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Structures and stability of N_7^+ and N_7^- clusters

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Abstract. Ab initio molecular orbital theory and density functional theory have been used to study nine isomers of N_7 ionic clusters with low spin at the HF/6-31G*, MP2/6-31G*, B3LYP/6-31G*, and B3LYP/6-311(+)G* levels of theory. All stationary points are examined with harmonic vibrational frequency analyses. Four N_7^+ isomers and five N_7^- isomers are determined to be local minima or very close to the minima on their potential-energy hypersurfaces, respectively. For N_7^+ and N_7^-, the energetically low lying isomers are open-chain structures (C_{2v} and C_{2v} or C_2). The results are very similar to those of other known odd-number nitrogen ions, such as N_5^+, N_9^+, and N_9^-, for which the open-chain structures are also the global minima. This research suggests that the N_7 ionic clusters are likely to be stable and to be potential high-energy-density materials if they could be synthesized.

Key words: Nitrogen cluster – Ab initio calculation – Density functional theory method – N_7^+ – N_7^-

1 Introduction

There has been intense interest in homoatomic nitrogen clusters and their ions because they are good candidates for high-energy-density materials (HEDM), which can be used as propellants or explosives. A lot of theoretical investigations have been reported on even-number nitrogen clusters [1–6]; however, until now none of them have been synthesized.

After molecular nitrogen was isolated in 1772 [7], the azide ion N_3^- was the first nitrogen ionic cluster synthesized (in 1890) [8]. More than a century later, Christe et al. [9] synthesized the AsF_6^- salt of N_5^+ by reacting $N_2F^+AsF_6^-$ with HN_3 in anhydrous hydrogen fluoride at −78 °C in 1998. The cation N_5^+ is the first new all-nitrogen species to be synthesized in isolatable quantities in more than a century. It is very surprising that the first synthesized nitrogen cluster (N_x $x>3$) is a cation containing an odd number of nitrogen atoms rather than an even-number nitrogen cluster. More odd-number nitrogen clusters, such as N_3 [2, 10], N_3^+ [2, 10], N_5 [2, 11], N_5^- [2, 11,12], N_5^+ [2, 9, 11, 13, 14], N_7 [2, 15, 16], N_7^- [2, 17], N_9 [2, 18], N_9^- [2, 18], and N_9^+ [2, 18], have been studied.

Christe et al. [9] identified the novel cation N_5^+ as a C_{2v} symmetry structure by means of NMR and vibrational (IR, Raman) spectra. The experimental results are consistent with their own CCSD (T)/6-311+G (2d) theoretical results that N_5^+ has an open-chain structure with C_{2v} symmetry. Wang et al. [11] found that the most stable neutral N_5 isomer is a complex with weak $N_2{\cdot}N_3$ bonding and C_{2v} symmetry, while the most stable anion, N_5^-, is a complex with weak $N_2{\cdot}N_3^-$ bonding and the same symmetry. We reported previously [15] that the most stable N_7 isomers are open-chain structures with C_s and C_2 symmetry. Both of them have almost identical energy at the UHF/6-31G*, UMP2/6-31G*, and B3LYP/6-31G* levels of theory. Recently, with the Gaussian-3 method, Wang et al. [16] found that the most stable isomer for the N_7 cluster consists of a five-membered ring and a N_2 side chain with C_s symmetry. For the N_7^- cluster, Michels et al. [17] demonstrated that the open-chain structure $(N_3–N–N_3)^-$ was a local minimum on the potential-energy surface at the HF/6-31G* and MP2/6-31G* levels. For the N_9, N_9^+, and N_9^- clusters, we previously studied them at the HF/6-31G*, B3PW91/6-31G*, B3LYP/6-31G*, and MP2/6-31G* levels of theory [18]. The results showed that the most stable radical N_9 cluster is an open-chain structure with C_{2v} symmetry and that of N_9^- is also an open-chain structure but with C_s symmetry. Only one stable structure of the N_9^+ with C_{2v} symmetry was reported. Bartlett [2] made a systemic investigation of the structures, energies, and spectra of purely nitrogen molecules from N_3 to N_{10}, as well as their cations and anions.

