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An Ab Initio Study of Potential Energy Surfaces for N_8 Isomers

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The potential energy surfaces and the nature of transition structures for the decomposition of three N_8 isomers (octaazapentalene, azidopentazole, and diazidodiimide) into 4 N_2 are investigated using ab initio methods. These isomers are all high-energy species, relative to molecular nitrogen, but are much lower in energy than the previously studied cubic structure. Second-order perturbation theory (MP2) predicts that the dissociation of octaazapentalene proceeds via isomerization to a linear molecule. The dissociation reaction of azidopentazole prefers ring breaking, at a cost of less than 20 kcal/mol, to breaking a bond in the side chain. The cis isomer of diazidodiimide is found to be slightly more stable than that of the trans isomer at the highest levels of theory used here. The coupled cluster (CCSD(T)) diazidodiimide dissociation barrier is computed to be about 20 kcal/mol. This barrier is only marginally sufficient to make this high energy density molecule metastable.

Introduction

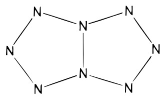
The study of high energy density materials (HEDM) [1,2] has been an important goal for the possible design of new fuels. In particular, several authors have proposed polynitrogen (N_x) compounds[1−14] as potential propellants, using a variety of computational methods. However, there are only a small number of experimentally known polynitrogen systems. Indeed, for many years, the only known pure nitrogen species were N_2 and N_3^-. Recently, a very exciting discovery, the experimental isolation of N_5^+ cation in a salt form, was reported.[10] This experiment suggests that a possible route to N_8 compounds may be the combination of N_5^+ and N_3^- species.

Most of the previous calculations on polynitrogen compounds have focused on the highly strained species tetrahedral N_4 [2−5] and cubic N_8[5−9] because their decomposition reactions into multiple N_2 molecules are expected to be highly exothermic. They are therefore candidates to be high-energy fuels. However, in order for such species to be viable as new fuels, the energy barriers that prevent their decomposition, isomerization, or bimolecular destruction must be sufficiently high to provide stability under the conditions in which fuels would normally be stored. It is therefore desirable to have all such barriers more than 20, and preferably more than 30, kcal/mol. Therefore, one should examine all possible dissociation routes for any new fuel candidates.

Generally, the study of potential energy surfaces of high-energy species is expected to be more complex than those of simpler compounds. The fact that they are, by definition, metastable suggests that low-lying electronic states can approach or cross the ground state. An important example is tetrahedral N_4. Although this species appears to have a large (> 50 kcal/mol) activation energy for decomposition on its adiabatic ground-state potential energy surface, Yarkony[3] has shown that a crossing with the repulsive first triplet state lowers the barrier to just over 30 kcal/mol via spin−orbit coupling. This makes N_4 a less viable high-energy species than originally thought, despite its high adiabatic barrier caused by a symmetry forbidden least motion decomposition.

Cubic N_8 is an isoeletronic analogue to the highly strained hydrocarbon cubane (C_8H_8).[15,16] Even though it is experimentally unknown, the least motion unimolecular decomposition of cubic N_8, like its hydrocarbon analogue, is symmetry forbidden and therefore expected to have a large barrier. Thus, it has been the subject of several theoretical studies to investigate its structure and dissociation mechanisms.[5−9] However, recent studies have shown that nonleast motion pathways reduce the calculated barrier to less than 20 kcal/mol.[8,9] This is insufficient to make this material metastable in a practical sense.

On the basis of theoretical studies, several possible isomers of the N_8 system have been reported.[7−9,14] In particular, the previous work by Nguyen and Ha,[14] Gagliardi et al.,[8b] and this laboratory [9] noted that three of these isomers, octaazapentalene (**1**, two fused aromatic five-membered rings), azidopentazole (**2**, a five-membered ring with an azide side chain), and diazidodiimide (**3**, linear structure: N3−N═N−N3) appear to be much lower in energy than cubic N_8 but are still much higher in energy than four N_2 molecules. Very recently, Gagliardi and co-workers examined the dissociation of **2** and the isomerization of **1** → **2**,[8b] using multireference second-order perturbation theory. In the present study, the potential energy surfaces and the dissociation mechanisms for all three of these N_8 isomers are investigated using ab initio methods.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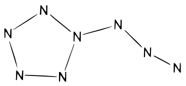
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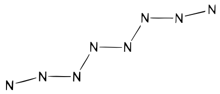
3a

