

Regular article

Structures and stability of N_9 , N_9^- and N_9^+ clusters

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Received: 15 June 1999 / Accepted: 11 October 1999 / Published online: 14 March 2000

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Abstract. Ab initio molecular orbital calculations for N_9 , N_9^- and N_9^+ isomers were carried out at the HF/6-31G*, B3PW91/6-31G*, B3LYP/6-31G* and MP2/6-31G* levels of theory. Stable equilibrium geometric structures were determined by harmonic vibrational frequency analyses at the HF/6-31G*, B3PW91/6-31G* and B3LYP/6-31G* levels of theory. The most stable free-radical N_9 cluster is structure **1** with C_{2v} symmetry and that of anion N_9^- is structure **3** with C_s symmetry. Only one stable structure of the N_9^+ cation with C_{2v} symmetry was predicted. Their potential application as high-energy-density materials has been examined.

Key words: Nitrogen clusters – Ab initio molecular orbital calculation

1 Introduction

A lot of theoretical investigations have been reported in the literature on nitrogen clusters [1–12]. These theoretical investigations on even-number nitrogen clusters have drawn the conclusion that they are likely to be candidates for high-energy-density materials (HEDMs) [2, 8]; however, how to synthesize them is still an open question. At present only three bulk species which contain only nitrogen atoms are known experimentally. Except for N_2 and N_3^- , they were not prepared until 1998, when N_5^+ was synthesized and characterized as a hexafluoroarsenate at the end of 1998 by Christe et al. [13]. The N_5^+ cation is the first new all-nitrogen species to be synthesized in isolable quantities in more than a century. Pentazoles (RN_5) have had a long history of controversy regarding their stability and isolation since Lifschitz reported the synthesis of the silver salt, AgN_5 . This synthesis was promptly refuted [14]. Further attempted syntheses were not successful until 1957,

when Huisgen and Uzi [15] reported the synthesis of the phenylpentazole derivative. In addition to even-number nitrogen clusters, there have also been theoretical publications on possible stable N_7 free-radical isomers [16] as well as N_3^- , N_5^- and N_7^- [17–19]. The most stable N_7 isomers are open-chain C_s and C_2 structures having almost identical total energy. This work suggests the possibility that nitrogen clusters with odd-number nitrogen atoms are likely to be stable and to be potential HEDMs if they can be synthesized. Glukhovtsev et al. [2] found that N_8 (C_s) with an N_5 five-membered ring and an N_3 open structure is the isomer with the lowest energy. In the present article, we report an ab initio study of N_9 clusters, i. e., another odd-number nitrogen cluster. Geometric structures of neutral and ionic N_9 isomers are optimized theoretically; however, no local minima containing the cyclic N_5 form are found. Only four isomers with lower spin and one isomer with higher spin for N_9 are definitely local minima on the UHF/6-31G*, B3PW91/6-31G* and B3LYP/6-31G* potential energy hypersurfaces (PES) (Fig. 1). The geometries of the N_9^- and N_9^+ clusters are also fully optimized at the HF/6-31G*, B3PW91/6-31G*, B3LYP/6-31G* and MP2/6-31G* levels of theory. Finally, the estimates of the energy difference between nitrogen clusters and 9/2 N_2 are determined using HF, B3PW91, B3LYP and MP2 methods and these structures are confirmed as HEDM candidates.

2 Computational method

Ab initio molecular orbital (MO) calculations were carried out by using the Gaussian 94 program package. All calculations were done on an SGI O₂ workstation and an Origin 2000 server. Equilibrium geometric structures of N_9 clusters and their corresponding ions, N_9^+ and N_9^- , were fully optimized at the HF/6-31G*, B3PW91/6-31G*, B3LYP/6-31G* and MP2/6-31G* levels of theory. Vibrational frequencies were computed at the HF/6-31G*, B3PW91/6-31G* and B3LYP/6-31G* levels. The default integration convergence accuracy of Gaussian 94 was applied in the present article.

3 Results and discussion

3.1 N_9 clusters

Perspectives of five N_9 isomers are shown in Fig. 1. The optimized geometric parameters, total energies and zero-point energies of neutral N_9 clusters are listed in Tables 1–3.

It appears that neutral N_9 should be a free radical. Nevertheless, in five free-radical N_9 isomers optimized at the HF/6-31G*, B3PW91/6-31G*, B3LYP/6-31G* and MP2/6-31G* levels four of the structures are stable with all-real vibrational frequencies and the other one (structure 4) is unstable with imaginary frequencies at the B3PW91/6-31G* level or dissociates at the B3LYP/6-31G* level.

Open-chain structure 1, with C_{2v} symmetry, is the lowest in energy among the N_9 isomers at the four

levels. Harmonic vibrational frequency analysis shows that structure 1 is a local minimum (the lowest vibrational frequency is 97.6 cm^{-1} at the HF/6-31G* level, 87.4 cm^{-1} at the B3PW91/6-31G* level and 87.5 cm^{-1} at the B3LYP/6-31G* level). Similar to open-chain N_6 [20–22] and N_7 [16], the most stable isomer of N_9 among its corresponding isomer is with open-chain structure. As shown in Table 1, the bond length of N6–N8 (about 1.123 \AA) in structure 1 is somewhat longer than the experimental triple-bond length of 1.094 \AA of the nitrogen molecule, N_2 , and the bond length of N6–N4 (about 1.265 \AA) is longer by 0.013 \AA than the experimental value of $\text{HN}=\text{NH}$ (1.252 \AA). The distances N4–N2 and N1–N2 lie in-between the double-bond length of $\text{HN}=\text{NH}$ (1.252 \AA) and the experimental single-bond length of $\text{H}_2\text{N}-\text{NH}_2$ (1.449 \AA) at the four levels. The central bond angles ($\angle 312$) are 108.0° at the four levels. Of particular interest is the hypervalent

