STRUCTURES OF STERICALLY ENCUMBERED 1,9-BIS(ARYLTHIO)-DIBENZOTHIOPHENES AND DETECTION OF THEIR DITHIA DICATIONS IN CONCENTRATED SULFURIC ACID BY ^{1}H-NMR

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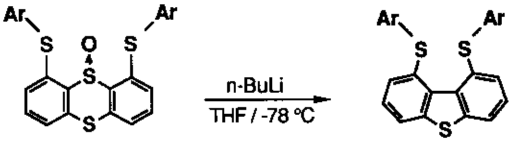
Abstract - 1,9-Bis(arylthio)dibenzothiophenes (**1**) and their monooxides (**2**) were prepared and the structures of the phenyl derivatives (**1a**) and (**2a**) were determined by X-ray crystallographic analysis. The dithia dications (**3**) were generated on dissolution of compounds (**1**) and (**2**) in concentrated sulfuric acid-d_2 and their structures were characterized by ^{1}H-nmr spectroscopy.

Dithia dications are of considerable interests because of their unusual bonding modes and reactivities as electron-acceptors.[1] Recently, we found a convenient preparation of sterically congested 1,9-dithiodibenzothiophenes (**1**) in which the two outer sulfur atoms are close together and hence interact transannularly.[2] Therefore, these compounds may provide new sources for encumberd dithia dications by treating with appropriate oxidants. This paper reports the X-ray crystallographic analysis of 1,9-bis(phenylthio)dibenzothiophene (**1a**) and its monooxide (**2a**). The formation of dithia dications of **1a-e** in conc. D_2SO_4 by the ^{1}H-nmr studies is also presented.

1,9-Bis(arylthio)dibenzothiophenes (**1a-e**) were prepared by the intramolecular ring contraction (ligand coupling



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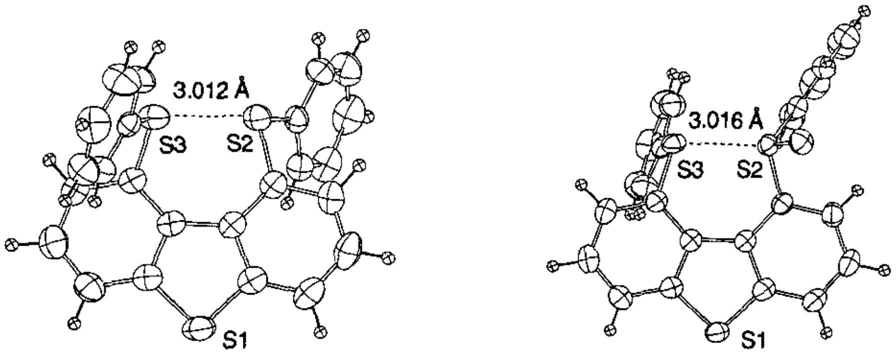
1a :Ar = Ph : 65%
1b : *o*-Tol : 53%
1c : *m*-Tol : 56%
1d : *p*-Tol : 63%
1e : 3,5-Xylyl : 55%

Scheme 1

This paper is dedicated to Prof. M. Hamana for his 75 years birthday.

