are rationalized by this model. The quantitative (VEH) calculations indicate that PIBFV could have a very small band gap, making it an interesting experimental target.

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Do Stable Isomers of N_3H_3 Exist?

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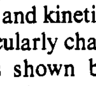
Abstract: The potential energy surface of the unknown N_3H_3 molecule is investigated by using ab initio coupled-cluster and many-body perturbation theory. Five stable isomers of N_3H_3 are identified. In decreasing order of stability, these are triazene, triimide, *cis*-triimide, triaziridine, and *cis*-triaziridine. The infrared spectra of the principal isomers are predicted at the MBPT(2) level by using newly developed analytical second-derivative techniques and are compared to SCF predictions. The thermochemical quantities of enthalpy, entropy, Gibbs free energy, and heat capacity at constant volume are also computed. The predicted IR spectra and these thermochemical properties should aid experimental attempts to synthesize and isolate these compounds, some of which should be observable in low-temperature matrices.

I. Introduction

For many years chemists have studied small ring compounds such as cyclopropane and cyclobutane. These systems are made thermodynamcially unstable and kinetically reactive by ring strain. Thus, their synthesis is particularly challenging. These compounds also interest kineticists, as shown by the fact that the rearrangement of cyclopropane to its open-chain isomer is one of the most studied unimolecular reactions.[1]

A compound similar to cyclopropane can be imagined, in which the methylene units ($-CH_2-$) are replaced by nitrenes ($-NH-$). This ring system of nitrogen is called triaziridine (**1**). It has never been synthesized and isolated. To predict the structure and properties of triaziridine and of other N_3H_3 isomers, we have performed theoretical investigations of the N_3H_3 hypersurface by using the modern computational procedures of ab initio coupled-cluster (CC) and many-body perturbation theory (MBPT), including analytical MBPT energy-derivative techniques.



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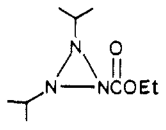
Triaziridine is a member of a class of inorganic compounds called homocycles, of which the sulfur S_8 is perhaps the best known. Homocycles in general have received little theoretical or experimental attention; however, triaziridine and its alkyl derivatives have been the subject of some investigations.

In 1977 Kim, Gilje, and Seff[2] reported the serendipitous synthesis of a minute amount of triaziridine on a zeolite crystal in a capillary. They used ammonia in an attempt to reduce the silver ions trapped in a silver-exchanged zeolite, but an X-ray crystal structure of the resulting zeolite indicated the presence of triaziridine facially complexed to the silver ions. The three nitrogen atoms formed an equilateral triangle, but the positions of the three hydrogen atoms could not be determined due to the proximity of the heavy silver atom. The N–N bond length in the ring was 1.49 Å, and the length of the Ag–N bond was 2.59 Å. Further evidence of the formation of triaziridine came from high resolution mass spectroscopy of the gases exiting the zeolite. Peaks representing both $N_3H_3^+$ and $N_3H_2^+$ were observed while the zeolite was between room temperature and 75 °C, suggesting that the N_3H_3 molecule possesses remarkable stability in the gas phase. Despite this observation, neither these investigators nor any other research team has repeated this synthesis of triaziridine.

In spite of this evidence for the formation of triaziridine, there are still many questions about the molecule and its synthesis that remain unanswered. If ammonia is converted to triaziridine, hydrogen gas should be a byproduct, but hydrogen was never observed. The silver ions presumably catalyze the conversion, but do they also stabilize the product through complexation? What is the arrangement of the hydrogens in triaziridine? In the zeolite one expects that the hydrogens are located on the side of the ring opposite the silver ion so that charge repulsion is minimized, but this may not be the structure of the molecule in the gas phase. The mass spectral data suggest that a molecule with empirical formula N_3H_3 is present, but is it triaziridine or one of its isomers?

More recently the synthesis of two alkyl derivatives of triaziridine has been reported by Leuenberger, Hoesch, and Dreiding.[3] They were able to make and isolate 1-(ethoxycarbonyl)-*trans*-2,3-diisopropyltriaziridine (**2**) and 2,3-(*cis*-1,3-cyclopentyl)-1-(methoxycarbonyl)triaziridine (**3**). On standing at room temperature compound **2** thermolyzed to the corresponding azimine (**4**). This reaction proceeded with a half-life of 3 days. Although one would expect triaziridine itself to be even less stable than an alkyl derivative, this observation is not inconsistent with the stability that Kim et al. observed.



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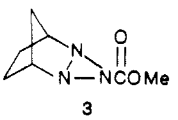

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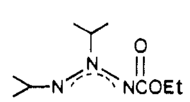

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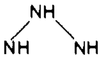
The triaziridine ring structure may not be a minimum on the potential energy surface of N_3H_3. It could, for example, relax directly to triimide (**5**). This structure is commonly known as azimine, but we choose to call it triimide to emphasize its similarity to such compounds as diimide and trimethylene. Another possible structure is triazine (**6**), which has an N–N double bond.



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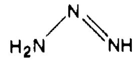

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Triazene has long been thought to be an intermediate in the oxidation of hydrazine.[4] The proposed mechanism includes the formation of hydrazyl radicals (N_2H_3) which combine to form tetrazine (N_4H_6). Triazene and ammonia are then produced from the unimolecular decomposition of tetrazine. More recent studies by pulse radiolysis have provided further evidence for this mechanism.[5]

Before 1984 only limited investigations of the N_3H_3 surface were reported. In 1973 Lathan et al. reported STO-3G SCF geometries of triaziridine and two of its isomers, *cis*-triaziridine and triazene.[6] Howell and Kirschenbaum investigated the cis–trans isomerization of triazene about its double bond at the SCF STO-3G level.[7] Hiberty and Leforestier showed that triimide had strong diradical character, in keeping with the expectation that triimide is a 1,3-dipole.[8] Triaziridine was mentioned in a recent paper on inorganic aromaticity by Gimarc and Trinajstič.[9] The arrangement of the six p_z electrons in the π orbitals of the molecule would obey the Huckel $4n + 2$ rule for aromaticity and lead to a planar, D_{3h} geometry. However, a simple Huckel calculation or application of Frost's rule revealed that both bonding and antibonding orbitals in the π system are filled, causing the net resonance energy of the π system to be zero. With these qualitative molecular orbital considerations Gimarc and Trinajstič concluded that triaziridine is "not aromatic but saturated" and that the hydrogen atoms will not lie in the plane of the nitrogen ring. This prediction agreed with the structure found earlier by Lathan et al.

Triaziridine is isoelectronic with cyclopropane, which thermally rearranges to propene. This reaction is thought to proceed through an intermediate or transition state known as the trimethylene diradical which is isoelectronic with triimide. The activation enthalpy of this reaction is in the range of 56–65 kcal/mol.[1] The overall enthalpy of reaction to propene is −8 kcal/mol.

Triimide is also isoelectronic with ozone, which has a bent, open structure in its ground state. In the late 1960's and early 1970's theoretical chemists predicted that a cyclic form of ozone is stable.[10] This conformation of ozone is isoelectronic with triaziridine and cyclopropane. In 1978–1979 several good calculations of these two forms of ozone placed the energy difference between them in the range of 20–30 kcal/mol.[11,12] The open form of ozone is more stable due to the contribution of its π system to bonding. The trimethylene compound of carbon is well-known and cyclic, while the triatomic species of oxygen is well-known and open. However, the trinitrene compound of nitrogen is unknown. Nitrogen lies between carbon and oxygen in the periodic table, so triimide and triaziridine appear to lie in the middle of a trend from cyclic, σ-bonded molecules to open, π-bonded molecules as one moves across the first row from left to right. It is not clear which form of trinitrene is more stable; moreover, the possibility exists that neither form is a local minimum on the N_3H_3 energy surface.

In 1984 Nguyen, Kaneti, Hoesch, and Dreiding addressed this question.[13] They carried out an SCF investigation of the N_3H_3 surface by using two split-valence basis sets, 3-21G and 6-31G. Their geometry optimization of triimide indicated that it is a minimum on the surface, but they did not confirm this by calculating eigenvalues of the force constant matrix. They reported that the energy of triimide is lower than triaziridine's for both basis sets. In the 3-21G basis set triimide is 10 kcal/mol lower in energy; at 6-31G this difference increases to 30 kcal/mol.

Nguyen et al. also reported that both triimide and triazene are planar. While this is not surprising for the 1,3-dipolar triimide, it is an interesting result for triazene since it implies that the $-NH_2$ group has flattened to increase the overlap of the unshared pair with the N–N double bond. As Nguyen et al. point out, this result is corroborated by the observation that synthesized derivatives of triazene are planar. Again, however, eigenvalues of the force constant matrix were not computed.

The goal of previous theoretical investigations has been to determine the relative electronic energies of the N_3H_3 isomers. These studies have been performed at the SCF level only; the effects of electron correlation have not been examined. Only small basis sets have been used in previous investigations, and polarization functions have never been used during geometry optimizations. Other important aspects of the chemistry of N_3H_3, such as thermodynamic stability, kinetic lability, vibrational frequencies, and electronic excitations have not been investigated.

Considering the theoretical and experimental interest in the N_3H_3 system, we feel that this system deserves a more extensive theoretical examination. We have searched for optimum structures at the correlated level by using polarized basis sets. These structures have been characterized by vibrational analysis, which also allows us to compute their infrared spectra. For the most important N_3H_3 isomers, we have computed infrared spectra by using electron correlation. The structures and vibrational frequencies of the molecules allow us to compute their thermochemical properties, including Gibbs free energy. Whenever possible, we have tried to compute properties that can be directly measured in the laboratory. Our goal is to examine aspects of the chemistry of N_3H_3 that current electronic structure theory can address and to do so at a level of ab initio quantum chemistry that enables us to make accurate predictions of the chemical and physical properties of this molecular system.

