Theoretical study of N_4X (X = O, S, Se) systems

Li Ping Cheng · Win Qian Cao

Abstract A series of N_4X (X = O, S, Se) compounds have been examined with ab initio and density functional theory (DFT) methods. To our knowledge, these compounds, except for the C_{2v} ring and the C_{3v} towerlike isomers of N_4O, are first reported here. The ring structures are the most energetically favored for N_4X (X = O and S) systems. For N_4Se, the cagelike structure is the most energetically favored. Several decomposition and isomerization pathways for the N_4X species have been investigated. The dissociation of C_{2v} ring N_4O and N_4S structures via ring breaking and the barrier height are only 1.1 and −0.2 kcal mol^{-1} at the CCSD (T)/6-311+G*//MP2/6-311+G* level of theory. The dissociation of the cagelike N_4X species is at a cost of 12.1–16.2 kcal mol^{-1}. As for the towerlike and triangle bipyramidal isomers, their decomposition or isomerization barrier heights are all lower than 10.0 kcal mol^{-1}. Although the C_S cagelike N_4S isomer has a moderate isomerization barrier (18.3–29.1 kcal mol^{-1}), the low dissociation barrier (−1.0 kcal mol^{-1}) indicates that it will disappear when going to the higher CCSD(T) level.

Keywords Ab initio · Dissociation or isomerization barrier · HEDMs · N_4X

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Introduction

Since many all-nitrogen compounds decompose to yield chemically inert N_2, such processes offer very attractive energy in an environmentally friendly way. For purposes of energy storage, such compounds are exceptionally useful; however, they are not the only compounds of high nitrogen content suitable for this purpose. Heteroatomic nitrides with high N content are also potential HEDMs. For example, some NO clusters, such as the smallest diatomic nitride oxide, are very energetic molecules. In fact, diatomic NO is known experimentally to be an explosive in the liquid state, with an enthalpy of about 21.6 kcal mol^{-1} relative to N_2 and O_2 products at 298 K [1]. Evangelisti [2] have studied some NO clusters, N_2O_3, N_4O_6, and N_8O_{12}, with D_{3h}, T_d, and O_h symmetries, respectively, at SCF and MP2 levels of theory. He pointed out these systems also show characteristics of HEDMs. To reinforce the notion that very high-energy metastable forms of N_4 can exist, Engelke et al. [3] have employed an experimental and theoretical study on $[N_3O]^+$. They observed this cation via time-of-flight spectroscopy, as a metastable species whose lifetime is at least 0.52 μs. Another possible candidate is nitrosyl azide (N_4O), a heteroatom nitride whose decomposition products would be "virtually pure hot air" thus making it an ideal, environmentally friendly high-energy propellant [4]. Attempts to identify and synthesize nitrosyl azide date back to the beginning of last century [5–7]. Despite N_4O plays important roles in many reactions, the isotopic labeling experiments clearly confirmed it to exist as a reaction intermediate [5], and Lucien [6] found that it decomposes even at temperatures as low as −50 °C to from nitrous oxide and nitrogen. In view of the instability of nitrosyl azide, Lucien [6] attempted to produce it at lower-temperatures. Despite numerous difficulties, a yellowish

substance was obtained at temperatures below $-30\ ^{\circ}C$, and it was identified as nitrosyl azide based on physical properties, decomposition studies and inferences made from infrared absorption spectra. Following a procedure similar to that of Lucien, Schultz et al. [7] also produced a pale yellow solid. Raman spectrum combined with theoretical harmonic vibrational frequencies from MP2/6-31+G(d) level identified this solid as an open trans-chain N_4O species. To estimate the kinetic stability of this molecule, Schultz et al. explored two possible dissociation pathways [8]. The first pathway involved conversion into a cis-isomer, then a cyclic form, followed by its dissociation into N_2 and linear N_2O. The highest barrier for this process computed at the MP2/6-31+G(d) level was only 6.7 kcal mol^{-1}. A transition state for the direct dissociation into N_2 and cyclic N_2O was also found, which indicates a barrier of 24.2 kcal mol^{-1}. Other isomers of N_4O have been considered including a C_{2v} ring structure (**1a**) [4] and a C_{3v} towerlike structure (**1c**) [9]. However, the barrier height for the unimolecular dissociation of the ring molecule is only 1.0–2.0 kcal mol^{-1} [4], and the corresponding barrier for the C_{3v} towerlike structure is only 5.6 kcal mol^{-1} at the CCSD(T) level of theory [9].