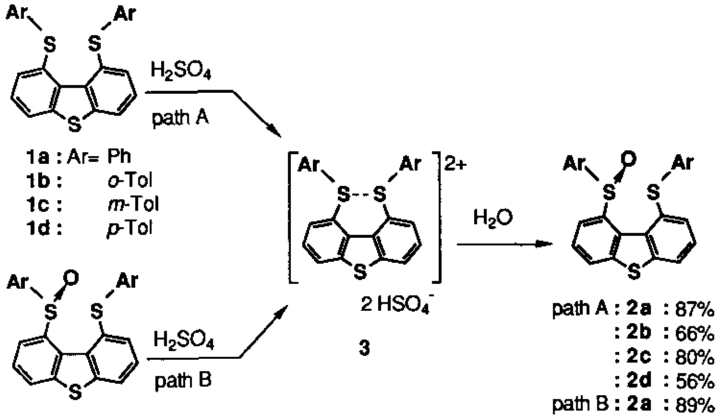


1a Figure 1 **2a**

reaction[3]) of the corresponding 4,6-disubstituted thianthrene-5-oxides with n-butyllithium (Scheme 1),[2,4] and then were oxidized with an equimolar amount of *m*-chloroperbenzoic acid (mCPBA) to afford the monooxides (**2**) in good yields. The structural analysis of compounds (**1a**) and (**2a**) were performed by X-ray crystallographic analysis (Figure 1).[5] The molecular structure of **1a** indicates that the central thiophene ring is considerably distorted due to the steric repulsion between the two phenylthio groups attached at the C_1 and the C_9 atoms but the distance between the two sulfur atoms is 3.012 Å which is within van der Waals contact (3.70 Å).[6] The two phenyl rings are located at anti orientation and are close to the dibenzothiophene ring. The structure of sulfoxide (**2a**) indicates that the dibenzothiophene skeleton is roughly the same and the S-S contact is also 3.016 Å and the O-S_2-S_3 angle is 158.8 ° suggesting that both the sulfenyl and the sulfinyl sulfur atoms interact transannularly. The ^{1}H-nmr spectra of the S-phenyl rings of **1a** and **2a** appear at **1a**: 6.95-7.01 (*o*-H) and 7.06-7.16 (*m,p*-H); **2a**: 6.76 (*o*-H, PhS), 7.04-7.13 (*m,p*-H, PhS), 7.29-7.38 (*m,p*-H, PhSO), 7.63-7.68 (*o*-H, PhSO). Other derivatives of **1** and **2** also have the likely chemical shifts to **1a** and **2a**. The transannular bond formation between the two sulfur atoms in the phenylthio groups in **1a** would be supported by the lower oxidation potential (0.86 V) as compared to dibenzothiophene (1.31 V).[7]

In order to generate the dithia dications (**3**) the sulfides (**1**) and sulfoxides (**2**) were dissolved in conc. D_2SO_4 and their ^{1}H-nmr spectra were measured according to our procedures employed previously.[1] The identical ^{1}H-nmr spectra were observed by dissolving either **1** or **2** in conc. D_2SO_4. Either the H_2SO_4 solution of **1** or **2** gave the corresponding sulfoxide in good yield after hydrolysis of the solution demonstrating that the dication (**3**) should be formed (Scheme 2).[8]

On dissolution of **1a** and **2a** in conc. D_2SO_4, unexpectedly, broadening of the phenyl protons attached to the phenylthio groups in the ^{1}H-nmr spectra of the dication (**3a**) was observed and the two protons shift to upfield at 5.89 ppm (2H) as a broad singlet together with 6.93 ppm (2H), 7.18 ppm (4H) and 7.61 ppm (2H) respectively (Figure 2).[9] The signal at 5.89 ppm is attributed to the two ortho-protons at the phenylthio group since in the



Scheme 2

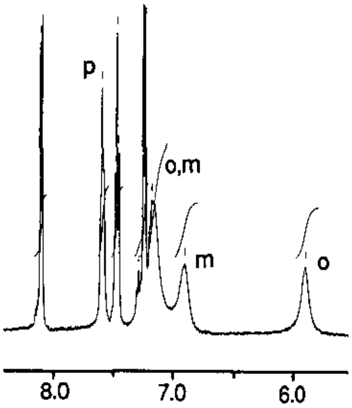


Figure 2. 500 MHz ^{1}H-nmr spectra of dication (**3a**) in D_2SO_4.

signals of **2d** (Ar=*m*-Tol) and **2e** (Ar=3,5-Xylyl) in D_2SO_4 only the shifts at 5.89, 7.18 and 7.61 ppm are remained unchanged. The signal at 7.61 ppm (t, J=7.5 Hz, 2H) is determined to be the para-protons due to the disappearance of this signal from **2d** (Ar=*p*-Tol). Thus the remaining four protons at 7.18 and 6.93 ppm are assigned to be the meta-protons. Furthermore, 1,9-bis(*o*-deuterated phenylthio)dibenzothiophene (**1a**-d_2) was synthesized and was dissolved in conc. D_2SO_4 for measurement of the ^{1}H-nmr. In the spectrum, the peak areas correspnding to two protons decreased from 5.89 and 7.18 ppm indicating that the assignment of the ^{1}H-nmr of the dication (**3a**-d_2) in D_2SO_4 is reasonable. The ^{1}H-nmr spectra of **1a** and **2a** indicate clearly that the two phenyl rings at the sulfur atoms tend to overhang to the dibenzothiophene ring and the protons at the *o*- and *m*-positions are magnetically non-equivalent in the dithia dication (**3a**). Other substituted dibenzothiophenes (**1b**-**e**) show the identical ^{1}H-nmr behaviors, particularly, in 3,5-xylyl derivative (**1e**) two sharp methyl singlets appeared in the spectrum. These results demonstrate that the free rotation of the S-C (phenyl) bond should be restricted or pyramidal inversion at the sulfonium sulfur atoms in **3** does not take place at 27 °C. The broadening of the ^{1}H-nmr by the presence of cation radical may be eliminated since in the reaction of **2a** in D_2SO_4 does not exhibit esr absorption.[10] Dithia dication (**3a**) is unusually stable in conc. H_2SO_4 even at 70 °C for several hours. By elevating the temperature, the two ortho-protons coalesced at 67 °C into a singlet at 6.56 ppm. The spectrum was recovered back to the original one by lowering the temperature to 27 °C. Thus, the spectrum change by varying the temperature is attributed to the free rotation of the phenyl rings and the free energy of the rotation is calculated to be $\Delta G^{\ddagger} = 63$ kJmol^{-1} at 67 °C.

