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Theoretical study of structures and stabilities of C_mN_2 ($m = 1$–14) ions

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Abstract

Geometrical and electronic properties of C_mN_2 ($m = 1$–14) positively and negatively charged clusters have been investigated by hybrid B3LYP functional at the respective 6-311G(d) and 6-311+G(d) levels. Our results revealed that C_mN_2 ($m = 2$–14) cationic ions and C_mN_2 ($m = 6$–14) anions form linear conformer with $D_{\infty h}$ symmetry except for $C_{11}N_2^+$ cationic ion whereas C_mN_2 ($m = 1$–5) anions form chain-like arrangements. Two N atoms favor to bond at ends in linear and chain-like configurations. Both calculated HOMO–LUMO gaps and adiabatic ionization potentials showed that the C_mN_2 ($m = 1$–14) clusters with even m are more stable than those with odd m. The second difference in energy for $C_mN_2^+$ ($m = 1$–14) ions revealed that the cationic ions with even m are more stable than those with odd m, which is consistent with the observed cationic even–odd alternation of the TOF signal intensities. The relative stability of anions is in opposition to that of cationic clusters.

Keywords: C_mN_2 charged clusters; DFT theory; Geometries; Stability; Mass spectrometry

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1. Introduction

Recently, a great deal attention has been paid to study of carbon nitride (CN) film since this material is, theoretically, harder than diamond [1,2]. In an ultrahigh vacuum environment, carbon nitride films [3,4] can be obtained by carbon–nitrogen cluster depositions. Since the cluster-assembled materials may have uncommon properties, information about the geometric structure and electronic ground state of these clusters is of primary importance. Up to now the structure and electronic state of neutral C_mN_n ($m = 2$–10, $n = 1$–2) clusters have been theoretically well understood [5–8]. There are a number of well-known experimental procedures [9–11] for producing carbon–nitrogen clusters in the laboratory. In some variations of these mass spectrometric techniques, the clusters were observed in ionic forms. On the other hand, it is well known that the loss or acceptance of an electron would introduce significant structural distortions to corresponding neutral clusters. The structures of neutral clusters are therefore expected to be less reliable in interpreting the anionic geometries. Hence, it is of interest to carry on an investigation in the carbon–nitrogen ions. Cao and Peyerimhoff [10] and Lee [12] successively reported a study of NC_4N^+ and NC_6N^+ ions with density functional theory (DFT). Pascoli and Lavendy [13] investigated C_mN^- anions with B3LYP, MP2, MP4, QCISD(T) and CCSD(T) and drew a conclusion: (1) the B3LYP predictions appear reliable not only for the geometries and vibrational frequencies but also for the energies for small and medium-sized heteroatom-containing carbon clusters, (2) MP2 calculations appear to be insufficiently accurate for the energies of anionic carbon clusters under the influence of the high spin contamination of the HF reference wave function in the MP2 method. No systematic study of geometries and relative stabilities has been reported for C_mN_2 ions.

In this work, we systematically carried out density functional calculations on C_mN_2 ions of up to 16 atoms. DFT methods have been shown to provide good accuracy at relatively low computational cost. The charged-induced structural changes in these ions will be discussed.

The rest of the paper is organized as follows. In Section 2, a brief description of the computational method used in this work was given. Section 3 of this report is devoted to a detailed discussion on the geometries, electronic states and

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relative stability. Finally, our conclusions were drawn in Section 4.

2. Computational methods

Initial geometry optimizations were performed at the B3LYP/6-31G(d) level without any symmetry constraint, except for those needed to maintain a particular geometry. These minimized cationic and neutral structures were finally optimized with B3LYP/6-311G(d) method. The anions were finally optimized at the B3LYP/6-311+G(d) level. Harmonic vibrational frequencies were calculated at the final level to characterize the stationary points as minima or transition state structures on the potential energy surfaces of corresponding clusters. All of the obtained most stable charged and neutral C_mN_2 clusters were characterized as energy minima without imaginary frequencies. Partial charges were given with Mulliken atomic charges. The first ionization potentials and electron affinities of various C_mN_2 clusters were calculated with adiabatic approximation. All calculations were carried out using the Gaussian'98 program [14] on Dell Precision 650 workstations.

