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# Electronic Structure of Sulfanenitriles[#]

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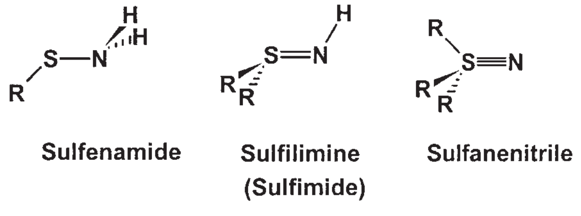
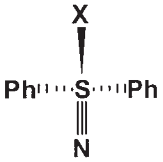
Ab initio calculations have been carried out to analyze the electronic structure of organosulfur compounds with $S{\equiv}N$. The electronic structures of $R_3S{\equiv}N$, $R(O)S{\equiv}N$, and $RS{\equiv}N$ have been compared. The calculations suggest that the S–N interactions should be taken as a hybrid of the $S{\equiv}N$ triple bond and the $S^+$–$N^-$ single bond. The balance between the two resonating structures shift towards a $S{\equiv}N$ triple-bonded arrangement with an increase in the electronegativity of substituents on sulfur. The strength of the Lewis basicity of sulfanenitriles has been estimated by studying their proton affinities and the complexation energies with $BH_3$. On the potential energy surface of $H_3S{\equiv}N$, this hypervalent compound has been shown to be a high-energy local minimum; although its 1,2-H shift isomers are all more stable, the barrier for the 1,2-shift is very high.

Compounds bearing a sulfur–nitrogen bond are of special interest due to the possibilities of sulfur possessing different oxidation states and coordination numbers, forming single, double, and triple bonds with nitrogen (Scheme 1). $\lambda^6$-sulfanenitriles (also known as thiazynes) are unusual compounds having a $S{\equiv}N$ triple bond.[1] The inorganic chemistry of thiazynes has been explored by Glemser et al.,[2] mainly based on $FS{\equiv}N$ (**A**) and $F_3S{\equiv}N$ (**B**) systems (Scheme 2). Tchir and Spratley[3d,e,f] have generated the sufanenitrile $HO$–$S{\equiv}N$ from HNSO, and several theoretical and experimental studies have been carried out on this molecule. Nakamura et al.[3c] have performed theoretical studies on $HS$–$S{\equiv}N$ as a part of their ab initio MO study on the isomers of $HNS_2$. The organic chemistry of $\lambda^6$-sulfanenitriles is being extensively studied by Yoshimura et al.,[4] for example **C**–**J** (Scheme 3). Among the different $\lambda^6$-sulfanenitriles, the fluorothiazynes ($FAr_2S{\equiv}N$) have been found to be useful reagents to prepare a variety of $\lambda^6$-sulfanenitriles and other compounds with S–N bonds.[12] $\lambda^6$-Sulfanenitriles are constitutional isomers of sulfoximines (sulfoximides); for example, alkoxysulfanenitriles (**E**) are rather unstable and their exposure to an acid, base, or heat rapidly rearranges them to the corresponding sulfoximine (**K**) (Scheme 4).[13] The S–N bond length in sulfanenitriles is in the order of ~1.41–1.47 Å, indicating strong S–N interactions.[4] The S–N stretching frequencies for organic $\lambda^6$-sulfanenitriles have been found to be in the range of ~1250–1360 cm$^{-1}$. Sulfane-



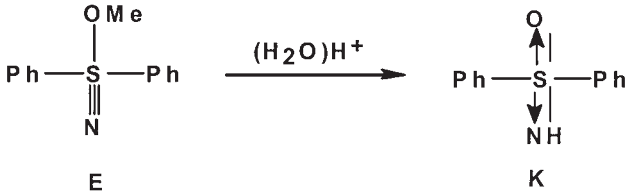
Scheme 1.

Scheme 2.



| Molecule | X | S≡N (Å) | Ref. |
|---|---|---|---|
| C | F | 1.444 | 5 |
| D | Ph | 1.462 | 5 |
| E | OMe | 1.441 | 7 |
| F | $NR_2$ | - | 8 |
| G | Me | - | 9 |
| H | $N{=}SPh_2$ | 1.467 | 10 |
| I | $N{=}SPh_2R$ | 1.456 | 10 |
| J | Heterocyclic | 1.470 | 11 |

Scheme 3.



Scheme 4.

