J. Am. Chem. Soc. **1996,** *118,* 227−228

Isotriazene: A Surprisingly Stable Minimum on the N_3H_3 Surface

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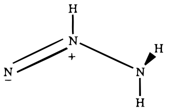
Received October 11, 1994

In the course of a reinvestigation of the N_3H_3 energy surface to find transition states and reaction intermediates, we have discovered an unusual molecule that has a hypervalent nitrogen atom and a hypovalent nitrogen atom, yet has an energy lower than some of the isomers reported in earlier investigations. Isotriazene (**1**) has been optimized at the SCF, MBPT(2), and CCSD(T) levels of theory; at each level the energy of isotriazene is lower than the energy of the triaziridines, which are ring molecules on the N_3H_3 surface.



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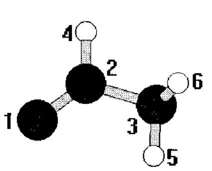
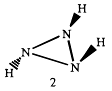


In 1984 Nguyen, Kaneti, Hoesch, and Dreiding carried out an *ab initio* investigation of the N_3H_3 energy surface at the SCF level using the split valence basis sets 3-21G and 6-31G; they found seven minima on the surface.[1] These seven minima can be divided into three subsets: the triaziridines (or cyclotriazanes), cyclic $(NH)_3$, which appear as either the *cis,trans* (*c,t*) isomer (**2**) or the less stable *c,c* isomer (**3**); the azimines or triimides, open-chain $(NH)_3$, which exist as three diastereomers, *t,t* (**4**), *c,t* (**5**), and *c,c* (**6**); and the triazenes, $HN{=}NNH_2$, which occur as either the *t* (**7**) or *c* isomer (**8**) about the N═N bond.



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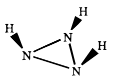

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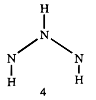

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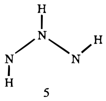

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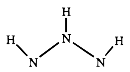

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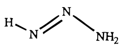

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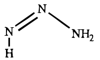

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In 1988 we reported results of investigations on five of these seven isomers at the SCF, MBPT(2), MBPT(4), and CCSD+T(CCSD) levels of theory using polarized basis sets.[2] All these investigations indicate that the triazenes are the most stable structures, followed by the triimides and then the triaziridines.

Recently we investigated the surface for transition states in an effort to sort out the reactions that convert one isomer to another. We stumbled upon the isotriazene structure and were surprised to find that its electronic energy is less than that of *c,t*-triaziridine (**2**). Isotriazene has been optimized at the SCF, MBPT(2), and CCSD(T)[3] levels of theory using the DZP basis set we used in our earlier study; at these levels a complete vibrational analysis has been carried out to be sure that the structure is a minimum on the surface. At the SCF level the optimum isotriazene structure is lower in energy than both *c,c*-triimide (**6**) and *c,t*-triaziridine (**2**). The optimum structure at the MBPT(2) level has an energy above that of *c,c*-triimide but still below that of *c,t*-triaziridine. Calculations at higher levels of theory using the MBPT(2) structures show that isotriazene is 10−12 kcal/mol lower in energy than *c,t*-triaziridine. These calculations were performed with Gaussian 92.[4]

Because isotriazene is such an unusual structure, we carried out additional tests to be sure that it is a real feature of the N_3H_3 surface: (1) A UHF/DZP optimization led to the same structure with the same energy. (2) The stability of the wave function was tested using single-excitation configuration interaction (stability test available in Gaussian 92).[5] The wave function was found to be stable with respect to perturbations from excited configurations. (3) Using Gaussian 94[6] isotriazene was optimized and vibrationally analyzed at the MBPT(2) level of theory (frozen core) using a 6-311+G (2df,2pd) basis set. The optimum structure is very close to that of MBPT(2)/DZP, and the vibrational analysis yielded frequencies and intensities consistent with those obtained using MBPT(2)/DZP. We conclude that the DZP basis set we have used extensively in our exploration of the N_3H_3 surface is adequate for isotriazene. This calculation also supports the use of MBPT(2) for our study, because correlated calculations employing triple-ζ basis sets such as this one are known to recover more correlation than smaller basis sets.[7] (4) Just as we have done previously for *t,t-triimide* (ref 2), we carried out a GVB optimization of isotriazene using the DZP basis set to assess the contribution of the lowest excited singlet configuration. Our GVB calculation yielded CI-like coefficients of 0.9837 for the ground state configuration and −0.1797 for the excited configuration, leading to orbital occupancies of 1.935 and 0.065, respectively. This result indicates that there is very little contribution from the excited singlet configuration. We conclude that a single determinant wave function is a good model for isotriazene, and our correlation calculations based on the single determinant wave function are reliable. (5) Using Gaussian 94 isotriazene has been optimized at the CCSD(T) level of theory using the DZP basis set. The structure obtained is virtually the same as that obtained using the MBPT(2)/DZP model; therefore, we conclude that there is no significant contribution from static correlation effects. These results demonstrate that isotriazene is a real molecular form of N_3H_3 and not a numerical artifact of inadequate theoretical investigation.

Table 1 contains the optimized internal coordinates of isotriazene. The amino group contains a typical pyramidal, sp^3 nitrogen atom and is rotated to a position such that one hydrogen is nearly in the N_3 plane. As a result, the other amino hydrogen is nearly perpendicular to the N_3 plane, so isotriazene has no plane of symmetry and could exist as a pair of enantiomers.

