8890 *J. Phys. Chem. A* **1999,** *103,* 8890−8894

Density Functional Theory Studies of Hexamethylene Triperoxide Diamine

Andrzej Wierzbicki* and Eugene Cioffi

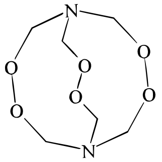
Department of Chemistry, University of South Alabama, Mobile, Alabama 36688

Received: June 21, 1999; In Final Form: September 9, 1999

Hexamethylene triperoxide diamine (HMTD) is a powerful initiating explosive belonging to the family of triperoxide energetic materials. Single-crystal X-ray studies of this compound have revealed exactly planar 3-fold coordination about the two bridgehead nitrogen atoms. We have performed density functional theory B3LYP/6-31+G(d) calculations of HMTD to study the electronic nature of this very unusual coordination and to analyze the energetics and structure of this high-energy compound. The calculated geometry of HMTD was found to agree very well with the X-ray data. The vibrational spectrum of this molecule was also calculated and favorably compared to a diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) single-crystal spectrum.

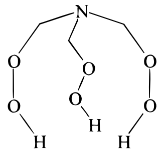
Introduction

1,6-Diaza-3,4,8,9,12,13-hexabicyclo[4.4.4]tetradecane, hexamethylene triperoxide diamine (HMTD)



is a powerful initiating explosive belonging to the family of triperoxide energetic materials. Its explosive properties have been known since 1885, when it was synthesized for the first time by Legler.[1] Although relatively sensitive to shock and more powerful than most initiating explosives, HMTD has not been of any major commercial importance, since it decomposes slowly,[2] and in the recent years this compound has been found to be of limited interest to science as well. However, when the crystallographical structure of HMTD was revealed for the first time,[2] it became evident that from an electronic structure point of view the HMTD molecule could be very interesting because of a very uncommon, exactly planar 3-fold coordination about the two bridgehead nitrogen atoms. There was some concern that the observed planar geometry about the nitrogen atoms could also result from the disorder between in and out conformations of the nitrogen atoms.[2] However, attempts to refine the entire structure with the isotropic half nitrogen atoms on either side of the carbon atom planes[2] led to a conclusion that the appropriate model most likely consists of single nitrogen atoms with carbon atoms arranged around them in a planar 3-fold conformation.

An independent way to exclude the possibility that this exactly planar conformation of nitrogen is an artifact of X-ray structure determination and/or crystal packing can be achieved using high level of theory computational studies. In this paper we present our density functional theory (DFT) studies of HMTD that have been applied to elucidate the electronic structure and geometry of this unusual molecule. We address the question "Does a planar 3-fold conformation about the nitrogen atoms represent an energetically stable form of the HMTD molecule in a vacuum, and if so, what are the reasons for this unusual geometry?" We have computed optimized structures and harmonic vibrational frequencies for the HMTD molecule using density functional theory as implemented in the Gaussian94[3] and Gaussian98[4] computational chemistry programs. The optimized geometry of HMTD very favorably compares with the X-ray geometry, and the calculated DFT harmonic vibrational frequencies very favorably compare with our single-crystal DRIFTS spectra. For comparison purposes we have also performed B3LYP/6-31G+(d) full geometry optimization and harmonic frequency calculations for [bis(hydroperoxymethyl)-amino]hydroperoxymethane, methylene trihydroperoxyamine (MTHA),



the "open cage" analogue of HMTD.

Computational Details

Density functional calculations using Gaussian 94[3] and Gaussian 98[4] were carried out on Cray C94 and SGI Octane 250 computers. In all-electron calculations we employed the Becke hybrid three-parameter DFT method[5] using the Lee, Yang, and Parr correlation functional[6] (B3LYP) and the 6-31G(d) and 6-31G+(d) polarized split valence basis sets.[7−12] The latter basis set includes diffuse functions, which are recommended for the description of lone-pair electrons. The default grid option was chosen for numerical integration of matrix elements. DFT calculations for the HMTD molecule using the 6-31+G(d) basis set involved a total of 110 electrons with 290 contracted Gaussian basis functions consisting of 496 primitive Gaussians, whereas calculations using the 6-31G(d) basis set involved a total of 110 electrons with 234 contracted Gaussians consisting of 440 primitives. For all models considered, C_1 symmetry was used throughout full optimization and subsequent frequency calculations. Analytical harmonic vibrational frequen-

---

* To whom correspondence should be addressed.

