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Synthesis and Structure of (MeN)Ph$_2$S=C=SPh$_2$(NMe)

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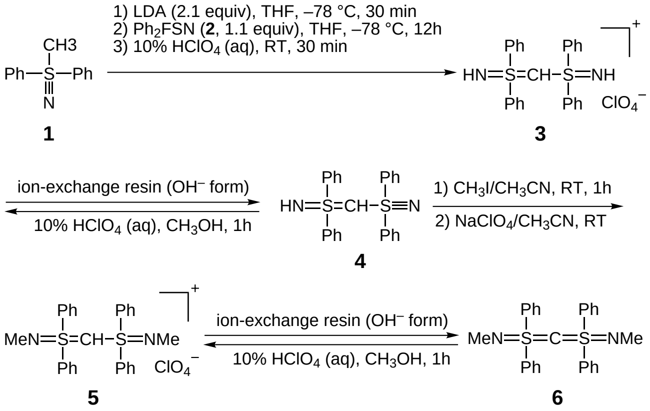
(X)R$_2$S=C=SR$_2$(X) can be regarded as the isoelectronic carbon analogue of the [(X)R$_2$S=N=SR$_2$(X)]$^+$ ion (R = Ar, alkyl; X = lone pair, NH, O).[1] There has, however, been little reported on this compound to date.[2] In view of its chemical properties and structural features, investigation of this compound has posed an interesting challenge. Herein, we report the first synthesis, isolation, and crystal structure of (MeN)Ph$_2$S=C=SPh$_2$(NMe) (**6**), prepared by the α-proton abstraction of a new type of iminosulfonium ylide [(MeN)Ph$_2$S=CH–SPh$_2$(NMe)]$^+$ (Scheme 1).



Scheme 1. Synthesis of **6**.

α-Lithiation of methyldiphenyl-λ^6-sulfanenitrile (**1**)[3a] with lithium diisopropylamide (LDA), followed by treatment with fluorodiphenyl-λ^6-sulfanenitrile (**2**)[3b] and acidification with perchloric acid afforded **3** in 66% yield. This compound was further treated with ion-exchange resin IRA-410 (OH$^-$ form) to give **4**[4–6] almost quantitatively. The reaction of **4** with methyl iodide in CH$_3$CN at room temperature and then treatment with NaClO$_4$ afforded precursor **5**, which was isolated in 26% yield by recrystallization from MeOH and diethyl ether.[7] The desired compound **6** was prepared in essentially quantitative yield by passing a methanolic solution of **5** through a column of the above basic resin.[6] The compositions of **3**–**6** were identified by NMR (except for **4**) and IR spectroscopy, as well as elemental analysis, and the molecular structures of **5** and **6** were determined by X-ray crystallographic analysis (Figure 1 and 2).[8]

The X-ray structure of **6** indicates the following characteristic properties (Figure 2). Each sulfur center is associated with one imido and two phenyl groups, in a pseudo-tetrahedral arrangement. The bond angles N1-S1-C1 and

