

Structural Isomers and Excited States of HN₃

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Multiconfigurational wavefunctions were adopted to study structural isomers, their isomerization reactions and excited states of HN₃. In addition to the known linear isomer, two new structural isomers were found. The three isomers can be classified as *sp*, *sp*² and *sp*³ hybridized species, respectively. The *sp*³ hybridized species turned out to be the second most stable. Large reaction barriers among these species prevent thermal isomerizations. A low-lying ³A' exists with a relative energy of 13.5 kcal/mol. Dramatic re-hybridization and bond elongation was found in the first excited ¹A''.

Key Words : NH₃ isomers, Excited state, Multi-configuration, Silicon surface

Introduction

The molecular properties of HN₃ have attracted a great deal of attentions. The basic properties such as conformational isomers and vibrational frequencies of ground state HN₃ were studied with MP2¹ and DFT² theories. As an isoelectronic compound of HNCO, the photodissociation and the corresponding excited states of HN₃ have been also studied extensively.^{3,4} On the other hand, among alternative nitrogen sources, hydrazoic acid (HN₃) has been considered as the most efficient compound in the preparation of thin film.⁵ The nitridation of silicon surfaces for insulating and passivating layers is an important process in the semiconductor industry. Although nitrogen gas and ammonia are convenient sources for the formation of silicon nitride, they require high temperature environments. The adsorptions and thermal decompositions of HN₃ with various surfaces such as Si(100)-2x1,⁶ Ge(100)-2x1,⁷ etc. have been studied.

However, in spite of the previous studies, the basic molecular properties of HN₃ are not sufficiently understood. In the current paper, the low energy structural isomers as well as the low-lying excited states of HN₃ were investigated with the help of multiconfigurational wavefunctions.

Computational Details

Dunning's triple zeta quality basis sets augmented with polarization functions and diffuse functions on both heavy and hydrogen atoms were adopted throughout this study, which are collectively denoted as TZV++(d,p).⁸ The Hessian matrix (matrix of energy second derivatives) was computed and diagonalized for all stationary points to characterize them. Intrinsic reaction coordinate (IRC) calculations were conducted to verify that each saddle point connects the two minima of interest.

In order to consistently describe entire potential energy surface, CASSCF (complete active space self-consistent field)⁹ wavefunction was used throughout this study. Active

space is composed of the full valence space of HN₃ molecule (13 orbitals and 16 electrons). Alexander *et al.*¹⁰ have used an active space of 16 valence electrons with 11 orbitals. Although the terminal N-N σ orbital is doubly occupied with a very low orbital energy, it is included in the current active space. To recover the dynamic electron correlation, single-point energy calculations with MRMP2(16,13)/TZV++(d,p) (multireference second order perturbation theory) method¹¹ were performed at the CASSCF(16,13) optimized geometries. All calculations were performed with GAMESS (general atomic and molecular electronic structure system).¹²

Results and Discussion

Structural Isomers of HN₃. Full geometry optimizations with CASSCF(16,13)/TZV++(d,p) yielded three structural isomers, which are presented in Figure 1 along with the MRMP2 relative energies. Among these, the global minimum **I1** is well known as a planar molecule belonging to C_s point group. The calculated bond lengths of H-N₁, N₁-N₂, N₂-N₃ are in good agreements with Microwave data¹³ (1.015, 1.243 and 1.134 Å, respectively). The calculated angles of H-N₁-N₂ and N₁-N₂-N₃ are also in good agreements with the experimental values of 108.8 and 171.3°, respectively. The nearly linear configuration of N₁-N₂-N₃ indicates that the N₂ is *sp* hybridized.

The isomer **I2** and **I3** are new species which have not been reported before. **I2** turned out to be the least stable species with a relative energy of 78.1 kcal/mol as compared to the most stable **I1**. Since the N₁-N₂ bond length of **I2** is in between the corresponding **I1** and **I3**, the central nitrogen N₂ can be better considered to be *sp*² hybridization. Due to the geometric constraints, unusually long N₁-N₃ bond length of 2.01 Å exists. The corresponding bonding and antibonding orbitals of N₁-N₃ are presented in Figure 2(a) and 2(b) along with NOON(Natural orbital Occupation Numbers) values. Although a large radical character exists, they clearly indicate that a s bond exists between N₁ and N₃.

