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A Quantum Chemical Theoretical Study of Decomposition Pathways of N_9 (C_{2v}) and N_9^+ (C_{2v}) Clusters

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Dissociation pathways of N_9 (C_{2v}) and N_9^+ (C_{2v}) clusters have been investigated by ab initio molecular orbital theory and density functional theory methods. The reactants and products involved were optimized at the HF/6-31G*, B3PW91/6-31G*, B3LYP/6-31G*, and MP2/6-31G* levels of theory. Transition states of decomposition processes were found and characterized on the HF/6-31G*, B3PW91/6-31G*, and B3LYP/6-31G* potential energy surfaces (PES). At the above levels, the barrier heights of the process $N_9 \rightarrow N_6 + N_3$, with zero point energy corrections, are predicted to be 15.3, 31.8, and 32.9 kcal/mol. Similarly, those of the second step $N_6 \rightarrow 3N_2$ are 8.2, 16.3, and 14.4 kcal/mol. The barrier height of $N_9^+ \rightarrow N_7^+ + N_2$ is 2.1 kcal/mol, and that of second step $N_7^+ \rightarrow N_2 + N_5^+$ is 4.3 kcal/mol at the B3LYP/6-311+G*//B3LYP/6-31G* level. The potential applications of N_9 and N_9^+ as high-energy density materials were examined.

Introduction

The intense scientific and popular interest in C_n molecule has naturally raised the question whether other important cluster species have been systematically overlooked. Are there any stable molecules made of pure nitrogen? Many stable structures have been predicted theoretically for all-nitrogen clusters.[1−13] Although N is an isoelectronic analogue to CH and many stable complexes of $(CH)_n$, such as benzene (C_6H_6) and polyalkyne, have been known, corresponding nitrogen clusters ($n > 3$) have not been prepared. The main reason for this is due to the differences of the nitrogen−nitrogen triplet (226.9 kcal/mol), double (100.2 kcal/mol), and single (38.4 kcal/mol) bond energies. Therefore, nitrogen clusters are of great interest as high-energy density materials.[1,2] Christe et al.[14] synthesized the AsF_6^- salt of N_5^+ by the reaction of $N_2F^+AsF_6^-$ with HN_3 in anhydrous hydrogen fluoride at −78 °C. Prior to this new work, only molecular nitrogen (N_2) and the azide ion (N_3^-) had been isolated, although a few other species were seen fleetingly in gas-phase chemistry. The N_5^+ cation is the first new all-nitrogen species to be synthesized in isolatable quantities in more than a century.

The metastability of molecules and whether they can be synthesized depend on the activation energy of decomposition; therefore, theoretical studies of the decomposition mechanisms of polynitrogen structures are of great interest.

Dissociation energies of N_4 (T_d, D_{2h}) with the B3LYP method, computed with various basis sets, converge to the G2 value.[15−19] The Woodward−Hoffmann forbidden dissociation of N_4 (T_d) to $2N_2$ has been explored at several levels of ab initio molecular orbital theory. The barrier to dissociation at the CASSCF (12,12)/DZP level of theory is 63.0 kcal/mol. The barrier of dissociation for N_4 (D_{2h}) to $2N_2$ at the G2 level is calculated to be 2.5 kcal/mol.[19]