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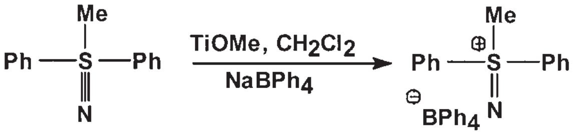
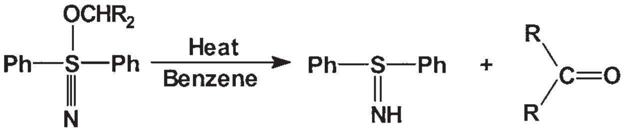


Scheme 5.



Scheme 6.

nitriles are highly basic,[8] and afford corresponding salts upon a treatment with acids; for example, the p$K_a$ values of the conjugate acid of triphenylthiazyne has been found to be 7.44.[6] Sulfanenitriles can be readily alkylated to give the corresponding iminosulfonium salts[9] (Scheme 5). Pyrolysis of amino-[8a] and alkoxysulfanenitriles[8b] afford sulfilimines (Scheme 6). Thus, thiazynes show rich chemistry, and are useful reagents in organosulfur chemistry.

Though sulfanenitriles have an acceptable Lewis structure, the hypervalency of sulfur should make these compounds high-energy systems. This is supported by the fact that the $\lambda^6$-sulfanenitriles become converted to sulfilimines or sulfoximines in many reactions. Even the $\equiv$N in sulfanenitriles has been shown to be very different from that in cyanides, R–C$\equiv$N,[14] for example, $\lambda^6$-sulfanenitriles have been shown to be highly basic compared to simple nitriles. The electronic structure of heterocyclic $\lambda^6$-sulfanenitrile (**J**) was described using B3LYP/6-31+G* calculations and Natural Bond Orbital analysis.[15] A strong donation of the electron density from the p$\pi$ of nitrogen to the $\sigma^*_{\text{S–C}}$ orbitals has been shown to be present in (**J**). The relative stability of systems with S$\equiv$N has been shown to be less than that of their isomers. For example, HS$\equiv$N has been shown to be less stable than S=NH by about 23.6 kcal/mol at the CCSD(T)/CC-pVQZ level. Also, the barrier for a 1,2-H shift in HNS has been predicted to be about 67.7 kcal/mol.[16] Similarly, FN$\equiv$S is more stable than FS$\equiv$N by about 26.2 kcal/mol with a barrier for a 1,2 shift in FNS of 59.6 kcal/mol at the MP2/6-31+G* level.[17] It is also important to know the complete electronic description of sulfanenitriles and the effect of substituents on the electronic distribution. In this paper we report the electronic structure of $\lambda^6$-sulfanenitrile $R_3S{\equiv}N$ and compare it with that of RS$\equiv$N and R(O)S$\equiv$N. We also report the variation in the S$\equiv$N interactions as a function of substituents on sulfur, and study the potential energy surface of $H_3SN$ to understand the relative stability. This work is a continuation of our studies on S–N interactions.[18]

## Methods of Calculation

Ab initio molecular orbital (MO)[19] and density functional calculations (DFT)[20] were carried out using the GAUSSIAN98W[21] package, the windows version of the GAUSSIAN98 suite of programs. Complete optimizations were been performed on $R_3S{\equiv}N$, **1–11** (Table 1) at the HF/6-31+G* and B3LYP/6-31+G* levels. For comparisons, calculations were carried out on RS$\equiv$N, **12–16** (Table 2) and on R(O)S$\equiv$N, **17–21** (Table 3). The potential energy surface of $H_3S{\equiv}N$ was probed at the HF/6-31+G*, B3LYP/6-31+G*, MP2(full)/6-31+G*, and G2 levels (Fig. 1).[22–26] The frequencies were computed analytically for all of the optimized species at the HF/6-31+G* level in order to characterize each stationary point as a minimum or a transition state, and to determine the zero-point vibrational energies (ZPE). The ZPE values obtained at the HF/6-31+G* level were scaled by a factor of 0.9153.[27] The atomic charges in all of the structures were obtained using the Natural Population Analysis (NPA) method within the Natural Bond Orbital (NBO) approach[28] using the B3LYP/6-31+G* geometries to understand the electron distribution in these molecules. A second-order energy analysis was carried out using the NBO method to understand the delocalizations present in these molecules at the B3LYP/6-31+G* level. In this paper, the geometric and energetic parameters obtained at B3LYP/6-31+G* are employed in the discussion, unless otherwise specifically mentioned.

