J. Phys. Chem. A **2004,** *108,* 4679−4684

Structures of Nitrogen-Rich Sulfides: SN_5 and SN_6

Li Jie Wang[†] **and Marek Z. Zgierski***

Steacie Institute for Molecular Sciences, National Research Council, Ottawa, K1A 0R6, Canada

Received: August 27, 2003; In Final Form: March 2, 2004

Structures of nitrogen-rich sulfides SN_5 and SN_6 (neutral molecules and ions) with low spin are optimized and characterized by harmonic vibrational frequency analysis using ab initio and density functional theory methods. Their stability is studied by evaluating dissociation barriers and by comparison of their total energies with those of $^1/_8S_8 + {}^x/_2N_2$ ($x = 5, 6$). The important role d orbitals play in nitrogen-rich sulfides is discussed. We have identified two charged SN_5 structures and three charged SN_6 structures that can be good candidates for high-energy density materials.

1. Introduction

Recently, nitrogen-rich compounds have attracted interest because of their possible use as high-energy density materials (HEDMs)[1−4] provided one finds those that have a high dissociation energy barrier and a facile synthesis. Similar to the problem of pure nitrogen clusters, the stability and synthesis methods of nitrogen-rich compounds are challenging because of the metastable nature of nitrogen clusters.

Bartlett[5] suggested some nitrogen-rich clusters formed by N, O, and H for use as HEDMs. The properties of other kinds of nitrogen cluster, $(Ar)_n(N_2)_m{}^+$ and benzene$(N_2)_n$, were studied by Adams[7] and Hiraoka et al.[6] Hammerl and Klapotke studied the nitrogen-rich clusters CN_x both experimentally and theoretically.[8] Gagliardi and Pyykkö[9,10] designed and calculated the structures of ScN_7 and N_5−metal−N_7 and their dissociation pathways. We have also designed some structures of nitrogen-rich sulfides, SN_4 and SN_3,[11,12] and some possible reaction pathways for synthesizing the nitrogen-rich ionic compounds $HN_8{}^+$, $N_4H_2F^+$, and $N_7H_2{}^+$.[13−15]

The N−N single bond has an energy of 39 kcal/mol, while that for N═N is 100 kcal/mol, and N≡N has an energy of 228 kcal/mol at 298 K.[16] Nitrogen compounds containing single and double bonds therefore release substantial amounts of energy when they dissociate into N_2 molecules. Consequently, storing the maximum amount of energy in a polynitrogen molecule would mean having the largest number of single bonds. However, nitrogen atoms have lone pairs of electrons repelling each other, so their single bonds are much weaker than, for example, a carbon−carbon single bond. At the most fundamental level, a molecule will exist only if it has an energy barrier high enough to keep it away from dissociation. Although N−N single bonds store more energy, the stability of a molecule would suggest that it must have enough double bonds to ensure adequate bond strength to keep it intact. The SN bond has very special properties in part due to the diffuse electron density on the sulfur atom and also to the d-type symmetry of a part of the electron distribution, resulting in such unusual properties as rotation-independent conjugation in some compounds.[17−19] The special role of d orbitals in the representation of diffuse electron densities has also been the subject of detailed studies.[20−22] The special properties of the sulfur atom with its large atomic radius and loose electron density make it a good candidate to link well with nitrogen clusters. Nitrogen sulfide, NS, is known to play key roles in both combustion and atmospheric chemistry.[23] Ongstad and co-workers[24] reported the photodissociation dynamics of S_4N_4 at 222 and 248 nm. Most studies of S_xN_x are on the structures of alternating atoms of N and S. Collins et al.[25] studied the electronic ground state of the dinitrogen sulfide (N_2S) molecule. An aromatic cation with an N_3 unit, $S_2N_3{}^+$, was studied by theory and experiment.[26] The $S_2N_3{}^+$ ion represents the first binary SN ring with an N_3 unit.

Of course, the structure of the PES for SN_m becomes increasingly more complex with increasing m, and a richer family of possible molecules can be expected. One cannot expect to find simple rules based on m alone; however, as more information becomes available, it is possible that one will be able to find some trends.

In this paper, the main task is to investigate nitrogen-rich sulfur compounds, the neutral and ionic structures SN_5 and SN_6, which store energy and are stable enough so that they could exist.

