

First Isolation and Molecular Structure of Bis(2,2'-biphenylene)sulfuranyl Bis(tetrafluoroborate) [8-S-4(C4)]²⁺

Soichi Sato, Hitomi Ameta, Ernst Horn, Ohgi Takahashi, and Naomichi Furukawa*

Tsukuba Advanced Research Alliance Center and Department of Chemistry University of Tsukuba, Tsukuba, Ibaraki 305, Japan

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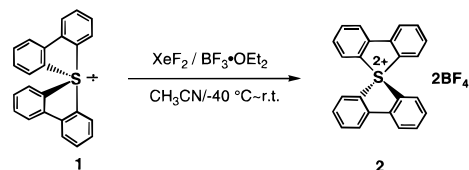
Sulfurane dication species (R₄S²⁺)X²⁻ belong to the isoelectronic molecules of the corresponding silanes (R₄Si) and phosphonium salts (R₄P⁺)X⁻ but only a few studies have been presented.¹ If the central sulfur atom of the compounds obeyed the Lewis octet rule such as a [8-S-4]²⁺, they should have tetrahedral structures of sp³ hybridization at the central sulfur atom.

The first generation of organosulfurane(IV) dication species (H₄S²⁺) has been suggested by Olah et al.² in the H–D exchange reaction of trihydridosulfonium ion (H₃S⁺) which is protonated H₂S in a FSO₃D·SbF₅ and FSO₃H–SbF₅–SO₂ solution (magic acid), and the structure of the intermediate has also been predicted by *ab initio* theoretical calculations. Similarly, they have reported several other organosulfurane(IV) dications having ligands containing hydrogen and carbon atoms which are quite unstable species and have to date not been detected or isolated. Instead of the Olah procedure using sulfonium salts with strong acids, we intended to generate R₄S²⁺ from the hypervalent sulfuranes by oxidative removal of the lone-electron pair.

Recently, we have succeeded in the first isolation and structural determination of bis(2,2'-biphenylene)sulfurane [10-S-4(C₄)] (**1**) as a stable sulfurane(IV) having only carbon ligands.³ We considered that this sulfurane would be a suitable precursor to provide the desired dication. Therefore, we tried the reaction of bis(2,2'-biphenylene)sulfurane (**1**) with xenon difluoride (XeF₂) in the presence of BF₃·OEt₂ and indeed obtained the bis(2,2'-biphenylene)sulfurane dication, [8-S-4(C₄)]²⁺ (**2**) as an amazingly stable bis(tetrafluoroborate) salt.⁴ Here, we communicate the first isolation and structural determination of bis(2,2'-biphenylene)sulfurane dication (**2**) having only carbon ligands. Also included in this paper are the results on *ab initio* calculation of the dication **2** showing the charge distribution of the molecule and a new ligand coupling reaction.

The sulfurane **1** was reacted with 1 mol equiv of xenon difluoride in the presence of BF₃·OEt₂ in dry CH₃CN at –40 °C (Scheme 1). After the solvent was removed at room temperature, the residue was washed with CHCl₃ at room temperature, and bis(2,2'-biphenylene)sulfurane bis(tetrafluoroborate) (**2**) was isolated as a stable moisture-insensitive yellow powder in 62% yield. The product **2** was identified by ¹H, ¹³C, and ¹⁹F NMR, mass spectroscopy, and elemental analysis.⁵

Scheme 1



Examination of the ¹H and ¹³C NMR spectra of the compound **2** reveals that the two phenyl rings of biphenylene groups are in equivalent states. There are two doublet and two triplet peaks in the ¹H NMR spectrum and six peaks in the ¹³C NMR spectrum. All of the ¹H NMR chemical shifts appear at unusually low field compared with those of the corresponding sulfurane **1**. The ¹⁹F and ¹¹B NMR spectra of **2** show each signal of the tetrafluoroborate anion (BF₄⁻) as a single peak. These results indicate that the yellow compound **2** has a symmetrical structure and contains BF₄⁻ as counter anions. The dication **2** was also characterized by its parent peaks in the FAB-MS spectra and by elemental analysis.

