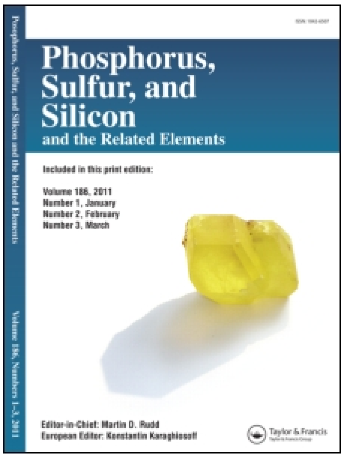

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HIGH-SYMMETRY CHIRAL ORGANOSULFUR COMPOUNDS: 6,7-DITHIO-DIBENZO[*c*,*e*][1,2]DITHIIN AND 5,6-DITHIO-DIBENZOTHIOPHENE

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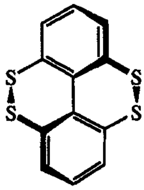
The title organosulfur compounds **1** and **2** were prepared via Newman-Kwart rearrangment of the tetrathiocarbamate of 2,2′,6,6′-tetrahydroxybiphenyl. The 2,2′,6,6′-tetramercaptobiphenyl **3a**, hitherto unknown, is not stable and it oxidizes easily to the bisdisulfide **1**. An X-ray crystallographic analysis of **1** is reported.

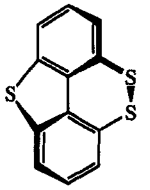
Key words: High symmetry chiral organosulfur compounds; 6,7-dithiodibenzo[*c*,*e*][1,2]dithiin, X-ray of; 5,6-dithio-dibenzothiophene; 2,2′,6,6′-tetramercaptobiphenyl.

The tetrathiol **3a** can be used as a ligand and as precursor of a number of chiral organosulfur reagents of D_2-symmetry, similarly to those recently reported by us based on the binaphthyl skeleton.[1] Here, we describe the synthesis of its bis(disulfide) **1**[2] which arised when we attempted to generate **3a** with the same method used for the preparation of 1,1′-dibenzo-2,2′-dithiol[3] or 1,1′-dinaphtho-2,2′-dithiol.[4]

Generation of the tetraalkoxy anion of tetrahydroxybiphenyl **3b**[5] with sodium hydride in dimethylformamide (DMF) and its treatment with dimethylthiocarbamoyl chloride afforded modest yield of the tetracarbamoyl derivative **3c**. The latter, upon thermolysis underwent Newman-Kwart rearrangement to the tetratransposed



1



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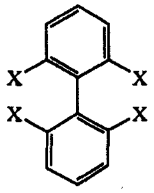

3a (X = SH)
3b (X = OH)
3c [X = OC(S)NMe$_2$]
3d [X = SC(O)NMe$_2$]
3e (X = Br)

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‡ Author to whom inquiries concerning the X-ray crystal structure analysis should be directed.