Since N_3^- and N_5^+ have been synthesized, it can be expected that N_7 ions may be the next object to be synthesized. Therefore, it is worth investigating the N_7

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ionic clusters theoretically. The aim of this research was to predict the plausible equilibrium structures, energies, and vibrational frequencies of the N_7^+ and N_7^- isomers using ab initio molecular orbital theory and density functional theory (DFT) methods. Four N_7^+ isomers (**1–4**) and five N_7^- isomers (**5–9**) were found to be stable structures.

2 Computational method

The geometries were fully optimized at the Hartree–Fock (HF), MP2, and DFT levels of theory. Here, the MP2 method employed is one using the frozen-core approximation and the DFT method is B3LYP which is a hybrid HF/DFT approach with Becke's three parameter hybrid exchange functional and the Lee, Yang, and Parr nonlocal correlation functional [19, 20]. The basis set used was the standard 6-31G* basis set, which is of double-zeta contraction quality plus six d-like polarization functions. The harmonic vibrational frequencies were determined via analytic second derivative methods at the HF/6-31G*, B3LYP/6-31G*, and MP2/6-31G* levels. For the N_7^+, we employed the 6-311G* basis set, along with the B3LYP method, to examine the effect of different basis sets, while for the N_7^-, we employed the 6-311 + G* basis set to examine a similar effect. The 6-311G* basis set is a standard triple-zeta plus polarization basis set, whereas the 6-311 + G* basis set is further augmented with diffuse functions [21]. In addition to the structural and energetic results, the bonding in these isomers was also discussed using the natural localized molecular orbital (NLMO) analyses, which were carried out at the B3LYP/6-31G* level of theory and are based on the optimized geometries at the same level. Throughout, bond lengths are given in angstroms, bond angles in degrees, total energies in hartrees, and relative energies and zero-point vibrational energies (ZPE) in kilocalories per mole.

All the computations were carried out with the Gaussian98 program package [22].

3 Results and discussion

The geometric structures and the optimized geometric parameters of the N_7^+ and N_7^- isomers are shown in Figs. 1 and 2. The total energies, the ZPE, and the relative energies with ZPE correction are listed in Tables 1 and 2. The lowest vibrational frequencies and their corresponding modes are exhibited in Table 3.

3.1 N_7^+ isomers

It was reported that the open-chain structure is the most stable species for N_5^+ [9] and N_9^+ [18]. Similarly, the C_{2v} symmetry open-chain structure **1** (Fig. 1a) for N_7^+ is also the lowest in energy. It is energetically lower than structure **2** (Tables 1, 2) by 46.4 kcalmol^{-1} (HF/6-31G*), 27.1 kcalmol^{-1} (B3LYP/6-31G*), 27.6 kcalmol^{-1} (MP2/6-31G*), and 29.5 kcalmol^{-1} (B3LYP/6-311G*). Table 3 shows that structure **1** is a local minimum on the energy hypersurface with the lowest vibrational frequency being 139, 130, 123, and 131 cm^{-1} at the four levels, respectively. Bartlett also obtained the open-chain structure N_7^+ as a local minimum at the B3LYP/aug-cc-PVDZ level [2].