Furthermore, we have succeeded in determining the structure of the product **2** by X-ray crystallographic analysis. Single crystals of **2** were formed by recrystallization from a CH₃CN/Et₂O solution at –20 °C. The crystallographic data and numerical details for the compound **2** are given in ref 6. The molecular structure of dication **2** and the adopted numbering scheme are illustrated by an ORTEP plot in Figure 1, together with a selected list of bond distances and angles.

The unit cell consists of four asymmetric units containing ³/₂[S(C₁₂H₈)₂·(BF₄)₂] and *ca.* two H₂O molecules. One of the dications and a BF₄⁻ anion are located on a crystallographic 2-fold axis of symmetry, while a second BF₄⁻ anion is disordered about a center of symmetry. The central sulfur atom of the dications has a distorted tetrahedral bonding geometry

(5) For **2**: mp 231–233 °C (dec); ¹H NMR (270 MHz, CD₃CN, room temperature (rt)) δ 7.92 (t, *J* = 7.5 Hz, 4H, 4-ArH), 8.24 (d, *J* = 7.5 Hz, 4H, 3-ArH), 8.36 (t, *J* = 7.5 Hz, 4H, 5-ArH), 8.59 (d, *J* = 7.5 Hz, 4H, 6-ArH); ¹³C NMR (68 MHz, CD₃CN, rt) δ 115.7, 128.2, 132.2, 135.6, 142.6, 143.6; ¹⁹F NMR (254 MHz, CD₃CN, rt) δ –151.6 (relative to CFCl₃); ¹¹B NMR (87 MHz, CD₃CN, rt) δ –20.4 (relative to (CH₃O)₃B); IR (KBr, cm⁻¹) 3426(b) (H₂O) (only recrystallized compounds); FABMS *m/z* 355 ([M – 2BF₄ + F]⁺), (matrix nitrophenyl octyl ether). Anal. Calcd for C₂₄H₁₆B₂F₈S: C, 56.52; H, 3.16. Found: C, 56.20; H, 3.30 (not recrystallized compound). Each chemical shift was determined by two-dimensional shift correlation (¹H–¹H and ¹³C–¹H COSY) spectra. All NMR spectra were recorded on a JEOL EX-270.

(6) Crystallographic data for compound **2**: ³/₂[S(C₁₂H₈)₂·(BF₄)₂]·2.07(H₂O), *M_w* = 802.38, orthorhombic, space group *Pbcn* (No. 60), *a* = 15.335(5) Å, *b* = 20.333(7) Å, *c* = 23.562(5) Å, *V* = 7346(3) Å³, *d_{calcd}* = 1.45 g/cm³, *Z* = 8, *F*(000) = 3261.60, *μ* = 2.1 cm⁻¹. A transparent yellow crystal of dimensions 0.45 × 0.50 × 0.80 mm was analyzed on a Rigaku AFC-7R four-circle diffractometer at 296 K. A total of 7446 unique reflections were collected in the range 2.8 < 2θ < 50°. An intensity check of three standard reflections showed that no significant decay had occurred during the data collection. The data were corrected for Lorentz and polarization effects, and secondary extinction (coefficient = 4.81100e-08). No crystal absorption corrections were applied. The structure was solved by direct methods. The initial E map revealed the non-hydrogen atoms of the sulfurane dications. In subsequent difference Fourier syntheses, the BF₄⁻ molecules were located and their disorder was modeled. Further refinements and difference maps revealed residual electron density peaks which with the help of an infrared spectrum were identified as two water molecules (*ν*(O–H) = 3426 cm⁻¹ disordered over several sites. The disorder of effectively four BF₄⁻ molecules and of the lattice water accounts for the higher than normal *R*-values. All carbon hydrogen atoms were added at calculated positions (C–H = 0.97 Å) but not refined. The neutral atom scattering factors used in the refinements were taken from Cromer and Waber¹⁴ and corrected for anomalous dispersion.¹⁵ Only the 3142 reflections with *I* > 3.00σ(*I*) were used in the refinements. The final cycle of refinement included 379 variable parameters and converged with *R* = 0.067 and *R_w* = 0.062. The remaining maximum and minimum electron density features in the final difference Fourier map are equal to 0.34 and –0.43 e/Å³, respectively, with the maxima located at a distance of 1.04 Å from a fluorine atom of a disordered BF₄⁻ molecule. All calculations were performed on an Indy workstation using the *teXsan* crystallographic software package from Molecular Structure Corp. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

