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## Theoretical study of $[XN_5]^-$ ( $X=O, S, Se, Te$ ) systems

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**Abstract** A series of  $[XN_5]^-$  ( $X=O, S, Se, Te$ ) compounds has been examined with ab initio and Density Functional Theory (DFT) methods. The five-membered nitrogen ring series of structures are global minima and may exist or be characterized due to their significant dissociation barriers (29.7–32.7 kcal mol<sup>-1</sup>). Nucleus-independent chemical shifts (NICS) criteria and the presence of  $(4n+2)$   $\pi$ -electrons confirmed that the five-membered nitrogen ring in their structures exhibits characteristics of aromaticity. Thus, the strong stability of the five-membered nitrogen ring structures may be attributed partially to their aromaticity.

**Keywords** Ab initio · HEDMs ·  $[XN_5]^-$  · Aromaticity · NICS

### Introduction

Many all-nitrogen compounds decompose to yield chemically inert  $N_2$  with a large release of energy. 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 high-energy-density materials (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<sup>-1</sup> relative to  $N_2$  and  $O_2$  products at 298 K [1]. Another possible candidate is nitrosyl azide ( $N_4O$ ), an unstable oxide of nitrogen whose decomposition products

would be “virtually pure hot air”, thus making it an ideal, environmentally friendly high-energy propellant [2]. Following this principle, the present paper reports some possible structures of heteroatomic nitrides  $[XN_5]^-$  ( $X=O, S, Se, Te$ ).

On the experimental side, only a few nitrogen clusters are known.  $N_5^+$  was made as a cation in bulk compounds in 1999 [3]. Recently, Cacace et al. [4] demonstrated the existence of the tetranitrogen molecule,  $N_4$ , as a metastable species with a lifetime exceeding one microsecond at 298 K. Vij et al. [5] reported the first experiment detection of the long-sought pentazolate anion by cleaving the C–N bond of suitably substituted phenylpentazoles. These new discoveries indicate a bright future for experimental polynitrogen chemistry. In addition to pure nitrogen clusters, other nitrogen-rich compounds have also attracted interest because of their possible use as HEDMs [6–15]. To reinforce the notion that very high-energy metastable forms of  $N_4$  can exist, Engelke et al. [6] reported 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  $\mu$ s. In view of the instability of  $N_4O$ , Lucien [7] approached the problem via low-temperature techniques. In spite of numerous explosions, low yields, and other experimental difficulties, a yellowish substance was produced at temperatures below  $-30^\circ\text{C}$ . Bartlett [8] suggested some nitrogen-rich clusters formed by N, O, and H for use as HEDMs. Several transition-metal complexes of all-nitrogen planar cyclic ligands have been investigated theoretically. Complexes such as  $Fe(\eta^5-N_5)_2$  [9],  $Sc(\eta^7-N_7)$  [10],  $M(\eta^6-N_6)$  [11], and  $(\eta^5-N_5)M(\eta^7-N_7)$  ( $M=Ti, Zr, Hf, Th$ ) [12] were found to be energetically lower than the corresponding  $N_n^q$  systems. Evangelisti [13] 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 the SCF and MP2 levels of theory. He pointed out that these systems also show characteristics of HEDMs. Wang and Zgierski [14] have identified some nitrogen-rich sulfides  $SN_5$  and  $SN_6$  (neutral

