5186823806,-1.804915381\N,-0.8811903203,2.2761608511,2.3855378677\
O,-0.7629627117,2.8649808004,3.4747126815\H,2.3023419147,0.4646875859,
-0.0472683786\H,3.3792055147,-0.9735379776,-1.4084063603\H,0.406178216
4,-2.5648649329,-2.4132353018\H,-1.8100688724,-1.8511885514,-1.5238736
606\H,-2.8985357235,0.7626759597,-0.4855744623\H,-2.9891807602,-0.6879
189815,0.5169268678\H,-2.2098106725,0.7962423084,1.1466211116\H,0.0848
519451,1.1669317833,0.868001108\\Version=x86-Linux-G98RevA.11.1\HF=-47
6.81945\S2=2.006946\S2-1=0.\S2A=2.000026\RMSD=2.841e-09\RMSF=1.661e-06
\Dipole=1.2571763,-2.7073819,-3.2012249\PG=C01 [X(C7H8N1O2)]\\@

[NO˙˙Trp]˙

1\1\GINC-CURIE\Freq\UB3LYP\6-311G(d,p)\C9H9N2O1(1-,3)\JESSE\27-Jun-200
3\0\\#N GEOM=ALLCHECK GUESS=TCHECK UB3LYP/6-311G(D,P) FREQ\\single try
ptophan ring structure associated with nitrosonium ion triplet.\\-1,3\
N,-0.2127672693,-0.6837773063,-0.8596567177\C,-0.2855045837,-0.0663611
601,0.3569636076\C,0.9199039442,0.6761843468,0.5667683321\C,1.72870710
83,0.4712744837,-0.6001512052\C,0.9891313588,-0.3580449531,-1.42182108
71\C,1.0731373022,1.3974393986,1.7639361812\C,0.0546770583,1.370656540
8,2.7071787447\C,-1.12701715,0.6329556374,2.4807729488\C,-1.3102506894
,-0.0896956372,1.3102516284\C,3.0893962047,1.0382430309,-0.8714104091\
H,0.1651007407,1.9251848339,3.6346311246\H,1.9772492385,1.9706597696,1
.952129204\H,-2.2101568659,-0.6630504196,1.1168872309\H,-1.9062599508,
0.6322709492,3.2369908711\H,3.0860980083,2.13628007,-0.8845315779\H,3.
8233763432,0.7348508675,-0.1131088605\H,3.4664298986,0.7024326287,-1.8
422623782\H,-0.9946178687,-1.3245188882,-1.3016404718\H,1.2474703311,-
0.7479152445,-2.3973336064\N,-2.1307715525,-2.2539757106,-1.8431296375
\O,-2.8803751804,-1.9047291969,-2.7796486873\\Version=x86-Linux-G98Rev
A.11.1\HF=-533.2017048\S2=2.007184\S2-1=0.\S2A=2.000028\RMSD=2.597e-09
\RMSF=2.019e-06\Dipole=2.7778682,2.1118816,2.0277447\PG=C01[X(C9H9N2O1)]
\\@

[NO˙˙Trp]˙ (not in Figure 4)

1\1\GINC-CURIE\Freq\UB3LYP\6-311G(d,p)\C9H9N2O1(1-,3)\JESSE\25-May-200

3\0\\#N GEOM=ALLCHECK GUESS=TCHECK UB3LYP/6-311G(D,P) FREQ\\single try
ptophan ring structure associated with nitrosonium ion triplet.\\-1,3\
O,-3.8011812718,-0.0632915142,-1.9002827199\N,-3.4613471402,-1.1443222
261,-1.3865324384\C,-0.9925324452,1.3481897627,-0.7743191791\C,-0.1826
318376,2.4211742962,-0.3700404162\C,1.0094374272,2.2150198949,0.332005
679\C,1.3526649002,0.8918007524,0.6280283461\C,0.543830038,-0.20660277
99,0.2326704281\C,-0.643378015,0.0294729299,-0.4915481655\H,-1.9251440
195,1.5114320213,-1.3042722421\C,1.1870063023,-1.404778667,0.710149396
\C,2.3306365599,-1.0125081417,1.3595463444\N,2.4477469665,0.3741047773
,1.2959990108\H,-1.3228654549,-0.7623104963,-0.8038345268\H,1.63905765
48,3.0466293686,0.6356669686\H,-0.486415664,3.4368107186,-0.6075018653
\C,0.6851893665,-2.8030498668,0.5207394598\H,-0.3330331077,-2.91487993
14,0.9082682333\H,0.6414602175,-3.0744514118,-0.5400997275\H,1.3262138
091,-3.5302325027,1.0293697121\H,3.1391254148,0.9185430719,1.780189092
4\H,3.0849187625,-1.6059956686,1.8548187526\\Version=x86-Linux-G98RevA
.11.1\HF=-533.170634\S2=2.00751\S2-1=0.\S2A=2.000031\RMSD=1.586e-09\RM
SF=2.934e-06\Dipole=4.8158542,0.6589446,2.3037463\PG=C01 [X(C9H9N2O1)]
\\@