10.1021/jp992040z CCC: $18.00

TABLE 1: Comparison of Experimental and Calculated Bond Distances, Bond Angles, and Dihedral Angles for HMTD and MTHA

	HMTD					MTHA
bond or angle[a]	exptl[b]	B3LYP/6-31+G(d)	B3LYP/6-31G(d)	HF/6-31+G(d)	HF/6-31G(d)	B3LYP/6-31+G(d)
N1−C1	1.426	1.435	1.434	1.425	1.425	1.440
N2−C2′	1.417	1.435	1.434	1.425	1.425	
O1−O2	1.456	1.459	1.458	1.388	1.390	1.450
C1−O1	1.410	1.427	1.424	1.402	1.400	1.443
C2′−O2′	1.432	1.427	1.423	1.402	1.400	
C1−N1−C1′	120.00	119.94	119.89	119.94	119.89	117.72
C2−N2−C2′	119.98	119.92	119.91	119.94	119.89	
N1−C1−O1	116.62	117.85	118.27	117.11	117.41	115.60
C1−O1−O2	107.34	107.29	106.86	108.27	108.07	109.56
O1−O2−C2	105.18	107.31	106.86	108.27	108.04	102.09
O2−C2−N2	115.68	117.89	118.27	117.11	117.38	
N1−N2	3.294	3.411	3.418	3.338	3.356	
C1−O1−O2−C2(−H)	129.33	129.35	129.74	130.24	130.73	78.18
C1−H1a	0.950	1.096	1.096	1.082	1.082	1.093
C1−H1b	0.950	1.097	1.097	1.082	1.082	1.094
C2′−H2a′	0.951	1.096	1.096	1.082	1.082	
C2′−H2b′	0.950	1.097	1.097	1.082	1.082	
H1a−C1−H1b	109.49	109.84	109.60	109.65	109.46	110.75
H2a′−C2′−H2b′	109.40	109.85	109.61	109.65	109.46	
N1−C1−H1a	107.65	108.81	108.53	108.92	108.80	110.34
N1−C1−H1b	107.66	110.27	110.02	110.08	109.92	109.24
N2−C2′−H2a′	107.86	108.81	108.56	108.92	108.81	
N2−C2′−H2b′	107.82	110.24	110.02	110.08	109.94	
O1−O1′	3.585	3.612	3.596	3.537	3.526	3.184
O1−O2′	4.127	4.140	4.128	4.044	4.033	4.032
O2−O2′	3.608	3.606	3.598	3.537	3.526	3.873
N1−C1−O1−O2	−72.65	−71.03	−71.17	−70.01	−70.06	−83.50

[a] Bond lengths in Å, bond angles and dihedral angles in degrees. [b] Experimental data from ref 2.

cies were computed for all structures to confirm that local minima on the potential energy surface had been found. B3LYP/6-31+G(d) calculations on MTHA involved a total of 82 electrons with 208 contracted Gaussian basis functions consisting of 356 primitive Gaussians.

For comparison purposes a model of the HMTD molecule was constructed using the X-ray fractional coordinates and a single-point B3LYP/6-31+G(d) energy calculation was conducted with the X-ray-derived geometry. Hartree−Fock 6-31G(d) and 6-31+G(d) geometry optimizations on HMTD were also performed.

Experimental geometry was obtained from X-ray fractional coordinates using materials science modeling software Cerius^2 (version 3.8).[13] Molecular graphics were generated using the Spartan[14] (version 4.1.1) interface for Gaussian 94 and Gaussian 98.