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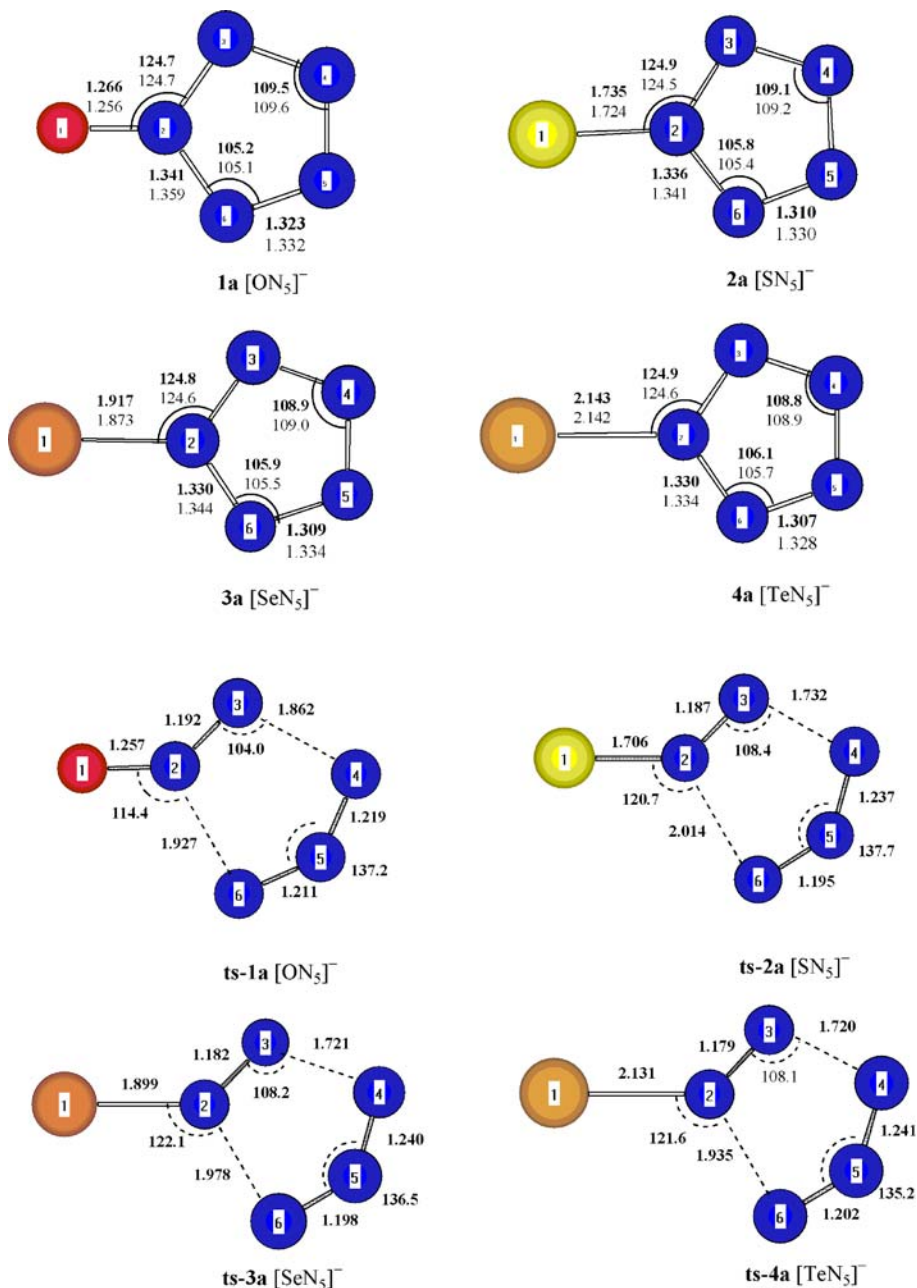
molecules and ions) with low spin using ab initio and density functional theory methods. Recently, we have designed some heteroatomic nitrides  $[XN_3]^+$  ( $X=O, S, Se, Te$ ) [15] and some possible dissociation or isomerization pathways for these compounds.

In this paper, our main goal is to model nitrogen-rich compounds  $[XN_5]^-$  ( $X=O, S, Se, Te$ ) that can store large amounts of energy and yet are stable enough for potential application as HEDMs. Since the atoms of O, S, Se, and Te are in the same column of the periodic table, their  $[XN_5]^-$  type compounds should be similar in geometries and properties. Thus, we also attempt to find some stability rules for this series of compounds.