For structure **1**, the terminal bond length of N4–N6 (or N5–N7) is 1.077, 1.118, 1.144, and 1.110 Å at the HF/6-31G*, B3LYP/6-31G*, MP2/6-31G*, and B3LYP/6-311G* levels of theory, respectively. It is slightly longer than the experimental triple-bond length, 1.098 Å, of a nitrogen molecule [23], except for the HF value. It is known that electron correlation would increase the optimized bond lengths. As usual, the MP2 method is known to overestimate electron correlation effects and this results in some geometrical parameters being different from those of the HF method. Nguyen et al. [25] suggested that the true bond lengths lie between the HF and MP2 values for molecules of this type. Since the bond lengths obtained from B3LYP just lie between the HF and MP2 values, and the 6-311(+)G* basis set is better than that of 6-31G*, we mainly use the B3LYP/6-311(+)G* results unless otherwise indicated in discussing the geometries of the molecules. As shown in Fig. 1a, the bond lengths of N1–N2 (or N1–N3) and N2–N4 (or N3–N5) are 1.297 and 1.317 Å, respectively. They lie between the double-bond length of HN=NH (1.252 Å) and the aromatic N–N bond length (1.350 Å), indicating that there is conjugation, to some extent, over these bonds. Natural population analysis shows that most positive charge of this cation lies on the atoms N6 (or N7) (0.32) and N4 (or N5) (0.23).

We also investigated the geometry composed of a five-membered ring along with one or two side chains. We tried several possible structures, but only structures **2** and **3**, containing a five-membered ring and an N_2 chain, were found to be stable species (Fig. 1).

Recently Wang et al. [16] suggested that the same structure as **2** is the global minimum for the neutral N_7 cluster; however, structure **2** for the N_7^+ cluster lies energetically higher than **1**. Although it is a local minimum with the HF and MP2 methods, it has an imaginary frequency with the B3LYP method. When following the normal mode of an imaginary vibrational frequency, it collapses to a $N_5^+ \cdot N_2$ complex (**2**-complex) with C_s symmetry (Fig. 1a).

Structure **3**, obtained only by the HF method, has a spiro structure in which the three- and five-membered rings are perpendicularly fused to each other. It lies energetically higher than **1** by 80 kcalmol^{-1} at the HF/6-31G* level; however, with the B3LYP and MP2 methods, structure **3** collapses to another C_{2v} symmetry complex (**3**-complex). As shown in Fig. 1b, it contains an N_3 three-membered ring and two N_2 fragments.

We also tried several structures with a four-membered ring, but only structure **4** (Fig. 1b) with C_{3v} symmetry was obtained with all real vibrational frequencies. Structure **4** is composed of three fused four-membered rings. It has quite a high energy, higher than structure **1** by 275.9, 220.3, 215.4, and 232.2 kcal mol^{-1}, respectively, at the four levels of theory used.

In view of the instabilities of the three N_7^+ isomers (**2**, **3** and **4**), there will be no further discussion for these isomers.

The structures with six-membered rings were also investigated; however, none of them were found to be local minima.

In addition, we also obtained several complexes with lower energies and we will carry out further investigations on them later.