Lauderdale et al.[6] have also discussed nitrogen clusters and predicted N_8 clusters with ab initio self-consistent field (SCF), coupled-cluster (CC), and Moller−Plesset perturbation theory (MPn) methods. Their SCF results agree qualitatively with those of Engelke and Stine.[9] From symmetry arguments, they deduced that N_8 should have a significant barrier to decomposition. By correlating the orbitals of N_8 with those of $4N_2$ through D_{2h} symmetry, they obtained an orbital crossing between occupied and unoccupied orbitals, which demonstrated that N_8 corresponds asymptotically to an excited state of $4N_2$ molecules on the D_{2h} energy surface. The decomposition of N_8 to $4N_2$ is thus symmetry-forbidden along this reaction pathway. Similarly, the decomposition via a D_{2d} pathway is also forbidden, and it was therefore expected that N_8, if it could be formed, would be relatively stable. To understand the dissociation channels of N_8, we have presented some results[3] from a study of the isomerization reaction from high-energy azacubane structure to the more stable azapentalene structure. This reaction may occur via a series of intermediate metastable structures with moderately low barriers (10−20 kcal/mol). Five local minima on the energy surface have been found, and the transition states between two consecutive minima have also been determined. Recently, Gagliardi et al.[10] and Chung et al.[11] investigated that possible dissociation reaction of N_8 isomers to $4N_2$. The calculations have determined the relative energies of the two isomers and the two transition states involved in the decomposition process.

There seems to be a lack of appreciation within the group of workers doing quantum-chemical calculations on pure nitrogen energetic materials (N_{2n+1}, $n > 2$) in that the electrically neutral "linear" forms are not the most interesting geometrical structures as HEDMs. This is because these forms probably have radical (i.e., unpaired electron) characteristics and, therefore, will be highly reactive. Additionally, the various atomic centers on such species carry significant Mulliken electrical charges and, therefore, will be subject to nucleophilic or electrophilic attack.

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The primary interest in the linear forms is their role as intermediates in the decomposition of the probably more kinetically stable (and higher-energy) polycyclic forms containing the same number of nitrogen atoms. Concerning the ionic forms of such structures, perhaps they could be kinetically stabilized in salt forms—as in the recent isolation of a salt of N_5^+. However, in most metal salts, the high molecular weight of the metal will significantly degrade the performance characteristics of the material as HEDM. Therefore, the value of the calculations on the structures reported is in their ability to cast light on the properties of the decomposition intermediates of polycyclic nitrogen molecular forms.

Besides the reports about the decomposition mechanisms of N_{2n} clusters, there are only a few studies on N_{2n+1} clusters, such as N_3^-, N_7, N_5^-, N_5^+, and N_7^-.[4,5,20−23] No decomposition mechanism studies of odd clusters have been reported. The most stable N_7 isomers are open-chain C_S and C_2 structures having almost identical total energies.[5] This work suggests the possibility that neutral nitrogen clusters with odd-numbers of nitrogen atoms may be stable and would be HEDMs if they could be synthesized. Matsunaga[24] has identified all-nitrogen cations by MS/MS spectrometry from pulsed laser irradiation of cyanuric triazide. $(N_2)_n^+$ and $N(N_2)_n^+$ have been widely studied by ion mass spectrometry.[25−29] The N_9^+ cluster has been reported as a high-intensity cluster ion source for fast-beam experiments.[29]

Geometric structures of N_9 and N_9^+ clusters have been optimized in our previous work.[12] The structures of the N_9 cluster were designed in analogy to those of $(CH)_n$ because a CH group and N are isoelectronic. In such structures, the linear forms are the most stable isomers. In this paper, we attempt to find some of the possible pathways of decomposition for N_9 (C_{2v}) and N_9^+ (C_{2v}) and to determine the energy barriers of these reactions. Finally, we examine the possibilities of N_9 and N_9^+ clusters as HEDMs candidates.

Computational Methods

Equilibrium geometries of reactants and products have been optimized with ab initio molecular orbital (MO) theory and density functional theory (DFT) methods. The DFT functionals used in the present work include B3PW91 (Becke's three-parameter hybrid functional and Perdew and Wang's 1991 gradient-corrected correlation functional) and B3LYP (B3 and the nonlocal correlation of Lee, Yang, and Parr). The basis set used in this paper is the standard 6-31G*, which is a split-valence plus polarization basis set introduced by Pople and coworkers. Some calculations of single-point energies used the 6-311+G* basis set. Spin-restricted wave functions were used for all the closed-shell systems, and spin-unrestricted wave functions were employed for the open-shell species. The vibrational frequencies and zero-point energies (ZPE) were evaluated from analytical second derivatives calculated at some levels. To confirm that the transition state connects the reactant and product, we also performed intrinsic reaction coordinate (IRC) calculations at some levels of theory. All calculations were carried out with the Gaussian 94 program[30] on a SGI O2 workstation and an Origin 2000 server.