II. Synopsis of Theory

The stability and identification of unknown molecules like N_3H_3 rest upon geometry optimizations that locate minima and transition states and upon accurate predictions of the relative energies of the isomeric forms. Ab initio SCF calculations are frequently helpful in this regard, but *predictive accuracy* usually demands that electron correlation be included to a high accuracy. Among the most accurate correlation methods available today are coupled-cluster (CC) theory[14-18] and its finite-order many-body perturbation theory (MBPT) approximations.[16-19]

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Points of zero force on molecular energy surfaces are located by minimizing first derivatives of the energy with respect to nuclear displacement. These points are subsequently characterized by solving for the eigenvalues of the force constant matrix (the mass-weighted second-derivative matrix). A stable molecular structure is a local minimum on the energy surface; therefore, all the eigenvalues of its force constant matrix will be positive. A transition state is located at a maximum along the reaction path and a minimum for all displacements orthogonal to this path. Thus, one of its eigenvalues will be imaginary. The harmonic vibrational frequencies are related to the eigenvalues of the force constant matrix, and the intensities of the vibrational transitions are related to the derivative of the dipole moment with respect to nuclear displacement. Thus, second derivatives of the energy with respect to nuclear displacement coupled with first derivatives of the dipole moment give rise to a prediction of the infrared spectrum.

Analytic first and second derivatives of the SCF potential energy surface have been widely available for some time,[20] but SCF vibrational frequencies are generally found to be too high compared to experiment by ~10–15%. Analytic first derivatives of the simplest correlated model, MBPT(2), have been available as well,[20] but analytic MBPT(2) second derivatives have become available only recently.[21] However, other applications of our MBPT(2) analytical second derivative methods have now been reported.[22,23] Even though MBPT(2) is the simplest model for the inclusion of electron correlation, it typically accounts for >90% of the basis set correlation energy.[17,24] Consequently, the harmonic frequencies computed at the MBPT(2) level of theory with a reasonable basis set provide a vast improvement over SCF frequencies as they are expected to be within ~5% of experiment.[25]

Once optimum geometries are obtained for the various isomers of N_3H_3, their relative energies are studied at higher levels of correlation including MBPT(4) and CC theory.

Coupled-cluster theory is built upon the exponential ansatz; that is, the solution to the Schrodinger equation is

$$\Psi = \exp(T)|0\rangle \tag{1}$$

where $|0\rangle$ is some reference function, often the SCF solution. The operator is separated into single, double, and higher clusters

$$T = T_1 + T_2 + T_3 + \ldots \tag{2}$$

each of which is defined in terms of a set of coefficients (amplitudes) and second-quantized operators

$$T_1 = \sum_{i,a} t_i^a a^\dagger i \tag{3a}$$

$$T_2 = 1/4 \sum_{\substack{i,j,\\a,b}} t_{ij}^{ab} a^\dagger i b^\dagger j \tag{3b}$$

$$T_3 = 1/36 \sum_{\substack{i,j,k,\\a,b,c}} t_{ijk}^{abc} a^\dagger i b^\dagger j c^\dagger k \tag{3c}$$

The indices $i, j, k, \ldots$ represent orbitals (operators) that are occupied in $|0\rangle$, while $a, b, c, \ldots$ are orbitals (operators) pertaining to excited correlating orbitals. Inserting eq 1 into the Schroedinger equation, we obtain

$$\exp(-T)\mathrm{H}\exp(T)|0\rangle = E|0\rangle \tag{4}$$

from which projection on the left by $\langle 0|$ gives the energy. In the case of an SCF reference, this energy is

$$E = E_{\mathrm{SCF}} + \Delta E \tag{5}$$

$$\Delta E = \sum_{\substack{i<j\\a<b}} \langle ij||ab\rangle(t_{ij}^{ab} + t_i^a t_j^b - t_j^a t_i^b) \tag{6}$$

The integral $\langle ij||ab\rangle$ represents an antisymmetrized two-electron integral. Similarly, projection of eq 4 onto a sufficient set of excited determinants Φ^* provides equations for the coefficients t_i^a, t_{ij}^{ab}, t_{ijk}^{abc}, ...

$$\langle \Phi^*|\exp(-T)\mathrm{H}\exp(T)|0\rangle = 0 \tag{7}$$

The coupled equations are solved by using an iterative method.[26] Many-body perturbation theory (MBPT) can be viewed as arising from the low-order iterations of the CC equations.

The first reasonable approximation to the correlated wave function is to assume $T = T_1 + T_2$ when $|0\rangle$ is usually the SCF solution. This defines the coupled-cluster singles and doubles (CCSD) model.[16] The first iteration of the equation for the T_2 amplitudes and subsequent substitution into the energy expression (eq 6) yields the second-order energy, MBPT(2). The next iteration of the T_2 equation gives rise to MBPT(3). On the third iteration of the CCSD equations, the T_1 amplitudes are allowed to couple with the T_2 amplitudes, resulting in the fourth-order MBPT contributions: S(4), D(4), and Q(4). S, D, Q indicate that the contributions arise from single, double, and quadruple excitations, respectively. The quadruples arise from $T^2/2$ in the exponential expansion of T_2.[16] Note that single and quadruple excitations have their first contribution to the correlation energy in fourth-order MBPT. The fourth-order MBPT terms included in the CCSD model are, therefore, defined as SDQ-MBPT(4). Higher iterations of the CCSD equations introduce some effects of triple excitations such as T_2T_1 and $T_1^3/3!$ as well as other contributions to higher orders of MBPT.

Improving the approximation to $T = T_1 + T_2 + T_3$, defines the CCSDT model.[27,28] This model differs from the CCSD model first in fourth order, since the "connected" part of the triples introduces $T(4)$, the fourth-order contribution of the triple excitations. At fourth order, we have the complete SDTQ-MBPT(4) approximation. Although all T_1 and T_2 terms and all their possible products are included in the CCSD model, computational limitations force us to restrict ourselves to a partial inclusion of T_3. Hence, in this paper, we utilize an approximation to CCSDT that introduces some infinite-order character in T_3 to correct the $T(4)$ triples contribution. This model is identified as CCSD + T(CCSD)[22,29] and has been demonstrated to give results close to the full CCSDT values.[28]

The harmonic vibrational analysis of a molecule also allows us to compute its zero-point energy. Each vibration contributes one-half the energy of its fundamental transition to the zero-point energy of the molecule. The sum of the zero-point energy and the electronic energy gives the internal energy of the molecule at 0 K.

The contribution to the enthalpy made by rotation, translation, and excited vibrations at a given temperature may also be computed. For a nonlinear molecule at sufficiently high temperatures, rotation and translation will each contribute $1.5RT$ to the internal energy. For the enthalpy an additional PV term (RT for an ideal gas) is needed. The vibrational contribution to the enthalpy depends on the Boltzmann distribution of excited states, which can be computed at any temperature from the vibrational frequencies of the molecule. Thus, given a vibrational analysis of the molecule, the enthalpy at standard temperature and pressure may be calculated.

Finally, the translational and vibrational contributions to entropy are easily calculated at a given temperature and pressure, and the

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computation of the rotational entropy simply requires the determinant of the inertia tensor. Thus, the entropy of a molecule may be computed, and the Gibbs free energy then follows from definition.

III. Summary of Computational Procedures

SCF optimum geometries for triazene, triaziridine, triimide, *cis*-triimide, and *cis*-triaziridine are determined by using the ACES program system[30] following preliminary STO-3G and 6-31G* studies with GAUSSIAN 82.[31,32] The SCF calculations use a single-configuration restricted Hartree–Fock (RHF) wave function to represent these closed-shell singlet isomers. The Gaussian-type orbital basis used for the geometry optimizations performed with ACES is a double-ζ plus polarization (DZP) basis consisting of Dunning's contracted double-ζ bases for hydrogen and nitrogen[33] (a 1.2 scale factor is used in the hydrogen basis) augmented by the optimum polarization functions (nitrogen d function, exponent = 0.902; hydrogen p function, exponent = 0.7) of Redmon, Purvis, and Bartlett.[34] This DZP basis set comprises 111 uncontracted basis functions which yield 63 symmetry-adapted basis functions that compose the nitrogen [4s2p1d] and the hydrogen [2s1p] contracted Gaussian set.

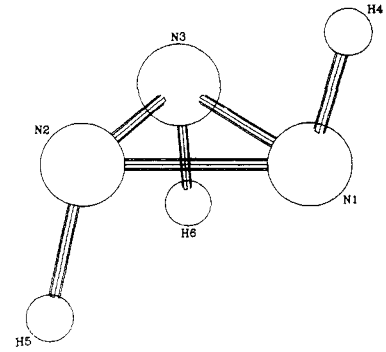
Single-point MBPT(2)[35] calculations at the 6-31G* optimum geometries are performed by using a program written to take advantage of molecular symmetry.[36] In these correlated computations the molecular orbitals representing the nitrogen 1s core orbitals are frozen. Using ACES, single-point correlated calculations are then performed on all five isomers by using the SCF-DZP optimized geometries at various levels of MBPT and CC theory. No molecular orbitals are frozen in these computations. SCF vibrational frequencies and infrared intensities are also reported for all five isomers at these geometries. With the exception of triaziridine, only frequencies are reported for the 6-31G* basis set. To calculate infrared intensities, the derivative of the dipole with respect to nuclear displacement must be determined. Electric fields for these computations are produced by using point charges.[37]

By using ACES we then determine MBPT(2) optimum geometries and corresponding MBPT(2) vibrational frequencies and infrared intensities for triazene, triimide, and triaziridine. As with the SCF intensities, the necessary electric fields are produced by point charges. At these correlated optimized geometries, the single-point calculations at various levels of MBPT and CC theory are repeated to yield consistent relative energies. Once again, no molecular orbitals are frozen.

