forms an angle of 169·1° with the previous plane. The deviations of O(1) and O(2) from this plane of the five-membered ring are 0·73 and 0·15 Å, respectively. Except for C(2) five C atoms of the six-membered ring are nearly coplanar but the tendency toward a boat conformation is indicated by the mean absolute deviation of 7° (Table 4, deposited) of the torsion angles from the ideal boat: 0, 0, 28, −56, 54, −27°, cyclically starting from the double bond (Bucourt & Hainaut, 1965). The acetyl and hydroxyl substituents are quasiaxial in a *trans* position. All observed bond lengths are within the expected ranges.

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Acta Cryst. (1990). C**46**, 804–807

Structures of 4,5-Bis(methylthio)-2*H*-1,3-dithiole-2-thione and its 2-Oxo Analogue. Precursors to Organic Multisulfur π Donors

By Ole Simonsen

Department of Chemistry, Odense University, DK-5230 Odense M, Denmark

and K. S. Varma, A. Clark and A. E. Underhill

Department of Chemistry and Institute for Molecular and Biomolecular Electronics, University College of N Wales, Bangor, Gwynedd LL57 2DG, Wales

(*Received* 19 *June* 1989; *accepted* 17 *August* 1989)

Abstract. 4,5-Bis(methylthio)-2*H*-1,3-dithiole-2-thione, $C_5H_6S_5$ (BTDTT), $M_r = 226·40$, monoclinic, $P2_1/c$, $a = 7·543\ (2)$, $b = 12·480\ (2)$, $c = 9·896\ (1)$ Å, $\beta = 99·81\ (1)°$, $V = 918·0\ (5)$ Å^3, $Z = 4$, $D_m = 1·62\ (1)$, $D_x = 1·638$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 1·14$ mm^{-1}, $F(000) = 464$, $T = 295$ K. $R = 0·027$ for 1928 unique observed reflections. 4,5-Bis(methylthio)-2*H*-1,3-dithiole-2-one, $C_5H_6OS_4$ (BTDTO), $M_r = 210·34$, monoclinic, $P2_1$, $a = 11·087\ (2)$, $b = 9·198\ (2)$, $c = 4·194\ (2)$ Å, $\beta = 96·03\ (2)°$, $V = 425·2\ (4)$ Å^3, $Z = 2$, $D_m = 1·62\ (1)$, $D_x = 1·643$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 1·01$ mm^{-1}, $F(000) = 216$, $T = 295$ K, $R = 0·026$ for 1261 unique observed reflections. The dithiole ring in both BTDTT and BTDTO is planar. Torsion angles involving the CH_3—S groups and the C═C bond vary between −121 and −178°. The endocyclic C—S bonds are shorter than the exocyclic C—S single bonds. The two endocyclic C—S bonds in the S—C—S region of the ring in BTDTO are longer than those in BTDTT. The S···S contact distances have values between 3·54 and 3·68 Å.

Introduction. The quest for molecular metals and superconductors has concentrated on multisulfur π donors and ligands over the past five years. This is due to the discovery in 1983 of a new family of organic superconductors based on 3,4;3′,4′-bis(ethylenedithio)-2,2′,5,5′-tetrathiafulvalene (BEDT-TTF) (Parkin, Engler, Schumaker, Lagier, Lee, Scott & Greene, 1983). The compound initially studied, β-(BEDT-TTF)$_2$I$_3$, had a superconductivity transition temperature (T_c) of approximately 1·6 K, but the value of T_c has been raised to 10·4 K in (BEDT-TTF)$_2$ Cu(SCN)$_2$ (Kikuchi, Murata, Honda, Namiki, Saito, Kobayashi, Ishiguro & Ikemoto, 1987). The related ligand, dmit, has also been shown to give rise to a series of molecular metals and superconductors (Kobayashi, Kim, Sasaki, Kato, Kobayashi, Moriyama, Nishio, Kajita & Sasaki, 1987; Clark, Underhill, Parker & Friend, 1989).

As part of an extensive investigation into molecular conductors we have prepared and determined the crystal structure of 4,5-bis(methylthio)-2*H*-1,3-dithiole-2-thione BTDTT and 4,5-bis(methylthio)-2*H*-1,3-dithiole-2-one BTDTO to study the influence of the *exo* heteroatom attached to C(1) on the structures of the multisulfur π systems.