Results and Discussion

The optimized equilibrium geometric parameters, obtained at the several levels of theory, for the reactants, transition states and products, are listed in Table 1. The relative energies and ZPE's are presented in Table 2.

TABLE 1: Geometrical Parameters of Reactants, Transition States, and Products Involved in the N_9 and N_9^+ Dissociation Process (6-31G*)[a]

species	parameter	B3PW91	B3LYP
N_9	r12	1.305	1.309
(C_{2v})	r24	1.364	1.373
	r64	1.255	1.261
	r86	1.135	1.137
	a213	107.4	107.5
	a124	106.5	106.4
	a246	111.9	111.5
	a468	169.6	173.1
N_6	r12	1.432	1.448
(C_{2h})	r13	1.242	1.247
	r35	1.139	1.141
	a312	109.7	109.0
	a531	171.3	171.3
N_3	r	1.182	1.184
N_2	r	1.110	1.106
TS1	r12	1.161	1.171
(C_S)	r13	1.529	1.481
	r24	2.577	2.458
	r35	1.334	1.345
	r46	1.176	1.193
	r35	1.187	1.266
	r68	1.259	1.126
	r79	1.137	1.138
	a312	119.0	119.0
	a421	107.7	106.6
	a531	102.7	103.3
	a642	97.7	99.0
	a753	113.2	112.4
	a468	179.8	179.7
	a579	170.2	169.9
TS2	r12	1.288	1.303
(C_1)	r13	1.427	1.427
	r24	1.427	1.428
	r46	1.130	1.131
	r35	1.130	1.131
	a312	116.8	116.0
	a421	116.8	116.0
	a531	148.0	149.0
	a642	148.0	149.0
N_9^+	r12	1.316	1.320
(C_{2v})	r28	1.296	1.300
	r64	1.314	1.326
	r86	1.117	1.118
	a213	104.5	104.7
	a124	107.9	107.9
	a246	110.3	110.0
	a468	165.0	176.0
N_7^+	r12	1.265	1.302
(C_{2v})	r24	1.359	1.321
	r46	1.077	1.118
	a312	111.0	108.6
	a124	107.0	109.6
	a357	169.0	165.2
N_5^+	r12	1.325	1.306
(C_{2v})	r24	1.080	1.119
	a312	107.9	112.1
	a421	168.6	166.0
TS3	r12	1.277	1.354
(C_S)	r13	1.314	1.303
	r24	1.264	1.236
	r35	1.226	1.311
	r46	1.367	1.542
	r35	1.508	1.313
	r68	1.077	1.111
	r79	1.074	1.120
	a312	105.8	104.2
	a421	111.0	111.2
	a531	110.7	108.2
	a642	106.8	108.8
	a753	105.3	110.0
	a468	169.0	153.2
	a579	167.2	165.8
TS4	r12	1.287	1.323
(C_S)	r13	1.222	1.232
	r24	1.342	1.315
	r35	1.586	1.586
	r46	1.078	1.119
	r57	1.075	1.110
	a312	113.0	114.4
	a124	107.0	109.1
	a135	104.6	108.0
	a246	169.0	165.0
	a357	165.9	151.8

[a] The bond lengths are in Å, and bond angles are in deg.