3. Results and discussion

For C_n clusters with $n = 3$–10, ab initio calculations [15,16] predicted linear structures for odd n and cyclic forms for even n, and there is experimental evidence for both linear and ring geometries [17,18]. Larger clusters form monocyclic or bicyclic rings [19], and many with $n > 28$ give rise to fullerene structures [20]. These geometries indicate that C atoms tend to attain small atomic coordination (hybridization with sp or sp^2 character mainly) forming few strong bonds at small clusters while an even number of atoms with large atomic coordination lead to multiple bonds and the formation of the fullerenes, nanotubes, onions (multishell spherical concentric fullerenes) in the larger clusters. On the other hand, previous works [6,21–23] have revealed that the substitution of two C atoms by two N atoms does not essentially modify the original carbon cluster structure in C_n clusters, and the neutral and singly charged carbon clusters with one or two heteroatoms prefer linear or cyclic conformations with $n < 20$. Hence, the calculated geometries of C_mN_2 ($m = 1$–14) singly charged ions should prefer chain or cyclic forms. The current effort was mainly focused on searching for the minimum energy configuration in chain and cyclic forms and studying structural distortions upon charging.

The minimum energy geometric sketches of C_mN_2 anions are shown in Fig. 1. The energetically low-lying geometric ions are given in Fig. 2. The minimum energy structures of C_mN_2 ($m = 2$–14) cationic and C_mN_2 ($m = 6$–14) anionic clusters form linear arrangements with $D_{\infty h}$ symmetry except for $C_{11}N_2^+$ ion whereas C_mN_2 ($m = 1$–5) anions form chain-like configurations. Two N atoms favor to bond at ends in linear and chain-like structures.

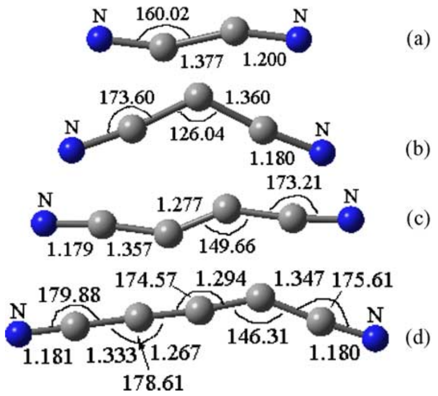

Fig. 1. Minimum energy structures of anionic clusters (a–d).

3.1. Geometry

3.1.1. CN_2

Armstrong et al. [5] investigated three different neutral and cationic isomers at B3LYP/6-311+G(2df) level. We support their predictions that the lowest-energy neutral CN_2 molecule is a N–C–N ($D_{\infty h}$, $^3\Sigma_g^-$) conformer. A linear N–N–C ($C_{\infty v}$, $^3\Sigma$) is 1.29 eV less stable. Their difference in energy and energy ordering are quite similar to previous calculation (1.26 eV [5]) on neutral molecule.

Their energy ordering is changed in the cationic configuration. The linear N–C–N ($D_{\infty h}$) is slightly higher in energy, 0.22 eV, than the N–N–C ($C_{\infty v}$) conformer. The N–N and N–C bond lengths for N–N–C cationic ion are 1.165 and 1.232 Å, respectively. Their energy difference is also quite analogous to the previous result (0.25 eV [5]). For all other members of this series, those linear isomers having terminal nitrogen atoms are the lowest energy configuration.

The energy ordering of two linear structures is preserved in the anion. The linear N–C–N ($D_{\infty h}$) is more stable than that linear N–N–C ($C_{\infty v}$) by 2.02 eV.

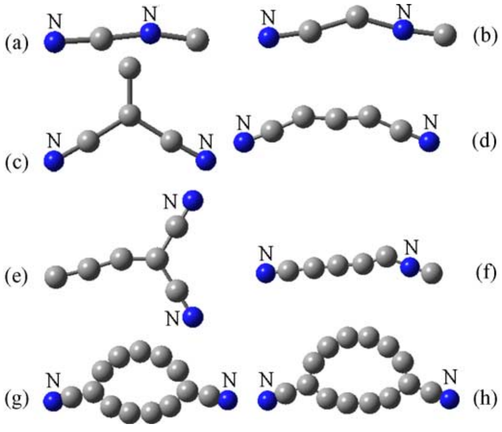

Fig. 2. Energetically low-lying isomers of C_mN_2 cationic and anionic clusters (a–h).

3.1.2. C_2N_2

C_2N_2 has a linear N–C–C–N ($D_{\infty h}$, $^1\Sigma_g^+$) minimum energy with $d_{C–C} = 1.3751$ Å and $d_{C–N} = 1.1551$ Å. The differences in calculated bond lengths and experimental values [24] are smaller than 0.6% and there exists a systematic trend in the remaining small errors. Botschwina [25] studied NCCN molecule with MP2, CCSD, CEPA-1 and CCST(T) methods, and their bond lengths are closer to experimental data [24] than ours. Two linear N–C–N–C ($C_{\infty v}$, $^1\Sigma$) and C–N–N–C ($D_{\infty h}$, $^1\Sigma_g^+$) isomers are 1.04 and 3.10 eV less stable above minimum energy, respectively.

