

Liping Cheng · Qianshu Li · Wenguo Xu ·
Shaowen Zhang

A computer-aided quantum chemical study of the N_{15}^- cluster

Received: 2 October 2002 / Accepted: 13 January 2003 / Published online: 12 March 2003
© Springer-Verlag 2003

Abstract Ab initio (RHF, MP2) and Density Functional Theory (DFT) methods have been used to examine six isomers of the N_{15}^- cluster with the 6-31+G* basis set. Different from the known odd-numbered anionic N_7^- , N_9^- , and N_{11}^- clusters, in which the open-chain structures are the most stable species, the most stable N_{15}^- isomer is structure **1** (C_1), which may be considered as a complex between the fragments cyclic N_5^- (D_{5h}) and staggered N_{10} (D_{2d}). The decomposition pathways of structure **2** (C_S), containing two aromatic N_5 rings connected by a N_5 chain, and the open-chain structure **3** (C_{2v}) were studied at the B3LYP/6-31+G* level of theory. Relative energies were refined at the level of B3LYP/6-311+G(3df,2p)//B3LYP/6-31+G*+ZPE (B3LYP/6-31+G*). The barriers for N_2 and N_5^- (D_{5h}) fission reactions for structure **2** are predicted to be 18.2 and 14.2 kcal mol⁻¹, respectively. The corresponding $N_2+N_3^-$ fission barrier for structure **3** is predicted to be 11.2 kcal mol⁻¹. Supplementary material is available for this article if you access the article at <http://dx.doi.org/10.1007/s00894-003-0118-0>. A link in the frame on the left on that page takes you directly to the supplementary material.

Electronic Supplementary Material Supplementary material is available for this article if you access the article at <http://dx.doi.org/10.1007/s00894-003-0118-0>. A link in the frame on the left on that page takes you directly to the supplementary material.

Keywords Nitrogen cluster · Ab initio · High-energy-density materials (HEDM) · N_{15}^-

Introduction

Three pure nitrogen chemical species in bulk compounds are experimentally known, i.e., N_2 , N_3^- [1] and N_5^+ . [2] The last was synthesized in 1999. Furthermore, there is the new evidence for the existence of the tetranitrogen molecule, N_4 , as a metastable species whose lifetime exceeds 1 μ s at 298 K. [3] Could other “polynitrogen molecules” exist? In recent years, the hypothetical existence of polynitrogen clusters has been the focus of many theoretical studies. [4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29] Besides their theoretical interest, these intriguing structures have received attention because of their possible use as high-energy-density materials (HEDM).

Although most theoretical studies treated even-numbered nitrogen clusters, [3, 4, 5, 6, 7, 8, 9, 10, 11] it is surprising that, besides the particularly stable nitrogen molecule, N_2 , the synthesized nitrogen clusters [N_n ($n>2$)] are not even-numbered nitrogen clusters but two ionic odd-numbered clusters N_3^- and N_5^+ . Therefore, more and more attention was paid to odd-numbered nitrogen clusters, such as N_3^- , [1] N_3 , [12] N_3^+ , [13] N_5 , N_5^- , N_5^+ , [14, 15, 16, 17] N_7 , [18, 19] N_7^- , N_7^+ , [20, 21, 22] N_9 , N_9^- , N_9^+ , [23, 24] N_{11} , N_{11}^+ , N_{11}^- , [25, 26] and $N(N_3)_4^+$ [21] etc.

It is well known that the pentazole anion N_5^- (D_{5h}) can be expected to be particularly stable due to the aromatic character of the π -electron system. [7] For N_7^- , Michels et al. [20] demonstrated that the open chain, diazidamide structure, $(N_3-N-N_3)^-$, is a local minimum at the RHF/6-31+G* and MP2/6-31+G* levels of theory. Our recent calculation [21] for N_7^- also confirmed that the energetically low-lying isomer is the open-chain structure with C_{2v} or C_2 symmetry. In addition, we have also investigated the N_9^- cluster. [23] Computational results showed that the most stable anion N_9^- is an open-chain structure but with C_S symmetry. For the larger odd-numbered anionic cluster, N_{11}^- , we [26] recently found that, similar to the N_7^- and N_9^- clusters, the open chain structure with C_{2v} symmetry is the global minimum.

L. Cheng · Q. Li (✉) · W. Xu · S. Zhang
School of Chemical Engineering and Materials Science,
Beijing Institute of Technology,
100081 Beijing, P.R. China
e-mail: QSLi@bit.edu.cn
Tel.: +86-10-68912665
Fax: +86-10-68912665

Based on the previous investigations on the odd-numbered anionic clusters, it seems that generally the most stable known odd-numbered anionic isomers are the open-chain structures. Is this conclusion applicable to the N_{15}^- cluster? To answer this question, we now report a theoretical study on the N_{15}^- cluster.

Nitrogen clusters are of significant interest as HEDM for propulsion and explosive applications. The critical properties for effective HEDM molecules are high dissociation barrier and facile syntheses. Therefore, it is very valuable to search all possible synthesis and dissociation routes for any new fuel candidates. Although a large body of theoretical studies has already been devoted to the polynitrogen clusters, [4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29] they were mainly focused on the structures and energies of various polynitrogen isomers and only a few studies [15, 17, 22, 27, 29] on their synthesis and decomposition mechanism were reported. For instance, Wang et al. [27] predicted the synthesis reaction pathway of N_6 (C_{2h}) from HN_3 and N_3F . Gagliardi et al. [15] reported a theoretical study on the formation of the nitrogen cluster N_{10} from the ionic species N_5^+ and N_5^- . Nguyen et al. [17] have discussed the decomposition of the pentazole N_5^- (D_{5h}) into $N_3^-+N_2$ and reinforced the view that the pentazole anion is a relatively stable cyclic species with a moderately high energy barrier (110–114 kJ mol^{-1}). Our recent study [22] showed that the *gauche* C_2 form N_7^- can very easily dissociate into $N_3^-+N_2+N_2$ with only 5.0 kcal mol^{-1} and 1.2 kcal mol^{-1} energy barriers at the B3LYP/6-311+G(3df,2p)//B3LYP/6-31+G(d) and G2(MP2)//MP2/6-31+G(d) levels of theory, respectively.