[NO⁻Trp]⁻ (not in Figure 4)

1\1\GINC-CURIE\Freq\UB3LYP\6-311G(d,p)\C9H9N2O1(1-,3)\JESSE\13-Jun-200
3\0\\#N GEOM=ALLCHECK GUESS=TCHECK UB3LYP/6-311G(D,P) FREQ\\single try
ptophan ring structure associated with nitrosonium ion triplet.\\-1,3\
N,-1.6090449445,-0.037667351,-2.1393474015\C,-1.6653446408,0.024771119
2,-0.7622271317\C,-0.3283049175,0.1075200405,-0.2899031906\C,0.5426833
484,0.0699896823,-1.4401552213\C,-0.2716956572,-0.0358759479,-2.538647
9371\C,-0.0794639485,0.1781072643,1.096263971\C,-1.1772809035,0.167838
3632,1.9539155926\C,-2.4951697133,0.0910514153,1.4712069691\C,-2.76425
01534,0.0171707094,0.1046097617\C,2.0378908164,0.1643481089,-1.4110249
033\H,-1.0100183063,0.213459744,3.0255738036\H,0.9425732592,0.20665789
94,1.4736105927\H,-3.78253822,-0.0463600096,-0.267995584\H,-3.32244016
12,0.0860079242,2.1753071619\H,2.3667952675,1.205145997,-1.3009944363\
H,2.4582081492,-0.3591107979,-0.5451496946\H,2.4778527801,-0.229668573
6,-2.333446335\H,-2.3895891549,-0.2390066692,-2.7387757643\H,-0.014917
7488,-0.0942736689,-3.5860999287\O,2.9908171576,-0.1419796368,1.614324
6043\N,3.8309237288,-0.5789811181,2.4363682425\\Version=x86-Linux-G98R
evA.11.1\HF=-533.1727235\S2=2.00734\S2-1=0.\S2A=2.000029\RMSD=1.235e-0
9\RMSF=2.037e-06\Dipole=-4.4181958,0.3928699,-3.299419\PG=C01[X(C9H9N2
O1)]\\@

[NO⁻Trp]⁻ (not in Figure 4)

1\1\GINC-CURIE\Freq\UB3LYP\6-311G(d,p)\C9H9N2O1(1-,3)\JESSE\17-Jun-200
3\0\\#N GEOM=ALLCHECK GUESS=TCHECK UB3LYP/6-311G(D,P) FREQ\\single try
ptophan ring structure associated with nitrosonium ion triplet.\\-1,3\
C,-1.6518662346,-0.1379015118,-2.2381138667\C,-1.6577978302,-0.1418269
231,-0.8381131902\C,-0.4592964895,-0.152633059,-0.0762694982\C,0.78880
26151,-0.1551862712,-0.7323010604\C,0.787603463,-0.1483964528,-2.12616
65764\C,-0.4064815512,-0.1416425981,-2.8668592297\C,-0.8297359842,-0.1
315900906,1.3183218354\C,-2.2005474628,-0.1058703348,1.3547046479\N,-2
.7096761424,-0.1393276565,0.0550447515\C,0.1226041821,-0.1569035611,2.
4735312608\N,3.1950040706,0.3727598872,1.3509610566\O,4.3129541907,0.8
928030732,1.474275078\H,1.7365400326,-0.1417167984,-2.6538024752\H,1.7
177401799,-0.1282352972,-0.1603785797\H,-2.5742895725,-0.1294941881,-2
.8116048928\H,-0.3613992011,-0.1377361213,-3.9524290816\H,0.527558977,

-1.1637099298,2.6334772146\H,1.0027080593,0.4698211656,2.2840079949\H,
-0.3677887539,0.1606288443,3.400062813\H,-3.6723688819,0.0092455113,-0
.1904619995\H,-2.8693381071,-0.0835485722,2.20248179\\Version=x86-Linu
x-G98RevA.11.1\HF=-533.1742167\S2=2.00696\S2-1=0.\S2A=2.000027\RMSD=1.
392e-09\RMSF=5.320e-06\Dipole=-4.972335,-0.6236385,-1.3263047\PG=C01
[X(C9H9N2O1)]\\@