Computational Methods

All minima and transition states were obtained using second-order perturbation theory (MP2)[17,18] with the 6-31G* basis set. The MP2/6-31G* Hessians (matrices of energy second derivatives) were calculated in order to verify whether the stationary points are local minima or saddle points. Minimum energy pathways connecting the reactants and products were confirmed using the intrinsic reaction coordinate (IRC) method with the Gonzalez−Schlegel second-order algorithm.[19] Triplet surfaces

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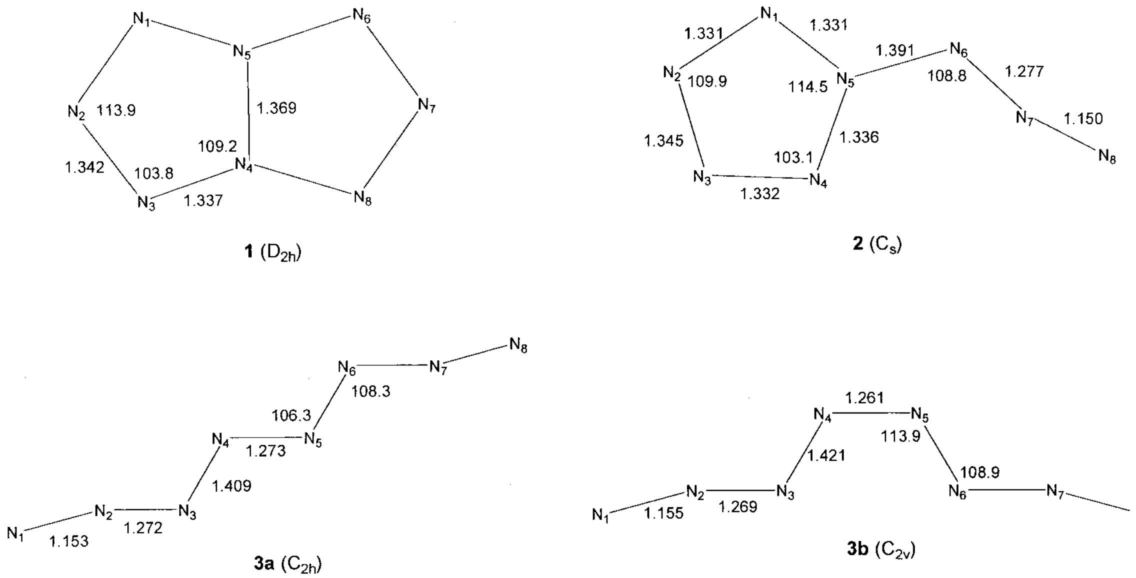


1 (D_{2h})

2 (C_s)

3a (C_{2h})

3b (C_{2v})

Figure 1. MP2 Optimized Molecular Structures for Three N_8 Isomers.

TABLE 1. Energy Difference (kcal/mol) among N_8 Isomers.

calculational level	1	2	3a	3b	cubic[c]
MP2/6-31G*[a]	14.7	0.0	17.5	14.6	245.3
CCSD(T)/6-311G*[b]	17.2	0.0	15.0	13.8	224.4
ΔH [b,d]	−247.4	−230.2	−245.2	−244.0	−454.6

[a] Includes zero point vibrational energy. [b] CCSD(T)/6-311G*//MP2/6-31G* level. [c] N_8 isomer with cubic structure. [d] Exothermicity for $N_8 \rightarrow 4N_2$ reaction

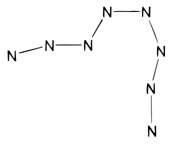
were considered with restricted open-shell MP2 single-point energy calculations [20,21] at the singlet geometries. To achieve more reliable energetics, CCSD(T) [22] single-point energy corrections were obtained with the 6-311G* basis set. All of the RHF and MP2 calculations in this study were performed using the GAMESS electronic structure program.[23] The Gaussian94 program[24] was used for the CCSD(T) calculations.