The present system becomes a new alternative process for generation of dithia dications. Elucidation of the crystalline structure of **3** is now in progress.

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RFERENCES AND NOTES

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2. N. Furukawa, T. Kimura, Y. Horie, and S. Ogawa, Heterocycles, 1991, 32, 675.
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4. **1b** (Ar=*o*-Tol); mp 126 °C; 500 MHz ^{1}H-nmr ($CDCl_3$) δ 7.73 (dd, J_1=7.8 Hz, J_2=1.2 Hz, 2H, Ar-H), 7.37 (dd, J_1=7.8 Hz, J_2=1.2 Hz, 2H, Ar-H), 7.34 (t, J=7.8 Hz, 2H, Ar-H), 7.08-6.30 (m, 8H, Ar-H) 2.06 (s, 6H, CH_3); ir (KBr) 1446, 1388, 741, 704 cm^{-1}; ms (m/z) 428 (M^+); Anal. Calcd for $C_{26}H_{20}S_3$: C, 72.85; H, 4.70. Found: C, 72.99; H, 4.74.
5. Crystal date for **1a**; $C_{24}H_{16}S_3$, monoclinic, space group $P2_1/n$, a=17.862(2), b=8.050(2), c=13.594(2) Å, β=95.74(1)°, V=1938.4(5) Å^3, z=4, D_x=1.373 gcm^{-3}, μ (Mo-kα)=0.372 mm^{-1}, R=0.0526 ($_w$R=0.0744); **2a**; $C_{24}H_{16}S_3O$, monoclinic, space group $P2_1/n$, a=9.972(4), b=8.835(4), c=21.915(9) Å, β=92.21(4)°, V=1929.4(1) Å^3, z=4, Dx=1.434 gcm^{-3}, μ (Cu-kα)=3.546 mm^{-1}, R=0.028 ($_w$R=0.027).
6. I. Hargittai and B. Rozsondai, 'The Chemistry of Organic Selenium and Tellurium Compounds Volume 1,' ed. by S. Patai and Z. Rappoport, John Wiley and Sons, New York, 1986, p. 63.
7. Cyclic voltammetry was measured using Ag/(0.01 M) $AgNO_3$ as a reference electrode (scan rate: 200 mV/s) at 25 °C in acetonitrile.
8. **2b** (Ar=*o*-Tol); mp 197 °C; 500 MHz ^{1}H-nmr ($CDCl_3$) δ 8.02 (d, J=7.9 Hz, 1 H, Ar-H), 7.90 (d, J=7.9 Hz, 1H, Ar-H), 7.85 (d, J=7.8 Hz, 1H, Ar-H), 7.81 (d, J=7.8 Hz, 1H, Ar-H), 7.59 (t, J=7.9 Hz, 1H, Ar-H), 7.49 (d, J=7.0 Hz, 1 H, Ar-H), 7.42 (t, J=7.8 Hz, 1H, Ar-H), 7.28-7.19 (m, 2H, Ar-H), 7.10-7.03 (m, 2H, Ar-H), 7.00-6.94 (m, 2H, Ar-H), 6.64 (d, J=7.8 Hz, 1H, Ar-H), 2.07 (s, 3H, CH_3), 1.83 (s, 3H, CH_3); ir (KBr) 1021 cm^{-1}; ms (m/z) 444 (M^+); Anal. Calcd for $C_{26}H_{20}OS_3$: C, 70.23; H, 4.53. Found: C, 70.05; H, 4.45.
9. Fast atom bombardment (FAB) mass spectrum of dication (**3a**) was measured by JEOL JMX-SX102: (m/z) 595 (MH^+), 497 ($(M-HSO_4^-)^+$).
10. The esr spectra of **1a** was observed in conc. H_2SO_4 as one broad singlet with g= 2.0058 and then the signal was degraded gradually. Very weak signal was obtained initially for **2a** in similar condition. On the other hand ^{1}H-nmr spectra of **1a** and **2a** in D_2SO_4 were not changed for one week.

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