[NO guanine]$^-$

1\1\GINC-KOHN\Freq\UB3LYP\6-311G(d,p)\C5H5N6O2(1-,3)\CRISTINA\28-Dec-2
003\0\\#N GEOM=ALLCHECK GUESS=TCHECK UB3LYP/6-311G(D,P) FREQ\\one guan
ine with no-, using standard orientation from guanine-tri-no-.log\\-1,
3\N,-0.4264495692,-1.6404816755,-0.0416358639\C,0.7363943605,-1.000402
4491,-0.1483956203\N,0.8521753865,0.3679060079,-0.1852681079\C,-0.2169
810822,1.2996816585,-0.1431085093\C,-1.4805157913,0.6028672969,-0.0391
141928\C,-1.4680845633,-0.7899985107,0.0098289691\O,-0.0063403721,2.49
88697681,-0.189859148\N,1.8870789785,-1.688546087,-0.2555411336\H,1.82
45867019,0.7279204564,-0.1959843454\H,2.7743803955,-1.1370592004,-0.19
87401869\H,1.8341145632,-2.6726977641,-0.0571112733\N,-2.77611824,1.08
87420904,0.036173865\C,-3.5277201838,0.0267905647,0.1284225113\N,-2.79
19127774,-1.1488003066,0.1184705621\H,-3.1295592277,-2.0954674584,0.17
48413144\H,-4.6053114616,0.0202681096,0.2060085474\O,3.6617634356,0.28
54244831,-0.1559750651\N,4.3694902333,0.4567586115,0.8980664925\\Versi
on=x86-Linux-G98RevA.11.1\HF=-672.6790982\S2=2.007267\S2-1=0.\S2A=2.00
0028\RMSD=5.234e-09\RMSF=1.243e-05\Dipole=-4.1605116,-2.8164438,-0.343
0183\PG=C01 [X(C5H5N6O2)]\\@

[C_6H_6 NO C_6H_6]$^+$

1\1\GINC-KOHN\Freq\RB3LYP\6-311G(d,p)\C12H12N1O1(1+)\CRISTINA\27-Oct-2
002\0\\#N GEOM=ALLCHECK GUESS=TCHECK RB3LYP/6-311G(D,P) FREQ\\2c6h6-no
-cat-4\\1,1\O,-0.8481157717,-1.1540523585,-0.8543196362\N,-0.399749145
2,-0.177334034,-0.6161715199\C,-1.4443607712,1.9883356808,-1.679556771
\C,-1.1539693955,2.5409835219,-0.4236236167\C,0.1749900486,2.727324208
9,-0.0296496364\C,1.2126038534,2.3357855705,-0.8709423091\C,0.92851287
3,1.7616917977,-2.1169722817\C,-0.4009904854,1.6036447914,-2.530037281
\H,-2.4745413511,1.8777949691,-1.9980255759\H,-1.9621808154,2.85358303
24,0.2270565932\H,0.3944110927,3.1850423458,0.9275565433\H,2.242846395
7,2.4868323776,-0.5712864698\H,1.7374041925,1.4717108255,-2.7772779435
\H,-0.620223762,1.1928866139,-3.5089284525\C,0.653467962,-3.1016979881
,0.8797786032\C,1.5869507543,-2.0716481835,0.9103535571\C,1.2650866376
,-0.8693003667,1.5456570175\C,0.0257219079,-0.7195531934,2.1963787438\
C,-0.8948902644,-1.7632638145,2.1902170647\C,-0.5910566918,-2.94471331
67,1.5129682369\H,0.8890691542,-4.0364727286,0.3847972955\H,2.55704854
46,-2.1985344096,0.4448338393\H,1.989579341,-0.0643776216,1.5807634089
\H,-0.1958270348,0.2003342362,2.724581206\H,-1.8413800908,-1.660905615
5,2.7073666447\H,-1.3054340475,-3.7596691693,1.4988926759\\Version=x86
-Linux-G98RevA.11.1\HF=-594.2811571\RMSD=3.164e-09\RMSF=3.451e-06\Dipo
le=-0.3340586,0.1031595,-0.6276249\PG=C01 [X(C12H12N1O1)]\\@

[Phe NO Phe]$^+$

1\1\GINC-HAMMERHEAD9\Freq\RB3LYP\6-311G(d,p)\C14H16N1O1(1+)\JGAULD\29-
Mar-2003\0\\#N GEOM=ALLCHECK GUESS=TCHECK RB3LYP/6-311G(D,P) FREQ\\san
dwich structure of no-cat with phe\\1,1\C,-1.9916032653,2.1232808382,-
1.6489543328\C,-2.1612967509,2.2872691415,-0.2821120376\C,-1.049260240
9,2.3292884266,0.5765607544\C,0.2439362937,2.2386903644,0.0029561829\C

,0.413799555,2.1175568937,-1.3741657325\C,-0.7011965445,2.0292814752,-2.2012822968\C,-1.2178475744,2.554136796,2.052534436\N,-0.7003714359,-0.2941285435,0.2857370388\O,-0.9740025985,-0.5959353794,-0.7413389906\C,1.133595861,-1.9050931501,1.2987748124\C,1.9390352441,-1.1500337964,0.4124741936\C,1.9996357656,-1.4607788226,-0.9418920253\C,1.2314022359,-2.5078921438,-1.4467213564\C,0.4449963548,-3.2843151526,-0.5771880409\C,0.4055174839,-2.9933324521,0.7765287172\C,1.1376852549,-1.6214341253,2.7742991583\H,2.5404511174,-0.3401699523,0.8102928625\H,2.6368835966,-0.8859883899,-1.6030146887\H,1.2657724012,-2.7496814761,-2.5023560813\H,-0.1247569357,-4.1185703406,-0.9692940286\H,-0.1909095623,-3.6036268617,1.4456693794\H,0.1639147701,-1.817527439,3.228035219\H,1.8612233956,-2.2757689513,3.2731558876\H,1.4291560246,-0.5925153144,2.9914517299\H,-3.1588531393,2.3792887992,0.1326352235\H,-2.8571516983,2.0812818462,-2.2998370159\H,-0.5807453908,1.921118164,-3.2725429915\H,1.410763677,2.0805683549,-1.7962683275\H,1.1106323909,2.3117470612,0.6508602498\H,-1.206279674,3.6289662734,2.2655658138\H,-0.4065531905,2.1045826971,2.6284895146\H,-2.1693249809,2.1629326122,2.4168353115\\Version=DEC-AXP-Linux-G98RevA.11\HF=-672.9449234\RMSD=4.676e-09\RMSF=2.766e-06\Dipole=-0.3641513,-0.1774173,0.0107651\PG=C01 [X(C14H16N1O1)]\\@

