



# First preparation and crystal structure of heterocyclic $\lambda^6$ -sulfanenitrile, 2,2'-biphenylene(phenyl)- $\lambda^6$ -sulfanenitrile

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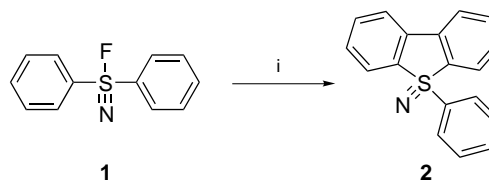
**Abstract**—The first heterocyclic  $\lambda^6$ -sulfanenitrile, 2,2'-biphenylene(phenyl)- $\lambda^6$ -sulfanenitrile is prepared and its molecular and electronic structures are determined by X-ray crystallographic analysis and quantum chemical calculations, respectively. © 2001 Elsevier Science Ltd. All rights reserved.

The chemistry of  $\lambda^6$ -sulfanenitrile bearing an SN triple bond shows some interesting and fascinating features. A number of reports on the preparation and reactions of  $F_3S\equiv N$  and its derivatives have appeared<sup>1,2</sup> but to date there has been no report on the preparation of a heterocyclic compound containing a thiazyl group ( $S\equiv N$ ) in the ring system. In view of its chemical properties and structural features, investigation of this heterocyclic compound has posed an interesting challenge. Recently, we prepared fluoro(diphenyl)- $\lambda^6$ -sulfanenitrile (**1**) and further reported the formation of alkoxy-, amino-, imido-, and phenyl- $\lambda^6$ -sulfanenitriles from the reaction of **1**.<sup>2</sup> These results prompted us to examine the reaction of **1** with 2,2'-dilithobiphenyl which might lead to the isolation of 2,2'-biphenylene(phenyl)- $\lambda^6$ -sulfanenitrile (**2**). Herein, we describe the first preparation and crystal structure determination of the title compound **2**.

The reaction of fluoro- $\lambda^6$ -sulfanenitrile **1** with 1.1 equiv. amount of 2,2'-dilithobiphenyl in anhydrous THF under an argon atmosphere at  $-78^\circ\text{C}$  gave a novel heterocyclic  $\lambda^6$ -sulfanenitrile **2** (Scheme 1). Compound **2** was isolated by silica-gel column chromatography and recrystallized from  $\text{CH}_2\text{Cl}_2$ -hexane in 32% yield.<sup>3</sup>  $^1\text{H}$  and  $^{13}\text{C}$  NMR, IR, and mass spectral data and elemental analysis were consistent with the structure of hydrated **2** ( $2 \cdot n\text{H}_2\text{O}$ ), and elemental analysis of the

dehydrate product by heating at  $60^\circ\text{C}$  under vacuum conditions also gave satisfactory results. Examination of the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of compound **2** reveals that the two phenyl rings of the biphenylene group are in equivalent states. The IR absorption of **2** due to the SN stretching band is present at  $1261\text{ cm}^{-1}$ , which is similar to that of triphenyl- $\lambda^6$ -sulfanenitrile ( $1267\text{ cm}^{-1}$ ).<sup>2c</sup>

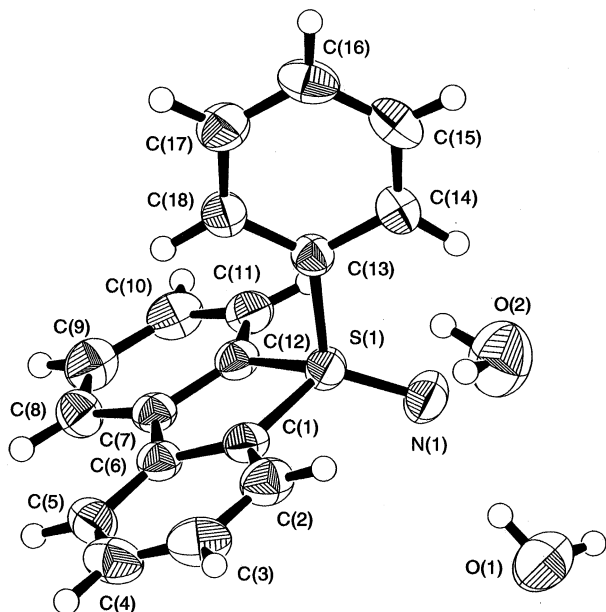
The crystal structure of **2** was determined by X-ray crystallographic analysis.<sup>4</sup> The crystal lattice consists of  $\lambda^6$ -sulfanenitriles **2** and two types of water molecules. The distances between the oxygen and nitrogen atoms are  $2.865(4)$  ( $d_{\text{O1}\cdots\text{N1}}$ ) and  $2.985(3)$  Å ( $d_{\text{O2}\cdots\text{N1}}$ ), respectively. These values are very close to the sum of the van der Waals radii ( $2.94$  Å) of the two elements<sup>5</sup> and are indicative of the  $\text{OH}\cdots\text{N}$  hydrogen bond. The X-ray structure of **2** indicates the following characteristic properties (Fig. 1). The dibenzothiophene ring system is essentially coplanar, with the phenyl rings inclined by only  $0.7^\circ$ . The corresponding angles in dibenzothiophene, and dibenzothiophene 5-oxide and -tosylimide, and methyl-dibenzothiophenium salt are similarly small ( $1.6$ ,  $4.4$ ,  $3.7$ , and  $1.1^\circ$ , respectively).<sup>6</sup> The nitrogen