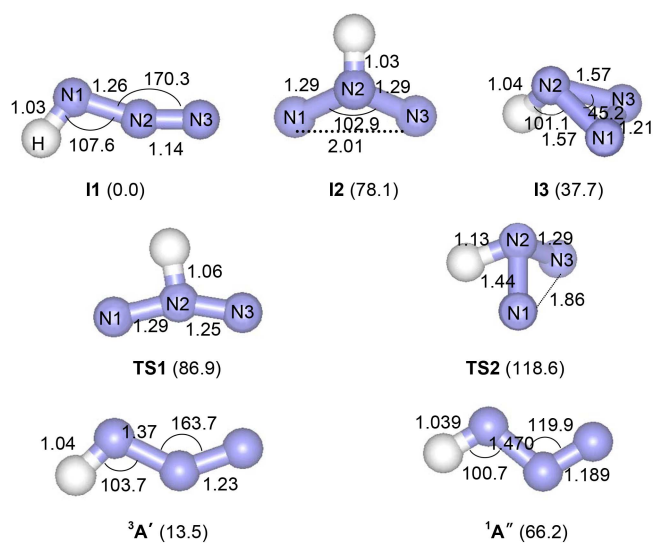


Figure 1. Optimized geometries of the three isomers, isomerization transition states, and excited states of HN_3 as obtained with CASSCF(16,13) TZV++(d,p). MRMP2 Energies are in kcal/mol. The distances and the angles are in angstroms and in degrees, respectively.

The C_s isomer **I3** is calculated to be the second most stable species with a relative energy of 37.7 kcal/mol. Unlike **I2**, **I3** has a clear pyramidal configuration implying sp^3 hybridization of the center N2. As a result, N2-N1 and N2-N3 bonds become a single bonds elongated by 0.28 Å as compared to those of **I2**. At the same time, N1-N3 bond distance significantly reduced by 0.8 Å, implying an increase of bond order. In fact, the natural orbitals as shown in Figure 2(c-f) clearly show that the N1-N3 bond of **I3** is composed of a strong s and a p bond with very little contributions of anti-bonding characters. Therefore, even though isomer **I2**

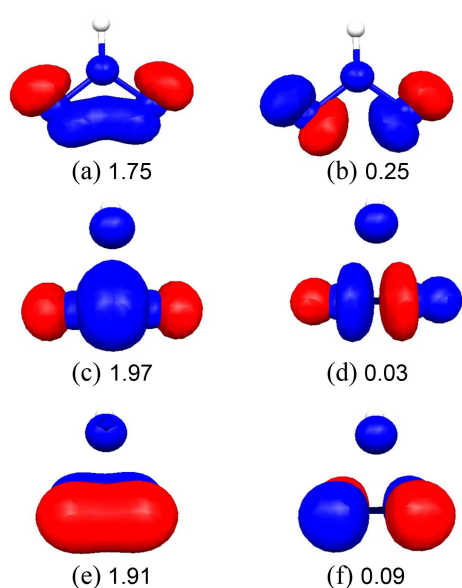


Figure 2. Selected Natural Orbitals of **I2** (a, b) and **I3** (c,d,e,f) along with Natural Orbital Occupation Numbers (NOON). The NOON represents the orbital occupation numbers.

and **I3** appear to have similar triangular N-N-N ring, their chemical bonding configurations are different. In short, the three structural isomers of **I1**, **I2** and **I3** can be identified as sp , sp^2 and sp^3 species, respectively.