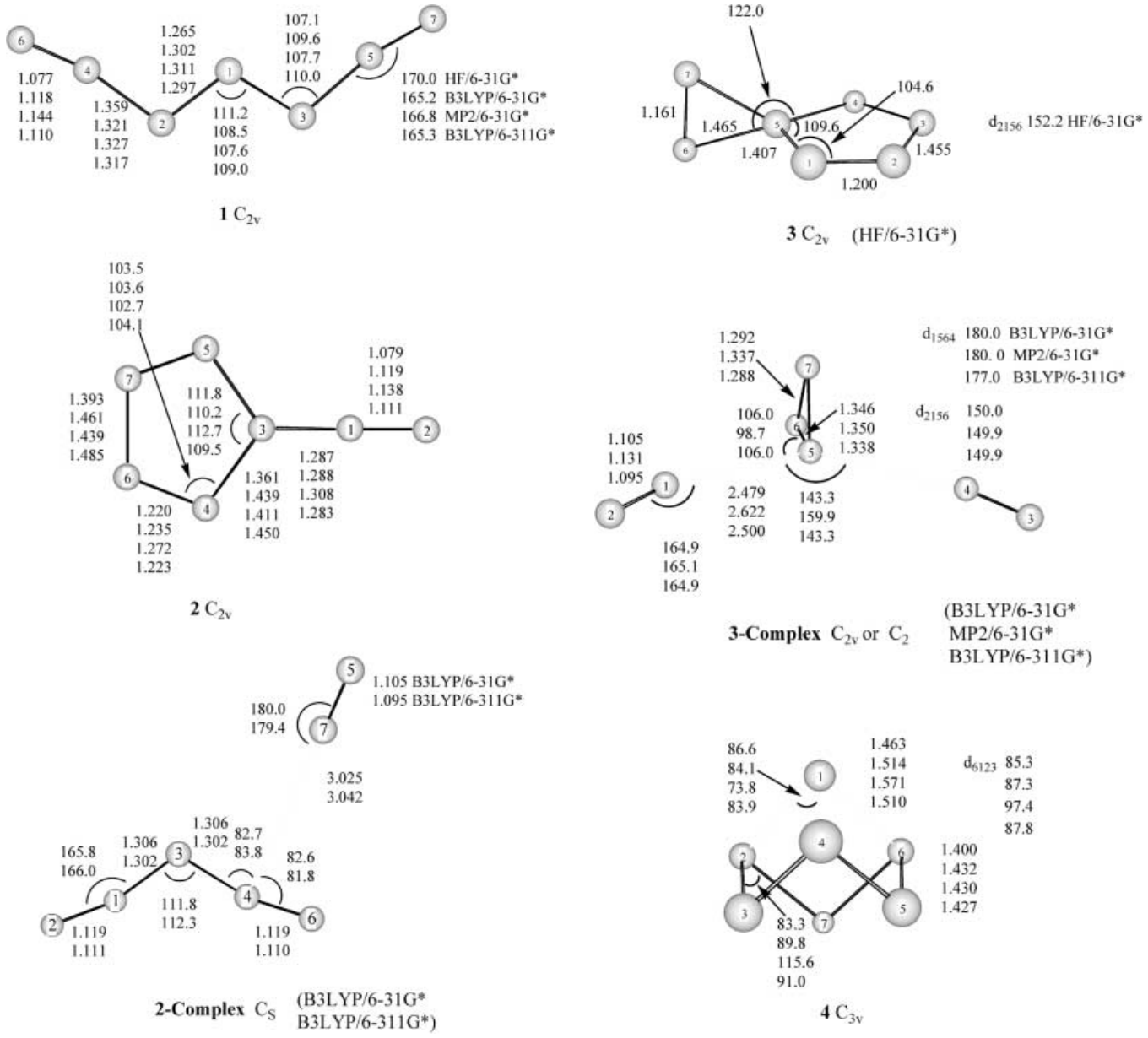

Fig. 1. a Structures **1**–**2** of N_7^+, with bond lengths in angstroms and bond angles in degrees. **b** Structures **3**–**4** of N_7^+, with bond lengths in angstroms and bond angles in degrees

3.2 N_7^- isomers

The open-chain structure **5** of N_7^-, as shown in Fig. 2a, is characterized as a minimum with all real vibrational frequencies at the HF/6-31G* and B3LYP/6-31G* levels; however, there are two imaginary frequencies ($113i$ and $27i$ cm^{-1}) at the MP2/6-31G* level and an imaginary frequency ($119i$ cm^{-1}) at the B3LYP/6-311 + G* level. Following the imaginary vibrational frequency, a structure with C_2 symmetry (the value of the dihedral angle of N3–N1–N2–N4 is 150.2° and 175.4° with the MP2 and B3LYP methods, respectively) with all-real vibrational frequency was obtained. Michels et al. [17] previously suggested that an open-chain structure with C_2 symmetry is a local minimum at the RHF/6-31 + G* and MP2/6-31 + G* levels of theory. Structure **5** has a slightly higher energy than structure **6** with the HF/6–1G* and B3LYP/6-31G* methods; however, it lies energetically lower than **6** with the more accurate MP2/6-31G* and B3LYP/6-311 + G* methods by 3.2 and 3.7 $kcalmol^{-1}$, respectively (Table 2). Therefore, structure **5** (C_{2v} or C_2) can be regarded to be the most stable species among the N_7^- clusters.