In the present study, besides geometric optimization and vibrational frequency analysis, we have also performed calculations on the decomposition pathways of some low-lying energetic N_{15}^- species in an attempt to provide a theoretical foundation for synthesizing HEDM.

Computational method

Geometries were fully optimized with restricted Hartree–Fock (RHF), density functional theory (DFT), and second-order perturbation theory (MP2). [30] The DFT method used in the present work comprises the combinations of Becke’s three-parameter nonlocal functionals [31] with the nonlocal correlation of Lee, Yang, and Parr

[32] or with the Perdew–Wang 1991 correlation functionals, [33] herein denoted as B3LYP and B3PW91, respectively. The MP2 method employed is one using the frozen core approximation. The basis set we used is the 6-31+G*, which is a split-valence double-zeta polarization basis set augmented with the diffuse functions. [34] To characterize the nature of the stationary points and to determine the zero-point energy (ZPE) corrections, harmonic vibrational frequencies were also calculated at the RHF/6-31+G*, B3LYP/6-31+G*, and B3PW91/6-31+G* levels of theory. For transition states, the minimum energy pathways connecting the reactants and products were confirmed using the intrinsic reaction coordinate (IRC) method with the Gonzalez–Schlegel second-order algorithm. [35, 36] Final energies were refined at the B3LYP/6-311+G(3df,2p)//B3LYP/6-31+G*+ZPE (B3LYP/6-31+G*) level of theory. In addition to the structural and energetic investigations, the natural population and Wiberg bond indices (WBI) analyses were also presented using the natural bond orbital procedure (NBO). [37, 38, 39, 40] All computations were carried out with the Gaussian 98 program package. [41]

Throughout this paper, bond lengths are given in ångströms, bond angles in degrees, total energies in hartrees, and relative and zero-point vibrational energies in kcal mol^{-1} .

Results and discussion

The optimized structures for six N_{15}^- isomers are shown in Figs. 1 and 2. The total energies, zero-point energies (ZPE), and the relative energies corrected by ZPE of the N_{15}^- isomers are summarized in Tables 1 and 2. The six isomers are all local minima on their potential energy surfaces (PES) at the above levels of the theory.

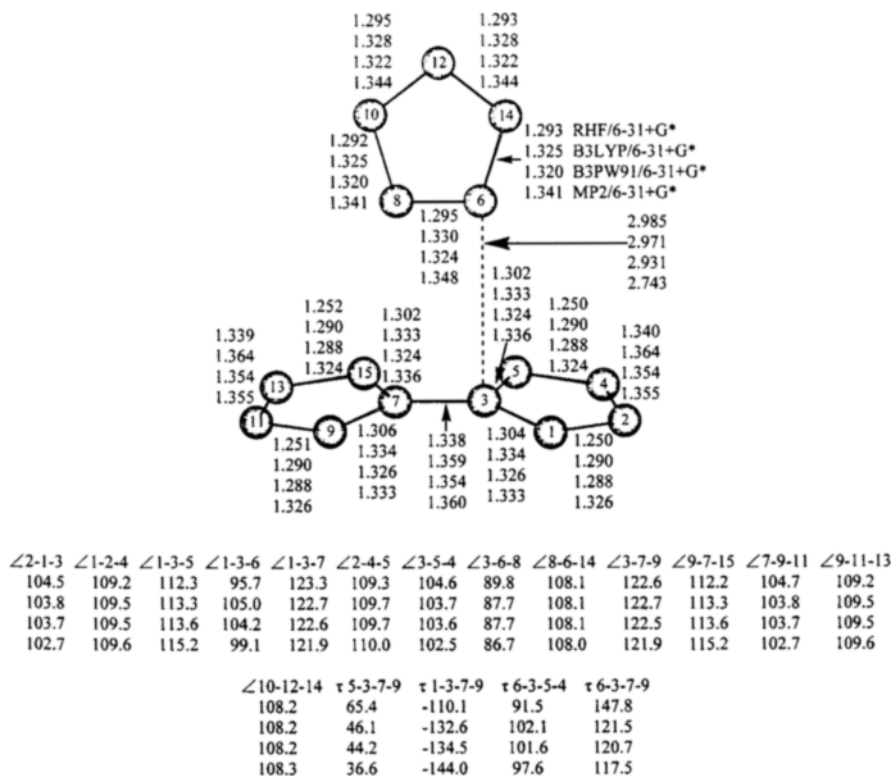
Minimum energy N_{15}^- isomers

It can be seen in Table 2 that the energetic stability ordering of the six N_{15}^- isomers is **1>2>3>4>5>6** at all levels of the theory. Energetically speaking, **1** (C_1), as shown in Fig. 1a, is the most stable species among these six isomers. Examining the structure of **1**, as well as its NBO results, this anion may be considered as a complex between the fragments cyclic N_5^- (D_{5h}) and staggered N_{10} (D_{2d}). At the B3LYP/6-311+G(3df,2p)//B3LYP/6-31+G*