Experimental Details

In a modification of literature procedures,[15,16] hexamethylenetetramine (35.7 mmol, 5.0 g) was dissolved in 50% aqueous hydrogen peroxide (25 mL) with stirring at <2 °C (ice/NaCl). While the temperature was maintained at <2 °C, finely powdered citric acid monohydrate (40 mmol, 8.4 g) was added in small portions over a 30 min period. Stirring was continued for an additional 5 h at <2 °C, and the mixture was allowed to slowly warm to room temperature overnight with continuous stirring. Following gentle filtration of the opaque mixture, washing with 2 × 100 mL of ice−water and 35 mL of anhydrous MeOH and drying under gentle vacuum, the product was obtained as small, nearly colorless crystals (4.6 g; 62%), mp 151−152 °C (dec) [lit. mp 144−145 °C,[15] 154 °C [16]]. ^{1}H NMR: δ 4.80 (s).

Melting points were taken with a Thomas−Hoover capillary apparatus and are uncorrected. NMR spectra were run on a JEOL GFX-400 spectrometer using $CDCl_3$ with TMS as an internal standard. Diffuse reflectance infrared Fourier transform spectroscopy single-crystal infrared spectra were run on a Nicolet Magna 550 FTIR spectrometer equipped with a NicPlan FTIR microscope, SpectraTech FTIR objective, and a SpectraTech HATR attachment. DRIFTS resolution was set at 1 cm^{-1}, with 2048 spectra acquired; standard postacquisition processing employed Kubelka−Munk conversion. The DRIFTS spectrum was acquired using a single crystal of HMTD of approximately 1.0 mm × 0.2 mm × 0.2 mm dimensions in less than 6 min.

Results and Discussion

The structural parameters of HMTD and MTHA as determined by the Gaussian 94 and Gaussian 98 implementations of the B3LYP and HF models are summarized in Table 1. Experimental bond lengths, bond angles, and dihedrals were obtained from the fractional coordinates, as determined by the X-ray analysis.[2] An excellent agreement in the overall structure of DFT-calculated HMTD molecular structure has been achieved when compared to the experimental data, as seen in Table 1. In particular, a very unusual, planar geometry on the nitrogen atoms was successfully reproduced in the B3LYP/6-31+G(d) calculations (Figure 1). The calculated C−N−C angle is equal to 119.93°, versus the experimental 119.99° (Figure 1). It is necessary to mention here that while comparing the structural data, one should observe that the experimental structure of HMTD shows a small asymmetry between its lower (atomic indices 1) and upper (atomic indices 2) parts. This unexpected asymmetry also shows in our calculated structure of HMTD, but it is only minor (Table 1). The symmetry breaking observed in the experimental data is responsible for shortening of some bonds and decreasing angle values. For example, the experimental N1−C1 bond length is 1.426 Å, but N2−C2′ is 1.417 Å; the C1−O1 bond value is 1.410 Å, whereas C2′−O2′ is 1.432 Å; the C1−O1−O2 bond angle is equal to 107.34°, while O1−

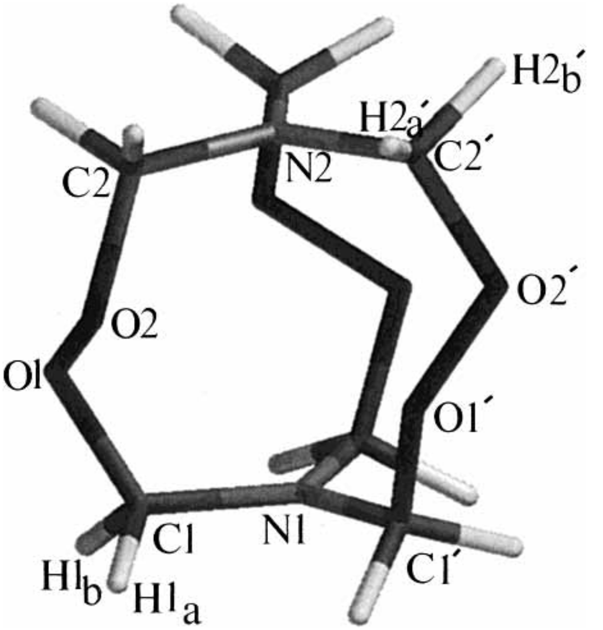


Figure 1. HMTD geometry and atom labeling.