The terminal bond length of structure **5** (i.e., N4–N6 or N5–N7) is 1.163 Å. It is substantially longer than the experimental triple-bond length 1.098 Å of the nitrogen molecule [23]. The bond length of N2–N4 (or N3–N5) is 1.216 Å, which is slightly shorter than the double-bond length of HN = NH (1.252 Å). The bond length of N1–N2 (or N1–N3) (1.414 Å) is near the single-bond length of H_2N–NH_2 (1.449 Å) [23], thus, it can be regarded as a typical single bond. Figure 2a also shows that all the

central angles (i.e., ∠312, ∠124 and ∠135) are somewhat smaller than 120° and the terminal angles (∠642 and ∠753) are close to 180° at the four theoretical levels.

The NLMO analysis suggests that, in structure **5**, the bonds of N2–N4 (or N3–N5) and N4–N6 (or N5–N7) are both double bonds and that the N1–N2 (or N1–N3) bond

Table 1. Total energies (*E*) (hartree) and the zero-point energy (*ZPE*) (kcalmol^{-1}) for the N_7 ionic isomers

Isomers		HF/6-31G*		B3LYP/6-31G*		MP2/6-31G*		B3LYP/6-311(+)G*	
		E	ZPE	*E*	ZPE	*E*	ZPE	*E*	ZPE
N_7^+	**1** ($^1A_1$, C_{2v})	– 380.63 78285	20.1	– 382.74 55189	18.3	– 381.762 0915	17.8	– 382.8410 263	18.3
	2 ($^1A_1$, C_{2v})	– 380.58 28783	22.0	– 382.70 10962	17.6	– 381.717 5044	17.5	– 382.7925 165	17.4
	3 ($^1A_1$, C_{2v})	– 380.51 18566	21.0						
	4 ($^1A_1$, C_{3v})	– 380.19 85726	20.3	– 382.39 15689	16.5	– 381.427 6679	23.4	– 382.4678 092	16.3
N_7^-	**5** ($^1A_1$, C_{2v})	– 380.86 65255	18.6	– 383.06 84178	16.6	– 382.049 0312	16.7	– 383.1972 773	16.2
	6 ($^1A'$, C_s)	– 380.89 10304	21.3	– 383.07 09098	17.9	– 382.046 8966	18.1	– 383.1934 480	17.8
	7 ($^1A'$, C_s)	– 380.75 19910	20.4	– 383.04 74172	17.3	– 382.065 9622	16.9	– 383.1651 563	17.1
	8 ($^1A'$, C_s)	– 380.86 89812	21.8	– 383.04 65696	17.9	– 382.035 8498	17.4	– 383.1617 991	17.8
	9 ($^1A_1$, C_{2v})	– 380.65 01134	16.6	– 382.88 64277	16.2	– 381.919 0882	57.1	– 383.0053 634	15.7

Table 2. Relative energies (kcal mol^{-1}) with ZPE correction for the N_7 ionic isomers

Isomers		HF/6-31G*	B3LYP/6-31G*	MP2/6-31G*	B3LYP/6-311(+)G*
N_7^+	**1** ($^1A_1$, C_{2v})	64.1	44.0	61.1	48.4
	2 ($^1A_1$, C_{2v})	110.5	71.1	88.7	77.9
	3 ($^1A_1$, C_{2v})	144.1			
	4 ($^1A_1$, C_{3v})	340.0	264.3	276.5	280.6
N_7^-	**5** ($^1A_1$, C_{2v})	0.0	0.0	0.0	0.0
	6 ($^1A'$, C_s)	−12.7	−0.3	3.2	3.7
	7 ($^1A'$, C_s)	73.7	13.8	−10.0	20.8
	8 ($^1A'$, C_s)	1.7	15.0	9.5	23.6
	9 ($^1A_1$, C_{2v})	133.8	113.8	121.0	119.6