Table 1 Total energies [E (Hartrees)] and the zero-point energies [(ZPE) (kcal mol^{-1})] for six N_{15}^- isomers

Isomers N_{15}^-	RHF/6-31+G*		B3LYP/6-31+G*		B3PW91/6-31+G*		MP2/6-31+G* E
	E	ZPE	E	ZPE	E	ZPE	
1 (C_1)	-816.44156	51.3	-821.06478	44.2	-820.75017	45.1	-818.97315
2 ($^1A', C_5$)	-816.42183	51.0	-821.05711	44.1	-820.74104	45.0	-818.93051
3 ($^1A_1, C_{2v}$)	-816.32341	45.6	-820.97922	40.2	-820.64987	41.0	-818.82897
4 (C_1)	-816.30758	45.6	-820.96725	40.2	-820.63835	41.0	
5 (C_1)	-816.28025	47.4	-820.94664	41.2	-820.62272	42.0	
6 ($^1A', C_5$)	-816.22811	48.6	-820.91163	41.8	-820.59310	42.8	

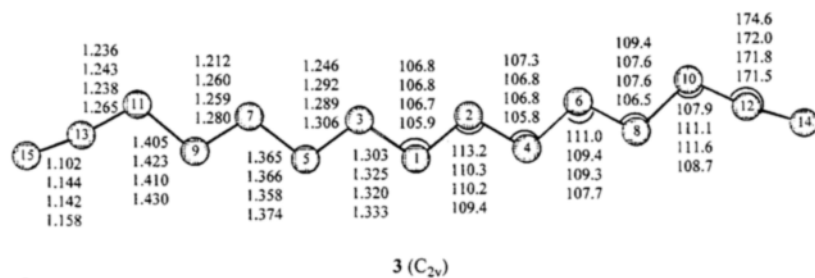
Fig. 1 Structures (a) 1, (b) 2, and (c) 3 of the N_{15}^- cluster, showing bond distances in Å and bond angles in degrees



a

1 (C_1)

b

2 (C_5)

c

3 (C_{2v})

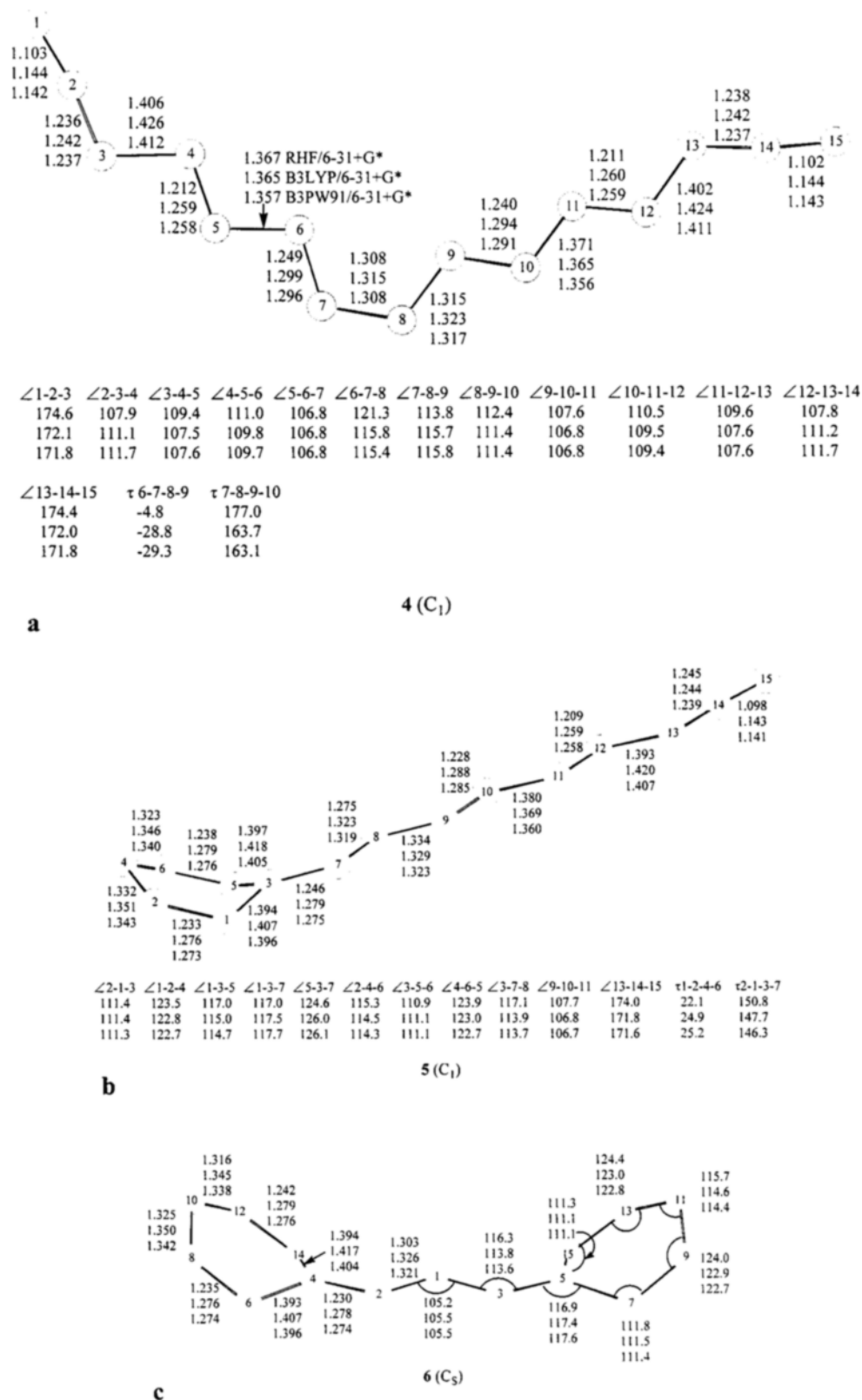


Fig. 2 Structures (a) 4, (b) 5 and (c) 6 of N_{15}^- cluster, showing bond distances in Å and bond angles in degrees

