

Isolation and Molecular Structure of the Organo-persulfuranes [12-S-6(C6)]

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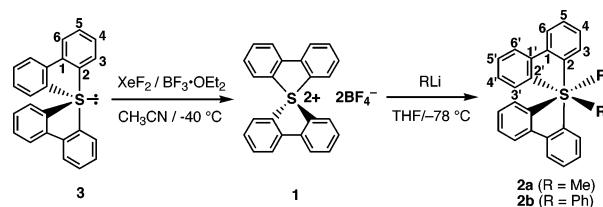
Hypervalent (hypercoordinated) compounds with unusual valences on main group elements have attracted considerable attention due to their extraordinary structure and reactivity.¹ Unlike typical stable organic compounds, hypervalent compounds do not obey the octet rule.

Recently, stable tetra- and hexacoordinated organo-chalcogen compounds (organo-chalcogenuranes and -perchalcogenuranes²) have been prepared. Strong electron-withdrawing ligands stabilize hypervalent structures that possess characteristic three-center–four-electron (3c–4e) bonds. Even organo-persulfuranes, which have two aryl ligands, can be isolated when the other four ligands are strongly electron-withdrawing.³ The stability of hypervalent compounds increases as the period number of the central atom increases. The syntheses of hexacoordinated organo-chalcogen compounds, such as persulfuranes and perselenuranes, which have only aryl or alkyl ligands, are extremely difficult, although a few organo-pertelluranes [12–Te–6(C6)] that consist of all carbon ligands have recently prepared.⁴ Schaefer et al. conducted a theoretical study on hexamethylpersulfurane (CH₃)₆S and concluded that (CH₃)₆S could be synthesized.⁵ However, organo-persulfurane [12–S–6(C6)], which contains only carbon ligands, has yet to be synthesized.

We have successfully isolated and determined the structure of bis(2,2′-biphenylene)sulfuranyl bis(tetrafluoroborate) [8–S–4(C4)]²⁺ (**1**), which is a stable organo-sulfuranyl dication that contains only carbon ligands.⁶ This unique organo-sulfur species was generated via an unstable bis(2,2′-biphenylene)difluoroper-sulfurane, which was produced by the fluorination of the corresponding sulfurane **3**.⁷ We hypothesized that **1**, which has a high electrophilicity, would be a suitable precursor to provide the desired organo-persulfurane with only carbon ligands. Indeed, the reaction of **1** with organo-lithium reagents gave bis(2,2′-biphenylene)di-C-substituted persulfurane [12–S–6(C6)] (**2**) as an amazingly stable solid. Herein, we communicate the first synthesis, isolation, and structural determination of bis(2,2′-biphenylene)dimethyl- and diphenylpersulfuranes (**2a,b**) as novel species that contain only carbon ligands.

Sulfuranyl dication **1** was treated with 2 molar equiv of methyl- and phenyllithium in dry THF at –78 °C. After removing the solvent at 0 °C, the crude product was purified by column chromatography (silica gel/CHCl₃) to give stable and moisture-insensitive colorless crystals of bis(2,2′-biphenylene)dimethyl- and diphenylpersulfurane (**2a,b**) in 7 and 53% yield, respectively. The ¹H and ¹³C NMR spectra of **2** in the aromatic region reveal that the two phenyl rings of the biphenylene groups are nonequivalent. There are four doublet and four triplet peaks in the ¹H NMR spectrum and 12 peaks in the ¹³C NMR spectrum, which are

Scheme 1. Synthesis of Persulfurane **2**



assigned to the two biphenylene ligands on the sulfur atom. Furthermore, the ¹H NMR signal of each 3′-hydrogen atom in persulfuranes (VI) **2** appears at an unusually high field [δ 6.15 (**2a**) and 6.61 (**2b**)] compared to that (δ 7.71) of bis(2,2′-biphenylene)-sulfurane **3**.⁷ This upfield shift is characteristic of the *cis* configuration as seen in *cis*-bis(2,2′-biphenylene)perchalcogenuranes, such as bis(2,2′-biphenylene)difluoroper-selenurane, bis(2,2′-biphenylene)dihaloper-tellurane, and the bis(2,2′-biphenylene) *Te*-oxide dimer.⁸ This result indicates that the aromatic ring of the neighboring biphenylene group shields the 3′-proton of **2**. Thus, **2** has an octahedral structure and a *cis* configuration with respect to the methyl or phenyl ligands. Single crystals of **2a** were formed by recrystallization from CHCl₃ at room temperature. X-ray crystallographic analysis was used to determine the novel structure of **2a**. Figure 1 shows an ORTEP plot of the molecular structure