The energy ordering is partially changed in the cationic ion. The linear N–C–C–N ($D_{\infty h}$) is most favorable conformation. The linear N–C–N–C with an imaginary bending mode frequency lies at 0.94 eV higher in energy. Its bending mode frequency shows a tendency of trying to vibrate the middle carbon atom along radial direction and leads to a bent chain 2(a), which locates at 0.62 eV less stable above the minimum energy.

The linear N–C–C–N ($D_{\infty h}$) configuration is a transition state with an imaginary bending mode frequency in anionic state. Its bending mode frequency shows a tendency of contrarily vibrating two carbon atoms along transverse direction and results in a bent chain 1(a), which is lowest energy state (C_{2h}, ^2B_u). Their difference in energy is 0.02 eV. An isomer [quite similar to 2(a)] is the third most stable state, locating at 1.09 eV higher in energy above the lowest energy state.

3.1.3. C_3N_2

Blanksby et al. [26] has experimentally and theoretically investigated neutral, cationic and anionic C_3N_2 clusters. We support their predictions that the lowest-energy neutral, cationic and anionic configurations are linear, linear and bent chain, respectively. Linear neutral conformer N–C–C–C–N ($D_{\infty h}$, $^3\Sigma_g^-$) is energetically most favorable. Two bent chains C_{2v} ($^1A_1$) [quite similar to 1(b)] and C_s ($^3A''$) [quite similar to 2(b)] locate at 0.80 and 1.24 eV above the minimum energy, respectively.

The energy ordering is partially changed in the cationic ion. The linear N–C–C–N–C with an imaginary bending mode frequency locates 0.48 eV higher in energy. Its bending mode frequency makes linear conformer bent and conduces to a bent chain 2(b) (C_s, $^2A'$), which is 0.47 eV less stable above the linear N–C–C–C–N ($D_{\infty h}$, $^2\Pi_u$). A comparison of our bond lengths and previous calculations (B3LYP/6-31G+(d) [26]) shows their differences are 0.6% (N–C) and 0.4% (C–C) for NC_3N ($D_{\infty h}$) cationic conformer, respectively.

The linear N–C–C–C–N ($D_{\infty h}$) isomer is a transition state with an imaginary bending mode frequency in anionic state. Its bending mode frequency results in a bent chain 1(b), which is lowest energy state (C_{2v}, $^2B_1$). Their difference in energy is 0.20 eV. There are no experimental bond lengths and angles available. The differences in our geometric parameters and calculations (B3LYP/6-31G+(d) [26]) are smaller than 0.8% (bond angles) and 0.9% (bond lengths), respectively. An isomer (C_s, $^2A''$) [similar to 2(b)] is the third most stable state, lying 1.31 eV higher in energy above the lowest energy state.

3.1.4. C_4N_2

Smith et al. [27] produced N–C–C–C–C–N, N–C–C–C–N–C and C–N–C–C–N–C isomers in an argon matrix and measured their vibrational frequencies. The lowest energy C_4N_2 isomer (N–C–C–C–C–N, $D_{\infty h}$) is the linear arrangement of nuclei in the $^1\Sigma_g^+$ electronic state. Our calculations indicate the existence of three linear energetically low-lying isomers except the minimum energy. The linear structures N–C–C–C–N–C ($C_{\infty v}$, $^1\Sigma$), C–N–C–C–N–C ($D_{\infty h}$, $^1\Sigma_g^+$) and C–C–C–N–C–N ($C_{\infty v}$, $^1\Sigma$) are 1.07, 2.22 and 2.60 eV higher in energy relative to the minimum energy, respectively.

Lee [12] and Cao and Peyerimhoff [10] have successively investigated the NC_4N^+ ion with DFT. The linear NC_4N^+ was predicted to be the most stable form, which is consistent with our results. The strongest vibrational band ν_4 of linear NC_4N^+ was predicted to be 2133.3 cm^{-1}. A comparison of calculated and experimental frequency (2010 cm^{-1} [29]) shows a good agreement if the calculated value is scaled by factor 0.957. The linear isomers N–C–C–C–N–C ($C_{\infty v}$), C–N–C–C–N–C ($D_{\infty h}$) and C–C–C–N–C–N ($C_{\infty v}$) are 0.69, 1.51 and 1.70 eV higher, respectively, in energy above the linear N–C–C–C–C–N ($D_{\infty h}$, $^2\Pi_u$).