1. Geometric Structures. Open-chain N_9, with C_{2v} symmetry (Figure 1), is a local minimum, and its lowest vibrational

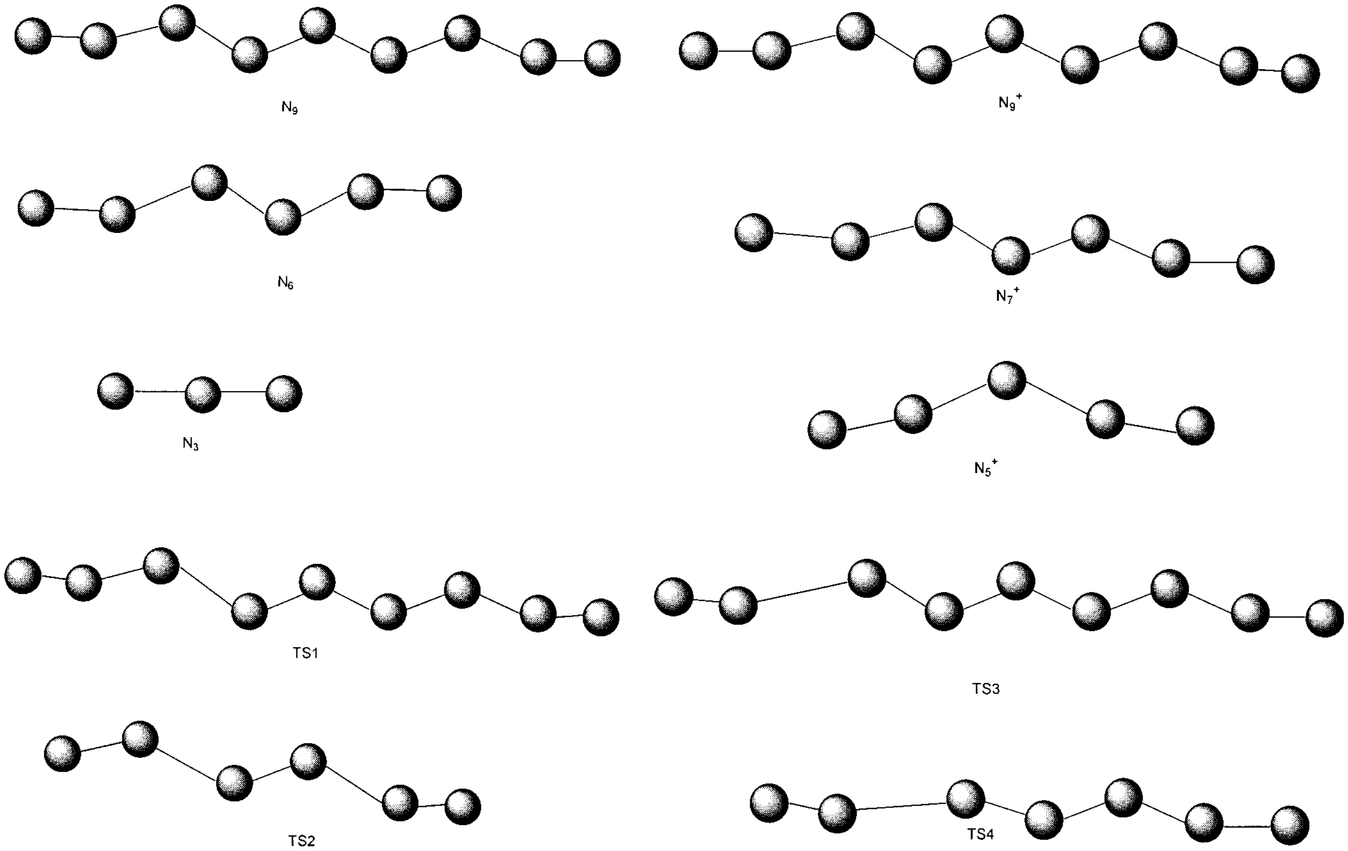

Figure 1. Geometric structures of N_9^+ and N_9 dissociation systems.

