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Communication

Synthesis and Properties of $Ph_2S(=N-(Ph_2)S\equiv N)_2$

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A new type of λ^6-sulfanenitrile with an SN triple bond at both ends, $Ph_2S(=N-(Ph_2)S\equiv N)_2$ (**5**), was prepared in excellent yield from the one-pot synthesis of diphenylsulfimide (Ph_2SNH) with fluoro(diphenyl)-λ^6-sulfanenitrile ($Ph_2FS\equiv N$) in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene. Its molecular structure was determined by X-ray crystallographic analysis. Compound **5** reacted further with methyl triflate and trifluoromethanesulfonic anhydride to afford the corresponding bis-N-methylated and -N-sulfonated compounds.

Inorganic rings and chains based on skeletons of nitrogen, sulfur, and/or heteroatoms have attracted considerable attention because of their structures and reactivities. They also offer potential access to new materials with interesting and useful properties.[1,2] Recently, we have described the synthesis of $Ph_2(X)S=N-(Ph_2)S\equiv N$ [X = LP (**3**), HN= (**4**), and O=] and established that fluoro(diphenyl)-λ^6-sulfanenitrile ($Ph_2FS\equiv N$) (**2**) is a potentially useful building block in S−N−S chemistry.[3] Moreover, the crystal and electronic structures of **3** and **4** were elucidated by X-ray crystallographic analysis and quantum chemical calculations, respectively.[4] In a further extension of these studies, we have examined the reaction of **2** with **3**. Surprisingly, it was found that the reaction gives a new type of λ^6-sulfanenitrile with an SN triple bond at both ends, $Ph_2S(=N-(Ph_2)S\equiv N)_2$ (**5**). We also have reported that the reaction of diphenylsulfimide (Ph_2SNH, **1**) with **2** affords the corresponding **3**.[3a] These results prompted us to explore the possibility that **5** could be produced in one-pot synthesis via reaction of **1** with a large excess of **2**. In this Communication, we report a high-yielding and efficient method for the preparation and crystal structure determination of the title compound, as well as reactivities of the terminal nitrogens.

The reaction of **1** with an excess amount (5 equiv) of **2** in CH_3CN at 50 °C for 48 h, followed by simple acid extraction to remove side products and treatment with ion-exchange resin IRA-410 (OH^- form), afforded **5** in 54% yield after purification by recrystallization from CH_2Cl_2−ether.[5] The side products were mainly diphenylsulfoximide ($Ph_2OS=NH$)[6] and diphenylsulfoxide ($Ph_2S=O$). The formation of **5** is obviously a multistep sequence (Scheme 1). The