[Tyr-NO-Tyr]$^+$

1\1\GINC-HAMMERHEAD5\Freq\RB3LYP\6-311G(d,p)\C14H16N1O3(1+)\JGAULD\13-Mar-2003\0\\#N GEOM=ALLCHECK GUESS=TCHECK RB3LYP/6-311G(D,P) FREQ\\sandwich structure of no-cat with tyr\\1,1\O,-0.026655557,-0.5218585873,-1.0214264872\N,0.0101921051,0.5861116774,-0.9133930821\C,-1.8659810826,0.5964338853,1.2604392912\C,-2.1296874181,-0.763023702,1.2382268296\C,-2.7420467788,-1.3356130149,0.1107550256\C,-3.1000141228,-0.5192038628,-0.9833217658\C,-2.8320615987,0.8306086054,-0.9455935046\C,-2.1760971987,1.4245667252,0.16152738\H,-1.4186551977,1.0365209758,2.1443887014\H,-1.8882009755,-1.3823719722,2.0959521295\O,-3.0397736447,-2.6402661669,0.0131999715\H,-2.831837154,-3.1089798672,0.8307934124\H,-3.5978906768,-0.9780887705,-1.8284560844\H,-3.1236664818,1.4545743638,-1.7833712785\C,-1.9791782999,2.9142537259,0.221217019\H,-1.6369682733,3.3139394671,-0.7363497617\H,-2.927352334,3.4097269199,0.455015408\H,-1.2627918193,3.1981475412,0.99323815\C,2.8591310435,0.6550927176,-0.9944159352\C,2.2630569015,1.2796650014,0.1297481424\C,1.9233531736,0.4635345653,1.2287028863\C,2.1009824399,-0.9094974697,1.1915020312\C,2.6549071639,-1.5098327543,0.0482244845\C,3.0421147932,-0.7083489928,-1.0468305222\H,3.1727360755,1.2666655331,-1.8333962262\H,3.494215744,-1.1902518332,-1.904776381\O,2.8687155449,-2.8296293482,-0.0641833569\H,2.647143408,-3.291237642,0.7538730249\H,1.837921786,-1.5197307061,2.0494195905\H,1.5216935376,0.9231735234,2.1245536849\C,2.1609584434,2.7782305489,0.203636542\H,3.1438092994,3.2120539201,0.4156730133\H,1.4836782998,3.1000772179,0.9958024461\H,1.8199045244,3.2058365339,-0.742236697\\Version=DEC-AXP-Linux-G98RevA.11\HF=-823.4421913\RMSD=8.582e-09\RMSF=1.338e-06\Dipole=0.0041176,-0.0478479,0.6526204\PG=C01 [X(C14H16N1O3)]\\@

[Trp-NO-Trp]$^+$

1\1\GINC-POPLE\Freq\RB3LYP\6-311G(d,p)\C18H18N3O1(1+)\CRISTINA\12-May-2003\0\\#N GEOM=ALLCHECK GUESS=TCHECK RB3LYP/6-311G(D,P) FREQ\\sandwich structure of trp with no-cat\\1,1\C,-1.6850574224,2.3675418188,-0.0722616871\C,-1.3729595211,1.8805864011,1.21477843\C,-0.1526477645,2.2370134755,1.8075869234\C,0.7939784723,2.9839043581,1.1039012154\C,0.5374

