First Preparation of a Sulfurane with Four Carbon–Sulfur Bonds: Synthesis and Molecular Structure of Bis(2,2′-biphenylylene)sulfurane†

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The first stable pentacoordinated sulfur compound with four carbon–sulfur bonds, bis(2,2′-biphenylylene)sulfurane **1**, is prepared and its molecular structure is determined by X-ray crystallographic analysis.

A number of hypervalent organic sulfur compounds, sulfuranes, have been prepared.[1] However, of the compounds bearing four carbon ligands only tetra(pentaflurophenyl)-sulfurane has been observed directly by ^{19}F NMR at low temperature.[2] Although the formation of sulfuranes bearing four carbon ligands has been postulated for a long period in the substitution reactions of sulfonium salts or sulfoxides with organolithium or Grignard reagents,[3] no one has ever succeeded in the detection or isolation of the compounds. Recently, we have reported the first crucial evidence for the formation of tetraphenylsulfurane as an intermediate in the reaction of triphenylsulfonium salt or diphenyl sulfoxide with phenyllithium by a low temperature NMR experiment.[4] We now report here the first synthesis and the structural characterization of a new stable sulfurane with four carbon–sulfur bonds, bis(2,2′-biphenylylene)sulfurane **1**.[5]

Compound **1** was synthesized as follows (Scheme 1). Dibenzothiophene 5-oxide (200 mg, 1.0 mmol) in anhydrous tetrahydrofuran (THF, 10 ml) was treated with trimethylsilyl trifluoromethanesulfonate (0.25 ml, 1.3 mmol) under an N_2 atmosphere at −78 °C. After stirring at 0 °C for 30 min, the mixture was cooled to −78 °C and was treated with 1.0 mol dm^{-3} 2,2′-dilithiobiphenyl‡ (1.0 ml, 1.0 mmol) in diethyl ether solution. The whole mixture was stirred at

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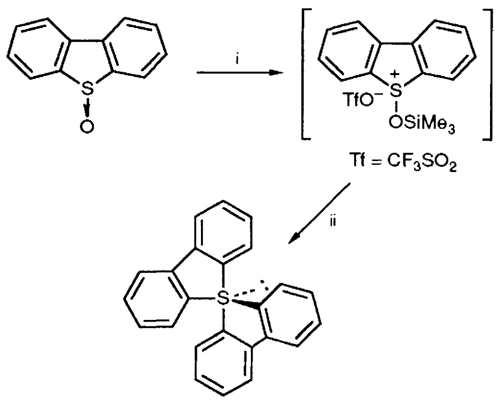
† 5,5′-Spirobi(5λ^5-benzo[*b*]thiophene).

‡ This compound was prepared by the reaction of 2,2′-diiodobiphenyl in diethyl ether with two equivalents n-butyllithium at −78 °C under an N_2 atmosphere.



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Scheme 1 *Reagents*: i, trimethylsilyl trifluoromethansulfonate in THF; ii, 2,2′-dilithiobiphenyl in diethyl ether–THF

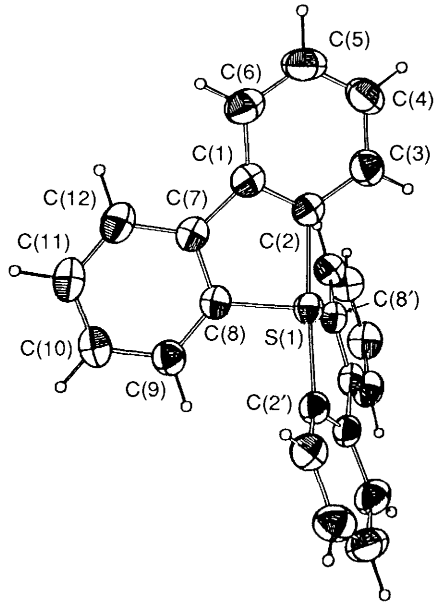

Fig. 1 ORTEP drawing of **1**. Selected bond distances (Å) and angles (°) are as follows: S(1)–C(2) and S(1)–C(2′) 1.926(2), S(1)–C(8) 1.813(2), S(1)–C(8′) 1.814(2), C(1)–C(2) 1.383(3), C(1)–C(6) 1.389(3), C(1)–C(7) 1.458(3), C(2)–C(3) 1.384(3), C(3)–C(4) 1.375(3), C(4)–C(5) 1.391(3), C(5)–C(6) 1.384(3) C(7)–C(8) 1.389(3), C(7)–C(12) 1.404(3), C(8)–C(9) 1.382(3), C(9)–C(10) 1.386(3), C(10)–C(11) 1.379(3), C(11)–C(12) 1.379(3); C(2)–S(1)–C(2′) 175.19(9), C(2)–S(1)–C(8) 86.39(8), C(2)–S(1)–C(8′) 95.96(8), C(8)–S(1)–C(8′) 121.52(9), S(1)–C(2)–C(1) 111.4(1), S(1)–C(8)–C(7) 113.7(1), C(2)–C(1)–C(7) 111.6(2), C(1)–C(7)–C(8) 114.9(2).