To be viable as useful fuels, materials must be stable enough to be synthesized and stored without isomerization or decomposition. In other words, the energy barriers that prevent their decomposition and isomerization must be sufficiently high to provide stability. Generally, it is desirable to have all such barriers higher than 20 kcal mol^{-1}, and preferably higher than 30 kcal mol^{-1} [10]. According to this principle, none of the three reported N_4O species is stable and to be used as useful fuels. Therefore, it is necessary to study N_4O further and identify the isomers that are likely to be stable and to be observed experimentally.

In the present study, we will continue to study N_4O, and we expect to find new isomers. Because the atoms of O, S, and Se are in the same column of the periodic table, their N_4X-type compounds should be similar in geometries and properties. Therefore, we also study N_4S as well as N_4Se and attempt to find some stability rules for this series of compounds.

Computational methods

All calculations were performed using the Gaussian 03 program package [11]. We initially optimized geometries and calculated the harmonic vibrational frequencies for N_4X (X = O, S, and Se) at the B3LYP/6-311+G* level of theory, where B3LYP is the DFT method using Becke's three-parameter gradient-corrected functional [12] with the gradient-corrected correlation of Lee, Yang, and Parr [13] and 6-311+G* is the split-valence triple-ζ plus polarization

basis set augmented with diffuse functions [14]. Then, the geometries were refined and the vibrational frequencies were calculated at the level of second-order Møller-Plesset perturbation theory (MP2) [15] with the 6-311+G* basis set. Stationary points were characterized as minima without any imaginary vibrational frequency and a first-order saddle point with only one imaginary vibrational frequency. 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 [16]. Final energies were refined at the CCSD(T)[17]/6-311+G*//MP2/6-311+G*+ ZPE(MP2/6-311+G*) or CCSD(T)[17]/6-311+G*//B3LYP/ 6-311+G* + ZPE(B3LYP/6-311+G*) level of theory. In addition to the structural and energetic investigations, the natural population and Wiberg bond indices (WBIs) analyses were also presented using the NBO procedure [18, 19].

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

Results and discussion

The optimized structures for three N_4X systems are illustrated in Fig. 1. The total energies, zero-point energies (ZPE), relative energies (with ZPE corrections), and number of imaginary frequencies are tabulated in Table 1.

