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Structures and properties of 1,4-dithiins and related molecules

Miguel A. Mendez-Rojas,(1) **Satish G. Bodige,**(1) **Krzysztof Ejsmont,**(1)
and William H. Watson(1)*****

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A series of organosulfur compounds was characterized by NMR, IR, mass spectroscopy, cyclic voltammetry, and chemical analyses. The crystal structures of six compounds were determined: 1,3-dithioleno[4,5-*e*]naphtho[2,3-*b*]1,4-dithiin-2,5,10-trione (**1b**), $P\bar{1}$, $a = 7.665(4)$, $b = 7.997(4)$, $c = 11.443(5)$ Å, $\alpha = 91.311(8)$, $\beta = 92.516(8)$, $\gamma = 117.53(7)^\circ$; 6,7-dimethylbenzo[1,2-*b*]1,3-dithioleno[4,5-*e*]1,4-dithiin-2,5,8-trione (**2b**), $P2_1/m$, $a = 3.933(1)$, $b = 12.864(2)$, $c = 11.943(3)$ Å, $\beta = 99.161(4)^\circ$; 6-phenyl-2-thioxo-6-hydrocyclopenta[2,1-*b*]1,3-dithioleno[4,5-*e*]1,4-dithiin-5,7-dione (**3a**), $C2/c$, $a = 32.408(6)$, $b = 3.8743(8)$, $c = 27.123(5)$ Å, $\beta = 125.171(7)^\circ$; 6-phenyl-1,3-dithioleno[4,5-*e*]3-pyrrolino[3,4-*b*]1,4-dithiin-5,7-trione (**3b**), $P2_1/n$, $a = 7.9712(9)$, $b = 6.1976(7)$, $c = 55.978(6)$ Å, $\beta = 91.096(1)^\circ$; 2,3,7,8-tetramethylthianthrene-1,4,6,9-tetraone (**4**), $P2_1/c$, $a = 4.195(1)$, $b = 17.924(5)$, $c = 9.682(3)$ Å, $\beta = 98.509(5)^\circ$; 3H,6H-1,4-oxathiino[6′,5′-2,1]naphtho[3,4-*e*]1,4-oxathiin-2,7-dione (**5**), $P2_1/n$, $a = 9.3522(7)$, $b = 7.8782(6)$, $c = 17.118(1)$ Å, $\beta = 93.171(1)^\circ$. Several structures exhibited significant S–S intermolecular interactions, suggesting that the molecules might be precursors for preparing nonmetallic conductors.

KEY WORDS: S–S intermolecular interactions; quinones; maleimides.

Introduction

Organosulfur compounds, and in particular systems containing 1,3-dithiole rings such as TTF, frequently are good electronic conductors and even superconductors. The 1,3-dithiole compounds act as electron donors, and short S–S intermolecular contacts are important contributors to the formation of a conduction band in the solid. When the 1,3-dithiole ring is fused to a quinone moiety, the molecules now become electron withdrawing and the semiquinone can be stabilized to form compounds which also exhibit good electrical conductivity.[1] Cyclic-voltammetry studies indicate that the bis-1,3-dithiolequinones are better electron acceptors than chloranil. Previously, we reported the synthesis and characterization of a variety of 1,3-dithiolequinones, tetrathiafulvalene analogues, and quinonedithiolate metal complexes.[2–4] In this paper we report the syntheses, structures, and properties of several quinone and maleimide dithiindithioles (Scheme 1). If these compounds are to be useful precursors for conducting solids, the important question must be whether or not the carbonyl oxygen atoms prevent short S–S intermolecular contacts.

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(1) Department of Chemistry, Texas Christian University, Box 298860, Fort Worth, Texas.

* To whom correspondence should be addressed; e-mail: w.watson@tcu.edu.

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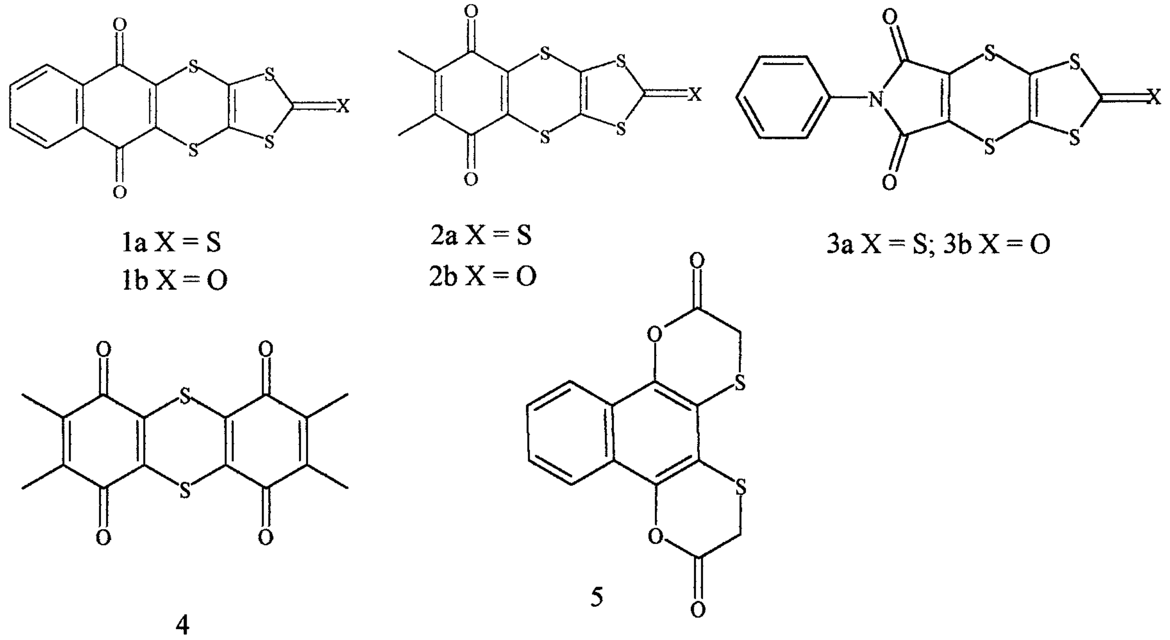


1a X = S
1b X = O

2a X = S
2b X = O

3a X = S; 3b X = O

4

5

Scheme 1.