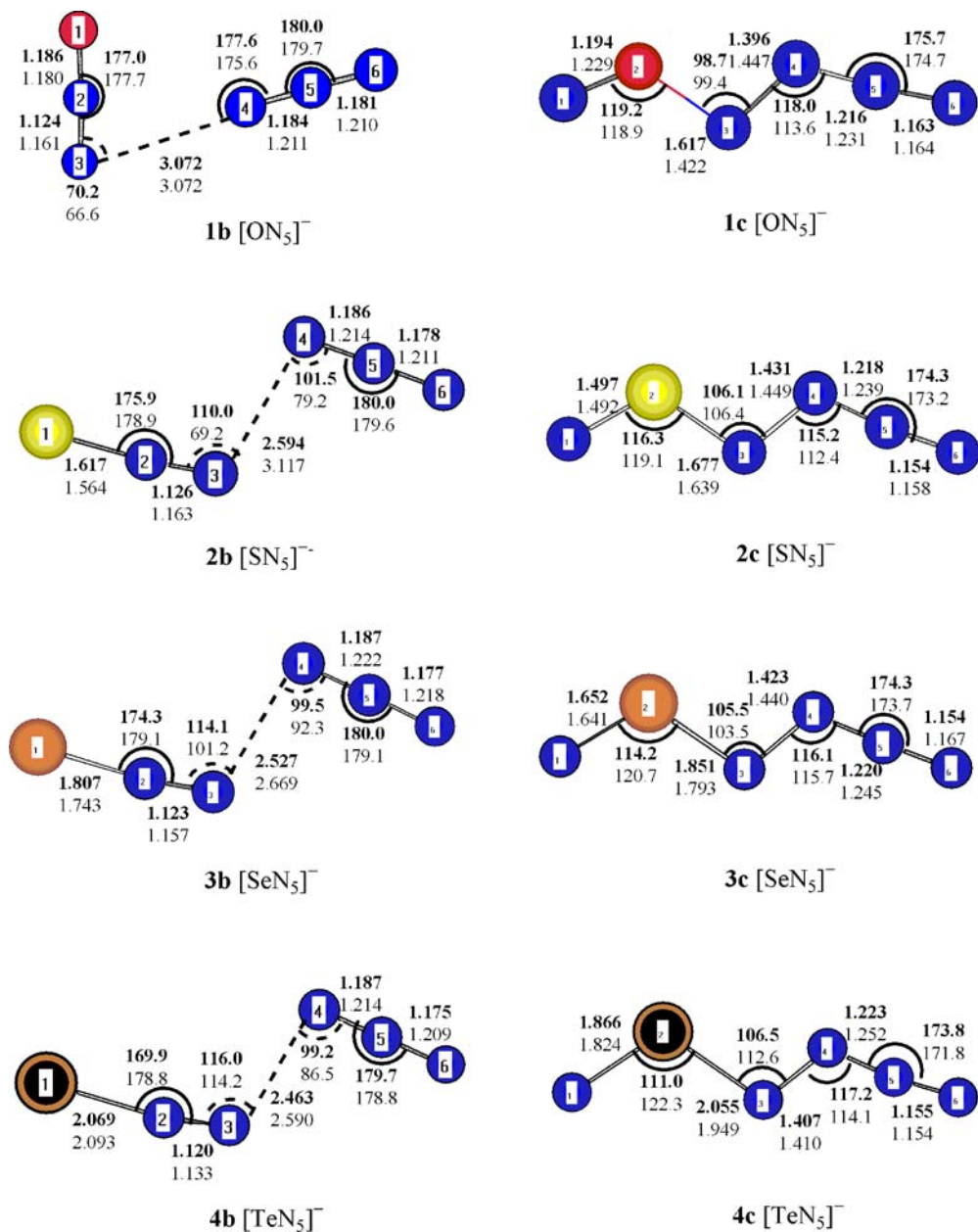
## Computational methods

All calculations were performed using the Gaussian 03 program package [16]. We initially optimized geometries and calculated the harmonic vibrational frequencies for  $[XN_5]^-$  ( $X=O, S, \text{ and } Se$ ) at the B3LYP/6-311+G(d) level of theory, where B3LYP is the DFT method using Becke's three-parameter gradient-corrected functional [17] with the gradient-corrected correlation of Lee, et al. [18] and 6-311+G(d) is the split-valence triple- $\zeta$  plus polarization basis set augmented with diffuse functions [19]. Then, the geometries of  $[ON_5]^-$  and  $[SN_5]^-$  were refined and the vibrational frequencies were calculated at the level of second-order