Geometric structures and energies of the N_4X species

The first member of the N_4X series is the N_4O system and we first performed ab initio calculations on a wide variety of singlet structures of N_4O by using two different and sophisticated theoretical methods. As exhibited in Fig. 1, besides the reported C_{2v} ring structure (**1a**) [4] and the C_{3v} towerlike structure (**1c**) [9], we have located two new structures, that is, the C_{2v} cagelike structure (**1b**) and the C_{3v} triangle bipyramidal structure (**1d**). Furthermore the C_{2v} ring isomer we located is the most energetically favored for all singlet N_4O species, in agreement with the results of Galbraith and Schaefer III [4]. For the heavier N_4X species, we focused mainly on the four low-lying structures initially obtained for N_4O. As shown in Fig. 1, we found that the C_{2v} ring isomer **2a** is the most energetically favored for N_4S system. As for the C_{2v} ring isomer of SeN_4, our optimization directly leads to a linear structure. However, harmonic vibrational frequencies calculations indicate that it is a first-order saddle point at the B3LYP and MP2 levels of theory. So, less attention will be paid to it in the present study. The cagelike structures (**1b**–**3b**), the towerlike structures (**1c**–**3c**), and the triangle bipyramidal structures (**1d**–**3d**) are all local minima for all N_4X systems. As shown
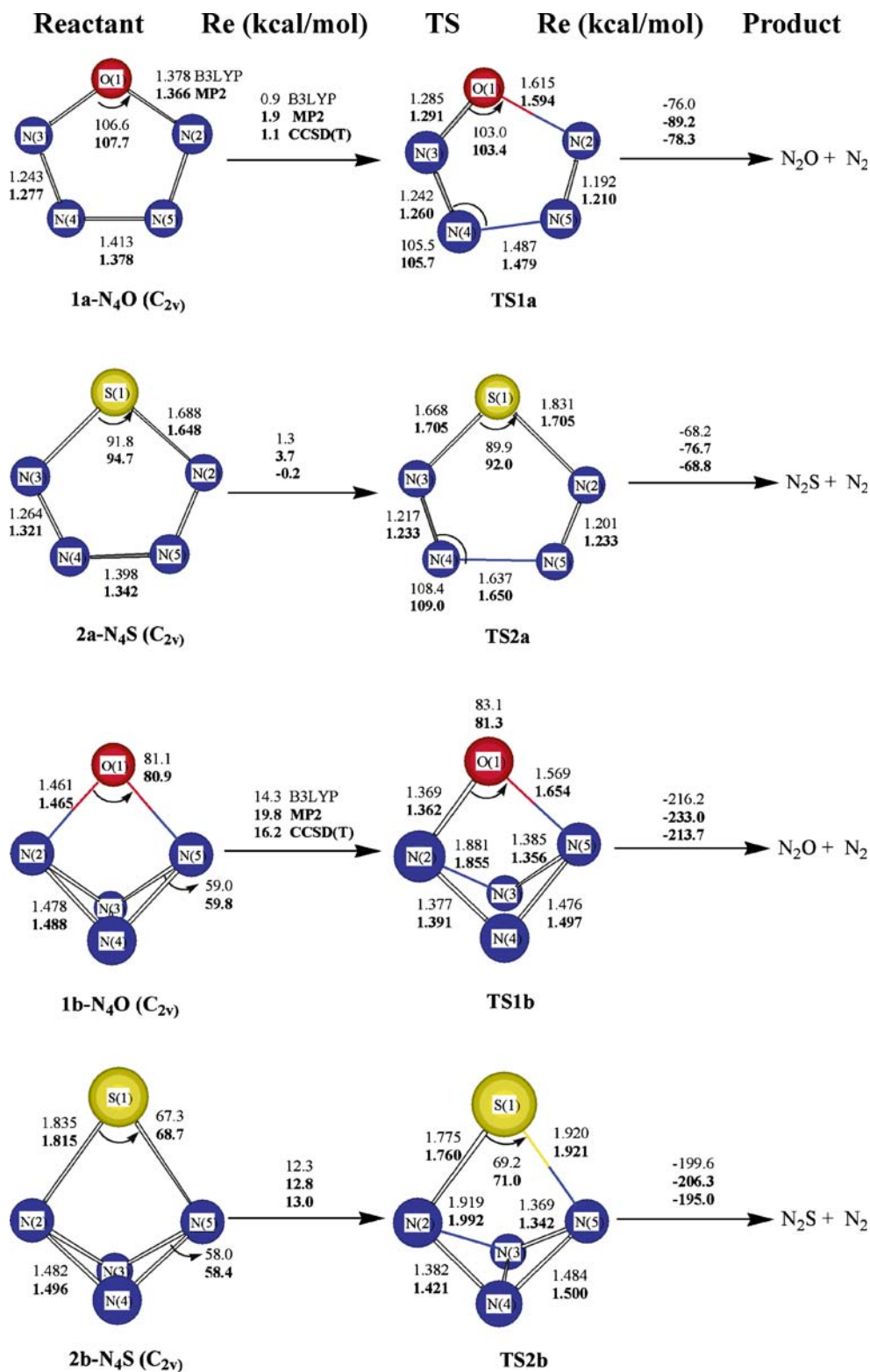
Fig. 1 Optimized geometries for reactants, transition states, products, and relative energies (RE) of N4X systems

in Table 1, the cagelike N_4O and N_4S structures are 120.4 and 113.0 kcal mol^{-1} higher in energy than their ring isomers at the CCSD(T) level of theory, respectively. The C_{3v} towerlike N_4X (X = O, S) isomers are energetically higher