Table 3. The lowest vibrational frequencies (cm^{-1}) for the N_7 ionic isomers

Isomers		HF/6-31G*	B3LYP/6-31G*	MP2/6-31G*	B3LYP/6-311(+)G*
N_7^+	**1** ($^1A_1$, C_{2v})	139 (A_1)	130 (A_1)	123 (A_1)	131 (A_1)
	2 ($^1A_1$, C_{2v})	56 (B_1)	76*i* (B_2)→C_s 28 (A″)	38 (B_1)	259*i* (B_2)→C_s 24 (A′)
	3 ($^1A_1$, C_{2v})	196 (B_1)	Complex C_{2v} 43 (A_1)	Complex C_{2v} 27 (B_1)	Complex C_{2v} 43 (A_1)
	4 ($^1A_1$, C_{3v})	293 (E)	350 (E)	465 (A_1)	348 (E)
N_7^-	**5** ($^1A_1$, C_{2v})	54 (B_1)	67 (B_1)	113*i* (A_2), 27*i* (B_1)→C_2 36 (B)	119*i* (A_2)→C_2 76 (B)
	6 ($^1A'$, C_s)	158 (A′)	170 (A′)	171 (A′)	179 (A′)
	7 ($^1A'$, C_s)	399 (A′)	136 (A″)	222 (A″)	130 (A″)
	8 ($^1A'$, C_s)	276 (A″)	217 (A′)	268 (A′)	206 (A′)
	9 ($^1A_1$, C_{2v})	109 (A_2)	62 (A_2)	72 (A_2)	22*i* (A_2)→ C_2 32 (A)