Results and Discussion

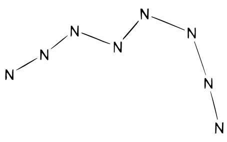
Minimum Energy Structures. The present study is focused on the N_2 dissociation mechanism and the nature of the potential energy surfaces of the three N_8 isomers **1**, **2**, and **3**. These structures are examined in the context of the nature of the transition structures on the potential energy surfaces that connect the three isomers with molecular nitrogen. The cis−trans isomerization of diazidodiimide (**3**) is also considered. The molecular structures for the N_8 isomers are illustrated in Figure 1, along with their computed MP2/6-31G* geometrical parameters. The relative energy differences of the three N_8 isomers are summarized in Table 1, along with CCSD(T) exothermicities for the dissociation reaction of N_8 isomers. The data for cubic N_8 is also included in this table for comparison. Both levels of theory, MP2/6-31G* and CCSD(T)/6-311G*, predict that **2** is the most stable isomer. CCSD(T) energies of the three N_8 isomers considered in the present study lie more than 230 kcal/mol below the cubic N_8 molecule. The CCSD(T) exothermicity for dissociation of cubic N_8 into 4 N_2 is estimated to be 454.6 kcal/mol. This means that the energies of the three N_8 isomers lie about halfway between cubic N_8 and 4 N_2 molecules.

Structure **1** is reminiscent of the structure of naphthalene, in that the two distinct ring bonds have similar lengths, whereas the bridge bond is somewhat longer than the other two. This reflects the delocalization of the 10 π electrons, yielding a nearly aromatic species. The CCSD(T) energy of **1** lies about 17 kcal/mol above **2**. The MP2 geometry for **2** has C_s symmetry, with the $-N_3$ chain lying in the same plane as the N_5 ring. The bond lengths in the N_5 ring in this isomer are also nearly equal, whereas the bond linking the ring with the N_3 chain is somewhat longer. The two bonds in the N_3 chain are shorter than the bonds in the ring, as is typical for an azide. The Mayer bond order [25] for the N7−N8 bond is 2.4, whereas that for the N6−N7 bond is 1.3.

Linear (open-chain) N_8 has two rotational isomers (trans: **3a**, cis: **3b**), shown in Figure 1. The cis isomer is 2.9 kcal/mol more stable than that of the trans at the MP2/6-31G* level. CCSD(T)/6-311G* reduces this energy difference to 1.2 kcal/mol. This is consistent with the preference of FN=NF for cis rather than trans.[26] In that system, the isomerization occurs via an inversion mechanism, and it is likely that this is also the case here, because rotation about the NN double bond requires considerably more energy.[27] Two additional rotamers can exist, corresponding to rotation of the $-N_3$ group in both cis and trans isomers. This would lead to structures **3c** and **3d**:



3c



3d

Hessian calculations confirm that these two rotamers are also local minima on the potential energy surface. The CCSD(T)/6-311G* energy of **3c** is 8.2 kcal/mol above the that of the cis (**3a**) isomer, whereas **3d** is 4.1 kcal/mol above that of the cis isomer.

Transition Structures and Reaction Barriers for Decomposition Reaction. The N_8 isomers of interest might dissociate either by direct elimination of one or more N_2 molecules, or via an intermediate N_8 structure (another isomer). Figure 2 illustrates several MP2 transition structures and their geometrical parameters. The energy differences between the minima (**1**, **2**, **3a**, and **3b**) and the corresponding transition structures are summarized in Table 2.