**Fig. 1** Optimized geometries (bond lengths in Å, bond angles in degrees) for some five-membered nitrogen ring  $[XN_5]^-$  species at the B3LYP (*bold font*) and MP2 levels of theory



**Fig. 2** Optimized geometries (bond lengths in Å, bond angles in degrees) for some  $[XN_5]^-$  species at the B3LYP (*bold font*) and MP2 levels of theory



Møller–Plesset perturbation theory (MP2) [20] with the 6–311+G(d) basis set. With respect to  $[SeN_5]^-$ , at the MP2 level we calculated its vibrational frequencies with 6–31+G(d) basis set using geometries optimized at the same level. The  $[TeN_5]^-$  system was optimized at the B3LYP and MP2 levels of theory, where the 6–311+G(d) basis set was used for nitrogen and the energy-adjusted Stuttgart ECPs were used on the heavier atom Te ( $Z=52$ ) [21]. 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 [22].

NICS for  $[XN_5]^-$  ( $X=O, S, Se$ ) were calculated with the GIAO-B3LYP/6–311+G(d)/B3LYP/6–311+G(d) method. NICS for  $[TeN_5]^-$  were evaluated by using the GIAO-B3LYP//B3LYP method [23, 24], where the 6–311+G(d) basis set was used for nitrogen and the STO-3G basis set was used on Te. Molecular Orbitals (MOs) of  $[XN_5]^-$  ( $X=O, S, \text{ and } Se$ ) were calculated at the B3LYP/6–311+G(d) level of theory. MOs of  $[TeN_5]^-$  was computed at the B3LYP level of theory, where the 6–311+G(d) basis set was used for nitrogen and the energy-adjusted Stuttgart ECPs were used on Te. All MO diagrams were made by using the MOLDEN 3.7 program [25].

Natural bond orbital (NBO) [26, 27] analyses were also performed to provide insight into the bonding nature and aromaticity of these species.

**Table 1** Total energies (E)<sup>a</sup>, zero-point energies (ZPE)<sup>b</sup>, and relative energies (RE)<sup>c</sup> for [XN<sub>5</sub>]<sup>-</sup> species

Species	B3LYP			MP2		
	E	ZPE	RE	E	ZPE	RE
<b>1a</b> (C <sub>2v</sub> )	-349.01646	16.2 (0)	0.0	-348.16626	16.1 (0)	0.0
<b>1b</b> (C <sub>s</sub> )	-349.01069	14.0 (0)	1.4	-348.17867	13.3 (1)	-10.6
<b>1c</b> (C <sub>s</sub> )	-348.84215	11.9 (1)	105.1	-347.95017	12.4 (1)	131.9
<b>2a</b> (C <sub>2v</sub> )	-672.02724	14.9 (0)	0.0	-670.79257	14.8 (0)	0.0
<b>2b</b> (C <sub>s</sub> )	-672.01526	12.4 (0)	5.0	-670.79043	11.5 (1)	-2.0
<b>2c</b> (C <sub>s</sub> )	-671.91903	11.8 (1)	64.8	-670.67330	12.3 (1)	72.3
<b>3a</b> (C <sub>2v</sub> )	-2675.37109	14.6 (0)	0.0	-2670.77260 <sup>e</sup>	14.8 (0)	0.0
<b>3b</b> (C <sub>s</sub> )	-2675.35424	11.9 (0)	7.9	-2670.76319 <sup>e</sup>	11.8 (0)	2.9
<b>3c</b> (C <sub>s</sub> )	-2675.23181	11.1 (0)	83.9	-2670.61974 <sup>e</sup>	11.9 (0)	93.0
<b>4a</b> (C <sub>2v</sub> ) <sup>d</sup>	-281.90944	14.4 (0)	0.0	-281.06122	14.4 (0)	0.0
<b>4b</b> (C <sub>s</sub> ) <sup>d</sup>	-281.89066	11.6 (0)	9.0	-281.04324	10.7 (1)	7.6
<b>4c</b> (C <sub>s</sub> ) <sup>d</sup>	-281.72784	10.3 (1)	109.9	-280.85867	10.9 (1)	123.6