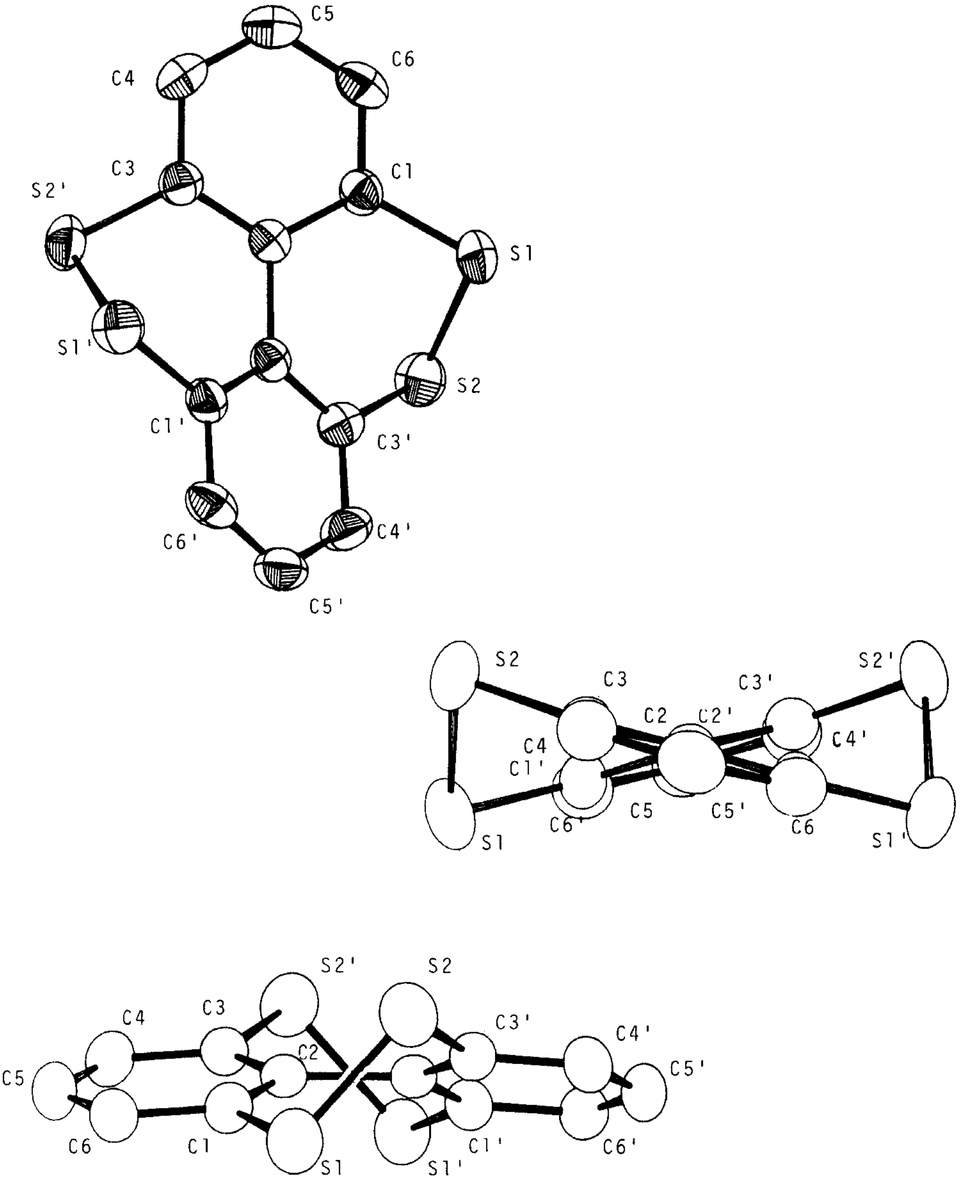
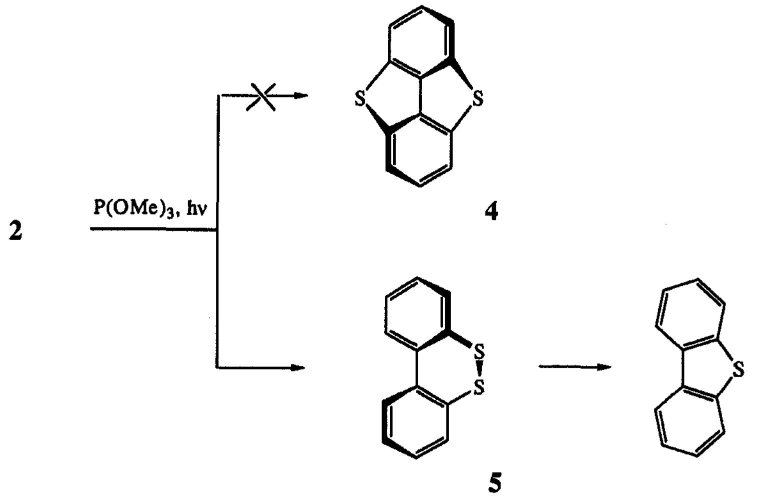


FIGURE 1 ORTEP drawing of **1** from three different perspectives. Hydrogen atoms have been omitted.

isomer **3d**. During the thermolysis, substantial quantities of the compound **2** were also produced. The mechanism with which this transformation occurs is still unclear but it is possible that **2** arises from a radical process. Upon hydrolysis of **3d** with potassium hydroxide and standard work up, the bisdisulfide **1** was obtained in 64% yield. The expected tetrathiol was not observed even though, under identical reaction conditions, related molecules afford the mercapto derivatives.[1,2] Reduction



of **1** with lithium aluminium hydride led to disappearance of the yellow color of **1**, but the isolation of **3a** from the reaction mixture was so far unsuccessful leading only to recovery of the starting material.

