



A COMPUTATIONAL INVESTIGATION ON THE NITROGEN-RICH C_2N_{10} , C_6N_{12} , AND C_6N_{20} COMPOUNDS BY DENSITY FUNCTIONAL METHODS

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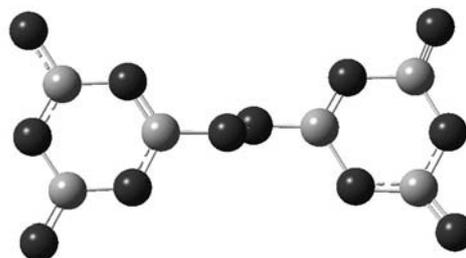
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The nitrogen-rich compounds of C_2N_{10} , C_6N_{12} , and C_6N_{20} molecules are optimized at the (U)B3LYP/6-31G(d) level. Total energies, IR, NMR chemical shifts, and equilibrium geometries of C_2N_{10} , C_6N_{12} , and C_6N_{20} molecules are calculated. The stabilities of C_2N_{10} and C_6N_{20} molecules are discussed. The predicted IR spectra and NMR chemical shifts as well as equilibrium geometries of C_6N_{20} molecules are in good agreement with available experimental measurements. Particularly, the high-energy-density nitrogen-rich C_6N_{12} molecule with nonet spin state and eight unpaired electrons is determined as the ground state with electronic state of 9A_g , reflecting that C_6N_{12} is a high-spin organic magnetism and molecular-spin material. Furthermore, the average N-N dissociation energy with respect to the removal of N_2 molecules from C_6N_{20} molecules is predicted, which corresponds to single N-N bond energy (40 Kcal/mol for the N-N single bond). On the basis of the calculated natural populations and natural electron configurations, the charge-transfer is discussed and N_3 chains in C_2N_{10} and C_6N_{20} molecules are bound tightly with triple covalent bonds.



INTRODUCTION

The design and synthetic high-energy-density nitrogen-rich materials have been extensively investigated theoretically and experimentally,¹⁻²² Nitrogen-rich compounds are expected to release a large amount of energy when they are decomposed into N_2 molecules; therefore, these species are potentially promising and interesting recently as high-energy-density materials.^{1,3,6} The pentanitrogen cation (N_5^+) in bulk compounds has been demonstrated to be the feasibility of experimentally pursuing polynitrogen-containing materials.^{2,7}

Although the cyclic N_5^- anion was identified in the gas phase, which opened the route to explore further pentazole derivatives, suggesting the possibility of preparing the $N_5^+N_5^-$ cluster, the synthetic scientists have given up trying to synthesize these all-nitrogen compounds because the calculated results indicate that they simply are too unstable to isolate as solids. The metastable N_4 and N_6^- diazide chain radicals were observed experimentally,^{9,10} and the N_4 -CH- N_5 ,¹² 1,2,4,5-tetrazine-based high-energy density materials¹³ have been investigated theoretically because these compounds can be utilized as the basis for the

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preparing the high-energy-density materials. Furthermore, employment of reliable predictive methods can help scientists to synthesize, characterize, and formulate new candidate energetic molecules and the nitrogen compounds.^{11,18}

Experimental measurements and theoretical calculations indicated that cyanuric azide (C_3N_{12}) is a planar C_{3h} symmetry.²¹ Moreover, the stepwise generations of the corresponding high-spin mononitrene, dinitrene, and trinitrene are observed by matrix IR and electronic paramagnetic resonance spectroscopy (EPRS)² and septet trinitrene was confirmed by EPRS, together with the verification by the UB3LYP/6-31G* calculations.² In addition, the synthesis and full characterization of an azobis (diazidorizine) C_6N_{20} ,⁴ BN_{17} , and PN_{17} ⁵ compounds are reported in that these high-nitrogen compounds with $N\equiv N$ triple bond dissociation energy of 945 KJ mol^{-1} form a unique class of energetic materials with very high positive heats of formation and the large number of inherently energetic N-N and C-N bonds contributes to the high heat of formation.^{5,16} A critical property for an effective high-energy-density material is a high dissociation energy barrier, and these compounds, besides being an interesting gambit to gain fundamental chemical knowledge, are potential candidates as commercial high-energy-density materials that may be used as explosives, propellants, and fireworks.²²

Nitrogen-rich compounds, which are potential high-energy-density materials, have been extensively investigated theoretically.^{7,11,18-21} Accurate CCSD(T) calculations show that N_5^- anion is a D_{5h} geometry,¹¹ lying 14.3 kcal/mol above $N_3^- + N_2$ with an energy barrier of 27.8 kcal/mol for dissociation. A variety of all-nitrogen N_n ($n=2-14, 48, 60$) compounds have been studied theoretically,¹⁹ however, all-nitrogen compounds are generally kinetically unstable.²⁴ The structures and relative energies of N_5XN_5 , X_2N_{10} ($X=C, N$),^{9,18} $M(N_5)_n^{2-}$ ($M=Si, Cr, Mo, \text{ and } W$),²³ and WN_n ¹⁴ as well as metal- $(N_5)_n$ ($n=1,2$) compounds^{24,25} have been predicted by using density functional methods while the high-energy-density materials with nitrogen-rich systems containing hydrogen, lithium, or aluminum have been reported.^{26,27} The N_8H^+ molecule, which consists of $N_5^+ + HN_3$, was successfully synthesized and calculated at the B3LYP/6-31++G** level, barrier heights of the synthetic pathway in the forward and reverse directions were predicted and the rate constant was obtained theoretically.²⁶ The kinetically stable

nitrogen-rich N_nO_m ($n=4,6; m=1-3$) clusters were calculated at the CCSD level,²⁸ the heat of formation was calculated and the covalent bonded O atom was found to stabilize the planar nitrogen rings.