Fig. 1. Geometric structures of N_9 , N_9^- and N_9^+ clusters

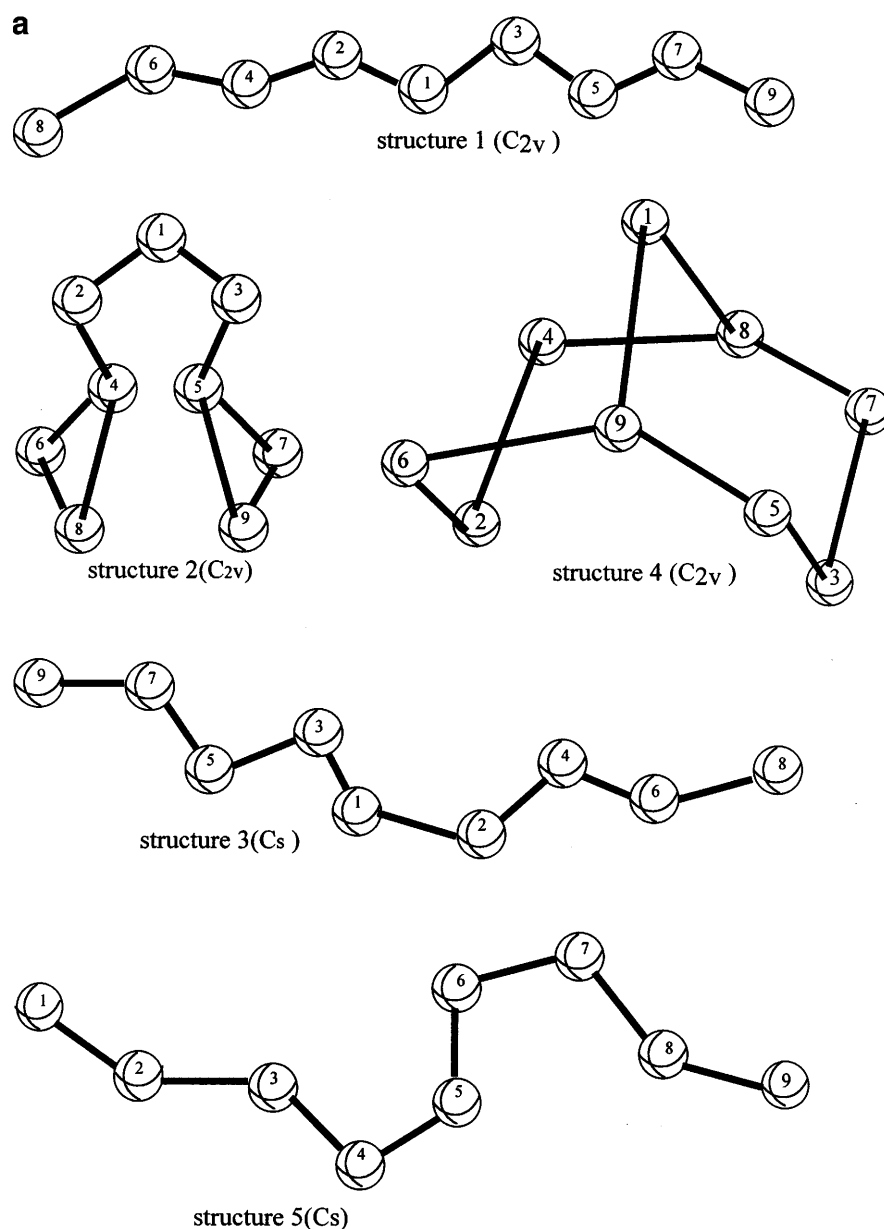
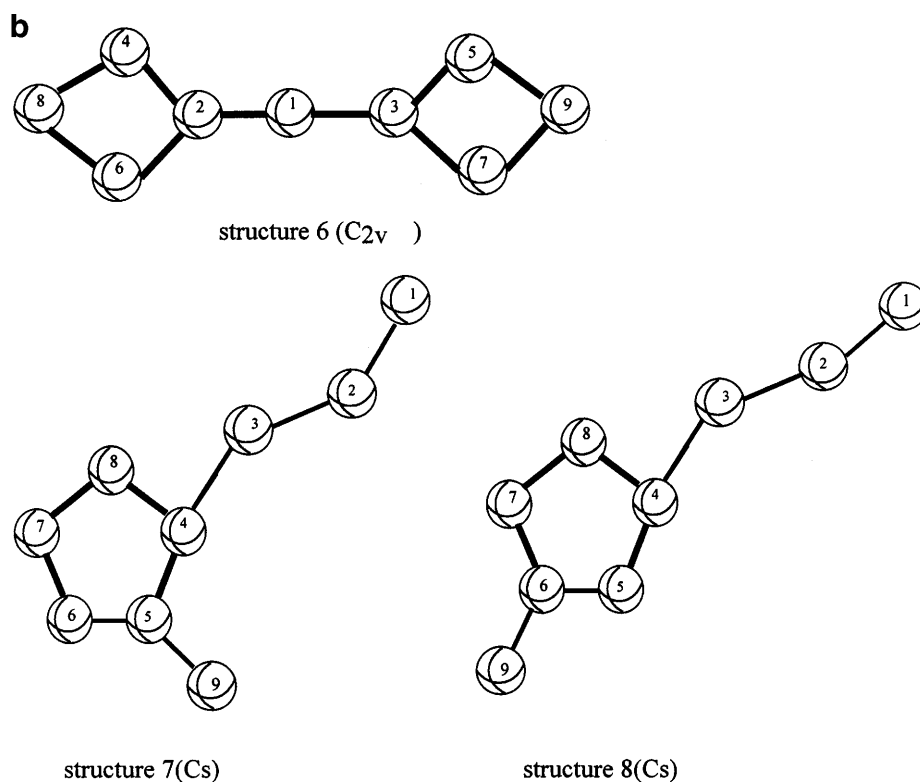


Fig. 1. (Contd.)



nature of structure **1**: the bond lengths of N6-N8 (about 1.123 Å) and N4-N6 (about 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 isomers [20–22] and N_7 isomers [16]; however, Glukhovtsev and Schleyer [22] suggested that none of the nitrogen atoms in the N_6 open-chain structures form more than four covalent bonds by natural bonding orbital analysis. The hypervalent nature of the open-chain nitrogen isomers can be questioned at present. Further appropriate studies exploring the hypervalent nature are necessary.

