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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 (\( C_{2s} \) and \( C_{3s} \) or \( C_2 \)). The results are very similar to other known odd-number nitrogen ions, such as \( N_3^+ \), \( N_3^- \), and \( N_5^- \), 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 \( \text{AsF}_6^- \) salt of \( N_5^+ \) by reacting \( \text{N}_2\text{F}^+ \) with \( \text{HN}_3 \) in anhydrous hydrogen fluoride at \(-78^\circ \text{C}\) in 1998. The cation \( N_3^+ \) 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 (\( N_4 \), \( x > 3 \)) is a cation containing an odd number of nitrogen atoms rather than an even-number nitrogen cluster. More odd-number nitrogen clusters, such as \( N_5 \) [2, 10], \( N_7^+ \) [2, 10], \( N_8 \) [2, 11], \( N_9 \) [2, 9, 11, 13, 14], \( N_{11} \) [2, 9, 11, 13, 14], \( N_{11} \) [2, 15, 16], \( N_{12} \) [2, 17], \( N_1 \) [2, 18], \( N_9 \) [2, 18], and \( N_{12} \) [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 \( N_2 \)–\( N_3 \) bonding and \( C_{2v} \) symmetry, while the most stable anion, \( N_5^- \), is a complex with weak \( N_2 \)–\( N_3^- \) bonding and the same symmetry. We reported previously [15] that the most stable \( N_7 \) isomers are open-chain structures with \( C_{2v} \) 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 \( N_3 \) side chain with \( C_4 \) symmetry. For the \( N_7^- \) cluster, Michels et al. [17] demonstrated that the open-chain structure (\( N_3 \)–\( N_5 \)–\( N_3 \)) was a local minimum on the potential-energy surface at the HF/6-31G* and MP2/6-31G* levels. For the \( N_9 \), \( N_6^- \), and \( N_8^- \) 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 \( N_6 \) cluster is an open-chain structure with \( C_{2v} \) symmetry and that of \( N_9^- \) is also an open-chain structure but with \( C_4 \) symmetry. Only one stable structure of the \( N_9^- \) with \( C_{2v} \) symmetry was reported. Bartlett [2] made a systematic 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 \( N_5^- \) and \( N_7^+ \) 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 \( N_7 \)
ionic clusters theoretically. The aim of this research was to predict the plausible equilibrium structures, energies, and vibrational frequencies of the N₄⁺ and N₇⁻ isomers using ab initio molecular orbital theory and density functional theory (DFT) methods. Four N₂⁺ isomers (1–4) and five N₇⁻ 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 N₂⁺, we employed the 6-31G* basis set, along with the B3LYP method, to examine the effect of different basis sets, while for the N₇⁻, we employed the 6-31 + G* basis set to examine a similar effect. The 6-31G* basis set is a standard triple-zeta plus polarization basis set, whereas the 6-31 + 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 (NLOM) 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 N₂⁺ and N₇⁻ 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 N₂⁺ isomers

It was reported that the open-chain structure is the most stable species for N₄⁺ [9] and N₆⁺ [18]. Similarly, the C₂ᵥ symmetry open-chain structure 1 (Fig. 1a) for N₂⁺ is also the lowest in energy. It is energetically lower than structure 2 (Tables 1, 2) by 46.4 kcal mol⁻¹ (HF/6-31G*), 27.1 kcal mol⁻¹ (B3LYP/6-31G*), 27.6 kcal mol⁻¹ (MP2/6-31G*), and 29.5 kcal mol⁻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 N₂⁺ as a local minimum at the B3LYP/aug-cc-PVVDZ 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 6-311G* basis set is better than that of 6-31G*, we mainly use the B3LYP/6-311G* 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 N₂ 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 N₇⁻ cluster; however, structure 2 for the N₇⁻ 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 N₃–N₂ complex (2-complex) with Cₛ 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 kcal mol⁻¹ at the HF/6-31G* level; however, with the B3LYP and MP2 methods, structure 3 collapses to another C₂ᵥ symmetry complex (3-complex). As shown in Fig. 1b, it contains an N₃ three-membered ring and two N₂ fragments.

We also tried several structures with a four-membered ring, but only structure 4 (Fig. 1b) with C₃ᵥ 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 N₂⁺ 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.