2. Computational Methods

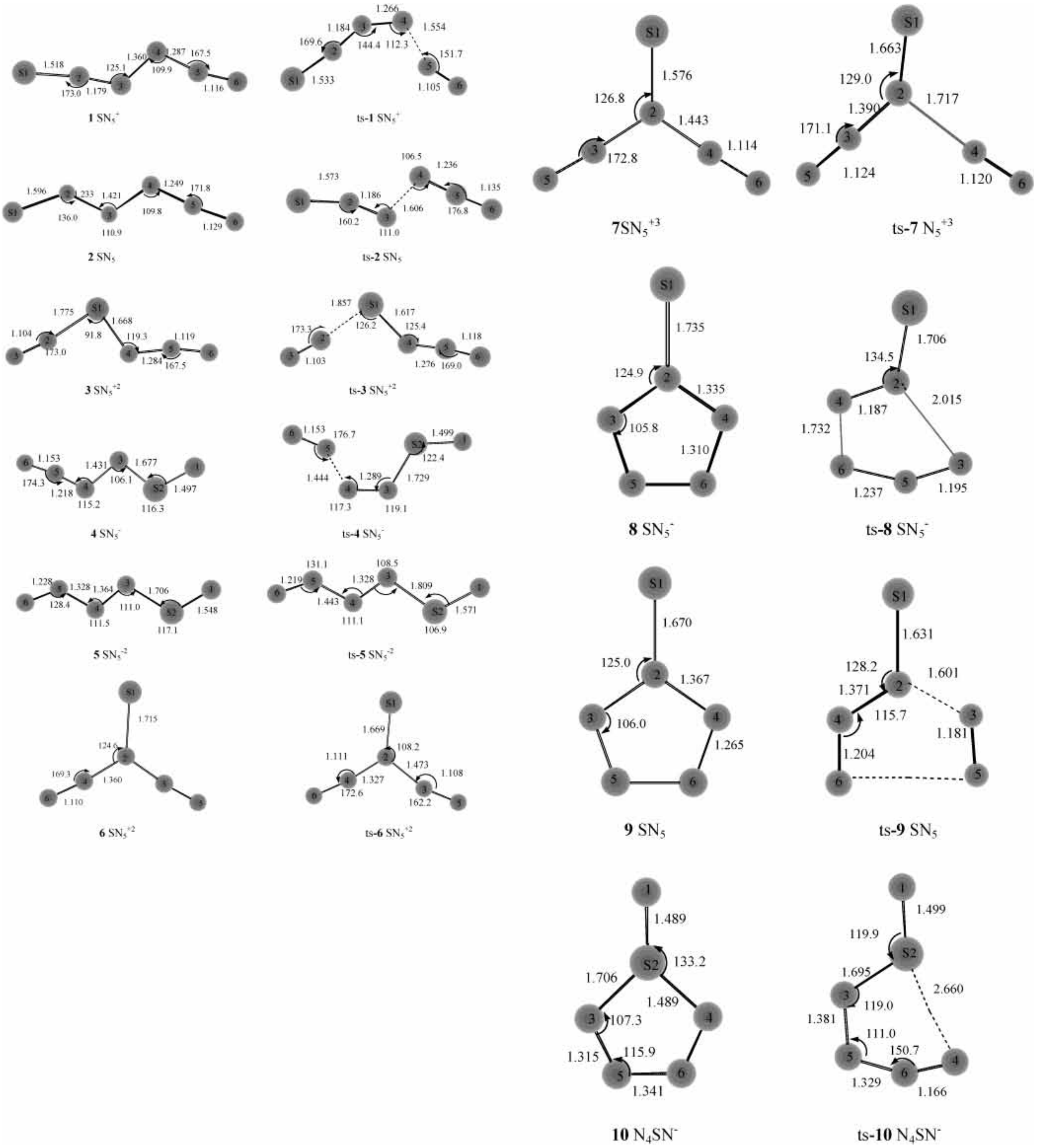
The geometries of the compounds SN_x have been optimized with ab initio and density functional methods at the levels of MP2/6-31G*, B3LYP/6-31G*, and B3LYP/6-311+G*, where B3LYP is a hybrid functional method using Becke's three-parameter nonlocal exchange functional[27] with the nonlocal correlation of Lee, Yang, and Parr,[28] and MP2 stands for the second-order Mϕller−Plesset (many-body) perturbation theory.[29] The designation 6-31G* refers to a standard split-valence double-ζ polarization basis set, while the 6-311+G* is a standard spit-valence triple-ζ polarization basis set augmented with diffuse functions.[30] To characterize the nature of the stationary points as either local minima or transition states, harmonic vibrational frequencies were also calculated at the levels of the above-mentioned theory. Minimum energy path calculations[31] were performed starting at the transition state structures with a coordinate step size of 0.1 (amu)$^{1/2}$ bohr. All calculations were carried out with the Gaussian 98 program package.[32]

---

* Corresponding author. Fax: 1-613-947-2838. E-mail: marek@ned.sims.nrc.ca.

[†] Present address: Department of Chemistry, Memorial University of Newfoundland, NL A1B 3×7, Canada.

10.1021/jp0310201 CCC: $27.50



1 SN_5^+ **ts-1** SN_5^+ **7** SN_5^{+3} **ts-7** N_5^{+3}

2 SN_5 **ts-2** SN_5

3 SN_5^{+2} **ts-3** SN_5^{+2} **8** SN_5^- **ts-8** SN_5^-

4 SN_5^- **ts-4** SN_5^-

5 SN_5^{-2} **ts-5** SN_5^{-2} **9** SN_5 **ts-9** SN_5

6 SN_5^{+2} **ts-6** SN_5^{+2}

10 N_4SN^- **ts-10** N_4SN^-

Figure 1. Parameters and geometric structures of SN_5 at the B3LYP/6-311+G* level. Distances are in angstroms and angles are in degrees.

3. Results and Discussion

3.1. Stability and Geometric Structures of SN_5. Ten stable structures of SN_5 (four cations, four anions, and two neutrals) and transition states (TS) were optimized and characterized to be minima or saddle points by harmonic vibrational frequency analysis at the B3LYP/6-311+G* level. Parameters of geometric structures, total energies, and relative energies are present in Figure 1 and Tables 1 and 2.