Table 1. The S–N Bond Lengths (in Å), S–N Stretching Frequencies[a] (cm$^{-1}$), Atomic Charges (e), and Total Energies (a.u.) of Substituted Sulfanenitriles, $R^1R^2R^3S{\equiv}N$ at B3LYP/6-31+G* Level

| | $R^1$ | $R^2$ | $R^3$ | S–N bond length | S–N stretching frequencies | Atomic charges | | Total energies | NBO analysis | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | S | N | | Number of lone pairs on N | Number of S–N bonds |
| **1** | H | H | H | 1.482 | 1100 | 0.952 | −1.021 | −454.541733 | 3 | 1 |
| **2** | F | H | H | 1.462 | 1171 | 1.296 | −0.886 | −553.824240 | 3 | 1 |
| **3** | F | F | H | 1.442 | 1342 | 1.743 | −0.824 | −653.089514 | 2 | 2 |
| **4** | F | F | F | 1.434 | 1377 | 2.193 | −0.804 | −752.332189 | 1 | 3 |
| **5** | Cl | H | H | 1.478 | 1233 | 0.975 | −0.805 | −914.175589 | 3 | 1 |
| **6** | Cl | Cl | H | 1.465 | 1237 | 1.065 | −0.715 | −1373.789082 | 2 | 2 |
| **7** | Cl | Cl | Cl | 1.453 | 1284 | 1.153 | −0.682 | −1833.387471 | 1 | 3 |
| **8** | Me | H | H | 1.480 | 1246 | 1.146 | −1.031 | −493.876984 | 3 | 1 |
| **9** | Me | Me | H | 1.480 | 1200 | 1.319 | −1.048 | −533.206583 | 3 | 1 |
| **10** | Me | Me | Me | 1.480 | 1190 | 1.488 | −1.070 | −577.535901 | 3 | 1 |
| **11** | Ph | H | H | 1.481 | 1253 | 1.184 | −1.014 | −685.616724 | 3 | 1 |

a) Scaled by 0.9163.

Table 2. The S–N Bond Lengths (Å), S–N Stretching Frequencies[a)] ($cm^{-1}$), Atomic Charges (e), and Total Energies (a.u.) of RSN at B3LYP/6-31+G* Level

| | R | S–N bond length | S–N stretching frequencies | Atomic charges | | Total energy | NBO Analysis | |
|---|---|---|---|---|---|---|---|---|
| | | | | S | N | | Number of lone pairs on N | Number of S–N bonds |
| **12** | H | 1.516 | 1050 | 0.618 | −0.631 | −453.431143 | 2 | 2 |
| **13** | Me | 1.510 | 1069 | 0.821 | −0.672 | −492.762863 | 2 | 2 |
| **14** | Ph | 1.509 | 1070 | 0.859 | −0.691 | −684.508917 | 2 | 2 |
| **15** | Cl | 1.465 | 1236 | 0.905 | −0.556 | −913.074547 | 2 | 2 |
| **16** | F | 1.456 | 1270 | 1.171 | −0.629 | −552.719170 | 1 | 3 |

a) Scaled by 0.9163.

Table 3. The Important Bond Lengths (Å), Bond Angles (degrees), S–N Stretching Frequencies[a)] ($cm^{-1}$), and Total Energies (a.u.) of the Different Molecules at B3LYP/6-31+G* Level

| Molecule | S–N | S–O | N–S–O | S–N stretching[a)] frequency | Total energy | NBO analysis | |
|---|---|---|---|---|---|---|---|
| | | | | | | Number of lone pairs on N | Number of S–N bonds |
| H(O=)S≡N (**17**) | 1.466 | 1.476 | 139.5 | 1308 | −528.6211423 | 2 | 2 |
| Me(O=)S≡N (**18**) | 1.469 | 1.483 | 135.9 | 1285 | −567.9536899 | 2 | 2 |
| Ph(O=)S≡N (**19**) | 1.470 | 1.482 | 135.1 | 1278 | −739.6981938 | 2 | 2 |
| Cl(O=)S≡N (**20**) | 1.462 | 1.470 | 138.2 | 1307 | −988.2227424 | 2 | 2 |
| F(O=)S≡N (**21**) | 1.457 | 1.464 | 140.8 | 1334 | −627.8623350 | 1 | 3 |

a) Scaled by 0.9163.