COMPUTATIONAL DETAILS

Due to the importance of accurate and reliable methods for estimation of density of energetic compounds, *ab initio* methods have been developed to predict density of some classes of energetic compounds. All calculations are performed with the Gaussian 98 program.³⁰ Geometrical optimizations of C_2N_{10} , C_6N_{12} , and C_6N_{20} systems are carried out at the Becke three-parameter Lee, Yang and Parr exchange-correlation functional (B3LYP) level employing 6-31G(d) basis sets. A systematic investigation of C_2N_{10} , C_6N_{12} , and C_6N_{20} molecules at the B3LYP/6-31G(d) level gives general and reasonable conclusions. B3LYP/6-31G(d) calculation of N_2 bond length gives 1.11 \AA , which is in good agreement with reported experimental and theoretical results (1.13 \AA ³¹ and 1.10 \AA ³²). B3LYP/6-31G(d) method is capable of providing results of very satisfactory and reasonable quality for the geometries, stabilities, and spectroscopic properties of C_2N_{10} , C_6N_{12} , and C_6N_{20} molecules. For each stationary point of each molecule, the character (local minimum, transition state, etc) was determined by the harmonic vibrational frequencies. Vibrational frequencies predicted at the B3LYP/6-31G(d) level were scaled by 0.9614 .³³ NMR chemical-shifts of carbon atoms in the isomers are computed with the Gauge-Independent Atomic Orbital (GIAO) method³⁴ after the geometry optimizations are performed at the B3LYP/6-311G** level. In addition, the total energies of C_6N_{20} and C_6N_{12} isomers (single point calculations) are calculated at the (U)MP2/6-311++G(2,d,p)//B3LYP/6-31G(d) level.

RESULTS AND DISCUSSION

1. C_2N_{10} isomers

The 3,6-di(azido)-1,2,4,5-tetrazine C_2N_{10} molecule has been synthesized.^{5,8} In order to give a systematic investigation of the C_2N_{10} molecule, the possible geometries of C_2N_{10} isomers (Figure 1) are optimized at the (U)B3LYP/6-31G(d) level.

The calculated total energies of the stable isomers are presented in Table 1. The bond lengths and the natural net populations of the stable geometries are

labeled in Figure 1, which are in good agreement with previous simulated results.^{7,9}

Table 1

Total energies and relative energies of C_2N_{10} isomers at the B3LYP/6-31G(d) level. (Units: E_T , hartree; ΔE , eV)

| Systems | C_s | C_{2v} | C_{2v} | C_{2v} | C_i | C_s | C_{2v} |
|------------|--------------|--------------|--------------|--------------|--------------|--------------|-------------|
| | A1 | A2 | A3 | A4 | A5 | A6 | A7 |
| E_T | -623.5266733 | -623.5275719 | -623.5248861 | -623.5048544 | -623.5050678 | -623.4839058 | -623.490193 |
| ΔE | 0.02 | 0.00 | 0.07 | 0.62 | 0.61 | 1.19 | 1.02 |