683122,3.4274297496,-0.1986602467\C,-0.7055292231,3.1385580431,-0.7591
735429\H,0.0596071788,1.9186427178,2.8204720284\N,-1.2407107591,3.4706
265303,-1.9801626361\N,-0.0658665694,-0.0229244146,0.0972661492\O,0.81
76271217,0.3674577044,-0.4589612481\C,1.5458962801,-1.0830159578,2.175
3628893\C,2.7660254168,-0.8707337825,1.5308927876\C,3.087003921,-1.556
0075325,0.3533734804\C,2.1725981932,-2.4871645915,-0.1359849279\C,0.91
52024801,-2.715040677,0.4907661074\C,0.5934718366,-1.963073305,1.64056
47428\N,2.2326351977,-3.3185498896,-1.2280918544\H,1.3251333409,-0.554
9799703,3.094487556\H,3.4820760045,-0.1741012839,1.9484931793\H,4.0373
158427,-1.3863064114,-0.1403281684\C,0.2257240228,-3.7172923498,-0.265
4763398\H,-0.348675797,-2.1207429708,2.1528351656\H,-2.1001994628,1.30
2842611,1.7735782585\C,-2.8289004903,2.2534205494,-0.9268908183\H,1.27
75289617,4.0081032129,-0.7378829151\H,1.7381507803,3.2346348334,1.5709
003435\C,-1.1209350427,-4.3063245786,0.0209450831\H,-1.3907509205,-5.0
522108816,-0.7281102521\H,-1.1396780128,-4.7968335862,0.998748415\H,-1
.9043905278,-3.5423063069,0.0244202581\H,3.0183719577,-3.415301169,-1.
8517163225\C,1.074603648,-4.0578599742,-1.2974258119\C,-2.510522148,2.
9498068404,-2.0737056411\H,-0.8000420272,4.0483679461,-2.6785009813\C,
-4.1207929642,1.5573361641,-0.628617085\H,-4.81214949,1.6354206378,-1.
468950266\H,-3.9690353839,0.4933419622,-0.4226450141\H,-4.6127772031,1
.9918380426,0.246716775\H,-3.1093869569,3.1210122546,-2.9550372252\H,0
.9377116179,-4.7896567639,-2.0787258118\\Version=x86-Linux-G98RevA.11.
1\HF=-936.17048\RMSD=3.784e-09\RMSF=1.599e-06\Dipole=0.5922395,0.15158
,-1.3668042\PG=C01[X(C18H18N3O1)]\\@

[guanine⁻NO⁻guanine]⁺

1\1\GINC-POPLE\Freq\RB3LYP\6-311G(d,p)\C10H10N11O3(1+)\QINGHANG\25-Jan
-2003\0\\#N GEOM=ALLCHECK GUESS=TCHECK RB3LYP/6-311G(D,P) FREQ\\two gu
anine with no+, from optimized guanine-no+.log, 2 rings are 90 degree\
\1,1\N,-1.7485805296,-0.6279674151,-2.2026967417\C,-0.9093287781,0.415
2628688,-1.9349576654\N,-1.1489091981,1.2830020383,-0.9318852096\C,-2.
2269963482,1.2211591756,0.0263128656\C,-3.1576040067,0.1633459528,-0.3
355753651\C,-2.8636589325,-0.6509464074,-1.4211898736\O,-2.2530599109,
1.9954216062,0.9428816384\N,0.1761273649,0.5584815593,-2.6833032824\H,
-0.4244654796,1.9722697838,-0.7344912338\H,0.3260864726,-0.0845425895,
-3.4443996271\H,0.9502539759,1.1059635762,-2.3021183516\N,-4.378856747
9,-0.1453090059,0.187328922\C,-4.8244715485,-1.133656073,-0.5520243177
\N,-3.9438431933,-1.4874134447,-1.5487928702\H,-4.0979794483,-2.168327
0367,-2.2786268971\H,-5.7690308772,-1.6389769215,-0.4202974771\N,-0.54
70557583,-2.1293968361,-1.7716113273\O,-1.1135129385,-2.9147146374,-1.
2086103937\N,3.5204530206,0.1258729944,2.5272257268\C,3.8006255475,1.3
279520298,2.071647402\N,3.1729128735,1.8678819749,0.970266498\C,2.1747
953774,1.2429610875,0.1975925465\C,1.8847870451,-0.0650018247,0.683824
0305\C,2.5811000137,-0.5097686686,1.8127640491\O,1.6888470924,1.869449
2688,-0.7532503732\N,4.7532960769,2.0681701906,2.6761413202\H,3.418629
155,2.7954592671,0.6454665355\H,5.1515887693,1.6977701562,3.5243351921
\H,4.8863507585,3.0450181097,2.4763121382\N,0.9803608605,-1.0323795713
,0.2627138926\C,1.1340034796,-2.0200886516,1.106227379\N,2.0860381071,
-1.760335766,2.064050382\H,2.373511517,-2.362395055,2.8222890408\H,0.5
937499822,-2.9550531549,1.0895762307\\Version=x86-Linux-G98RevA.11.1\H
F=-1215.1100948\RMSD=5.702e-09\RMSF=7.752e-06\Dipole=1.8498847,-1.7860
944,-0.8584367\PG=C01 [X(C10H10N11O3)]\\@