than their ring isomers by 122.4 and 127.1 kcal mol^{-1} at the CCSD(T) level of theory, respectively. The triangle bipyramidal N_4X (X = O, S) isomers are energetically higher than their ring isomers by 215.5 and 174.3 kcal mol^{-1} at the
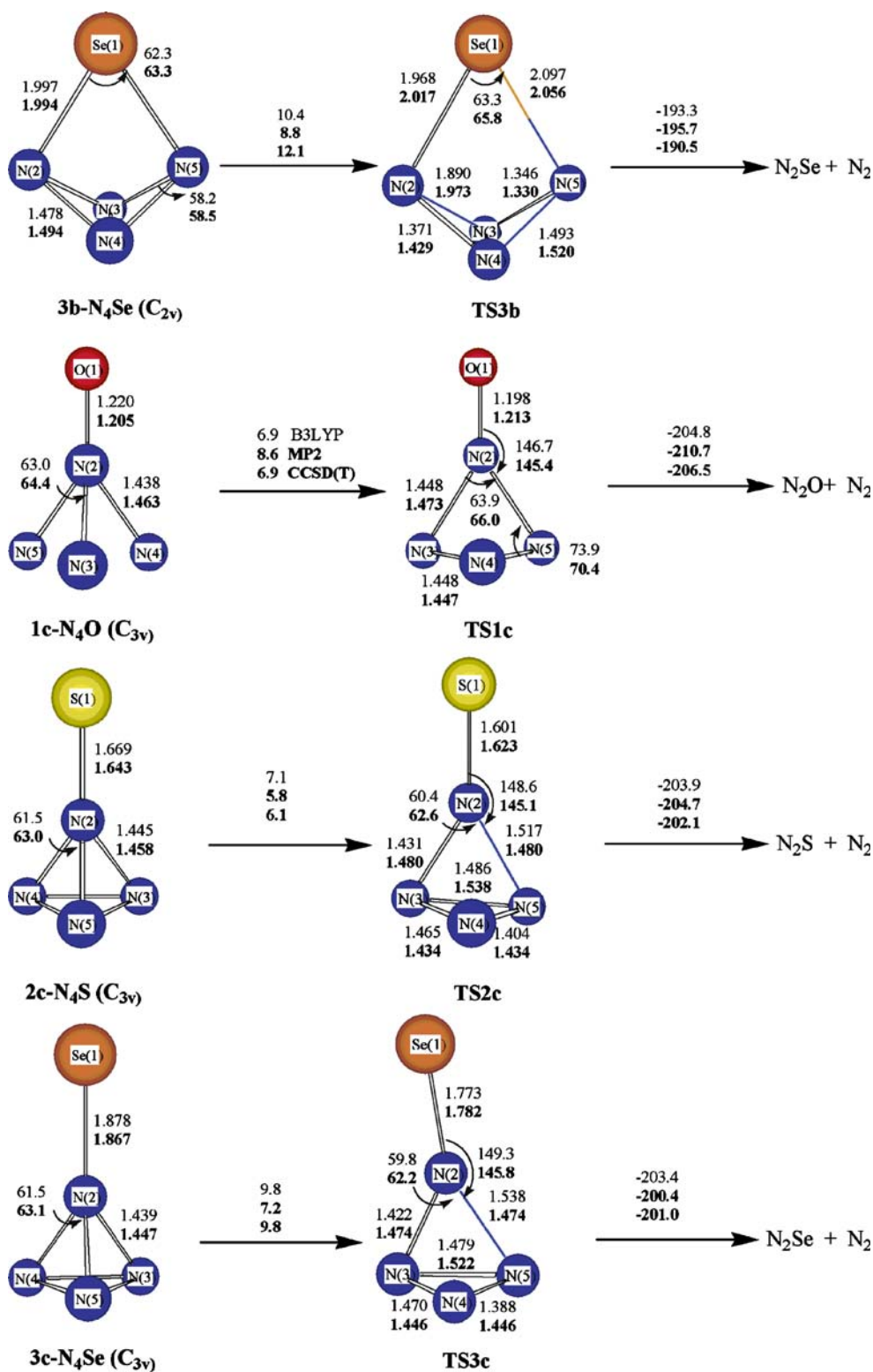
Fig. 1 (continued)

CCSD(T) level, respectively. For SeN$_4$, the cagelike structure was found to be lower in energy than the towerlike and triangle bipyramidal isomers by 12.4 and 69.9 kcal mol^{-1} at the CCSD(T) level, respectively.

