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Theoretical Studies of the N_6 Potential Energy Surface

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In addition to five previously studied isomers, two new isomers and a complex in the N_6 cluster were investigated at the B3LYP/6-311G(d) and MP2/6-311G(d) levels of theory. The effect of electron correlation on potential energy surfaces in the vicinity of the above eight structures of N_6 clusters was further examined at the CCSD/6-311G(d)//B3LYP/6-311G(d) level of theory. The calculated activation barriers for the isomerization and decomposition reactions were employed to predict dynamic stabilities of the N_6 isomers. It is suggested that only prismane, structure **2**, might possibly be a convenient and useful receptacle for the storage of energy. The rate constants of the isomerization reaction **2** → **3** are predicted using conventional transition state theory (TST) and canonical variational transition state theory (CVT), respectively.

Introduction

The understanding of the stability and structure of polynitrogen species has commanded extensive studies in recent years. A fundamental reason is that the nitrogen atom is isoelectronic with a CH group; thus, one might expect that stable structures containing the CH group could have nitrogen analogues. The practical interest of these structures is related to their possible use as environmentally friendly high-energy-density materials (HEDMs). A successful experimental synthesis of N_5^+ cation[1] in a salt form and the recent experimental detections of the N_4[2] and $[N_3O^+]$[3] were reported recently. These have received much public acclaim and have given impetus to theoretical predictions concerning the stability and structure of other possibly synthesizable N_n clusters.

Among the homonuclear nitrogen molecules, theoretical studies on N_6 isomers[4−16] have a substantial history; however, few have been studied experimentally.[17] Previous researchers have pointed out that the qualitative shape of the N_6 potential energy surface (PES) strongly depends on choice of theoretical model and basis set.[4,9−13,16] Therefore, although several N_6 isomers have been reported, as shown in Figure 1, only prismane **2**, dewarbenezene **3**, benzvalene **4**, and D_2 twist-boat form **5** are predicted to be minima at all the HF,[4,13] MP2,[4,13] and DFT[16] levels of theory. However, there exists a common recognition that open-chain diazide **1** is the global minimum of the PES, irrespective of its being an unstable state with one imaginary vibrational frequency at the correlated MP2/6-31G(d) level of theory.[4] At this level, the mode of the imaginary vibrational frequency corresponds to a rotation around the central N−N bond and its magnitude is so small, about 40i cm^{-1}, that the open-chain diazide **1** can be seen as a minimum or very close to the minimum.

To be viable as useful fuels, the polynitrogen species must be stable enough to be synthesized and stored without isomerization or decomposition. In other words, the energy barriers that prevent their isomerization and decomposition must be sufficiently high to provide stability. Generally, it is desirable to have all such barriers more than 20 kcal/mol, and preferably more than 30 kcal/mol for the polynitrogen compounds.[18]