The linear N–C–C–C–C–N ($D_{\infty h}$) is a transition state with an imaginary bending mode frequency in anionic state. Its bending mode frequency reveals that two carbon atoms contrarily vibrate along transverse direction and conduces to a bent chain 1(c), which is lowest energy state (C_{2h}, ^2A_g). Their difference in energy is 0.02 eV. A new isomer 2(c) (C_{2v}, $^2B_2$) is the third most stable state, lying at 1.01 eV higher in energy above the lowest energy state.

3.1.5. C_5N_2

Linear NC_5N ($D_{\infty h}$) molecule [7,8,27,28] was predicted to be lowest energy structure. We support their conclusions that the neutral C_5N_2 has a linear NC_5N minimum energy ($D_{\infty h}$, $^3\Sigma_g^-$). This is followed by a bent NC_5N (C_{2v}, $^3B_1$) [quite similar to 2(d)], which is 0.16 eV higher in energy. The next isomer in the energy ordering, at 0.79 eV above the minimum energy, is found to be a C_{2v} ($^1A_1$) configuration, which is derived from capping a carbon atom between two middle C atoms in N–C–C–C–C–N molecule.

The energy ordering is partially changed in the cationic state. A bent chain [quite similar to 2(d)] lies at 0.16 eV higher in energy above the lowest state NC_5N ($D_{\infty h}$). The linear NC_4NC ($C_{\infty v}$) becomes more stable and locates at 0.66 eV higher in energy.

The energy ordering is changed in the anion. In terms of energetic behavior, the most favorable anionic configuration is bent chain NC_5N (C_s) 1(d). The linear NC_5N ($D_{\infty h}$) and bent chain 2(d) locate at 0.011 and 0.014 eV, respectively. They are nearly degenerate.

3.1.6. C_6N_2

Chuchev and BelBruno [8] performed density functional calculations (B3LYP/cc-pVTZ) on C_6N_2 molecule and predicted the minimum energy geometry to be linear structure. We support their conclusions that the linear NC_6N ($D_{\infty h}$, $^1\Sigma_g^+$) is the most favorable state. There are three energetically low-lying linear species except the minimum energy. The linear species NC_5NC ($C_{\infty v}$, $^1\Sigma$), CNC_4NC ($D_{\infty h}$, $^1\Sigma_g^+$) and C_3NC_3N ($C_{\infty v}$, $^1\Sigma$) locate at 1.10, 2.23 and 2.60 eV higher in energy relative to the minimum energy, respectively.

Lee [12] studied the $C_4N_2{}^+$ and $C_6N_2{}^+$ cationic ions with BLYP method and the linear $C_6N_2{}^+$ was predicted to be the most favorable form, which is consistent with our results. The strongest vibrational band ν_2 of linear NC_4N^+ was predicted to be 2194.4 cm^{-1}. A comparison of calculated frequency and experimental observation (2093.8 cm^{-1} [30]) clearly indicates an excellent agreement if the calculated value is scaled by the same factor (0.957). The linear isomers NC_5NC ($C_{\infty v}$) and CNC_4NC ($D_{\infty h}$) locate at 0.76 and 1.57 eV higher, respectively, in energy relative to the minimum energy.

The energy ordering is partially changed in the anionic state. The most favorable anionic conformation is also linear ($D_{\infty h}$) form. The branched form 2(e) and bent chain 2(f) locate at 1.06 and 1.37 eV, respectively. The charged-induced structural relaxation appears to be small for this anion so that the neutral and anionic conformers have the same form. This cluster size is a watershed in structural rearrangement upon charging in C_mN_2 clusters. The structural changes induced by charging are small when cluster size is greater than number 7.

3.1.7. C_7N_2

The difference in singlet and triplet states of linear NC_7N molecule is 0.71 eV and the triplet state ($D_{\infty h}$, $^3\Sigma_g^-$) is most favorable in energy. This is followed by a branched form (C_s, $^1A'$), lying at 1.06 eV, which is derived from capping a C atom between 3rd and 4th atoms in N–C–C–C–C–C–C–C–N structure. A linear NC_6NC ($C_{\infty v}$, $^1\Sigma$) is 1.16 eV higher in energy.