Figure 1 shows the ORTEP representation of **1** from three different perspectives. In the crystal state the molecule possesses a C_2 symmetry and not the expected D_2 symmetry. In fact, the carbon atoms at the positions 1 and 4 [C(2) and C(5) in Figure 1] of the two phenyl rings are not in line but bent with an angle of 4.73°. The dyhedral angle between the two phenyl groups is of 29.92°. In other words the molecule in its crystal state does not contain an inversion center, but only a C_2 symmetry axis.

Attempts to desulfurize **2** to the bisthiophene **4**, isoelectronic with pyrene, with trimethylphosphite and UV light[6] gave the disulfide **5** instead.

Other methods of preparation of **1** or **3a** based upon alogen substitution on **3e** with thio derivatives[7] or coupling of 2,6-dithiosubstituted benzenes[8] have been so far unsuccessful.

EXPERIMENTAL

Melting points are uncorrected. ^{1}H NMR spectra were recorded on a Varian VXR300 at 300 MHz or a Varian EM360A spectrometers at 60 MHz. IR spectra were recorded on a Perkin-Elmer 983 spectrophotometer. Microanalysis were performed by Mr. Antonello Canu in the Department of Chemistry of the University of Sassari.

2,2′,6,6′-Tetra(N,N′-dimethylthiocarbamoyloxy)biphenyl **3c**. Sodium hydride (6.45 g, 161.3 mmol of a 60% dispersion in mineral oil) was added under nitrogen, in portions at 0°C during 30 min, to a solution of 2,2′,6,6′-tetrahydroxybiphenyl **3b** (8.0 g, 36.7 mmol) in dry DMF (135 mL). After 3.5 h at room temperature, dimethylthiocarbamoyl chloride (20 g, 161.8 mmol) was added and the reaction mixture was kept stirring at room temperature overnight then heated to reflux for 24 h. After cooling, the reaction mixture was poured into 800 mL of 1% aqueous potassium hydroxide. The solid which separated was filtered and washed with water, dissolved in dichloromethane and made neutral with 5% hydrochloric acid. The organic phase was finally dried over sodium sulfate and concentrated under vacuum to give a solid which was recrystallized from dichloromethane-ethanol: 3.8 g (18% yield), mp 248°C. ^{1}H-NMR ($CDCl_3$, TMS) δ (ppm): 2.97 (12H, s), 3.22 (12H, s), 7.27–7.41 (6H, m). IR (KBr disk): 2929, 1602, 1531, 1448, 1412, 1393, 1297, 1285, 1263, 1225, 1165, 1135, 797, 785, 750, 733 cm^{-1}. Elem. Anal (Calcd for $C_{24}H_{30}O_4N_4S_4$): C, 50.72 (50.86); H, 5.20 (5.33); N, 9.70 (9.88).

2,2′,6,6′-Tetra(N,N′-dimethylcarbamoylthio)biphenyl **3d** *and 5,6-dithiodibenzothiophene* **2**. The tetrathiocarbamoyl derivative **3c** (1g, 1.76 mmol) into a 50-mL Pyrex test tube was heated under nitrogen at 250–255°C for 40 min. The crude reaction mixture was dissolved in dichloromethane and flash-cromathographed on silica gel eluting with a dichloromethane-ethyl acetate gradient. There were eluted sequentially 0.2 g (47% yield) of **2** and 0.55 g (55% yield) of **3d**.

2. mp 126 °C (benzene). ^{1}H-NMR (CDCl$_3$, TMS) δ (ppm): 7.25 (2H, d, J = 9.0 Hz), 7.40 (2H, t, J = 9.0 Hz), 7.70 (2H, d, J = 9.0 Hz). IR (KBr disk): 2931, 1564, 1406, 1396, 1312, 1173, 762, 701 cm^{-1}. Elem. Anal (Calcd for $C_{12}H_6S_3$): C, 58.27 (58.50); H, 2.33 (2.45).

TABLE I

Crystal structure parameters for **1**.

formula	$C_{12}H_6S_4$
FW	278.4
crystal system	orthorhombic
space group	Pbcn (N. 60)
a, Å	10.355(1)
b, Å	7.085(1)
c, Å	15.189(2)
V, Å^3	1114.3(2)
Z	4
D_{calc}, g/cm^3	1.66
F(000)	568.00
$\mu_{calc.}$,cm^{-1}	7.37
diffractometer	Philips PW1100
radiation	MoKα (λ = 0.7107 Å)
scan type	ϑ–2ϑ
2θmax, deg	56°
unique reflections	1342
observed reflections with $F>7\sigma(F)$	1027
no. of variables	85
R	0.035
Rw [$w = 1/\sigma^2(F) + 0.0006F^2$]	0.042
highest map residual e/A^3	0.37