Structures **3** and **5**, with C_s symmetry, are also open-chain structures. Structures **3** and **5**, can be discussed similarly to structure **1**. Structures **3** and **5** are characterized as a local minimum having all-real vibrational frequencies at the UHF/6-31G*, B3PW91/6-31G* and B3LYP/6-31G* levels, respectively (Tables 1, 2). At the HF/6-31G* level, the bond length (in structure **3**) characters of N1-N2 (1.266 Å), N1-N3 (1.300 Å), N2-N4 (1.371 Å) and N3-N7 (1.350 Å) lie in-between the experimented double-bond length (1.252 Å) of N_2H_2 and the single-bond length (1.449 Å) of H_2N-NH_2 . The bond lengths for N5-N7 (1.258 Å) and N4-N6 (1.258 Å) are near to that of $HN=NH$ and bond length of N7-N9 (1.102 Å) is near to the bond length of $N\equiv N$ (1.094 Å). The relative energy of structure **3** is slightly higher than that of structure **1** and that of structure **5** is slightly higher than that of structure **3**.

Charge distribution analyses of N_9 clusters were carried out at the HF/6-31G*, B3PW91/6-31G* and B3LYP/6-31G* levels. The total values of the electron

density calculated at the HF/6-31G* level for N_9 isomers are shown in Fig. 2.

Compared the Mulliken charge distribution in structures **1** and **3**, the charge on N1 changes from -0.047 to -0.033 , that on N2 from -0.041 to -0.031 and that on N3 from -0.041 to -0.069 at the HF/6-31G* level. The Mulliken charges with density functional theory methods show a similar pattern, but the charge differences are smaller. Accordingly the bond length of N1-N2 in structure **1** is longer than that of N1-N2 in structure **3**. Based on the electron density on N1, N2 and N4 of structure **1**, we know that the repulsive force between the charges on N1 and N2 is smaller than that between N2 and N4, so the bond length of N1-N2 is shorter than that of N2-N4 at the HF/6-31G* level.

In view of the previous discussions, the electron density distribution on each nitrogen atom is consistent with the value of the bond length. This coincides with the inherent relations among charge density, bond order and bond lengths in covalent bond theory.

In the same manner, structures **2** and **4**, with C_{2v} symmetry, are also predicted to be the local minima on their PES with all-real vibrational frequencies at the HF/6-31G* level (Table 3). The bond length of N1-N2 (1.299 Å) of structure **2** lies in-between the bond length of a double bond (N_2H_2) and a single-bond (N_2H_4). The characters of the other bonds in structure **2** are all single bonds with bond lengths in the range 1.374–1.436 Å at the HF/6-31G* level or from 1.425 to 1.495 Å at the B3LYP/6-31G* level. However, the bond angles are smaller than the normal bond angle of the equivalent sp^3 hybrid orbital, some of which (< 468) are even smaller than 90° ; therefore, this isomer should be a strained

Table 1. The optimized geometric parameters of N₉ clusters (6-31G*). Bond lengths are given in angstroms and bond angles in degrees

Isomers	Parameter	HF	B3PW91	B3LYP	MP2	
N ₉	1 (C _{2v}) (² A ₂)	r12	1.298	1.305	1.309	1.288
		r24	1.352	1.364	1.373	1.417
		r46	1.256	1.255	1.261	1.287
		r68	1.102	1.135	1.137	1.129
		a213	108.0	107.4	107.5	108.0
		a421	107.5	106.5	106.4	106.0
		a246	109.0	111.9	111.5	171.8
		a468	173.1	169.6	173.1	104.0
	2 (C _{2v}) (² B ₁)	r12	1.299	1.289	1.290	
		r24	1.374	1.445	1.468	
		r46	1.436	1.415	1.425	–
		r68	1.295	1.294	1.296	
		a213	113.0	121.4	122.0	
		a421	107.0	103.4	103.0	
		a246	121.0	129.2	129.0	
		a468	54.0	62.8	63.0	
	3 (C _s) (² A'')	r12	1.266	1.284	1.286	1.237
		r24	1.371	1.395	1.408	1.472
		r13	1.300	1.318	1.324	1.333
		r35	1.350	1.359	1.367	1.397
		r46	1.258	1.250	1.256	1.275
		r68	1.097	1.135	1.136	1.116
		r57	1.258	1.257	1.263	1.297
		r79	1.102	1.135	1.137	1.107
		a213	116.0	116.2	108.0	116.4
		a421	115.2	114.3	107.5	114.3
		a975	176.0	169.6	172.2	171.6
		a357	108.0	112.1	111.7	103.9
		a246	107.3	110.9	109.0	102.2
	a468	175.9	170.9	173.1	172.6	
	4 (C _{2v}) (² B ₂)	r18	1.395	1.392		
		r24	1.246	1.234		
		r95	1.517	1.680		
a487		125.0	121.9			
a426		125.0	133.8			
a248		101.2	97.6			
5 (C _s) (² A')	r12	1.098	1.136	1.134		
	r23	1.260	1.257	1.252		
	r34	1.360	1.403	1.390	–	
	r45	1.294	1.279	1.277		
	r56	1.301	1.338	1.277		
	r67	1.343	1.336	1.331		
	r78	1.267	1.289	1.330		
	r89	1.101	1.136	1.136		
	a123	173.0	170.7	170.6		
	a234	107.9	110.3	110.9		
	a345	114.9	114.4	114.4		
	a456	116.7	117.6	117.5		
	a567	113.4	113.4	111.9		
a678	116.0	118.2	118.3			
a789	171.5	165.2	165.5			

molecule. Although the energy of structure **2** at all levels is higher than those of the others, structure **2** should have certain rigidity and thus is mechanically stable due to the lowest frequency of 175.9 cm⁻¹ at the HF/6-31G* level, 168.4 cm⁻¹ at the B3PW91/6-31G* level and 163.0 cm⁻¹ at the B3LYP/6-31G* level.