$[C_6H_6NOC_6H_6]^-$

1\1\GINC-VLAD\Freq\UB3LYP\6-311G(d,p)\C12H12N1O1(1-,3)\CRISTINA\08-Jun
-2003\0\\#N GEOM=ALLCHECK GUESS=TCHECK UB3LYP/6-311G(D,P) FREQ\\2c6h6-
no-an-tbl no triplet\\-1,3\C,-0.7900247379,0.0428959886,-4.5588357904\
C,-0.9054921303,0.039608128,-3.1694195238\C,0.2451043348,0.007005216,-
2.3773106153\C,1.5023456788,-0.0220613339,-2.980122749\C,1.6170370153,
-0.0187561241,-4.3716423367\C,0.4689663666,0.0137841661,-5.1627529301\
O,-2.7511103353,0.0747249436,-0.5875543615\N,-1.7847159896,0.044941047
6,0.2078122176\C,-0.1767099167,-0.7076668773,2.8074352854\C,0.43428177
46,-1.425214582,3.8352771797\C,1.0763071203,-0.7508673439,4.8784657759
\C,1.1095969951,0.6417423113,4.8884575877\C,0.5008612417,1.3608556123,
3.8552515002\C,-0.1433557846,0.6880727163,2.8174864918\H,1.5482469487,
-1.3108649523,5.6808823444\H,0.4113522569,-2.511016177,3.8281881395\H,
-0.6989375796,-1.1801651281,1.9812149109\H,-0.6420605938,1.1968592347,
1.9983265029\H,0.5298124502,2.4465041114,3.8637200068\H,1.6074800254,1
.1669995523,5.6986490756\H,-1.8631221561,0.0614901881,-2.6554182638\H,
0.1088446686,0.0056218719,-1.2981594176\H,2.3971339524,-0.0474139168,-
2.3650214029\H,2.5977740769,-0.0414529433,-4.8383845551\H,0.5552539821
,0.0164476403,-6.2456594493\H,-1.683391169,0.0682163717,-5.1763277746\
\Version=x86-Linux-G98RevA.11.1\HF=-594.5702229\S2=2.007911\S2-1=0.\S2
A=2.000033\RMSD=3.921e-09\RMSF=2.381e-06\Dipole=2.4719071,-0.0642593,0
.0432924\PG=C01[X(C12H12N1O1)]\\@

[Phe NO Phe]$^-$

1\1\GINC-HAMMERHEAD8\Freq\UB3LYP\6-311G(d,p)\C14H16N1O1(1-,3)\JGAULD\2
3-May-2003\0\\#N GEOM=ALLCHECK GUESS=TCHECK UB3LYP/6-311G(D,P) FREQ\\s
andwich structure of no-an with phe no triplet\\-1,3\C,-2.6037285782,5
.1824375737,-1.27926314\C,-2.3544391982,4.582912937,-0.0443057528\C,-1
.6599225882,3.3718532608,0.0480232813\C,-1.203895552,2.7700647092,-1.1
361705505\C,-1.4560494859,3.3691194702,-2.3684010884\C,-2.1558166939,4
.5740270453,-2.4498009725\C,-1.4034729634,2.7025582212,1.3747938812\N,
1.1039284487,0.6229945073,0.6514085346\O,0.3257525176,0.1082390237,-0.
2006521465\C,1.3281086924,-3.2565508667,1.3268917341\C,1.3622105334,-2
.9246589794,-0.037323574\C,1.8005263662,-3.8576940575,-0.9744327848\C,
2.2180724798,-5.1293278614,-0.5785981818\C,2.1961584561,-5.4636148064,
0.7737108005\C,1.7551498555,-4.5315494299,1.7136331493\C,0.8285143095,
-2.2479626766,2.3304949031\H,1.0385167537,-1.9292922598,-0.3400094831\
H,1.8223162083,-3.5844559132,-2.025269815\H,2.5626289846,-5.8491090266
,-1.3151363148\H,2.5241437653,-6.446892587,1.0987234571\H,1.7441295061
,-4.7977403527,2.7676229077\H,1.1459376648,-1.2323797084,2.0608479176\
H,-0.2675549753,-2.2271063317,2.3381902073\H,1.166886438,-2.4933648435
,3.342479168\H,-2.7036354965,5.0649467451,0.8654075953\H,-3.1443093101
,6.1235606057,-1.3251180615\H,-2.3442000341,5.0365391243,-3.4141070672
\H,-1.0950427736,2.89153727,-3.2744832919\H,-0.6552146437,1.8313541393
,-1.0661202482\H,-1.4974660499,3.4127777309,2.2027866601\H,-0.41363392
24,2.2284911234,1.3929136174\H,-2.125515195,1.8945733064,1.5411199532\
\Version=DEC-AXP-Linux-G98RevA.11\HF=-673.2323179\S2=2.009072\S2-1=0.\
S2A=2.000043\RMSD=4.534e-09\RMSF=3.025e-06\Dipole=-0.9333811,-0.467672
9,-0.2427379\PG=C01 [X(C14H16N1O1)]\\@

[Tyr NO Tyr]$^-$

1\1\GINC-POPLE\Freq\UB3LYP\6-311G(d,p)\C14H16N1O3(1-,3)\CRISTINA\20-Au
g-2003\0\\#N GEOM=ALLCHECK GUESS=TCHECK UB3LYP/6-311G(D,P) FREQ\\sandw
ich structure of tyrosine with no anion triplet\\-1,3\O,-0.0028269756,