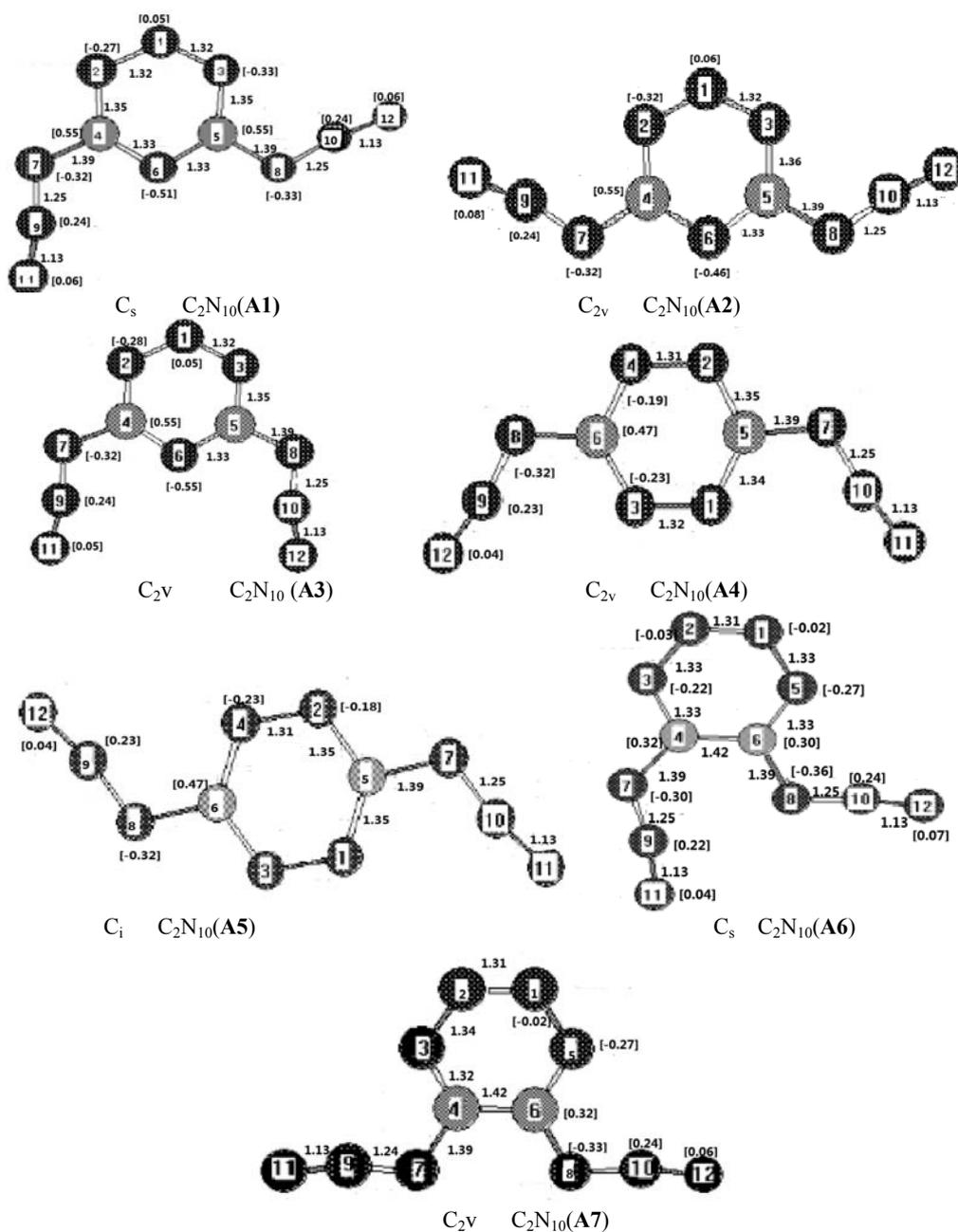


Fig. 1 – Equilibrium geometries of C_2N_{10} isomers with singlet spin multiplicity. [0.05] represents natural atomic net charge while the others represent calculated bond lengths, the numbers which are not in parentheses are bond lengths (Å).

For the meta-Diazo-*s*-tetrazine isomers (Figure 1, **A1**, **A2**, and **A3**), C_s and C_{2v} isomers are optimized, and total energy of C_{2v} **A2** isomer is about 0.56 kcal/mol lower than that of C_s isomer. Therefore, C_{2v} **A2** isomer is more stable than C_s **A1** and C_{2v} **A3** isomers. It is found that total energy difference between C_s **A1** and C_{2v} **A2** isomers equals to calculated rotational energy barrier of N(7)-N(9)-N(11) chain (0.56 kcal/mol). Furthermore, the shortest N-N bond lengths in C_s **A1** and C_{2v} **A2** isomers are shown to be triple bonds by natural orbital analysis. **A1**, **A2**, and **A3** units are the building blocks of the C_6N_{20} isomers, which will be discussed later.

Although the 3,6-di(azido)-1,2,4,5-tetrazine(para) C_2N_{10} isomer has been synthesized,^{5,8} the equilibrium geometry of D_{2h} C_2N_{10} isomer is considered firstly. The calculated results show that the D_{2h} isomer is not a stable structure because several imaginary frequencies are found. After appropriate distortion of the geometry, the new C_{2v} **A4** isomer is yielded as a stable geometry (Figure 1, **A4** and **A5**), and new C_i **A5** isomer is yielded after rearrangement of the N(8)-N(9)-N(12) chain. The calculated total energies of C_{2v} **A4** and C_i **A5** isomers show that C_{2v} **A4** isomer is about 0.13 kcal/mol higher in total energy than C_i **A5** isomer which results from the rotation of N(8)-N(9)-N(12) chain. Therefore, C_i **A5** isomer is more stable than C_{2v} **A4** isomer, which is consistent with the fact that only C_i **A5** isomer was found in the crystal and matches the conformation in the X-ray structure.⁸ The calculated geometry parameters of C_i **A5** have little deviations to the experimental measurements, and are in agreement with the experimental results.

Guided by the above calculated results, two new ortho-di(azido)-tetrazine isomers with C_{2v} and C_s symmetries are obtained (Figure 1, **A6** and **A7**) to be the only stable structures. The difference of total energies between C_{2v} and C_s isomers is due to rotation of N(7)-N(9)-N(11) chain, calculated difference of energy is 3.95 kcal mol⁻¹. The shortest N-N bond lengths in N3 chains of C_s C_2N_{10} isomer are the same as that of free N_2 molecule²³ and experimental value of 1.11 Å in the 3,6-di(azido)-1,2,4,5-tetrazine(para) isomer.⁹ According to calculated natural orbital analysis on N_3 chains of C_{2v} and C_s isomers, the shortest N-N bonds are triple bonds. In addition, the calculated geometries are in good agreement with previous reported results.⁹

On the basis of calculated data shown in Figure 1, it is easily found that rotation of N(8)-N(9)-N(12)

chain results in the different isomers. However, C_{2v} **A2** isomer is the most stable isomer. Moreover, **A1**, **A2**, and **A3** isomers with small energy difference are obviously stable than others, consequently, they are the building block for the new high-energy material.