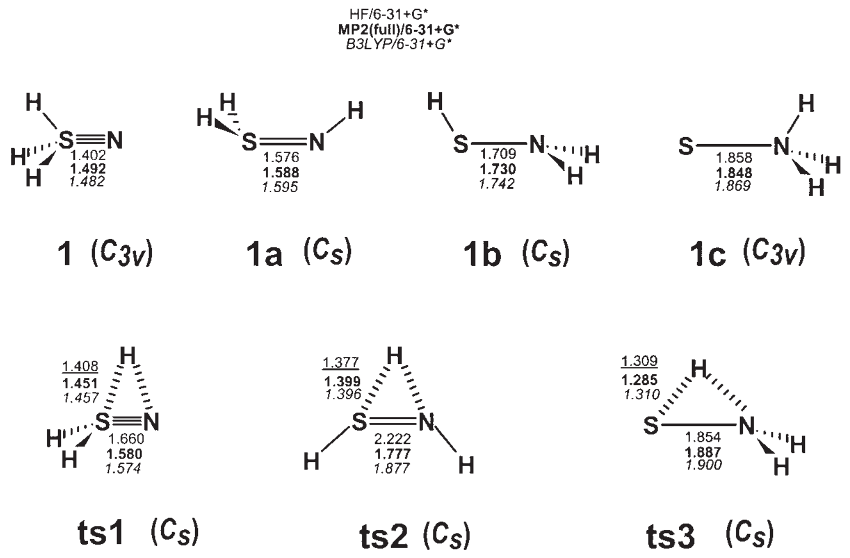


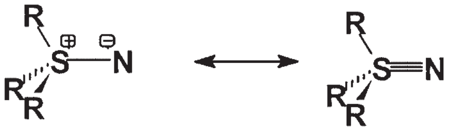
Fig. 1. The important geometrical parameters and the structure of sulfanenitrile **1**, and its isomers obtained by 1,2-H shift and their transition states.

## Results and Discussion

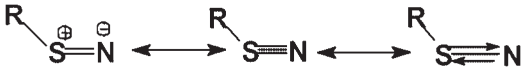
To understand the electronic structure of sulfanenitriles, complete optimizations were performed on $H_3S{\equiv}N$, **1** using the HF/6-31+G*, MP2(full)/6-31+G*, and B3LYP/6-31+G* levels. The estimated S–N bond lengths in **1** at the above levels are 1.402, 1.492, and 1.482 Å, respectively (Fig. 1). The estimated bond lengths at the electron-correlated levels are more closely comparable to the experimental observed bond lengths. Especially the S–N bond length, estimated at B3LYP/6-31G*, is relatively better than that at the MP2 level; hence, the B3LYP level data are reported in this paper. These short bond lengths indicate the presence of the S–N triple bond. **1** has an almost $C_{3v}$ symmetric structure with a N–S–H angle of ~123.5°.[29] Natural Population Analysis (NPA) shows that a large negative charge is present on nitrogen

(−1.021 e), and a strong positive charge is present on sulfur (0.952 e). The strong polarity between sulfur and nitrogen in **1** indicates that the ionic interactions are probably responsible for the short S–N bond length. Natural Bond Orbital (NBO) analysis suggested that only one bond is present across the sulfur and nitrogen, and three lone pairs of electrons are on N in **1**. This description of $H_3S{\equiv}N$ is much different from the expectations from an X-ray analysis of sulfanenitriles (Schemes 2 and 3).

Table 1 lists the important geometric and electronic parameters observed in $\lambda^6$-sulfanenitriles **1**–**11**. In all of the systems, the S–N bond lengths are in the order of ~1.43–1.48 Å, much smaller than in sulfenamides ($RS{-}NH_2$ (~1.70 Å)[18c]) and sulfilimines ($R_2S{=}NR$ (1.59 Å)[18h]). The S–N bond length in sulfanenitriles is highly sensitive to the substituents on sulfur. As the electronegativity of R increases, the S–N bond length decreases (Table 1). For example, the S–N bond length is about 1.480 Å in $Me_3SN$ **10** and is much shorter (1.434 Å) in $F_3SN$ **4**. The negative charge on nitrogen decreases with an increase in the electronegativity of R in $R_3S{\equiv}N$, suggesting a strong electron transfer from nitrogen to sulfur. NBO analysis shows a strong electron transfer (the second order delocalisation energy, $E^{(2)}$ for this interaction is 37.42 kcal/mol) from the $\pi$ orbitals of the S–N bond to the $\sigma^*$ orbitals of the S–F bond in **4**, which stabilizes the hypervalent state of sulfur.[30] NBO analysis on **4** at the B3LYP/6-31+G* level indicates that there are three S–N bonds and only one lone pair on nitrogen. The sulfur d-orbital occupancy is very low (0.15 e), but significant, in **4**. The two $\pi$ bonds in **4** are mainly due to the d$\pi$–p$\pi$ bond between sulfur and nitrogen, and the contribution from the 3d orbital of sulfur is 37%. NBO calculations on $Me_3S{\equiv}N$, **10** showed that there is no S–N triple bond. The electronic structure of **10** is similar to that of **1**. From an analysis of **1**–**11** it can be concluded that the S–N interactions in $\lambda^6$-sulfanenitriles consist of a resonance hybrid (Eq. 1). Highly electron withdrawing groups, like F, polarize the d orbitals on sulfur and increase the d$\pi$–p$\pi$ interactions between sulfur and nitrogen, but alkyl groups reduce such a possibility.