The MP2/6-31G* saddle point searches were unable to find a transition state corresponding to direct N_2 elimination from

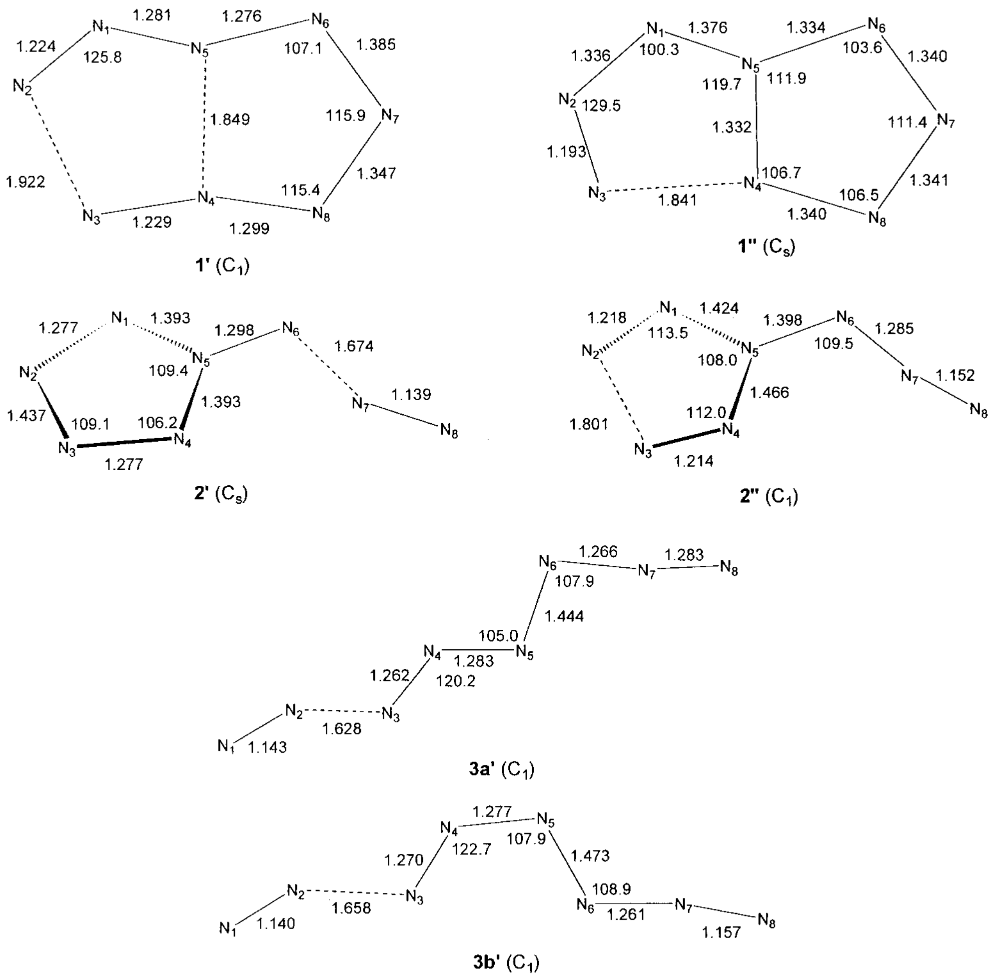


Figure 2. Transition Structures for N_2 Dissociation and Isomerization of N_8 Isomers.

TABLE 2. Energy Difference (kcal/mol) between N_8 Isomer and Transition States.

	1		2		3a	3b
calculational level	**1′**	**1″**	**2′**	**2″**	**3a′**	**3b′**
MP2/6-31G*[a]	32.2	19.8	21.7	12.8	27.2	24.9
CCSD(T)/6-311G*[b]	49.7	13.0	13.7	12.7	21.9	19.1

[a] Includes zero point vibrational energy. [b] CCSD(T)/6-311G*//MP2/6-31G* level.

1. This suggests that the dissociation of **1** proceeds via an isomerization. Indeed, two transition states (**1′** and **1″**) have been found that connect **1** to other isomers on the MP2 potential energy surface. Clearly, structure **1′** leads to the acyclic structure **3c**, whereas **1″** connects **1** and **2** (see Figure 1). The MP2/6-31G* energies of **1′** and **1″** are 32.2 and 19.8 kcal/mol higher than that of **1**, respectively, including zero-point vibrational corrections. The CCSD(T)/6-311G* values for these energies are 49.7 and 13.0 kcal/mol, respectively.