2. C_6N_{20} isomers

Three nitrogen-rich compound 4,4',6,6'-tetra(azido)azo-1,3,5-triazine (Figure 2) isomers, corresponding to a so-called α -isomer and two β -isomers, have been observed experimentally,^{5,7} On the basis of X-ray experimental results,^{5,7} the C_1 α -isomer is approximate centric molecular symmetry and four N3 chains direct to the direction of azo chain. The C(2)-N(1)-N(14)-C(15) and N(4)-C(2)-N(1)-N(14) dihedral angles of $\beta(1)$ -isomer (or $\beta(2)$ -isomer) maintaining C_1 (or C_i) center symmetry are 180 (or 180) and 97 (or 135)°, respectively (Table 2). Four N3 chains in $\beta(1)$ -isomer point to the reverse directions of α -isomer. The possible geometries of α -isomer, $\beta(1)$ -isomer, $\beta(2)$ -isomer, γ -isomer, ϵ -isomer, and δ -isomer are considered theoretically with a trans N(1)=N(14) group in azo chain that connects the two separate and essentially planar halves of the C_2N_{10} molecules, which are discussed above. In order to characterize the chemical properties of the 4,4',6,6'-tetra(azido)azo-1,3,5-triazine and to compare with available experimental results, several possible C_6N_{20} geometries based on the 4,4',6,6'-tetra(azido)azo-1,3,5-triazine are considered, geometrical optimizations of the possible isomers are performed. Furthermore, theoretical results show that the isomer with one triazine group being perpendicular to other has an imaginary frequency and corresponds to the transition state.

The first structure considered is the C_{2v} structure based on a cis-azo group, vibrational frequencies indicate that the planar C_{2v} C_6N_{20} isomer is not a local minimum. The optimized new C_2 isomer, obtained by slightly distorted C_{2v} geometry in the direction of the imaginary frequency, is found to be a local minimum (Figure 2). However, C_2 isomer has not been observed experimentally. This is accord with the fact that its total energy is higher than those of the following isomers that are based on a twist azo chain, which will now be discussed.

Table 3

Calculated total energies for different C₆N₂₀ isomers by using B3LYP/6-31G(d) method(units: hartree)

| System | C ₂ | α | β(1) | β(2) | γ | δ |
|----------------|----------------|---------------|---------------|---------------|---------------|---------------|
| ε | | | | | | |
| E _T | -1323.3627467 | -1323.3705468 | -1323.3685197 | -1323.3706338 | -1323.3696419 | -1323.3695771 |
| | 1323.3710794 | | | | | |

The structures with a twist azo chain are considered. C_{2h} α-isomer with azo chain and two triazine groups at the same plane, and C_s isomer with azo chain perpendicular to the two planar halves of molecules are optimized, which have several imaginary frequencies. Furthermore, the stable C_i geometry deviates slightly to the initial C_{2h} and C_s isomers (Figure 2). The calculated C(2)-N(1) bond length of the azo chain in C_i α-isomer is in good agreement with the available experimental results (1.21 and 1.43 Å for N(1)-N(14) and C(2)-N(1) bond lengths, respectively).³⁵ Furthermore, N(10)-N(12) and N(11)-N(13) bond lengths of the four N₃ chains equal to that of free N₂ molecule,²³⁻²⁵ reflecting that N(10) and N(11) atoms are tightly bound to N(12) and N(13) atoms with triple bonds, respectively; natural orbital analyses on N₃ chains of β-isomer and the previous calculated results on N₈H⁺ systems²⁴ support this finding. Additionally, experimental values of N(10)-N(12) and N(11)-N(13) bond lengths³⁵ are in good agreement with our calculated results.

C₁ β(1)-isomer is observed experimentally. However, final optimized C₁ geometry is slightly distorted from C_i geometry. The difference of total energies between β(1)-isomer and α-isomer isomers is 1.29 kcal mol⁻¹, in other words, the average rotational energy of each N₃ chain in C₁ β(1)-isomer is 0.32 kcal mol⁻¹, which is bigger than that of C₂N₁₀ (A3 or A4) isomer. The calculated N(1)-N(14) and N(1)-C(2) bond lengths in azo chain of C₁ β(1)-isomer deviate slightly to the experimental results of 1.20 and 1.45 Å.³⁵ The calculated N(11)-N(13) and N(10)-N(12) bond lengths equal to that of free N₂ molecule,^{23,24} reflecting that N(11)-N(13) and N(10)-N(12) bonds are formed with triple bonds. N(1)-N(14) bond length of C₁ β(1)-isomer is shorter than that of C_i α-isomer, indicating that the elongated N(1)-N(14) bond length of C_i α-isomer is resulted from the rotations of four N₃ chains.

C_i β(2)-isomer is observed experimentally⁵ and C_i β(2)-isomer can be seen as the intermediate of C₁ β(1)-isomer and C_i α-isomer. Total energy of C_i

β(2)-isomer is about 0.05 and 1.33 kcal mol⁻¹ lower than those of C_i α-isomer and C_i β(1)-isomer, respectively (Table 3). Therefore, C_i β(2)-isomer is more stable than their isomers above. On the basis of this finding, one can conclude that the rotational numbers of N₃ chains of nitrogen-rich C₆N₂₀ isomer affect total energy and N(1)-N(14) bond length; The N(10)-N(12) and N(11)-N(13) bond lengths in four N₃ chains are in good agreement with those of available experimental results³⁵ and with that of free N₂ molecule.²⁴ It obviously shows that inherently energetic (10)-N(12) and N(11)-N(13) bonds in four N₃ chains are formed with triple bonds. The calculated C(2)N(1)N(14) bond angle is equivalent to the experimental result of 112°.³⁵