Isomerization Processes. Potential energy surfaces of isomerization reactions among the predicted three isomers were explored and the resulted minima and transition state are presented in Figure 1. A planar transition state **TS1** in which the hydrogen is migrating from N1 to N2, connects the isomer **I1** and the isomer **I2** with a barrier height of 86.9 kcal/mol. Hydrogen migration is necessary to change hybridization of the center N2 from sp to sp^2 . Another transition state **TS2** connects **I2** and **I3** with an overall barrier height of 118.6 kcal/mol. The N2-N1 bond is longer than the N2-N3 in **TS2** by 0.15 Å indicating an asymmetric transition state. Since the backward reaction from **I3** to **I2** also experiences a large barrier, **I3** can be considered as a kinetically stable species. A direct isomerization path connecting **I1** and **I3** was not found. Large barriers among the possible isomers make thermal isomerizations difficult to occur. Since **I3** is both thermodynamically and kinetically stable, it has a good chance to exist. Experimental observations are highly expected.

Low-lying Excited States. Full geometry optimizations on the excited singlet and the triplet states of HN_3 were performed with the CASSCF(16,13)/TZV++(d,p) and the results are presented in Figure 1 along with the MRMP2 energies. A low-lying triplet state $^3\text{A}'$ with a relative adiabatic energy of 13.5 kcal/mol exists, while a low-lying $^3\text{A}''$ turned out to be repulsive and no minimum geometry was found. The N1-N2 and N2-N3 bond lengths of $^3\text{A}'$ are increased by about 0.11 and 0.09 Å as compared to those of ground state, respectively. The elongation of these bonds is due to the $\pi \rightarrow \pi^*$ transitions of out-of-plane nitrogen π electrons (See Fig. 3(a) and 3(b)).

More significant geometrical changes occur in the first excited $^1\text{A}''$ state. Unlike the ground electronic state geometry, the N1-N2-N3 angle becomes close to 120° , and the N1-N2 and N2-N3 bond lengths are increased by about 0.21 and 0.05 Å, respectively. Natural orbital analysis shows that it is mostly due to the out of plane π orbital (3d) and the

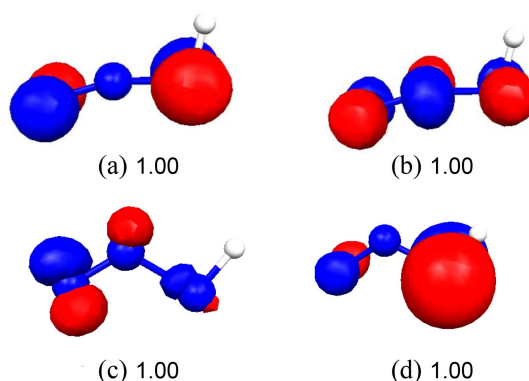


Figure 3. Selected Natural Orbitals of $^3\text{A}'$ (a, b) and $^1\text{A}''$ (c,d) along with Natural Orbital Occupation Numbers (NOON). The NOON represents the orbital occupation numbers.

in plane π^* orbital (3c). From the viewpoint of valence bond theory, one electron excitation from S₀ to S₁ accompanies a re-hybridization of the middle N atom from *sp* to *sp*², resulting a significant N1-N2-N3 bond angle change. Especially the N1-N2 bond is largely elongated in the ¹A'' state. In fact, the photodissociation study of HN₃ in its first excited singlet state reported that the breakage of this N1-N2 bond is the dominant fragmentation channel.⁴

Conclusions

Multiconfigurational wavefunctions were adopted to study possible structural isomers, their isomerization reactions and excited states of HN₃. Two new structural isomers (**I2** and **I3**) were found, of which isomer **I3** turned out to be thermodynamically and kinetically stable. **I1**, **I2** and **I3** can be identified as *sp*, *sp*² and *sp*³ hybridized species, respectively. The isomerization reactions among the possible isomers may not be feasible due to the large reaction barriers.

A low-lying ³A' exists with a relative energy of 13.5 kcal/mol. In contrast, ³A'' turned out to be repulsive and no minimum geometry was found. Dramatic re-hybridization and bond elongation occur in the first excited ¹A'', which has been recognized as the dominant photodissociation channel.

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