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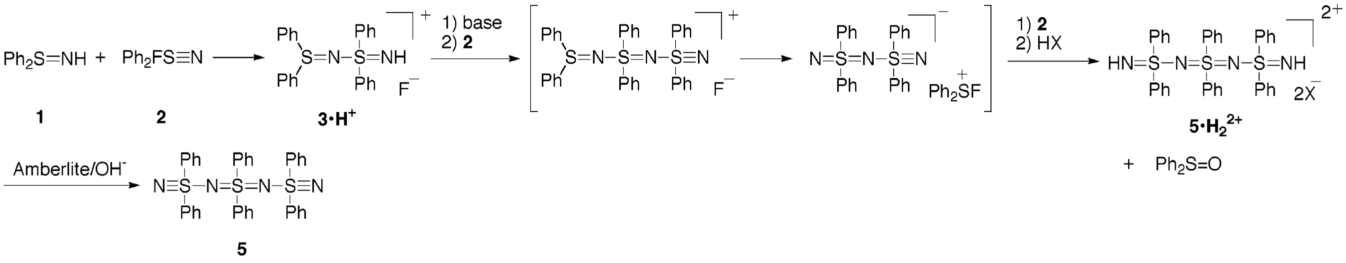
(5) A solution of $Ph_2SNH{\cdot}H_2O$ (**1**; 0.219 g, 1.0 mmol), Ph_2FSN (1.095 g, 5.0 mmol), and DBU (230 μL, ca. 1.5 mmol) in 1.0 mL of CH_3CN at 50 °C was stirred for 18 h. The reaction mixture was cooled in an ice bath and then dissolved in 10 mL of 3% HCl, and the aqueous solution was extracted with benzene (10 × 5 mL) to remove side products such as Ph_2OSNH and Ph_2SO. To the aqueous layer was added saturated $NaClO_4$(aq) (0.5 mL). The mixture was stirred for 30 min and the resulting white precipitate filtered off and washed with water to provide $[Ph_2S(=N-(Ph_2)S=NH)_2][2ClO_4]$ ($\mathbf{5}{\cdot}H_2^{2+}$) in almost pure quantitative yield. If necessary, the product was purified by recrystallization in CH_3CN−ether to give pure $\mathbf{5}{\cdot}H_2^{2+}$ as crystals. A solution of the residue $\mathbf{5}{\cdot}H_2^{2+}$ in methanol was passed through a column of Amberlite IRA-410 ion-exchange resin (strong base, OH^- form) followed by evaporation of the solvent to give **5** (dihydrate) in almost quantitative yield (0.631 g, 97%, relative to **1**). Further purification by recrystallization from CH_2Cl_2−ether produced dihydrated **5** as crystals. For $\mathbf{5}{\cdot}H_2^{2+}$: mp 228−229 °C (dec); ^1H NMR (400 MHz, CD_3CN) δ 7.53−7.62 (m, 12H), 7.75 (t, $J = 7.5$ Hz, 4H), 7.79 (t, $J = 7.5$ Hz, 2H), 7.89−7.91 (m, 4H), 7.93−7.96 (m, 8H); ^{13}C NMR (100 MHz, CD_3CN) δ 128.6, 129.9, 131.6, 131.9, 136.9, 137.9, 138.4; IR (KBr) 3247, 1031, 992 cm^{-1}; Anal. Calcd for $C_{36}H_{32}Cl_2N_4O_4S_3$: C, 53.00; H, 3.95; N, 6.87. Found: C, 53.07; H, 3.97; N, 6.87. For **5**: mp 139−140 °C (dec, dihydrate); ^1H NMR (400 MHz, $CDCl_3$) δ 7.23−7.30 (m, 12H), 7.36 (t, $J = 7.90$ Hz, 4H), 7.49 (t, $J = 7.42$ Hz, 4H), 7.86−7.91 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 126.7, 128.4, 128.6, 129.0, 130.6, 133.2, 138.7, 150.1; IR (KBr) 3373, 1313, 1170, 1157, 1045, 1017, 991 cm^{-1}. Anal. Calcd for $C_{36}H_{34}N_4O_2S_3$: C, 66.43; H, 5.27; N, 8.61. Found: C, 66.25; H, 5.24; N, 8.60.

10.1021/ic051523g CCC: $30.25

Scheme 1



key step seems to involve NH deprotonation of $3{\cdot}H^+$ followed by intermediary formation of $[Ph_2S{=}N{-}(Ph_2)S{=}N{-}(Ph_2)S{\equiv}N][F]$, which undergoes subsequently rapid decomposition, leading to $[Ph_2FS][Ph_2(N{\equiv})S{=}N{-}(Ph_2)S{\equiv}N]$. This intermediate further reacted with **2** and H_2O to give the corresponding **5** and $Ph_2S{=}O$. Thus, the addition of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU; ca. 1.1 equiv relative to **1**) as a base to avoid protonation of **1** and/or **3** shortened the reaction times and improved the yield of $Ph_2S({=}N{-}(Ph_2)S{\equiv}N)_2$ (**5**) to 97% yield.

The crystal structure of **5** was determined by X-ray crystallographic analysis.[7] The crystal lattice consists of **5** and water molecules. The distance between the oxygen and nitrogen atoms is 2.928(3) Å ($d_{O1}{\cdots}N1$). This value is very close to the sum of the van der Waals radii (2.94 Å) of two elements[8] and is indicative of the OH···N hydrogen bond. The X-ray structure of **5** indicates the following characteristic properties (Figure 1). **5** has an S-shaped C_s structure. The S(1)−N(1) bond length in **5** is 1.457(2) Å, which is very close to the SN triple bond length [1.435(2)−1.462 Å] of λ^6-sulfanenitriles.[4,9] The bridgings S(1)−N(2) and S(2)−N(2) bond lengths are 1.656(2) and 1.550(2) Å, respectively. These values lie between those of single and double bonds and are close to those of **3** and **4**.[4] The geometry around S(1) in **5** is a slightly distorted tetrahedral structure with two SN and two SC bonds. The bond angles of N(1)−S(1)−N(2) [123.47(10)°] and N1−S1−C [average 116.4(1)°] are larger but N(2)−S(1)−C [average 98.38(10)°] and C(1)−S(1)−C(2) [99.56(10)°] are smaller than the tetrahedral angle of 109.5°. The geometry around S(2) is also a slightly distorted tetrahedral structure with bond angles varying from 101.44(10)° to 121.8(2)°. The S(1)−N(2)−S(2) bond angle of 121.9(1)° is indicative of sp^2 hybridization at the N(2) atom.