C₁ γ-isomer is formed after rearrangement of four N₃ chains. Specifically, C₁ γ-isomer can be seen as a new intermediate of C_i α-isomer and C₁ β(1)-isomer forms. Total energy of C₁ γ-isomer is about 0.71 kcal mol⁻¹ lower than that of β(1)-isomer. However, C₁ γ-isomer is about 0.58 and 0.62 kcal mol⁻¹ higher in total energy than C_i α-isomer and C_i β(2)-isomer, respectively; the difference of total energies are resulted from the rotations of four N₃ chains. As can be seen from the findings related to the geometries of the examined systems, N(1)-N(14) bond lengths of azo chain of C₁ γ-isomer is the same as that of C_i β(2)-isomer, the calculated C(2)N(1)N(14) bond angle of C₁ γ-isomer is in good agreement with those of C_i α-isomer and C_i β(2)-isomer. According to calculated geometry parameters labeled in Figure 2, it is obvious that the calculated N-N bond length at the separate N₃ chains is different each other, however, the shortest N-N bond lengths of four N₃ chains are in good agreement with those of the experimental results⁵ and that of free N₂ molecule.²³⁻²⁵ Unfortunately, no experimental observation of this structure is reported. Additionally, δ-isomer and ε-isomer are considered and optimized also.

The natural charges of C₆N₂₀ isomers are calculated, which are labeled in Figure 2, natural

populations of C atoms are positive while natural populations of N atoms in two triazine groups are negative, however, N atoms in the shortest N-N bond in N₃ chains of C₆N₂₀ isomers are positive. On the basis of these findings, one notes that charges are transferred from C and N atoms (forming the shortest N-N bonds) to N atoms of triazine groups. Furthermore, charge-transfer in four N₃ chains is very small because N-N bonds in four N₃ chains of C₆N₂₀ isomers are formed with covalent bonds.

According to the calculated total energies of C₂ isomer, α -isomer, two β -isomers, C₁ γ -isomer, δ -isomer, and ϵ -isomer (Table 3), the differences of total energies are very small. However, ϵ -isomer is lower in total energy than those of $\beta(1)$ -isomer, α -isomer, C₁ γ -isomer, and δ -isomer. Therefore, ϵ -isomer corresponds to the lowest-energy structure.

3. IR spectra of C₆N₂₀ isomers

The calculated IR frequencies of triazine groups in C_i α -isomer are 811.8, 1008.9, 1424.3, and 1556.0 cm⁻¹ (Table 4), which correspond to experimental observations of 823, 1011, 1435, and 1549 cm⁻¹, respectively.⁵ Additionally, experimental results show that four N₃ chains of C_i α -isomer have three stretching vibration frequencies of 2132, 2155, and 2208 cm⁻¹, respectively.⁵ Comparison of the calculated active IR results with the available experimental observations shows a slight deviation.

The IR frequencies of C₁ $\beta(1)$ -isomer and C₁ $\beta(2)$ -isomer have been reported experimentally,⁵ the calculated IR frequencies for triazine groups in C₁ $\beta(1)$ -isomer and C₁ $\beta(2)$ -isomer are listed in Table 4. The calculated results show that the intense frequencies at about 1526.6 and 1549 cm⁻¹ correspond to the C-N stretching vibrational frequency of the triazine groups in C₁ $\beta(1)$ -isomer and C₁ $\beta(2)$ -isomer, respectively. The N-N bond stretching frequencies of N₃ chains in C₁ $\beta(1)$ -isomer are predicted to be 2205.2, 2216.6, and 2219.8(inactive) cm⁻¹, respectively; which are assigned as 2155 and 2132 cm⁻¹ being shown in experimental results.⁵ Furthermore, 2216.6 cm⁻¹ of $\beta(1)$ -isomer is predicted to be the intense band theoretically. As for the stretching vibrational frequencies of N₃ chains of $\beta(2)$ -isomer, experimental results of 2155 and 2132 cm⁻¹ are

associated to be the calculated 2217.1 and 2212.3 cm⁻¹, respectively. On the whole, the ranges of the calculated values of IR spectra are in good agreement with the available experimental results.⁵

The IR frequencies of γ -isomer, δ -isomer, and ϵ -isomer are calculated at the B3LYP/6-31G(d) level. According to the calculated results listed at Table 4, the calculated results show that C-N stretching vibrations of triazine of the isomers are about 1504-1551 cm⁻¹, corresponding to the intense bands of IR spectra. In addition, N₃ groups of the isomers generate the intense IR spectra peak of about 2211 cm⁻¹.

4. NMR chemical shifts of the C₆N₂₀ isomers

In order to calculate NMR chemical shifts of C(2), C(5) and C(6) atoms in C₆N₂₀ isomers, geometries of C₆N₂₀ isomers are reoptimized at the B3LYP/6-311G** level. The calculated results are listed at Table 5. For C₂ isomer, NMR chemical shifts are predicted as 181.6, 178.8, and 177.2 ppm (Table 5), respectively. The experimental α -isomer geometry has center symmetry, therefore, two NMR peaks are observed experimentally.⁵ However, our optimized α -isomer geometry with C_i symmetry deviates to the high-symmetry experimental result; consequently, three NMR chemical shifts are found theoretically. The calculated NMR chemical shifts for C(2), C(5), and C(6) atoms in C_i α -isomer compare well with the experimental values of 176.4 and 173.7 ppm. The calculated NMR chemical shifts for C(2), C(5), and C(6) atoms in $\beta(1)$ -isomer are predicted to be 184.35, 178.77, and 177.20 ppm, respectively; the calculated NMR chemical shifts of C(2) and C(6) atoms are assigned as the experimental observed 176.4 and 173.7 ppm, respectively (Table 5), which is in good agreement with experimental measurements of NMR values. However, the calculated NMR chemical shifts of C(2), C(5), and C(6) atoms of $\beta(2)$ -isomer are 182.97, 178.94, and 178.48 ppm, respectively; two NMR chemical shifts of C atoms of C₁ $\beta(1)$ -isomer should correspond to experimental measurements of 176.4 and 173.7 ppm, respectively. NMR chemical shifts of δ -isomer and ϵ -isomer are calculated also, unfortunately, no available experimental results are reported up to now.