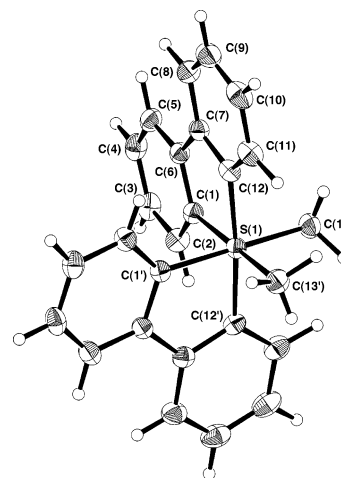


Figure 1. Labeled ORTEP drawing at the 50% ellipsoid probability level of **2a**.

of persulfurane **2a** and the adopted numbering scheme. The unit cell of **2a** consists of four [(C₁₂H₈)₂(CH₃)₂S] molecules without solvent. The racemic compound contains two types of sulfur centers. Each sulfur atom has two biphenylene ligands and two methyl ligands in the coordination sphere in both the Δ and Λ configurations. The central sulfur atom has a distorted octahedral geometry with the two methyl ligands *cis* to each other. The three S–C bond

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lengths are 1.891(2) [S(1)–C(13)], 1.919(2) [S(1)–C(12)], and 1.936(2) [S(1)–C(1)] Å, which are longer than the standard value of a S–C covalent bond (1.787 Å).⁹ The S(1)–C(12) and S(1)–C(13) bond lengths of **2a** are shorter than the S–C apical bond lengths [1.926(2) Å] of bis(2,2'-biphenylene)sulfurane (**3**).⁷ These results suggest that the 3c–4e bond of S(1)–C(12) is stronger than the corresponding apical bond in **3**. However, the length of S(1)–C(1) bond on the biphenylene plane is longer than those of the corresponding apical bond in **3**. As Mayer has suggested, the difference in length is due to the electron-donating property of the methyl group on the opposite side.¹⁰

The bond angles around the central sulfur atom range from 85.53(8) to 93.80(10)°. The three 3c–4e bonds are nearly perpendicular to each other. The bond angle of C(1)–S(1)–C(1') is equal to 89.0(1)°, which is smaller than that formed by the equatorial carbons and sulfur(IV) in sulfurane **3**. Hence, the distance between the hydrogen atoms at the 3'-position of the biphenylene groups and the aromatic ring in the other biphenylene group in **2** is shorter than that in **3**. The difference in the distance explains the shielding effect observed in the chemical shift for the protons at the 3'-position of **2** in the ¹H NMR spectrum.

Martin et al. have reported organo-persulfuranes [12–S–6(C2O2F2)] with a *cis* or *trans* configuration with regard to the two fluorine ligands and proposed that the stereoisomers interconverted via a dissociative mechanism that involves a 10–S–5 cationic intermediate.^{3d,e} In contrast, only the *cis* configuration of persulfurane **2a** is observed. The unfavorable repulsive interaction between the 3'-protons of biphenylene ligands in the *trans* configuration may have caused the exclusive formation of the *cis* isomer.

To understand the electronic structure of persulfurane **2a**, a single-point ab initio calculation was conducted using the crystal structure of **2a** at the B3LYP/6-311+G** level. The atomic charges were calculated by natural population analysis. Despite the fact that **2a** is neutral, the calculated charge of the sulfur atom in **2a** is +1.265. All the atoms directly bonded to the central sulfur atom are negatively charged (–0.175 [C(1)], –0.189 [C(12)], and –0.718 [C(13)]). Thus, the six bonds around the sulfur atom are very polar. Since the total 3d-orbital populations of sulfur are very small, 0.093 for **2a**, the 3d-orbitals are not the primary contribution to the S–C bonds. The occupancy of the 3s natural atomic orbital of sulfur in **2a** is 1.270. This contribution of the 3s-orbital and the S–C bond lengths obtained from the crystallographic data are consistent with the conclusions derived from the *extended Rundle–Musher Model* theory, which rationalizes the stability and properties of the 3c–4e bond of neutral hexacoordinated chalcogen species.^{1c,8b} These results of theoretical calculation of **2a** agree with the nature of hypercoordinated compounds reported by Schleyer et al.¹¹

The first stable persulfuranes with all carbon ligands were successfully obtained from **1**. This preparative strategy may be applicable to a variety of persulfurane derivatives, such as unsymmetrically ligated and/or chiral persulfuranes. Investigations that examine the reactivities of **2** toward nucleophiles and electron-donating species and examine the electrochemical properties are currently underway.

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Supporting Information Available: Details for synthesis, characterization, spectral data (PDF), and X-ray crystallographic file (CIF) for **2a**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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