In all of the geometry optimizations of triazene mentioned above, both SCF and MBPT(2), no symmetry restraints are enforced. However, Nguyen et al.[13] reported the optimum geometry of triazene to be planar. Thus, an SCF geometry optimization of triazene has been carried out with ACES by using the DZP basis set in which the molecule is constrained to C_s symmetry. The force-constant matrix is calculated and diagonalized to determine if the planar structure is a local minimum on the hypersurface, a transition state, or neither.

Triimide closely resembles the C_{2v} isomer of ozone whose ground state has long been reported to have multireference character.[12,38-40] In order to determine if our single-reference description of the ground state of triimide is adequate, generalized valence bond (GVB)[38,41] calculations are performed by using ACES. The geometry is optimized at the GVB level of theory, and GVB vibrational frequencies are computed with the DZP basis set. For comparison, single-reference RHF SCF, GVB, and MBPT(2) geometries are also determined for ozone. For these calculations we use a DZP basis set consisting of Dunning's contracted double-ζ basis for oxygen[33] plus the optimum polarization function of Redmon et al.[34] (oxygen d function, exponent = 1.211).

Table I. Optimum Geometries and Electronic Energies of Triaziridine[a]



bond or angle	SCF (6-31G*)[c]	SCF (DZP)[c]	MBPT(2) (DZP)[c]
	bond distances (Å) and bond angles (deg)		
N1–N2	1.416	1.414	1.470[b]
N2–N3	1.420	1.418	1.470[b]
H4–N1	1.003	1.004	1.025
H5–N2	1.005	1.006	1.027
θ(N2N1N3)	60.16	60.19	59.98
θ(N1N2N3)	59.92	59.91	60.01
θ(H4N1N2)	106.02	106.23	102.59
θ(H5N2N1)	105.67	105.78	102.39
θ(H5N2N3)	110.16	110.10	107.33
θ(H4N1N2H5)	155.88	155.88	159.58
θ(N2N3N1H4)	99.58	99.71	97.40
	−164.94244[d]	−164.98666[d]	−165.53732[d]

[a] Molecule has C_s symmetry. [b] These two calculated bond lengths differ in the next decimal place. [c] Basis set and level of theory. [d] Energy (au).

A transition state between the cyclic structure of triaziridine and the open structure of triimide is found by using the search procedure in GAUSSIAN 82. The transition state is started by an optimization with a STO-3G basis, from which we initiate a 6-31G* optimization. A single-point MBPT(2) calculation at the 6-31G* optimum geometry provides some measure of correlation effects on the transition state.

For the purposes of thermochemical comparisons the energies of molecule "pairs" on the N_3H_3 hypersurface are reported. Three pairs are considered: ammonia (NH_3) and nitrogen (N_2), triplet nitrene (NH) and *cis*-diimide (N_2H_2), and triplet nitrene and *trans*-diimide. These molecules are initially optimized at the SCF level in a 6-31G* basis set. MBPT(2) correlation energies are then computed for these optimum structures. In addition, ammonia and nitrogen are optimized by using the DZP basis set at both the SCF and MBPT(2) level. At each set of these DZP optimum geometries single-point MBPT and CC calculations are performed. At least one other pair exists on the N_3H_3 hypersurface: hydrazoic acid (N_3H) and hydrogen (H_2), but this pair has not been considered.

Thermochemical analyses of all N_3H_3 structures are performed by using PLOTGIBB.[42] The reference state for N_3H_3 is $^3/_2(N_2 + H_2)$. Thus, to compute heats of formation and free energies, electronic energy calculations and vibrational analyses are carried out on N_2 and H_2. We report thermochemical data at the SCF level of theory for both the 6-31G* and the DZP basis set and at the MBPT(2) level for the DZP basis set whenever corresponding frequencies are computed. In accordance with the convention that the enthalpies of elements in their standard states are zero, the enthalpy of nitrogen plus hydrogen is set to zero, and the other enthalpies are shifted accordingly. The temperature-entropy

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(30) ACES (Advanced Concepts in Electronic Structure) ab initio program system: Bartlett, R. J.; Purvis, G. D.; Fitzgerald, G. B.; Harrison, R. J.; Lee, Y. S.; Laidig, W. D.; Cole, S. J.; Magers, D. H.; Salter, E. A.; Trucks, G. W.; Sosa, C.; Rittby, M.; Pal, S. This program system performs SCF, MBPT, and CC calculations for electronic energies of molecules. Correlated calculations may be performed with RHF, ROHF, UHF, and other reference functions. The program also performs analytical first-derivative calculations at the SCF level and at various levels of MBPT and CC theory. It currently performs analytical second-derivative calculations at the SCF and MBPT(2) levels. Additional options in the program allow the prediction of excitation and ionization processes by using CC/MBPT theory. Currently the ACES programs employ J. Almloef's MOLECULE and R. Pitzer's integral packages.

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(42) PLOTGIBB: Salter, C. Project SERAPHIM, Eastern Michigan University, Ypsilanti, MI.

Table II. Vibrational Frequencies and Intensities of Triaziridine[a]

vibrational mode	vibrational frequencies (cm^{-1})		
	SCF (6-31G*)[b,d]	SCF (DZP)[c,d]	MBPT(2) (DZP)[c,d]
A′	3763 (7.18)	3758 (8.85)	3517 (0.943)
A′	3733 (0.437)	3739 (0.710)	3489 (0.758)
A″	3709 (1.21)	3718 (0.205)	3466 (0.326)
A′	1617 (0.103)	1579 (0.233)	1466 (0.142)
A″	1592 (24.8)	1563 (20.3)	1444 (12.1)
A″	1464 (50.7)	1438 (41.3)	1287 (46.3)
A′	1411 (63.0)	1380 (57.8)	1295 (43.9)
A′	1387 (3.52)	1413 (0.318)	1157 (21.2)
A′	1280 (103.7)	1261 (87.0)	1118 (60.2)
A″	1248 (45.5)	1232 (38.8)	1094 (30.6)
A′	956 (24.0)	972 (24.7)	796 (5.18)
A″	953 (28.4)	964 (28.4)	789 (7.62)

[a] Molecule has C_s symmetry. [b] Intensities are shown in parentheses in arbitrary units, scaled to match the SCF-DZP intensity of the smallest frequency. [c] Intensities are shown in parentheses in units of km/mol. [d] Basis set and level of theory.

product (TS) is then subtracted from the enthalpies to obtain the free energies.

IV. Results and Discussion

Results of the geometry optimizations of triaziridine are given in Table I along with a figure of the molecule. Triaziridine is found to have a $^1A'$ ground state with C_s symmetry; the SCF electronic configuration is

$$1a'^2 1a''^2 2a'^2 3a'^2 4a'^2 2a''^2 5a'^2 6a'^2 3a''^2 7a'^2 8a'^2 4a''^2$$

In Table I the usual shortening of bond lengths with a larger basis set is apparent in the SCF computations, while we observe the usual bond lengthening effect of correlation in the MBPT(2) results. The structures are similar to those reported by Nguyen et al., except that their results have all of the N–N bond lengths equal. In our results, the ring is not an equilateral triangle; the N2–N3 bond is slightly longer than the other N–N bonds, even though almost equal at the MBPT(2) level. Even if higher levels of correlation and a better basis set predicted these bond lengths to be equal, the molecule would still have C_s symmetry due to the location of the hydrogens. Nguyen et al. also report that the H5N2N1 angle is equal to the H5N2N3 angle, while we find that the H5N2N3 angle is larger. Here, the MBPT(2) geometry gives the largest difference between the angles.

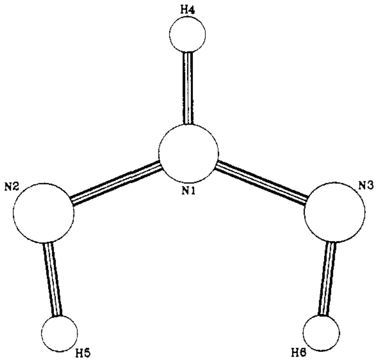
The effect of the cis hydrogen interaction on the optimum SCF geometry appears to increase as the basis set improves. However, the addition of electron correlation appears to diminish this effect; the substantial effect here is the rehybridization of the nitrogen atoms. As indicated in Table I, the bond angles at the nitrogen atoms decrease when the geometry is optimized with correlation. This decrease corresponds to an increase in the p-character of the bonds.

The vibrational frequencies and corresponding infrared intensities for triaziridine are reported in Table II. Note that a pair of frequencies near 1400 wavenumbers are reordered in the change from the smaller to the larger basis set at the SCF level of theory. Both of these vibrational modes have large contributions from the hydrogens bending with respect to the nitrogen ring. The 6-31G* basis should not be as accurate for frequencies involving such hydrogen motion as the DZP basis because it lacks polarization functions on the hydrogens. Studies have shown that SCF frequencies computed with a DZP basis set are usually closer to experimental results than those computed with a 6-31G* basis set for molecules comprised of first-row atoms.[25,43]

The SCF intensities for both basis sets are in fair agreement. The intensity of the vibrational mode with a frequency of 964 wavenumbers at the SCF-DZP level was chosen as the reference to scale the other 6-31G* intensities because this mode involves almost no hydrogen motion relative to the nitrogen ring.