Experimental

Melting points (uncorrected) were determined on a Thomas-Hoover apparatus. IR spectra were recorded on a Midac Systems FTIR at a spectral resolution of 4 cm^{-1} (KBr pellets). Mass spectra were obtained on a Finnigan quadrupole mass spectrometer. ^{1}H and ^{13}C spectra were recorded on a Varian XL300 spectrometer using CD_3Cl as solvent and TMS as an internal reference. Cyclic voltammetric studies were performed on a BAS CV-50W potentiostat using a three-electrode microcell with a Pt disk as the working electrode, a saturated calomel reference electrode, and a Pt wire as auxiliary electrode. Ferrocene was added to all samples as an internal reference, and the data corrected to that of the normal hydrogen electrode assuming the ferrocene couple is 0.400 V.[5] Cyclic voltammetry and UV–Vis data for compounds **1a**, **1b**, **2a**, **2b**, **3a**, and **3b** are given in Table 1.

Table 1. Voltammetric Data[a] and UV–Vis Absorption Data[b] for Compounds **1a**, **1b**, **2a**, **2b**, **3a**, and **3b**

Compound	$E_{1/2}$	Ep (irreversible)	λ (nm)
1a	−0.34	−0.60, −0.94	304, 377, 556
1b	−0.36	—	303, 532
2a	−0.27	1.63, 1.23, 0.25, −0.11, −1.33	304, 379, 578
2b	−0.31	—	296, 557
3a	—	−0.23, −0.75	303, 396
3b	—	−0.49	289, 474

[a] All voltammetric measurements use CH_3CN as solvent with 0.1 M $(n\text{-Bu})_4NClO_4$ as electrolyte at 293 K. All potentials are calibrated by reference to the standard ferrocene couple and referenced to the NHE value of 0.400 V.[5]
[b] $CHCl_3$ used as solvent.

Synthesis

1,3-Dithioleno[4,5-e]naphtho[2,3-b]1,4-dithiin-2,5,10-trione (1b)

To 1.68 g (2.20 mmol) of [Zn(4,5-disulfanyl-1,3-dithiole-2-thionate)$_2$](tetraethylammonium)$_2$ or [Zn(dmit)$_2$](TEA)$_2$ in acetone (20 mL) was added 1.00 g (4.40 mmol) of 2,3-dichloronaphthoquinone and the mixture stirred at room temperature (rt) overnight. The solid thione **1a** was recovered by vacuum filtration

(1.55 g, yield >99%). The sample was recrystallized from CH_2Cl_2 yielding dark green crystals, m.p. 354–355°C (lit.[6] 354–355°C). IR (cm^{-1}): 1663 (vs), 1586 (m), 1553 (m), 1493 (m), 1385 (w), 1275 (vs), 1134 (m), 1073 (vs), 794, 706, 635, 505. ^1H NMR ($CDCl_3$): δ 8.16 (dd, 2*p*-H), 7.80 (dd, 2*o*-H). MS (m/z) (%): 352 (46, M^+), 276 (20), 104 (24), 88 (100), 76 (87), 74 (11). Anal. Calcd. for $C_{13}H_4O_2S_5$: C, 44.30; H, 1.14. Found: C, 44.48; H, 0.99. The 1.55 g (4.40 mmol) of the thione **1a** was suspended in a mixture of chloroform (40 mL) and acetic acid (15 mL) and refluxed overnight with 3.22 g (10.1 mmol) of mercuric acetate. Solid HgS and unreacted mercuric acetate were removed by vacuum filtration. The organic phase was washed twice with 10 mL portions of water and then dried. The solvent was evaporated and the solid product recrystallized from CH_2Cl_2–isooctane yielding 0.56 g of black **1b**, m.p. 250–252°C (lit.[6] 250–252°C) (yield 38%). IR (KBr) (cm^{-1}): 1661 (vs), 1649 (sh), 1586 (m), 1557 (m), 1400 (w), 1275 (vs), 1134 (m), 903, 853, 795, 706, 636. ^1H NMR ($CDCl_3$): δ 8.16 (dd, 2*p*-H), 7.80 (dd, 2*o*-H). MS (m/z) (%): 336 (52%, M^+), 307 (44), 263 (13), 232 (17), 188 (13), 144 (14), 132 (37), 109 (82), 92 (11), 88 (80), 76 (100), 75 (13), 74 (21). Anal. Calcd. for $C_{13}H_4O_3S_4$: C, 46.41; H, 1.20. Found: C, 46.18; H, 1.16.

6,7-Dimethylbenzo[1,2-b]1,3-dithioleno[4,5-e] 1,4-dithiin-2,5,8-trione (2b)

To 1.40 g (4.77 mmol) of 2,3-dibromo-5,6-dimethylbenzoquinone in 10 mL of acetone was added 1.82 g of $[Zn(dmit)_2](TEA)_2$ (2.38 mmol) and the mixture stirred at rt overnight. The original orange solution turned green, and a precipitate formed immediately. The solid thione **2a** was recovered by vacuum filtration (1.57 g, yield >99%), m.p. >355°C. IR (cm^{-1}): 2988 (w), 1643 (s), 1572 (w), 1458 (vs), 1400 (m), 1277 (w), 1182 (s), 1165 (s), 1080 (vs), 1069 (sh), 1032 (m), 1007, 895, 791. ^1H NMR ($CDCl_3$): δ 2.09 (s, 6H). MS (m/z) (%): 330 (100, M^+), 286 (14), 254 (17), 110 (10), 88 (87), 76 (16). Anal. Calcd. for $C_{11}H_6O_2S_5$: C, 39.90; H, 1.80. Found: C, 39.74; H, 2.01. The reaction of the thione with mercury acetate was identical to that described above, giving 1.48 g of black **2b** (yield 99%), m.p. >355°C. IR (cm^{-1}): 1682 (2), 1651 (s), 1610 (sh), 1568 (s), 1506 (w), 1379 (w), 1265 (s), 1171 (s), 1117 (w), 1088, 1011, 907, 864, 777, 756, 704, 550, 469, 422. ^1H NMR ($CDCl_3$): δ 2.09 (2, 6H). MS (m/z) (%): 314 (75, M^+), 286 (60), 212 (31), 136 (32), 122 (10), 97 (38), 84 (100), 75 (21), 69 (87). Anal. Calcd. for $C_{11}H_6O_3S_4$: C, 42.02; H, 1.92. Found: C, 42.03, H, 1.78.

6-Phenyl-2-thioxo-1,3-dithioleno[4,5-e] 3-pyrrolino[3,4-b]1,4-dithiin-5,7-dione (3a)

To 0.857 g (3.54 mmol) of 2,3-dichloro-*N*-phenyl maleimide dissolved in acetone (30 mL) was added 1.35 g (1.77 mmol) of $[Zn(dmit)_2](TEA)_2$ and the mixture stirred at rt overnight. The green precipitate was recovered by vacuum filtration yielding 1.12 g of the thione **3a** (crude yield 99.2%). The product was recrystallized from dichloromethane, giving small dark green needles, m.p. 225°C (dec.). IR (cm^{-1}): 1768 (w), 1721 (vs), 1601 (m), 1499 (2), 1387 (s), 1202 (w), 1109 (sh), 1087 (vs), 897, 883, 808, 779, 756, 725, 681, 633, 577, 512, 496. ^1H NMR ($CDCl_3$): δ 7.47 (dd, 1H), 7.32 (d, 2H), 7.26 (d, 2H). MS (m/z) (%): 367 (100, M^+), 323 (25), 291 (8), 247 (9), 159 (22), 119 (11), 100 (15), 88 (97), 76 (16), 64 (16). Anal. Calcd. for $C_{13}H_5O_2S_5N$: C, 42.49; H, 1.37 N, 3.81. Found: C, 41.03; H, 1.40; N, 3.60.