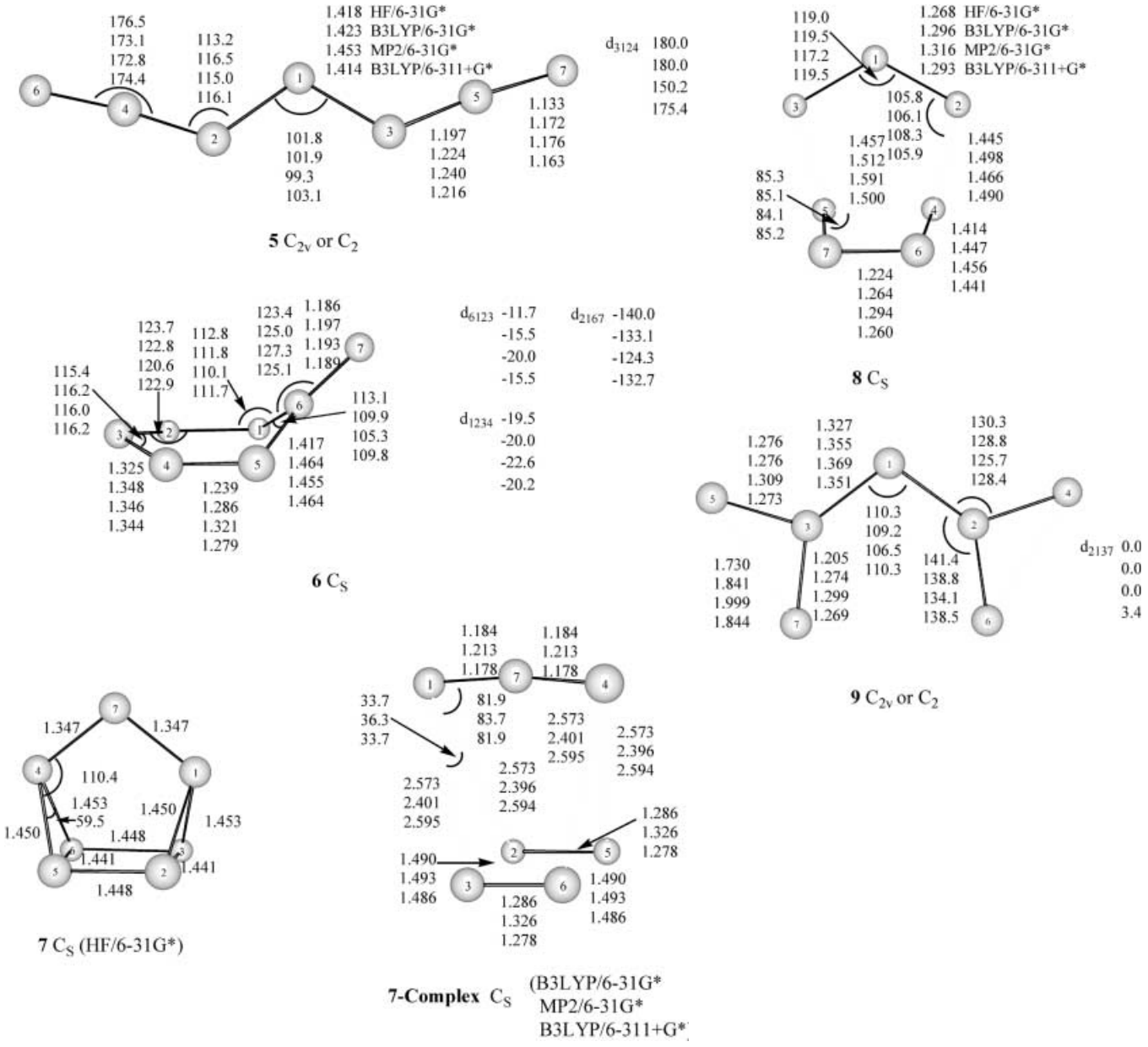

Fig. 2. a Structures **5**–**7** of N_7^-, with bond lengths in angstroms and bond angles in degrees. **b** Structures **8**–**9** of N_7^-, with bond lengths in angstroms and bond angles in degree

is a single bond. The negative charge of this anion mainly distributes on N1 (−0.40), N2 (or N3) (−0.18), and N6 (or N7) (−0.28).

As can be seen in Fig. 2a, structure **6** has C_s symmetry and contains a six-membered ring. The optimized geometries show that the six-membered ring favors the boat conformation. The vibrational frequencies of structure **6** are all real, so it is a local minimum on the potential-energy hypersurface.

For structure **6**, the bond length of N6–N7 is 1.189 Å and that of N1–N2 (or N4–N5) is 1.279 Å. Obviously, the N6–N7 bond is between double and triple bonds, while the N1–N2 (or N4–N5) bond is between aromatic and double bonds. The bond length of N1–N6 (or N5–N6) is 1.464 Å and that of N2–N3 (or N3–N4) is 1.344 Å, which are close to the single-bond length (1.449 Å) and the aromatic N–N bond length (1.35 Å), respectively. The situation of N1–(N6 = N7)–N5 is, geometrically and probably electronically, similar to that of N3–(N1 = N2)–N6 in structure **11a** studied by Fau and Bartlett [5]. The NLMO analysis indicates that the bonds of N1–N2, N4–N5 and N6–N7 are double bonds; the other bonds are single bonds. The negative charge of this anion mainly resides on N7 (−0.30) and N3 (−0.25).

The HF optimization of structure **7** results in a cage consisting of two five-membered rings, two trigonal rings, and one four-membered ring (Fig. 2a) with the bond lengths of N1–N7 (or N4–N7), N2–N3 (or N5–N6), and N2–N5 (N3–N6) being 1.347, 1.441, and 1.448 Å, respectively. The B3LYP and MP2 optimizations lead to a complex (structure **7**-complex) composed

Table 4. Dissociation energies to O_2 or N_2 (kcalmol^{-1} of each atom) with ZPE correction

