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Evidence of Through-Space Interaction between the Sulfur and Aromatic Ring on Photolysis of 1-(Phenylthio)-9-aryldibenzothiophenes

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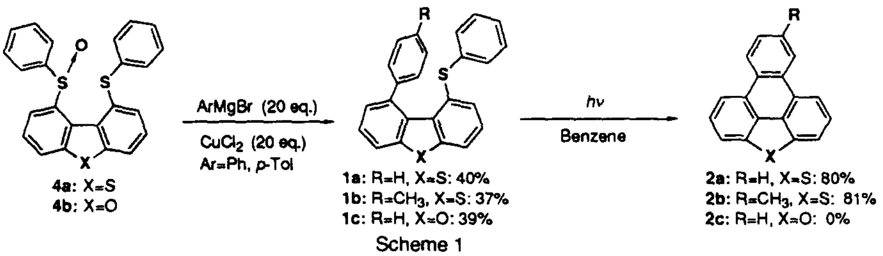
Abstract: Sterically congested 1-(phenylthio)-9-aryldibenzochalcogenophenes were prepared and photolyzed with a 400 W high pressure Hg lamp in benzene to afford triphenyleno[4,5-*bcd*]thiophenes.

A photolytic sulfur extrusion reaction of the cyclic sulfides in the presence of trialkyl phosphite has been known as a common methodology for preparation of strained molecules and cyclophanes.[1] Recently, we reported that the photolysis of 1,9-dichalcogenasubstituted dibenzochalcogenophenes (**3**) proceeded without trialkyl phosphite via concomitant dechalcogenization and cyclization reactions to produce dibenzo-[*bc,fg*][1,4]dichalcogenapentalenes and triphenyleno[4,5-*bcd*]chalcogenophenes.[2,3] Furthermore, it was revealed that this photolytic cyclization reaction of compounds **3** depends significantly on the distance between their two heteroatoms at the 1, 9 positions. Since a photolysis of 1,9-bis(phenylthio)dibenzothiophene (**3a**) was found to give a small amount of monodesulfurized product together with triphenyleno[4,5-*bcd*]thiophene (**2a**) and tribenzo[*bc,e,hi*][2,7]dithiaazulene, it is important to determine whether 1-(phenylthio)-9-phenyldibenzothiophene (**1a**) is an intermediate of the photolysis of **3a**, and to verify the effect of through-space interaction between the heteroatom and π-electrons of the aryl group in the photolytic reaction. Accordingly, 1-(phenylthio)-9-aryldibenzochalcogenophenes (**1**) were prepared and photolyzed with a 400 W high pressure Hg lamp. This communication describes the evidence of the effect of through-space interaction between the sulfur and the aryl group on photolysis of compounds **1**.



Scheme 1

Typically, compound **1a** was prepared as a colorless liquid in 40% yield from 1-(phenylsulfinyl)-9-(phenylthio)dibenzothiophene (**4a**) on treatment with PhMgBr and anhydrous $CuCl_2$ in THF under argon (Scheme 1). The compound **1a** was found to be unstable in a chloroform solution as compared with **3a** which has two sulfur atoms in close proximity at 1, 9 positions, and to decompose gradually without shielding to produce **2a**. Hence, compound **1a** was irradiated with a high pressure Hg lamp in benzene under argon for 10 h to produce **2a** in 80% yield. 1-(Phenylthio)-9-(*p*-tolyl)dibenzothiophene (**1b**) and 1-(phenylthio)-9-

phenyldibenzofuran (**1c**) were obtained by a similar procedure as colorless crystals from **4a** and 1-(phenylsulfinyl)-9-(phenylthio)dibenzofuran (**4b**), respectively (Scheme 1).[4] Whereas the photolysis of **1b** gave 9-methyl triphenyleno[4,5-*bcd*]thiophene (**2b**) in 81% yield, the photolysis of **1c** did not proceed at all, suggesting that the through-space interaction between the sulfur atom and the phenyl group of **1c** is weak as compared to that of **1a,b**, because of the shorter distance of the O-C bond of dibenzofuran ring than that of the S-C bond of dibenzothiophene ring.[3,5]

The structure of **1b** was determined by X-ray crystallographic analysis (Figure 1). The torsional angle of **1b** is 19.9° at the C_5-C_6-C_{16}-C_{15} positions revealing that the central dibenzothiophene ring is considerably distorted from the usual planar form due to steric repulsion between the sulfur atom and *p*-tolyl group attached at the 1, 9 positions. The dihedral angle between the dibenzothiophene and *p*-tolyl ring at C_{15}-C_{21} positions is 150.58° and the length of C_{15}-C_{21} bond is 1.499 Å. Interestingly, the distance between S_2 and C_{21} atoms at the 1, 9 positions is 2.99 Å which is rather shorter than the van der Waals contact of a carbon and a sulfur atom (S-C: 3.55 Å).[5]

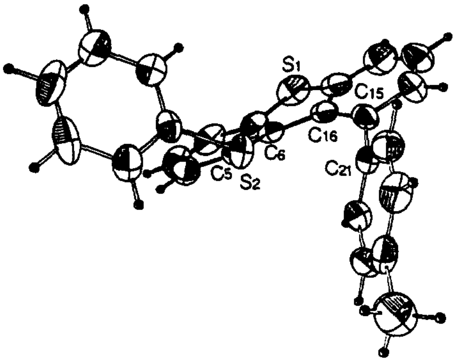


Figure 1. The ORTEP Drawing of **1b**.

Furthermore, the oxidation potential and the λ_{max} values of UV spectra of **1b** and **1c** explain the different reactivities of these two compounds as well as those of **3a** and 1,9-bis(phenylthio)dibenzofuran:[3] the oxidation potential (Ep): **1b**, 0.96 V; **1c** 1.06 V;[6] λ_{max} (CH_2Cl_2): **1b** (361 nm); **1c** (329 nm). These results indicate that the through-space interaction exists between the sulfur atom and the *p*-tolyl group of **1b** and accelerates the photolytic cyclization reaction of **1b**. Further investigation of this photolytic reaction is in progress in this laboratory.

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References and Notes

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4. **1b**: mp 152.5-153.5 °C ^{1}H-HMR (500 MHz, $CDCl_3$) δ 2.44 (s, 1H), 6.78-6.81 (m, 2H), 7.03-7.07 (m, 3H), 7.14 (dd, J=7.9, 1.0 Hz, 1H), 7.24 (d, J=8.0 Hz, 2H), 7.25 (t, J=7.9 Hz, 1H), 7.32 (d, J=8.0 Hz, 2H), 7.41 (dd, J=7.5, 1.0 Hz, 1H), 7.50 (t, J=7.5 Hz, 1H), 7.71 (dd, J=7.9, 1.0 Hz, 1H); MS (m/z) 382 (M^+); Anal. Calcd for $C_{25}H_{18}S_2$: C, 78.49; H, 4.74. Found: C, 78.50; H, 4.67; the crystal data: orthorhombic, Aba2, a=18.575 (1) Å, b=16.624 (2) Å, c=12.542 (1) Å, v=3872.7 Å^3, Z=8, ρ=1.31 g/cm^3, μ(Mo-Kα)=2.7 cm^{-1}, R=0.036 (Rw=0.036).
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6. Measurement of oxidation potential for **1b** and **1c** was carried out by cyclic voltammetry using Ag/(0.01 M)$AgNO_3$ as a reference electrode in acetonitrile at 25 °C (scan rate: 200 mV/s).

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