6-Phenyl-1,3-dithioleno[4,5-e]3-pyrrolino [3,4-b]1,4-dithiin-2,5,7-trione (3b)

The conversion of the thione **3a** to the **3b** was identical to the procedure above, yielding 1.16 g (yield, 99%) of black crystals, m.p. 290–293°C. IR (cm^{-1}): 1711 (vs), 1607 (w), 1505 (w), 1402 (w), 1115 (m), 1071 (w), 891 (w), 791 (w), 748 (w),

Table 2. Crystal, Collection, and Refinement Data for Compounds **1b**, **2b**, **3a**, **3b**, **4**, and **5**

Compound	**1b**	**2b**	**3a**	**3b**[a]	**4**	**5**
Chemical formula	$C_{13}H_4O_3S_4$	$C_{11}H_6O_3S_4$	$C_{13}H_5NO_2S_5$	$C_{13}H_5NO_3S_4$	$C_{16}H_{12}O_4S_2$	$C_{14}H_8O_4S_2$
CCDC deposit no.	CCDC-1003/5986	CCDC-1003/5987	CCDC-1003/5988	CCDC-1003/5989	CCDC-1003/5990	CCDC-1003/5991
Formula weight	336.40	314.40	367.48	301.24	332.38	304.31
Color/shape	Black/needle	Black/platelet	Dark green/needle	Black/prism	Dark green/prism	
Temperature, K	213(2)	213(2)	213(2)	213(2)	213(2)	213(2)
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P2_{1/m}$	$C2/c$	$P2_{1/n}$	$P2_{1/c}$	$P2_{1/n}$
Unit cell dimensions						
a, Å	7.665(4)	3.933(1)	32.408(6)	7.8712(9)	4.195(1)	9.3522(7)
b, Å	7.997(4)	12.864(2)	3.8743(8)	6.1976(7)	17.924(5)	7.8782(6)
c, Å	11.443(5)	11.943(3)	27.123(5)	55.978(6)	9.682(3)	17.118(1)
α, deg	91.311(8)	90.0	90.0	90.0	90.0	90.0
β, deg	92.516(8)	99.161(4)	125.171(7)	91.096(1)	98.509(5)	93.171(1)
γ, deg	117.53(7)	90.0	90.0	90.0	90.0	90.0
Volume, Å^3	670.7(5)	596.6(3)	2783(1)	2730.2(5)	720.0(4)	1259.3(2)
Z	2	2	8	8	2	4
Density (calculated), mg/m^3	1.800	1.750	1.754	1.710	1.533	1.605
Absorption coefficient, mm^{-1}	0.766	0.790	0.833	0.703	0.385	0.432
Diffractometer/scan	Bruker Smart 1000	Bruker Smart 1000	Bruker Smart 1000	Bruker Smart 1000	Bruker Smart 1000	Bruker Smart 1000
θ range for data collection, deg	1.78–23.29	1.73–23.25	1.54–22.50	4.14–24.99	2.27–22.50	2.38–22.50
Reflections measured	2819	2697	7478	10,044	2947	5162
Independent reflections (R_{int})	1763 (0.0625)	906 (0.1119)	1820 (0.0750)	4496 (0.0332)	945 (0.0836)	1647 (0.0323)
Observed reflections [$I > 4\sigma(F_o)$]	1462	804	1527	4112	761	1392
Data/restraints/parameters	1763/0/198	906/0/87	1820/0/191	4496/0/380	945/0/103	1647/0/182
Extinction coefficient	0.000(4)	0.049(6)	0.00001(8)	0.00001(1)	0.000(2)	0.002(1)
Goodness of fit on F^2	1.020	1.108	1.009	1.376	1.078	1.056
Final $R1$, $wR2$ indices [$I > 2\sigma(I)$]	0.0400; 0.1046	0.0361; 0.1018	0.0284; 0.0610	0.0675;0.1337	0.0419; 0.1182	0.0270; 0.0734
R indices (all data)	0.0489; 0.1103	0.0397; 0.1042	0.0373; 0.0632	0.0735;0.1356	0.0519; 0.1225	0.0325; 0.0758

[a] Detector moved from 5.0 to 7.0 cm because of length of one axis.

727 (w), 685 (w). ^{1}H NMR ($CDCl_3$): δ 7.47 (dd, 1H), 7.32 (d, 2H), 7.26 (d, 2H). MS (m/z) (%): 353 (16), 352 (15), 351 (87, M^+), 325 (13), 324 (11), 322 (67), 247 (21), 171 (12), 159 (21), 129 (11), 120 (17), 119 (62), 100 (19), 91 (28), 90 (11), 88 (100), 84 (13), 77 (10), 76 (29), 64 (27), 63 (12). Anal. Calcd. for $C_{13}H_5NO_3S_4$: C, 44.42; H, 1.43. Found: C, 44.20; H, 1.55.

2,3,7,8-Tetramethylthianthrene-1,4,6,9-tetraone (4)

Compound **4** was obtained as side reaction in the formation of metal tetrathiolate complexes. To 0.47 g (6.85 mmol) of ammonium sulfide dissolved in 10 mL of methanol and 1 mL of water at −70°C (dry ice/acetone) 1.0 g (3.42 mmol) of 2,3-dibromo-5,6-dimethyl-benzoquinone in 20 mL of methanol was added. The mixture was stirred for 1 h under an inert atmosphere (N_2). The initial yellow solution turns purple during this time. The mixture was warmed to 0°C , and at this point the purple color fades and a dark green suspension forms almost immediately. $NiCl_2 \cdot 6H_2O$ (0.246 g, 1.04 mmol) is added and stirred for 1 h, followed by the addition of tetrabutylammonium

Table 3. Atomic Coordinates (10^4) and Equivalent Isotropic Displacement Parameters (10^3 Å^2) for **1b**