TABLE 2: Relative Energies (kcal/mol) with ZPE (kcal/mol) Correction of Species in N_9 and N_9^+ Decomposition System[a]

	B3PW91/6-31G*		B3LYP/6-31G*		B3LYP[a]/6-311+G*
species	*E*	ZPE	*E*	ZPE	*E*
N_9	0.0	23.6	0.0	23.1	0.0
$N_3 + N_6$	9.1	21.7	7.4	21.3	0.0
TS1	31.8	19.5	32.9	25.1	35.4
N_6	0.0	15.6	0.0	15.3	0.0
$3N_2$	−155.0	10.5	−160.1	10.5	−168.9
TS2	16.3	12.5	14.4	12.3	15.4
N_9^+	0.0	24.2	0.0	23.7	0.0
$N_2 + N_7^+$	−53.2	22.2	−55.0	21.8	−57.5
TS3	2.9	22.6	2.2	22.2	2.1
N_7^+	0.0	17.0	0.0	18.3	0.0
$N_2 + N_5^+$	−38.5	16.5	−40.6	16.3	−39.5
TS4	4.1	17.0	4.1	16.7	4.3

[a] Single-point energy in B3LYP/6-311+G*//B3LYP/6-31G* with ZPE correction in B3LYP/6-31G*.

frequencies are 97.6 cm^{-1} (HF/6-31G*), 87.4 cm^{-1} (B3PW91/6-31G*), and 87.5 cm^{-1} (B3LYP/6-31G*). As shown in Table 1, the bond length of N6−N8 (ca. 1.123 Å) is somewhat longer than the experimental triple-bond length 1.094 Å of N_2, and the bond length of N6−N4 (ca. 1.265 Å) is longer by 0.013 Å than the experimental value for HN=NH (1.252 Å). The bond lengths of N4−N2 and N1−N2 lie between the experimental double-bond length of HN=NH (1.252 Å) and single-bond length of H_2N-NH_2 (1.449 Å).[31] The central bond angles (∠312) are all 108.0° at the four levels. Of particular interest is the hypervalent nature of structure N_9: the bond lengths of N6−N8 (ca. 1.123 Å) and N4−N6 (ca. 1.265 Å) imply that it may be a highly nonclassical structure, with N6 and N7 being hypervalent. The results are similar to those of the open-chain N_6[32] and N_7 [5] isomers. There is little spin contamination, for the computational values of S**2 are nearly 0.75 in the open-shell system. Therefore, we considered the results of calculation to be reliable. However, Glukhovtsev et al.[33] concluded from nature bonding orbital (NBO) analysis that none of the N atoms in the N_6 open-chain structures form more than four covalent bonds. The hypervalent nature for open-chain nitrogen isomers can be questioned at present.[5] Further appropriate studies exploring the hypervalent nature are necessary.

Open-chain structures of N_9^+ (C_{2v}), N_7^+ (C_{2v}), N_6 (C_{2h}), and N_5^+ (C_{2v}) were also optimized at the HF, B3PW91, B3LYP, and MP2 levels of theory with the 6-31G* basis set. They are all local minima. In the structure of N_9^+ (C_{2v}), the bond lengths of N1−N2, N2−N4, and N4−N6 lie between those of NH_2-NH_2 and NH=NH, and the bond length of N6−N8 is nearly equal to that of N≡N. Similar statements apply to N_7^+ (C_{2v}), N_6 (C_{2h}), and N_5^+ (C_{2v}).

2. Decomposition Process of N_9 (C_{2v}). *a. First Decomposition Process: N_9 (C_{2v}) → N_6 (C_{2h}) + N_3 ($D_{\infty h}$).* The decomposition mechanism of the open-chain N_9 cluster with C_{2v} symmetry was exammed at the three levels of theory. First, the open-chain N_9 cluster may decompose into N_6 (C_{2h}) and N_3 ($D_{\infty h}$), and the transition state (TS1) was found on the HF/6-31G*, B3PW91/6-31G*, and B3LYP/6-31G* PES. During the process N_9 (C_{2v}) → N_6 (C_{2h}) + N_3 ($D_{\infty h}$), the bond length of N2−N4 increases, with the symmetry changing from C_{2v} to C_S, and the other bond lengths and bond angles change slightly. For example, in the TS1 structure ($N_6 \cdots N_3$), the optimized N6−N8 distance (1.118 Å at HF/6-31G*, 1.176 Å at B3PW91/6-31G*, and 1.126 Å at B3LYP/6-31G*) differs from that of N6−N8 (1.102, 1.135, and 1.137 Å at above levels) in stable N_9 (C_{2v}) by only −0.016, 0.041, and 0.011 Å, respectively. Only the separation of N2−N4 (1.762, 2.577, and 2.458 Å at the above levels) is longer than that of N2−N4 (1.352, 1.364, and 1.373 Å) in stable N_9. The distance between N2−N4 suggests that the charge attraction between N2 and N4 be weakened. Thus, the bond of N2−N4 would break easily, and N_9 (C_{2v}) would dissociate into two species: N_3+N_6.