The energy ordering is partially changed in the cationic ion. The bent chain N–C–C–C–C–C–C–C–N (C_s, $^2A'$) [similar to 2(d)] and linear NC_6NC ($C_{\infty v}$) locate at 0.02 and 0.76 eV higher in energy relative to the linear NC_7N ($D_{\infty h}$), respectively.

The energy ordering is partially changed in the anionic state. The most favorable structure is also linear form NC_7N ($D_{\infty h}$). A branched form (C_{2v}, $^2B_1$) [similar to 2(e)] and a bent chain N–C–C–C–C–C–C–N–C (C_s, $^2A''$) [similar to 2(f)] locate at 0.87 and 1.44 eV, respectively.

3.1.8. C_8N_2

The linear NC_8N is the most stable and its triplet state energy is 2.15 eV higher above the singlet state. There are two low-lying linear species except the minimum energy. The linear isomers NC_7NC ($C_{\infty v}$, $^1\Sigma$) and CNC_6NC ($D_{\infty h}$, $^1\Sigma_g^+$) are 1.10 and 2.24 eV higher in energy, respectively.

The energy ordering is preserved in the cationic ion. The linear NC_7NC ($C_{\infty v}$) and CNC_6NC ($D_{\infty h}$) are 0.82 and 1.67 eV higher in energy relative to the linear NC_8N, respectively. Agreiter [30] produced NC_8N^+ cationic cluster, but no experimental bond lengths and vibrational frequencies were reported. Our bond lengths and vibrational frequencies should be useful for future experimental investigations.

The energy ordering is partially changed in the anion. The most favorable anionic conformer is also linear form NC_8N ($D_{\infty h}$). A branched form (C_{2v}, $^2B_2$) [similar to 2(e)] and a bent chain (C_s, $^2A'$) [similar to 2(f)] locate at 1.12 and 1.40 eV, respectively.

3.1.9. C_9N_2

The singlet state energy is 0.64 eV higher above the triplet state for linear NC_9N molecule. A bent chain NC_9N (C_{2v}, $^3B_1$) [similar to 2(d)] and a linear NC_8NC ($C_{\infty v}$, $^3\Sigma$) locate at 0.27 and 1.15 eV higher, respectively, above the minimum energy.

The energy ordering is preserved in the cationic state. The bent chain NC_9N (C_{2v}) and linear NC_8NC ($C_{\infty v}$) locate 0.25 and 0.82 eV higher, respectively, above the minimum energy.

The energy ordering is also preserved in the anionic state. The linear form NC_9N ($D_{\infty h}$) is most favorable conformer. A bent chain NC_9N (C_{2v}) [similar to 2(d)] and linear NC_8NC ($C_{\infty v}$) lie 0.30 and 1.43 eV higher, respectively, above the minimum energy.

3.1.10. $C_{10}N_2$

The singlet state of linear $NC_{10}N$ molecule is more stable than its triplet states by 1.88 eV. Similar to C_8N_2 molecule, two linear NC_9NC ($C_{\infty v}$, $^1\Sigma$) and CNC_8NC ($D_{\infty h}$, $^1\Sigma_g^+$) species are 1.12 and 2.26 eV higher in energy, respectively.

The energy ordering is preserved in the cationic state. Similar to C_8N_2 cluster, the linear NC_9NC ($C_{\infty v}$) and CNC_8NC ($D_{\infty h}$) are 0.87 and 1.74 eV higher in energy relative to the linear $NC_{10}N$ ($D_{\infty h}$), respectively.

The energy ordering is partially changed in the anion. The most favorable isomer $C_{10}N_2{}^-$ is also linear form $NC_{10}N$ ($D_{\infty h}$). Similar to C_8N_2 anion, a branched form (C_{2v}) [similar to 2(e)] and a linear NC_9NC ($C_{\infty v}$) locate at 1.20 and 1.40 eV higher in energy, respectively.

3.1.11. $C_{11}N_2$

The singlet state energy is 0.59 eV higher above the triplet state for linear $NC_{11}N$ molecule. Similar to C_9N_2 molecule, a bent chain $NC_{11}N$ (C_{2v}, $^3B_1$) locates 0.28 eV higher in energy above minimum energy. This followed by a linear isomer $NC_{10}NC$ ($C_{\infty v}$, $^3\Sigma$), which is 1.15 eV higher in energy.

The energy ordering is preserved in the cationic state. Similar to C_9N_2 cluster, the bent chain $NC_{11}N$ (C_{2v}) and linear $NC_{10}NC$ ($C_{\infty v}$) locate 0.26 and 0.87 eV higher above the linear $NC_{11}N$ ($D_{\infty h}$) cationic state, respectively.