Atom	x	y	z	$U_{\text{eq}}{}^a$
C(1)	2086(4)	9299(4)	9530(3)	25(1)
C(2)	2291(4)	8940(4)	8273(3)	25(1)
C(3)	954(4)	7387(4)	7662(3)	27(1)
C(4)	−831(4)	5935(4)	8197(3)	27(1)
C(5)	−1105(4)	6287(4)	9433(3)	26(1)
C(6)	−2731(4)	4967(5)	9969(3)	31(1)
C(7)	−2980(4)	5256(5)	11132(3)	33(1)
C(8)	−1590(4)	6844(5)	11770(3)	34(1)
C(9)	50(4)	8171(5)	11246(3)	29(1)
C(10)	305(4)	7893(4)	10076(3)	24(1)
C(11)	3673(4)	10565(4)	6266(3)	27(1)
C(12)	3183(5)	11685(5)	4196(3)	40(1)
C(13)	2374(4)	9005(5)	5671(3)	30(1)
O(1)	3380(3)	10668(3)	10080(2)	33(1)
O(2)	−1938(3)	4514(3)	7620(2)	39(1)
O(3)	3312(4)	12556(4)	3342(2)	61(1)
S(1)	4500(1)	10644(1)	7736(1)	30(1)
S(2)	4525(1)	12699(1)	5562(1)	36(1)
S(3)	1642(1)	9206(1)	4241(1)	39(1)
S(4)	1205(1)	6743(1)	6226(1)	40(1)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 4. Atomic Coordinates (10^4) and Equivalent Isotropic Displacement Parameters (10^3 Å^2) for **2b**

Atom	x	y	z	$U_{\text{eq}}{}^a$
S(1)	4531(2)	6209(1)	9224(1)	29(1)
S(2)	2379(2)	6343(1)	11512(1)	29(1)
O(1)	1022(5)	5449(2)	7074(2)	41(1)
C(1)	737(6)	6388(2)	7091(2)	25(1)
C(4)	−2960(7)	6313(2)	5176(2)	34(1)
C(5)	3723(5)	6987(2)	10372(2)	24(1)
C(3)	−1178(6)	6977(2)	6123(2)	24(1)
C(2)	2429(5)	6982(2)	8104(2)	22(1)
O(3)	519(7)	7500	13139(2)	42(1)
C(6)	1534(9)	7500	12247(3)	29(1)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 5. Atomic Coordinates (10^4) and Equivalent Isotropic Displacement Parameters (10^3 Å^2) for **3a**

Atom	x	y	z	$U_{\text{eq}}{}^a$
S(1)	2669(1)	−616(2)	648(1)	26(1)
S(2)	1912(1)	285(2)	909(1)	25(1)
S(3)	2564(1)	3703(2)	2061(1)	25(1)
S(4)	3483(1)	3754(2)	2091(1)	28(1)
S(5)	1493(1)	2355(2)	1593(1)	38(1)
O(1)	3432(1)	−1207(5)	299(1)	32(1)
O(2)	4425(1)	4809(5)	2068(1)	35(1)
N(1)	4055(1)	1731(6)	1168(1)	24(1)
C(1)	3577(1)	262(7)	764(1)	24(1)
C(2)	3287(1)	848(7)	1027(1)	21(1)
C(3)	2535(1)	936(7)	1156(1)	21(1)
C(4)	1961(1)	2154(7)	1523(1)	24(1)
C(5)	2840(1)	2524(7)	1694(1)	21(1)
C(6)	3584(1)	2460(7)	1558(1)	22(1)
C(7)	4084(1)	3188(8)	1659(1)	25(1)
C(8)	4459(1)	1662(7)	1089(1)	25(1)
C(9)	4921(1)	317(7)	1542(1)	31(1)
C(10)	5301(1)	262(8)	1456(1)	39(1)
C(11)	5221(1)	1464(8)	928(2)	42(1)
C(12)	4756(1)	2745(8)	480(1)	40(1)
C(13)	4372(1)	2904(7)	561(1)	31(1)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 6. Atomic Coordinates (10^4) and Equivalent Isotropic Displacement Parameters (10^3 Å^2) for **3b**

Atom	*x*	*y*	*z*	U_{eq}[a]
C(1)	10037(10)	−55(16)	1090(2)	30(2)
C(2)	9866(10)	485(14)	1349(2)	27(2)
C(3)	9621(10)	−130(14)	1817(2)	27(2)
C(4)	8471(11)	−59(17)	2254(2)	35(2)
C(5)	8805(10)	1762(15)	1835(2)	30(2)
C(6)	9036(10)	2363(13)	1370(2)	26(2)
C(7)	8618(10)	3166(15)	1123(2)	30(2)
C(8)	9249(11)	1878(18)	710(2)	36(2)
C(9)	9864(13)	3710(20)	604(2)	45(3)
C(10)	9868(16)	3880(20)	359(2)	59(3)
C(11)	9231(16)	2270(30)	220(2)	70(4)
C(12)	8613(14)	390(30)	325(2)	61(4)
C(13)	8600(13)	210(20)	571(2)	49(3)
C(14)	3685(10)	5097(15)	1096(2)	29(2)
C(15)	4034(10)	5362(14)	1357(2)	27(2)
C(16)	3753(11)	4804(15)	1823(2)	31(2)
C(17)	3303(11)	5633(14)	2283(2)	30(2)
C(18)	4541(10)	6701(14)	1863(2)	28(2)
C(19)	4842(10)	7224(14)	1393(2)	25(2)
C(20)	5090(10)	8306(16)	1159(2)	30(2)
C(21)	4401(10)	7250(15)	731(2)	30(2)
C(22)	3751(12)	9152(16)	638(2)	36(2)
C(23)	3734(13)	9450(20)	391(2)	44(3)
C(24)	4364(15)	7860(20)	244(2)	59(3)
C(25)	5012(15)	5990(20)	341(2)	55(3)
C(26)	5034(13)	5661(18)	586(2)	41(3)
N(1)	9260(8)	1639(13)	966(1)	32(2)
N(2)	4394(8)	6908(12)	985(1)	29(2)
O(1)	10719(8)	−1619(11)	1009(1)	41(2)
O(2)	7862(8)	4811(12)	1072(1)	41(2)
O(3)	8179(9)	−411(13)	2458(1)	51(2)
O(4)	2964(8)	3626(11)	1001(1)	39(2)
O(5)	5803(8)	9974(11)	1123(1)	36(2)
O(6)	2905(9)	5585(12)	2486(1)	46(2)
S(1)	10703(3)	−1211(4)	1569(1)	32(1)
S(2)	9589(3)	−1835(4)	2064(1)	37(1)
S(3)	7812(3)	2341(4)	2102(1)	37(1)
S(4)	8484(3)	3811(4)	1619(1)	36(1)
S(5)	3462(3)	3359(4)	1555(1)	38(1)
S(6)	2777(3)	3573(4)	2068(1)	34(1)
S(7)	4455(3)	7782(4)	2150(1)	36(1)
S(8)	5608(3)	8373(4)	1659(1)	30(1)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 7. Atomic Coordinates (10^4) and Equivalent Isotropic Displacement Parameters (10^3 Å^2) for Compound **4**