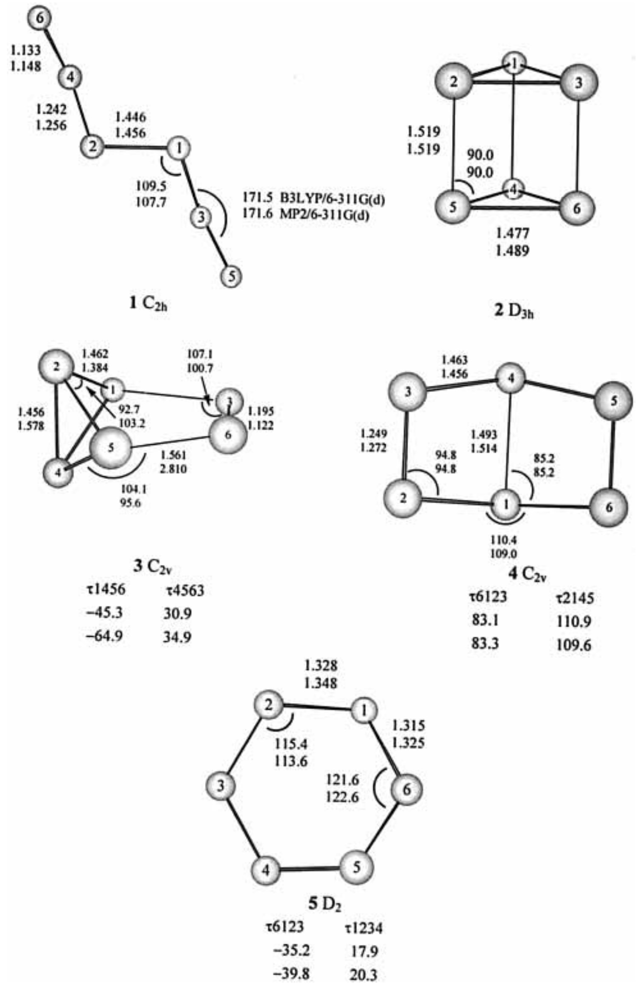

Figure 1. Equilibrium structures for **1**−**5**.

Structures and stabilities of some isomers of N_6 in the singlet electronic states have been well studied theoretically; however, their isomerization and decomposition pathways have not

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received as much attention. To the best of our knowledge, only the decomposition mechanisms and synthesis pathway of the open-chain diazide **1** has been well established to date.[19−21] Therefore, investigations of the isomerization and decomposition mechanisms of the various other N_6 isomers are of interest. To get a deeper insight into the dynamics of N_6 clusters, we have done such calculations on the five previously studied N_6 isomers and on two new isomers. In addition, the rate constants of the isomerization reaction $\mathbf{2} \rightarrow \mathbf{3}$ are also predicted. We hope that this new information will assist future experimental work.

Computational Details

The Gaussian 98 program[22] was used for density functional theory (DFT),[23] second-order perturbation theory (MP2),[24−31] and coupled cluster (CC)[32] method calculations. The core orbitals were kept frozen. The 6-311G(d) basis set was utilized throughout. Optimized geometries and vibrational frequencies for N_6 isomers were obtained at the B3LYP[33,34]/6-311G(d) and MP2/6-311G(d) levels, while those for the transition states were obtained at the B3LYP/6-311G(d) level. The calculation of the vibrational frequencies were performed in order to characterize the stationary points as minima with no imaginary frequencies or as transition states with one imaginary frequency. To confirm the minimum energy pathways connecting the reactants and products, intrinsic reaction coordinate (IRC) calculations were performed at the B3LYP/6-311G(d) level. The importance of ab initio electron correlation on the relative energy of various isomers and transition states was further examined by single-point calculations using the CCSD/6-311G* (coupled cluster theory with single and double excitations) method based on the DFT-optimized geometries with the same basis set. Unless otherwise noted, all geometries are those calculated at the B3LYP/6-311G (d) level and all energies are those determined at the CCSD/6-311G(d)//B3LYP/6-311G(d) level, including zero-point energy corrections (unscaled) from frequency calculations at the B3LYP/6-311G (d) level.

The POLYRATE 8.2[35] program was used to evaluate the reaction rate constants at various temperatures. For purposes of comparison, calculations of the reaction rate constants were carried out by conventional transition state theory (TST) and canonical variational transition state theory (CVT). The latter is based on varying the dividing surface along a reference path to minimize the rate constant. The CVT rate constants were also corrected using the small-curvature tunneling (SCT) transmission coefficient,[36,37] which is based on the centrifugal-dominant small-curvature semiclassical adiabatic ground state (CD-SCSAG) method.

Results and Discussion

1. N_6 Isomers. The structures considered are depicted in Figures 1 and 2, and their relative energies are summarized in Table 1; the point groups and ground electronic state symmetries are also given. Note that the symbol "τ" on the figures stands for the dihedral angle.