Experimental. BTDTT was prepared by methylating sodium 4,5-dimercapto-1,3-dithiole-2-thione (Poleschner, John, Hoppe & Fanghänel, 1983). BTDTO was prepared by treatment of BTDTT with mercuric acetate (Varma, Bury, Harris

Table 1. *Fractional coordinates* ($\times 10^4$) *and equivalent isotropic thermal parameters of non*-H *atoms with e.s.d.'s in parentheses*

	x	y	z	B_{eq}(Å^2)
BTDTT				
S(1)	1405 (1)	1277·3 (8)	2502·1 (9)	4·29 (7)
S(2)	2122 (1)	−798·4 (6)	4059·4 (7)	3·25 (5)
S(3)	3432 (1)	−2159·2 (7)	6562·1 (9)	4·00 (6)
S(4)	4196 (1)	144·4 (7)	8224·7 (8)	3·49 (6)
S(5)	2871 (1)	1194·4 (6)	5500·3 (8)	3·16 (5)
C(1)	2090 (4)	587 (2)	3953 (3)	2·9 (2)
C(3)	2934 (4)	−908 (2)	5813 (3)	2·7 (2)
C(4)	3267 (4)	32 (2)	6489 (3)	2·7 (2)
C(31)	1882 (5)	−3008 (3)	5473 (4)	4·3 (3)
C(41)	2468 (6)	881 (3)	8857 (4)	4·5 (3)
BTDTO				
S(2)	3935·3 (6)	4542 (4)	3879 (2)	3·56 (5)
S(3)	1206·5 (6)	4386 (4)	3965 (2)	4·01 (6)
S(4)	1319·7 (6)	1351 (4)	2 (2)	3·29 (5)
S(5)	4030·6 (7)	1733 (3)	591 (2)	3·72 (5)
O(1)	5959 (2)	3288	2504 (8)	5·8 (2)
C(1)	4872 (2)	3193 (5)	2357 (8)	3·8 (2)
C(3)	2561 (2)	3632 (5)	2927 (6)	2·7 (2)
C(4)	2606 (2)	2349 (5)	1415 (6)	2·8 (2)
C(31)	1668 (3)	6085 (5)	5749 (9)	4·7 (3)
C(41)	1655 (3)	−402 (5)	1834 (7)	3·9 (2)

& Underhill, 1987). Yellow needles of BTDTT and light yellow needles of BTDTO were obtained by recrystallization from absolute ethanol. The density was determined by flotation in a mixture of CCl_4 and CH_2BrCl.

Crystals of size 0·10 × 0·16 × 0·52 mm (BTDTT) and 0·07 × 0·23 × 0·40 mm (BTDTO) were investigated on an Enraf–Nonius CAD-4F diffractometer with graphite-monochromatized Mo $K\alpha$ radiation. The lattice parameters were determined from setting angles for 23 reflections (BTDTT) with $10·78 < \theta < 14·26°$ and 24 reflections (BTDTO) with $9·65 < \theta < 15·61°$. The intensities of 2667 unique reflections were measured for BTDTT (h: $0\rightarrow 10$, k: $0 \rightarrow 17$, l: $-13 \rightarrow 13$) with $2·0 < \theta < 30·0°$. 1928 reflections with $I > 2·5\sigma(I)$ were used in the refinement process together with 'less-than' reflections [$I < 2·5\sigma(I)$] with calculated values greater than the observed (2444 contributing reflections). The intensities of 1302 unique reflections for BTDTO (h: $0 \rightarrow 15$, k: $0 \rightarrow 12$, l: $-5 \rightarrow 5$) with $2·0 < \theta < 30·0°$, 1261 with $I > 2·5\sigma(I)$, were used in the refinement process together with 'less-than' reflections ($I < 2·5\sigma(I)$] with calculated values greater than the observed (1291 contributing reflections). $\omega/2\theta$ scan technique was used with scan angles $\Delta\omega = (1·60 + 0·35\tan\theta)°$ for both structures. Three reflections were used for orientation control every 100 reflections (BTDTT: 252, 204, 253; BTDTO: $\bar{1}41$, $\bar{4}\bar{3}1$, 252). An intensity stability check was made every third hour of exposure time by using 204 (BTDTT) and $\bar{1}41$ (BTDTO). The intensities were corrected for Lorentz and polarization effects. Absorption was ignored. The structures were solved with direct methods, full-matrix least-squares refinement of anisotropic non-H atoms. Positional H-atom parameters from $\Delta\rho$ maps. Refinements of H(x,y,z) using reflections with $(\sin\theta)/\lambda < 0·40$ Å^{-1}, and fixed isotropic temperature factors. The function $\sum w(\Delta|F|)^2$ was minimized. Average $(w\Delta|F|)^2$ was almost independent of $|F_o|$ by using $w = 1$ when $|F_o| < 32$ else $w = (32/F_o)^2$ for both BTDTT and BTDTO. The refinement converged to final $R =$