Table 2 Relative energies (kcal mol⁻¹) with zero-point energy corrections for six N₁₅⁻ isomers

Isomers	RHF/6-31+G*	B3LYP/6-31+G*	B3PW91/6-31+G*	MP2/6-31+G*
1 (C ₁)	0.0	0.0	0.0	0.0
2 (¹ A',C ₅)	12.1	4.7	5.6	26.8
3 (¹ A ₁ ,C _{2v})	68.4	49.7	58.8	90.5
4 (C ₁)	78.4	57.2	66.1	
5 (C ₁)	97.3	71.1	76.9	
6 (¹ A',C ₅)	131.2	93.7	96.3	

Table 3 Dissociation energies (kcal mol⁻¹) to 6 N₂+N₃⁻ at the B3LYP/6-31+G(3df,2p)//B3LYP/6-31+G* and MP2/6-31+G* levels of theory

N ₁₅ ⁻ isomer	1 (C ₁)	2 (C ₅)	3(C _{2v})	4(C ₁)	5(C ₁)	6(C ₅)
B3LYP	263.4	267.0	306.5	314.3	330.4	355.3
MP2	264.9	291.7	355.4			

level, the binding energy for **1** is calculated to be 9.7 kcal mol⁻¹. Natural population analysis confirms that this complex consists of two moieties, N₅⁻ and N₁₀. The sum of the charges on the N6 (-0.230), N8 (-0.230), N10 (-0.174), N12 (-0.182), and N14 (-0.174) atoms is about -1.0, corresponding to that of the N₅⁻ moiety, and that on the other nitrogen atoms is about 0.0, corresponding to that of a neutral N₁₀ moiety. As the distance (2.743–2.985 Å) between the N3 and N6 atoms is so long, we predict the interaction between the atoms of the above N₅ ring and the atoms of the other two N₅ rings appears to be a long-range Coulomb induced force.

As shown in Fig. 1b, structure **2** (C₅) contains two five-membered rings connected by an N₅ chain. It is the second most stable isomer and energetically less stable than **1** by 12.1, 4.7, 5.6, and 26.8 kcal mol⁻¹ at the RHF/6-31+G*, B3LYP/6-31+G*, B3PW91/6-31+G*, and MP2/6-31+G* levels of theory, respectively. Different from the structure of the corresponding neutral molecule, [28] structure **2** is not a planar molecule; there is a dihedral angle (about 150°) between the two five-membered rings and the center N₅ chain. As shown in Fig. 1, most of its bond lengths in the two terminal N₅ rings are close to the aromatic N–N bond length (1.350 Å). [7] In the center N₅ chain, the bond lengths of N1–N2 (or N1–N3) and N2–N4 (or N3–N5) are also close to the aromatic N–N bond length (1.350 Å). However, the bond lengths of the two bridge bonds N4–N6 and N5–N7 are closer to the single-bond length of H₂N–NH₂ (1.449 Å). All the WBI of bonds in the two terminal N₅ rings of **2** are more than 1.2, the corresponding values in the center chain are more than 1.3, but the WBI of the two bridge bonds N4–N6 and N5–N7 are about 1.0. Therefore, the two terminal N₅ rings and the center N₅ chain may form three small isolated conjugation systems. Natural population analysis indicates that the net negative charges of this isomer mainly lie on the atoms N1, N4 (N5), N10 (N11) and N12 (N13), which are -0.208, -0.116, -0.120, and -0.115, respectively.

Structure **3** is an open-chain structure with C_{2v} symmetry, different from the anions of N₇⁻ (C_{2v} or C₂), [21] N₉⁻ (C₅) [23] and N₁₁⁻ (C_{2v}); [26] this isomer is not the most stable species in the N₁₅⁻ system. As listed in Table 2, it is energetically higher than **1** by 68.4, 49.7,

Table 4 Electron affinities (eV) of N₁₅⁻ isomers corresponding to neutral molecules

Isomer	Electron affinity	
	B3LYP/6-31+G*	MP2/6-31+G*
1 (C ₁)	6.47	7.96
2 (¹ A',C ₅)	5.93	8.07
3 (¹ A ₁ ,C _{2v})	5.31	8.87
4 (C ₁)	5.05	
5 (C ₁)	5.14	
6 (¹ A',C ₅)	5.21	

58.8, and 90.5 kcal mol⁻¹ at the RHF/6-31+G*, B3LYP/6-31+G*, B3PW91/6-31+G*, and MP2/6-31+G* levels of theory, respectively. Natural population analysis gives the result that the net negative charges of this isomer lie mainly on the atoms N1, N4 (N5), N8 (N9) and N10 (N11), which are -0.176, -0.163, -0.105, and -0.190, respectively.

As shown in Fig. 2a–c, the remaining three structures **4–6** are all local minima on their PES at the above levels of the theory, but they are all high-lying energetic species, about 57–132 kcal mol⁻¹ less stable than **1**. In view of their instability, they will be no further discussion for these isomers.