Structure **4** can be visualized as a derivative of the N₆ (D_{3h}) isomer. The bond length of N6-N9 (1.517 Å) at the HF/6-31G* level in structure **4** is slightly longer by 0.068 Å than the experimental N-N bond length in N₂H₄ (1.449 Å). The bond length of N1-N9 (1.395 Å) lies in-

between that of a single bond (N₂H₄) and a double bond (N₂H₂), and the bond length of N2-N4 (1.246 Å) is slightly shorter by 0.006 Å than that of N₂H₂; therefore, structure **4** is a local minimum at the HF/6-31G* level with the lowest frequency of 210.4 cm⁻¹. However, the bond length of N5-N9 (1.680 Å) is too long at the B3PW91/6-31G* level and dissociates into 3N₃ at the B3LYP/6-31G* level, i.e., structure **4** can be divided into three fragments N9-N1-N8, N6-N2-N4 and N5-N3-N7 due to the N-N bonds which are broken. Generally speaking, the results at the B3PW91/6-31G* and

Table 2. The optimized geometric parameters of N_9^- and N_9^+ clusters (6-31G*). Bond lengths are given in angstroms and bond angles in degrees

Isomers		Parameter	HF	B3PW91	B3LYP	MP2
N_9^-	1 (C_{2v}) (1A_1)	r12	1.264	1.294	1.298	1.309
		r24	1.436	1.437	1.456	1.473
		r46	1.209	1.223	1.230	1.247
		r68	1.119	1.157	1.160	1.167
		a213	114.6	112.1	112.0	111.0
		a421	106.0	105.1	105.0	103.6
		a246	110.0	114.4	114.0	111.7
		a468	176.0	187.4	173.0	180.0
	2 (C_{2v}) ($^1A'$)	r12	1.271	1.300	1.304	–
		r24	1.417	1.428	1.443	–
		r46	1.368	1.378	1.387	–
		r68	1.330	1.384	1.390	–
		a213	120.0	120.8	121.0	–
		a421	103.5	104.2	104.0	–
		a246	133.0	133.0	132.0	–
		a468	51.0	59.9	60.0	–
	3 (C_s) ($^2A''$)	r12	1.262	1.293	1.296	1.281
		r24	1.254	1.253	1.233	1.153
		r13	1.441	1.446	1.466	1.480
		r35	1.470	1.223	1.227	1.468
		r68	1.119	1.565	1.694	1.161
		r79	1.116	1.157	1.157	1.215
		a213	122.0	124.0	128.0	167.0
		a421	105.0	105.5	105.0	105.0
	4 (C_{2v}) (1A_1)	r18	1.425	1.400	1.409	1.406
		r24	1.266	1.324	1.331	1.353
		r48	1.433	1.356	1.364	1.372
		a248	104.0	111.4	111.5	111.4
		a426	119.6	117.8	118.0	117.4
		a184	119.7	116.3	116.3	116.4
		a213	180.0	121.1	180.0	–
		a421	141.0	140.9	141.3	–
	6 (C_{2v}) (1A_1)	r12	1.237	1.266	1.269	–
		r84	1.291	1.333	1.334	–
		r42	1.422	1.427	1.446	–
		r26	1.412	1.427	1.442	–
a213		180.0	121.1	180.0	–	
a421		141.0	140.9	141.3	–	
a842		84.8	84.6	85.0	–	
a621		130.0	128.4	129.0	–	
N_9^+	1 (C_{2v}) (1A_1)	r12	1.292	1.315	1.320	1.327
		r24	1.253	1.296	1.300	1.210
		r46	1.386	1.314	1.326	1.333
		r68	1.076	1.117	1.118	1.109
		a213	106.0	104.5	104.7	108.0
		a421	110.0	107.9	107.9	106.0
		a246	106.6	110.3	110.0	104.0
		a468	176.0	174.8	176.0	172.0

B3LYP/6-31G* levels are more reliable when considering electron correlation effects; thus, structure **4** is predicted to be unstable.

Furthermore, structures **1** (4A_2) and **3** ($^4A''$) with spin multiplicity of **4** were also investigated at the HF/6-31G* level and were determined to be unstable with one imaginary frequency.

3.2 N_9^- clusters

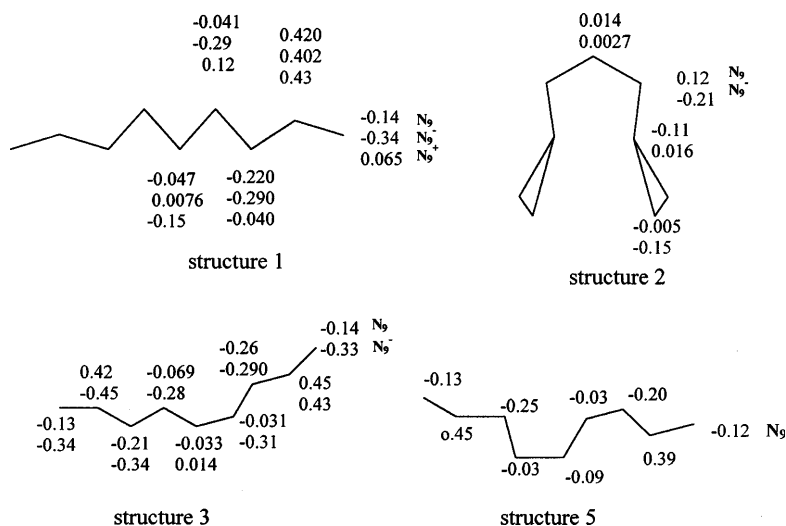
The optimized geometric parameters of ionic N_9 clusters are listed in Table 2. Five geometric structures of N_9^-

isomers were optimized at the HF/6-31G*, B3PW91/6-31G*, B3LYP/6-31G* and MP2/6-31G* levels of theory. Four structures were determined to be local minima on their PES with all-real vibrational frequencies. Structure **1** (N_9^-), with C_{2v} symmetry, and structure **3** (N_9^-), with C_s symmetry, are predicted to be stable and to have nearly the same total energies. Structure **3** is slightly lower in energy than structure **1**, and we can discuss these two structures in a similar way to neutral cluster structures **1** (N_9) and **3** (N_9). The single bond character in anionic structures **1** (N_9^-) and **3** (N_9^-) differs slightly from that of H_2N-NH_2 (1.449 Å). At the HF/6-31G* and MP2/6-31G* levels, the bond lengths in

Table 3. Total energies (E) (hartrees) and the zero-point energy (ZPE) (kcal/mol) for the N_9 , N_9^- and N_9^+ isomers. The integers in parentheses are the number of imaginary vibrational frequencies