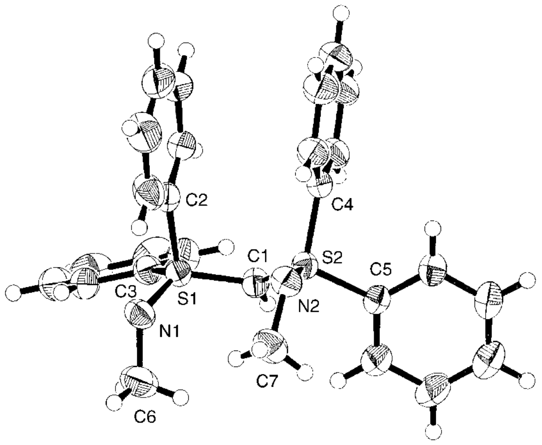


Figure 1. ORTEP drawing of **5** (50% probability thermal ellipsoids for all non-hydrogen atoms, perchlorate anion is omitted for clarity). Selected bond lengths [Å] and angles [°]: S1-N1 1.526(2), S1-C1 1.695(2), S1-C2 1.780(3), S1-C3 1.802(3), S2-N2 1.531(2), S2-C1 1.691(2), S2-C4 1.788(3), S2-C5 1.802(3), N1-C6 1.479(4), N2-C7 1.469(4); N1-S1-C1 123.1(1), N1-S1-C2 103.4(1), N1-S1-C3 112.5(1), C1-S1-C2 107.8(1), C1-S1-C3 102.4(1), C2-S1-C3 106.6(1), N2-S2-C1 119.6(1), N2-S2-C4 103.4(1), N2-S2-C5 115.4(1), C1-S2-C4 110.7(1), C1-S2-C5 102.1(1), C4-S2-C5 104.9(1), S1-N1-C6 117.3(2), S2-N2-C7 118.0(2), S1-C1-S2 118.0(1).

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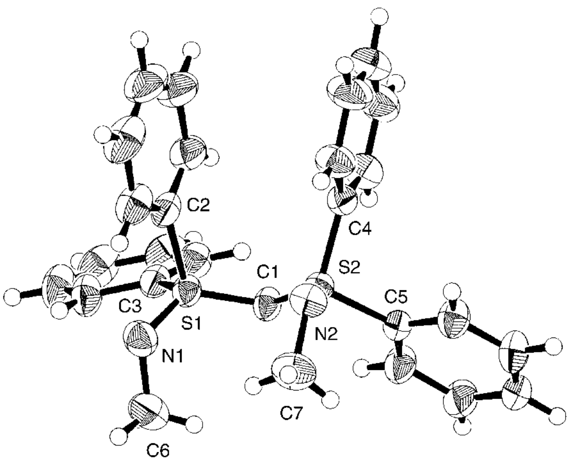
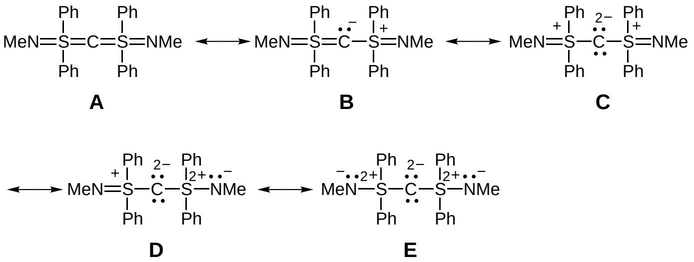


Figure 2. ORTEP drawing of **6** (50% probability thermal ellipsoids for all non-hydrogen atoms). Selected bond lengths [Å] and angles [°]: S1-N1 1.553(10), S1-C1 1.635(4), S1-C2 1.801(2), S1-C3 1.802(4), S2-N2 1.550(8), S2-C1 1.636(2), S2-C4 1.799(4), S2-C5 1.808(4), N1-C6 1.464(4), N2-C7 1.470(5); N1-S1-C1 124.1(2), N1-S1-C2 102.2(2), N1-S1-C3 110.6(3), C1-S1-C2 115.4(1), C1-S1-C3 101.9(3), C2-S1-C3 100.5(1), N2-S2-C1 128.1(2), N2-S2-C4 101.1(3), N2-S2-C5 110.1(3), C1-S2-C4 111.6(1), C1-S2-C5 102.1(1), C4-S2-C5 101.0(3), S1-N1-C6 115.2(2), S2-N2-C7 115.7(3), S1-C1-S2 116.8(2).