-1.2819403722,-0.0009254293\N,-0.0376858494,-1.0526247082,1.2545173202
\C,4.1472584898,0.758854107,1.1191602145\C,3.1101484004,0.0038754612,0
.5848659766\C,3.3076904624,-0.7149595953,-0.6088075408\C,4.5645214793,
-0.6475349126,-1.2273484411\C,5.5885462479,0.1146851522,-0.6730573976\
C,5.4059276392,0.8362853159,0.5093526969\H,3.9697693724,1.3038923057,2
.0433022608\H,2.1468163606,-0.0525693204,1.083468979\O,2.3564845564,-1
.4688557597,-1.1823365448\H,1.4845721085,-1.40085429,-0.6958683072\H,4
.7145104536,-1.2031235183,-2.1466622582\H,6.5526112696,0.1484786479,-1
.1749230359\C,6.5152136309,1.6710834378,1.1075833343\H,7.4377424466,1.
5736055144,0.5283142538\H,6.2558133975,2.7361743217,1.1340010749\H,6.7
404727234,1.3717121794,2.1377403142\C,-5.5106076635,0.4348415027,-0.85
70975\C,-5.4676221129,0.8016190577,0.4914905572\C,-4.2739263535,0.5624
351517,1.1822219123\C,-3.1673151367,-0.0186660539,0.5725194151\C,-3.22
64288189,-0.385489468,-0.7836093015\C,-4.41668877,-0.1475118864,-1.488
1754675\H,-6.4185973911,0.6101246993,-1.4293229393\H,-4.4561888523,-0.
4244222535,-2.5360934677\O,-2.2019136358,-0.9495126206,-1.442784461\H,
-1.3965772196,-1.0607558714,-0.8599089263\H,-2.2514682822,-0.195211739
2,1.1301088585\H,-4.2024620903,0.8399473286,2.2311597383\C,-6.66949116
46,1.4030253563,1.1836296642\H,-6.372437138,2.1550940548,1.9212800581\
H,-7.2586084144,0.6454498304,1.7164425029\H,-7.3394773376,1.8880453301
,0.4673423975\\Version=x86-Linux-G98RevA.11.1\HF=-823.7633918\S2=2.007
808\S2-1=0.\S2A=2.000032\RMSD=2.032e-09\RMSF=1.153e-06\Dipole=-0.04254
24,1.430815,0.1957535\PG=C01[X(C14H16N1O3)]\\@

[Trp¨NO¨Trp]¯

1\1\GINC-KOHN\Freq\UB3LYP\6-311G(d,p)\C18H18N3O1(1-,3)\CRISTINA\22-May
-2003\0\\#N GEOM=ALLCHECK GUESS=TCHECK UB3LYP/6-311G(D,P) FREQ\\sandwi
ch structure of trp with no-anion triplet\\-1,3\C,-4.0556653928,0.2180
649974,0.6151298048\C,-3.0995952103,-0.5702681126,1.2779157164\C,-3.55
27760105,-1.5705012228,2.1297775161\C,-4.9269870587,-1.803690171,2.329
2554148\C,-5.8902659576,-1.0402646024,1.6807018903\C,-5.4389159004,-0.
0312240294,0.8246548739\H,-2.8300899842,-2.1921042494,2.6481304281\N,-
6.1377075808,0.8755120007,0.0570078787\N,-0.016679975,-0.0506344926,-0
.7006523286\O,-0.0728407139,0.239672711,0.5260320608\C,3.582935426,-2.
1719691685,-1.6939307577\C,4.9567390926,-2.477050961,-1.741953967\C,5.
9095204976,-1.5947550621,-1.2467721066\C,5.4484209986,-0.3923724742,-0
.7025196583\C,4.065653664,-0.0684435443,-0.6510262546\C,3.1202744087,-
0.9788888887,-1.1527134928\N,6.1359539578,0.6644075281,-0.1449923815\H
,2.8666930331,-2.8891125283,-2.0815903987\H,5.2799101676,-3.4213261189
,-2.1701267845\H,6.9687379581,-1.8328867254,-1.2807702156\C,3.94423819
63,1.2306460446,-0.0283027678\H,2.0519924267,-0.7509734422,-1.10660816
22\H,-2.035321716,-0.392725908,1.1214721013\C,-3.9460722012,1.31226057
64,-0.3233249119\H,-6.9500247258,-1.2232177992,1.833206419\H,-5.242264
4115,-2.5976746405,2.9997028655\C,2.6718754143,1.9836568239,0.20863550
62\H,2.8557501427,2.8824917399,0.8061970196\H,2.2151440723,2.288263989
8,-0.7391702693\H,1.9099627166,1.3692919122,0.700313843\H,7.1245799916
,0.6891421335,0.0300718381\C,5.2190902675,1.6290234354,0.2693568452\C,
-5.2285553438,1.6702175219,-0.6397321404\H,-7.1347791109,0.8921068091,
-0.0619765108\C,-2.6745360492,1.9236430354,-0.8222433845\H,-2.87793082
17,2.6780430378,-1.5892648476\H,-2.1195284618,2.3980698673,-0.00657198
58\H,-1.9839315799,1.1708703216,-1.2227310108\H,-5.5807794439,2.442807
2041,-1.3072828036\H,5.561367599,2.5380522681,0.7417510509\\Version=x8
6-Linux-G98RevA.11.1\HF=-936.4285365\S2=2.009178\S2-1=0.\S2A=2.000045\
RMSD=6.159e-09\RMSF=2.883e-06\Dipole=0.0706581,0.620786,0.1804241\PG=C