To explore the scope of the functionalization of terminal thiazyl nitrogens ($S^{VI}{\equiv}N$) in **5**, the reaction of **5** with methyl triflate (TfOMe) was first examined (Scheme 2). When **5** reacted with 1 equiv of TfOMe in CH_2Cl_2 at 0 °C for 1 h, the corresponding $[Ph_2(N{\equiv})S{-}N{=}(Ph_2)S{=}N{-}(Ph_2)S{=}NMe][TfO]$ (**6**) was obtained in 98% yield.[10] Interestingly, the reaction of **5** with excess of TfOMe under the same conditions as those above led to a straightforward formation of $[Ph_2S({=}N{-}(Ph_2)S{=}NMe)_2][2TfO]$ (**7**) in 98% yield.[11] This result indicates that the methylation of pre-

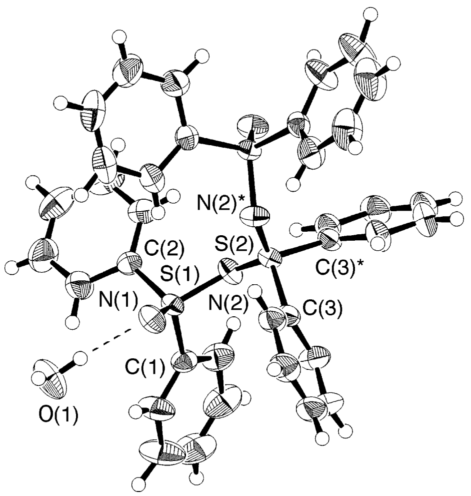
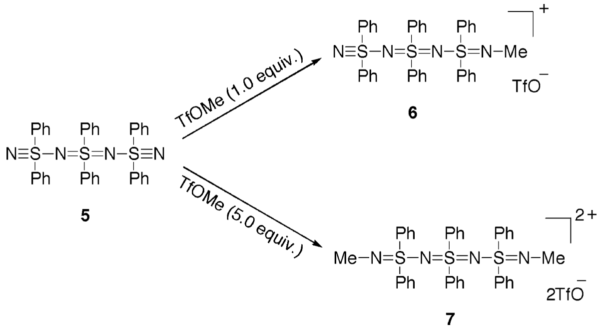


Figure 1. ORTEP drawing of **5** [50% probability thermal ellipsoids for all non-hydrogen atoms; the water molecule ($H_2O(1)^*$) is omitted for clarity; the hydrogen bond is dashed]. Selected bond lenghs [Å] and angles [deg]: S(1)−N(1) 1.457(2), S(1)−N(2) 1.656(2), S(1)−C(1) 1.808(2), S(1)−C(2) 1.804(2), S(2)−N(2) 1.550(2), S(2)−C(3) 1.781(2); N(1)−S(1)−N(2) 123.47(10), N(1)−S(1)−C(1) 115.8(1), N(1)−S(1)−C(2) 117.0(1), N(2)−S(1)−C(1) 98.73(10), N(2)−S(1)−C(2) 98.03(10), C(1)−S(1)−C(2) 99.56(10), N(2)−S(2)−N(2)* 121.8(2), N(2)−S(2)−C(3) 112.94(10), N(2)−S(2)−C(3)* 101.44(10), C(3)−S(2)−C(3)* 105.6(1).

Scheme 2



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(6) $Ph_2OS{=}NH$ was easily formed by the hydrolysis of $Ph_2FS{\equiv}N$ (**2**) in acidic conditions: Dong, T.; Fujii, T.; Murotani, S.; Ono, S.; Morita, H.; Shimasaki, C.; Yoshimura, T. *Bull. Chem. Soc. Jpn*. **2001**, *74*, 945−954.

(7) Crystal data for **5**, $C_{36}H_{34}N_4O_2S_3$, with Mo Kα (λ = 0.710 69 Å) radiation: MW = 650.87, colorless plate, monoclinic, a = 26.830(2) Å, b = 8.968(2) Å, c = 17.906(2) Å, β = 128.616(4)°, V = 3366.6(8) $Å^3$, T = 296 K, space group $C2/c$ (No. 15), Z = 4, μ(Mo Kα) = 2.58 cm^{-1}, 5304 reflections measured, 4910 unique (R_{int} = 0.015), R = 0.040, R_w = 0.053, GOF = 1.20.