Atom	*x*	*y*	*z*	U_{eq}[a]
S(1)	3539(2)	4221(1)	8934(1)	46(1)
O(1)	6414(6)	2960(1)	10133(2)	60(1)
O(2)	−825(6)	4752(1)	6758(2)	61(1)
C(1)	6323(7)	4246(2)	10479(3)	40(1)
C(2)	7473(7)	3478(2)	10870(3)	42(1)
C(3)	9832(7)	3356(2)	12151(3)	45(1)
C(4)	10717(8)	2552(2)	12447(4)	60(1)
C(5)	2581(7)	5171(2)	8721(3)	40(1)
C(6)	199(8)	5297(2)	7446(3)	43(1)
C(7)	−926(7)	6058(2)	7041(3)	44(1)
C(8)	−3206(8)	6119(2)	5698(3)	60(1)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

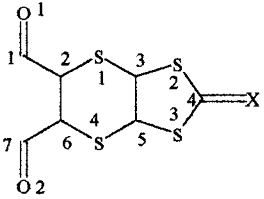
iodide (0.764 g, 2.07 mmol) with stirring for an additional hour. A dark greenish black precipitate was recovered by vacuum filtration and recrystallized from chloroform, yielding 0.274 g (24% yield) of small green-black plates, m.p. >330°C. IR (cm^{-1}): 1645 (s), 1559 (s), 1437 (w), 1383 (w), 1281 (m), 1192 (s), 1090 (w), 772 (w), 702 (w). ^{1}H NMR: δ 2.03 (s, 12H). Anal. Calcd. for $C_{16}H_{12}O_4S_4$: C, 57.81; H, 3.64. Found: C, 57.71; H, 3.86.

Table 8. Atomic Coordinates (10^4) and Equivalent Isotropic Displacement Parameters (10^3 Å^2) for Compound **5**

Atom	*x*	*y*	*z*	U_{eq}[a]
S(1)	−2636(1)	6558(1)	10710(1)	44(1)
S(2)	−70(1)	8374(1)	11679(1)	47(1)
O(1)	2402(1)	9297(2)	10676(1)	41(1)
O(4)	−1940(1)	5804(2)	9033(1)	43(1)
C(14)	−914(2)	6734(2)	9476(1)	34(1)
C(7)	1295(2)	8353(2)	10313(1)	34(1)
C(11)	−1051(2)	7092(2)	10252(1)	33(1)
C(6)	1460(2)	7993(2)	9508(1)	32(1)
C(1)	326(2)	7166(2)	9079(1)	33(1)
C(10)	87(2)	7916(2)	10682(1)	35(1)
C(5)	2699(2)	8464(2)	9119(1)	39(1)
C(2)	490(2)	6772(2)	8280(1)	41(1)
O(2)	3533(2)	10360(2)	11718(1)	64(1)
C(3)	1701(2)	7229(3)	7930(1)	48(1)
C(4)	2811(2)	8078(3)	8349(1)	46(1)
C(9)	1818(2)	8186(3)	11945(1)	48(1)
C(12)	−3786(2)	6887(2)	9843(1)	45(1)
C(8)	2652(2)	9366(3)	11470(1)	44(1)
O(3)	−4103(2)	4768(2)	8844(1)	71(1)
C(13)	−3348(2)	5737(3)	9210(1)	46(1)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 9. Selected Bond Distances (Å) and Angles (deg) for Compounds **1b**, **2b**, **3a** and **3b** (3b$_a$ and 3b$_b$ Indicate Two Independent Molecules)



	1b	**2b**	**3a**	**3b**$_a$	**3b**$_b$
Bond distance					
C(1)─O(1)	1.220(3)	1.213(3)	1.204(3)	1.204(7)	1.194(7)
C(1)─C(2)	1.490(4)	1.495(3)	1.491(4)	1.500(7)	1.502(7)
C(2)─S(1)	1.760(3)	1.763(2)	1.737(3)	1.730(5)	1.739(5)
C(2)─C(6)	1.342(4)	1.334(5)	1.338(3)	1.330(7)	1.329(7)
S(1)─C(3)	1.760(3)	1.767(2)	1.770(3)	1.770(6)	1.769(5)
C(3)─S(2)	1.752(3)	1.747(2)	1.741(3)	1.747(5)	1.748(5)
C(3)─C(5)	1.328(4)	1.319(5)	1.351(3)	1.332(8)	1.342(8)
S(2)─C(4)	1.785(4)	1.785(2)	1.739(3)	1.783(6)	1.784(6)
C(4)─X	1.194(4)[a]	1.196(4)[a]	1.773(3)[b]	1.201(7)[a]	1.203(7)[a]
C(4)─S(3)	1.781(4)	—	1.739(3)	1.776(6)	1.780(6)
S(3)─C(5)	1.741(3)	—	1.738(3)	1.746(6)	1.750(5)
C(5)─S(4)	1.756(3)	—	1.773(3)	1.767(5)	1.768(6)
S(4)─C(6)	1.757(3)	—	1.734(3)	1.733(6)	1.730(5)
C(6)─C(7)	1.494(4)	—	1.503(4)	1.506(7)	1.501(7)
C(7)─O(2)	1.213(3)	—	1.198(3)	1.197(7)	1.193(6)
Bond angle					
O(1)─C(1)─C(2)	120.3(2)	119.5(2)	126.8(3)	127.2(5)	127.0(5)
C(1)─C(2)─S(1)	113.3(2)	114.9(2)	119.8(2)	120.8(4)	121.5(4)
S(1)─C(2)─C(6)	124.9(2)	124.3(8)	131.3(2)	130.3(4)	129.7(4)
C(1)─C(2)─C(6)	121.6(3)	120.8(1)	108.9(2)	108.9(5)	108.7(5)
C(2)─S(1)─C(3)	99.0(1)	98.5(1)	98.3(1)	97.9(3)	98.5(3)
S(1)─C(3)─C(5)	124.3(3)	124.5(8)	130.0(2)	129.8(4)	129.6(4)
C(3)─C(5)─S(4)	125.6(3)	—	130.5(2)	129.1(4)	129.0(4)
C(5)─S(4)─C(6)	98.7(2)	—	98.9(1)	97.9(3)	98.5(3)
C(2)─C(6)─S(4)	124.5(2)	—	131.8(2)	130.8(4)	131.3(4)
C(3)─S(2)─C(4)	95.8(2)	95.2(1)	97.3(1)	95.6(3)	96.5(3)
S(2)─C(4)─S(3)	112.3(2)	112.9(2)	112.6(2)	112.4(3)	112.2(3)
S(4)─S(3)─C(5)	96.0(2)	—	97.4(1)	96.5(3)	96.4(3)
S(3)─C(5)─C(3)	118.1(3)	118.3(9)	116.3(2)	116.9(4)	117.7(4)
S(2)─C(4)─X	124.2(3)	123.5(1)	123.6(2)	123.6(5)	123.4(5)
S(4)─C(6)─C(7)	113.2(2)	—	119.7(2)	120.3(4)	119.3(4)
O(2)─C(7)─C(6)	119.2(3)	—	126.3(3)	126.7(5)	127.1(5)

[a] X = O.
[b] X = S.