(1)

Sulfanenitriles with single substitution on sulfur (**12**–**16**) also show similar characteristics (Table 2), where the S–N bond length is in the range of 1.45–1.52 Å. The S–N bond length decreases, the S–N stretching frequency increases, and the negative charge on nitrogen decreases, with an increase in the electronegativity of R in RSN. NBO analysis on HSN shows that it has two S–N bonds ($\sigma$ and $\pi$) and two lone pairs on nitrogen, one of which shows a strong $n_N \rightarrow \sigma^*_{S-H}$ negative hyperconjugative interaction ($E^2$ is 57.54 kcal/mol). The d-orbital participation in the S–N $\pi$ bond is negligible. NBO analysis on FSN shows that there are three bonds (one $\sigma$ and two $\pi$) and only one lone pair. The d-orbital participation is much less (~3.7) in **12**. In the case of RSN, it should also be considered that a resonance hybrid between the given electronic arrangements (Eq. 2) is a more appropriate description compared to either of the structures.


(2)

The electronic structure of RS–N indicates that these systems can be treated as singlet nitrenes with –SR substitution. In a general nitrene (R–N), there are six electrons around nitrogen. RS substitution stabilizes the nitrenes by donating a lone pair of electrons from sulfur to nitrogen, and completes the octet arrangement around nitrogen in RS–N. When the R in RS–N is fluorine, the negative hyperconjugative interactions become triggered, leading to the partial triple bond between sulfur and nitrogen. This description of the RSN systems satisfies all of the observed reactions of RSN.[2e]

To quantitatively estimate the Lewis basic character of sulfanenitriles, studies have been carried out on the protonation and complexation with $BH_3$ of **1**, **4**, **12**, **16**, and **17** (Tables 4 and 5). The protonation energies of $H_3S{\equiv}N$ and $F_3S{\equiv}N$, respectively, are 223.7 and 168.7 kcal/mol at the B3LYP/6-31+G* level. This clearly indicates that $H_3S{\equiv}N$ is a much stronger base compared to that of $F_3S{\equiv}N$. Similarly, the protonation energy of $HS{\equiv}N$ (196.4 kcal/mol) is much stronger than that of $FS{\equiv}N$ (165.3 kcal/mol at B3LYP/6-31+G*). This data indicates that substitution by electronegative groups on sulfur decreases the Lewis-basic character of sulfanenitriles. The protonation energy of $H_3S{\equiv}N$ and $HS{\equiv}N$ are much higher than that of $HC{\equiv}N$ (172.7 kcal/mol at the B3LYP/6-31+G* level[18h] and 170.4 kcal/mol experimental[31]), which has been recognized as being one of the very weak Lewis bases.[32] The protonation energy of **1** indicates that it is a much stronger Lewis base than $H_2C{=}NH$ and $NH_3$ and close to that of $MeNH_2$, whose protonation energies at B3LYP/6-31+G* are 213.9, 211.8, and 222.5 kcal/mol, re-

Table 4. The Important Bond Distances (Å), Bond Angles (in degrees), Total Energy, and Stabilization Energy due to Protonation at B3LYP/6-31+G* Level

| Molecule | S–N | N–H | S–N–H | Total energy[a)] | Energy[b)] |
|---|---|---|---|---|---|
| $H_3S{\equiv}NH^+$ | 1.529 | 1.025 | 116.0 | −454.898267 | 223.7 |
| $F_3S{\equiv}NH^+$ | 1.441 | 1.023 | 132.1 | −752.601106 | 168.7 |
| $HS{\equiv}NH^+$ | 1.536 | 1.034 | 119.3 | −453.744242 | 196.4 |
| $FS{\equiv}NH^+$ | 1.488 | 1.032 | 122.6 | −552.982749 | 165.3 |
| $H(O)S{\equiv}NH^+$ | 1.496 | 1.031 | 121.8 | −528.918013 | 147.5 |
| $HC{\equiv}NH^+$ | 1.139[c)] | 1.018 | 179.2[d)] | −93.703906 | 172.6 |

a) Absolute energy in atomic units. b) Stabilization energy due to protonation (in kcal/mol). c) N–C. d) C–N–H.