The eight structures are minima on the B3LYP potential energy surface (PES). However, at the MP2 level, structure **1** has one imaginary frequency, which agrees well with what has been obtained by Engelke;[4] the other seven structures have all real frequencies. The calculated energies, optimized geometries, and vibrational frequencies for diazide (**1**), prismane (**2**), dewarbenezene (**3**), benzvalene (**4**), and D_2 twist-boat form (**5**) are all in a good agreement with what has been reported earlier;[2,9,11,14] thus, no further discussion of these isomers will be given.

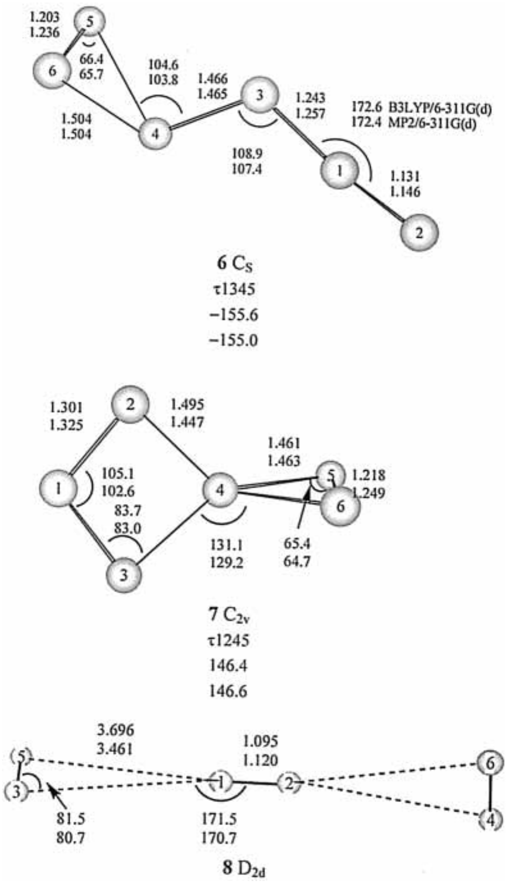

Figure 2. Equilibrium structures for **6**−**8**.

TABLE 1: Relative Energies (kcal/mol) for N_6 Isomers

	B3LYP/6-311G(d)+ZPE	CCSD/6-311G(d)// B3LYP/6-311G(d)
1 (^1A_g, C_{2h})	0.0	0.0
2 ($^1A_1'$, D_{3h})	155.2	137.2
3 ($^1A_1$, C_{2v})	79.8	65.5
4 ($^1A_1$, C_{2v})	68.3	55.2
5 (^1A, D_2)	31.2	26.5
6 ($^1A'$, C_S)	33.6	25.3
7 ($^1A_1$, C_{2v})	90.2	82.8
8 ($^1A_1$, D_{2d})	−158.4	−200.8

Two new intriguing isomers and a complex are illustrated in Figure 2. Structure **6** is the second most stable one among the considered isomers and lies 25.3 kcal/mol higher in energy than structure **1**. It is composed of a three-membered ring and a N_3 tail, and the bonds of N1−N2 and N1−N3, N5−N6 have triple and double bond character, respectively. The other bonds have the single bond characters, at least, in terms of their lengths. Structure **7** has a spiro-structure in which the three- and four-membered rings are perpendicularly fused to each other (Figure 2). It is less stable than structures **1** and **6** by about 82.8 and 57.5 kcal/mol, respectively. Its geometric parameters indicate that the four bonds around atom 4 have single bond characters and the other bonds have double or close to double bond characters. Structure **8** is a complex, which consists of three N_2 fragments.

2. Isomerization and Transition States. The geometric structures of the transition states as well as their optimized parameters for the isomerization reactions are presented in Figure 3, and their relative energies and symmetries are listed in Table 2.