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(4) Compounds in this paper are designated by the *N–X–L* formalism where *N* is the number of valence-shell electrons in the atom *X* which are formally involved in bonding *L* as ligands to *X*. See: Perkins, C. W.; Martin, J. C.; Arduengo, A. J.; Lau, W.; Alegria, A.; Kochi, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 7753.

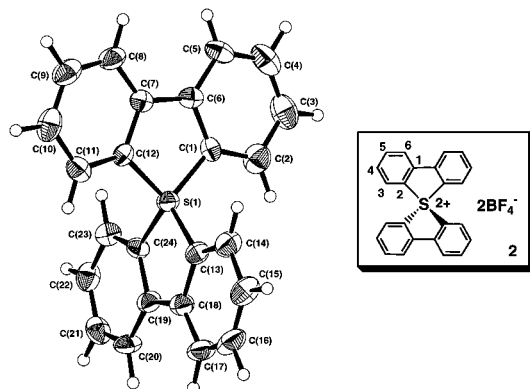


Figure 1. An ORTEP (50% probability ellipsoids) view of **2** showing the atomic numbering scheme employed. Bond distances (Å) and a selected list of angles (deg) for the non-hydrogen atoms: S(1)–C(1) 1.747(6); S(1)–C(12) 1.749(6); S(1)–C(24) 1.758(6); C(2)–C(3) 1.37(1); C(6)–C(7) 1.455(8); C(3)–C(4) 1.38(1); C(7)–C(8) 1.384(8); S(1)–C(13) 1.761(6); C(4)–C(5) 1.39(1); C(8)–C(9) 1.38(1); C(5)–C(6) 1.374(9); C(9)–C(10) 1.36(1); C(1)–C(2) 1.369(9); C(1)–C(6) 1.396(8); C(10)–C(11) 1.39(1); C(11)–C(12) 1.377(9); C(1)–S(1)–C(12) 94.9(3); C(1)–S(1)–C(13) 118.3(3); C(1)–S(1)–C(24) 117.5(3); S(1)–C(12)–C(7) 108.8(5); C(12)–S(1)–C(13) 115.9(3); S(1)–C(12)–C(11) 125.8(5); C(12)–S(1)–C(24) 116.9(3); S(1)–C(13)–C(14) 125.5(5); C(13)–S(1)–C(24) 95.1(3); S(1)–C(13)–C(18) 108.0(5); S(1)–C(24)–C(23) 125.9(5); S(1)–C(24)–C(19) 108.4(5); S(1)–C(1)–C(6) 108.9(5); S(1)–C(24)–C(23) 125.9(5).

Table 1. Charge Distribution (Natural Population Analysis) and Mulliken Bond Orders of Sulfurane Dication **2** (Average Values)

quantity	variable	2
charges ^a	S(1)	+1.594
	C(1)	–0.306
	C(2)	–0.108
	C(3)	–0.164
	C(4)	–0.087
	C(5)	–0.145
	C(6)	–0.018
bond order ^a	Ar–H	+0.233
	S(1)–C(1)	0.949
hybridization ^b	S(1)–C(1)	sp ^{2.91–3.01}

^a Average values. ^b Hybridization of the bonding orbitals of S(1).

with the two biphenylene groups. This result is in agreement with the calculated results reported by Olah et al., which suggest that the sulfurane dication as a tetrahedral structure is more stable than a planar structure.² The least-squares planes of two biphenylene groups in compound **2** are perpendicular to each other. The average of S–C bond distance is 1.753 Å, and the bond angles range from 94.9(3) to 118.3(3)°. The S–C distances are quite normal and comparable with the reference value of 1.787 Å.⁷