O2−C2 is 105.18°. This asymmetry is also responsible for a relatively large difference between the experimental N1−N2 distance, which is 3.294 Å, and the calculated value of 3.411 Å. This symmetry breaking also contributes substantially to the differences in the dipole moments calculated for these structures. The B3LYP/6-31+G(d) calculated dipole moment for the "distorted" experimental geometry is 0.176 D, whereas the B3LYP/6-31+G(d) optimized structure has a negligible dipole moment of only 0.010 D. Overall, our DFT calculations show a very good agreement between the B3LYP/6-31+G(d) optimized geometry and the experimental one. The calculated bond lengths are slightly longer, which is expected for the B3LYP/6-31+G(d) calculations.[17] Bond angles and dihedral angles are also remarkably well reproduced (Table 1). Table 1 also shows a very good agreement between the B3LYP/6-31+G(d) and B3LYP/6-31G(d) calculations, indicating that the diffuse functions provide only a small refinement to the optimized geometry. Comparison of DFT and HF results clearly indicates that the Hartree−Fock level is sufficient for the general structural determination of this lone-pair-rich molecule, with the exception of oxygen−oxygen interaction distances. This is especially evident in the O1−O2 bond length, which is poorly reproduced at the HF level. A good agreement between the HF/6-31+G(d) and HF/6-31G(d) calculations (Table 1) shows that the inadequacy of the HF calculations lies not in the basis character but rather reflects its fundamental lack of correlation effects. It is interesting to note that the HF/6-31+G(d) calculations reproduce relatively well the planar 3-fold conformation about the nitrogen atoms; the C1−N1−C1′ angle is 119.94°.

There were two major hypotheses put forward to explain the unusual planar 3-fold conformation about the nitrogen atoms in HMTD.[2] One of them seeks the explanation in electronic effects, another in steric effects. The discussion of both effects was based on the comparison with the carbon analogues and did not decisively give credit to either one. First, to assess the steric effect, we compared the HMTD structure to the structure of MTHA, which also has both a methylamine part and three peroxide bonds, but its cage is open on one end. Since, to our knowledge, no experimental data are available, for the purpose of discussion we have to rely on the B3LYP/6-31+G(d) calculated structure, which we will assume to be adequate, bearing in mind an excellent agreement between the calculated and experimental data for HMTD as seen in Table 1. In MTHA the calculated conformation about the nitrogen atom represents an *out* conformation, and as one can see from Table 1, the C1−