<sup>a</sup>Total energies in Hartree<sup>b</sup>Zero-point energies in kcal mol<sup>-1</sup>. The integers in parentheses are number of imaginary frequencies (NIMAG)<sup>c</sup>The relative energies with ZPE corrections in kcal mol<sup>-1</sup><sup>d</sup>The 6-311+G\* basis set was used for nitrogen and the energy-adjusted Stuttgart ECPs were used on Te<sup>e</sup>The 6-31+G\* basis set was used for [SeN<sub>5</sub>]<sup>-</sup> at the MP2 level of theory

## Results and discussion

The optimized structures for four [XN<sub>5</sub>]<sup>-</sup> systems are illustrated in Figs. 1 and 2. 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 [XN<sub>5</sub>]<sup>-</sup> species

We first performed ab initio calculations on a wide variety of singlet structures of [ON<sub>5</sub>]<sup>-</sup> by using two different and sophisticated theoretical methods. As shown in Figs. 1 and 2, we have located three structures, that is, the five-membered nitrogen ring structure (**1a**), the N<sub>2</sub>O...N<sub>3</sub><sup>-</sup> adduct (**1b**) and the chain-shaped structure (**1c**). Furthermore, the five-membered nitrogen ring structure we located is the most energetically favored for all singlet [ON<sub>5</sub>]<sup>-</sup> species at the B3LYP level considered here. For the heavier [XN<sub>5</sub>]<sup>-</sup> species, we focused mainly on the three low-lying structures initially obtained for [ON<sub>5</sub>]<sup>-</sup>. The five-membered nitrogen ring structure (**2a**) and the chained-shaped structure (**2c**) of [SN<sub>5</sub>]<sup>-</sup> had been previously computed by Wang and Zgierski [14] at the MP2/6-31G(d), B3LYP/6-31G(d), and B3LYP/6-311+G(d) levels of theory. In the present

**Table 2** Dissociation barriers (kcal mol<sup>-1</sup>) corrected by ZPE of some five-membered nitrogen ring species at the B3LYP/6-31+G\* level of theory

1a	2a	3a	4a
32.7	29.9	29.8	29.7

study, we calculated them at the MP2/6-311+G(d) and B3LYP/6-311+G(d) levels of theory. As listed in Table 1, the five-membered nitrogen ring structures (**1a-4a**) are global minima for all four [XN<sub>5</sub>]<sup>-</sup> systems at the B3LYP level of theory. The N<sub>2</sub>O...N<sub>3</sub><sup>-</sup> adducts (**1b-4b**) are local minima for [XN<sub>5</sub>]<sup>-</sup> (X=O, S, Se, Te) systems at the B3LYP level of theory, but first-order saddle points for [ON<sub>5</sub>]<sup>-</sup>, [SN<sub>5</sub>]<sup>-</sup>, and [TeN<sub>5</sub>]<sup>-</sup> systems at the MP2 level of theory. Different from other similar structures, the N<sub>2</sub>O...N<sub>3</sub><sup>-</sup> adduct **3b** of [SeN<sub>5</sub>]<sup>-</sup> is a local minimum at the MP2/6-31+G(d) level of theory. The chain-shaped structures (**1c-4c**) are local minima for [SeN<sub>5</sub>]<sup>-</sup> system, whereas first-order saddle points for [ON<sub>5</sub>]<sup>-</sup>, [SN<sub>5</sub>]<sup>-</sup>, and [TeN<sub>5</sub>]<sup>-</sup> systems at the two used levels of theory.