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Table 1. Optimum Geometries and Electronic Energies of Isotriazene[a]

	bond distances (Å) and bond angles (deg)		
bond or angle	SCF	MBPT(2)	CCSD(T)
N1−N2	1.1955	1.1966	1.2076
N2−N3	1.4182	1.4727	1.4863
N2−H4	1.0141	1.0457	1.0430
N3−H5	1.0042	1.0239	1.0254
N3−H6	1.0053	1.0240	1.0259
θ(N1N2N3)	126.0	127.1	126.8
θ(H4N2N1)	123.8	126.8	126.6
θ(H4N2N3)	110.0	105.9	106.4
θ(H5N3N2)	105.4	102.7	102.6
θ(H6N3N2)	107.9	105.9	105.7
θ(H5N3H6)	107.9	107.1	106.7
θ(H5N3N2N1)	8.41	−8.61	−8.50
θ(H6N3N2N1)	−106.0	−120.9	−120.1
θ(H4N3N2N1)	175.1	175.2	174.6
N1−N3 dist	2.3313	2.3930	2.4115
H4−H5 dist	2.7882	2.8205	2.8315
	2.86[b]	3.22[b]	
	−165.01469[c]	−165.54864[c]	−165.59614[c]

[a] DZP basis set. [b] Dipole moment (Debye). [c] Energy (au).

We attempted a C_s-symmetry locked optimization of isotriazene in which the amino group is rotated down to straddle the N_3 plane and away from H4. At the SCF/DZP level the C_s-symmetric structure we found is in fact a transition state: its energy is just 0.6 kcal/mol higher than that of the optimum isotriazene structure. Thus there is virtually no barrier to rotation around the N−N bond, so isotriazene can easily interconvert between its two enantiomeric forms.

The geometry of isotriazene is remarkably different from that of *t*-triazene (**7**). To promote overlap between the unshared pair of electrons on the amino group and the π-system of the N═N bond, *t*-triazene's amino group has a flat, sp^2 nitrogen atom; as a result, *t*-triazene is nearly planar.[8] In contrast, the amino group in isotriazene is pyramidal, like an aliphatic amine, and isotriazene is far from planar. This significant structural difference immediately suggests that in isotriazene there is no substantial overlap between the unshared pair and the N═N bond. This conclusion is supported by the observation that in isotriazene the N−N bond is longer and the N═N bond is shorter than the corresponding bonds in *t*-triazene. Isotriazene's N2−H4 bond is unusually long; this suggests that the bond is weakened by the formal positive charge on N2.

Isotriazene has a large charge separation across its double bond. A Mulliken population analysis on the MBPT(2)/DZP structure reveals a −0.280 charge on N1 and a +0.230 charge on N2 (charges of attached hydrogens summed into nitrogen charges). Isotriazene's dipole moment is 3.22 D (MBPT(2)/DZP), twice as large as the dipole moment of *c,t*-triaziridine (**2**), 1.49 D. The large charge separation and dipole moment indicate that isotriazene's electronic structure is less stable than *c,t*-triaziridine's, which makes the lower total energy of isotriazene surprising. Two recent *ab initio* investigations of the strain energy of small-ring molecules calculate *c,t*-triaziridine's strain energy at roughly 30−31 kcal/mol[9] (which is slightly larger than the strain energy of cyclopropane, 25−28 kcal/mol). Given isotriazene's unusual electronic structure, it would be reasonable to assume that the relative stability of isotriazene compared to triaziridine must be due to relief of steric strain.

The structure of isotriazene suggests two possible intramolecular reactions: (1) conversion to *t*-triazene (**7**) by a 1,2 hydrogen shift in which H4 moves to N1 and (2) a fragmentation to ammonia and nitrogen if H4 moves to the N3 amino group. We have located transition states on the N_3H_3 surface that we can tentatively assign to these two reactions: at the MBPT(2) level with zero-point energy correction the barrier heights for these reactions are 42 and 11 kcal/mol, respectively.

We have been unable to locate any earlier work, theoretical or experimental, on isotriazene, although Nguyen *et al.*[1] did speculate about the possibility of a "structure such as ...$H_2N{-}NH^+{=}N^-$." Nor have we uncovered a synthesis of an organic derivative of isotriazene. Organic derivatives of both *c,t*- and *c,c*-triaziridine have been synthesized and isolated,[10] and triaziridine itself has probably been synthesized inside a silver-exchanged zeolite,[11] so it is reasonable to speculate on the possibility of synthesizing derivatives of the more stable isotriazene. Substituents at N2 with appropriate electron-donating ability might be able to stabilize the charge on N2 and block the fragmentation reactions mentioned above. Aryl substituents on the amino group might be able to create overlap into the N═N bond. Either of these two effects could enhance the electronic stability of the compound, permitting synthesis and isolation. The chemistry of a substituted isotriazene, with its negatively charged and probably very nucleophilic nitrogen atom, could be exciting.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by ACS, for support of this research under ACS-PRF 28449-B4. We thank J. D. Madura, University of South Alabama Chemistry Department, and the Alabama Supercomputing Authority for making the Alabama Cray available for MBPT(2) frequency calculations and CCSD(T) optimization. Thanks also to David Magers of Mississippi College for helpful discussions and to Dan Libby and Dave Langhus of Moravian College for reviews of the literature.

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(8) Triazene is either planar or almost planar, depending on the basis set used. See the discussion in ref 2.

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