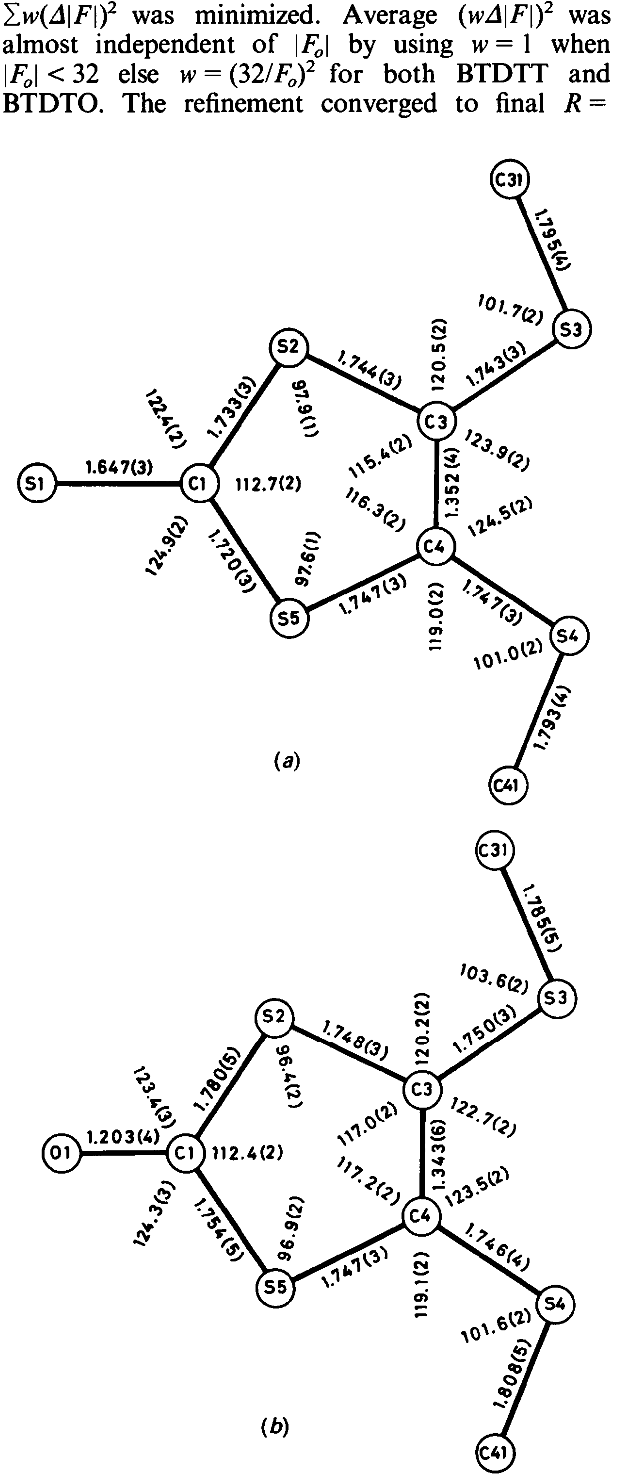


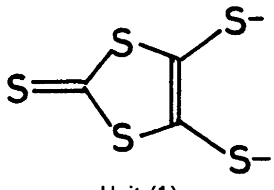
Fig. 1. Bond distances (Å), angles (°) and the atomic numbering scheme for the compounds (*a*) BTDTT, and (*b*) BTDTO. E.'s.d.'s are in parentheses.