Structures **1** (C_S, $^1A'$), **2** (C_S, $^2A'$), and **3** (C_S, $^2A''$) are chain-shaped structures with different charges. In structure **1** (SN_5^+), a sulfur atom connects a chain-shaped N_5, and the N3−N4 bond is longer than the other N−N bonds. Structure **1** dissociates into $SN_3^+ + N_2$ with a barrier of 14.5 kcal/mol at the B3LYP/6-311+G* level. When an electron is added to cation **1**, stable neutral molecule **2** is obtained. The bonds S−N2, N2−N3, and N3−N4 in structure **2** are slightly longer than those in structure **1** since an increased electron density results in a repelling force between these atoms. The **ts-2** (imaginary frequency 400i) is a transition state of **2** dissociating into $SN_2 + N_3$ with a barrier of 2.7 kcal/mol. Addition of another electron causes breaking of the N3−N4 bond and dissociation of SN_5^- into $SN_2^- + N_3$. Structure **3** (SN_5^{+2}) has a sulfur atom connecting two fragments,

TABLE 1: Total Energies (Hartree)/ZPVE (kcal/mol) of SN_x ($x = 5, 6$) at the Ab Initio and DFT Levels with Basis Set 6-31G*

		6-31G*		6-311+G*
SN_m		B3LYP	MP2	B3LYP
SN_5	**1** (SN_5^+)	−671.46577/13.7	−670.20565/13.9	−671.56484/13.8
	2 (SN_5)	−671.76948/13.2	−670.46187/17.1	−671.87405/13.2
	3 (SN_5^{+2})	−670.92016/12.6	−669.65505/19.0	−671.01952/12.5
	4 (SN_5^-)	−671.79212/12.2	−670.50743/12.7	−671.91903/11.8
	5 (SN_5^{-2})	−671.63189/10.9	−670.27617/10.7	−671.79893/10.2
	6 (SN_5^{+2})	−670.85612/12.8	−669.61506/22.1	−670.95790/12.9
	7 (SN_5^{+3})	−670.02964/12.3	−668.81290/11.6	−670.13225/12.4
	8 (SN_5^-)	−671.91736/15.1	−670.64159/15.1	−672.02724/14.9
	9 (SN_5)	−671.79545/14.6	−670.52770/15.0	−671.89269/14.5
	10 (SN_5^-)	−671.79396/12.7	dissociated	−671.90895/12.4
SN_6	**11** (SN_6^{-2})	−726.43801/14.6	−724.98547/14.7	−726.60806/14.6
	12 (SN_6^-)	−726.56185/15.3	−725.09314/17.7	−726.69763/15.2
	13 (SN_6)	−726.47381/15.9	−725.06051/15.8	−726.59409/15.9
	14 (SN_6^+)	−726.17614/16.1	−724.73752/22.2	−726.29026/16.1
	15 (SN_6^{+2})	−725.66908/16.7	−724.29706/18.3	−725.78153/16.6
	16 (SN_6)	−726.46166/15.0	−725.04422/15.0	−726.58509/14.9
	17 (SN_6^{-2})	−726.47477/17.0	−725.04195/17.1	−726.63344/16.8
	18 (SN_6^-)	−726.60898/17.3	−725.17651/19.8	−726.73438/17.1
	19 (SN_6)	−726.50635/17.4	−725.10104/17.3	−726.61834/17.3
	20 (SN_6)	−726.50371/16.7	−725.10454/16.8	−726.61926/16.6
	21 (SN_6^{-2})	−726.42033/15.9	−724.98319/16.0	−726.58010/15.8
	22 (SN_6)	−726.35063/15.3	−724.95482/13.4	−726.45403/15.2
	23 (SN_6)	−726.12248/14.3	−724.75198/13.0	−726.22382/14.3
	24 (SN_6^{+2})	−725.65660/15.4	−724.28907/15.4	−725.76950/16.1
	25 (SN_6)	−726.52498/16.2	−725.12508/16.3	−726.64458/16.1

TABLE 2: Relative Energies (kcal/mol) Corrected by ZPVE of the Neutral SN_x Corresponding to Thermodynamic Stability ($^x/_2N_2 + {}^1/_8S_8$) at DFT Levels

	B3LYP/6-31G*	B3LYP/6-311+G*
$^1/_8S_8 + {}^5/_2N_2$	0.0	0.0
SN_5 (**2**)	150.8	157.3
SN_5 (**9**)	135.9	147.3
$^1/_8S_8 + 3N_2$	0.0	0.0
SN_6 (**13**)	188.0	192.7
SN_6 (**16**)	194.7	197.3
SN_6 (**19**)	169.5	178.1
SN_6 (**20**)	170.4	180.7
SN_6 (**22**)	264.7	283.3
SN_6 (**23**)	406.8	426.8
SN_6 (**25**)	156.2	164.6