SCF theory overestimates the strength of bonding; as a consequence the vibrational frequencies are too high. The MBPT(2) model corrects for this shortcoming of SCF theory, lowering the frequencies by as much as 250 wavenumbers in the N–H stretches of triaziridine. Reordering of frequencies is also common when correlation is included. The same pair of frequencies near 1400 wavenumbers which switched order at the SCF level with the change of basis set reorder again at the MBPT(2) level of theory. This time a third frequency is also involved in the rearrangement. In general, for molecules of first-row atoms, MBPT(2) frequencies computed with DZP basis sets are usually within 5% of experimental results (usually within 2% of experimental frequencies computed with harmonic empirical force fields), while frequencies computed at the SCF level with the same DZP basis sets are only within 15%.[25]

Table III. Optimum Geometries and Electronic Energies of Triimide[a]



bond or angle	bond distances (Å) and bond angles (deg)			
	SCF (6-31G*)[b]	SCF (DZP)[b]	GVB (DZP)[b]	MBPT(2) (DZP)[b]
N1–N2	1.255	1.257	1.278	1.305
H4–N1	1.005	1.009	1.004	1.023
H5–N2	1.008	1.010	1.011	1.033
Θ(N2N1N3)	135.43	135.27	134.11	135.87
Θ(H4N1N2)	112.29	112.37	112.95	112.07
Θ(H5N2N1)	108.14	108.43	108.15	105.35
	−164.96537[c]	−165.00993[c]	−165.05168[c]	−165.58110[c]

[a] Molecule has C_{2v} symmetry. [b] Basis set and level of theory. [c] Energy (au).

Rather than perform the often costly and time-consuming determination of vibrational frequencies at the correlated level, many researchers use a simple scaling factor to lower their SCF frequencies into the experimental range. Obviously, scaling SCF frequencies does not truly correct for correlation effects, because correlation does not affect each frequency by the same amount. Nevertheless, such scaling often yields good agreement with experimental frequencies. On the other hand, computed vibrational intensities cannot be scaled to account accurately for correlation. Note that some of the intensities for triaziridine change only a little with the inclusion of correlation effects while others change dramatically. The relatively strong SCF-DZP intensity of 24.7 km/mol is reduced by a factor of more than four. One study has shown that SCF calculations of infrared intensities using a DZP basis set for molecules comprising first-row atoms yield results which frequently differ from experiment by over 100%. MBPT(2) computations using the same bases yield intensities that are typically within 30% of the experimental values.[25]

Results of the geometry optimizations of triimide are reported in Table III along with a figure of the molecule. Triimide has a $^1A_1$ ground state with C_{2v} symmetry, but the assignment of an optimal reference function to describe this ground state is not as clear as with triaziridine. Triimide closely resembles the C_{2v} $^1A_1$ ground state of O_3 whose single-reference RHF SCF electronic configuration is

$$1a_1^2 1b_2^2 2a_1^2 3a_1^2 2b_2^2 4a_1^2 5a_1^2 1b_1^2 3b_2^2 4b_2^2 6a_1^2 1a_2^2$$

but ozone is not described well by a single-reference function. Due to the biradical character of its ground state, O_3 has a second important reference whose configuration is

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[43] Yamaguchi, Y.; Frisch, M.; Gaw, J.; Schaefer, H. F., III; Binkley, J. S. *J. Chem. Phys.* **1986**, *84*, 2262.

$$O_3(\text{core})4b_2^2 6a_1^2 2b_1^2$$

Similarly, the $^1A_1$ ground state of triimide has a single-reference RHF SCF electron configuration of

$$1a_1^2 1b_2^2 2a_1^2 3a_1^2 2b_2^2 4a_1^2 3b_2^2 5a_1^2 1b_1^2 6a_1^2 4b_2^2 1a_2^2$$

but the determinant whose configuration is

$$\text{triimide(core)}6a_1^2 4b_2^2 2b_1^2$$

may be too important to limit the description of triimide to single-reference SCF. For convenience, all future references to the above configurations will refer to the primary reference determinant as the a_2 configuration and the secondary reference determinant as the b_1 configuration for both ozone and triimide.

In order to validate our single-reference SCF computations and our MBPT(2) calculations built upon the single-reference SCF function, we performed a generalized valence bond (GVB) geometry optimization for triimide and computed corresponding GVB vibrational frequencies. Simple GVB calculations such as we performed are identical with multiconfiguration self-consistent-field (MCSCF) calculations limited to two closed-shell configurations. This description is equivalent to an open-shell RHF calculation in which the orbitals are nonorthogonal. Our GVB calculation for triimide using the DZP basis set yielded CI-like coefficients of 0.9568 for the a_2 configuration and −0.2906 for the b_1 configuration. By squaring these coefficients and multiplying by two, we obtain orbital occupancies for the GVB orbitals, which are a measure of the biradical character.[44,40] The orbital occupancy is 1.831 for the a_2 configuration and 0.169 for the b_1 configuration. Thus, in this scheme the RHF single configuration represents 91.5% of the GVB wave function compared to 95% for more typical closed-shell ground states. Furthermore, the b_1 configuration is a double excitation out of the a_2 configuration and MBPT(2) correlates the ground-state reference with such double excitations. We therefore conclude that the MBPT(2) model is adequate for the geometry, vibrational frequencies, and intensities of triimide even though the single-reference SCF model may have deficiencies.

In Table III the similarity of the SCF and GVB values of triimide's internal coordinates is apparent. The fact that the GVB values correspond more closely with the SCF results than with those at MBPT(2) should not be surprising. While it is true that some correlation has been included in the GVB wave function, the degree of correlation is much smaller than that obtained at the MBPT(2) level. The additional correlation of the MBPT(2) calculation leads to shorter bond lengths.

The planar structure of triimide allows strong π bonding to take place. The π-structure of triimide is similar to that of the propenyl anion or ozone (see below), with four electrons in the three p orbitals. The 6-31G* Mulliken population analysis of the SCF electronic density shows that the central nitrogen is almost uncharged (−0.06). Nguyen et al. found the central nitrogen had a charge of −0.23 at 3-21G with the same type of SCF population analysis. The Lowdin population analysis of the SCF-DZP electronic density yields a charge of +0.73 for the central nitrogen atom. All such population analyses are nonphysical measurements, yet they provide a means for succinctly summing the physical electronic density into qualitative electronic occupations for each nuclear center. The different types of population analyses rarely differ qualitatively, so we may directly compare them. Thus, we see that the electronic density of the π-system increases on the terminal nitrogens as the basis set is improved.

Another easy way to view the electronic density is to sum the density into bonding regions. By using the SCF bond order scheme of Natiello et al.,[45] the DZP-SCF N–N bonds for triimide are calculated to have a bond order of 1.74. For triaziridine, the N1–N2 and N1–N3 bonds have a bond order of 1.14, and the bond order of the N2–N3 bond is 1.12. Comparison with the following list of SCF bond orders adds perspective to these N_3H_3 values: ethane, 1.2; benzene, 1.5; and ethene, 2.2.[45] Thus, we see that the N–N bonds in triaziridine are single bonds, and the N–N bonds in triimide are halfway between single and double bonds.

Table IV. Vibrational Frequencies and Intensities of Triimide[a]

vibrational mode	vibrational frequencies (cm^{-1}) SCF (6-31G*)[e]	SCF (DZP)[b,e]	GVB (DZP)[e]	MBPT(2) (DZP)[b,e]
A_1	3781	3761 (49.9)	3813	3573 (28.9)
B_2	3687	3701 (19.7)	3686[c]	3435 (11.4)
A_1	3686	3697 (4.67)	3686[c]	3428 (7.10)
B_2	1794	1767 (260.7)	1824	1771 (22.3)
A_1	1695	1673 (7.85)	1644	1517 (16.0)
B_2	1612	1595 (839.3)	1660	1569 (11.1)
B_2	1441	1426 (136.1)	1407	1298 (77.2)
A_1	1392	1389 (24.1)	1338	1163 (11.4)
B_1	1283	1263 (171.9)	1136	1093 (180.2)
B_1	912	896 (88.7)	794	778 (25.7)
A_2[d]	849	823 (0.00)	791	756 (0.00)
A_1	713	706 (47.4)	683	622 (38.0)

[a] Molecule has C_{2v} symmetry. [b] Intensities are shown in parentheses in units of km/mol. [c] These two calculated frequencies differ in the next decimal place. [d] IR vibrational transition is forbidden by symmetry. [e] Basis set and level of theory.

We calculated geometries for O_3 at the single-reference SCF, MBPT(2), and GVB levels so that we could compare the accuracy of each level with known experimental results. The experimental equilibrium bond length r_e is 1.2717 Å, and the experimental equilibrium bond angle Θ_e is 116.8°.[46] At the single-reference SCF level, the theoretical value of r_e is 1.1987 Å, and the value of Θ_e is 119.2°. The GVB model predicts r_e to be 1.2487 Å and Θ_e to be 115.5°. The coefficients from the GVB calculation were 0.8962 for the a_2 configuration and −0.4437 for the b_1 configuration. These coefficients in turn yield orbital occupancies of 1.606 and 0.394, respectively. We see that ozone exhibits more biradical character than triimide because the single-reference RHF configuration accounts for only 80.3% of the GVB wave function. One further indication that an RHF single-reference description of the ground state of triimide is more accurate than an equivalent treatment of the ground state of ozone is that the lowest unoccupied molecular orbital (LUMO) in the single-reference RHF calculation of ozone has negative energy ($\epsilon = -0.01023$ au), while the energy of the corresponding LUMO for triimide is positive ($\epsilon = 0.12092$). Of course, both LUMO's have b_1 symmetry and represent the highest occupied molecular orbitals in the b_1 configurations for each system. Finally, MBPT(2) computations yield 1.2933 Å as the value for r_e and 116.7° as the value for Θ_e. Thus, we see that good agreement with experiment is obtained at the MBPT(2) level for a system with more biradical nature than triimide.