Isomers	HF/6-31G*		B3PW91/6-31G*		B3LYP/6-31G*		MP2/6-31G*
	E	ZPE	E	ZPE	E	ZPE	E
$C_{2v}({}^2A_2, 1) N_9$	-489.73826	24.9(0)	-492.28450	23.6(0)	-492.47792	23.1(0)	-491.13058
$C_{2v}({}^2B_1, 2) N_9$	-489.498989	24.7(0)	-492.09410	23.0(0)	-492.27685	22.2(0)	-
$C_s({}^2A'', 3) N_9$	-489.73022	24.9(0)	-492.28121	23.3(0)	-492.47467	22.9(0)	-491.13052
$C_{2v}({}^2B_2, 4) N_9$	-489.51728	25.4(0)	-492.12064	21.2(3)	(Dissociated)	-	(Dissociated)
$C_s({}^2A'', 5) N_9$	-489.72529	24.7(0)	-492.27967	23.2(0)	-492.47311	22.8(0)	-
$C_{2v}({}^1A_1, 1) N_9^-$	-489.74522	25.8(0)	-492.36588	23.3(0)	-492.55729	22.9(0)	-491.2525
$C_{2v}({}^1A', 2) N_9^-$	-489.49433	26.7(0)	-492.17953	23.5(0)	-492.35814	22.7(0)	-
$C_s({}^2A'', 3) N_9^-$	-489.74601	26.0(0)	-492.37306	23.2(0)	-492.56561	22.6(0)	-491.2743
$C_{2v}({}^1A_1, 4) N_9^-$	-489.62543	28.3(0)	-492.25867	24.2(1)	-492.43968	23.1(1)	-491.1667
$C_{2v}({}^1A_1, 6) N_9^-$	-489.65065	27.3(0)	-492.27646	23.9(0)	-492.46014	23.1(1)	-
$C_{2v}({}^1A_1, 1) N_9^+$	-489.46239	26.0(0)	-491.98758	24.2(0)	-492.18227	23.7(0)	-490.9066

Fig. 2. Total value electron density plot calculated at the Hartree – Fock level for N_9 , N_9^- and N_9^+ clusters



structure **1** are in the range from 1.435 (N4-N2) to 1.473 Å (N5-N3) and in structure **3** (N_9^-) from 1.441 (N4-N2) to 1.480 Å (N5-N3). It is already known that inclusion of electron correlation can usually increase optimized bond lengths and enlarge differences among distinct single bonds. As usual, the MP2 method is known to overestimate the electron correlation effect and this results in some geometrical parameters being different from those of the HF method. Nguyen and co workers [23] suggested that the true bond lengths lie between the HF and MP2 values for molecules of this type. Structures **1** (N_9) and **3** (N_9^-) are reasonable local minima on both the HF/6-31G* and B3LYP/6-31G* PES and they would be possible candidates for experimental preparation.

Structure **6** can be regarded as coming from N_8 cubane isomer derivatives. Structures **4** and **6** (N_9^-) with C_{2v} symmetry calculated at the HF/6-31G* level are predicted to be local minima with all-real vibrational frequencies (Table 3). Some bond lengths of these two structures are nearly the same as that of H_2N-NH_2 and others lie in-between the bond length of a double bond and a single bond. Structure **4** is predicted to be unstable on the B3LYP/6-31G* PES with one imaginary frequency of $236.9i \text{ cm}^{-1}$ and on the B3PW91/6-31G* PES with a frequency of $216.2i \text{ cm}^{-1}$. Structure **6** is also a

local minimum on the B3PW91/6-31G* PES with a minimum frequency of 68.4 cm^{-1} , but on the B3LYP/6-31G* PES it has a small imaginary frequency of $14i \text{ cm}^{-1}$. Since the imaginary value is so small and the value is real with other methods, structure **6** may be considered as a stable structure.

The geometry parameters of structure **2** (N_9^-) with C_{2v} symmetry are similar to those of neutral N_9 (structure **2**), but only the bond lengths of N4-N6 and N6-N8 are shortened. Structure **2** is also predicted to be stable at the HF/6-31G*, B3PW91/6-31G* and B3LYP/6-31G* levels. The change in the charge distribution is shown in Fig. 2.

3.3 N_9^+ clusters

The systems of N_9^+ clusters as high-intensity-cluster ion sources can be used for various fast-beam spectroscopies [24]. Only one structure of the N_9^+ cluster, the open-chain N_9^+ , is found to be a local minimum with a lowest frequency of 98.1 cm^{-1} (HF/6-31G*), 95.0 cm^{-1} (B3PW91/6-31G*) and 91.6 cm^{-1} (B3LYP/6-31G*). Compared with the N_9^- anion and the neutral N_9 isomer (structure **1**), the bond length of N4-N2 in N_9^+ is shortened, that of N6-N4 is lengthened and the others have no obvious differences.

It was reported [2] for N_8 that the isomer with the lowest energy is the structure with a five-membered ring and an open N_3 chain. Based on the structure, we started the optimization from the N_9 isomers (structures **7** and **8**) containing a five-membered ring. From structure **7** for N_9 , N_9^+ and N_9^- , the result dissociated into $N_7 + N_2$, $N_5 + 2N_2$ and an open-chain N_9 , respectively; thus, structure **7** is not a stable structure. Similarly to this, from structure **8**, the geometries for N_9 , N_9^+ and N_9^- also dissociated into $N_5 + 2N_2$, $N_5 + 2N_2$ and $N_3 + 3N_2$, respectively, i.e., structures N_9 , N_9^+ and N_9^- containing the five-membered ring, we have designed at present, are not local minima.

Although the reaction path $N_9 \rightarrow 9/2 N_2$ cannot be analyzed and discussed on the corresponding PES in the present work, the energies of the N_2 molecule are -108.942 , -109.4771 and -109.518 au at the HF/6-31G*, B3PW91/6-31G* and B3LYP/6-31G* levels, respectively. The relative energies for isomers **1–5** are much higher than for $9/2 N_2$ molecules (Table 5) and are also taken as the formal measures of the energy content.

