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First Isolation and Characterization of Sulfenium Cation Salts Stabilized by the Coordination of Two Nitrogen Atoms

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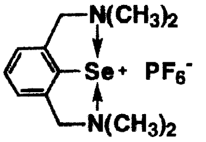
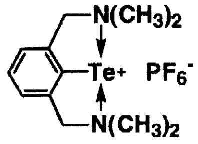
Abstract: *The remarkably stable sulfenium cation salts were prepared from the reaction of 2,6-bis(dimethylamino)methyl-1-lithiobenzene with sulfur dichloride. These compounds have been characterized by various NMR and elemental analysis. A single crystal X-ray structure determination revealed that two amino groups coordinate directly to the cationic sulfur atom.* © 1998 Elsevier Science Ltd. All rights reserved.

Sulfenium cation species (RS^+) have long been considered to be unstable and very reactive as strong electrophilic reagents.[1] In general, two approaches for the preparation of sulfenium cation species have been reported. The first one is the heterolysis of the S–X bond of the neutral precursors which contain a relatively weak sulfur-X bond (X = electronegative heteroatoms).[2] The second method is the electrochemical anodic oxidation of various disulfides.[3] Although the formation of sulfenium cation salts has been proposed in many studies, it is controversial whether the corresponding free cation exists or not. To date, there is no report describing the actual structure of the sulfenium cation salts. Recently, the analogous selenenium and tellurenium cation salts (**1** and **2**) were first prepared and isolated as a result of their stabilization by employing two neighboring amino ligands, namely, dimethylaminomethyl groups.[4] This ligand is widely used for isolating unstable species, and a number of studies have already been reported.[5] As a result of applying this ligand, we have succeeded in the isolation of sulfenium cation salts as remarkably stable crystals. Here we report the first isolation, crystal structure, and properties of sulfenium cation salts stabilized by two amino groups.

Chart 1



1



2

1,3-Bis[(dimethylamino)methyl]benzene **3** was easily lithiated by *n*-BuLi in anhydrous ether at room temperature under an argon atmosphere to yield 1,3-bis(dimethylaminomethyl)-2-lithiobenzene *in situ*. The

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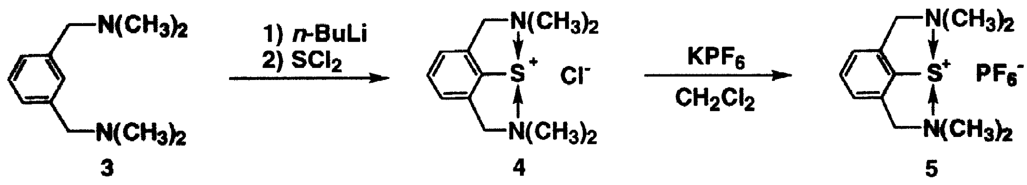
ether solution containing the lithiated compound **4** was added dropwise to a 1 molar equiv of sulfur dichloride (SCl_2) in dry ether. After the removal of the solvent at room temperature, the corresponding sulfenium chloride **4** having Cl^- as the counter anion was isolated as stable yellow needle-like crystals in 20% yield.[6] Furthermore, when the product **4** was treated with the potassium hexafluorophosphate (KPF_6) in CH_2Cl_2 the 2,6-[bis(dimethylaminomethyl)phenyl]sulfenium hexafluorophosphate **5** was produced in 56% yield as shown in Scheme 1.[6] The products **4** and **5** were identified by ^1H, ^{13}C, ^{19}F, and ^{31}P NMR, mass spectroscopy, and elemental analysis.

Scheme 1



The ^1H NMR signals of the benzylic and four methyl protons in **4**, measured in $CDCl_3$ at room temperature, appear at 4.31 ppm and at 2.96 ppm as singlets, respectively. These chemical shifts of those protons of **4** appear at a lower field than those of 1,3-bis(dimethylaminomethyl)-2-methylthiobenzene. These results indicate that each amino group coordinates to the cationic sulfur. The ^1H NMR spectrum of **5**, measured in $CDCl_3$ at room temperature, exhibits almost the same signals as **4**, and no significant difference in their chemical shifts was observed. The proton-decoupled ^{31}P and ^{19}F signals of **5** appeared at –145.4 ppm as the septet and –73.5 ppm as the doublet due to the spin-spin coupling between the phosphorus and fluorine nuclei ($^1J_{P-F}$ = 707 Hz) which is derived from PF_6^- counter anion. The molecular of structures of both **4** and **5** except for their counter anion parts were reasonably characterized by the fragmentation peaks derived from their parent peaks in their EI-MS spectra.

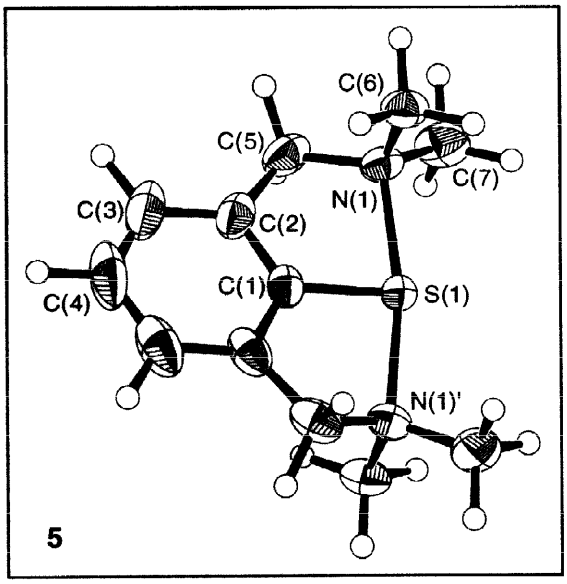


Figure 1. An ORTEP drawing (drawn at 50% probability level) of **5**. N(1)' is related to N(1) by a two-fold axis of symmetry. Selected bond distances (Å) and angles (°) of the non-hydrogen atoms of **5** are given below (e.s.d.'s in parenthesis),