As listed in Table 1, the N<sub>2</sub>O...N<sub>3</sub><sup>-</sup> adducts (**1b-4b**) are 1.4, 5.0, 7.9, and 9.0 kcal mol<sup>-1</sup> higher in energy than their five-membered nitrogen ring ones at the B3LYP level of theory, respectively. The corresponding values at the MP2

**Table 3** Energies (kcal mol<sup>-1</sup>) of [XN<sub>5</sub>]<sup>-</sup> Relative to [XN]<sup>-</sup>+2N<sub>2</sub>

Species	B3LYP	MP2
<b>1a</b> (C <sub>2v</sub> )	7.5	12.9
<b>1b</b> (C <sub>s</sub> )	35.4	50.4
<b>1c</b> (C <sub>s</sub> )	112.6	144.8
<b>2a</b> (C <sub>2v</sub> )	11.5	11.9
<b>2b</b> (C <sub>s</sub> )	16.6	9.9
<b>2c</b> (C <sub>s</sub> )	76.3	84.2
<b>3a</b> (C <sub>2v</sub> )	6.2	43.5
<b>3b</b> (C <sub>s</sub> )	14.1	46.4
<b>3c</b> (C <sub>s</sub> )	90.1	136.5
<b>4a</b> (C <sub>2v</sub> )	-5.9	-16.6
<b>4b</b> (C <sub>s</sub> )	3.1	-9.0
<b>4c</b> (C <sub>s</sub> )	104.0	107.0



**Table 4** Calculated NICS values with GIAO-B3LYP/6-311+G\*\*//B3LYP/6-311+G\* method for the five-membered nitrogen ring species  $[\text{ON}_5]^-$ ,  $[\text{SN}_5]^-$  and  $[\text{SeN}_5]^-$  and GIAO-B3LYP//B3LYP method for  $[\text{TeN}_5]^-$  species

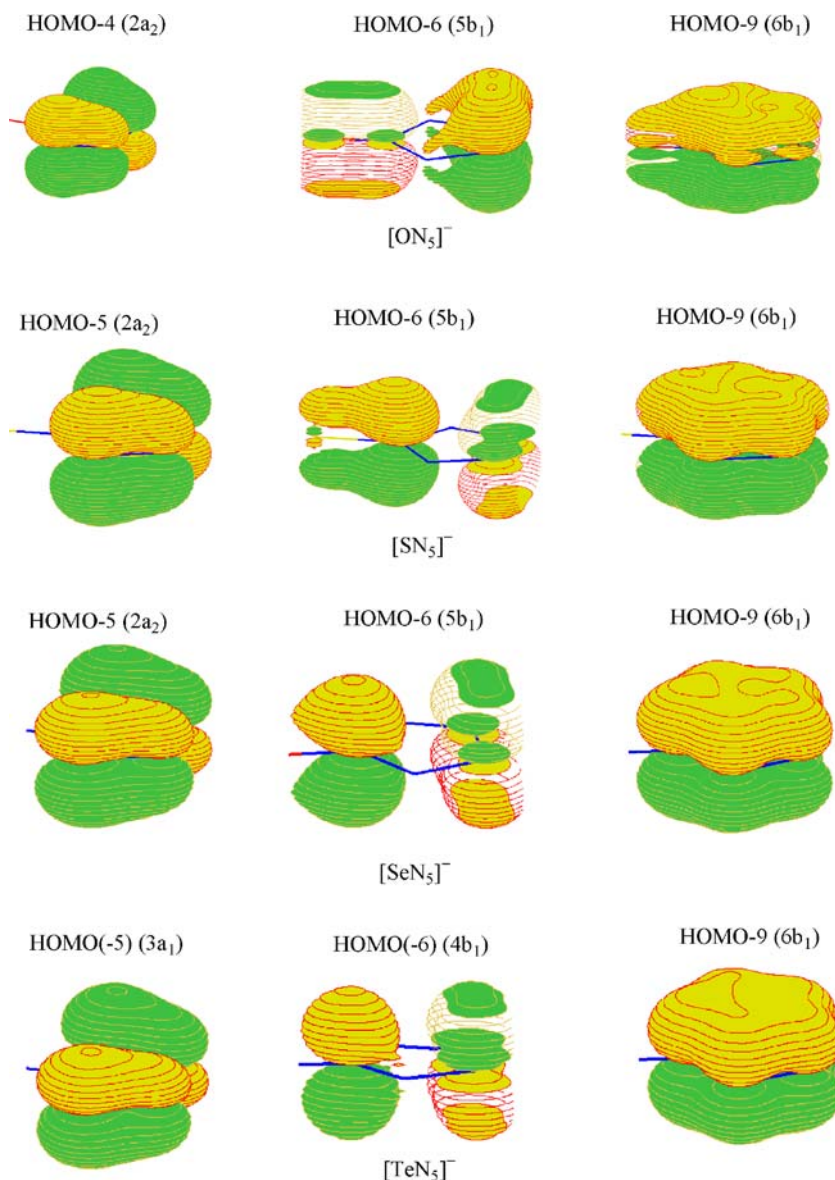
Species	NICS (0.0)	NICS (0.5)	NICS (1.0)	NICS (1.5)
<b>1a</b> ( $C_{2v}$ )	-12.27	-14.31	-12.01	-7.37
<b>2a</b> ( $C_{2v}$ )	-14.05	-16.50	-13.91	-8.57
<b>3a</b> ( $C_{2v}$ )	-14.80	-17.40	-14.72	-9.14
<b>4a</b> ( $C_{2v}$ )	-15.88	-18.30	-15.52	-9.91