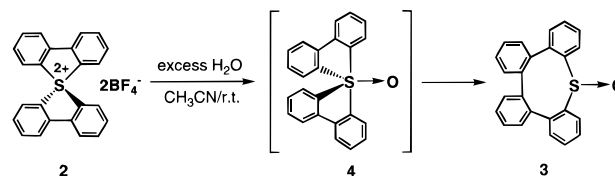
In order to elucidate the electronic structure of organosulfurane dication **2**, a single-point *ab initio* calculation was carried out using the data from the crystal structure of **2**. The calculation was carried out at the RHF/6-31G* level using Spartan 3.1,⁸ and atomic charges were calculated by the natural population analysis.⁹ The charge of the S atom in **2** was calculated to be +1.594, and the carbon atoms, especially those bonded to the central S atom, are negatively charged, as shown in Table 1. The remainder of the positive charge is carried by the hydrogen atoms (+0.233), and this may explain the low-field shift in the ¹H NMR spectrum of **2**.

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Scheme 2



The Mulliken bond orders of the four S–C bonds are approximately 0.95, indicating that these bonds are essentially single bonds. The natural bond orbital (NBO) analysis⁹ showed that the four natural hybrid orbitals (NHOs) of the sulfur atom concerning the four S–C bonds are almost sp³ (sp^{2.91}–sp^{3.01}) and consistent with the tetrahedral bonding structure. Though there is an appreciable sulfur 3d-orbital population (0.066), the electronic structure around the central S atom can be approximately described by a Lewis structure.

Mews et al. have reported that the reaction of *S*-(dimethylamino)-*S,S*-difluorothiazine with (MeOSO)⁺MF₆[–] (M = As, Sb) as an alkylating agent leads to the first detectable organosulfurane(IV) dication, [(Me₂N)₂SF₂]²⁺ 2MF₆[–], in quantitative yield, characterized by NMR spectroscopy.¹⁰ Recently, Dehnicke et al. have reported the first isolation of the organosulfurane(IV) dication, [S(NPMe₃)₄]Cl₂, which was characterized by X-ray crystal analysis.¹¹ However, these compounds have been described as a dication of hexavalent sulfur species rather than the organosulfurane(IV) dication species, because the N atoms on the ligands are indicative of sp² hybridization from both the X-ray crystal analysis results and theoretical calculation.

This organosulfurane dication **2** did not react with atmospheric moisture or crystal lattice water but reacted with excess water or dilute alkali solution at room temperature to give the ring-reorganized cyclic sulfoxide, tetrabenzo[*b,d,f,h*]thionin *S*-oxide (**3**), quantitatively (Scheme 2).¹² The structure of sulfoxide **3** was determined by X-ray crystallographic analysis. The formation of this sulfoxide **3** can be explained by a carbon–carbon ligand coupling reaction of the corresponding sulfuranyl oxide **4** intermediate which was produced from the reaction of the compound **2** with water.¹³ However, the sulfuranyl oxide **4** has not been detected under the present reaction conditions.

The present results provide a novel procedure for the synthesis of the organosulfur(IV) dication, and further work on other organochalcogen dication species [8–X–4, (X = S, Se, Te)]²⁺ is currently underway in our laboratory.

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Supporting Information Available: Textual presentation of experimental data and tables of crystal data, positional parameters, thermal parameters, root mean-square amplitudes, and bond distances and angles (24 pages). See any current masthead page for ordering and Internet access instructions.

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(12) For **3**: mp 253 °C (dec); ¹H NMR (270 MHz, CDCl₃, rt) δ 6.71–7.44 (m, 14H, ArH), 7.74–7.82 (m, 2H, ArH); ¹³C NMR (68 MHz, CDCl₃, rt) δ 125.8, 126.2, 126.9, 127.4, 127.4, 127.4, 127.9, 128.2, 128.2, 128.7, 128.9, 129.1, 129.6, 130.2, 131.2, 133.6, 137.2, 138.0, 138.5, 139.7, 139.8, 140.1, 142.1, 143.1; IR (KBr, cm^{–1}) 1046 (S–O); MS *m/z* 352 (M⁺); HRMS calcd for C₂₄H₁₆OS (M⁺) 352.0922, found 352.0920.

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