3H,6H-1,4-oxathiino[6′,5′-2,1]naptho[3,4-e] 1,4-oxathiin-2,7-dione (5)

Thiolacetic acid (3.2 mL) was added at 40°C with stirring to 10 mL pyridine. To this solution 2.27 g (10 mmol) of 2,3-dichlorobenzoquinone was added and the temperature raised to 80°C for 1 h. The solution was cooled to 25°C and 8 mL of acetic anhydride was added. After 30 min the solution was cooled to 0°C and the precipitate was filtered, washed with ethanol, and air-dried, yielding 2.45 g of **13** (yield 80.6%), m.p. 276–277°C. The physical properties agree with literature values.[7]

Table 10. Selected Bond Distances (Å) and Angles (deg) for Compound **4**

Bond distance	
C(1)—C(2)	1.489(4)
C(1)—S(1)	1.757(3)
C(1)—C(5a)	1.342(4)
C(2)—O(1)	1.214(4)
C(2)—C(3)	1.484(4)
C(3)—C(7a)	1.348(4)
S(1)—C(5)	1.754(3)
C(5)—C(6)	1.486(5)
C(6)—C(7)	1.478(5)
C(6)—O(2)	1.223(4)
Bond angle	
C(1)—C(2)—C(3)	119.9(3)
C(1)—C(2)—O(1)	118.7(3)
C(3)—C(2)—O(1)	121.4(3)
C(2)—C(1)—C(5a)	120.2(3)
C(2)—C(1)—S(1)	110.0(2)
C(1)—S(1)—C(5)	100.8(1)
S(1)—C(1)—C(5a)	129.7(3)
S(1)—C(5)—C(6)	111.1(2)
C(5)—C(6)—C(7)	120.7(3)
C(5)—C(6)—O(2)	118.0(3)
C(7)—C(6)—O(2)	121.3(3)

Table 11. Selected Bond Distances (Å) and Angles (deg) for Compound **5**

Bond distance	
C(1)—C(6)	1.415(3)
C(1)—C(14)	1.418(3)
C(6)—C(7)	1.423(3)
C(7)—C(10)	1.369(3)
C(7)—O(1)	1.393(2)
O(1)—C(8)	1.366(2)
C(8)—O(2)	1.198(2)
C(8)—C(9)	1.485(3)
C(9)—S(2)	1.758(2)
S(2)—C(10)	1.805(2)
C(10)—C(11)	1.418(3)
C(11)—C(14)	1.370(2)
C(11)—S(1)	1.756(2)
S(1)—C(12)	1.803(2)
C(12)—C(13)	1.488(3)
C913)—O(3)	1.193(2)
C(13)—O(4)	1.368(2)
C(14)—O(4)	1.398(2)
Bond angle	
C(7)—O(1)—C(8)	123.1(2)
O(1)—C(8)—O(2)	117.1(2)
O(1)—C(8)—C(9)	117.0(1)
O(2)—C(8)—C(9)	125.9(2)
C(8)—C(9)—S(2)	110.3(1)
C(9)—S(2)—C(10)	95.46(9)
S(2)—C(10)—C(7)	120.8(2)
O(1)—C(7)—C(10)	122.7(2)
C(10)—C(11)—C(14)	119.4(2)
S(1)—C(11)—C(14)	120.5(1)
C(11)—C(14)—O(4)	122.4(2)
S(1)—C(12)—C(13)	109.7(1)
C(12)—C(13)—O(3)	126.4(2)
O(3)—C(13)—O(4)	117.2(2)
C(12)—C(13)—O(4)	116.4(2)
C(13)—O(4)—C(14)	122.7(2)

X-ray analysis

X-ray data for compounds **1b**, **2b**, **3a**, **3b**, **4**, and **5** were collected at 213 K on a Bruker SMART 1000 diffractometer using Mo Kα radiation. Because of a long unit cell dimension in compound **3b**, the detector was moved from the normal 5-cm distance to 7 cm. The frames were integrated with the Saint software package[8] using a narrow-frame integration algorithm, and the structures were solved and refined using SHELXTL.[9] All structures were checked using the PLATON[10] program package. The positions of hydrogen atoms were found in difference maps or were calculated. Table 2 contains crystal and refinement data for all compounds. Atomic coordinates for all compounds are given in Tables 3–8, while selected bond distances and angles are given in Tables 9–11.

Discussion

The cyclic voltammetry data in Table 1 indicate that the two oxo-quinone derivatives **1b** and **2b** exhibit a reversible one-electron wave at $E_{1/2} = -0.36$ and -0.31 V respectively, while the thione-quinone derivatives **1a** and **2a** exhibit irreversible processes in addition to reversible waves at -0.34 and -0.27 V. The $E_{1/2}$ values for the oxo derivatives are slightly more negative than those of the corresponding thiones. Benzoquinone gives two one-electron waves at -0.50 and -1.33 V while the more easily reduced tetrachlorbenzoquinone is shifted to $+0.06$ and -0.82 V. The sulfur atom does not shift the one-electron reduction significantly, but it leads to a number of irreversible side reactions. Electrocrystallization will