level are  $-10.6$ ,  $-2.0$ ,  $2.9$ , and  $7.6$  kcal mol $^{-1}$ , respectively. The chain-shaped structures (**1c–4c**) are energetically higher than their global minima by 105.1, 64.8, 83.9, and 109.9 kcal mol $^{-1}$  at the B3LYP level of theory. The corresponding values at the MP2 level are 131.9, 72.3, 93.0, and 123.6 kcal mol $^{-1}$ .

As shown in Fig. 1, for each set of the similar structural  $[\text{XN}_5]^-$  species, the heavier the  $X$  atom is, the longer the  $X$ –

N distances are. The covalent radius for nitrogen is 0.70 Å; the corresponding values for O, S, Se, and Te are 0.66, 1.04, 1.17, and 1.37 Å [28], respectively. Obviously, in the five-membered nitrogen ring structures, the  $X$ –N bond distances in  $[\text{ON}_5]^-$  and  $[\text{SN}_5]^-$  systems are slightly shorter than the sum of covalent radii of the corresponding  $X$  atoms and nitrogen, but the  $X$ –N bond distances in  $[\text{SeN}_5]^-$  and  $[\text{TeN}_5]^-$  systems are slightly longer than the sum of the covalent radii of the corresponding  $X$  atoms and nitrogen. In the other two series of structures, except for the O2–N3 bond in **1c**, all  $X$ –N bond distances are slightly shorter than the sum of covalent radii of the corresponding  $X$  atoms and nitrogen at the B3LYP level of theory. Regarding the N–N bond distances in the five-membered nitrogen ring structures, all N–N bond distances tend to equalization. In terms of NBO analysis, for the five-membered nitrogen ring structures (**1a–4a**) and the  $\text{N}_2\text{O}\dots\text{N}_3^-$  adducts (**1b–4b**), along group 6, going from O to Te, the heavier the  $X$  atom is, the smaller the calculated  $\text{XN}$  Wiberg

**Fig. 3** Some  $\pi$ -bonding molecular orbital contour figures of the five-membered nitrogen ring series of structures



bond index (WBI) is, suggesting that the less electronegative the  $X$  atom is, the more polar the  $XN$  bond would be. In the chain-shaped structures (**1c–4c**), the WBIs of  $N1–X2$  are close to that of a double bond (2.0), but the WBIs of  $X2–N3$  are close to that of a single bond (1.0). The calculated NN WBIs in the five-membered nitrogen ring structures range from 1.2 to 1.5, which are between the standard values of single-bonds and double-bonds, indicating delocalization.

We have investigated some decomposition channels for the five-membered nitrogen ring  $[XN_5]^-$  species using the B3LYP method. The optimized transition structures are shown in Fig. 1. The dissociation barriers are listed in Table 2.

Four transition structures **ts–1a**, **ts–2a**, **ts–3a**, and **ts–4a** with  $C_s$  symmetry were located on the potential energy surfaces (PESs). As shown in Fig. 1, we cannot that, compared with the five-membered nitrogen ring structures (**1a–4a**), the bond lengths of  $N3–N4$  and  $N2–N6$  in the transition structures are stretched to eliminate  $N_3$  and  $N_2X$  molecules. The barriers for dissociation are 32.7, 29.9, 29.8, and 29.7 kcal mol $^{-1}$  for  $X=O, S, Se,$  and  $Te$  at the B3LYP level of theory, respectively, indicating high kinetic stability.