As shown in Fig. 1, for each set of the similar structural N$_4$X species, the heavier the X atom is, the longer the X-N distances are. Regarding the N-N bond distances in the N$_4$X compounds, the N-N bond distances in the C$_{2v}$ ring
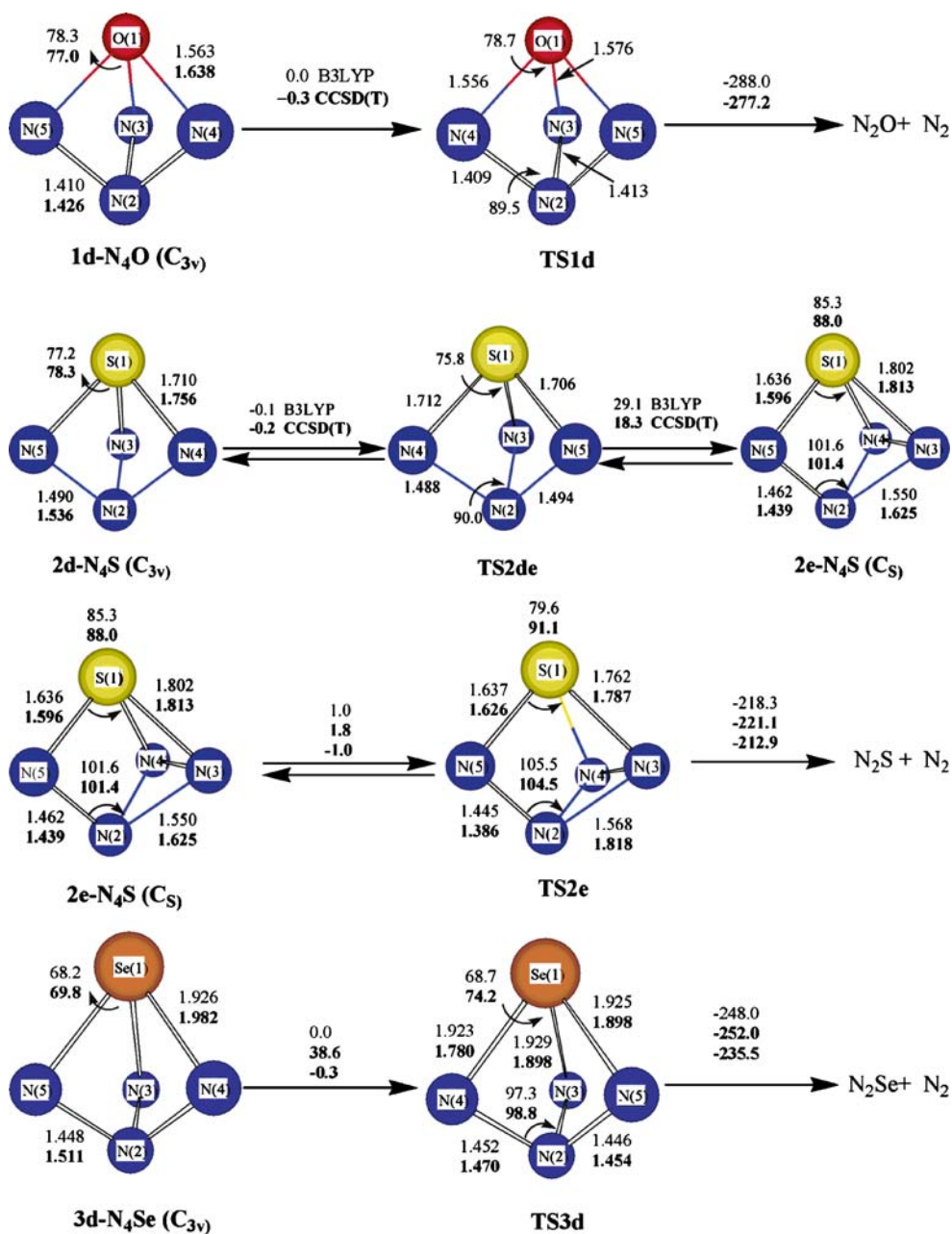
Fig. 1 (continued)