Table 5. The Important Bond Distances (Å), Bond Angles (in degrees), Total Energy, and Stabilization Energy due to Complexation with $BH_3$ at B3LYP/6-31+G* Level

| Molecule | S–N | N–B | B–H | S–N–B | Total energy[a)] | Energy[b)] |
|---|---|---|---|---|---|---|
| $H_3S{\equiv}NBH_3$ (**22**) | 1.504 | 1.661 | 1.221 | 102.5 | −481.194765 | 23.91 |
| $F_3S{\equiv}NBH_3$ (**23**) | 1.410 | 1.672 | 1.205 | 179.9 | −778.957288 | 6.30 |
| $HS{\equiv}NBH_3$(**24**) | 1.578 | 1.463 | 1.236 | 125.5 | −480.114230 | 42.76 |
| $FS{\equiv}NBH_3$(**25**) | 1.472 | 1.485 | 1.227 | 158.8 | −579.373118 | 24.40 |
| $H(O)S{\equiv}NBH_3$(**26**) | 1.506 | 1.567 | 1.215 | 115.3 | −555.266769 | 19.25 |
| $HC{\equiv}NBH_3$(**27**) | 1.150[c)] | 1.070 | 1.207 | 179.4[d)] | −120.074964 | 19.71 |

a) Absolute energy in atomic units. b) Stabilization energy due to the complexation with $BH_3$ (in kcal/mol). c) N–C. d) C–N–B.

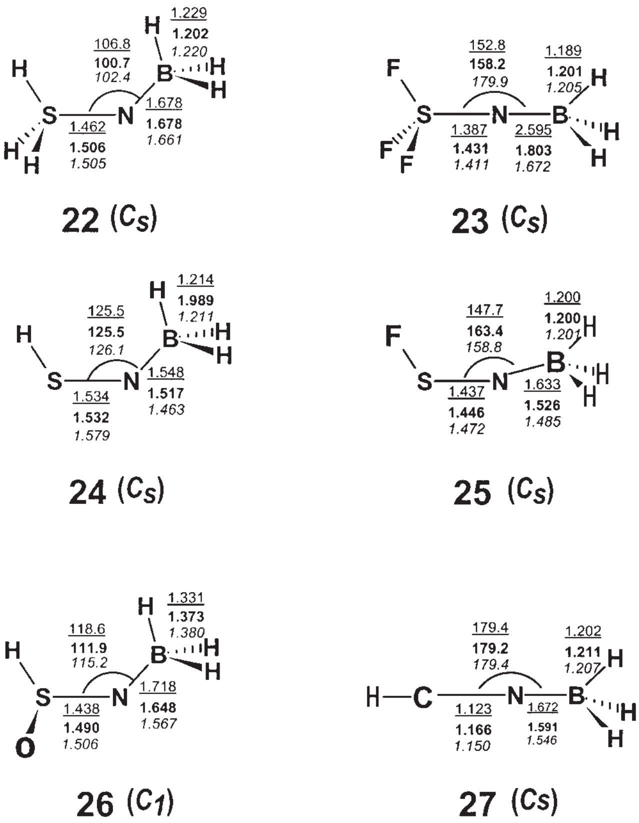


Fig. 2. The important geometrical parameters of the complexes of **1**, **4**, **12**, **16**, **17**, and **HCN** with $BH_3$ at various levels HF/6-31+G*, **MP2(Full)/6-31+G***, and *B3LYP/6-31+G** levels.

spectively.[18h] The protonation energy of $H_3S{\equiv}N$ is slightly less than that $H_2S{=}NH$ (234.8 kcal/mol at the B3LYP/6-31+G* level).[33]

Figure 2 shows the structural parameters of sulfanenitrile–$BH_3$ complexes at the HF/6-31+G*, B3LYP/6-31+G*, and MP2(full)/6-31+G* levels. The N–B bond length in **22** is 1.661 at the B3LYP/6-31+G* level, indicating a coordination-type interaction. The S–N–B angle is 102.4° at the same level, indicating that the lone pair of electrons in $H_3SN$ are in an $sp^3$ orbital, rather than an sp orbital. The energy of stabilization due to the formation of **22** is 23.9 kcal/mol at the B3LYP/6-31+G* level (Table 5). In $F_3SN$–$BH_3$, **23**, the coordination bond is much weaker than that in **22**. This is indicated by an increase in the N–B bond length (by 0.011 Å) and the S–N–B bond angle (by 77.5°), and a decrease in the stabilization energy (by 17.6 kcal/mol) at the B3LYP/6-31+G* level. These changes are also accompanied by a decrease in the S–N bond length in **23** (1.411 Å) relative to that in **22** (1.505 Å). The increase in the S–N–B angle in **23** (179.9°) relative to that in **22** (102.4°) indicates that the directionality of the nitrogen lone pair in $H_3SN$ is different from the directionality of the nitrogen lone pair in $F_3SN$. A similar trend in the S–N–B bond angle increase is observed between **24** (125.5°) and **25** (158.8°). The stabilization energy due to the formation of **24** (42.7 kcal/mol) is much stronger than that of **25** (24.4 kcal/mol), supporting the observation that electronegative substituents decrease the Lewis basicity of sulfanenitriles. The Lewis basicity values of **1** and **12** are much stronger than that of $HC{\equiv}N$ because the energy of stabilization values due to complexation with $BH_3$ are 23.9, 42.7, and 19.7 kcal/mol at the B3LYP/6-31+G* level.