N_2 and N_3. Two S−N bonds are very different, and the longer one connects the N_2 fragment. The positive charges mainly reside on atoms 1, 3, 5, and 6. Structure **3** dissociates into $SN_3^{2+} + N_2$ with a barrier of 0.2 kcal/mol, that is, **3** is a very unstable cation. When an electron is added to **3**, a stationary point is obtained with one imaginary frequency of 139i cm^{-1}. The vibrational mode of this imaginary frequency puts atom 2 out of the plane. Then, the symmetry of SN_5^+ is reduced from C_S to C_1, and SN_5^+ dissociates into $SN^+ + 2N_2$. Likewise, the new species SN_5 and SN_5^-, obtained from **3** by the addition of two and three electrons, dissociate into SN_2 (linear) + N_3 and $SN^- + 2N_2$, respectively. Structures **4** (NSN_4^-) and **5** (NSN_4^{-2}) are the only stable structures among the species formed by a sulfur atom connecting a nitrogen atom and chainlike nitrogen cluster N_4. The **ts-4** (imaginary frequency 758i cm^{-1}) and **ts-5** (imaginary frequency 761i cm^{-1}) are dissociation transition structures of ions **4** and **5**. The low dissociation barriers of **4** and **5** of 11.2 and 1.7 kcal/mol, respectively, show that they are not stable enough. NSN_4^+, NSN_4^{-3}, and NSN_4 dissociate into $SN^+ + 2N_2$, $SN_2^{-2} + N_3^-$, and $SN + 2N_2$, respectively. Structures **6** (SN_5^{+2}) and **7** (SN_5^{+3}) possess C_{2v} symmetry and differ in the total charges. The symmetry of the ground state of **6** is $^2B_1$while that of **7** is $^1A_1$. Removal of an electron from **6** leads to a marked contraction of the SN bond (by 0.14 Å) due to nearly a 2-fold increase of the charge on the sulfur atom (from +0.6 to +1.12). The **ts-6** (imaginary frequency 501i cm^{-1}) and **ts-7** (imaginary frequency 955i cm^{-1}) are dissociation transition structures of ions **6** and **7**. In the dissociation processes, the N2−N4 bond is broken. The barrier heights for **6** and **7**, dissociating into $N_2 + SN_3^{+2}$ and $N_2 + SN_3^{+3}$, respectively, are 0.1 and 61.0 kcal/mol at the B3LYP/6-311+G* level. The high dissociation barrier of structure **7** shows that it is stable enough to be used as an HEDM in combination with suitable counterions.

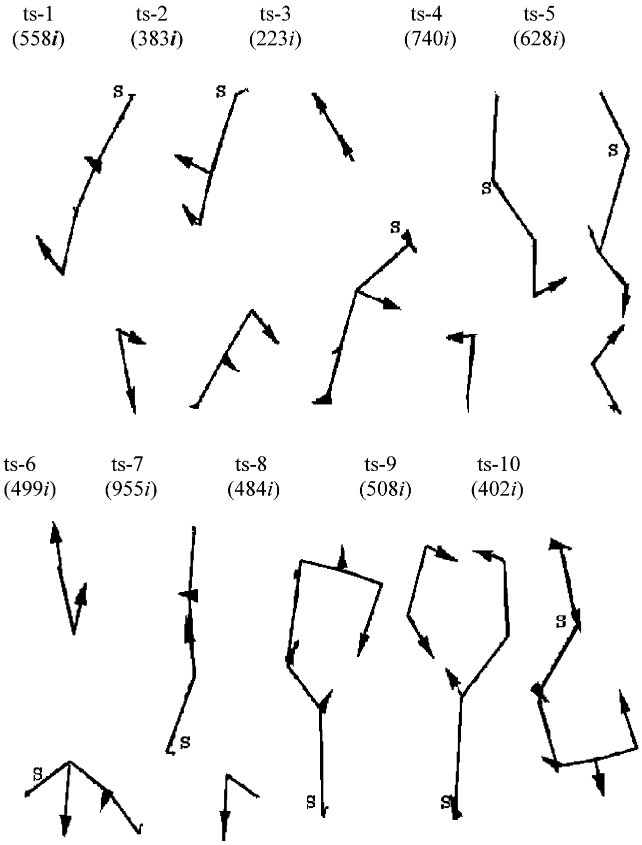


Figure 2. Imaginary frequency normal modes of the 10 transition state structures of SN_5.

Structures **8** SN_5^- (C_{2v}, $^1A_1$) and **9** SN_5 (C_{2v}, $^2B_1$) are both formed by a sulfur atom connecting a pentagon N_5 with different charges. The main difference is that S−N is longer by 0.065 Å in **8** than in **9**. Structures **ts-8** (484i) and **ts-9** (508i) are two transition states of the **8** and **9** dissociation processes. The dissociation pathways of these two structures are different although in both cases the N_5 pentagon is broken. In structure **8**, the N4−N6 and N2−N3 bonds break, then **8** dissociates into $SN_2 + N_3^-$ with a barrier height of 29.9 kcal/mol at the B3LYP/6-31G* level. For structure **9**, the N2−N3 and N5−N6 bonds break and **9** dissociates into $SN_3 + N_2$. However, the barrier for dissociation is in this case only 2.0 kcal/mol at the B3LYP/6-31G* level indicating the high instability of **9**. Addition of another electron to structure **8** causes dissociation of SN_5^{-2} into $S^- + N_5^-$. Only anion **8** is reasonably stable.

