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FIRST PREPARATION OF DIBENZO[*bc,fg*][1,4]DITHIAPENTALENE AND DETERMINATION OF THE STRUCTURE BY X-RAY ANALYSIS

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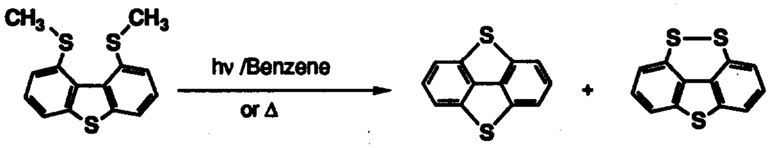
Abstract: New stable dibenzo[*bc,fg*][1,4]dithiapentalene (1) was prepared by heating 1,9-bis(methylthio)-dibenzothiophene in a glass tube. The X-ray analysis of 1 reveals clearly that it has a completely planar structure. Repeated scanning of cyclic voltammetry of 1 shows an analogous voltammogram with that of polythiophene.

There are four isomeric thienothiophenes among which thieno[3,4-*c*]thiophene, called nonclassical thiophene, is somewhat unstable since it must use unusual bonding orbitals of the sulfur atoms to accommodate 10π electrons for resonance stabilization.[1] Several stable thieno[3,4-*c*]thiophenes bearing four substituents such as tetraphenylthieno[3,4-*c*]thiophene (5) have been reported.[2] As a new stable thieno[3,4-*c*]thiophene derivative, we found that dibenzo[*bc,fg*][1,4]dithiapentalene (1),[3] the dithio analog of dibenzo[*cd,gh*]pentalene which was prepared by Trost and his co-workers,[4] was obtained serendipitously upon thermolysis or photolysis of 1,9-bis(methylthio)dibenzothiophene (3).[5] This communication reports the results of the first preparation of a new stable dithiapentalene (1) and determination of the structure by X-ray crystallographic analysis.

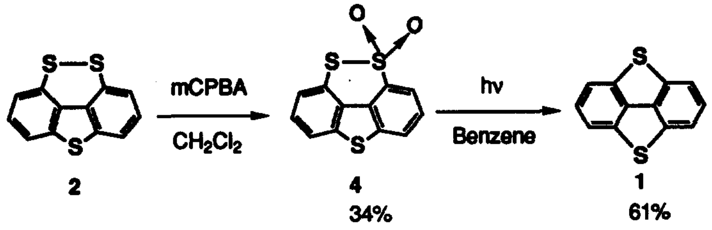


3

Photolysis : 1 11% 2 16%
Thermolysis : <1% 61%

Scheme 1

When 3 was placed in a long pyrex tube and heated gently with a burner flame, dithiapentalene (1) (<1%) was obtained together with thieno[2,3,4,5-*lmn*][9,10]dithiaphenanthrene (2) (61%) after purification with column chromatography and preparative HPLC.[6,7] However, photolysis of 3 with a 400 W high-pressure mercury lamp for 10 h gave 1 and 2 in 11% and 16% yields respectively (Scheme 1). Interestingly, it was found that the photolysis of thiosulfonate (4) which was prepared by oxidation of 2 with *m*-chloroperbenzoic acid (mCPBA)[8] proceeded cleanly under irradiation for 72 h to afford **1** as the sole product in 61% yield together with the recovered **4** in 33% yield (Scheme 2).[9]



Scheme 2

The UV spectrum of pentalene **1** lacks the visible band at around 530 nm observed in tetraphenylthieno[3,4-*c*]thiophene (**5**) corresponding to the biradical structure,[1b] which suggests that the pentalene **1** should have neither a biradical nor a charged structure and the character of **1** was different from that of **5**. Therefore, X-ray crystallographic analysis of **1** was performed and the structure was shown in Figure 1.[10] The result indicates clearly that pentalene **1** is a completely planar molecule belonging to the point group D_{2h}. The C-S bonds of the thiophene rings are 1.791 and 1.792 Å which are considerably longer than those of **5** (1.706 Å).[1b] Furthermore, the benzene rings of **1** are considerably distorted (C_1-C_3-C_4*, 128.5 °; C_2-C_1-C_3, 116.1 °; C_1-C_2-C_5, 116.8 °; C_2-C_5-C_6*, 125.7 °) from those of a normal hexagonal structure. The bond length of C_3-C_3* (1.386 Å) is shorter than that of **5** (1.452 Å) suggesting that the two benzene rings are stabilized by conjugation and the two sulfur atoms participate less in the essential π-conjugation than the usual thiophene ring.

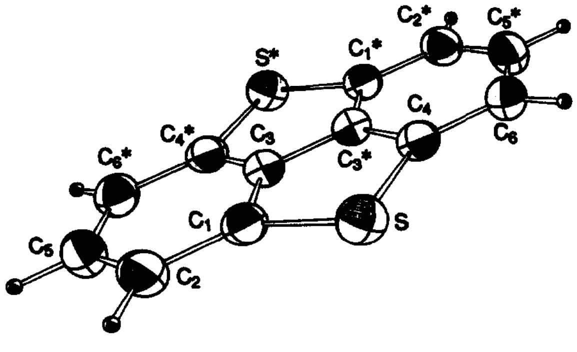


Figure 1. X-Ray Crystallographic Analysis of 1.