structures tend to equalization. In the cagelike and towerlike series, the N-N bond lengths are more close to the single-bond length 1.449 Å of H_2N-NH_2 [20]. In the triangle bipyramidal series, some N-N bond lengths, such as N2-N3 (N4 or N5), are very close to that of the single bond length. However, the other N-N distances, such as N3-N4 (N5) and N4-N5, are much longer than that of a single bond. In terms of NBO analysis, the calculated NN Wiberg bond indices (WBI) in the C_{2v} ring structures (**1a**–**2a**) are between the standard values of single-bond (1.0) and double-bond (2.0), indicating delocalization. While in

the cagelike and towerlike series (**1b**–**3b** and **1c**–**3c**), the NN WBIs are very close to that of the single bond. Regarding the triangle bipyramidal series, the WBIs of N2-N3(N4 or N5) range from 0.8 to 1.0, indicating that these bonds are all single-bond. That all WBIs of N3-N4(N5)and N4-N5 bonds are about 0.5 supports that these NN bonds are possibly partly ionic and partly covalent. Along group 6, going from O to S, the calculated WBIs of X1-N2(N3) in the C_{2v} ring structures (**1a**–**2a**) range from 1.0 to 1.2, which are closer to the standard values of single-bond (1.0); the calculated WBIs of X1-N2(N5) in the cagelike structures

Table 1 Total energies (E)[a], zero-point energies (ZPE)[b], and relative energies (RE)[c] for N_4X species

Species	B3LYP/6-311+G*			MP2/6-311+G*			CCSD(T)/6-311+G* //MP2/6-311+G*	
	E[a]	ZPE[b]	RE[c]	E[a]	ZPE[b]	RE[c]	E[a]	RE[c]
1a-N_4O (C_{2v})	−294.16129	12.4 (0)	0.0	−293.45667	12.3 (0)	0.0	−293.49392	0.0
1b- N_4O (C_{2v})	−293.95732	11.1 (0)	126.7	−293.25291	10.4 (0)	126.0	−293.29909	120.4
1c- N_4O (C_{3v})	−293.96303	10.7 (0)	122.7	−293.26941	9.6 (0)	114.8	−293.29455	122.4
1d- N_4O (C_{3v})	−293.81649	8.8 (0)	212.8	−293.15308	23.0 (0)	201.2	−293.16749	215.5
2a-N_4S(C_{2v})	−617.17864	10.9 (0)	0.0	−616.09246	10.9 (0)	0.0	−616.13330	0.0
2b- N_4S (C_{2v})	−616.98499	9.7(0)	120.3	−615.89791	9.2 (0)	120.4	−615.95057	113.0
2c- N_4S (C_{3v})	−616.96898	9.2(0)	129.9	−615.88751	8.1 (0)	125.8	−615.92636	127.1
2d- N_4S (C_{3v})	−616.88851	8.4(0)	179.6	−615.85596	18.6 (0)	156.1	−615.86782	174.3
2e- N_4S (C_S)	−616.93534	8.6(0)	150.4	−615.85538	8.3 (0)	146.2	−615.89799	145.1
3b-N_4Se (C_{2v})	−2620.32895	9.2(0)	0.0	−2618.16197	8.5(0)	0.0	−2618.21187	0.0
3c-N_4Se (C_{3v})	−2620.31133	8.9(0)	10.8	−2618.15201	8.1(0)	5.8	−2618.19140	12.4
3d-N_4Se (C_{3v})	−2620.22235	7.4(0)	65.1	−2618.11984	21.0(0)	38.9	−2618.12038	69.9

[a] Total energies in Hartree. [b] Zero-point energies in kcal mol^{-1}. The integers in parentheses are number of imaginary frequencies (NIMAG). [c] The relative energies with ZPE corrections in kcal mol^{-1}.