As can be seen in Figure 2, two bonds (N2−N3 and N4−N5) in **1′** lengthen to form the acyclic N_8 molecule, whereas the adjacent bonds (N1−N2, N1−N5, and N3−N4) shorten as the electron density is redistributed. The N3−N4 bond length in **1″** increases by about 0.5 Å from **1**, on the way to forming **2**, whereas the N2−N3 bond length decreases by about 0.15 Å.

One can imagine three possible dissociation mechanisms for **2**: (a) the side chain can break to eliminate N_2, (b) the ring can break, eliminating N_2, and (c) the ring can open. Although RHF transition states that correspond to all three processes can be found, the ring opening transition state does not exist on the MP2 potential energy surface. The MP2/6-31G* saddle point structures corresponding to side chain breaking (**2′**) and ring breaking (**2″**) lie 21.7 and 12.8 kcal/mol above **2**, respectively. The corresponding CCSD(T)/6-311G* results are 13.7 and 12.7 kcal/mol, respectively.

The side chain in the transition structures **2′** and **2″** lies perpendicular to the ring plane, as can be seen in Figure 2. The MP2/6-31G* IRC corresponding to side chain breaking leads from transition state **2′** directly to dissociation into $4N_2$. On the other hand, starting from transition state **2″**, the IRC leads to $N_2 + N_6$. Two bonds (N2−N3 and N1−N5) break to form these products. It was shown in the previous paper [9] that dissociation from N_6 to $3N_2$ proceeds with only a small barrier. Therefore, isomer **2** does not appear to be a useful high-energy species. Gagliardi and co-workers[8b] examined only the ring-opening mechanism for **2**. Although they assumed the transition state leads directly to $4N_2$, the minimum energy path illustrated that it was in fact connected to the intermediate products N_2 and N_6. Their calculated barrier height, 14.1 kcal/mol, is similar to our prediction of nearly 13 kcal/mol. For the cases in which they used a much larger basis set, the barrier increased to 19.3 kcal/mol; they drew the same conclusion that **2** is not a viable high-energy species.

As discussed above, the cis and trans isomers of **3**, **3a**, and **3b**, are nearly degenerate. The corresponding MP2/6-31G* transition states, **3a′** and **3b′**, correspond to dissociation into $N_2 + N_6$. The corresponding MP2/6-31G* barriers are about 27 and 25 kcal/mol, respectively, including the zero point vibrational energies. CCSD(T)/6-311G* calculations at the MP2 geometries lower these barriers to about 20 kcal/mol. Generally, a reaction proceeds through the pathway that has the lowest barrier. Accordingly, it does not seem reasonable to consider any of the N_8 isomers to be suitable as new fuels because their lowest reaction barriers are all less than or equal to 20 kcal/mol at the highest level of theory used in this work.

Because these are all high-energy species, it is of interest to consider the lowest triplet surface as well. Single point ROHF MP2 triplet calculations at all singlet isomer geometries suggest that singlet−triplet crossings are unlikely because the triplets lie at least 30 kcal/mol above the singlets.

Conclusions

The mechanisms for the dissociation of several N_8 isomers and the nature of their potential energy surface have been investigated with the MP2 and CCSD(T) methods. It is suggested that the dissociation mechanism of **1** proceeds via isomerization into other isomers. The CCSD(T) barriers leading from **1** to **2** and **3** are 13.0 and 49.7 kcal/mol, respectively. For isomer **2** the CCSD(T) barrier height for ring breaking is about 13 kcal/mol, whereas the barrier for side chain breaking is about 14 kcal/mol.

For the acyclic N_8 isomers (**3a** and **3b**), the CCSD(T) dissociation barrier heights are about 20 kcal/mol, so the acyclic isomer appears to be the most metastable of the three N_8 structures considered in the present work. Because all three isomers have barriers of 20 kcal/mol or less for dissociation or isomerization, N_8 does not appear to be a viable fuel in any of its isomeric forms.

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