Vibrational frequencies and intensities for triimide are listed in Table IV. In general, the GVB frequencies lie between the SCF and the MBPT(2) values, but three GVB frequencies are actually higher than the corresponding SCF values. Note that the fifth and sixth vibrational modes reorder from the SCF level when correlation effects are added and that the GVB and MBPT(2) orderings are identical. The largest difference between the SCF and MBPT(2) level is shown in the infrared intensities for the fourth and sixth vibrational modes. These SCF values are obviously too high; the SCF intensity of 839.3 is over 75 times larger than the corresponding MBPT(2) result. Both values are probably a manifestation of the inadequacy of the single-reference RHF SCF wave function.

Table V contains the optimized internal coordinates for triazene along with a figure of the molecule. The ground state of triazene is ^1A and is well-described by a single reference closed-shell RHF SCF wave function. The optimized structures are roughly similar to those found by Nguyen et al.,[13] but our structures are not planar. Further investigation revealed that the SCF energy difference

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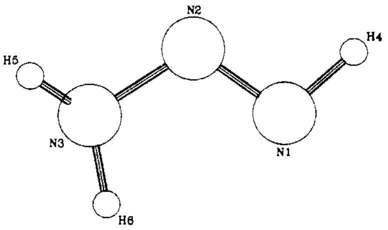
(44) Hayes, E. F.; Siu, A. K. Q. *J. Am. Chem. Soc.* **1971**, *93*, 2090.

(45) Natiello, M. A.; Reale, H. F.; Medrano, J. A. *J. Comput. Chem.* **1985**, *6*, 108.

(46) Tanaka, T.; Morino, Y. *J. Mol. Spectrosc.* **1970**, *33*, 538. Lichtenstein, M.; Gallagher, J. J.; Clough, S. A. *J. Mol. Spectrosc.* **1971**, *40*, 10.

Table V. Optimum Geometries and Electronic Energies of Triazene[a]



bond or angle	bond distances (Å) and bond angles (deg) SCF (6-31G*)[b]	SCF (DZP)[b]	MBPT(2) (DZP)[b]
N1–N2	1.217	1.220	1.274
N2–N3	1.348	1.346	1.365
H4–N1	1.008	1.009	1.029
H5–N3	0.996	0.997	1.012
H6–N3	1.002	1.003	1.021
θ(N1N2N3)	113.90	113.93	111.59
θ(H4N1N2)	106.82	106.89	103.82
θ(H5N3H6)	114.65	115.37	114.81
θ(H5N3N2)	110.92	111.45	110.52
θ(H6N3N2)	113.59	114.16	113.57
θ(H4N1N2N3)	177.01	177.25	176.09
θ(H6N3N2N1)	21.33	20.77	21.21
	−165.01412[c]	−165.05823[c]	−165.60259[c]

[a] Molecule has no symmetry. [b] Basis set and level of theory. [c] Energy (au).

Table VI. Vibrational Frequencies and Intensities of Triazene[a]

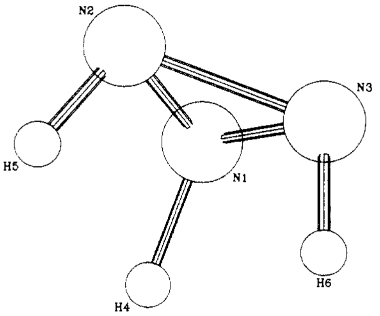
vibrational mode[b]	vibrational frequencies (cm^{-1}) SCF (6-31G*)[d]	SCF (DZP)[c,d]	MBPT(2) (DZP)[c,d]
N3–H5 stretch	3898	3914 (38.8)	3731 (34.7)
N3–H6 stretch	3744	3755 (14.7)	3541 (9.35)
N1–H4 stretch	3685	3692 (0.973)	3468 (0.041)
N1–N2 stretch	1889	1873 (103.9)	1540 (46.9)
H5–N3–H6 stretch	1817	1787 (54.1)	1647 (47.3)
N2–N1–H4 bend	1643	1615 (6.66)	1476 (6.76)
N2–N3–H5 bend	1414	1389 (48.6)	1262 (44.6)
N2–N3 stretch	1211	1213 (83.4)	1133 (49.4)
H4 out-of-plane deformtn	1068	1055 (49.8)	952 (41.6)
H6 out-of-plane deformtn	764	717 (353.8)	684 (341.1)
N1–N2–N3 bend	686	679 (5.67)	635 (6.79)
H5 out-of-plane deformtn	518	517 (80.8)	501 (83.2)

[a] Molecule has no symmetry. [b] The dominant internal coordinate is used to label each normal mode of vibration. [c] Intensities are shown in parentheses in units of km/mol. [d] Basis set and level of theory.

between the planar conformation and the energetically optimum nonplanar conformation is 2 kcal/mol for the 6-31G* basis and 1.3 kcal/mol for the DZP basis. Contrary to this trend, we found that the optimum SCF geometry with the 6-31G basis is planar, as Nguyen et al. reported. By using the bond order analysis for triazene, we found the N1–N2 bond to be a double bond (bond order = 2.13) and the N2–N3 bond to be a single bond (bond order = 1.302), as expected.

With use of the STO-3G basis, the 6-31G* basis, and the DZP basis set, we found that the optimum SCF structure of triazene is not planar. Apparently the split-valence basis sets used by Nguyen et al. favor a planar structure. One would presume this is due to a bias of the split-valence basis sets in favor of overlap between the N–N double bond and the unshared pair of electrons on the sp^2 nitrogen atom. Such an overlap would be enhanced by a planar structure. However, Nguyen et al. report that the electron pairs in the double bond and on the sp^2 nitrogen are "rather localized". Of course, we observe the same localization in our nonplanar structures. Nevertheless, the small overlap that we do observe is certainly one of the chief reasons that our optimum structures are as close to planarity as they are.

Table VII. Optimum Geometries and Electronic Energies of *cis*-Triaziridine[a]



bond or angle	bond distances (Å) and bond angles (deg) 6-31G*[b]	DZP[b]
N1–N2	1.421	1.419
H4–N1	1.006	1.007
θ(N1N2N3)	60.00	60.00
θ(H4N1N2)	109.74	109.62
θ(H4N1N2N3)	101.96	101.88
	−164.92202[c]	−164.96860[c]

[a] Molecule has C_{3v} symmetry. [b] SCF level of theory and basis set. [c] Energy (au).

Table VIII. Vibrational Frequencies and Intensities of *cis*-Triaziridine[a]

vibrational mode	vibrational frequencies (cm^{-1}) 6-31G*[d]	DZP[b,d]
A_1	3713	3730 (0.030)
	3667	3689 (1.38)
E	3667	3689 (1.38)
	1591	1561 (54.8)
E	1591	1561 (54.8)
A_1	1451	1412 (1.47)
A_1	1389	1409 (0.449)
A_2[c]	1379	1362 (0.00)
	1224	1206 (4.33)
E	1224	1206 (4.33)
	931	944 (26.3)
E	931	944 (26.3)

[a] Molecule has C_{2v} symmetry. [b] Intensities are shown in parentheses in units of km/mol. Intensities for degenerate vibrational frequencies should be summed to give one value for the mode; for example, the E mode of 3667 wavenumbers has an overall calculated intensity of 2.76 km/mol. [c] IR vibrational transition is forbidden by symmetry. [d] SCF level of theory and basis set.

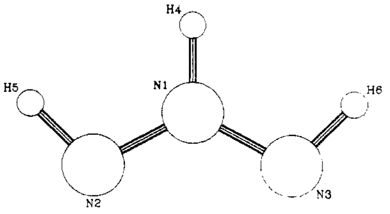
The vibrational frequencies and intensities of triazene are presented in Table VI. For this molecule the SCF infrared intensities are quite similar to those reported at the MBPT(2) level of theory; only two differ substantially. However, once again we observe a reordering of two of the frequencies, the N1–N2 stretch and the H5–N3–H6 bend, with the inclusion of electron correlation. We also calculated SCF-DZP frequencies for the planar conformation. We found the planar conformation to be a transition state; it has a single imaginary frequency of 517i corresponding to the out-of-plane deformation of the hydrogens. Therefore, we expect the harmonic approximation to break down for the lowest frequency mode of vibration of triazene, due to the presence of a degenerate well separated by a small barrier of 1–2 kcal/mol.

cis-Triaziridine, a form of triaziridine with all hydrogens on the same side of the nitrogen ring, was investigated at the SCF level of theory. The predicted geometry and vibrational frequencies and intensities of *cis*-triaziridine using the 6-31G* and DZP basis sets are shown in Tables VII and VIII. *cis*-Triaziridine has C_{3v} symmetry; its ground-state configuration is given by

$$1a_1^2 1e^4 2a_1^2 2e^4 3a_1^2 4a_1^2 3e^4 4e^4$$

The N–N bond lengths in *cis*-triaziridine are nearly identical with the N_2–N_3 bond length in triaziridine when the same basis sets

Table IX. Otimum Geometry and Electronic Energy of *cis*-Triimide[a]



bond or angle	bond distances (Å) and bond angles (deg) DZP[b]
N1-N2	1.258
H4-N1	1.013
H5-N2	1.005
Θ(N2N1N3)	125.25
Θ(H4N1N2)	117.37
Θ(H5N2N1)	107.37
	−164.99448[c]

[a] Molecule has C_{2v} symmetry. [b] SCF level of theory and basis set. [c] Energy (au).