(**1b–2b**) range from 0.9 to 1.0, which are also close to that of the single-bond (1.0). In the towerlike structures, the calculated WBIs of S1-N2 and Se1-N2 ranging from 0.8 to 1.0 are very close to that of the single bond. However, for the towerlike N_4O, the WBI of O1-N2 is 1.4, which is between the standard values of single-bond (1.0) and double-bond (2.0). In the triangle bipyramidal structures, from O to Se, the WBIs of X1-N3 (N4 or N5) range from 0.8 to 1.0, indicating these bonds are all single bonds. Natural population analysis shows that positive charges mainly populate on the S and Se atoms for N_4S and N_4Se systems, respectively. While for the N_4O system, things are different. Negative charges reside mainly on the O atoms for all four singlet N_4O isomers. This trend can be rationalized with the strong electronegativity of the oxygen atom.

Table 2 Energies (kcal mol^{-1}) of N4X relative to $N_2 + N_2O$

Species	B3LYP/ 6-311+G*	MP2/ 6-311+G*	CCSD (T) /6-311+G* //MP2/6-311+G*
1a-N_4O(C_{2v})	75.1	87.3	77.2
1b- N_4O (C_{2v})	201.9	213.2	197.5
1c- N_4O (C_{3v})	197.9	202.1	199.6
1d- N_4O (C_{3v})	288.0	288.5	292.8
2a-N_4S(C_{2v})	66.9	73.0	69.0
2b- N_4S (C_{2v})	187.3	193.5	182.0
2c- N_4S (C_{3v})	196.8	198.9	196.0
2d- N_4S (C_{3v})	246.5	229.2	243.3
2e- N_4S (C_S)	217.3	219.2	214.0
3b- N_4Se (C_{2v})	182.9	187.9	179.4
3c- N_4Se (C_{3v})	193.6	193.8	191.8
3d- N_4Se (C_{3v})	248.0	226.9	249.3

The energy differences relative to $N_2X + N_2$ molecules are listed in Table 2 and it appears that all N_4X species would be very energetic materials.

Transition structures and reaction barriers for decomposition and isomerization reactions

In the present study the decomposition and isomerization reactions for the N_4X (X = O, S, Se) systems were investigated at the B3LYP and MP2 level of theory. The optimized structures for reactants, transition states, and products are shown in Fig. 1. The energy differences (with ZPE corrections except for SeN_4 at the MP2 and CCSD(T) levels) between reactants and transition states and transition states and products are inserted between their corresponding structures.

Dissociation channels

(a)   The C_{2v} ring N_4X (C_{2v}) → N_2X (linear) + N_2 (X = O, S)

These dissociations proceed in a straightforward manner with simple bond fissions. The transition states **TS1a** and **TS2a** were located on the potential energy surfaces (PES). As shown in Fig. 1, we can note that, compared with the C_{2v} ring structures, the two bond lengths of X1-N2 and N4-N5 in the transition states are stretched to eliminate the N_2X molecules whereas those of N2-N5 are actually compressed and almost become the triple N≡N bond. The barriers for dissociation are 1.9 and 3.7 kcal mol^{-1} for X = O and S at the MP2/6-311+G* level of theory, respectively. Single point calculations at the CCSD (T) level decrease these values to 1.1 and −0.2 kcal mol^{-1}, respectively. These reactions are thus expected to occur easily. Therefore, the C_{2v} ring N_4O species could not be regarded as suitable candidates for new

fuels and the corresponding N4S minimum apparently disappears when going to the higher CCSD(T) level.