The energy differences relative to 6N₂+N₃⁻ molecules are listed in Table 3 and it appears that these six N₁₅⁻ isomers would be very energetic materials. Based on our investigations on the neutral N₁₅ molecules, [28] the electron affinities (EAs) of all N₁₅⁻ isomers can then be easily calculated and they are tabulated in Table 4.

Transition structures and reaction barriers for decomposition reactions

Since the low-energy species always receive attention, we shall, in the present study, examine their possible decomposition pathways with B3LYP. However, isomer **1** is a weak ion–molecule complex. Since the decomposition of a weak complex is generally a simple and easy bond cleavage and barrier-free process, we need not further explore its decomposition mechanism. Therefore,

Fig. 3 Structures of dissociation products N_{10} (C_S), N_5^- (D_{5h}), N_{13}^- (C_1), N_{10} (C_{2h}), N_3^- , and N_2 , showing bond distances in Å and bond angles in degrees

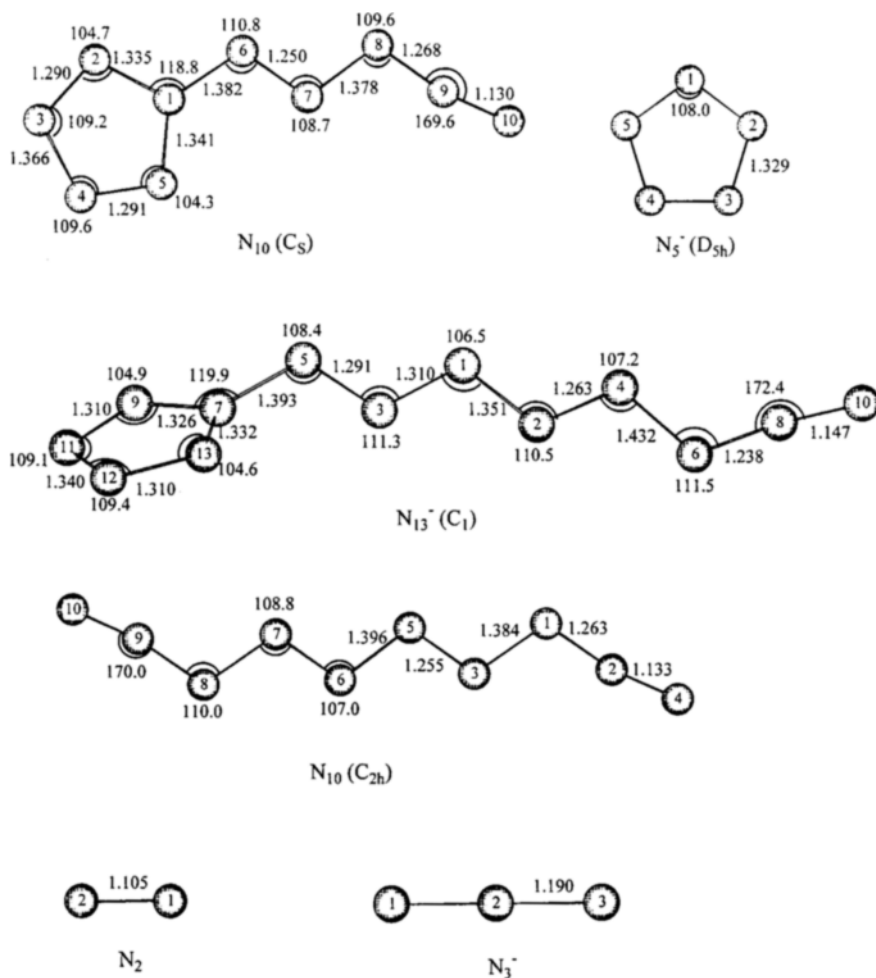


Table 5 Total energies [E (Hartrees)] and the zero-point energies [(ZPE) (kcal mol^{-1})] for the reactants, complex, transition states, and products

Species	B3LYP/6-31+G*		B3LYP/6-311+G(3df,2p)//B3LYP/6-31+G*+ZPE
	E	ZPE	E
2 N_{15}^- (C_S)	-821.05711	44.1	-821.29874
N_{13}^- (C_1)	-711.56546	36.6	-711.77905
N_2 ($D_{\infty h}$)	-109.52978	3.5	-109.56684
TS1 (C_1)	-821.02253	41.5	-821.26558
N_5^- (D_{5h})	-273.76309	13.5	-273.84178
N_{10} (C_S)	-547.26741	28.3	-547.43516
Complex (C_1)	-821.05087	42.6	-821.29622
TS2 (C_1)	-821.03011	42.2	-821.27311
3 N_{15}^- (C_{2v})	-820.97922	40.2	-821.22952
N_{10} (C_{2h})	-547.24212	26.8	-547.41372
N_3^- ($D_{\infty h}$)	-164.24473	6.7	-164.29706
TS3 (C_S)	-820.95537	37.8	-821.20782

we only predict the possible decomposition mechanisms for isomers **2** and **3**.

The geometric structures and the optimized geometric parameters for the reactants, products, transition states, and complex are shown in Figs. 1, 2, 3, and 4. The total energies, zero-point energies (ZPE), and the relative energies corrected by ZPE of the reactants, products,

transition states, and complex are tabulated in Tables 5 and 6. Figure 5 plots an energy diagram that presents the relative energies including ZPE corrections of stationary points on the PES of isomers **2** and **3**. In the following discussions, we will mainly use the B3LYP/6-311+G(3df,2p)//B3LYP/6-31+G*+ZPE (B3LYP/6-31+G*) results unless otherwise indicated.