0·027, $wR = 0{\cdot}033$, $S = 2{\cdot}54$, and $(\Delta/\sigma)_{\max} = 0{\cdot}07$ for BTDTT and $R = 0{\cdot}026$, $wR = 0{\cdot}027$, $S = 4{\cdot}26$, and $(\Delta/\sigma)_{\max} = 0{\cdot}002$ for BTDTO. Min. and max. values in final $\Delta\rho$ maps were $-0{\cdot}4$, $0{\cdot}3\ \text{e}\ \text{Å}^{-3}$ for BTDTT and $-0{\cdot}3$, $0{\cdot}4\ \text{e}\ \text{Å}^{-3}$ for BTDTO. Scattering factors from *International Tables for X-ray Crystallography* (1974). Computer programs from *SHELX*76 (Sheldrick, 1976) and *XRAY*76 (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976). The positional and thermal parameters are given in Table 1.*

Discussion. The bond distances and bond angles are shown in Fig. 1 with the atomic numbering scheme. Figs. 2 and 3 show projections of the crystal structures along the *c* axis. The dithiole ring in both BTDTT and BTDTO is essentially planar as the maximum deviation from a least-squares plane defined by the thiole ring atoms is 0·013 and 0·018 Å respectively for BTDTT and BTDTO. The two S—CH_3 groups make different torsion angles with the values C(41)—S(4)—C(4)—C(3): −121·6 (3) (BTDTT), −126·8 (3)° (BTDTO) and C(31)—S(3)—C(3)—C(4): 156·2 (2) (BTDTT), −178·1 (3)° (BTDTO).

Although the structures of the molecules can be formally drawn with single bonds between C and S within the ring, there will be some delocalized π bonding through the interaction of the sulfur *d* orbitals with the C=C and C=S (C=O) π bonds. This is evidenced by the short C—S bond distance within the ring (< 1·76 Å) compared with the S—CH_3 bond length (> 1·785 Å). The C—S bond length differences can also be rationalized in another way. The more '*s* character' in an orbital, the closer it is to the nucleus, consequently the exocyclic S—C(sp^3) bonds will be longer than the S—C(sp^2) bonds. It might be anticipated that replacing S(1) by the more electronegative O atom will remove electron density from C(1). Such an effect would be expected to result in an increase in the C(1)—S distances within the ring. This is clearly observed.

There have been a number of crystal structures determined for metal complexes of the related ligand 4,5-dimercapto-1,3-dithiole-2-thione (dmit) (Lindqvist, Andersen, Sieler, Steimecke & Hoyer, 1982; Matsubayashi, Takahashi & Tanaka, 1988).



Unit (1)

The bond lengths and angles of unit (1) are similar in both the methyl derivatives and the metal complexes, suggesting that the bonding within the unit is similar in both cases and demonstrates the covalent nature of the metal to sulfur bond. Apparently there exists a significant difference between C(1)—S(2) and C(1)—S(5) within the same molecule.

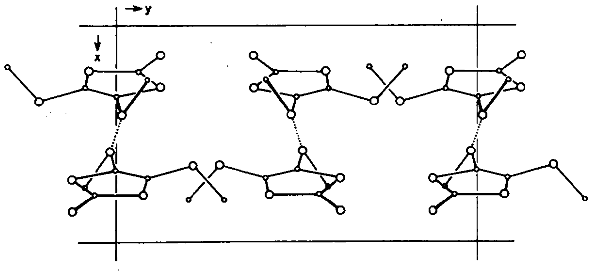


Fig. 2. The crystal structure of BTDTT projected down the *z* axis. Large circles: S atoms, small circles: C atoms, black circles: O atoms. The dotted lines represent S···S contact distances less than 3·7 Å.

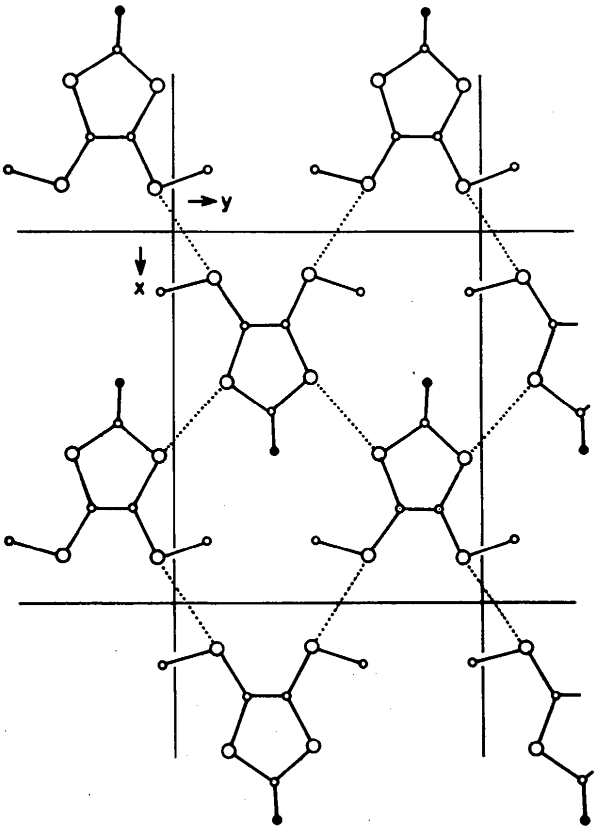


Fig. 3. The crystal structure of BTDTO projected as in Fig. 2.