The high energy content of these N_9 isomers suggests that they may be useful as explosives or propellants, as noted in previous studies of the N_8 structure [10, 25–27]. An effective propellant is characterized by a high ratio of energy release to mass and by a high specific impulse, I_{sp} [28]. The ratios of the energy released to mass and I_{sp} are listed in Tables 6 and 7 as well as those of other HEDM candidates for comparison. At the HF and MP2 levels of theory the nitrogen compounds give dissociation energies (per mole of atoms) which are 1–3 times greater than those of the oxygen HEDM. Leininger et al. [10] 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 456 s. We see that N_9 (structure **2**), N_9^- (structure **2**) and N_9^+ (structure **1**) clusters outperform the standard oxygen/hydrogen mixture as propellants, while N_9 (structures **1, 3, 5**) and N_9^- (structures **1, 3, 6**) perform somewhat worse than the standard, according to the I_{sp} estimates.

Although structure **2** is clearly the most energetic, at the present there seems no obvious synthesis route to it due to it being such a high-lying structure on the PES. Structures **1, 3, 5** and **6** appear to be the most realistic targets for synthesis. Although structure **1, 3, 5** and **6** are not as energetic as the others, they are higher in energy than $9/2 N_2$ molecules, making them possible HEDMs (Table 7).

4 Summary

We have obtained the possible stable N_9 structures (**1, 2, 3, 5**) and stable N_9^- structures (**1, 2, 3, 6**) and stable N_9^+ . We have predicted their geometries, electronic structures and harmonic vibrational frequencies. The most stable isomer of N_9 is structure **1** (C_{2v}) and that of N_9^- is structure **3** (C_s). Only one open-chain N_9^+ cluster with C_{2v} symmetry was found in our present study. Analyses of dissociation energies and the I_{sp} of N_9 , N_9^- and N_9^+ isomers suggest that the possible stable N_9 , N_9^- and N_9^+ clusters could be potential HEDMs. The dissociation mechanism of polynitrogen should be further studied in future work.

Table 4. Relative energies (kcal/mol) of N_9 isomers (6-31G*)

Species	HF	B3PW91	B3LYP
$C_{2v}(^2A_2, \mathbf{1})$	0.0	0.0	0.0
$C_{2v}(^2B_1, \mathbf{2})$	149.8	118.8	125.2
$C_s(^2A'', \mathbf{3})$	5.0	1.8	1.8
$C_{2v}(^2B_2, \mathbf{4})$	139.1	100.3	–
$C_s(^2A'', \mathbf{5})$	7.9	2.6	2.7

Table 5. Relative energies (kcal/mol) of N_9^- and N_9^+ isomers (6-31G*)

Isomers	HF	B3PW91	B3LYP
$\mathbf{1}(C_{2v}) N_9^-(^1A_1)$	0.3	4.6	5.5
$\mathbf{2}(C_{2v}) N_9^-(^1A')$	158.5	121.6	130.2
$\mathbf{3}(C_s) N_9^-(^1A')$	0.0	0.0	0.0
$\mathbf{4}(C_{2v}) N_9^-(^1A_1)$	77.9	72.7	79.5
$\mathbf{6}(C_{2v}) N_9^-(^1A_1)$	61.1	61.2	66.6

Table 6. Dissociation energies to N_2 (kcal/mol of N atom)

	O_6	O_8	N_8 (D_{2d})	N_8 (D_{2h})	N_9				N_9^-				N_9^+
					1	2	3	5	1	2	3	6	1
HF	22.7	21.6	39.9	34.3	34.8	51.4	35.4	38.5	34.3	51.8	33.6	41.0	54.0
B3LYP	–	–	–	–	24.6	38.5	24.8	24.9	19.0	33.0	18.5	25.8	45.1
MP2	16.8	15.4	34.6	27.7	33.8	–	35.9	–	27.5	–	25.9	–	51.6
Ref.	[29]	[30]	[10]	[10]									

Table 7. Specific impulse (s) for N_9 , N_9^- and N_9^+ clusters as high-energy-density material candidates

	N_9				N_9^-				N_9^+
	1	2	3	5	1	2	3	6	1
HF	418	508	422	424	415	510	411	453	521
B3LYP	351	440	353	354	309	407	305	360	476
MP2	412	–	425	–	372	–	361	–	509

Supplementary material

Table 1. Harmonic vibration frequencies (cm^{-1}) and IR intensity (in *parentheses*) of stable N_9 clusters (6-31G*)