Table X. Vibrational Frequencies and Intensities of *cis*-Triimide[a]

vibrational mode	vibrational frequencies (cm^{-1}) DZP[b,d]	vibrational mode	vibrational frequencies (cm^{-1}) DZP[b,d]
A_1	3765 (0.702)	B_2	1413 (840.6)
B_2	3754 (21.4)	A_1	1369 (0.0004)
A_1	3634 (3.51)	B_1	1153 (6.92)
B_2	1871 (230.7)	B_1	863 (138.6)
A_1	1689 (14.0)	A_1	734 (0.511)
B_2	1580 (240.0)	A_2[c]	670 (0.00)

[a] Molecule has C_{2v} symmetry. [b] Intensities are shown in parentheses in units of km/mol. [c] IR vibrational transition is forbidden by symmetry. [d] SCF level of theory and basis set.

are used, while SCF theory predicts that the energy lies 11–13 kcal/mol above triaziridine. Thus, the energy difference is due to the two additional cis hydrogen interactions. Although the cis form of triaziridine is not as stable as the trans form, it is of particular interest since it may more closely resemble the form of triaziridine trapped in the silver-exchanged zeolite by Kim et al.[2]

If the geometry of *cis*-triaziridine were optimized at the MBPT(2) level, we would expect the N–N bond distance to be slightly larger than the 1.470 Å bond distance of triaziridine at this level. This bond distance is within 0.02 Å of the experimental N–N bond length that Kim et al. observed. Also, the larger experimental distance could be due to the presence of the silver.

In triimide, the terminal hydrogens lie on the opposite side of the nitrogen ring from the middle hydrogen. Additional conformations of triimide in which one or both terminal hydrogens rotate to the opposite side of the chain are also possible. The cis conformation, where both hydrogens have rotated so that all three hydrogens lie on the same side of the nitrogen chain, was optimized at the SCF level of theory. The predicted geometry and vibrational frequencies and intensities of *cis*-triimide using a DZP basis are shown in Tables IX and X. *cis*-Triimide has C_{2v} symmetry; its ground-state configuration is

$$1a_1^2 1b_2^2 2a_1^2 3a_1^2 2b_2^2 4a_1^2 5a_1^2 3b_2^2 1b_1^2 4b_2^2 6a_1^2 1a_2^2$$

As expected the N–N bond distances in *cis*-triimide are similar to the N–N bond distances in triimide. The energy of the cis conformer is higher due to the increased dipole moment caused by placing the positively charged hydrogens on one side of the molecule and the negatively charged nitrogens on the other side.

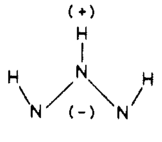


Table XI. Optimum Geometries, Electronic Energies, and Vibrational Frequencies of "Pair" Molecules

molecule	SCF (6-31G*)[e]	SCF (DZP)[e]	MBPT(2) (DZP)[e]	experiment[e]
H_2				
r(H-H)	0.730	0.736	0.740	0.740[a]
E (au)	−1.12683	−1.13100	−1.15842	
ν	4642	4637	4574	4395[a]
N_2				
r(N-N)	1.078	1.080	1.135	1.094[a]
E (au)	−108.94395	−108.96046	−109.29786	
ν	2758	2720	2129	2360[a]
NH_3				
r(N-H)	1.003	1.003	1.017	1.011[b]
θ(HNH)	107.18	107.82	105.68	106.6[c]
E (au)	−56.18436	−56.20890	−56.41235	
ν				d
E	3823	3847	3702	3444
A_1	3690	3712	3551	3337
E	1849	1797	1699	1627
A_1	1209	1121	1124	950
NH ($^3\Sigma^-$)				
r(N-H)	1.024			
E (au)	−54.95942			
trans-N_2H_2				
r(N-N)	1.216			
r(N-H)	1.015			
θ(HNN)	107.54			
E (au)	−109.99477			
cis-N_2H_2				
r(N-N)	1.215			
r(N-H)	1.018			
θ(HNN)	113.07			
E (au)	−109.98350			

The header of columns 2–5 is "bond distances (Å), bond angles (deg), and vibrational frequencies (cm^{-1})".

[a] Reference 47. [b] Reference 48. [c] Reference 49. [d] Reference 51. [e] Basis set and level of theory.

The conformation where only one hydrogen is rotated is energetically more stable than the cis structure (see the 6-31G study by Nguyen et al.[13]), but our objective was to see if the anomalous intensities predicted by SCF theory for triimide would also arise in other triimide conformations. The symmetry of the cis structure made it the computationally attractive candidate. The intensities of the B_2 vibrational modes whose frequencies are 1871, 1580, and 1413 are all found to be unreasonably large. Again we expect that the anomalous results are due to the shortcomings of the single-reference SCF description of a molecule with biradical character.

Components of selected molecular "pairs" on the N_3H_3 potential energy surface (hydrogen, nitrogen, ammonia, triplet nitrene, *trans*-diimide, and *cis*-diimide) were optimized at the SCF level of theory by using 6-31G* basis sets. Hydrogen, nitrogen, and ammonia were optimized by using DZP basis sets at the SCF and MBPT(2) levels of theory as well. Also, vibrational frequencies for these three molecules were computed at all three levels. The results of these calculations are given in Table XI. The geometries of the known molecules agree well with experiment,[47–49] and the triplet nitrene optimization, based upon the unrestricted Hartree–Fock SCF model, agrees with an earlier work.[50] The experimental frequencies reported for H_2 and N_2 are actually experimental frequencies computed with a harmonic force field.[47] The DZP-MBPT(2) calculated frequencies for H_2 and N_2 still differ by 4.07% and 9.79%, respectively. The calculated values for N_2 are especially poor due to the difficulty in describing the triple bond. Note that the DZP-MBPT(2) value for the bond

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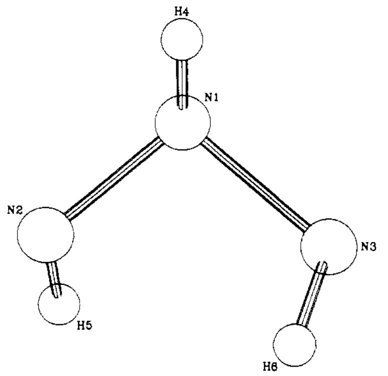
(47) Herzberg, G. *Spectra of Diatomic Molecules*; Van Nostrand Reinhold Company Inc.: New York, 1950.

(48) Kuchitsu, K.; Guillory, J. P.; Bartell, L. S. *J. Chem. Phys.* **1968**, *49*, 2488.

(49) Benedict, W. S.; Plyler, E. K. *Can. J. Phys.* **1957**, *35*, 1235.

(50) Lathan, W. A.; Hehre, W. J.; Curtiss, L. A.; Pople, J. A. *J. Am. Chem. Soc.* **1971**, *93*, 6377.

Table XII. Optimum Geometry and Electonic Energy of the Transition State[a]



bond or angle	bond distances (Å) and bond angles (deg)
	6-31G*[b]
N1–N2	1.271
N1–N3	1.429
N1–H4	1.004
N2–H5	1.004
N3–H6	1.010
Θ(N2N1N3)	97.01
Θ(H4N1N2)	114.97
Θ(H4N1N3)	117.68
Θ(H5N2N1)	105.56
Θ(H6N3N1)	104.22
Θ(H4N1N2H5)	173.97
Θ(H5N2N1N3)	−61.03
Θ(H6N3N1N2)	−50.55
	−164.84915[c]

[a] Transition state which lies between triaziridine and triimide. It has no symmetry. [b] SCF level of theory and basis set. [c] Energy (au).

distance is off by 0.041 Å for N_2, yet within 0.003 Å for both H_2 and NH_3. The experimental frequencies reported for NH_3 are true experimental values.[51] The average error for the DZP-MBPT(2) frequencies for NH_3 is 9.2%. This error is slightly larger than is usually obtained at the MBPT(2) level with a DZP basis set.

Our predicted transition state between triaziridine and triimide has no symmetry. The lengths of the two N–N bonds are not equal, but even if they were, the positions of the hydrogen atoms are sufficient to eliminate all symmetry. In Tables XII and XIII, we present the internal coordinates and vibrational frequencies predicted by single-reference SCF theory with a 6-31G* basis set. In triaziridine H5 and H6 lie below the ring plane; in the transition state H6 has moved above the nitrogen plane. H5 and H6 are destined for the nitrogen plane in triimide; in the transition state it appears that H6 has moved too far. The geometry of the transition state suggests that the N1–N3 bond lengthens so that it can rotate with less steric hindrance. Apparently one hydrogen rotates past the nitrogen plane first to minimize the interaction between the two hydrogens.

In order to substantiate our claim that the transition state lies between triaziridine and triimide on the potential surface, GAUSSIAN 80 optimizations using the transition state as the initial structure were performed. The searches yielded triimide as the final optimized structure. Furthermore, analysis of the motions of the atoms in the normal mode associated with the imaginary frequency indicate that the transition state is moving toward triimide.

The activation energy of triaziridine is predicted to be about 58.5 kcal/mol at the SCF level, but this estimate is probably too high. Single-point MBPT(2) calculations lower the activation energy by 38.8 kcal/mol. One other potential problem exists with our SCF prediction of the transition state. We have shown that triimide has some biradical character, and therefore a single-reference RHF treatment may have deficiencies. If deficiencies are possible for a minimum on the potential surface, they are certainly likely at a saddle-point.

Table XIII. Vibrational Frequencies of the Transition State[a]

vibrational mode[b]	vibrational frequencies (cm^{-1})
	6-31G*[c]
N2–H5 stretch	3752
N1–H4 stretch	3736
N3–H6 stretch	3627
H5–N2–N1 bend	1705
H6–N3–N1 bend	1618
N1–N2 stretch	1511
H4–N1–N3 bend	1459
H4 out-of-plane deformtn	1182
H5 out-of-plane deformtn	941
H6 out-of-plane deformtn	891
N1–N3 stretch	655
ring opening	1167i

[a] Transition state which lies between triaziridine and triimide. It has no symmetry. [b] The dominant internal coordinate is used to label each normal mode of vibration. [c] SCF level of theory and basis set.