Structure **10** (NSN_4^-) is formed by a nitrogen atom connecting to a sulfur atom in a five-membered ring, SN_4. The **ts-10** is a transition state for **10** dissociation into $NSN^- + N_3$ with a barrier of 11.4 kcal/mol. Structures of type **10** but with different charges, +1, −2, and neutral, dissociate into $SN^+ + 2N_2$, $SN^- + N_4^-$, and $SN + 2N_2$.

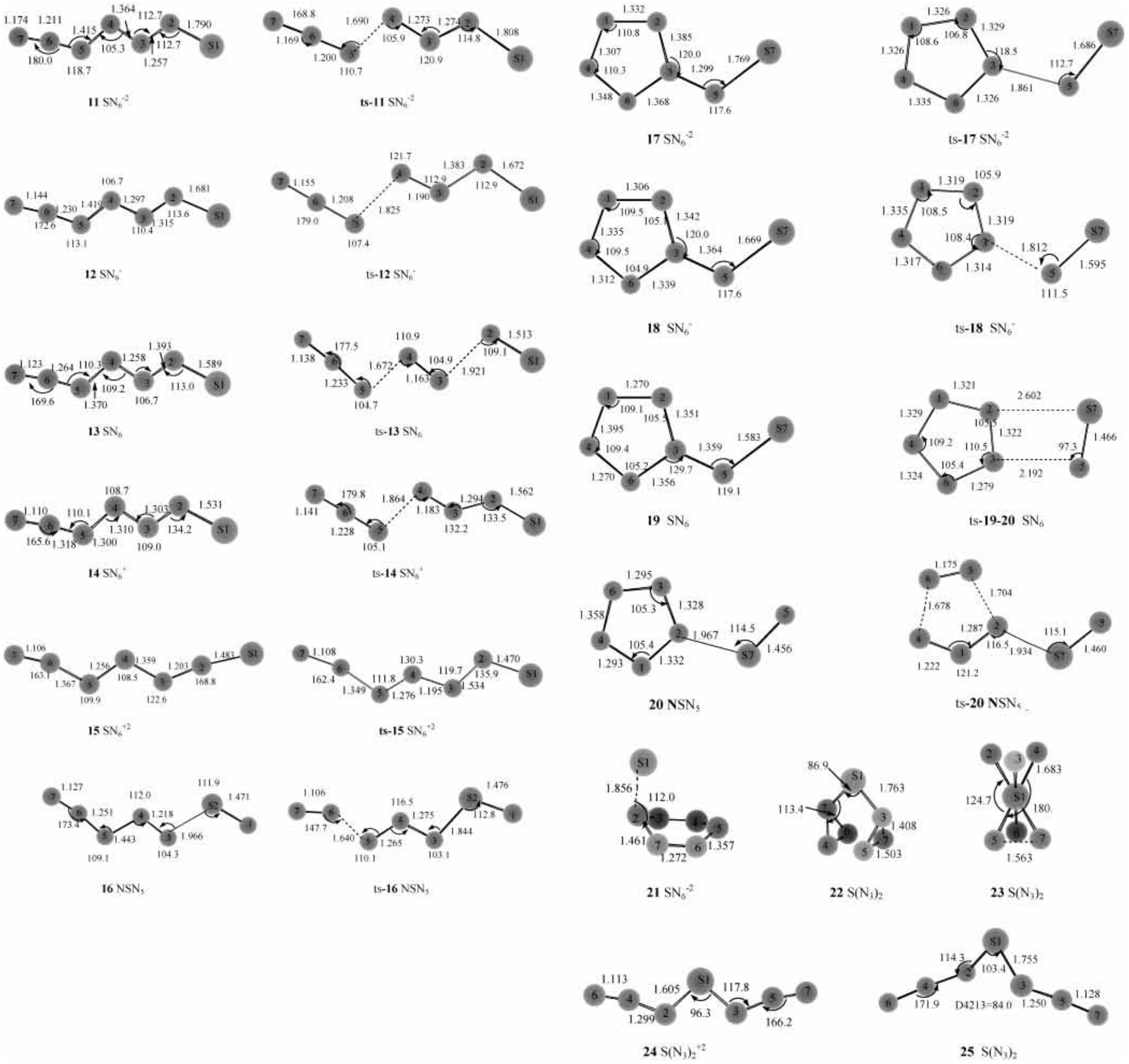


Figure 3. Parameters and geometric structures of SN_6 at the B3LYP/6-311+G* level. Distances are in angstroms and angles are in degrees.

In order to verify the dissociation paths, the reaction-coordinate vectors (the imaginary frequencies of the normal modes of the transition state structures) are shown in Figure 2.

3.2. Stability and Geometric Structures of SN_6. Fifteen species of SN_6 (seven neutral molecules, five negative ions, and three positive ions) were found to possess stable structures, characterized by all real frequencies. Their total energies, the parameters of the geometric structures, and the reaction-coordinate vectors are listed in Table 1 and Figures 3 and 4.