Species	HF	B3LYP	B3PW91
$1(^2A_2)$ freq.(IR)	97.6(0)	87.5(0)	87.4(0.1)
	211.3(2.6)	95.6(0)	96.1(0.1)
	586.6(26.2)	122.8(0)	124.8(0)
	785.7(9.8)	187.4(0.5)	189.3(0.8)
	1216.0(69.0)	258.9(0)	259.7(0)
	1217.0(34.0)	300.2(1.7)	302.7(1.6)
	1304.0(3.0)	306.3(0.1)	308.7(0.1)
	1445.6(0.2)	438.5(0.2)	445.3(0.2)
	1293.0(386.0)	497.2(11.0)	503.7(10.6)
	2263.0(3015.0)	501.7(0)	508.1(0)
	2303.7(273.0)	538.0(12.2)	546.1(12.3)
	104.0(0.2)	698.9(60.1)	705.1(54.6)
	124.7(0)	724.0(4.7)	728.5(4.4)
	304.4(0)	993.7(283.8)	1030.2(186.4)
	319.3(0)	1037.4(77.2)	1070.6(159.0)
	328.5(1.5)	1131.2(7.8)	1155.9(8.7)
	482.5(0)	1211.8(4.2)	1250.5(3.6)
	537.0(15.5)	1241.0(328.1)	1277.0(327.1)
	537.6(0)	1360.9(2.0)	1381.2(2.0)
	803.5(13.0)	2215.6(1778.2)	2245.2(1808.7)
$2(^2B_1)$ freq.(IR)	1135.6(3.7)	2239.6(85)	2269.3(87.0)
	640.5(10.0)	168.4(0)	219.3(0.8)
	1326.0(9.7)	212.3(4.1)	229.5(0)
	1636.0(10.2)	259.9(1.4)	301.0(0.9)
	1647.0(10.0)	332.2(2.4)	354.8(15.0)
	75.9(0)	365.5(1.0)	444.3(2.6)
	235.5(4.4)	436.5(0)	509.4(0)
	290.0(2.8)	512.5(3.6)	585.4(1.8)
	360.5(0.1)	556.6(0)	625.0(7.3)
	414.6(0)	596.9(3.7)	667.6(7.1)
	457.2(0)	658.2(4.1)	668.4(0)
	478.9(17.8)	762.2(0.5)	688.8(2.6)
	589.0(4.9)	832.8(220.0)	745.5(204.0)
	616.4(2.3)	850.7(0)	893.1(1)
	833.0(4.9)	891.1(312.7)	937.8(1.1)
	948.0(0)	929.2(0)	979.8(13.3)
	1002.0(16.4)	956.7(28.0)	1071.5(5.6)
	1051.0(31.8)	1121.5(1.5)	1081.0(0.6)
	1079.6(191.0)	1252.9(2.9)	1219.5(17.2)
	1124.0(5.1)	1368.4(94.0)	1342.6(170.0)
1187.0(37.3)	1456.1(255.8)	1430.1(35.7)	
$3(^2A'')$ freq.(IR)	1284.7(1.7)	1541.6(0.7)	1437.5(2.3)
	101.6(0.8)	45.9(0.1)	31.6(0.1)
	579.4(10.0)	88.7(0.2)	89.1(0.2)
	738.8(28.5)	101.2(0)	103.5(0)
	840.8(14.0)	156.9(0.3)	158.4(0.3)
	1202.0(37.6)	192.7(0.9)	194.1(0.8)
	1217.8(78.0)	286.9(2.7)	290.3(2.0)
	1244.7(490.0)	431.4(2.9)	435.9(2.4)
	1300.0(27.2)	443.8(2.5)	446.1(2.3)
	1393.0(33.0)	503.5(1.3)	510.1(1.4)
	2274.0(2168.0)	552.5(7.2)	558.0(7.1)
	2326.5(769.4)	589.3(12.0)	597.2(9.1)
	646.6(1.9)	647.6(67.1)	655.0(58.5)
	1112.5(2.6)	750.9(81.1)	769.8(56.8)
	103.8(0.1)	902.9(256.2)	935.2(247.8)
	131.0(0)	1018.2(66.7)	1058.4(85.7)
	209.3(0.6)	1118.8(40.4)	1139.9(31.2)
	216.9(0.4)	1185.9(419.6)	1220.0(435.6)
	322.6(0.3)	1229.1(45.4)	1263.3(39.7)
	451.8(0.6)	1337.1(30.7)	1359.4(34.2)
486.8(5.9)	2215.4(1323.0)	2244.7(1346.0)	

Table 1. (Continued)

Species	HF	B3LYP	B3PW91
$5^2(A'')$ freq.(IR)	543.2(16.0)	2240.9(327.7)	2270.4(340.3)
	59.0(1.2)	38.4(1.1)	39.3(1.1)
	114(0)	103.2(0.6)	102.7(0.5)
	121.3(1.7)	104.4(0.1)	103.1(0.1)
	204.3(0.6)	176.8(0.2)	175.6(0.1)
	300.9(3.4)	275.2(3.2)	172.6(3.5)
	319.6(0.1)	295.7(1.0)	292.1(1.1)
	446.1(8.8)	376.3(3.7)	367.3(3.6)
	447.8(0.3)	433.4(2.3)	426.6(3.0)
	577.8(9.3)	502.8(5.6)	496.0(5.0)
	531.8(12.4)	557.3(4.8)	552.3(5.1)
	673.6(10.3)	618.4(46.2)	610.5(56.9)
	759.1(36.5)	692.5(29.2)	683.3(33.0)
	933.4(12.6)	860.0(9.8)	840.8(25.9)
	1044.6(102.5)	919.8(108.6)	878.4(88.6)
	1092.2(153.0)	982.7(34.2)	935.8(51.1)
	1198.7(175.4)	1049.9(46.2)	1015.8(61.5)
	1247.4(355.6)	1172.2(259.6)	1141.1(349.4)
	1295.4(82.7)	1251.5(184.8)	1219.9(159.3)
	1390.6(42.2)	1390.4(40.8)	1374.4(45.0)
2214.5(1351.1)	2201.1(637.6)	2171.0(624.7)	
2320.7(1197.5)	2269.5(814.9)	2240.6(796.1)	

Table 2. Harmonic vibrational frequencies (cm^{-1}) and IR intensity (in *parentheses*) of N_9^- and N_9^+ clusters

Isomers	HF	B3LYP	B3PW91
$1(C_{2v}) \text{N}_9^-(^1A_1)$	46.6(2.7)	51.1(0.3)	55.5(0.3)
	210.0(21.0)	86.6(0)	89.8(0)
	609.8(36.0)	95.2(0.2)	95.5(0.26)
	610.0(154.0)	186.6(16.2)	189.5(18.2)
	736.0(49.0)	273.3(2.7)	279.1(2.8)
	1487.0(2550.0)	279.1(0)	283.6(0)
	1586.0(21.0)	342.4(2.5)	344.6(2.4)
	2335.0(3638.0)	376.0(0.5)	394.8(0.8)
	2373.0(217.0)	478.5(0)	477.9(0)
	608.7(0)	481.5(19.4)	481.3(18.7)
	143.2(13.7)	564.8(45.3)	571.2(46.5)
	816.0(15.0)	618.1(64.2)	644.1(65.6)
	100.9(0)	723.1(6.3)	729.0(5.8)
	1121.0(9.0)	852.1(36.1)	885.4(37.2)
	1423.0(16.4)	974.7(2.6)	1012.4(2.8)
	68.8(0)	1264.3(64.3)	1293.3(74.2)
	105.8(0)	1282.7(4.9)	1307.6(4.9)
	307.0(3.0)	1326.7(2.4)	1348.5(2.4)
	329.5(0)	1380.6(600.4)	1415.0(614.3)
	392.0(6.2)	2169.6(2359.8)	2205.8(2404.6)
471.5(0.2)	2193.3(73.5)	2229.5(74.4)	
$2(C_{2v}) \text{N}_9^-(^1A')$	176.6(0.3)	215.9(1.0)	163.1(0)
	395.0(25.0)	222.8(0)	203.7(4.2)
	393.8(0.6)	291.3(1.0)	252.8(2.2)
	1050.8(0)	347.3(13.9)	320.1(1.6)
	634.0(1205)	423.0(2.8)	323.1(1.9)
	721.0(194.0)	491.3(0)	415.7(0)
	1284.6(25.0)	552.4(2.6)	457.2(8.8)
	1204.3(2.3)	604.3(21.0)	543.1(0)
	744.0(13.0)	652.5(0.0)	582.6(4.8)
	1126.0(16.0)	658.3(6.8)	649.5(3.8)
	1181.0(42.0)	662.6(3.3)	743.8(0)
	1367.0(80.0)	708.5(197.2)	794.0(223.9)
	1013.3(9.0)	851.4(0)	817.6(0)
	1418.0(3.0)	901.5(1.9)	860.4(343.1)
	1561.0(511.0)	932.2(16.5)	892.2(0)
	1647.0(2.7)	1043.7(0.8)	923.4(40)
	789.3(0)	1058.6(7.0)	1097.2(0.6)