Tables 4 and 5 list the observed trends in protonation and complexation with $BH_3$ for **1**, **4**, **12**, **16**, and **17**. These observed trends are similar between these two processes when the comparison is made between $H_3SN$ vs $F_3SN$ and HSN vs FSN pairs, as discussed above. However, they are not comparable when we compare the $H_3SN$ vs HSN and $F_3SN$ vs FSN pairs. These deviations are mainly attributable to the differences in the charge distributions in protonated and $BH_3$ complexed systems. In the protonated system the positive charge is strongly delocalised, and hence the protonation energy may not be taken as a measure of the Lewis basicity of sulfanenitriles alone. For example, $H_3SNH^+$ may be treated as a protonated species of sulfilimine ($H_2SNH$), rather than the protonated product of ($H_3SN$). On the other hand, the $BH_3$ complexed systems do not suffer from this dichotomy. Hence, the trends in the complexation energies noted in Table 5 are more representative trends for estimating the of Lewis basic character if sulfanenitriles.

Thus, the study on protonation and complexation with $BH_3$ clearly suggests that the electronic structures of $H_3SN$ and $F_3SN$ (**1**, **4**) are on the two extremes of the spectrum of the electronic structure described in Eq. 1, $H_3SN$ preferring an $S^+$–$N^-$ arrangement and $F_3SN$ preferring $S{\equiv}N$ type arrangement. The electronic structure of $Me_3SN$, $Me_2HSN$, $MeH_2SN$, and $PhH_2SN$ are all similar to that of $H_3SN$, indicating that alkyl or phenyl substituents on sulfur prefer the $S^+$–$N^-$ type of electronic distribution in $\lambda^6$-sulfanenitriles. This is supported by the fact that $R_3SN$ are found to be more basic compared to $F_3SN$, where R = alkyl.[4]

Table 6. The Relative Energies (in kcal/mol) of the Various $H_3SN$ and Its Various Isomers Obtained by 1,2-H Shift at the Various Different Levels

| Method | ΔE | | | Barrier for 1,2-H shift | | |
|---|---|---|---|---|---|---|
| | **1 − 1a** | **1a − 1b** | **1b − 1c** | **1 − 1a** | **1a − 1b** | **1b − 1c** |
| HF/6-31+G* | 77.79 | 58.69 | 8.52 | 126.82 | 97.21 | 57.76 |
| MP2(full)/6-31+G* | 61.56 | 52.12 | 11.82 | 113.05 | 88.77 | 45.51 |
| B3LYP/6-31+G* | 64.29 | 48.86 | 11.20 | 110.30 | 83.30 | 43.37 |
| G2 | 59.75 | 40.98 | 16.83 | 99.78 | 73.95 | 42.94 |
| G2MP2 | 59.16 | 40.00 | 17.74 | 98.93 | 73.11 | 43.18 |

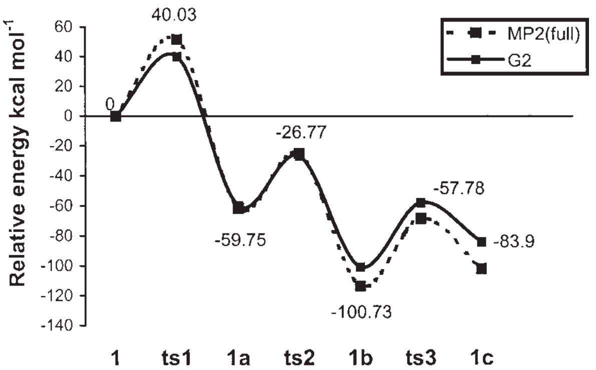


Fig. 3. The potential energy diagram of sulfanenitrile **1** and other conformers obtained by 1,2-H shift, the G2 value are included in the figure.