Since the electrochemical characters of **1** would be attractive properties, the oxidation potentials of **1** and **2** were measured with cyclic voltammetry in acetonitrile at 20 °C, using a Pt electrode, Ag/0.01 M $AgNO_3$ as a reference electrode (electrolyte: 0.1 M $NaClO_4$; scan rate: 200 mV/s). The oxidation potentials of these compounds are listed as follows: **1** (E_p=1.16 V, irreversible); **2** ($E_{1/2}$=0.91 V, reversible); dibenzothiophene (E_p=1.31 V, irreversible).[11] The cyclic voltammogram of **1** after 20 repeated scannings reveals nearly the same behavior of polythiophene on electrolysis (Figure 2).[12] Actually, the electrode was found to be coated with a yellow compound but the structure has not been determined. Investigation into the chemical properties of **1** is underway.

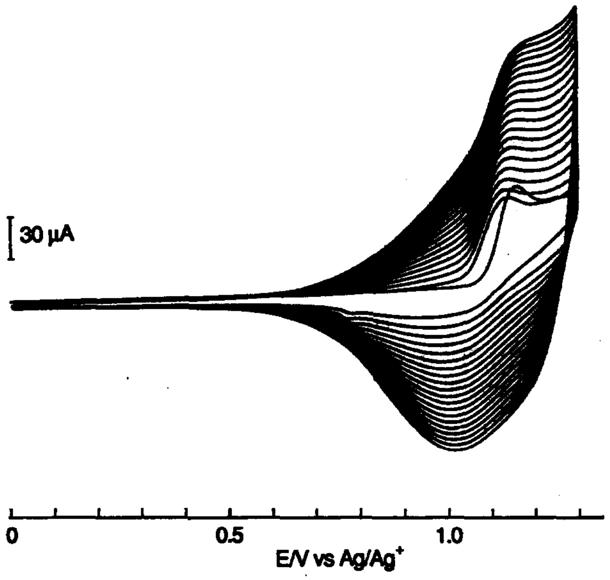


Figure 2. Cyclic Voltammogram of 1 (0.82 mM) after 20 Times Scannings in CH_3CN at 20 °C (Using Pt Electrode, Ag/0.01 M $AgNO_3$ as Reference Electrode; Electrolyte: 0.1 M $NaClO_4$; Scan Rate: 200 mV/s).

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6. **1**: mp 165 °C (sublimed); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.73 (d, J=7.7 Hz, 4H, Ar-H), 7.60 (t, J=7.7 Hz, 2H, Ar-H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 141.6, 135.7, 128.3, 116.2; MS (m/z) 214 (M^+); UV (CH_3CN) λ_{max} nm (ε) 243 (32000), 270 (4300), 329 (1900); Anal. Calcd for $C_{12}H_6S_2$: C, 67.25; H, 2.82. Found: C, 67.34; H, 2.90; **2**: mp 132.5-133 °C (lit 126 °C)[7]; ^{1}H-NMR (270 MHz, $CDCl_3$) δ 7.71 (d, J=7.9 Hz, 2H, Ar-H), 7.40 (t, J=7.9 Hz, 2H, Ar-H) 7.25 (d, J=7.9 Hz, 2H, Ar-H); MS (m/z) 246 (M^+).
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8. **4**: mp 220-221; ^{1}H-NMR (270 MHz, $CDCl_3$) δ 8.17 (dd, J_1=8.1 Hz, J_2=0.5 Hz, 1H, Ar-H), 8.03 (dd, J_1=7.6 Hz, J_2=0.5 Hz, 1H, Ar-H), 7.94 (dd, J_1=8.1 Hz, J_2=0.5 Hz, 1H, Ar-H), 7.78 (t, J=8.1 Hz, 1H, Ar-H), 7.62 (t, J=7.6 Hz, 1H, Ar-H), 7.49 (dd, J_1=7.6 Hz, J_2=0.5 Hz, 1H Ar-H); ^{13}C-NMR (67 MHz, $CDCl_3$) δ 141.3, 140.9, 137.2, 130.9, 128.4, 127.9,127.7, 127.0, 126.8, 123.7, 122.3, 115.5; IR (KBr) 1317, 1149 (SO_2) cm^{-1}; MS (m/z) 278 (M^+); Anal. Calcd for $C_{12}H_6O_2S_3$: C, 51.78; H, 2.17. Found: C, 51.68; H, 2.22.
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10. The Crystal Data for **1**; $C_{12}H_6S_2$, Monoclinic, Space Group $P2_1/c$, a=7.641(1) Å, b=4.000(0) Å, c=14.909(2) Å, β=95.23(6) °, V=453.8 Å^3, z=2, D_x=1.57 g/cm^3, μ(Mo-Kα)=5.1 cm^{-1}, R=0.029 (R_w=0.033), (temp. 23±1 °C); Bond Lengths (Å): S-C_1, 1.791(2); S-C_4, 1.790(2); C_1-C_3, 1.377(3); C_4-C_3*, 1.375(3); C_3-C_3*, 1.386(3); C_1-C_2, 1.397(3); C_4-C_6, 1.395(3); C_2-C_5, 1.399(4); C_5-C_6*, 1.406(4). Bond Angles (deg.): C_1-S-C_4, 92.3(1); S-C_1-C_3, 108.0(2); C_1-C_3-C_3*, 115.7(2); C_3-C_3*-C_4, 115.8(2); S-C_4-C_3*, 108.1(2); S-C_1-C_2, 135.8(2); S-C_4-C_6, 135.8(2); C_3*-C_4-C_6, 116.1(2); C_4-C_6-C_5*, 116.8(2). The Partial Torsional Angles (deg.): C_4-S-C_1-C_2, 179.94(29); C_4-S-C_1-C_3, 0.26(20); C_1-S-C_4-C_6, 179.81(28); S-C_1-C_2-C_5, -179.79(22); C_3-C_1-C_2-C_5, -0.08(35).
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