**Scheme 1.** (i) 2,2'-Dilithobiphenyl, THF,  $-78^\circ\text{C}$ .

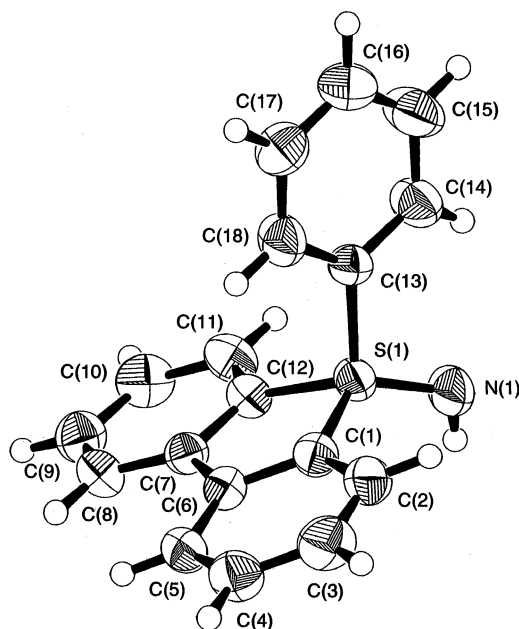
**Keywords:**  $\lambda^6$ -sulfanenitrile; heterocyclic compounds; X-ray crystallographic analysis; quantum chemical calculations.

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**Figure 1.** The molecular structure of **2**. Selected bond distances (Å) and bond angles (°): S(1)–N(1), 1.470(2); S(1)–C(1), 1.794(2); S(1)–C(12), 1.794(2); S(1)–C(13), 1.804(2); N(1)–S(1)–C(1), 121.9(1); N(1)–S(1)–C(12), 120.9(1); N(1)–S(1)–C(13), 115.0(1); C(1)–S(1)–C(12), 90.57(10); C(1)–S(1)–C(13), 101.71(9); C(12)–S(1)–C(13), 102.22(9).

bonded to sulfur assumes a pseudoequatorial position (torsion angle C–C–S1–N1: ca. 127°) in the dibenzothiofene ring system, whereas the phenyl group bonded to sulfur assumes a pseudoaxial position (torsion angle C–C–S1–C13: ca. 104°). The S1–N1 bond length



**Figure 2.** The molecular structure of **3**. For clarity, the chloride anion is omitted. Selected bond distances (Å) and bond angles (°): S(1)–N(1), 1.503(3); S(1)–C(1), 1.773(4); S(1)–C(12), 1.779(4); S(1)–C(13), 1.771(4); N(1)–S(1)–C(1), 121.1(2); N(1)–S(1)–C(12), 121.7(2); N(1)–S(1)–C(13), 106.7(2); C(1)–S(1)–C(12), 92.1(2); C(1)–S(1)–C(13), 106.5(2); C(12)–S(1)–C(13), 107.1(2).

(1.470(2) Å) in **2** is close to the SN triple bond length (1.441–1.462 Å) of organic  $\lambda^6$ -sulfanenitrile.<sup>2a,c,d,e</sup>

To evaluate the electronic structure of  $\lambda^6$ -sulfanenitrile **2**, a single-point calculation with the natural population analysis (NPA) and natural bond orbital (NBO) analyses<sup>7–9</sup> was carried out at the B3LYP/6-31+G(d) level using the data from the crystal structure of **2**. The NPA charges of the S and N atoms were calculated to be 1.623 and –1.085, respectively, and the carbon atoms bonded to the sulfur atom are more negatively charged (–0.267 to –0.296) than the other carbon atoms (–0.047 to –0.206). The NBO procedure for identifying the bonds and lone pairs of the S–N unit in **2** clearly showed four  $\sigma$  bonds, and three lone pairs, one with  $sp^{0.3}$  orbital and another with essentially a nearly unhybridized 2p orbital. The  $\pi$  type nitrogen lone pairs ( $P_\pi(N)$ ) are highly depleted (occupancies: 1.50 and 1.56 e), and donate strongly into the  $\sigma_{S-C}^*$  antibonding orbitals as well as into the sulfur d orbitals. With the formation of the natural localized molecular orbital (NLMO)<sup>8b</sup> from the NBOs, the  $P_\pi(N)$  orbitals delocalize by 12–14% onto hybrids on the sulfur (almost  $pd^{0.14}$ – $pd^{0.18}$ ). The ratio between the total lone pair occupancy depletion at the N atom and the total 3d orbital population at the S atom is 0.98:0.12 (8.2:1), and the NPA/NLMO bond orders of SN and SC are 1.47 and 0.82 (average), respectively.<sup>10</sup> These results indicate that ionic bonding and  $P_\pi(N) \rightarrow \sigma_{S-C}^*$  negative hyperconjugation exist in  $\lambda^6$ -sulfanenitrile **2**.