We also became interested in exploring the possibility of S–N triple bonded systems other than RSN and $R_3SN$. One such possibility seems to be strongly favorable, i.e. R(O=)S≡N. Table 3 gives the geometric parameters, S–N stretching frequencies, and the total energies of H(O=)S≡N (**17**), Me(O=)S≡N (**18**), Ph(O=)S≡N (**19**), Cl(O=)S≡N (**20**), and F(O=)S≡N (**21**). All of the systems are stable minima on the respective potential energy surfaces. The S–N bond lengths in **17**–**21** are in the order of 1.46–1.47 Å at the B3LYP/6-31+G* level. The S≡N bond lengths have shortened in R(O)S≡N relative to RS≡N, (R = H, Me, Ph); for example, the S–N bond length in **18** (1.469 Å) is shorter than in **13** (1.510 Å). NBO analysis of Me(O)S≡N shows that there is an S–N sigma bond, an S–N ($p\pi$–$p\pi$) bond an S–N anomeric $\pi$ bond ($n_N \rightarrow \sigma^*_{\text{S–O}}$ negative hyperconjugation) bonds in this system. The complexation energy due to the formation of a H(O)S≡N–$BH_3$ complex is 19.25 kcal/mol, which is less than that of $H_3S$≡N (23.91) and HSN (42.76 kcal/mol). This indicates a weaker Lewis basic character of R(O)S≡N systems relative to $R_3SN$ and RSN. The above discussion indicates that the R(O)S≡N are stable sulfanenitriles with an electronic structure similar to that of $R_3S$≡N and RSN, but less basic than both. It is worth attempting to synthesize them.

On the potential energy surface of $H_3S$≡N, **1** has been found to be least stable (Fig. 3, Table 6). Calculations at all levels suggest that the isomers of **1** are more stable than **1**. A 1,2-H shift in **1** would give sulfilimine **1a**, which is about 60 kcal/mol more stable than **1** at the G2 level. An additional 1,2-H shift would give isomer **1b** (sulfenamide), which is about 100 kcal/mol (G2) more stable than **1**. A 1,2-H shift of the third hydrogen would give $H_3N$–S (**1c**), which is about 84 kcal/mol (G2) more stable than **1**. The S–N bond length in these systems increases in the order **1** < **1a** < **1b** < **1c**, along the expected lines of bond order decrease. Detailed studies on sulfilimine (**1a**) and sulfenamide (**1b**) have been reported earlier.[18] In this paper we consider the most stable arrangements of **1a** (*syn*) and **1b** (*anti*) for discussion. **1a** has a partial double-bond character (S–N $\sigma$ bond and partial $d\pi$–$p\pi$ bond). **1b** has a regular S–N $\sigma$ bond with additional anomeric partial $\pi$ interaction (negative hyperconjugative interactions). **1c** has a highly elongated S–N bond length (~1.85 Å) and the S–N interactions should be considered as a Lewis base ($NH_3$) → Lewis acid (S) coordinating interactions as in *N*-sulfide. NBO analysis shows that sulfur atom in **1c** has three lone pairs with a negative charge of 1.995 e. The lower energy of **1c** over **1** indicates that the hypervalent arrangement in **1** is much more strained in relation to that in **1c**. The 1,2-H shift in **1** to give **1a** goes through the transition state (**TS1**) with a barrier of 40.03 kcal/mol at the G2 level; for the backward 1,2-H shift the energy barrier is 99.78 kcal/mol at the same level. The high-energy barriers prevent **1** → **1a** conversion, but even under mild reaction conditions it should be possible to convert sulfanenitriles to sulfilimines; through ionic paths, the reactions shown in Schemes 4 and 6 are examples of this phenomenon. The 1,2-H shift in **1a** to give **1b** is also a high-energy process with a barrier of 32.98 kcal/mol at the G2 level and should be thermodynamically forbidden. Conversion from **1b** to **1c** via the transition state **TS3** is also a thermodynamically forbidden path with a barrier of about ~43 kcal/mol at the G2 level. A potential energy surface search indicates that sulfanenitriles are in an electronically unstable arrangement, and are highly energetic species; their conversion to more stable isomers is thermodynamically forbidden, but even mild reaction conditions are sufficient to convert them to more stable isomers.

## Conclusions

The electronic structure of $\lambda^6$-sulfanenitriles has been explored using ab initio MO and DFT methods. The electronic structures of $R_3S$≡N has been shown to be a resonance hybrid of the $R_3S^{\oplus}$–$N^{\ominus}$ arrangement, and the $R_3S$≡N arrangement the balance lies towards $R_3S^{\oplus}$–$N^{\ominus}$ when R is alkyl and aryl. This electronic arrangement helps in the stronger Lewis basity of $\lambda^6$-sulfanenitriles.

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