Structures **11**−**15** are chain-shaped, formed by a S atom connecting an N_6 chain with different charges. Structure **11**, SN_6^{-2} (C_S, $^1A'$), is a negative ion, and the negative charge distributes on S1, N2, N4, N5, and N7. Structure **ts-11** is a transition state structure (imaginary frequency 458i cm^{-1} at the B3LYP/6-311+G* level) on the way to dissociation of structure **11**. Bond N4−N5 is lengthened to 1.690 Å, and then **11** breaks into $N_3^- + SN_3^-$. Structure **11** is not stable enough with the low dissociation barrier of 4.2 kcal/mol at the B3LYP/6-311+G* level. Structure **12** is obtained from **11** by removal of an electron. The bond lengths in **12**, SN_6^-, have some changes compared with those in structure **11** since the charge distribution is different. Structure **ts-12** is a transition state structure (imaginary frequency 291i cm^{-1}) on the way of structure **12** dissociating into $N_3 + SN_3^-$. Similar to the low barrier of structure **11** dissociation, that of **12** is only 6.3 kcal/mol at the B3LYP/6-311+G* level. Structure **13** is a neutral SN_6 species with the barrier of 13.4 kcal/mol for dissociation into $N_3 + N_2 + SN$. Structure **ts-13** is a transition state (imaginary frequency 308i cm^{-1}) for the dissociation reaction of **13**. Structures **14** and **15** are two positive ions derived from neutral molecule **13**. Shortening of the length of the S−N bond is observed with the removal of electrons. This agrees with the charge distribution upon ionization (see Table 3). Structures **ts-14** and **ts-15** are transition states for dissociation (714i cm^{-1} and 760i cm^{-1}) of structures **14** and **15** with the barriers of 43.3 and 27.0 kcal/mol, respectively. The dissociation pathway of structure **15** is different from those of **11**−**14**, with the N2−N3 bond broken. Structure **16** (NSN_5) is a neutral formed by a sulfur atom

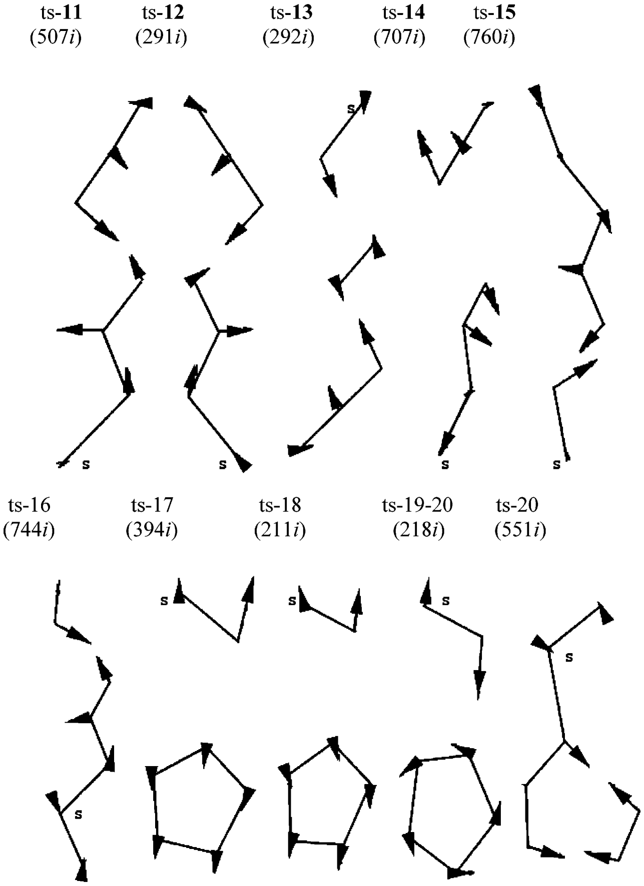


Figure 4. Imaginary frequency normal modes of the 10 transition state structures of SN_6.

TABLE 3: Dissociation Barriers (kcal/mol) Corrected by ZPVE of All Species (Except the Barrier for the Isomerization between 19 and 20) at the B3LYP/6-311++G Level**

SN_5	**1** (SN_5^+)	14.5
	2 (SN_5)	2.7
	3 (SN_5^{+2})	0.2
	4 (SN_5^-)	11.2
	5 (SN_5^{-2})	1.7
	6 (SN_5^{+2})	0.1
	7 (SN_5^{+3})	61.0
	8 (SN_5^-)	29.9
	9 (SN_5)	2.0
	10 (SN_5^-)	11.4
SN_6	**11** (SN_6^{-2})	4.2
	12 (SN_6^-)	6.3
	13 (SN_6)	13.4
	14 (SN_6^+)	43.3
	15 (SN_6^{+2})	27.0
	16 (SN_6)	16.3
	17 (SN_6^{-2})	23.1
	18 (SN_6^-)	7.5
	19 (SN_6)	22.3(isom)
	20 (SN_6)	12.4

connecting a nitrogen atom and a chainlike N_5. The **ts-16** is a transition state for **16** dissociating into $NSN_3 + N_2$ with the barrier of 16.3 kcal/mol. The cation and anion structures, from addition and removal an electron from **16**, dissociate into $SN^+ + N_5$ and $SN^- + N_3 + N_2$. The chainlike structures N−N−S−N−N−N−N, with charges of ±2, ±1, and 0, all dissociate. Thus, a single charged cation is the most stable among the investigated NSN_5 chainlike structures.