01[X(C18H18N3O1)]\\@

[guanine-NO-guanine]$^-$

1\1\GINC-N17\Freq\UB3LYP\6-311G(d,p)\C10H10N11O3(1-,3)\CRISTINA\07-Nov
-2004\0\\#N GEOM=ALLCHECK GUESS=READ SCRF=CHECK GENCHK UB3LYP/6-311G(D
,P) FREQ\\2gua+no-an-tr-2\\-1,3\N,-2.4435395123,-5.2576481494,0.417146
699\C,-1.4373083379,-4.3075826211,0.4766762775\C,-1.2097413824,-3.9052
504454,1.7909069588\N,-2.1024723933,-4.6333812207,2.5404879205\C,-2.81
53453416,-5.4275700697,1.6555443367\N,-0.3260920059,-3.0110918987,2.27
16832641\C,0.4093371852,-2.4598702233,1.3131732248\N,0.2714834654,-2.7
677659381,-0.0166203588\C,-0.6489980057,-3.7051823764,-0.5714372945\N,
1.3635038712,-1.5673548878,1.6490798424\O,-0.6872233543,-3.8944451126,
-1.773172264\O,2.5998211089,-0.2235018157,-0.5277115647\N,2.0670397562
,-0.8781695668,-1.4659350529\N,0.6816248879,1.3565057655,-2.674406871\
C,0.5376080578,2.3872249009,-1.8130088429\N,-0.2689557785,3.3923290687
,-2.1315058612\C,-0.2780393341,4.3600964518,-1.1955024197\C,0.41704503
62,4.4338075214,0.0097468226\C,1.2855751459,3.3386809291,0.3680431885\
N,1.2701725461,2.345335258,-0.6541052677\N,-1.013187235,5.5200645828,-
1.248143381\C,-0.7314023182,6.226484836,-0.0890512412\N,0.1178720388,5
.6068245384,0.6825829606\O,1.967657041,3.1853568773,1.364810493\H,1.85
38904687,1.5142733472,-0.4794654546\H,0.0147026532,1.3341800754,-3.427
6359955\H,1.1229530299,0.4734998687,-2.3769240609\H,-1.6358320905,5.77
57171994,-1.9970009349\H,-1.1871375663,7.1842533056,0.1153055989\H,0.8
598993299,-2.2565617653,-0.6954100287\H,1.3521032251,-1.2533174522,2.6
041642554\H,1.8697266074,-1.0193895313,0.946495568\H,-2.1990049346,-4.
5748527535,3.5410331935\H,-3.5878708026,-6.1016481695,1.9956312211\\Ve
rsion=IA32L-G03RevC.01\State=3-A\HF=-1215.4263833\S2=2.008048\S2-1=0.\
S2A=2.000035\RMSD=4.972e-09\RMSF=3.915e-05\Dipole=-2.3493289,1.0093684
,0.9300877\PG=C01[X(C10H10N11O3)]\\@

Vita Auctoris

Name: Cristina Baciu

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Year of Birth: 1966

EDUCATION

• **M. Sc. Candidate** **2001-present**

University of Windsor, Windsor, ON, Canada

• **Associate Degree Analyst-Programmer for PC** **1996**

Romanian Management Institute, Bacau, Romania

• **B. Sc. Degree in Chemical Engineering** **1993**

Technical University IASI, Romania

RESEARCH AND WORK EXPERIENCE

• **Research Assistant** **2001-present**

• **Teacher Assisstant**

University of Windsor, Windsor, ON, Canada

• **EGS Trade, Bucharest, Romania** **1997-1999**

Marketing Manager in a Chemical Company

• **Condus S.A., Buhusi, Romania** **1993-1997**

Quality Control Manager in a Chemical Company

PUBLICATIONS

• Baciu, C.; Gauld, W. J. *J. Phys. Chem. A*, **2003**, 107, 9946.

• Baciu, C.; Cho, K-B.; Gauld, J. W. *Eur. J. Mass Spectrom.* **2004,** accepted

• Baciu, C.; Cho, K-B.; Gauld, J. W. **2004,** submitted

PRESENTATIONS

• C. Baciu, M.Henry, J. Robinet, Q. Jin and J. W. Gauld *Interaction of NO and Its Ions With Aromatic Biomolecules*; Poster presentation at IUPAC and CSC Conference, London, ON, 2004.

• C. Baciu and J. W. Gauld *Computational Studies on Copper-Nitrosothiol Complexes;* Poster presentation at IUPAC and CSC Conference, Ottawa, ON, 2003.

• C. Baciu and J. W. Gauld *Theoretical Studies of S-nitrosothiols*; Oral presentation, Chemical Biology Discussion Weekend, University of Windsor, ON, 2003.

• C. Baciu and J. W. Gauld *Theoretical Studies of S-nitrosothiols;* Poster presentation at CSC Conference, Vancouver, BC, 2002.

AWARDS AND SCHOLARSHIPS

• John & Anne Cristescu Memorial Scholarship, for scholar year 2001-2002.