The lowest-energy structure **1**, diazide, can rotate around the N1−N2 bond through transition state **TS1/1′** to give **1′**. As

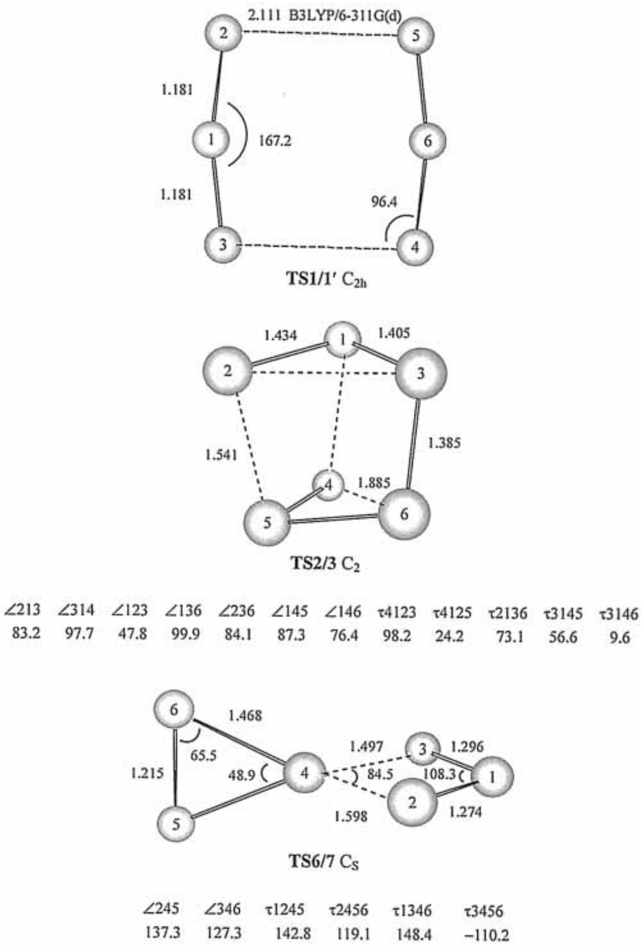

Figure 3. Structures of transition states for isomerization reactions.

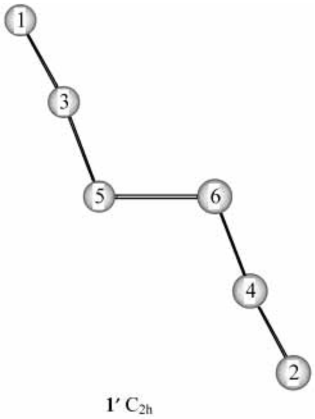

Figure 4. Equilibrium structures **1′** resulting from torsion of **1**.

TABLE 2: Relative Energies (kcal/mol) for the Transition States of the N_6 Isomerization Reactions

	B3LYP/6-311G(d)+ZPE	CCSD/6-311G(d)//B3LYP/6-311G(d)
TS1/1′ (^1A_g, C_{2h})	23.2	29.4
TS2/3 (^1A, C_2)	185.2	171.6
TS6/7 ($^1A'$, C_S)	90.1	84.0

shown in Figure 4, structure **1′** is the same as the corresponding **1** with exception of the numbering. The activation barrier for the interconversion of **1** to **1′** via the monorotating process, in which the bond of N1−N2 rotates 180° to reach **TS1/1′**, is 29.4 kcal/mol. The high barrier height is probably due in part to the energy required to stretch the N1−N2 bond, whose length is 1.446 Å in diazide **1**, while is 2.111 Å in **TS1/1′**. That is, a strong single bond in **1** changes into a weak van der Waals interaction in **TS1/1′**. IRC calculations for **TS1/1′** confirmed that a transition state indeed connects **1** and **1′**.