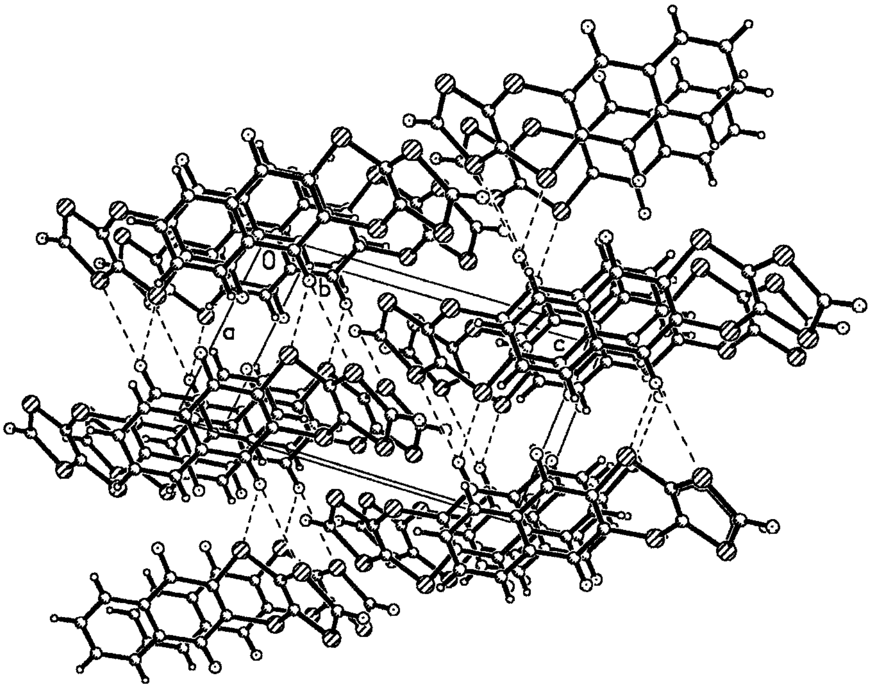


Fig. 1. Packing diagram for compound **1b**.

be attempted with the voltage maintained slightly more negative than Ep for the anodic wave. Both maleimide compounds **3a** and **3b** exhibit only irreversible processes at all scan rates. Compounds **1b** and **2b** exhibit two absorption maxima in the UV–Vis region (Table 1) while an additional absorption band around 378 nm is observed for the thiones **1a** and **2a**. Both the thione **3a** and the oxo-analogue **3b** exhibit two absorption bands.

Packing diagrams of compounds **1b**, **2b**, **3a**, and **3b** are shown in Figs. 1–4. The four molecules are folded by 42.3 (1)° (**1b**), 52.9(1)° (**2b**), 4.4(1)° (**3a**), 18.3(3)° (**3b**), and 19.7(3)° (**3b**′) along the S—S axes of the dithiin six-membered rings. A density functional calculated geometry for structure **1** gave a folding angle of 37.9° and a value of 0.7° for **3**. The quinone oxygen atoms in **1** are calculated to be out of the phenyl plane by 6.0° while the oxygen atoms in **3** are out of the plane by 0.9°. The maleimide six-membered dithiin moieties may be more planar because of the smaller repulsion from the carbonyl lone pairs. In the crystal structures the molecular entities on either side of this S—S axes are planar except for the *N*-phenyl rings which are twisted out of the plane of the maleimide ring by 53.4(2)° in **3a** and by 53.6(3)° and 53.2(3) in **3b**.

Compound **1b** (Fig. 1) exhibits two intermolecular S–O interactions smaller than the sum of van der Waals (vdv) radii (~3.30 Å), S(1)—O(2)′ = 3.048(3) Å and S(2)—O(2)′ = 3.264(3) Å. There are no short S–S interactions observed. The molecules are well-packed, lying nestled in vertical columns with centers of gravity separated by 3.566(3) Å. Intracolumn interactions are weak and there are no two- or three-dimensional networks.

Compound **2b** (Fig. 2) exhibits three sulfur intermolecular interactions at approximately the sum of the vdv radii, S(1)—S(1′) = 3.610(2) Å, S(1)—S(2′) = 3.656(2) Å, and S(2)—O(1′) = 3.258(2) Å. The molecules pack in nestled columns along the short axis, with centroids of the planes separated by 3.993(2) Å in this direction.

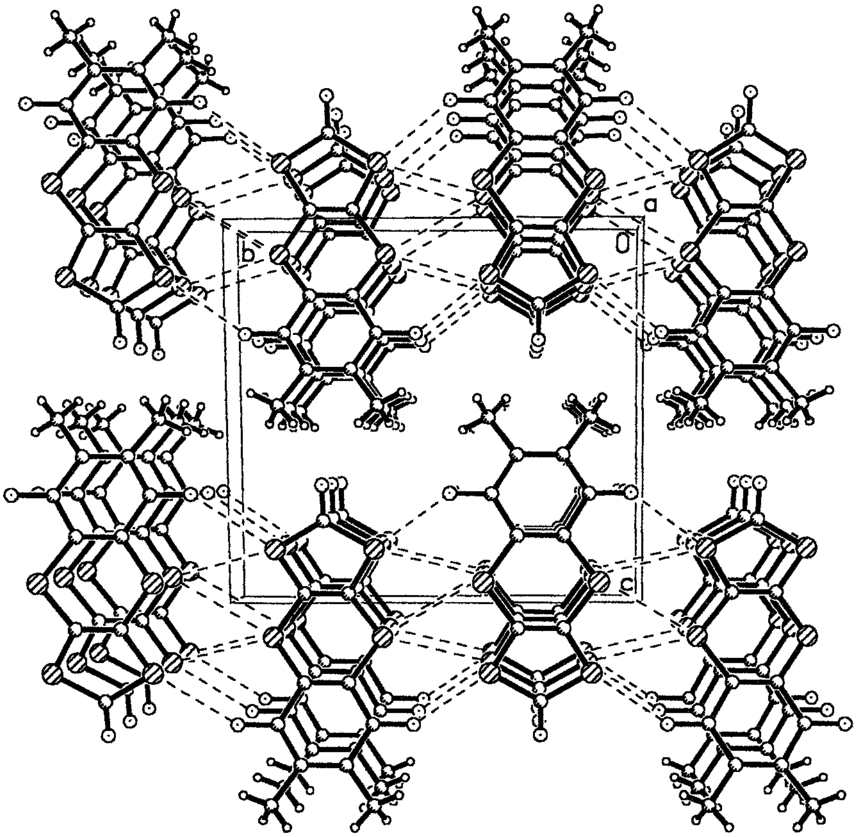


Fig. 2. Packing diagram for compound **2b**.

Compound **3a** (Fig. 3) is potentially the most interesting compound with three S—S and two S—O distances significantly shorter than the sum of vdv radii: S(1)—S(1)′ = 3.353(1) Å, S(3)—S(3)′ = 3.276(1) Å, S(3)—S(5)′ = 3.438(1) Å, S(1)—O(1)′ = 3.208(3) Å, and S(2)—O(1′) = 3.203(3) Å. The S(2)—S(3)′ = 3.623(1) Å is approximately the sum of the vdv radii. The molecules are packed canted to the short axis, with the short interactions occurring between stacks forming one-dimensional ribbons running through the structure. The interactions along the stacks exceed the vdv contacts for the S and O atoms.