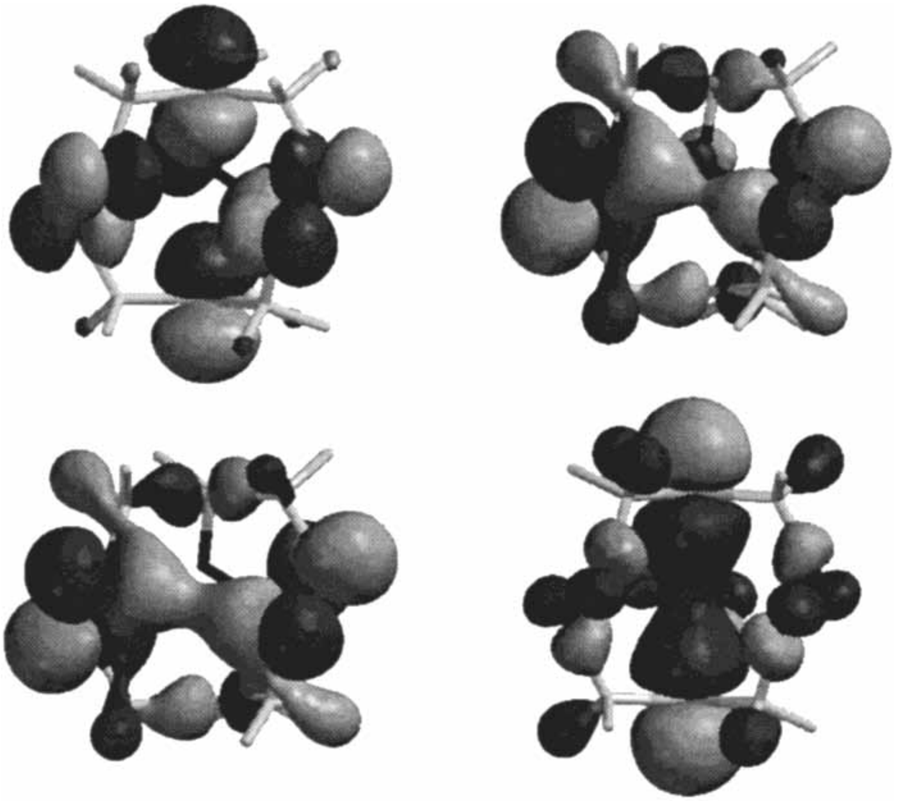


Figure 2. (a, b) Top row showing HOMO and HOMO-1 orbitals of HMTD, left and right, respectively. (c, d) Bottom row showing HOMO-2 and HOMO-3 orbitals of HMTD, left and right, respectively.

N1−C1′ bond value is 117.72°. When the HMTD and MTHA structures are compared (Table 1), one can see that the nonbonded O1−O1′ distance in HMTD (3.612 Å) is much larger than in MTHA (3.184 Å), and conversely, the nonbonded O2−O2′ distance in MTHA (3.873 Å) is greater than that in HMTD (3.606 Å). To close the cage, while starting from the MTHA structure, one must move the O1−O1′ oxygens much further apart while bringing the O2−O2′ oxygens a little bit closer. We argue that this transformation will result in bringing the nitrogen from an *out-of-plane* (MTHA) toward an *in-plane* position (HMTD) by creating a strain on the nitrogen conformation via the N1−C1−O1 angle. In other words to close the cage, one needs to rearrange the oxygen distances by modifying the "soft" bond angles and dihedrals (involving the peroxide bonds), which in turn "pull" the nitrogens inward via the relatively hard to compromise angles on the carbons. One should realize that lowering the nitrogen atom through the plane is also an energetically "soft" mode, requiring relatively little energy; the inversion barrier for nitrogen for most tertiary amines does not exceed 6 kcal/mol, for example.[18] We can see the evidence of this effect by inspecting the calculated N1−C1−O1 angles of both of these molecules. Namely, the N1−C1−O1 angle in MTHA (115.60°) is much closer to the "natural" N−C−C angle in most organic compounds (114.1°); the N1−C1−O1 angle for HMTD (117.85°) is obviously strained.

Another argument in favor of the steric versus electronic hypotheses is that the planar conformation could be easily obtained at a relatively low level of theory. For example, as seen in Table 1, even the HF/6-31G(d) model gives for the C1−N1−C1′ angle a very close to planarity value of 119.89°. The nitrogen−nitrogen and oxygen−oxygen repulsions given as an argument in support of an electronic explanation of the flat conformation on nitrogen atoms[2] do not seem to be valid, since nitrogen−nitrogen repulsion in HMTD would even further pucker the *out* conformation seen in MTHA. Furthermore, if the oxygen−oxygen repulsion were crucial, the calculated "unconstrained" O1−O1′ nonbonded distance in MTHA would be far greater than the value shown in Table 1. In fact the distance is much less in MTHA than in HMTD (Table 1).