TABLE 3: The Reaction Rate Constants (cm^3 $molecule^{-1}$ s^{-1}) for the 2 → 3 Reaction

T (K)	TST	CVT	CVT/SCT
500.00	$4.3936 \times 10^{+00}$	$4.1869 \times 10^{+00}$	$3.3453 \times 10^{+01}$
600.00	$6.9554 \times 10^{+02}$	$6.6745 \times 10^{+02}$	$2.9499 \times 10^{+03}$
700.00	$2.6123 \times 10^{+04}$	$2.5192 \times 10^{+04}$	$7.7039 \times 10^{+04}$
800.00	$3.9820 \times 10^{+05}$	$3.8542 \times 10^{+05}$	$9.2137 \times 10^{+05}$
1000.00	$1.8176 \times 10^{+07}$	$1.7682 \times 10^{+07}$	$3.1319 \times 10^{+07}$
1250.00	$3.8875 \times 10^{+08}$	$3.7970 \times 10^{+08}$	$5.5087 \times 10^{+08}$
1500.00	$3.0047 \times 10^{+09}$	$2.9423 \times 10^{+09}$	$3.8181 \times 10^{+09}$
1750.00	$1.2967 \times 10^{+10}$	$1.2720 \times 10^{+10}$	$1.5413 \times 10^{+10}$

As seen in Figure 3, prismane **2** may evolve through transition state **TS2/3**, at a considerable energy cost of 34.4 kcal/mol, to give dewarbenezene **3** which is 71.7 kcal/mol below **2**. The high barrier for the above isomerization is probably due to the need to cleavage of several bonds of **2**, i.e., N2−N3 and N4−N6 bonds, whose distances each elongate from 1.477 Å in **2** to 1.885 Å in **TS2/3**. IRC calculation for **TS2/3** confirmed that a transition state connects **2** with **3**.

For the isomerization of **6** to **7**, through **TS6/7**, there is activation energy of 58.7 kcal/mol. This high barrier is partly due to the energy required to form a tight four-membered ring in **TS6/7**. Nevertheless, the activation barrier for the reverse reaction, i.e., ring-opening process from **7** to **6**, is predicted to be only 1.2 kcal/mol. In **TS6/7**, the triple N1≡N2 bond of **6** changes its triple character (1.131 Å) into double character (1.274 Å). The geometry of **TS6/7** is remarkably similar to **7**. All of the bond lengths change slightly with the exception of N2−N4 bond distance elongating from 1.495 Å in **6** to 1.598 Å in **TS6/7**.

3. **The Rate Constants for the N_6 Isomerization Reaction 2 → 3.** The rate constants for the isomerization reaction from the **2** to **3** were calculated using the POLYRATE 8.2[35] program. For the purpose of comparing the rate constants of the above isomerization reaction, the rate constants using the TST, CVT, and CVT/SCT methods were calculated to obtain the forward reaction rate constants, as shown in Table 3. It is observed that the TST and CVT rate constants are quite close to each other, indicating that variational effects are very small. It is seen that the rate constants of CVT/SCT are larger than the TST and CVT rate constants. This result implies that the small-curvature tunneling corrections are necessary. From the above discussion, we conclude that the theoretical CVT/SCT rate constants are probably more reliable.

4. Decomposition and Transition States. Figure 5 presents the geometric structures of the transition states for the decomposition reactions, and Table 4 summarizes their relative energies, point groups, and electronic state symmetries. Some of N_6 isomers have a concerted decomposition process; i.e., the elimination of two N_2 molecules, such as **1**, **5**, and **6** isomers, while other isomers **3**, **4**, and **7** decompose in a stepwise process with the first step of being the elimination of one N_2 molecule.

The N1−N3 and N2−N4 bonds of **1** may be cleaved via **TS1-diss** with a barrier of just 18.1 kcal/mol to give the complex **8** which is lower in energy than **1** by 200.8 kcal/mol. The above results agree well with what has been point out by Gagliardi[19] and Nguyen.[20] The only difference being that, in our research, a complex occurs in this elimination process as indicated by IRC calculations.