Fig. 4 Structures of **TS1–3** and **Complex**, showing bond distances in Å and bond angles in degrees

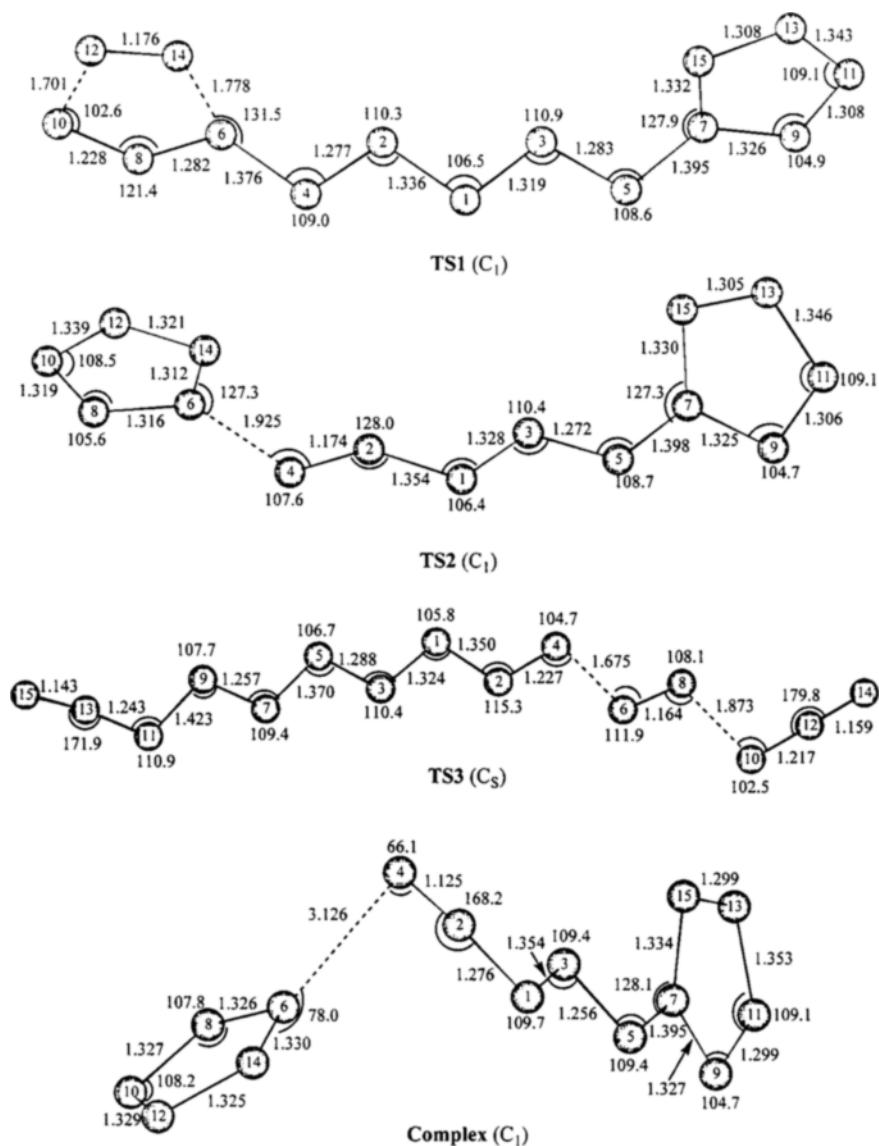


Table 6 Relative energies (kcal mol⁻¹, corrected by ZPE) of species on the N₁₅⁻ PES

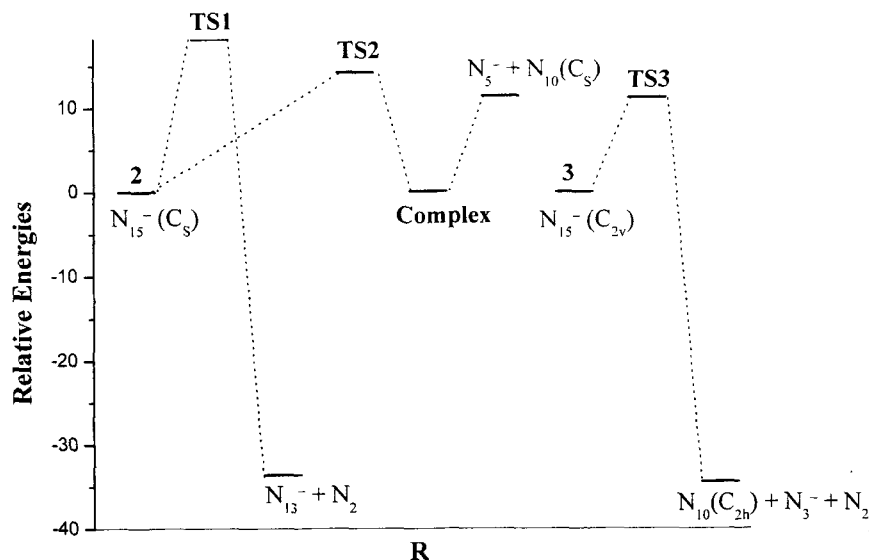
Species	B3LYP/6-31+G* <i>E</i>	B3LYP/6-311+G(3df,2p)//B3LYP/6-31+G*+ZPE (B3LYP/6-31+G*) <i>E</i>
2 N ₁₅ ⁻ (C _s)	0.0	0.0
N ₁₃ ⁻ (C ₁) + N ₂	-27.9	-33.6
N ₁₀ (C _s) + N ₅ ⁻ (D _{5h})	14.4	11.4
TS1 (C ₁)	19.1	18.2
Complex (C ₁)	2.4	0.1
TS2 (C ₁)	15.0	14.2
3 N ₁₅ ⁻ (C _{2v})	0.0	0.0
N ₁₀ (C _{2h}) + N ₃ ⁻ + N ₂	-26.7	-34.4
TS3 (C _s)	12.6	11.2