Structures **17** SN_6^{-2} (C_S, $^1A'$) and **18** SN_6^- (C_1) are formed by a pentagon N_5 connecting a fragment SN. Their stability was studied by evaluating the energy barriers to dissociation. SN_6^{-2} is stable enough because the barrier is 23.1 kcal/mol at the B3LYP/6-311+G* level. The low barrier of 7.5 kcal/mol for structure **18** depicts that it is not stable enough. Structures **ts-17** and **ts-18** are transition states of **17** and **18** dissociating into $N_5^- + SN^-$ and $N_5^- + SN$ with imaginary frequencies 394i cm^{-1} and 267i cm^{-1}, respectively. The fewer electrons, the more the S−N bond is shortened and, correspondingly, the less stable the structure. This agrees with the charge distribution and shows the opposite trend to the chainlike molecules **11**−**14**. Structures **19** (SN_6, C_S) and **20** (NSN_5, C_S) are neutral molecules in which the SN group connects the pentagon N_5 either through a nitrogen atom or a sulfur atom, respectively. **20** has an energy that is lower by 1.2 kcal/mol than that of **19** at the B3LYP/6-311+G* level. Ionic structures NSN_5^+, NSN_5^-, and NSN_5^{-2}, similar to **20**, dissociate into $N_2 + N_3 + SN^+$, $N_5^- + SN$, and $N_5^- + SN^-$, respectively. The **ts-19**−**20** (imaginary frequency 200i cm^{-1}) is a transition state of the isomerization reaction between structures **19** and **20** with a barrier of 22.3 kcal/mol**.** The dissociation reaction of **20** proceeds with a barrier of 12.4 kcal/mol. The structures, formed by the five-membered ring SN_4 and two nitrogen atoms, are all unstable. Species with total electric charges ±2, ±1, and 0 were investigated.

Structure **21** (SN_6^{-2}, C_S) is a negative ion formed by a six-membered ring N_6 connecting to a sulfur atom. The S−N bond (1.856 Å) is longer than that in the other species. The species **22** (C_{2v}) and **22** (D_{3d}), all of the type $S(N_3)_2$,[12] are formed by a S atom connecting two N_3 triangles in different ways. The relative energy of species **22** and **23** is 283.3 and 426.8 kcal/mol higher than $3N_2 + {}^1/_8S_8$ at the B3LYP/6-311+G* levels, respectively. Structure **23**, of D_{3d} symmetry, has the highest energy among the six neutral species. In the above-studied structures (except **23**), the common feature is that they are formed by a sulfur atom that connects to each nitrogen cluster via a single bond. The structures in which connection of each nitrogen cluster couples to the center sulfur with two single bonds are studied in a separate work.

Structure **24** (C_{2v}, $S(N_3)^{+2}$), with C_{2v} symmetry, is of the type $S(N_3)_2$ too.[12] It is formed by a sulfur atom connecting two N_3 fragments by one single S−N bond. A neutral structure (C_{2v}, similar to **24**) was found to be saddle point with two imaginary frequencies. However, a stable neutral molecule **25** was obtained when the symmetry was reduced from C_{2v} to C_2. Structure **25** is the most stable one among the six neutral species studied here. The negative ion with C_2 symmetry is a saddle point characterized by one imaginary frequency with the DFT method. When optimized according to the imaginary frequency vibrational mode, a stable negative complex (not planar) is obtained, $N_3S\cdots N_3$. The thermodynamical stability of the neutral structures was also calculated by comparing their total energies with that of $3N_2 + {}^1/_8S_8$. The results are collected in Table 2.

3.3. Importance of the d Orbitals of the Sulfur Atom in Nitrogen-Rich Sulfides. The special role of d orbitals in the representation of diffuse electron densities and the special properties of the sulfur atom with its large atomic radius and loose electron density make sulfur a good candidate to link well with nitrogen clusters. The calculated sulfur−nitrogen bond with a d orbital is shorter than that without d orbitals, and also the more nitrogen atoms connect to sulfur, the more important the role of the d orbitals becomes. Three different kinds of structures (**13**, **19**, **20**, **23**) have been calculated. Structures **13** and **19** both contain the sulfur atom at the end of the molecules. The length of the S−N bond in the optimized geometric structure is less than 1.6 Å if the d orbitals are included; however, it is over 1.68 Å without d orbitals. Structure **20** is formed by the sulfur atom connecting to one nitrogen atom and to one pentagonal nitrogen cluster; the S−N bond length is similar to those of **13** and **19**.

However, for structure **23**, the length of S−N in the optimized geometric structure is less than 1.7 Å with the d orbitals and more than 1.92 Å without d orbitals. Even more important is the finding that the optimized structure **23** without d orbital is not a minimum having two imaginary frequencies. Clearly, N atoms prefer sp^3 hybridization, and in structures with six bonds around a sulfur atom, this atom prefers an sp^3d^2 hybridization. The required 12 electrons are obtained from the 6 valence electrons of S and the single electron from each nitrogen atom linked to sulfur.