Compound **3b** (Fig. 4) has one axis of 56.45(3) Å with two independent molecules per cell. There are three S–S and three S–O interactions slightly smaller than the sum of vdv contacts: S(1)—S(4)′ = 3.562(2) Å, S(4)—S(8) = 3.572(2) Å, S(5)—S(6)′ = 3.561(2) Å, S(2)—O(3) = 2.936(5) Å, S(6)—O(6)′ = 3.278(5) Å, and S(7)—O(6)′ = 3.165(5) Å. These interactions form a linear connectivity throughout the structure.

Because the maleimide structures **3a** and **3b** are nearly planar and exhibit significantly shorter S–S interactions, they may prove useful in the preparation of conducting charge transfer complexes or electrocrystallized ionic species. Replacement of the phenyl ring by donor and acceptor groups is being investigated currently.

In compound **4** (Fig. 5) the three six-membered rings are completely planar (σ_p = .007 Å), with the oxygen atoms out of the plane by 0.008(2)–0.045(2) Å and the methyl groups by 0.045(4)–0.071(3) Å. There are no significant S–S

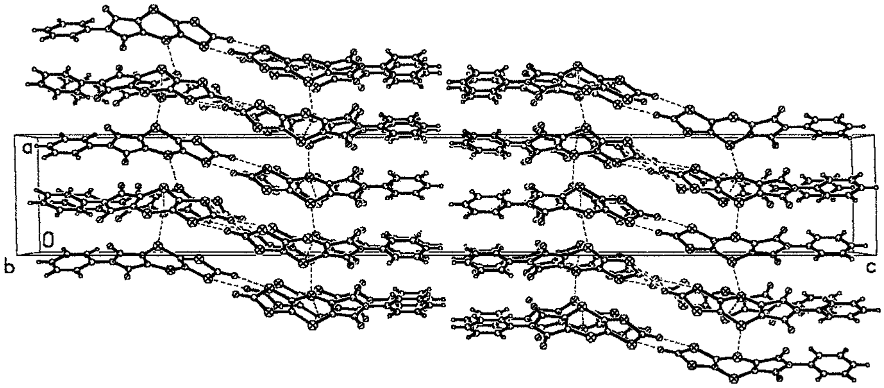


Fig. 3. Packing diagram for compound **3a**.

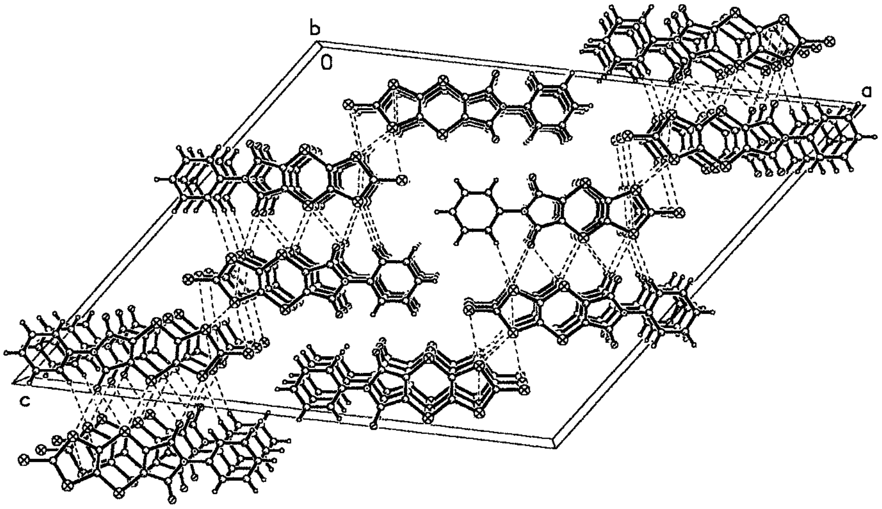


Fig. 4. Packing diagram for compound **3b**. Part of the central column has been removed for clarity.

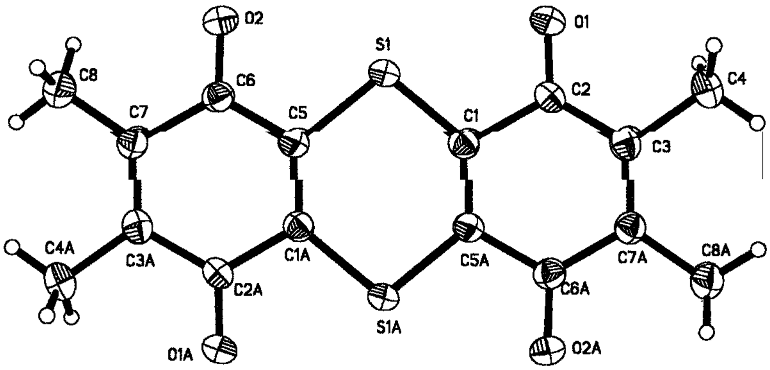


Fig. 5. Thermal ellipsoid plot for compound **4**. Thermal ellipsoids are drawn at the 35% probability level.

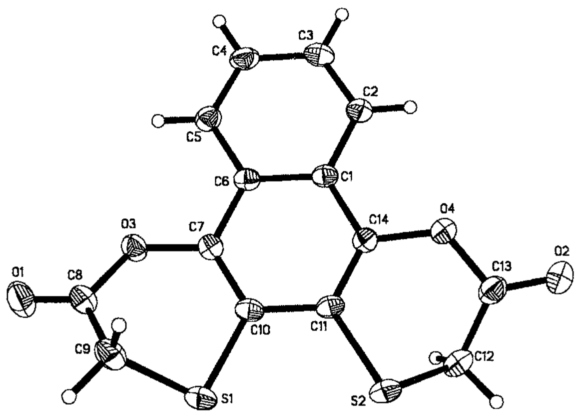


Fig. 6. Thermal ellipsoid plot of compound **5**. Ellipsoids are drawn at the 35% probability level.

or S–O intermolecular interactions. The closest intermolecular centroid approach is 3.723(2) Å.

In compound **5** (Fig. 6) the two heterocyclic rings adopt almost perfect screw-boat conformations.[11] One S atom is above and the other below the plane of the benzene ring. The two benzene rings are planar. There are no short intermolecular S or O interactions of interest.

Although the metallic behavior of a neutral molecular species has been reported recently,[12] combinations of ionic species or charge-transfer complexes usually are necessary for high electrical conductivity. In many of these species S–S or Se–Se intermolecular interactions lead to the formation of conduction bands. The present study indicates that the dithiin molecules with quinone functionalities are capable of packing with short S–S intermolecular interactions and may be suitable vehicles for preparing ionic or charge transfer metallic conductors. Since the dithiin molecules tend to accept electrons and TTF derivatives donate electrons, the formation of charge transfer salts is under investigation currently. This study indicates that S–S interactions might be expected in spite of the quinone and maleimide oxygen atoms. Further investigations into this series have been stimulated by the recent report of superconductivity in a dithian system.[13]

Acknowledgment

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