Table 4

Comparison of experimental observed IR data (cm^{-1}) with intensities and calculated data for various geometries of 4,4',6,6'-tetra(azido)azo-1,3,5-triazine and experimental results are from Ref 5

| Exp | calculated results | | | | | |
|---------|--------------------|------------|------------|------------|-----------|------------|
| | α | $\beta(1)$ | $\beta(2)$ | γ | δ | ϵ |
| 2208(s) | | | | 2216.0(s) | 2216.5(s) | 2218.2(s) |
| 2155(s) | 2215.3(w) | 2216.6(s) | 2217.1(m) | 2211.89(s) | 2212.1(s) | 2212.4(s) |
| 2132(s) | 2213.6(s) | 2205.2(w) | 2212.3(s) | 2205.5(m) | 2205.3(s) | 2211.6(s) |
| 1549(s) | 1556.0(s) | 1525.1(s) | 1544.3(s) | 1551.2(s) | 1542.7(s) | 1504.6(s) |
| 1521(s) | 1487.1(m) | 1514.8(s) | 1498.4(s) | 1528.1(s) | 1528.7(s) | 1504.6(s) |
| 1435(s) | 1424.3(w) | 1423.5(m) | 1424.1(m) | 1427.2 (s) | 1424.9(s) | 1428.0(m) |
| 1161(s) | 1191.8(w) | 1209.9(w) | 1188.9(w) | 1191.9(m) | 1187.0(s) | 1187.9(s) |
| 1011(s) | 1008.9(w) | 994.0(w) | 993.9(w) | 1008.1(m) | 1001.5(s) | 1011.2(s) |
| 823(s) | 811.8(w) | 812.1(w) | 812.2(w) | 811.8(m) | 812.2(s) | 803.2(s) |

where (s), (w), and (m) represent strong, weak, and moderate in intensities, respectively. Unit: cm^{-1}

Table 5

NMR chemical shifts of C atoms in C_6N_{20} isomers. The experimental results are from Ref. 5

| Systems | C_2 | α | $\beta(1)$ | $\beta(2)$ | γ | δ | ϵ | exp |
|---------|--------------|----------|------------|------------|----------|----------|------------|-----|
| C(2) | 178 | 182 | 184 | 183 | 180 | 183 | 180 | 176 |
| C(5) | 182 | 180 | 179 | 179 | 178 | 177 | 177 | |
| C(6) | 177 | 178 | 177 | 179 | 176 | 175 | 177 | 174 |

Unit: ppm for NMR chemical shifts of C atoms.

5. C_6N_{12} isomer

The previous experimental results shown that generation of 2,4,6-trinitreno-1,3,5-triazine upon the photolysis of 2,4,6-triazido-1,3,5-triazine is observed, the 2,4,6-trinitreno-1,3,5-triazine with a septet ground state is confirmed by experimental and theoretical methods.² On the basis of the finding on the 2,4,6-trinitreno-1,3,5-triazine, one infers that generation of new C_6N_{12} isomer with high spin configuration (Figure 3) from the nitrogen-rich 4,4',6,6'-tetra(azido)azo-1,3,5-triazine compound is possible. Consequently, C_6N_{12} isomer is designed upon release of four N_2 molecules from C_6N_{20} isomers. Specifically, the C(2)-N(1)-N(10) chain connecting two separate planar halves of molecules is found. The calculated total energies of $\text{C}_i \text{C}_6\text{N}_{12}$ isomer with $S=0, 1, 2, 3,$ and 4 are $-885.0428513, -885.0860792, -885.128507684, -885.1169015,$ and -885.1590433 hartrees, respectively. Unfortunately, geometry optimization on C_6N_{12} isomer with $S=5$ turns out to be an unstable structure. Furthermore, spin density is not influenced by the spin and stabilities are generally increased as spin S goes from 0 to 4. The large energy gap between $^9\text{A}_g$ and $^7\text{A}_g$ states is $26.47 \text{ kcal mol}^{-1}$, which is bigger than $19.18 \text{ kcal mol}^{-1}$ of the energy gap between $^9\text{A}_g$ and $^5\text{A}_g$ states, B3LYP method can be used for the cluster with the larger gaps between nearest spin states. Natural electron configurations of N(8), N(9), N(18), and N(17) atoms are $2s^{0.87}2p^{2.47}$ and $2s^{0.85}2p^{0.79}$ for