b. Second Decomposition Process: N_6 *(*C_{2h}*)* → $3N_2$ *(*$D_{\infty h}$*).* A similar trend was observed for the process N_6 (C_{2h}) → $3N_2$ ($D_{\infty h}$). Transition-state positions (TS2) were found on the HF/6-31G*, B3PW91/6-31G*, and B3LYP/6-31G* PES. Compared with stable N_6 (C_{2h}) at the above three levels of theory, in the structure of TS2, the bond length of N1−N2 shortens, and N4−N2, N1−N3 increases. The angles ∠135 and ∠246 both change from 171.3° to 148.0°. The symmetry changes from C_{2h} to C_1 during the deformation of the reactant N_6 toward the TS2. During the reaction process, the bonds N2−N4 and N1−N3 would break, and N_6 (C_{2h}) would dissociate into $3N_2$. The pathway has been confirmed by an IRC calculation.

c. Barriers and Release Energy. The energy barrier heights for N_9 (C_{2v}) → N_6 (C_{2h}) + N_3 ($D_{\infty h}$) are 15.3 kcal/mol (HF/6-31G*) 31.8 kcal/mol (B3PW91/6-31G*), 32.9 kcal/mol (B3LYP/6-31G*), and 35.4 kcal/mol (B3LYP/6-311+G*). The results with B3PW91/6-31G*, B3LYP/6-31G*, and B3LYP/6-311+G* are in good agreement. Since electron correlation is included in the DFT methods, we consider that the DFT results are more reliable. The theoretical energy barrier height for TS1 at our best level is predicted to be 35.4 kcal/mol. These results imply that N_9 (C_{2v}) has a significant energy barrier to dissociation. Those of N_6 (C_{2h}) → $3N_2$ ($D_{\infty h}$) are 8.2, 16.3, 14.4, and 15.4 kcal/mol at the above levels. Similar to the case of N_9, we expect that the barrier heights for N_6 predicted by the DFT methods are more reliable, the best prediction being 15.4 kcal/mol. It is concluded that N_6 is not stable enough to be considered as a candidate for high-energy density material.

The high-energy content of the N_9 and N_6 isomers suggests that they may be useful as explosives or propellants. An effective propellant is characterized by a high ratio of energy released per unit mass and by a high specific impulse, I_{sp}.[34,35] Specific impulses can be estimated using Rosen's formula, i.e., $I_{sp} = 265\sqrt{\Delta H_f/M}$, where ΔH_f is taken as the propellant's energy release and M is its molecular weight. Schaefer[35] et al. used a 4.7:1 weight mixture of O_2 to H_2 as a comparison propellant, and their estimated value for the I_{sp} of this mixture is 456s. I_{sp} estimates for N_9 and N_6 are 418 and 462 s (HF/6-31G*), 356 and 352 s (B3PW91/6-31G*) and 351 and 360 s (B3LYP/6-31G*). Thus, the N_9 cluster is not as powerful a propellant as the O_2/H_2 mixture.