N2-S2-C1 (124.1(2) and 128.1(2)°, respectively), those involving the bridging C1 atom, are considerably larger than the other sulfur-centered bond angles (N-S-C; av. 106.0°, C-S-C; av. 105.4°). The bonds between the sulfur centers and the bridging carbon atom are of similar size, as are the two terminal S–N bonds, and the four bonds between the sulfur centers and phenylic carbon atoms. The bridging S–C1 bonds in **6** (1.635(4) and 1.636(2) Å) are shorter than their counterparts in **5** (1.695(2) and 1.691(2) Å) and in iminosulfonium phenacylide (1.672(2) Å[3a]). In contrast, the terminal S1–N1 and S2–N2 bonds (1.553(10) and 1.550(8) Å, respectively) are slightly longer than those in **5** (1.526(2) and 1.531 Å) and in iminosulfonium phenacylide (1.538(2) Å[3a]). Interestingly, the S1-C1-S2 angle in **6** (116.8(2)°) is almost the same as the corresponding angle in **5** (118.0(1)°), and is indicative of sp^2 hybridization of the C1 atom. These findings suggest that the S1-C1-S2 bonds have double ylidic character, such as is found in carbodiphosphoranes, $R_3P{=}C{=}PR_3$,[9] and thus the canonical Lewis structures of **B**–**E** are anticipated (Scheme 2).

To evaluate the electronic structure of **6**, ab initio calculations were carried out on a model compound, (MeN)$Me_2S{=}C{=}SMe_2$(NMe) (**7**), where the phenyl groups in **6** are all replaced by methyl groups.[10] Calculations by geometry optimization, the natural population analysis (NPA), and the natural bond orbital (NBO) analyses were performed at the B3LYP/6-311+G(2d,p) level.[11] There is a reasonably good agreement between the bond lengths and angles of the N-S-C-S-N unit in the optimized structure (Figure 3), and those in the X-ray structure of **6**. As indicated by NPA and NBO analysis, the N-S-C-S-N unit in **7** has strongly polarized S–C and S–N bonds. The NPA charges at the two sulfur atoms, the two nitrogen atoms, and the central carbon atom are calculated to be +1.603 (S1), +1.594 (S2), −1.000 (N1), −0.997 (N2), and −1.228 (C1), respectively. The NBO procedure for identifying bonds and lone pairs of the N-S-C-S-N unit in **7** clearly showed ten σ bonds and six lone pairs. Therefore, the canonical structure **E** in Scheme 2 shows the best Lewis representation of the electronic configuration of **6**. The pσ and p lone pairs of the central carbon atom (C1) are highly depleted, with occupancies of 1.74e and 1.52e. NBO second-order perturbation analysis[11b, 12] of **7** indicates five strong orbital interactions of the lone pair (p-LP, pσ-LP) at the central carbon atom with the antibonding σ* orbitals of the S–N and S–C bonds, and the interaction of a lone pair at each terminal nitrogen atom with $\sigma^*_{S\text{-}C1}$ and $\sigma^*_{S\text{-}C}$ orbitals. These results indicate that ionic bonding, as well as LP(C1) →σ* and LP(N) →σ* negative hyperconjugation exist in **7**.



Scheme 2. Structural representation of **6**.

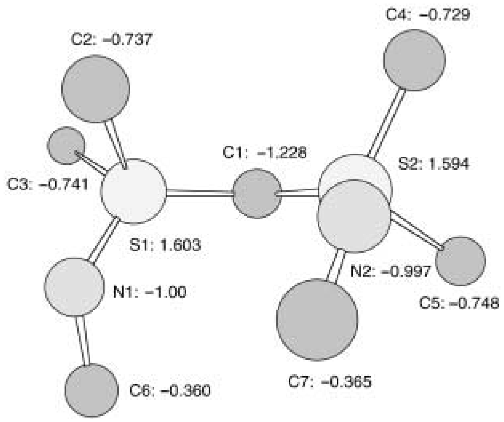


Figure 3. View of the B3LYP/6-311+G(2d,p) optimized structure and charge distribution (natural charge analysis) of **7** (all hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: S1-N1 1.565, S1-C1 1.646, S1-C2 1.824, S1-C3 1.831, S2-N2 1.567, S2-C1 1.650, S2-C4 1.819, S2-C5 1.836, N1-C6 1.460, N2-C7 1.465; N1-S1-C1 124.9, N1-S1-C2 99.4, N1-S1-C3 111.5, C1-S1-C2 117.6, C1-S1-C3 100.8, C2-S1-C3 100.3, N2-S2-C1 129.6, N2-S2-C4 99.1, N2-S2-C5 112.5, C1-S2-C4 110.8, C1-S2-C5 102.0, C4-S2-C5 99.2, S1-N1-C6 117.1, S2-N2-C7 118.1, S1-C1-S2 120.0.