Decomposition process of **2**, N₁₅⁻ (C_s) → **TS1** (C₁) → N₁₃⁻ (C₁) + N₂

The ring breaking reaction of **2** (C_s) into N₁₃⁻ (C₁) and N₂ was studied at the B3LYP/6-31+G* level of theory. The search for a transition state leads to a structure with C₁

symmetry. The calculation of the harmonic vibrational frequencies confirmed that the structure is a transition state, with one imaginary frequency equal to 531i cm⁻¹. As shown in Fig. 4, we can note that, compared with structure **2**, the two bond lengths of N10–N12 and N6–N14 in **TS1** are stretched whereas that of N12–N14 is

Fig. 5 Potential energy surfaces of **2**, $N_{15}^- (C_S)$ and **3**, $N_{15}^- (C_{2v})$ at the B3LYP/6-311+G(3df,2p)//B3LYP/6-31+G*+ZPE (B3LYP/6-31+G*) level of theory



actually compressed and almost becomes a triple $N\equiv N$ bond. A barrier for dissociation of $19.1 \text{ kcal mol}^{-1}$ was obtained at the B3LYP/6-31+G* level of theory. Single point calculation at the B3LYP/6-311+G(3df,2p)//B3LYP/6-31+G*+ZPE (B3LYP/6-31+G*) level decreases this value to $18.2 \text{ kcal mol}^{-1}$. Since the dissociation barrier is close to 20 kcal mol^{-1} [29], it seems reasonable to consider **2** as a candidate for HEDM along this dissociation path.

Decomposition process of **2**, $N_{15}^- (C_S) \rightarrow \text{TS2} (C_1) \rightarrow \text{Complex} \rightarrow N_5^- (D_{5h}) + N_{10} (C_S)$

With the distance between N4 and N6 atoms lengthening, the structure transfers into an intermediate (**Complex**) through **TS2** (C_1). The **Complex** is a local minimum on the PES, as shown by its all real harmonic frequencies at the B3LYP/6-31+G* level of theory. Natural population analysis confirms that the complex consists of two moieties, N_5^- and N_{10} . The sum of the charges on N6, N8, N10, N12, and N14 atoms is -1.0 , corresponding to that of N_5^- moiety, and that on the other nitrogen atoms is about 0.0 , corresponding to that of neutral N_{10} moiety. As shown in Fig. 4, in the structure of the **Complex**, the N6 atom of $N_5^- (D_{5h})$ connects the N4 atom of $N_{10} (C_S)$ through long-range Coulomb induced force. The long distance (3.126 \AA) between N4 and N6 atoms in the **Complex** suggests that the charge attraction force between N4 and N6 is greatly weakened. Thus, the bond of N4–N6 would break and $N_{15}^- (C_S)$, **2** would be decomposed into $N_{10} (C_S)$ and $N_5^- (D_{5h})$. To verify that the transition state really connects the **Complex** and structure **2**, an IRC calculation was also performed beginning with the transition state **TS2** at B3LYP/6-31+G*. The geometries of the two species obtained from IRC calculation are very close to those from the geometry optimization calculations.

The dissociation barrier at the B3LYP/6-311+G(3df,2p)//B3LYP/6-31+G* +ZPE (B3LYP/6-31+G*) level is $14.2 \text{ kcal mol}^{-1}$. It is not high enough to regard **2** as a suitable candidate for preparation and handling in bulk quantities.

Decomposition process of **3**, $N_{15}^- (C_{2v}) \rightarrow \text{TS3} (C_S) \rightarrow N_{10} (C_{2h}) + N_3^- (D_{\text{oh}}) + N_2$

The dissociation of **3** (C_{2v}) was investigated at the B3LYP/6-31+G* level of theory. A transition state **TS3** (C_S) with one imaginary frequency $333i \text{ cm}^{-1}$ was found lying about $11.2 \text{ kcal mol}^{-1}$ above **3** at the B3LYP/6-311+G(3df,2p)//B3LYP/6-31+G*+ZPE (B3LYP/6-31+G*) level of theory. The typical bond distances and angles of **TS3** are shown in Fig. 4. **TS3** leads to the formation of the neutral $N_{10} (C_{2h})$ species and N_2 , N_3^- fragments. This is rather obvious by looking at the structure of the TS and the vibrational mode of the imaginary frequency that corresponds to the breaking of the N4–N6 and N8–N10 bonds. Natural population analysis confirms the presence of the N_3^- part. The negative charges reside mainly on the atoms N10 and N14 of the N_3^- , which are -0.299 and -0.183 , respectively.

Summary

Six minimum energy isomers of N_{15}^- cluster are reported in this paper. Different from the known odd-numbered anionic N_7^- , N_9^- , and N_{11}^- clusters, in which the open-chain structures are most stable, the most stable N_{15}^- isomer is structure **1** (C_1), which may be considered as a complex between the fragments cyclic $N_5^- (D_{5h})$ and staggered $N_{10} (D_{2d})$. We have examined the decomposition mechanisms of isomers **2** and **3**. For isomer **2**, the N_2 -eliminating barrier, close to 20 kcal mol^{-1} , suggests that it

seems reasonable to consider it as a candidate for HEDM along this dissociation path, but the corresponding value for the N_5^- (D_{5h}) fission reaction is only $14.2 \text{ kcal mol}^{-1}$. Since a reaction generally proceeds through the pathway that has the lowest barrier, it does not seem reasonable to regard **2** as a new fuel. With respect to isomer **3**, the small dissociation barrier for the $N_2+N_3^-$ fission reaction of only $11.2 \text{ kcal mol}^{-1}$ indicates that this isomer of N_{15}^- is not stable kinetically.