The  $\lambda^6$ -sulfanenitrile **2** is not hydrolyzed under either acidic or alkaline conditions. Treatment of **2** with hydrochloric acid afforded quantitatively the corresponding 2,2'-biphenylene(phenyl)(imino)sulfonium chloride (**3**), which is also a new type of compound.<sup>11</sup> The structure of **3** was determined by X-ray crystallographic analysis (Fig. 2).<sup>12</sup> Measurement of the basicity of **2** is important for estimating its nucleophilicity and the character of the SN bond. The  $pK_a$  value of the conjugate acid of **2** was determined by potentiometric titration using 0.1 M hydrochloric acid at 25°C to be 6.36. The present results provide a novel procedure for the synthesis of heterocyclic compound **2**, and further work on other heterocyclic  $\lambda^6$ -sulfanenitriles is currently underway in our laboratory.

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- The side-products were mainly biphenyl (20%), dibenzothiophen (6%), and triphenyl- $\lambda^6$ -sulfanenitrile (7%). The phenyl- $\lambda^6$ -sulfanenitrile should be formed by the reaction of **1** with the phenyl anion generated from ligand exchange reaction.<sup>2c</sup> A complex reaction mixture including some unidentified products was also obtained. For **2**: mp 198–200°C (dec.); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.39 (t,  $J=6.6$  Hz, 2H), 7.47 (t,  $J=6.6$  Hz, 1H), 7.50 (t,  $J=8.0$  Hz, 2H), 7.65 (t,  $J=8.0$  Hz, 2H), 7.66 (d,  $J=6.6$  Hz, 2H), 7.78 (d,  $J=8.0$  Hz, 2H), 7.89 (d,  $J=8.0$  Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  121.5, 124.1, 125.2, 129.1, 130.8, 132.0, 133.4, 133.6, 144.7, 145.3; IR (KBr) 1261 cm<sup>-1</sup> (SN); MS ( $m/z$ ) 275 (M<sup>+</sup>). Calcd for C<sub>18</sub>H<sub>13</sub>NS: C, 78.51; H, 4.76; N, 5.09. Found: C, 78.41; H, 5.02; N, 5.12.
- Crystal data of **2**: C<sub>18</sub>H<sub>17</sub>NO<sub>2</sub>S,  $M=311.40$ , monoclinic,  $a=20.686(2)$ ,  $b=13.563(1)$ ,  $c=16.234(2)$  Å,  $\beta=136.246(4)^\circ$ ,  $U=3149.9(7)$  Å<sup>3</sup>,  $T=296$  K, space group  $C2/c$  (no. 15),  $Z=8$ ,  $\mu(\text{Mo K}\alpha)=2.12$  cm<sup>-1</sup>, 4711 reflections measured, 4597 unique ( $R_{\text{int}}=0.015$ ). The final  $R$  value was 0.044. Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 162038 for compound **2**.
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- For **3**: mp 239–241°C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.59 (t,  $J=7.6$  Hz, 2H), 7.64 (t,  $J=8.0$  Hz, 2H), 7.72 (t,  $J=7.6$  Hz, 1H), 7.85 (t,  $J=8.0$  Hz, 2H), 7.86 (d,  $J=7.6$  Hz, 2H), 8.15 (d,  $J=8.0$  Hz, 2H), 8.20 (d,  $J=8.0$  Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  123.72, 127.05, 127.09, 130.66, 132.11, 132.67, 135.26, 135.49, 135.55, 137.09; IR (KBr) 1072 cm<sup>-1</sup> (SN); FAB ( $m/z$ ) 276 (M<sup>+</sup>-Cl<sup>-</sup>). Calcd for C<sub>18</sub>H<sub>14</sub>CINS: C, 69.33; H, 4.53; N, 4.49. Found: C, 69.11; H, 4.64; N, 4.40.
- Crystal data of **3**: C<sub>18</sub>H<sub>16</sub>CINS,  $M=311.83$ , triclinic,  $a=10.125(1)$ ,  $b=10.655(1)$ ,  $c=8.3269(9)$  Å,  $\alpha=111.777(7)^\circ$ ,  $\beta=101.727(9)^\circ$ ,  $\gamma=91.309(9)^\circ$ ,  $U=812.0(2)$  Å<sup>3</sup>,  $T=296$  K, space group  $P\bar{1}$  (no. 2),  $Z=2$ ,  $\mu(\text{Mo K}\alpha)=3.56$  cm<sup>-1</sup>, 4982 reflections measured, 4978 unique ( $R_{\text{int}}=0.018$ ). The final  $R$  value was 0.049. Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 162039 for compound **3**.