The energy ordering is partially changed in the anionic species. The chain $NC_{11}N$ (C_{2v}, $^2B_1$) is a little bent and the most favorable conformer. The bent chain $NC_{11}N$ (C_{2v}) and a branched form (C_{2v}, $^2B_1$) [similar to 2(e)] lie 0.32 and 1.12 eV higher in energy.

3.1.12. $C_{12}N_2$

The linear structure $NC_{12}N$ is the most stable and its triplet state energy is 1.68 eV higher above the singlet state. Similar to the $C_{10}N_2$ molecule, the linear $NC_{13}NC$ ($C_{\infty v}$, $^1\Sigma$) and a planar C_{2v} ($^1A_1$) ring are 1.12 and 1.72 eV higher in energy, respectively. This is first time that a cyclic structure appears as one of the energetically lowest three isomers in this series. For pure carbon C_n clusters, the geometric change from chain to ring was observed around $n = 10$ [15]. However, similar change appears around $m = 12$ [22] in Si_2C_m clusters. This change has not appeared up to $m = 14$ in C_mN_2 clusters.

The energy ordering is partially changed in the cationic ion. Similar to $C_{10}N_2$ cluster, the linear $NC_{11}NC$ ($C_{\infty v}$) and $CNC_{10}NC$ ($D_{\infty h}$) are 0.90 and 1.82 eV higher in energy relative to the linear $NC_{12}N$ ($D_{\infty h}$), respectively.

The energy ordering is partially changed in the anion. The most favorable isomer $C_{12}N_2^-$ is also linear form $NC_{12}N$ ($D_{\infty h}$). Similar to $C_{10}N_2$ anion, a branched form [similar to 2(e)] and the linear NC_9NC ($C_{\infty v}$) locate at 1.30 and 1.47 eV, respectively.

3.1.13. $C_{13}N_2$

The singlet state energy is 0.55 eV higher above the triplet state for linear $NC_{13}N$ molecule. This is followed by a bent chained $NC_{13}N$ (C_{2v}, $^3B_1$) isomer, which is 0.21 eV higher in energy. The third is a linear isomer $NC_{12}NC$ ($C_{\infty v}$, $^3\Sigma$), being 1.15 eV higher in energy.

The energy ordering is preserved in the cationic state. Similar to $C_{11}N_2$ cluster, the bent chain $NC_{13}N$ (C_{2v}) and linear $NC_{12}NC$ ($C_{\infty v}$) isomers lie 0.20 and 0.90 eV higher, respectively, above the linear $NC_{13}N$ ($D_{\infty h}$) cationic cluster.

The energy ordering is partially changed in the anion. The linear form $NC_{13}N$ ($D_{\infty h}$) is most favorable anion. A bent chain $NC_{13}N$ (C_{2v}) and the ring-like form (C_{2v}, $^2B_1$) 2(g) lie 0.26 and 1.31 eV higher, respectively, above the minimum energy.

3.1.14. $C_{14}N_2$

The difference in singlet and triplet state of linear $NC_{14}N$ molecule is 1.54 eV. A linear $NC_{13}NC$ ($C_{\infty v}$, $^1\Sigma$) and a planar C_{2v} ($^1A_1$) structures [quite similar to 2(h)] are 1.13 and 2.21 eV higher, respectively, in energy above the minimum energy.

The energy ordering is preserved in the cationic state. The linear $NC_{13}NC$ ($C_{\infty v}$) and planar C_{2v} ($^2A_1$) ring 2(h) are 0.93 and 1.84 eV higher in energy relative to the linear $NC_{14}N$ ($D_{\infty h}$), respectively.

The energy ordering is partially changed in the anion. A linear $NC_{13}NC$ ($C_{\infty v}$) and a branched form [similar to 2(e)] are 1.36 and 1.38 eV higher in energy relative to the linear $NC_{14}N$ ($D_{\infty h}$), respectively.