References

1. Curtius Th (1890) *Chem Ber* 23:3023–3033
2. Christe KO, Wilson WW, Sheehy JA, Boatz JA (1999) *Angew Chem Int Ed Engl* 38:2004–2009
3. Cacace F, Petris G, Troiani A (2002) *Science* 295:480–481
4. Korkin AA, Balkova A, Bartlett RJ, Boyd RJ, Schleyer PvR (1996) *J Phys Chem* 100:5702–5714
5. Maana MR (2000) *Chem Phys Lett* 331:262–268
6. Bittererova M, Brinck T (2000) *J Phys Chem A* 104:11999–12005
7. Glukhovtsev MN, Jiao H, Schleyer PvR (1996) *Inorg Chem* 35:7124–7133
8. Gagliardi L, Evangelisti S, Barone V, Roos BO (2000) *Chem Phys Lett* 320:518–522
9. Leininger ML, Sherrill CD, Schaefer HF (1995) *J Phys Chem* 99:2324–2328
10. Chen C, Sun K-C, Shyu S-F (1999) *J Mol Struct (THEOCHEM)* 459:113–122
11. Klapötke TM, Harcourt RD (2001) *J Mol Struct (THEOCHEM)* 541:237–242
12. Wasilewski J (1996) *J Chem Phys* 105:10969–10982
13. Bartlett RJ, Structure and stability of polynitrogen molecules and their spectroscopic characteristics (to be published); <http://www.qtp.ufl.edu/~bartlett/>
14. Wang X, Hu H-R, Tian A, Wong NB, Chien S-H, Li W-K (2000) *Chem Phys Lett* 329:483–489
15. Gagliardi L, Orlandi G (2001) *J Chem Phys* 114:10733–10737
16. Nguyen MT, Ha T-K (2000) *Chem Phys Lett* 317:135–141
17. Nguyen MT, Ha T-K (2001) *Chem Phys Lett* 335:311–320
18. Li QS, Hu XG, Xu WG (1998) *Chem Phys Lett* 287:94–99
19. Wang X, Ren Y, Shuai MB, Wong NB, Li WK, Tian A (2001) *J Mol Struct (THEOCHEM)* 538:145–156
20. Michels HH, Montgomery JA, Christe KO, Dixon DA (1995) *J Phys Chem* 99:187–194
21. Liu YD, Zhao JF, Li QS (2002) *Theor Chem Acc* 107:140–146
22. Li QS, Zhao JF (2002) *J Phys Chem A* 106:5928–5931
23. Li QS, Wang LJ, Xu WG (2000) *Theor Chem Acc* 104:67–77
24. Li QS, Wang LJ (2001) *J Phys Chem A* 105:1203–1207
25. Li QS, Liu YD (2002) *Chem Phys Lett* 353:204–212
26. Liu YD, Yin PG, Guan J, Li QS (2002) *J Mol Struct (THEOCHEM)* 588:37–43
27. Wang LJ, Warburton P, Mezey PG (2002) *J Phys Chem A* 106:2748–2752
28. Cheng LP, Li QS (2003) *Int J Quantum Chem* (submitted)
29. Chung G, Schmidt MW, Gordon MS (2000) *J Phys Chem A* 104:5647–5650
30. Møller C, Plesset MS (1934) *Phys Rev* 46:618–622
31. Becke AD (1993) *J Chem Phys* 98:1372–1377
32. Lee C, Yang W, Parr RG (1988) *Phys Rev B* 37:785–789
33. Perdew JP, Wang Y (1992) *Phys Rev B* 45:13244–13249
34. Hehre WJ, Radom L, Schleyer PvR, Pople JA (1986) *Ab initio molecular orbital theory*. Wiley, New York
35. Gonzalez C, Schlegel HB (1989) *J Chem Phys* 90:2154–2161
36. Gonzalez C, Schlegel HB (1990) *J Phys Chem* 94:5523–5527
37. Carpenter JE, Weinhold F (1988) *J Mol Struct (THEOCHEM)* 169:41–62
38. Foster JP, Weinhold F (1980) *J Am Chem Soc* 102:7211–7218
39. Reed AE, Curtiss LA, Weinhold F (1988) *Chem Rev* 88:899–926
40. Reed AE, Weinstock RB, Weinhold F (1985) *J Chem Phys* 83:735–746
41. Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Zakrzewski VG, Montgomery JA, Stratman RE, Burant JC, Dapprich S, Millam JM, Daniels AD, Kudin KN, Strain MC, Farkas O, Tomasi J, Barone V, Cossi M, Cammi R, Mennucci B, Pomelli C, Adamo C, Clifford S, Ochterski J, Petersson GA, Ayala PY, Cui Q, Morokuma K, Malick DK, Rabuck AD, Raghavachari K, Foresman JB, Cioslowski J, Ortiz JV, Baboul AG, Stefanov BB, Liu C, Liashenko A, Piskorz P, Komaromi, I, Gomperts R, Martin RL, Fox DJ, Keith T, Al-Laham MA, Peng CY, Nanayakkara A, Gonzalez C, Challacombe M, Gill PMW, Johnson BG, Chen W, Wong MW, Andres JL, Gonzales C, Head-Gordon M, Replogle ES, Pople JA (1998) *Gaussian 98*. Gaussian, Pittsburgh, Pa.