In conclusion, the synthesis of **6** represents the first successful preparation of an organosulfur compound containing the $S^{VI}{=}C{=}S^{VI}$ unit, the molecular structure of which has been determined. In addition, the electronic structure of **7**, a model compound based on **6**, was predicted by ab initio molecular calculations.

Experimental Section

3: Lithium diisopropylamide (4.2 mL of 2.0 M solution in heptane/THF/ethylbenzene, 8.4 mmol) was added dropwise at −78 °C to a solution of **1** (861 mg, 4.0 mmol) in THF (50 mL) and stirred for 30 min. A solution of **2** (965 mg, 4.4 mmol) in THF (10 mL) was then added. The mixture was stirred for 12 h at −78 °C , warmed up to room temperature, and then quenched with 10% perchloric acid (10 ml) and then extracted with CH_2Cl_2. The solvent was evaporated under reduced pressure, and the residue was washed with MeOH and then recrystallized from EtOH/Et_2O to give colorless crystals of **3** (1.36 g, 66% yield), m.p. 175–176 °C. ^{1}H NMR (400 MHz, CD_3CN): $\delta = 5.08$ (s, 1H), 7.59–7.64 (m, 8H), 7.69–7.74 (m, 4H), 8.02–8.06 ppm (m, 8H); ^{13}C NMR (100 MHz, CD_3CN): $\delta = 49.3$, 127.9, 131.0, 135.2, 140.8 ppm; IR (KBr): $\tilde{\nu} = 3315$, 3269, 3094, 3062, 1095 cm^{-1}; elemental analysis calcd for $C_{25}H_{23}ClN_2O_4S_2$: C 58.30, H 4.50, N 5.44; found: C 58.29, H 4.46, N, 5.46.

5: A mixture of **4** (414 mg, 1.0 mmol) and methyl iodide (187 µL, 3 mmol) in acetonitrile (10 mL) was stirred at room temperature for 1 h. A solution of sodium perchlorate (184 mg, 1.5 mmol) in acetonitrile (10 mL) was added, and then the solvent was evaporated under reduced pressure. The residue was dissolved in water (10 mL) and extracted with CH_2Cl_2. After removal of the solvent, the residue was purified by recrystallization from MeOH/Et_2O to afford **5** as colorless crystals (152 mg),[7] m.p. 184–185 °C. ^{1}H NMR (400 MHz, CD_3CN): $\delta = 2.75$ (s, 6H), 5.18 (s, 1H), 7.52–7.57 (m, 8H), 7.65–7.70 (m, 4H), 7.87–7.90 ppm (m, 8H); ^{13}C NMR (100 MHz, CD_3CN): $\delta = 30.4$, 39.3, 128.9, 131.0, 135.3, 136.8 ppm; IR (KBr): $\tilde{\nu} = 2917$, 2872, 2803, 1194, 1091 cm^{-1}; elemental analysis calcd for $C_{27}H_{27}ClN_2O_4S_2$: C 59.71, H 5.01, N 5.16; found: C 59.72, H 4.97, N, 5.17.

6: A solution of **5** (100 mg) 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 **6** as a pale yellow powder (74 mg, 98%), m.p. 163–164 °C. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 2.62$ (s, 6H), 7.28–7.35 (m, 12H), 8.00 ppm (dd, $J_1 = 8.0$ Hz, $J_2 = 1.4$ Hz, 8H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 30.1$, 39.7, 127.7, 128.3, 130.5, 144.4 ppm; IR (KBr): $\tilde{\nu} = 2947$, 2840, 2776, 1147 cm^{-1}; elemental analysis calcd for $C_{27}H_{26}N_2S_2$: C 73.26, H 5.92, N 6.33; found: C 73.11, H 5.99, N, 6.29.