3.2. Structural relaxation

In CN_2 ($D_{\infty h}$) molecule, the carbon atom bears positive charge (0.292e), and each of nitrogen atoms has negative charge (−0.146e). However, both carbon and each of nitrogen atoms hold the same sign of electric charge (C 0.6e and N 0.4e, respectively) in CN_2 ($D_{\infty h}$) cationic configuration. Removal of an electron on ionization results in electrostatic interaction inversion from attraction to repulsion. The electrostatic interaction inversion accounts for the increase of C–N bond length in the cationic state. In C_2N_2 molecule, changes induced by ionization are quite noticeable. The structural changes involve a decrease of the C–C distance and an increase of the N–C distance to similar extents. They result from removing an electron from the highest occupied orbital (HOMO) with antibonding (C–C) and bonding (C–N) characters. In odd-number $C_{2m+1}N_2$ ($D_{\infty h}$) molecules except for CN_2, removal of an electron on ionization gives rise to decrease of all C–C bond lengths and decrease in total sum of bond lengths in $C_{2m+1}N_2$ ($D_{\infty h}$) cationic ions. In even-number $C_{2m}N_2$ ($D_{\infty h}$) molecules except for C_2N_2, removal of an electron on ionization results in increment of C–N bond lengths. Total decrease of C–C bond lengths is greater than sum of C–C and C–N bond-length increment. This explains the decrease in total sum of bond lengths in $C_{2m}N_2$ ($D_{\infty h}$) cationic ions.

In NCN^- ($D_{\infty h}$) anion, the carbon atom bears positive charge (0.14e), and each of nitrogen atoms has negative charge (−0.57e). The repulsive electrostatic force between N and N atoms is greater than attractive electrostatic interaction between N and C atoms. Hence, the C–N bond length increases upon affinity. The geometries of $C_2N_2^-$, $C_3N_2^-$, $C_4N_2^-$ and $C_5N_2^-$ for doublet states are all planar conformers, but they deviate more largely from the linear structures. Their bent forms result from second order Jahn-Teller effect [13]. The geometries of $C_mN_2^-$ ($m > 5$) for doublet states are all linear species. The C–N bond lengths of all $C_mN_2^-$ ($5 < m < 14$) increase upon charging. The sum of C–C and C–N bond-length increments is greater than total decrease of C–C bond lengths. This can account for the increase in total sum of bond lengths in $C_{2m}N_2$ ($D_{\infty h}$) anions.

3.3. Relative stability

We have adopted HOMO–LUMO gaps to explore the relative stability of the neutral clusters. The HOMO–LUMO gaps are plotted in Fig. 3(a). It is clear that the gap values are larger as even m and lower as odd m, which indicates that those C_mN_2 neutral clusters corresponding to even m are more stable. The large adiabatic ionization potential (AIP) of the corresponding neutral cluster is another indication of the stability of the clusters. The calculated AIP values of C_mN_2 are shown in Fig. 3(b). The AIP values hold the same

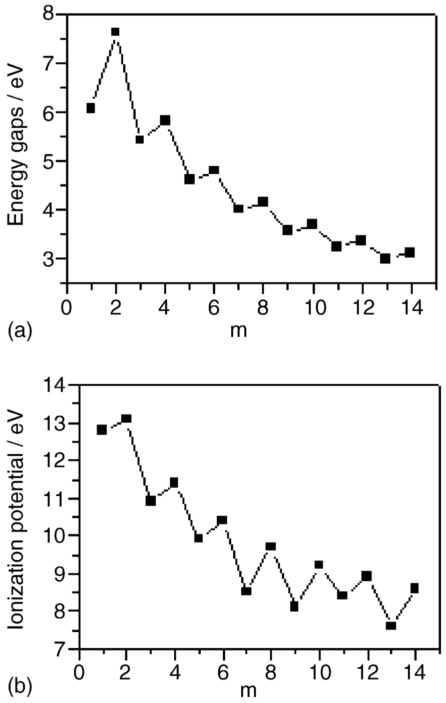

Fig. 3. (a) HOMO–LUMO gaps vs. *m*. (b) Adiabatic ionization potential vs. *m*.

trend as energy gaps. Both AIP and energy gap values tend to decrease with increasing number of total atoms. They reveal that the neutral C_mN_2 clusters are more instable with increasing cluster size, so this may be the reason why the larger neutral C_mN_2 clusters have not been observed until now.

The larger electron affinity of the corresponding cluster is another indication of the stability of the anions. The electron affinities are larger as odd *m* and lower as even *m* in Fig. 4, which shows that those $C_mN_2^-$ anions corresponding to odd *m* are more stable. The electron affinities have a flattening tendency with increasing cluster size, suggesting that their even–odd alternation of stability becomes more and more weaker with increasing cluster size.

To test the relative stabilities of $C_mN_2^+$ cationic ions further, the following energy variation of reactions is considered:

$$2(C_mN_2) \rightarrow C_{m+1}N_2 + C_{m-1}N_2$$

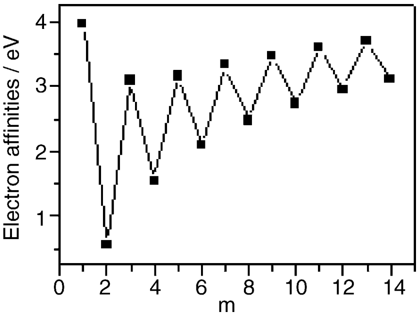

Fig. 4. Adiabatic electron affinities vs. *m*.