4. Summary

The calculations of the structures and stability of SN_x ($x = 5, 6$) present a wealth of such structures due to the presence of the sulfur atom, which connects nitrogen clusters as a bridge and makes it possible to connect a few nitrogen clusters together. We find that the nitrogen atoms have somewhat distorted sp^3 hybridization, and the sulfur atom has a distorted sp^3d^2 hybridization. These results demonstrate that the d orbitals play a very important role in nitrogen-rich sulfides. The stability of nitrogen-rich sulfides is a problem just the same as that of the all-nitrogen clusters. We have found three anions (**8**, **14**, **15**) and two cations (**7** and **17**) that have large enough energy barriers for dissociation to serve as good candidates for HEDMs. For charged species a condensed phase synthesis with suitable counterions must be investigated. In such a case, the actual charges at the various nitrogen atoms in the context of interactions between molecules will become important factors which would complicate the problem considerably. Stable charged clusters may form good candidates for HEDMs when they combine with appropriate counterions. Properties of such HEDMs will depend critically on the total charge of a cluster.

Supporting Information Available: Charge distributions of SN_x at the B3LYP/6-311+G* level. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Hammerl, A.; Klapotke, T. M. *Inorg. Chem.* **2002**, *41*, 906.

(2) Hammerl, A.; Klapotke, T. M.; Noth, H.; Warchhold, M. *Inorg. Chem.* **2001**, *40*, 3570.

(3) Chavez, D. E.; Hiskey, M. A.; Gilardi, R. D. *Angew. Chem., Int. Ed.* **2000**, *112*, 1861.

(4) Fraenk, W.; Haberader, T.; Hammerl, A.; Klapotke, T. M.; Krumm, B.; Mayer, P.; Noth, H.; Warchhold, M. *Inorg. Chem.* **2001**, *40*, 1334.

(5) Bartlett, R. *Chem. Ind.* **2000**, *21*, 140.

(6) Hiraoka, K.; Fujimaki, S.; Nasu, M.; Minamitsu, A. *J. Chem. Phys*. **1997**, *107*, 2550.

(7) Adams, J. E. *J. Chem. Phys*. **1998**, *109*, 6296.

(8) Hammerl, A.; Klapotke, T. M. *Inorg. Chem.* **2002**, *41*, 906.

(9) Gagliardi, L.; Pyykkö, P. *J. Am. Chem. Soc*. **2001**, *123*, 9700.

(10) Gagliardi, L.; Pyykkö, P. *J. Phys. Chem. A* **2002**, *106*, 4690.

(11) Wang, L. J.; Mezey, P. G.; Zgierski, M. Z. *Chem. Phys. Lett.* **2003**, *369*, 386**.**

(12) Wang, L. J.; Zgierski, M. Z.; Mezey, P. G. *J. Phys. Chem. A* **2003**, *107*, 2080.

(13) Wang, L. J.; Li, Q. S.; Warburton, P.; Mezey, P. G. *J. Phys. Chem. A* **2002**, *106*, 1872.

(14) Wang, L. J.; Mezey, P. G. *J. Phys. Chem. A* **2002**, *106*, 10391.

(15) Wang, L. J.; Mezey, P. G. *Chem. Phys. Lett.* **2002**, *363*, 87.

(16) Huheey, J. E.; Keiter, E. A.; Keiter, R. L. *Inorganic Chemistry*, 4th ed.; Harper-Collins: New York, 1993; p A31.

(17) Mezey, P.; Kucsman, A. *J. Chem. Soc., Faraday Trans. 2* **1972**, *68*, 2060.

(18) Mezey, P.; Kalman, A.; Kucsman, A. *Int. J. Sulfur Chem.* **1972**, *A2*, 187.

(19) Mezey, P.; Flakus, H. *J. Mol. Struct. (THEOCHEM)* **1989**, *186*, 117.

(20) Mezey, P.; Kapur, A. *Can. J. Chem.* **1980**, *58*, 559.

(21) Mezey, P.; Hass, E. C. *J. Chem. Phys.* **1982**, *77*, 870.

(22) Mezey, P.; Hass, E. C. *J. Comput. Chem.* **1983**, *4*, 482.

(23) Hassanzadeh, P.; Andrews, L. *J. Am. Chem. Soc.* **1992**, *114*, 83.

(24) Ongstad, A. P.; Lawconnell, R. I.; Henshaw, T. L. *J. Chem. Phys.* **1992**, *97*, 1053.

(25) Collins, C. L.; Yamaguchi, Y.; Schaefer, H. F., III. *J. Chem. Phys.* **1993**, *98*, 4777.

(26) Herler, S.; Mayer, P.; Nth, H.; Schulz, A.; Suter, M.; Vogt, M. *Angew. Chem., Int. Ed.* **2001**, *40*, 3173.

(27) Becke, A. D. *J. Chem. Phys*. **1993**, *98*, 5648.

(28) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, 37, 785.

(29) Moller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618.

(30) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley & Sons: New York, 1986.

(31) Gonzalez, C.; Schlegel, H. B. *J. Phys. Chem.* **1990**, *94*, 5523.

(32) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.5; Gaussian, Inc.: Pittsburgh, PA, 1998.