3. Decomposition Pathways of N_9^+ Are via Two Steps. *a.* N_9^+ *(*C_{2v}*)* → N_7^+ *(*C_{2v}*)* + N_2 *(*$D_{\infty h}$*).* The decomposition mechanism of the open-chain N_9^+ cluster, with C_{2v} symmetry, is different from that of N_9. Positions on the potential energy surfaces of N_9^+ and N_7^+ clusters decomposition were computed. The open-chain N_9^+ cluster decomposed into N_7^+ and N_2. A transition state (TS3) characterized by only one imaginary vibrational frequency was found at the HF/6-31G*, B3PW91/6-31G*, and B3LYP/6-31G* levels. During the process of N_9^+ (C_{2v}) decomposing into N_7^+ (C_{2v}) and N_2 ($D_{\infty h}$), the bond length of N7−N5 increases, with the symmetry changing from C_{2v} to C_S; the other bond lengths and bond angles change slightly. The optimized distance of N7−N9 (1.074 Å at HF/6-31G*, 1.110 Å at B3PW91/6-31G*, and 1.120 Å at B3LYP/6-31G*) in the structure TS3 is nearly equal to that in stable N_9^+ (C_{2v}), and only the bond length N5−N7 (1.508, 1.550, and 1.542 Å at the above three levels) increases. Thus, the bond of N5−N7 would break easily, and N_9^+ (C_{2v}) would dissociate into N_2 and N_7^+. IRC calculations, performed at the levels of HF/6-31G*, B3PW91/6-31G*, and B3LYP/6-31G*, also prove that the TS3 connects with N_9^+ and $N_2+N_7^+$.

b. N_7^+ *(*C_{2v}*)* → N_5^+ *(*C_{2v}*)* + N_2 *(*$D_{\infty h}$*).* Similar trends were observed in the process of N_7^+ (C_{2v}) → N_5^+ (C_{2v}) + N_2 ($D_{\infty h}$). A transition state (TS4) was found on the above PES. During the deformation process from the reactant (N_7^+) to the TS4, the bond length of N3−N5 increases, with the symmetry changing from C_{2v} to C_S; the other bond lengths and angles change slightly. These imply that the attraction between N3 and N5 is weaker and the bond N3−N5 in TS4 would break easily. IRC calculation also showed the pathway to being a channel of N_7^+ decomposition.

c. Barriers and Release Energy. The energy barrier height for $N_9^+(C_{2v})$ → $N_7^+(C_{2v})$ + $N_2(D_{\infty h})$ is 2.1 kcal/mol, and that of second step N_7^+ → N_2 + N_5^+ is 4.3 kcal/mol on the B3LYP/6-311+G*// B3LYP/6-31G* PES. That is, on the PES for N_9^+-(C_{2v}), the barrier to dissociation is much less than that for N_9. The relative energies of the N_9^+ (C_{2v}) decomposition process are shown in Table 4.

From above discussion, one concludes that N_9 is kinetically more stable than N_9^+. All calculations indicate that N_9^+ will not be a useful explosive or propellant because of its kinetic instability. I_{sp} estimates of N_9^+ and N_7^+, computed with the methods already mentioned, are 521s and 316s.

Summary

The decomposition pathways of N_9, N_6, N_9^+, and N_7^+ were found on HF/6-31G*, B3PW91/6-31G*, and B3LYP/6-31G* PES. The barrier heights of the dissociation processes, at our best level of theory, are 35.4 kcal/mol for N_9 (C_{2v}) → N_6 (C_{2h}) + N_3 ($D_{\infty h}$) and 15.4 kcal/mol for N_6 (C_{2h}) → $3N_2$ ($D_{\infty h}$). Those of N_9^+ (C_{2v}) → N_7^+ (C_{2v}) + N_2 ($D_{\infty h}$) and N_7^+ (C_{2v}) → N_5^+ (C_{2v}) + N_2 ($D_{\infty h}$) are 2.1 and 4.3 kcal/mol. From the barrier of the N_9 dissociation processes, we conclude that N_9 is metastable species and that it may be useful as a HEDM if it could be synthesized.

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