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52532 (27 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

This is also commonly observed for the metal complex (Bousseau, Valade, Legros, Cassoux, Garbauskas & Interrante, 1986; Groeneveld, Schuller, Kramer, Haasnoot & Reedijk, 1986), but there is no obvious explanation for this effect.

The variation in bond lengths observed between the different metal complexes probably reflects differences in intermolecular S···S interactions. In BTDTT there is only one S···S contact less than 3·7 Å [S(4)···S(4, $1-x$, $-y$, $2-z$), 3·535 (1) Å, whereas in BTDTO there are three weak S···S interactions at [S(3)···S(4, $-x$, $\frac{1}{2}+y$, $-z$), 3·592 (2), S(2)···S(5, $1-x$, $\frac{1}{2}+y$, $1-z$), 3·664 (2) and S(2)···S(5, $1-x$, $\frac{1}{2}+y$, $-z$), 3·681 (2) Å].

We would like to thank the SERC for support (to AEU and KSV). Financial support from the Danish Natural Science Research Council and Thomas B. Thriges Foundation for the purchase of the X-ray diffraction equipment is gratefully acknowledged.

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Acta Cryst. (1990). **C46**, 807–809

Structure of a Dimer Ketone* Formed *via* Fe(CO)$_5$-Promoted Coupling of 7-(*p*-Cyanophenoxy)norbornadiene to Carbon Monoxide

By Judith L. Flippen-Anderson, Richard Gilardi and Clifford George

Laboratory for the Structure of Matter, Naval Research Laboratory, Washington DC 20375, USA

and Alan P. Marchand and Paritosh R. Dave

Department of Chemistry, University of North Texas, PO Box 5068, Denton, Texas 76203, USA

(*Received* 22 *March* 1989; *accepted* 31 *July* 1989)

Abstract. (*syn,syn*)-1,4,4aα,4bβ,5,8,8aβ,9aα-Octahydro-10,11-di(*p*-cyanophenoxy)-1,4:5,8-dimethanofluoren-9-one, $C_{29}H_{22}N_2O_3$, $M_r = 446{\cdot}53$, triclinic, $P\bar{1}$, $a = 10{\cdot}186$ (2), $b = 11{\cdot}148$ (2), $c = 12{\cdot}052$ (2) Å, $\alpha = 110{\cdot}36$ (2), $\beta = 109{\cdot}90$ (2), $\gamma = 98{\cdot}68$ (2)°, $V = 1148{\cdot}8$ (4) Å^3, $Z = 2$, $D_x = 1{\cdot}29$ Mg m^{-3}, λ(Mo $K\alpha$) $= 0{\cdot}71073$ Å, $\mu = 0{\cdot}79$ mm^{-1}, $F(000) = 468$, $T = 225$ K, final $R = 0{\cdot}041$ for 2399 observed reflections. The central five-membered ring is planar with normal bond lengths and angles. The norbornene rings are fused to the central ring in an *anti* fashion and are under considerable strain showing both bond lengths (C—C distances as long as 1·559 Å) and angles (C—C—C angles as small as 94·2°) which deviate significantly from normal values.

Introduction. As part of an ongoing study of the thermal reactions of iron carbonyls with 7-substituted norbornadienes (Marchand & Hayes, 1977; Marchand, Earlywine & Heeg, 1986), the reactions of Fe(CO)$_5$ and of Fe$_2$(CO)$_9$ with 7-(*p*-cyanophenoxy)norbornadiene (1) were investigated. Compound (1) was synthesized *via* palladium(II)-

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* (*syn,syn*)-1,4,4aα,4bβ,5,8,8aβ,9aα-Octahydro-9-oxo-1,4:5,8-dimethanofluoren-10,11-diylbis(*p*-oxybenzonitrile).