TABLE II

Positional parameters and equivalent isotropic thermal parameters for **1**. U_e is defined as one third of the trace of the orthogonalized U_{ij} tensor.

atom	x	y	z	U_e
S(1)	0.46860(7)	0.2583(1)	0.43057(4)	0.0493(3)
S(2)	0.034689(7)	0.0435(1)	0.39529(4)	0.0500(2)
C(1)	0.5944(2)	0.2041(3)	0.3559(1)	0.0351(7)
C(2)	0.5669(2)	0.1574(3)	0.2679(1)	0.0304(6)
C(3)	0.6757(2)	0.1172(4)	0.2148(1)	0.0355(6)
C(4)	0.8009(2)	0.1301(4)	0.2467(2)	0.0440(9)
C(5)	0.8227(3)	0.1826(4)	0.3333(2)	0.0479(9)
C(6)	0.7200(3)	0.2181(4)	0.3874(2)	0.0443(8)

TABLE III

Bond lenghts (Å) and angles (deg) for **1** (e.s.d.).

S(1)-S(2)	= 2.047(1)	S(1)-C(1)	= 1.769(2)
C(1)-C(2)	= 1.407(3)	C(1)-C(6)	= 1.389(4)
C(2)-C(2')	= 1.488(3)	C(2)-C(3)	= 1.414(3)
C(3)-C(4)	= 1.388(3)	C(4)-C(5)	= 1.385(4)
C(5)-C(6)	= 1.366(4)		
S(2)-S(1)-C(1)	= 97.1(1)	S(1)-C(1)-C(6)	= 117.0(2)
S(1)-C(1)-C(2)	= 120.8(2)	C(2)-C(1)-C(6)	= 122.2(2)
C(1)-C(2)-C(3)	= 115.4(2)	C(1)-C(2)-C(2')	= 122.4(2)
C(2')-C(2)-C(3)	= 122.2(2)	C(2)-C(3)-C(4)	= 122.1(2)
C(3)-C(4)-C(5)	= 120.1(2)	C(4)-C(5)-C(6)	= 119.6(3)
C(1)-C(6)-C(5)	= 120.6(3)		

3d. mp 228–9°C (CH_2Cl_2-light petroleum). ^1H-NMR ($CDCl_3$, TMS) δ (ppm): 2.83 (24H, broad s), 7.44 (2H, t, J = 8.2 Hz), 7.66 (4H, d, J = 8.2 Hz). IR (KBr disk): 3010, 2914, 1650, 1578, 1448, 1356, 1250, 786, 774, 735 cm^{-1}. Elem. Anal (Calcd for $C_{24}H_{30}O_4N_4S_4$): C, 50.61 (50.86); H, 4.98 (5.33), N, 10.01 (9.89).

6,7-Dithio-dibenzo[c,e][1,2]dithiin **1**. To a solution of the tetracarbamoylthio derivative **2d** (80 mg, 0.14 mmol) in dry tetrahydrofuran (5 mL)—methanol (5 mL) was added dropwise potassium hydroxide (0.30 g) in methanol (5 mL). After 3 h at reflux, the reaction mixture was evaporated and the residue dissolved in dichloromethane and washed with 5% hydrochloric acid and water. After drying over anhydrous sodium sulfate, the organic phase was evaporated to leave a solid which was recrystallized from benzene-light petroleum. 0.025 g (64% yield), mp 207–10°C (benzene light petroleum). ^1H-NMR ($CDCl_3$, TMS) δ (ppm): 7.21 (2H, t, J = 6.0 Hz), 7.51 (4H, d, J = 6.0 Hz). IR (KBr disk): 2924, 2852, 1382, 1260, 1094, 802, 776 cm^{-1}. MS (70eV) m/z: 278 (M^+), 246 (M^+-S), 214 (246-S). Elem. Anal (Calcd for $C_{12}H_6S_4$): C, 51.50 (51.77); H, 1.96 (2.17).

X-ray structure determination. Crystal structure parameters are reported in Table I. The structure was phased by SHELX 86 programs and refined by blocked full matrix least squares using SHELX 76 programs. Thermal parameters of all non hydrogen atoms were anisotropic, hydrogen atoms were partially located on ΔF map but not refined. Figure 1 shows the ORTEP drawing of **1**, Table II reports positional parameters and Table III bonds lengths and angles. All crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, U.K.

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