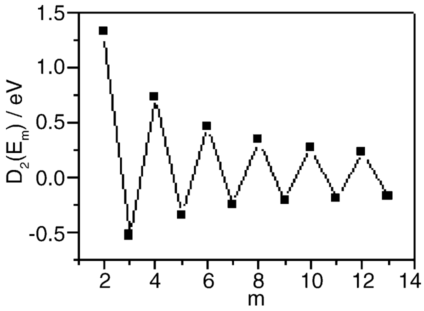

Fig. 5. Second difference in energy for cationic ions vs. *m*.

We define the energy variation in the formula as $D_2(E_m) = E_{m+1} + E_{m-1} - 2E_m$, which is the second difference in energy for cationic ions. Hence, we obtain the curves shown in Fig. 5 corresponding to the energy variations in the formula as *m*. It is evident that the $D_2(E_m)$ is larger as even *m* and lower as odd *m* in Fig. 5, which suggests that those $C_mN_2^+$ cationic species corresponding to even *m* are more stable. Hence, it can be excellent to explain why $C_2N_2^+$ and $C_6N_2^+$ in TOF mass spectra [11] are more stable. The $D_2(E_m)$ for cationic ions have a flattening trend with increasing number of total atoms, indicating that their stability appears a weak even–odd alternation with increasing cluster size.

3.4. General discussion

The stability alternation and the variation of spin state for neutral NC_mN clusters are a result of the number of available valence electrons. The electronic structure of neutral C_mN_2 cluster is similar to that of C_{m+2} cluster with polyacetylene structure. C_mN_2 cluster has a total $4(m + 2) + 2$ valence electrons and thus $2(m + 2)$ π electrons will be left to fill the $2(m + 2)$ π orbitals. As shown in [21], for C_mN_2 with odd size ($m + 2 = 2k + 1$), all $2k$ π bonding orbitals are filled up by $2(m + 2) = 4k + 2$ electrons and the remaining two electrons just fill in the 2 non-bonding orbitals. The π orbitals are doubly degenerate. Since each π orbital can be occupied by two electrons, two non-bonding orbitals (HOMO) are just half-filled. However, for C_mN_2 with even size ($m + 2 = 2k$), all $2(m + 2) = 4k$ electrons fill in $2k$ bonding orbitals and the HOMO is fully filled. Therefore, C_mN_2 with even size will be much more stable than those with odd size. Similar effect has been observed in linear carbon clusters with one or two heteroatoms [22].

For C_mN_2 with odd size, there are two non-bonding orbitals occupied by two electrons, in which electrons occupy degenerate states with a maximum number of unpaired electrons (Hund's rules). Hence, the C_mN_2 clusters with odd size have triplet minimum energy. However, for C_mN_2 with even size ($m + 2 = 2k$), all $2(m + 2) = 4k$ electrons fill in $2k$ bonding orbitals and the HOMO is fully filled. There is no unpaired electron in bonding orbitals, so they have singlet minimum energy. For singly charged C_mN_2 ions, they all have doublet minimum energy because there is only one unpaired electron in the highest occupied orbital.

4. Conclusions

C_mN_2 ($m = 2$–14) cationic and C_mN_2 ($m = 6$–14) anionic clusters form linear structures with $D_{\infty h}$ symmetry except $C_{11}N_2^+$ cationic ion whereas C_mN_2 ($m = 1$–5) anionic species form chain-like structure. Two N atoms favor to bond at ends in linear and chain-like conformer. The structural relaxation upon affinity becomes small when the number of total atoms is greater than 7. Both calculated HOMO–LUMO gaps and ionization potentials show that the C_mN_2 ($m = 1$–14) neutral clusters with even m are more stable than those with odd m. The second difference in energy reveals that the C_mN_2 ($m = 1$–14) cationic ions with even m are more stable than those with odd m, which is consistent with the observed even–odd alternation of the TOF signal intensities. The cationic stability appears a weak even–odd alternation with increasing cluster size. Our calculations indicate neutral and ionic C_mN_2 clusters are more instable with increasing cluster size.

Supplementary Information

Total electronic energies, the lowest vibrational frequencies, the strongest vibrational band, and bond lengths of the most stable configurations are included in Supplementary Information.

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