	O_6	O_8	N_7^+				N_7^-				
			1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
HF	22.7	21.6	60.6	65.8	72.0	100.0	39.9	38.1	50.4	40.1	59.0
B3LYP	–	–	53.7	57.5		85.1	24.5	24.4	26.5	26.6	40.7
MP2	16.8	15.4	59.1	63.1		89.9	33.2	33.7	31.8	34.5	50.7
Ref.	[27]	[28]									

of a four-membered N_4 ring and an open N_3 chain with the length of N1–N2 being 2.594 Å, as seen in Fig. 2b. Structures **7** and **7**-complex are less stable in energy than structure **5** by 73.7, 13.8, and 20.8 kcalmol^{-1} at the HF/6-31G*, B3LYP/6-31G*, and B3LYP/6-311 + G* levels, respectively, but are more stable by 10.0 kcalmol^{-1} at the MP2/6-31G* level. Table 3 shows that all the vibrational frequencies of structures **7** and **7**-complex are real, which indicates that they are local minima. NLMO analysis implies that, in structure **7**-complex, N1–N7 is a triple bond; the N2–N5 and N3–N6 bonds are double bonds and the other bonds are single bonds.

Structure **8** is also a local minimum without any imaginary vibrational frequencies. As shown in Fig. 2b, it contains a five-membered ring fused with a four-membered ring with C_s symmetry. It is energetically slightly higher than structure **5** by 1.7, 15.0, 9.5, and 23.6 kcalmol^{-1}, respectively, with the four levels used. From the structural perspective, the bond lengths of N1–N2 (or N1–N3) and N6–N7 (1.293 and 1.260 Å) are close to the double-bond length (1.252 Å), while other bond lengths are close to the typical single-bond length (1.449 Å). The NLMO results also confirm this conclusion.

The last structure optimized was **9**, seen in Fig. 2b with C_{2v} symmetry. It has no imaginary vibrational frequency at the HF/6-31G*, B3LYP/6-31G*, and MP2/6-31G* levels of theory, whereas it has a small imaginary vibrational frequency ($22i$ cm^{-1}) at the B3LYP/6-311 + G* level; thus, this structure is a local minimum or very close to a minimum. When following the imaginary vibrational frequency, we optimized a structure with C_2 symmetry (the value of the dihedral angle of N3–N1–N2–N4 is 3.4°) with all-real frequency. Structure **9** is the least stable species among the five N_7^- isomers and lies energetically higher by about 110–135 kcalmol^{-1} than structure **5**. Owing to its high energy, there will be no further discussion for this isomer.

Compared with the energy of the N_2 molecule (−108.9377345, −109.5185509, and −109.2552776 hartree at the HF/6-31G*, B3LYP/6-31G*, and MP2/6-31G* levels, respectively), the N_7 ionic clusters lie energetically much higher than 7/2 N_2. The dissociation energies for the nitrogen compounds (per mole of atoms) are shown in Table 4 along with those for the O_6 and O_8 systems for comparison. The relative energies with ZPE correction for the N_7^+ cations (**1**–**4**) are more than 50 kcalmol^{-1} per mole of nitrogen atoms, while those for the N_7^- anions (**5**–**9**) are more than 20 kcalmol^{-1}. Each of them is 2–5 times greater than those of the oxygen HEDM at the same level of theory (Table 4). The high energy content of these N_7 ionic clusters suggests that they may be useful as explosives or propellants just like other nitrogen clusters [1, 2].

4 Conclusions

The geometries, energies, harmonic vibrational frequencies, and bonding for four isomers of N_7^+ and five isomers of N_7^- have been reported using ab initio and DFT methods. Vibrational frequency analyses show that the nine isomers of the N_7 ionic clusters are minima or very close to the minima at the HF/6-31G*, B3LYP/6-31G*, MP2/6-31G*, and B3LYP/6-311(+) G* levels of theory. The most stable isomer of N_7^+ is structure **1,** with C_{2v} symmetry, similar to those for the known odd-number nitrogen cations (N_5^+ and N_9^+ clusters) with the open-chain structures. The most stable species for N_7^- is also an open-chain structure **5**, with C_{2v} or C_2 symmetry. From the analyses of the dissociation energies to N_2 molecules for the N_7 ionic compounds, it is suggested that if the N_7 ionic clusters could be synthesized, they are likely to be potential high-energy-density materials.

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