respective α -spin and β -spin orbitals, obviously indicating that there are two unpaired electrons at each of N(8), N(9), N(17), and N(18) atoms; and electronic state of $\text{C}_i \text{C}_6\text{N}_{12}$ isomer is $a_g^2 a_u^1 a_g^1 a_u^1 a_g^1 a_u^1 a_g^1 a_u^1 a_g^1$, indicating that there are totally eight unpaired electrons. On the basis of calculated total energies and analyses above, C_6N_{12} isomer with nonet spin state is selected as ground state. Computational results predict that C_6N_{12} isomer has high-spin ground state with large nonet-septet and nonet-quintet energy gaps; Furthermore, $\text{C}_i \text{C}_6\text{N}_{12}$ isomer with nonet spin state is perhaps the largest number of unpaired spin for a molecule among organic open shell species. On ground of equilibrium geometry of C_6N_{12} isomer, N(1)-N(10) and C(2)-N(1) bond lengths in azo chain are in good agreement with those of $\beta(1)$ -isomer. Thus, the removed four N_2 molecules from N3 chains do not influence bond lengths of azo chain seriously. One infers that C_6N_{12} isomer is a high-spin organic magnetism and molecular-spin material.

The natural populations of C_6N_{12} isomer are calculated. On the basis of natural charges of C_6N_{12} isomer, the charges in $\text{C}_i \text{C}_6\text{N}_{12}$ isomer are transferred from C atoms to N atoms. The charge-transfer between carbon and nitrogen atoms in triazine groups of $\text{C}_i \text{C}_6\text{N}_{12}$ isomer is bigger than that of C(5) and N(7) atoms. Furthermore, the charge-transfer between C(5) and N(7) atoms in high-spin $\text{C}_i \text{C}_6\text{N}_{12}$ molecule is smaller than those of C(5) and N(8) atoms in C_6N_{20} isomers.

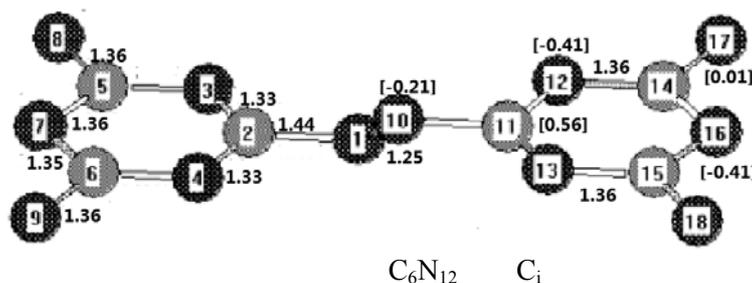


Fig. 3 – The equilibrium geometries of the most stable C_6N_{12} molecule with nonet spin configuration. [0.01] reprints the natural charge, the numbers which are not in parentheses are bond lengths (Å); the azo chain connects two planar halves of C_6N_{12} molecule.

According to the description of C_i C_6N_{12} formation above, C_i C_6N_{12} isomer is yielded with the aid of dissociations of four N_2 molecules from N3 chains of C_6N_{20} molecule. In a further series of investigations, we evaluate average C_6N_{20} fragmentation energy with respect to the removal of four N_2 molecules, defined according to the formula.^{36,37}

$$E_b = \frac{4E_T(N_2) + E_T(C_6N_{12}) - E_T(C_6N_{20})}{4}$$

where $E_T(N_2)$, $E_T(C_6N_{12})$, and $E_T(C_6N_{20})$ represent the total energies of the most stable N_2 , C_6N_{12} , and C_6N_{20} molecules, respectively; the corresponding values at the (U)MP2/6-31++G(2d,p)/(U)B3LYP/6-31G(d) level are -109.3229503, -883.1255464, and -1320.6429282 hartrees, respectively. E_b is the average dissociation energy with respect to the removal of one of four N_2 molecules. Thus, the average dissociation energy with respect to the removal of one of the four N_2 molecules at the (U)MP2/6-31++G(2d,p)/(U)B3LYP/6-31G(d) level is predicted to be 35.42 kcal mol⁻¹, which is comparable with single N-N bond energy (about 43 kcal mol⁻¹),²⁰ the average N-N dissociation energy gives a certification that N(8)-N(10) bond in N3 chains is a single bond. N(10) atom of N3 chains has four covalent bonds: one of four covalent bonds is bound to N(10) atom, others are bound tightly to N(12) atom with shortest N-N bond lengths as discussed above.

CONCLUSIONS

C_2N_{10} , C_6N_{12} , and C_6N_{20} isomers are investigated at the (U)B3LYP/6-31G(d) level. Total energies, natural populations, and equilibrium geometries of C_2N_{10} , C_6N_{12} , and C_6N_{20} isomers are calculated. The natural charges of the most stable C_2N_{10} , C_6N_{20} and C_6N_{12} isomers are calculated and discussed. The optimized

geometries on the possible C_6N_{20} isomers show the twist azo chain in C_6N_{20} isomers connecting the separate planar halves of C_2N_{10} molecule, which is confirmed by experimental results.¹³ Natural orbital analysis of four N3 chains of C_2N_{10} and C_6N_{20} isomers exhibit that the shortest N-N bonds are the triple covalent bonds. The NMR chemical shifts and IR frequencies of the possible C_6N_{20} isomers are calculated and discussed, which are in good agreement with experimental observations.