Tables 2. (Continued)

Isomers	HF	B3LYP	B3PW91
$3(C_s) N_9^-(^1A')$	253.3(0)	1197.7(17.0)	1234.2(3.3)
	564.5(0)	1311.8(161.3)	1342.0(65.2)
	643.9(0.3)	1386.3(40.2)	1415.2(303.4)
	479.9(0.2)	1394.3(1.7)	1514.5(0.3)
	48.3(0.2)	44.1(0)	55.3(0.1)
	99.0(3.0)	52.3(29.1)	77.5(0.4)
	307.0(5.5)	83.1(0)	88.7(0.1)
	459.0(20.0)	158.8(111.5)	178.1(14.2)
	611.0(25.0)	189.9(75.3)	226.0(0)
	658.0(18.0)	218.4(0)	248.5(31.5)
	678.0(140.0)	286.9(91.5)	368.0(94.9)
	661.0(2.0)	424.6(55.6)	461.1(108.1)
	622.7(0.8)	488.8(11.5)	488.4(10.9)
	73.7(0)	558.9(0.2)	567.4(0)
	211.5(1.4)	561.4(2.8)	584.6(4.1)
	264.8(0.1)	606.1(13.0)	586.4(12.4)
	809.0(84.0)	673.0(35.1)	688.7(50.1)
	929.0(13.0)	739.3(80.3)	770.0(45.0)
	1115.0(73.0)	918.6(67.1)	971.4(36.1)
	1404.0(687.0)	1217.0(202.9)	1250.4(194.1)
1428.9(60.0)	1296.3(7.4)	1316.4(1.3)	
1494.0(80.0)	1346.0(34.4)	1358.7(15.3)	
1556.0(1236.0)	1558.4(194.7)	1520.1(253.8)	
2344.0(3245.0)	2163.1(2102.2)	2206.4(2307.4)	
2382.0(513.0)	2195.5(341.7)	2232.0(197.9)	
$6(C_{2v}) N_9^-(^1A_1)$	63.6(0.0)	14.0i(0)	68.4(6.9)
	75.5(4.2)	52.7(6.4)	72.3(0)
	146.2(1.3)	128.1(2.0)	131.2(2.1)
	189.2(0)	155.3(0)	159.2(0)
	324.7(1.1)	280.5(2.9)	302.5(4.2)
	440.8(2.0)	370.7(0)	390.0(0)
	510.0(4.2)	435.8(0.6)	449.3(0.5)
	732.3(2.1)	589.7(1.1)	637.7(0.6)
	794.8(0)	638.7(24.2)	688.1(9.8)
	805.7(3.2)	702.4(0)	715.5(0)
	816.9(19.1)	714.2(1.4)	727.1(1.3)
	1191.5(15.5)	886.1(34.2)	914.2(49.8)
	1218.1(73.3)	1004.7(46.8)	1016.2(46.2)
	1254.5(487.0)	1060.1(19.6)	1090.9(17.9)
	1270.9(267.8)	1119.4(230.4)	1134.6(219.4)
	1286.1(75.8)	1176.2(51)	1205.5(50.6)
	1419.2(56.6)	1221.2(16.6)	1239.1(10.8)
	1495.6(31.1)	1270.8(45.3)	1293.1(48.2)
	1506.8(142.0)	1277.5(65.2)	1301.9(71.1)
	1772.6(25.9)	1505.7(5.3)	1531.2(5.7)
1810.3(1352.3)	1590.8(321.5)	1630.2(314.7)	
$1(C_{2v}) N_9^+(^1A_1)$	98.1(1.4)	94.6(1.0)	95.0(1.0)
	145.3(1.0)	107.9(0)	107.5(0)
	200.4(32.0)	144.7(0)	145.1(0)
	581.0(308.5)	191.4(3.4)	193.2(2.6)
	1227.0(3805.5)	287.9(2.4)	290.6(2.4)
	2731.0(19.0)	296.2(0)	295.3(0)
	2732.0(2.4)	304.7(2.2)	309.6(2.0)
	160.4(0)	435.5(0)	442.1(0.0)
	407.0(561.0)	526.3(20.8)	537.6(11.5)
	302.5(2.2)	530.9(1.9)	540.9(1.2)
	314.7(5.8)	548.3(0)	556.7(0)
	407.5(0)	697.1(67.4)	710.7(17.7)
	438.7(0)	717.0(1.2)	723.4(1.0)
	587.4(1.3)	871.8(1145.4)	918.0(1161.8)
	595.0(0)	942.3(9.0)	993.3(10.5)
	733.6(1.3)	1189.4(1649.2)	1222.9(1743.3)
	831.9(1.0)	1324.6(17.8)	1352.4(23.6)
	895.0(534.0)	1358.9(0)	1377.1(0)
	1548.0(81.0)	1388.7(4.5)	1420.0(4.9)
	1552.0(0)	2309.9(420.6)	2331.3(456.5)
1645.4(7.4)	2316.1(36.3)	2338.6(39.3)	

Acknowledgements. The present work was supported by the National Natural Foundation of China and the National Key Laboratory of Theoretical and Computational Chemistry of Jilin University.

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