(b) Cagelike N_4X (C_{2v}) → N_2X (linear) + N_2

In the process of the cagelike N_4X (C_{2v}) → N_2X + N_2, three transition states **TS1b**, **TS2b**, and **TS3b** were found lying about 16.2, 13.0, and 12.1 kcal mol^{-1} above the cagelike N4O, N4S, and N4Se species at the CCSD (T) level of theory, respectively. On the ways to forming **TS1b**, **TS2b**, and **TS3b**, with the bond distances of N2-N3 and X1-N5 increase, whereas the N2-N4 and N3-N5 bond distances decrease. Starting from **TS1b**, **TS2b**, and **TS3b**, the IRC calculations directly lead to dissociation into the linear N_2X (X = O, S, Se) and N2, respectively. Although the dissociation barriers of these series species are much higher than those of the C_{2v} ring structures, they also detract from the attractiveness of the cagelike N4X structures as suitable candidates for new fuels.

(c) Towerlike N_4X (C_{3v}) → N_2X (linear) + N_2

The decomposition mechanism of the towerlike N4X is investigated in our present work. As shown in Fig. 1, three tranision structures **TS1c**–**TS3c** were located. Starting from these transition structures, IRC calculation directly leads to dissociation into N_2X (X = O, S, and Se) and one N_2 molecule. The dissociation barriers are all lower than 10.0 kcal mol^{-1} at the CCSD(T) level of theory.

(d) Triangle bipyramidal N_4X (C_{3v}) → N_2X (linear) + N_2 (X = O, Se)

As shown in Fig. 1, these series of structures will apparently disappear when going to the CCSD(T) level, and the barriers for dissociation are only −0.3 kcal mol^{-1}. IRC calculations confirmed that the triangle bipyramidal N4O and N4Se species dissociation into linear N_2X and N_2 molecules via TS1d and TS3d, respectively. We have attempted to find possible transition states for dissociation of N4O (**1d**) at the MP2 level of theory, but failed.

Isomerization channels

We have located one transition structures **TS2de** for the triangle bipyramidal N4S (**2d**) isomer at the B3LYP level of theory. As shown in Fig. 1, the geometric structure of this transition state is very similar to that of **TS1d** and **TS3d**. However, starting from **TS2de**, the IRC calculation leads to another N4S isomer (**2e**). The transition state barrier going from **2d** to **2e** is −0.2 kcal mol^{-1} and from **2e** to **2d** is 18.3 kcal mol^{-1} at the CCSD(T)/6-311+G*//B3LYP/6-311+G* + ZPE (B3LYP/6-311+G*) level of theory. Therefore, the triangle bipyramidal N4S, **2d**, is not likely to exist at the CCSD(T) level and if it is formed in any process, it will transform into the **2e**. We have attempted to find possible transition states for the interconversions of the N4S isomers **2d** and **2e** at the MP2 level of theory, but failed.

To further investigate the stability of **2e**, possible channels of dissociation have been investigated. As shown in Fig. 1, a transition structure **TS2e** was located leading to further dissociation into N_2S + N_2. The activation barrier being only −1.0 kcal mol^{-1} and thus the corresponding minimum will apparently disappear when going to the higher CCSD(T) level.

Summary

We examined a series of N_4X (X = O, S, Se) compounds in the present study. To our knowledge, these compounds, except for N4O, are first reported here. Four singlet structures have been located for most N4X systems, that is, the C_{2v} ring, the C_{2v} cagelike, the C_{3v} towerlike, and the C_{3v} triangle bipyrmidal structures. Among them, the C_{2v} ring structures are the most energetically favored for N4S and N4Se systems, and the C_{2v} cagelike structure is the most energetically favored for N4Se systems. Thermodynamically, all known N4X species are local minima on their PES at the two used levels of theory. However, The barriers for dissociation of C_{2v} ring N4O and N4S structures are only 1.1 and −0.2 kcal mol^{-1} at the CCSD(T)/6-311+G(d)// MP2/6-311+G(d) level of theory. The dissociation of the cagelike N4X species is at a cost of 12.1–16.2 kcal mol^{-1}. The decomposition or isomerization barrier heights of the towerlike and triangle bipyramidal isomers are all lower than 10.0 kcal mol^{-1}. Although the C_S cagelike N4S isomer has a moderate isomerization barrier (18.3–29.1 kcal mol^{-1}), its dissociation barrier (−1.0 kcal mol^{-1} at the CCSD(T) level) is so low that it is still unlikely to exist and to be potential HEDMs.

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