S(1)–N(1) = 2.063(1), S(1)–C(1) = 1.758(2),
N(1)–C(5) = 1.487(3), N(1)–C(6) = 1.474(2),
N(1)–C(7) = 1.478(3), C(1)–C(2) = 1.383(2),
C(2)–C(3) = 1.393(3), C(2)–C(5) = 1.493(3),
C(3)–C(4) = 1.372(4),
N(1)–S(1)–N(1)' = 168.54(9), N(1)–S(1)–C(1) = 84.27(5),
S(1)–N(1)–C(5) = 105.5(1), S(1)–N(1)–C(6) = 106.1(1),
S(1)–N(1)–C(7) = 109.3(1), C(5)–N(1)–C(6) = 111.5(2),
C(5)–N(1)–C(7) = 112.8(2), C(6)–N(1)–C(7) = 111.2(2),
S(1)–C(1)–C(2) = 118.3(1), N(1)–C(5)–C(2) = 106.7(2)

Furthermore, the solid state structure of the sulfenium cation **5** was determined by X-ray diffraction (R = 0.037, R_w = 0.034). An ORTEP view of **5** is shown in Figure 1. In the solid state, the two neighboring amino nitrogens directly coordinate to the sulfur atom. Each of the S–N distances are equal to 2.063(1) Å, which is longer than a single covalent bond (1.74 Å)[7]. The N(1)–S(1)–N(1)' angle, 168.54(9) °, is distorted from a linear arrangement. The counter anion, PF_6^-, is independent of the cationic part of the sulfenium cation, since the closest contact (S(1)••••F(3) = 3.786(2)) is longer than the sum of the van der Waals' radii of a sulfur and a fluorine atom (2.20 Å).[7] The bicyclo ring on the sulfur and nitrogen atoms are distorted and the angle between the N(1), S(1), N(1)' and the benzene ring planes exhibited is 14.3(1)°. This X-ray data clearly indicates that in the solid state significant interactions exist between the sulfur and nitrogen atoms and the sulfenium cation is stabilized by the neighboring-group participation of the two nitrogen atoms.

In order to understand the electronic structure of sulfenium cation species single-point *ab initio* calculations were carried out using the crystal structure coordinates of **5**.[8] The charge on the S atom in **5** was calculated to be +0.550 and the two nitrogen atoms are negatively charged as shown in Table 1. The Mulliken and Löwdin bond orders of S(1)–N(1) of **5** are 0.379 and 0.539, respectively. These results indicate that the N–S–N bond have a three-center four-electron (3c–4e) hypervalent bonding system. The sulfur atom formally possesses ten valence electrons, the two S–N bonds being strongly polarized toward the nitrogen atoms. Finally, we notice that the total 3d orbital population evaluated by the natural population analysis is very small (0.025) indicating that the d orbitals are not primarily concerned with the 3c-4e bond in agreement with the current view of hypervalent species.[9]

Table 1. The charge distribution and bond orders of **5**

Atoms or Group	Charge (e)	Bonds	Bond Orders
S(1)	+0.550	S(1)–N(1)	0.379 (Mulliken)
N(1)	−0.535		0.539 (Löwdin)
C(1)	−0.235	S(1)–C(1)	0.945 (Mulliken)
C(2)	−0.057		1.067 (Löwdin)
C(3)	−0.146		
C(4)	−0.106		
C(5)	−0.160		
C(6)	−0.271		
C(7)	−0.302		
Benzene ring[a]	−0.196		
$H(CH_2)$	+0.219[b]		
$H(CH_3)$	+0.192[b]		

[a] Six carbons plus three hydrogens. [b] Averaged value.

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6. **4**; Yield 20%; colorless crystal; mp 130–133 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.96 (s, 12H), 4.31 (s, 4H), 7.26–7.27 (m, 3H, Ar-H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 47.9, 62.3, 125.4, 128.1, 130.1, 134.0; EI-MS (m/z) 223 (M^+–Cl); IR (KBr, cm^{-1}) 3400 (H_2O); Anal. Calcd for $C_{12}H_{19}Cl_1N_2S_1(H_2O)_2$: C, 48.88; H, 7.86; N 9.50. Found: C, 49.12; H, 7.93; N, 9.40. **5**; Yield 56%; colorless crystal; mp 168–170 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.86 (s, 12H), 4.11 (s, 4H), 7.26-7.27 (m, 3H, Ar-H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 47.8, 62.3, 125.3, 128.1, 128.7, 129.9; ^{19}F NMR (254 MHz, $CDCl_3$) δ –73.5 (d, J_{F-P} = 707 Hz); ^{31}P NMR (109 MHz, $CDCl_3$) δ –145.4 (sept, J_{P-F} = 707 Hz); EI-MS (m/z) 223 (M^+–PF_6). Anal. Calcd for $C_{12}H_{19}F_6N_2P_1S_1$: C, 39.13; H, 5.20; N 7.61. Found: C, 39.30; H, 5.29; N, 7.54.
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8. Single point *ab initio* calculations were carried out at the RHF/6–31G* level using Spartan 3.1.[10] Atomic charges were calculated by the natural population analysis.[11] This method is particularly preferred to the traditional Mulliken population analysis for analyzing the electronic wave function of hypervalent molecules which have strongly polar bonds.
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