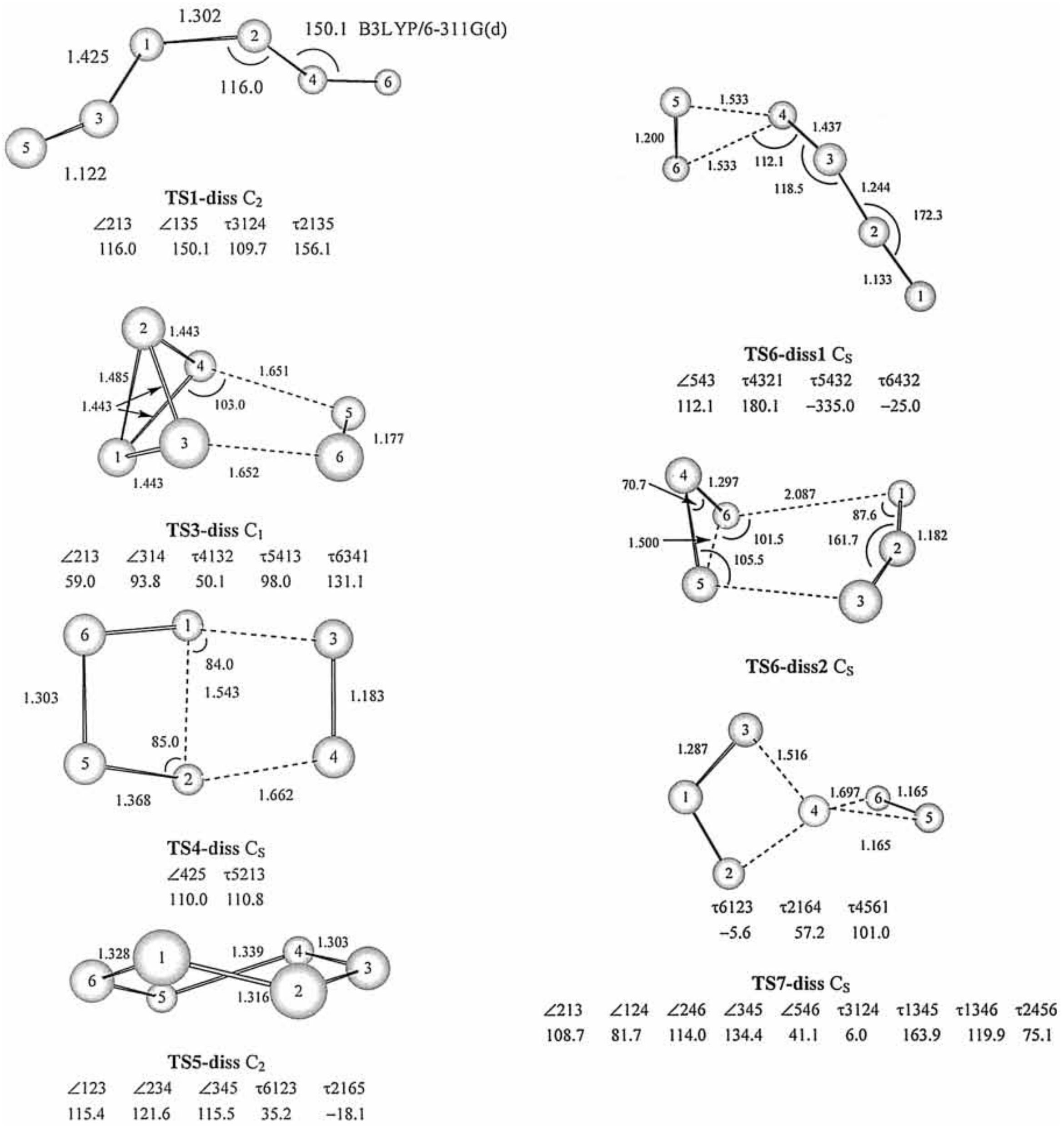

Figure 5. Structures of transition states for decomposition reactions.