To address the electronic structure impact on the molecular shape of HMTD, we have calculated and plotted several molecular orbitals. Figure 2a shows the highest occupied molecular orbital (HOMO) of HMTD. As can be seen from this figure, this is a predominantly antibonding orbital. For example, a positive lobe on the N1 atom points toward a negative lobe on N2. Figure 2b shows the HOMO-1 orbital in HMTD. We believe that this figure, together with the complementary Figure 2c of HOMO-2, is the key to the explanation of the nitrogen geometry in the HMTD molecule. In these figures one can see large, diagonal orbitals extending from O1 on one peroxide bridge to O2′ on another, additionally extending over the adjacent hydrogen atoms. The presence of these bonding orbitals helps to stabilize the cage geometry of HMTD. By allowing for the delocalization of electrons within these orbitals, the oxygen lone pair repulsion is decreased, compensating for the energy loss in changing from sp^3 to sp^2 hybridization at the nitrogen atoms. We see no evidence that MTHA has molecular orbitals extending between nonbonded oxygen pairs. The cage formation affords this overlap, which is highly directional and cannot be facilitated in MTHA. In Figure 2d one can see that the HOMO-3 orbital of HMTD represents a very interesting bonding orbital between the N1 and N2 nitrogen atoms extending over a 3.4 Å distance. One should consider the HOMO-3 with the HOMO orbital; together they most likely represent a net repulsive interaction between the nitrogen atoms. Our crude estimation involving comparisons between appropriate orbital energies of HMTD and MTHA gave a slightly positive energy (about 0.007 hartree) contribution.[19]

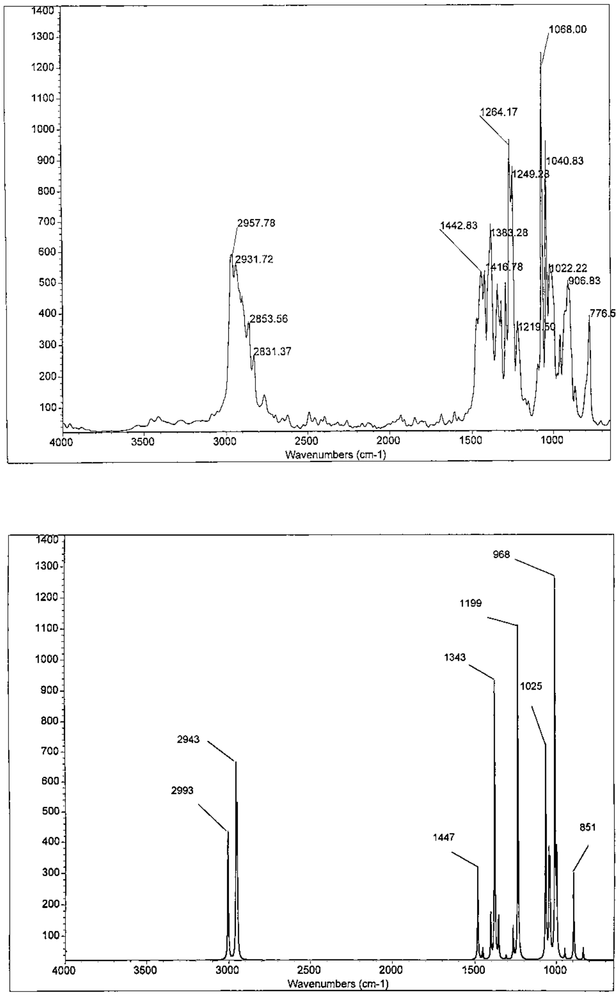


Figure 3. Single-crystal DRIFTS spectrum of HMTD (top) and simulated infrared gas-phase spectrum of HMTD (bottom). Calculated intensities were normalized to the maximum intensity of the experimental spectrum, and the calculated vibrational frequencies were scaled by a factor of 0.9613.[17] The simulated spectrum (bottom) was obtained by using a sum of Lorenzian line functions with the half-width set to 2.5 cm^{-1}.

In the past there was some controversy regarding the physical meaning of the Kohn−Sham (DFT) orbitals. Although it has been accepted that they are a good approximation to the Hartree−Fock orbitals, only recently has it been established[20] that the Kohn−Sham orbitals could be even more suitable in the qualitative molecular orbital theory than either Hartree−Fock or semiempirical orbitals.