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formed monocation derivative **6** is allowed despite the poor nucleophilic character of the terminal thiazyl nitrogen ($S^{VI}\equiv N$) because of the strongly electron-withdrawing cationic sulfur atom. Further, the reaction of **5** with a 2.2 equimolar amount of trifluoromethanesulfonic anhydride (Tf_2O) in CH_2Cl_2 at ambient temperature for 1 h gave the corresponding bis-N-sulfonated compound [$Ph_2S({=}N{-}(Ph_2)S{=}NTf)_2$][2TfO] (**8**) in 70%.[12]

In summary, we have demonstrated the formation of a new type of λ^6-sulfanenitrile **5** bearing the $N\equiv S^{VI}{-}N{=}S^{VI}{=}N{-}S^{VI}\equiv N$ backbone, the molecular structure of which has been determined. In addition, the nucleophilic character of both terminal nitrogen atoms in **5** can be recognized in the alkylation and sulfonation to yield the corresponding bis-iminosulfonium salts. Our current efforts include application of reactivities of the terminal nitrogen in **5** to the preparation of macromolecules.

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Supporting Information Available: Tables of crystallographic data of **5** (PDF and CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(10) For **6**: To a well-stirred solution of **5** (325 mg, 0.5 mmol) in CH_2Cl_2 (5 mL) at 0 °C was added TfOMe (57 μL, 0.5 mmol). After stirring for 1 h, ether was added and a white precipitate was produced. The precipitate was filtered and washed with ether to give **6** (381 mg) in 98% yield. Further purification by recrystallization from CH_2Cl_2−ether produced **6** as colorless crystals: mp 172−173 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.67 (s, 3H), 7.33−7.43 (m, 6H), 7.45−7.53 (m, 8H), 7.59−7.65 (m, 4H), 7.71−7.75 (m, 8H), 8.00 (d, $J = 7.6$ Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 31.1, 121.0 (q, $J_{CF} = 319$ Hz), 126.1, 128.0, 128.6, 128.8, 130.0, 130.2, 131.5, 134.4, 134.6, 134.9, 135.3, 148.7; IR (KBr) 1315, 1278, 1226, 1146, 1078, 1033, 979 cm^{-1}. Anal. Calcd for $C_{38}H_{33}F_3N_4O_3S_4$: C, 58.59; H, 4.27; N, 7.19. Found: C, 58.68; H, 4.33; N, 7.22.

(11) For **7**: To a well-stirred solution of **5** (325 mg, 0.5 mmol) in CH_2Cl_2 (5 mL) at 0 °C was added TfOMe (283 μL, 2.5 mmol). After stirring for 1 h, ether was added and a white precipitate was produced. The precipitate was filtered and washed with ether to give **7** (464 mg) in 98% yield. Further purification by recrystallization from CH_3CN−ether produced **7** as a white powder: mp 193−194 °C; ^{1}H NMR (400 MHz, CD_3CN) δ 2.63 (s, 6H), 7.58−7.65 (m, 12H), 7.77−7.82 (m, 12H), 7.87−7.93 (m, 6H); ^{13}C NMR (100 MHz, CD_3CN) δ 32.26, 121.95 (q, $J_{CF} = 318$ Hz), 129.31, 130.17, 131.56, 131.87, 131.93, 135.20, 136.96, 138.77; IR (KBr) 1262, 1226, 1162, 1070, 1031, 989 cm^{-1}. Anal. Calcd for $C_{40}H_{36}F_6N_4O_6S_5$: C, 50.94; H, 3.85; N, 5.94. Found: C, 50.87; H, 3.80; N, 6.02.

(12) Compound **8** is hygroscopic and was therefore isolated by converting it into the corresponding perchlorate **8′**. For **8′**: To a well-stirred solution of **5** (325 mg, 0.5 mmol) in CH_2Cl_2 (5 mL) at ambient temperature was added Tf_2O (185 μL, 1.1 mmol). After stirring for 1 h, the solvent was removed under reduced pressure. The residue was dissolved in MeOH (5 mL), and a saturated $NaClO_4$(aq) (0.25 mL) was added and then extracted with CH_2Cl_2. After removal of the solvent, the residue was purified by crystallization from CH_3CN−ether to afford [$Ph_2S({=}N{-}(Ph_2)S{=}NTf)_2$][$2ClO_4$] (**8′**; 378 mg) in 70% yield: mp 223−224 °C; ^{1}H NMR (400 MHz, CD_3CN) δ 7.68 (t, $J = 8.2$ Hz, 4H), 7.77 (t, $J = 8.2$ Hz, 8H), 7.91−7.97 (m, 12H), 8.01−8.08 (m, 12H); ^{13}C NMR (100 MHz, CD_3CN) δ 119.5 (q, $J_{CF} = 319$ Hz), 125.5, 129.9, 130.6, 131.4, 132.7, 133.0, 140.2, 141.7; IR (KBr) 1377, 1215, 1140, 1085, 1064, 1013, 989 cm^{-1}. Anal. Calcd for $C_{38}H_{30}Cl_2F_6N_4O_{12}S_5$: C, 42.26; H, 2.80; N, 5.19. Found: C, 42.08; H, 2.75; N, 5.17.