TABLE 4: Relative Energies (kcal/mol) for the Transition States of the N_6 Decomposition Reactions

	B3LYP/6-311G(d)+ZPE	CCSD/6-311G(d)//B3LYP/6-311G(d)
$\mathbf{N_4}$ (^1A_g, D_{2h}) + $\mathbf{N_2}$ ($^1\sigma_g$, $D_{\infty h}$)	−17.3	−8.8
$3N_2$ ($^1\sigma_g$, $D_{\infty h}$)	−167.0	−200.1
TS1-diss($3N_2$) (^1A, C_2)	14.5	18.1
TS3-diss(N_4+N_2) (C_1)	79.5	67.6
TS4-diss(N_4+N_2) ($^1A'$, C_s)	70.7	62.6
TS5-diss($3N_2$) (^1A, C_2)	31.4	26.4
TS6-diss1($3N_2$) ($^1A'$, C_s)	60.5	60.1
TS6-diss2($3N_2$) ($^1A'$, C_s)	37.9	30.9
TS7-diss(N_4+N_2) ($^1A'$, C_s)	91.9	91.3

The two N_2 elimination for **5** occurring via **TS5-diss** requires nearly no activation energy, −0.1 kcal/mol, however, this reaction is exothermic by 282.3 kcal/mol. The transition state **TS5-diss** is reactant-like.

Two transition states (Figure 5) have been found for the elimination of two N_2 molecules from **6**. The decomposition proceeds via **TS6-diss1** at a considerable energy cost of 34.8 kcal/mol, while that via **TS6-diss2** requires only 5.6 kcal/mol. **TS6-diss1** has a reactant-like structure, while **TS6-diss2** is geometrically different from reactant **6**, consisting of a triple-ring and an open-chain N_3 fragment. Decomposition of **6** is predicted to be exothermic by 225.4 kcal/mol.

The elimination of one N_2 molecule for isomers **3**, **4**, and **7** produce a D_{2h} symmetric N_4 molecule; these reactions are exothermic by 74.3, 64.0, 91.6 kcal/mol, respectively. The barriers for these decompositions are comparable and are fairly low, i.e., 2.1, 7.4, and 8.5 kcal/mol, respectively. As shown in Figure 5, **TS3-diss** has C_1 symmetry, **TS4-diss** and **TS7-diss** both have C_s symmetry, and the geometries of them are all similar to their corresponding reactants with exception of the elongations of some bonds.

Though we have made attempts to search for a decomposition pathway for isomer **2**, prismane, unfortunately, no transition structure could be located. It seems that the decomposition reaction of isomer **2** probably happens indirectly, i.e., **2** may first isomerize to **3**, then decompose into nitrogen molecules.

Conclusions

The potential energy surface and the nature of transition structures for the isomerization and decomposition reactions of N_6 isomers, including five previously reported isomers and two new isomers as well as a complex, were investigated at the B3LYP/6-311G(d) and CCSD/6-311G(d)//B3LYP/6-311G(d) levels of theory. All stationary points were characterized by harmonic vibrational frequency analyses; intrinsic reaction coordinates were calculated for all the transition structures at the B3LYP/6-311G(d) level of theory.

The above discussions show that all the isomers with exception of **2** have low activation energies, while **2** has a substantially high energy barrier for its isomerization reaction but no value of decomposition reactions could be found. We conjecture that only prismane, isomer **2**, has the possibility to be as a candidate for high-energy-density material among the known N_6 isomers.

Rate constants using TST, CVT, and CVT/SCT calculations for the N_6 isomerization reaction **2** → **3** were performed. The results imply that the small-curvature tunneling corrections are necessary in computing rate constants of this isomerization reaction. Therefore, we predict that the theoretical CVT/SCT rate constants are probably more reliable.

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