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[4] Compound **4** could not be isolated from the reaction mixture of lithiated **1** and **2**, and was therefore isolated by converting it into the corresponding perchloric salt **3** upon treatment with perchloric acid (See Experimental Section).

[5] Unexpectedly, ^{13}C NMR spectra of **4** showed only one set of phenyl groups, and methyne proton and carbon resonances were not observed in the temperature range −80 to 100 °C in CD_3OD and [D$_6$]DMSO. IR and elemental analyses were consistent with the structure of **4**, although the structure of **4** in the solution is still not certain. **4**: m.p. 155–156 °C; IR (KBr): $\tilde{\nu} = 1259$ cm^{-1} ($S{\equiv}N$); elemental analysis calcd for $C_{25}H_{22}N_2S_2$: C 72.43, H 5.35, N 6.76; found: C 72.36, H 5.38, N, 6.77.

[6] Compounds **4** and **6** are considerably basic. Treatment of **4** and **6** with perchloric acid afforded, almost quantitatively, **3** and **5**, respectively.

[7] The side products in the reaction with methyl iodide were **3** and the *N*-monomethylated compound, $[(MeN)Ph_2S{=}CH{-}SPh_2(NH)]^+$ $[ClO_4]^-$ (**8**). The structure of **8** is still preliminary as it has been difficult to effect the separation of **3** and **8** successfully.

[8] Crystal data for **5**: $C_{27}H_{27}ClN_2O_4S_2$, $M_r = 547.09$, monoclinic, space group $P2_1/n$, $Z = 4$, $a = 12.769(6)$, $b = 16.503(4)$, $c = 14.031(6)$ Å, $\beta = 115.99(3)^\circ$, $V = 2657(1)$ Å^3, $\rho_{calcd} = 1.367$ cm^{-1}. X-ray diffraction data were collected on a Rigaku AFC7R diffractometer with graphite monochromated Mo$_{K\alpha}$ radiation ($\lambda = 0.71069$ Å) at 296 K, and the structure was solved by direct methods (SIR 92) and expanded using Fourier techniques (DRIFT). The final cycle of full-matrix least-squares refinement was based on 5006 observed reflections ($I > 3\sigma(I)$) and 338 variable parameters and converged to $R = 0.050$ and $R_w = 0.071$. **6**: $C_{27}H_{26}N_2S_2$, $M_r = 442.64$, monoclinic, space group $P2_1/n$, $Z = 4$, $a = 7.40(5)$, $b = 15.63(8)$, $c = 20.36(6)$ Å, $\beta = 91.6(5)^\circ$, $V = 2352(20)$ Å^3, $\rho_{calcd} = 1.250$ cm^{-1}. X-ray diffraction data were collected on a Rigaku AFC7R diffractometer with graphite monochromated Mo$_{K\alpha}$ radiation ($\lambda = 0.71069$ Å) at 296 K, and the structure was solved by direct methods (SIR 92) and expanded using Fourier techniques (DRIFT). The final cycle of full-matrix least-squares refinement was based on 4039 observed reflections ($I > 3\sigma(I)$) and 280 variable parameters and converged to $R = 0.042$ and $R_w = 0.058$. CCDC-180279 (**5**) and CCDC-180280 (**6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

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Reaction of 2-Butyne with *nido*-[1,2-$(Cp^{*}RuH)_2B_3H_7$]: Improved Kinetic Control Leads to Metallacarboranes of Novel Composition and Structure[**]

Hong Yan, Alicia M. Beatty, and Thomas P. Fehlner[*]

The conventional route to metallacarboranes proceeds in a sequence of steps leading from polyborane to carborane to metallacarborane.[1–4] Although a fruitful strategy, it is also one in which strong bonds are formed before weak ones. Access to more diverse chemistry might arise by adoption of the reverse strategy, that is, formation of B–B/B–M before B–C/M–C bonds, thereby generating the most stable products

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