Relative energies for molecules and molecular pairs on the N_3H_3 hypersurface calculated at various levels of theory using SCF optimum geometries are reported in Table XIV. $^3/_2(N_2 + H_2)$ was chosen as the reference point for the relative energies so that it also could be chosen as the reference point for the relative enthalpies, since elements in their standard states at 298 K and 1 atmosphere pressure have zero enthalpies. Note that correlation lowers the relative energies of all of the N_3H_3 isomers and increases the relative energies of all the molecular pairs. While correlation stabilizes all of the N_3H_3 isomers relative to $^3/_2(N_2 + H_2)$, the relative energies of triimide and *cis*-triimide are lowered the most. This result is due to the coupled-cluster method attempting to recover the effects of the b_1 configuration. Contributions to the energy due to triple excitations are greatest for triimide and *cis*-triimide for the same reason. Certain triple excitations out of the a_2 configuration are equivalent to single excitations out of the b_1 configuration.

Relative energies for selected N_3H_3 isomers and molecular pairs calculated at MBPT(2) optimum geometries at various levels of theory are presented in Table XV. Relative energies at the highest level of theory employed, CCSD + T(CCSD), differ only slightly from corresponding values reported in Table XIV; all are increased by 0.5–2.0 kcal/mol.

Table XVI lists the thermochemical quantities computed from our ab initio results for the N_3H_3 isomers, hydrogen, nitrogen, and ammonia. For the transition state we calculate the thermodynamic activation parameters of Eyring; the imaginary frequency is ignored. The largest effect of free-energy corrections on the relative stability of the N_3H_3 isomers is to decrease the energy of the transition state relative to triimide and triaziridine by about 3 kcal/mol. The main reason the transition state has a smaller zero-point energy contribution than the other isomers is that it has only eleven vibrational modes.

Finally, we may simulate an experimental matrix-isolated spectrum by using a sum of Lorentzian line functions. The absorbance Y_i for each frequency point x_i is calculated as

$$Y_i(x_i) = \frac{1}{\pi}\sum_j \frac{S_j\Delta_j}{(x_i - \omega_j)^2 + \Delta_j^2}$$

where S_j represents the integrated absorbance of each band; Δ_j, the half bandwidth at half of the maximum absorbance; and ω_j, the frequency of the band center. The integrated absorbance is equal to the product of the calculated intensity, the path length, and the concentration, but these latter two variables are set to unity. The calculated frequencies are the frequencies of the band centers. For our unknown molecular systems, we use 2.5 wavenumbers for the half bandwidth of all peaks. This value is probably somewhat small for many of the peaks but should be a reasonable average value. We have plotted the infrared spectra for tria-

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(51) *Tables of Vibrational Frequencies*; Shimanouchi, T., Ed.; National Bureau of Standards, National Standards Data Service National Bureau of Standards 39, U.S. GPO, Washington, D.C., 1972; Vol. 1.

Table XIV. Relative Energies at SCF Optimum Geometries

molecule or molecular pair	relative energies (kcal/mol)						
	6-31G* basis set		DZP basis set				
	SCF	MBPT(2)	SCF	MBPT(2)	SDTQ-MBPT(4)	CCSD	CCSD + T(CCSD)
$^3/_2(N_2 + H_2)$[a]	0.0	0.0	0.0	0.0	0.0	0.0	0.0
$N_2 + NH_3$	-13.89	-8.44	-20.19	-18.15	-17.14	-18.62	-17.61
triazene	57.76	57.18	49.54	47.32	46.13	45.17	44.45
triimide	88.35	72.79	79.85	61.70	62.85	66.00	62.57
triaziridine	102.74	98.81	94.45	88.77	88.20	86.64	86.49
cis-triimide			89.55	71.57	72.54	75.18	71.73
cis-triaziridine	115.56	112.24	105.78	99.38	98.41	96.98	96.62
transition state[b]	161.28	137.62					
NH + *trans*-N_2H	95.37	137.31					
NH + *cis*-N_2H_2	102.44	143.65					

[a] The absolute energies (au) for $^3/_2(N_2 + H_2)$ are as follows: 6-31G*, SCF -165.10617, MBPT(2) -165.58845; DZP, SCF -165.13718, MBPT(2) -165.67320, SDTQ-MBPT(4) -165.71257, CCSD -165.69348, CCSD + T(CCSD) -165.71054. [b] Transition state lies between triaziridine and triimide.

Table XV. Relative Energies at the MBPT(2) Optimum Geometry[a]

molecule or molecular pair	relative energies (kcal/mol)					
	SCF	MBPT(2)	SDQ-MBPT(4)	SDTQ-MBPT(4)	CCSD	CCSD + T(CCSD)
$^3/_2(N_2 + H_2)$[b]	0.0	0.0	0.0	0.0	0.0	0.0
$N_2 + NH_3$	-22.72	-16.18	-17.86	-15.59	-18.12	-16.61
triazene	44.36	51.35	47.21	48.99	45.95	45.95
triimide	75.59	64.83	67.22	64.63	66.53	63.25
triaziridine	89.91	92.31	88.42	90.42	86.79	87.19

[a] DZP basis set. [b] The absolute energies (au) for $^3/_2(N_2 + H_2)$ are as follows: SCF, -165.12316, MBPT(2) -165.68442, SDQ-MBPT(4) -165.69983, SDTQ-MBPT(4) -165.72228, CCSD -165.69796, CCSD + T(CCSD) -165.71776.

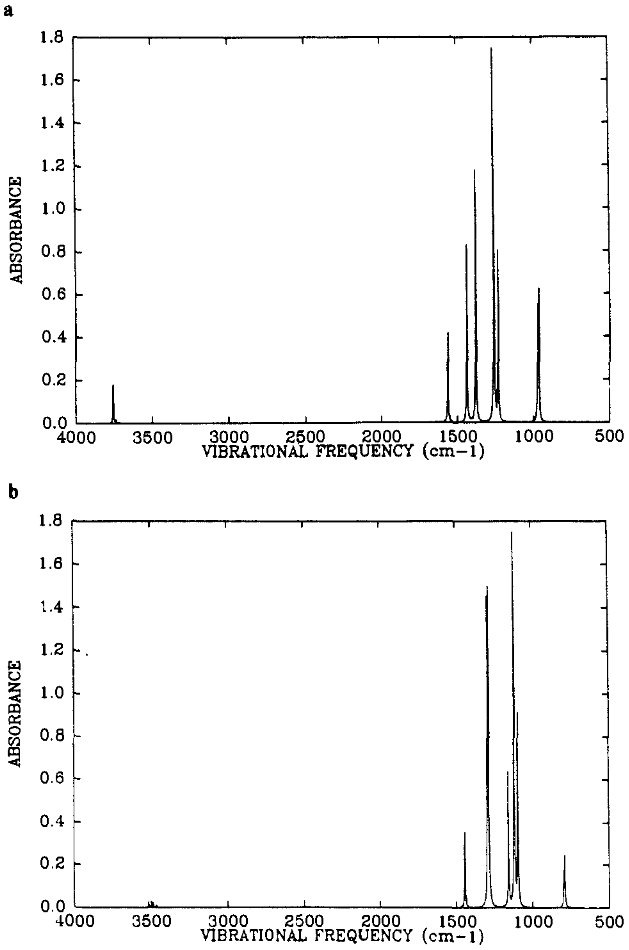

Figure 1. Spectra of triaziridine: (a) SCF IR and (b) E(2) IR.

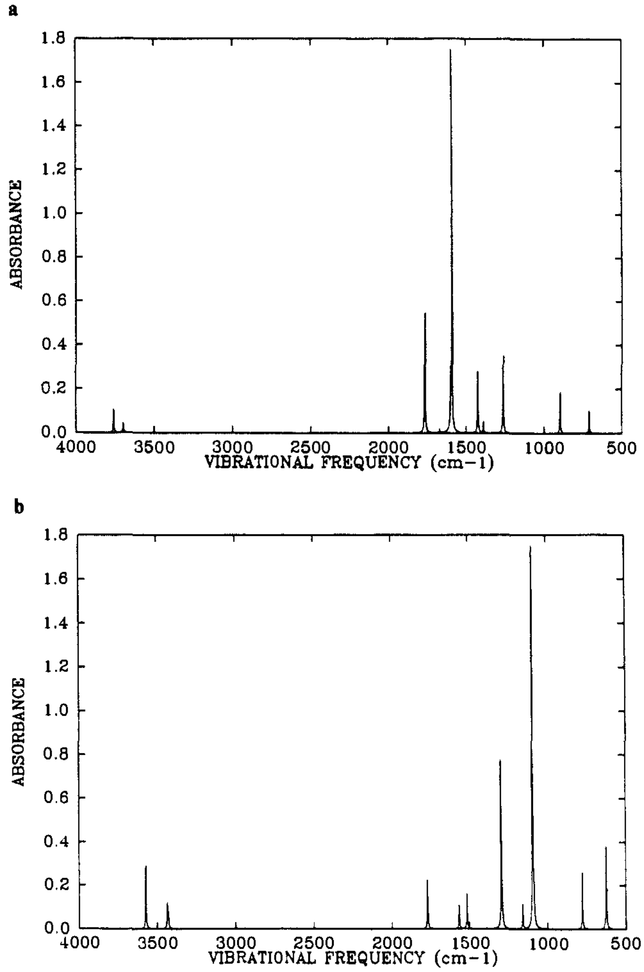

Figure 2. Spectra of triimide: (a) SCF IR and (b) E(2) IR.

ziridine, triimide, and triazene by using the computed MBPT(2) and SCF frequencies and intensities in Figures 1–3, respectively. Note that E(2) denotes MBPT(2) in each of these figures. The SCF infrared spectra for both cis isomers are presented in Figure 4. In all eight spectra, the largest absorption is normalized to the same absorption value. This normalization is made to help the calculated spectra more closely resemble an experimental spectrum and is equivalent to changing the path length and concentration for each system.