Frequency calculations yielded all positive frequencies, indicating that a stationary point has been found during the optimization. Calculated fundamental frequencies and infrared intensities were used to generate the infrared gas-phase spectrum of HTMD that very favorably compares with the experimental,[21] high-resolution single-crystal IR spectrum of HMTD (Figure 3).

Conclusions

In this paper we have performed density functional theory B3LYP/6-31+G(d) studies of HMTD in order to elucidate the unique, exactly planar, sp^2 hybridization at the two bridgehead nitrogen atoms, each bonded to the three CH_2 groups. Using the methods of computational chemistry, we have designed and studied MTHA, an open cage analogue, to explain the geometry of HMTD. Earlier attempts to explain the structure of HMTD on the basis of comparisons with carbon analogues[2] failed to provide insight into the formation of its unique features obviously because of the essential differences in electronic properties between these two systems. We have postulated that the formation of bonding orbitals, and thus charge delocalization between the adjacent peroxide bonds leading to decreased repulsion between lone electron pairs on oxygen atoms, may compensate the energy loss due to the sp^3 to sp^2 hybridization change on the nitrogen atoms.

The calculated geometry of HMTD was found to agree very well with the X-ray data. The vibrational spectrum of this molecule was also calculated and favorably compared to the diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) single-crystal spectrum.

Acknowledgment. We thank the Alabama Supercomputer Authority and Nichols Corporations for providing computer time on Cray C94. We also thank Dr. E. Alan Salter for his assistance in computational data collection and for numerous discussions related to the subject of this paper.

References and Notes

(1) Legler, L. *Ber. Dtsch. Chem. Ges.* **1885**, *18*, 3343.

(2) Schaefer, W. P.; Fourkas, J.; Tiemann, T. B. J. *J. Am. Chem. Soc.* **1985**, *107*, 2461.

(3) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94*, revision E.3; Gaussian Inc.: Pittsburgh, PA, 1995.

(4) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.6; Gaussian Inc.: Pittsburgh, PA, 1998.

(5) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(6) Parr, T. G.; Yang, W. *Density-Functional Theory of Atoms and Molecules*; Oxford University Press: New York, 1989.

(7) Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1971**, *54*, 724.

(8) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257.

(9) Hariharan, P. C.; Pople, J. A. *Mol. Phys.* **1974**, *27*, 209.

(10) Gordon, M. S. *Chem. Phys. Lett.* **1980**, *76*, 163.

(11) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213.

(12) Clark, T.; Chandrasekhar, J.; Spitznagel, G. W.; Schleyer, P. v. R. *J. Comput. Chem*. **1983**, *4*, 294.

(13) *Cerius²*, version 3.5; Molecular Simulations Inc.: San Diego, CA, 1997.

(14) *Spartan*, version 4.1.1; Wavefunction Inc.: Irvine, CA, 1996.

(15) Sülzle, D.; Klaeboe, P. *Acta Chem. Scand*. **1988**, *42*, 165.

(16) Vennerstrom, J. L. *J. Med. Chem*. **1989**, *32*, 64.

(17) Foresman, J. B.; Frisch, A. *Exploring Chemistry with Electronic Structure Methods*, 2nd ed.; Gaussian, Inc.: Pittsburgh, PA, 1996.

(18) Solomons, T. W. G. *Organic Chemistry*, 6th ed.; John Wiley and Sons: New York, 1996; p903.

(19) To estimate the energy of nitrogen−nitrogen lone pair interaction in HMTD, we have used the following approximation: $\Delta E = 2E^{\mathrm{HMTD}}(\mathrm{HOMO}) + 2E^{\mathrm{HMTD}}(\mathrm{HOMO\text{-}3}) - 4E^{\mathrm{MTHA}}(\mathrm{HOMO}) = 0.0068$ hartree.

(20) Baerends, E. J.; Gritsenko, O. V. *J. Phys. Chem. A* **1997**, *101*, 5383.

(21) Calculated frequencies were scaled by the factor of 0.9613 (see ref 17).