−78 °C for 1 h and at 0 °C for 30 min under an N_2 atmosphere. After evaporation of the solvent, the residue was washed with anhydrous diethyl ether (10 ml) and was extracted with anhydrous benzene (10 ml) under an N_2 atmosphere. The solvent was removed under reduced pressure, and the crude product was recrystallized from anhydrous THF at −20 °C to give **1** as orange rods in 96% yield.§

The structure of **1** in THF solution was characterized by NMR spectroscopy. By the ^1H and ^{13}C NMR spectra, each aryl ring of the biphenylylene was magnetically equivalent at room temperature.‡ Furthermore, these signals were unchanged at −100 °C suggesting that Berry pseudorotation[6] should take place rapidly in the NMR time scale even at low temperature, in contrast to the corresponding selenium and tellurium compounds.[7]¶

The crystal structure of **1** was confirmed by X-ray diffraction (Fig. 1).‖ The equatorial S(1)–C(8) and S(1)–(C8′) bond lengths have normal S–C values of 1.813(2) and 1.814(2) Å, respectively. The apical S(1)–C(2) bond length is 1.926(2) Å and is amongst the longest sulfur-aryl-carbon bonds ever known. The equatorial–equatorial, C(8)–S(1)–C(8′), bond angle is 121.52(9)° and is the largest ever known for the pentacoordinated sulfur compounds. The apical–apical, C(2)–S(1)–C(2′), bond angle of 175.19(9)° is approximately linear. Thus, compound **1** in the solid-state has a slightly distorted pseudo-trigonal-bipyramidal (Ψ-TBP) geometry with two apical S–C bonds, two equatorial S–C bonds, and the lone-pair electrons as the third equatorial position. The results represent the first structural characterization of a tetraorgano sulfurane consisting of two different kinds of S–C bonds.

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§ The activation energies ($\Delta G^{\ddagger}$) for pseudorotation of bis(2,2′-biphenylylene)selenurane and bis(2,2′-biphenylylene)tellurane were 13.1 and 9.2 kcal mol^{-1} (1 cal = 4.184 J), respectively.

¶ Compound **1**: m.p. 114–118 °C (decomp.); ^1H NMR (500 MHz, [$^2H_8$]THF) δ 7.23 (t, *J* 7.6 Hz, 4-ArH), 7.42 (t, *J* 7.6 Hz, 5-ArH), 7.71 (d, *J* 7.6 Hz, 3-ArH), 8.15 (d, *J* 7.6 Hz, 6-ArH); ^{13}C NMR (125 MHz, [$^2H_8$]THF) δ 122.9 (6-ArC), 127.3 (4-ArC), 128.2 (3-ArC), 128.8 (5-ArC), 134.5 (1-ArC), 148.6 (2-ArC). The chemical shifts were determined by two dimensional shift correlation (^1H–^1H- and ^{13}C–^1H-COSY) spectra. Exact mass calc for $C_{24}H_{16}S$ 336.0973, Found 336.0975; a satisfactory C and H analysis was obtained.

‖ *Crystal data* for **1**: $C_{24}H_{16}S$, M = 336.46, monoclinic, space group $C2/c$, a = 20.957(5), b = 10.372(1), c = 7.845(2) Å, β = 99.01(0)°, V = 1684.250 Å^3, D_c = 1.33 g cm^{-3}, Z = 4, $F(000)$ = 704, μ = 1.8 cm^{-1}. An orange rod-shaped crystal of dimensions 0.3 × 0.2 × 0.2 mm was used for measurements at 296 K on an Enraf-Nonius CAD4 diffractometer employing graphite-monochromated Mo-Kα radiation (λ = 0.70930 Å) using ω/2θ scan technique. The structure was solved by direct methods. 983 reflections having intensities greater than 3.0 times their standard deviation were used in the refinements. The final cycle of refinement included 138 variable parameters and converged with R = 0.031 and R_w = 0.032. All calculations were performed on a VAX computer using MolEN. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.