Table XVI. Thermodynamic Variables Computed at the SCF and MBPT(2) Levels of Theory

	thermodynamic variables at 298 K and 1 atm of pressure				
molecule or molecular pair	zero-point energy (kcal/mol)	enthalpy[a] (kcal/mol	entropy (cal/mol K)	Gibbs free energy (kcal/mol)	heat capacity at constant V (cal/mol K)
$^3/_2(N_2 + H_2)$					
6-31G*-SCF	15.87	0.0	115.12	−34.32	14.91
DZP-SCF	15.78	0.0	115.18	−34.34	14.90
DZP-MBPT(2)	14.37	0.0	115.51	−34.44	14.91
$N_2 + NH_3$					
6-31G*-SCF	27.16	−4.37	91.55	−31.67	11.17
DZP-SCF	26.94	−10.79	91.57	−38.09	11.24
DZP-MBPT(2)	25.17	−7.15	91.85	−34.53	11.27
triazene					
6-31G*-SCF	31.93	70.26	59.58	52.50	9.44
DZP-SCF	31.74	61.97	59.64	44.19	9.56
DZP-MBPT(2)	29.40	62.89	60.03	44.99	10.07
triimide					
6-31G*-SCF	32.66	101.44	57.60	84.27	8.29
DZP-SCF	32.45	92.84	57.65	75.65	8.39
DZP-MBPT(2)	30.02	76.88	58.17	59.53	9.19
triaziridine					
6-31G*-SCF	33.04	116.14	58.56	98.68	7.55
DZP-SCF	32.90	107.81	58.55	90.36	7.57
DZP-MBPT(2)	29.90	104.15	59.07	86.54	8.55
cis-triimide					
DZP-SCF	32.16	102.28	57.66	85.09	8.74
cis-triaziridine					
6-31G*-SCF	32.53	128.46	56.44	111.63	7.68
DZP-SCF	32.47	118.72	56.43	101.90	7.69
transition state					
6-31G*-SCF	30.13	171.85	59.28	154.18	8.30

[a] Enthalpies have been adjusted so that elements in their standard states have enthalpies of zero at 298 K and 1 atm of pressure.

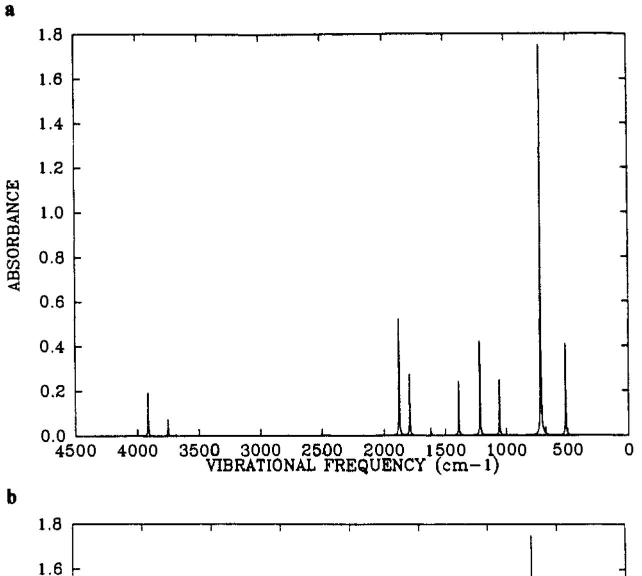

Figure 3. Spectra of triazene: (a) SCF IR and (b) E(2) IR.

In comparing the SCF-DZP infrared spectrum of triaziridine with the corresponding MBPT(2)-DZP spectrum in Figure 1, the importance of correlation is evident. Not only are the band centers shifted to lower frequencies as expected, but the relative intensities and the grouping of the peaks are different. The two spectra cannot be made to coincide by simply scaling the SCF values. In

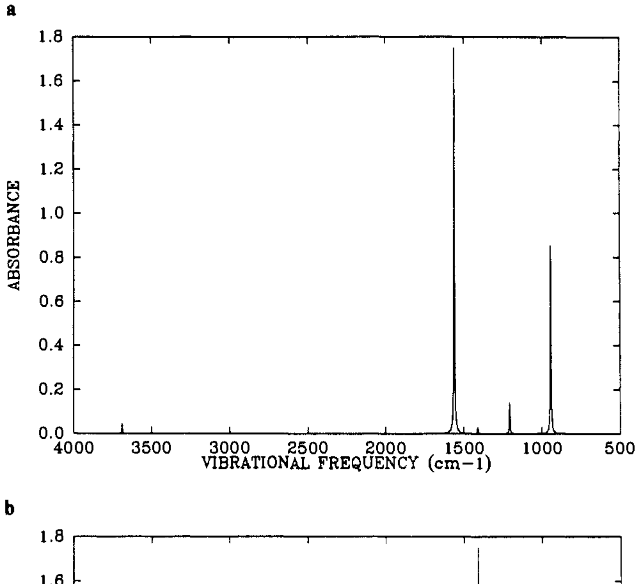

Figure 4. SCF IR spectra of (a) *cis*-triaziridine and (b) *cis*-triimide.

Figure 2, the difference in the SCF and MBPT(2) spectra of triimide is exaggerated due to the large anomalous SCF intensity of 839 km/mol. However, changes in relative peak heights may still be observed.

The two spectra of triazene in Figure 3 perhaps provide the best correspondence between the two levels of theory. At the MBPT(2) level the frequencies of the band centers are lower and the relative intensities of the stronger bands between 1000 and 2000 wavenumbers have leveled out to approximately the same peak height. Other than this, there appears to be little difference. However, recall that the order of two of the bands has shifted in the MBPT(2) results from the SCF order.

The SCF-DZP spectra for the two cis isomers are presented in Figure 4. The D_{3h} symmetry of *cis*-triaziridine causes many of the frequencies of its normal modes to be degenerate. This degeneracy is easily observed in the spectrum by the relatively few distinct band centers. As with triimide, the accuracy of the SCF spectrum for *cis*-triimide is diminished by the large anomalous intensities.

V. Conclusions

The optimum structures of triazene, triimide, and triaziridine have been determined for the 6-31G* basis set and the DZP basis set at the SCF level and for the DZP basis set at the MBPT(2) level of electron correlation. Relative electronic energies have been obtained with SDTQ-MBPT(4) and CCSD augmented by T(CCSD). The structures we have found agree with previously reported results, except that our results using polarized basis sets indicate that the structure of triazene is not exactly planar. Vibrational analyses of these structures have been carried out at all three levels of theory. We have predicted infrared spectra of the important isomers with electron correlation. The vibrational frequencies and moments of inertia have been used to compute thermochemical properties of the molecules, including the free energy.

Experimental and theoretical evidence suggests that some of these molecules can be isolated at room temperature. Low-temperature isolation of these compounds would very likely succeed. The predicted infrared spectra and thermochemical properties should aid experimental attempts to synthesize and isolate these compounds.

We feel we now have a good understanding of the relative thermodynamic stabilities of the N_3H_3 molecules, but we must do more work to understand the kinetic lability of these compounds. By using a 6-31G* basis set, we have found one SCF transition state between triaziridine and triimide. The energy barrier that this transition state represents is large enough for triaziridine to be fairly stable, but further work needs to be done with a larger basis set. In addition, this transition state deserves further attention because it appears to violate the Hammond postulate. Other transition states also need to be found to assess the kinetic stability of the various N_3H_3 isomers. Nguyen et al. claim to have found a variety of transition states on the N_3H_3 surface, but their description of the search routine leads us to believe their transition structures are not necessarily points of zero force on the surface. Interestingly, the transition state we report here is not one found by Nguyen et al. In future work we plan to make a systematic search for transition states by using large basis sets and correlation. Another goal is the computation of electronic spectra for the principal isomers using the newly developed equation-of-motion coupled-cluster excitation energy scheme.[52]

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Registry No. 1, 6572-31-2; *cis*-**1**, 108739-42-0; **6**, 15056-34-5; *cis*-**6**, 58729-78-5.

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[52] Rittby, M.; Magers, D. H.; Brown, R. E.; Bartlett, R. J., to be published.

A Protocol for Determining Enantioselective Binding of Chiral Analytes on Chiral Chromatographic Surfaces

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Abstract: A protocol for estimating binding energies of optical isomers to chiral surfaces used in chromatography is developed. The conformational states of the analyte and of the chiral stationary phase are explicitly treated. Enantioselective binding of (*S*)-(+)-2,2,2-trifluoro-1-(9-anthryl)ethanol to a chiral surface is found to be conformation dependent. Regions around the chiral stationary phase responsible for the enantiodifferentiation are located and a new chiral recognition model is presented as an alternative to a previously published model.

I. Introduction

Methods have been developed to separate optical isomers by direct resolution of enantiomeric mixtures. The most promising of these techniques utilize chromatographic separation with chiral stationary phases (CSP). While the search for suitable chiral phases has been challenging, some success has been achieved for gas, liquid, and planar chromatographies. These developments are summarized in several review articles,[1] proceedings of a

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[1] Leading references of reviews can be found in the following: Armstrong, D. W. *Anal. Chem.* **1987**, *59(2)*, 84A.