The energy differences relative to  $[XN]^- + 2N_2$  molecules are listed in Table 3 and it appears that most  $[XN_5]^-$  species would be energetic materials. Furthermore, all chain-shaped species (**1c–4c**) have higher dissociation energies. Therefore, it seems more reasonable to regard this series of species (especially the  $[SeN_5]^-$ ) as suitable candidates for HEDMs.

Aromaticity of the five-membered nitrogen ring in the  $[XN_5]^-$  species

#### Nucleus-independent chemical shift (NICS)

NICS, proposed by Schleyer and co-workers [29, 30], is an efficient and simple criterion in probing aromaticity, which is based on the negative of the magnetic shielding computed, e.g., at or above the geometrical centers of rings or clusters. Systems with (significant) negative NICS values are aromatic and systems with strongly positive NICS values are anti-aromatic. Non-aromatic cyclic systems should therefore have NICS values around zero. The more negative NICS, the more aromatic the system is. In this study, we firstly calculated NICS (0.0) by placing a ghost atom at the geometric centers of the nitrogen ring. To analyze the aromaticity further, we also calculated NICS (0.5), NICS (1.0) and NICS (1.5) values by placing a ghost atom above the geometric centers of the nitrogen ring by 0.5, 1.0, and 1.5 Å, respectively. As tabulated in Table 4, based on the calculated NICS values, all five-membered nitrogen rings are aromatic in the  $[XN_5]^-$  species according to the yardstick of a 50% value of benzene ( $-10.0$  at  $z=1.0$  Å) [31]. Furthermore, for each  $[XN_5]^-$  system, the aromaticity order is NICS (0.5) > NICS (0.0) > NICS (1.0) > NICS (1.5). It should be noted that NICS (0.0) values in

the ring plane are influenced by the local contributions of the  $N–N$   $\sigma$  bonds and lone pairs [30], and for the NICS (1.5) values the ghost atom is far from the geometric center of the ring. Therefore, it seems that the NICS (0.5) and NICS (1.0) values are better suited for the interpretation of  $\pi$ -contributions and to answer the question whether the  $[XN_5]^-$  species are really aromatic in the present study. In addition, the same NICS values give an increasing trend from O to Te. This trend may be attributed to the electronegativity of  $X$  atom. From O to Te, the heavier the  $X$  atom is, the less the electronegativity is, the less the  $X$  atom attracts electron density from the  $N_5$  ring, and thus the less aromatic the ring is.

#### The presence of $(4n+2)$ number of $\pi$ -electrons

Figure 3 shows that the  $\pi$ -bonding MOs of the  $N_5$  ring can be recognized easily in all  $[XN_5]^-$  species, even though the orders of some MOs are varied. They are only changed slightly by the presence of the heteroatoms. In each  $[XN_5]^-$  (**1a–4a**) system, altogether there are three  $\pi$ -bonding MOs in the five-membered nitrogen ring, involved six  $\pi$ -electrons and rendering aromaticity to this species.

Based on above analysis, we came to a conclusion that the five-membered nitrogen ring exhibits characteristics of aromaticity for these  $[XN_5]^-$  species.

#### Summary

We examined a series of  $[XN_5]^-$  ( $X=O, S, Se, Te$ ) compounds in the present study. Three singlet structures have been located for all  $[XN_5]^-$  systems, that is, the five-membered nitrogen ring structures, the  $N_2O\dots N_3$  adducts and the chain-shaped structures. Among them, the five-membered nitrogen ring structures are most stable and may exist or be characterized due to their significant dissociation barriers (29.7–32.7 kcal mol $^{-1}$ ).

Nucleus-independent chemical shifts (NICS) criteria and the presence of  $(4n+2)$   $\pi$ -electrons confirmed that the five-membered nitrogen ring in their structures exhibits characteristics of aromaticity. So the strong stability of this series of structures may be partially attributed to their aromaticity.

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