The new C_6N_{12} isomer with a twist azo chain connecting the two separate planar halves of molecule is formed by releasing of four N_2 molecules from N3 chains of C_6N_{20} isomers, the average dissociation energy of C_6N_{12} isomer at the (U)MP2/6-31++G(2d,p)/(U)B3LYP/6-31G(d) level is predicted, which is comparable with the single N-N bond energy. Theoretical results indicate that each of four N atoms in C_6N_{12} isomer, which does not localize at two triazine rings of C_6N_{12} isomer, has two unpaired electrons. In addition, C_6N_{12} isomer with nonet spin state is confirmed as the ground state, the electronic state is predicted to be 9A_g .

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REFERENCES

1. B. Tan, M. Huang, X. Long, J. Li, X. Yuan and R. Xu, *Int. J. Quantum Chem.*, **2015**, *115*, 84.
2. T. Sato, A. Narazaki, Y. Kawaguchi, H. Niino, G. Bucher, D. Grote, J. J. Wolff, H. H. Wenk and W. Sander, *J. Am. Chem. Soc.*, **2004**, *126*, 7846.
3. B.S. Tan, M. Huang, X.P. Long, J.S. Li, S. D. Yuan and R. J. Xu, *J. Phys. Chem. A*, **2015**, *115*, 84.
4. R. Haiges, S. Schneider, T. Schroer and K. O. Christe, *Angew. Chem. Int. Ed.*, **2004**, *43*, 4919.

5. M. H. V. Huynh, M. A. Hiskey, E. L. Hartline, D. P. Montoya and R. Gilardi, *Angew. Chem. Int. Ed.*, **2004**, *43*, 4924.
6. B. Hirshberg, R. Gerber and A. Krylov, *Nat. Chem.*, **2014**, *6*, 52.
7. M. H. V. Huynh, M. A. Hiskey, D. E. Chavez, D. L. Naud and R. D. Gilardi, *J. Am. Chem. Soc.*, **2005**, *127*, 12537.
8. H. J. Marcus and A. Remanick, *J. Org. Chem.*, **1963**, *28*, 2372.
9. Q. Wu, W. Zhu and H. Xiao, *Phys. Chem. Chem. Phys.*, **2014**, *16*, 21620.
10. F. Cacace, G. de Petris and A. Troiani, *Science*, **2002**, *295*, 481.
11. M. T. Nguyen and T. K. Ho, *Chem. Phys. Lett.*, **2001**, *335*, 311.
12. J. Guan, S. Zhang, W. Xu and Q. S. Li, *Structural Chemistry*, **2004**, *15*, 121.
13. T. Wei, W. Zhu, X. Zhang, Y.F. Li and H. Xiao, *J. Phys. Chem. A*, **2009**, *113*, 9404.
14. R. N. Zhao, *Main Group Chemistry*, **2016**, *15*, 243.
15. D. E. Chavez, M. A. Hiskey and R. D. Gilardi, *Angew. Chem.*, **2000**, *112*, 1861.
16. S. J. Shearer, G. C. Turrell, J. I. Bryant and R. L. Brooks, *J. Chem. Phys.*, **1968**, *48*, 1138.
17. M. A. Hiskey, N. Goldman and J. R. Stine, *J. Energ. Mater.*, **1998**, *16*, 119; **2000**, *18*, 219.
18. M. Straka and P. Pyykko, *Inorg. Chem.*, **2003**, *42*, 8241.
19. M. R. Manaa, *Chem. Phys. Lett.*, **2000**, *331*, 262.
20. M. N. Glukhovtsev, H. Jiao and P. V. R. Schleyer, *Inorg. Chem.*, **1996**, *35*, 7124.
21. W. H. Bragg, *Nature*, **1934**, *134*, 138.
22. S. Ritter, *C&EN*, **2004**, *10*, 44.
23. Q. Wu, W. Zhu and X. He, *PCCP*, **2014**, *16*, 21620.
24. Q. S. Li and J. F. Zhao, *J. Phys. Chem. A*, **2002**, *106*, 5367.
25. L. Gagliardi and P. Pyykko, *J. Phys. Chem. A*, **2002**, *106*, 4690.
26. L. J. Wang, Q. S. Li, P. Warburton and P. G. Mezey, *J. Phys. Chem. A*, **2002**, *106*, 1872.
27. E. P. Lee, J. M. Dyke and R. P. Claridge, *J. Phys. Chem. A*, **2002**, *106*, 8680.
28. K. J. Wilson, S. A. Perera, R. J. Bartlett and J. D. Watts, *J. Phys. Chem. A*, **2001**, *105*, 7693.
29. S. Rajca, A. Rajca, J. Wongsriratanakui, P. Butler and S. Choi, *J. Am. Chem. Soc.*, **2004**, *126*, 6972.
30. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle and J. A. Pople, *Gaussian 98*, Pittsburgh PA, **1998**.
31. B. M. Rice, E. F. C. Byrd and W. D. Mattson, *Struct. Bonding (Berlin)*, **2007**, *125*, 85.
32. J. J. P. Stewart, *J. Mol. Model.*, **2004**, *10*, 155.
33. A. P. Scott and L. Radom, *J. Phys. Chem.*, **1996**, *100*, 16502.
34. K. Wolinski, J. F. Hilton and P. Pulay, *J. Am. Chem. Soc.*, **1990**, *112*, 8251.
35. CCDC-235588 (α and β isomers) Cambridge database <http://www.ccdc.ac.uk/conts/retrieving.html>
36. R. N. Zhao, Y.H. Yuan, J. G. Han and Y. H. Duan, *Chem. Phys. Lett.*, **2016**, *648*, 41.
37. R. N. Zhao, *Rev. Roum. Chim.*, **2017**, *62*, 27.