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2,2′,6,6′-Tetraethoxycarbonyl-4,4′-bithiapyranylidene*

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Abstract. $C_{22}H_{24}O_8S_2$, orthorhombic, *Ibam*, a = 23·762 (9), b = 14·486 (2), c = 6·788 (3) Å, V = 2336 Å^3, Z = 4, D_c = 1·366, D_m = 1·36 (1) Mg m^{-3}, λ(Mo $K\alpha$) = 0·71073 Å. Full-matrix least-squares refinement based on 609 reflections having $F > \sigma(F)$ led to a final R of 0·057 and weighted R of 0·048. The space-group symmetry requires that the molecules of the title compound be either planar or disordered in the lattice; the planar model provides an adequate fit to the data. The molecular planes lie perpendicular to the c axis, the interplanar distance being $c/2$ (3·394 Å). The S—S axes of neighboring molecules are staggered with respect to each other by 88°.

Introduction. In our structural studies of the 1:1 salt of 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ) with 2,2′,6,6′-tetramethyl-$\Delta^{4,4'}$-bithiapyran (TMBTP) (Darocha, Titus & Sandman, 1979) and the 3:2 salt of TCNQ with $\Delta^{4,4'}$-bithiapyran (BTP) (Sandman, Epstein, Holmes, Lee & Titus, 1980), it was noted that the central double bond in cation radicals of TMBTP and BTP have relatively long lengths, 1·435 (3) and 1·429 (6) Å, respectively. In the structural chemistry of charge-transfer complexes, it is well established that oxidation of a molecular species results in small, but significant, alterations in its molecular structure. In order to examine the nature of these alterations in BTP complexes, we require structural data for a neutral BTP example. Since we have so far been unable to obtain X-ray-suitable crystals of either neutral BTP or TMBTP, we have studied the readily available (Sandman, Holmes & Warner, 1979) 2,2′,6,6′-tetraethoxycarbonyl BTP derivative (TCBTP). Initial results from this work have been reported (Titus, Lee & Darocha, 1979) and the structure of another neutral BTP derivative has since appeared (Luss & Smith, 1980).

Crystals suitable for X-ray analysis were obtained by slow cooling of warm benzene solution in a Dewar flask. Dark-green iridescent needles were isolated by suction filtration. The crystal used for data collection measured 0·08 × 0·05 × 0·25 mm and was mounted with its longest dimension nearly coincident with the φ axis of an Enraf–Nonius CAD-4 diffractometer. The data were collected by the Molecular Structure Corporation, College Station, Texas 77840. The cell parameters were obtained from a least-squares refinement of diffractometer settings for 25 reflections. A total of 946 reflections were collected up to a 2θ (Mo $K\alpha$) of 45°; from these reflections, a set of 907 independent reflections was obtained.

Three reflections were monitored periodically during the data collection; no significant changes were observed. The intensities were corrected for Lorentz and polarization effects, but not for absorption [μ(Mo $K\alpha$) = 2·71 cm^{-1}]. A data set consisting of the 609 reflections with $F > \sigma(F)$ was used for solution and refinement of the structure.

The structure was solved by Patterson and Fourier methods, and refined by full-matrix techniques to an R value $(=\sum |F_o| - |F_c|/|F_o|)$ of 0·057 and a weighted R $[=(\sum w||F_o| - |F_c||^2/\sum w|F_o|^2)^{1/2}]$ of 0·048. The quantity minimized was $\sum w(|F_o| - |F_c|)^2$ and the weight, w, was $[\sigma^2(F)]^{-1}$. Except for the H-atom thermal parameters (for which there were final shifts of 0·6σ), no parameter shifted more than 0·07σ in the final cycle.

The scattering factors employed for C, O, and S were those of Cromer & Waber (1965) and for H were those of Stewart, Davidson & Simpson (1965). The scattering factors of S were corrected for anomalous dispersion (Cromer & Liberman, 1970). The positional parameters are reported in Table 1.‡

* Alternative name: tetraethyl 4,4′-dithia-1,1′-bi-2,5-cyclohexadienylidene-3,3′,5,5′-tetracarboxylate.

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‡ Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36761 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Final atomic coordinates and isotropic thermal parameters*

E.s.d.'s are in parentheses.

	x^a	y^a	U_{eq}/U^b (Å^2)
S	1143 (1)	1954 (1)	61 (1)
C(1)	1212 (2)	767 (3)	43 (4)
C(2)	412 (2)	2030 (3)	43 (4)
C(3)	797 (2)	155 (3)	48 (4)
C(4)	54 (2)	1316 (3)	43 (4)
C(5)	206 (2)	348 (3)	36 (4)
C(11)	1819 (2)	473 (4)	53 (5)
C(12)	2439 (2)	−820 (4)	77 (6)
C(13)	2363 (3)	−1839 (5)	111 (7)
C(21)	215 (2)	3008 (4)	48 (4)
C(22)	−581 (3)	4007 (4)	76 (5)
C(23)	−1201 (3)	3912 (5)	114 (8)
O(11)	2202 (1)	1002 (2)	70 (4)
O(12)	1869 (1)	−439 (2)	67 (3)
O(21)	538 (2)	3648 (2)	68 (3)
O(22)	−337 (1)	3074 (2)	65 (3)
H(3)	943 (16)	−418 (29)	35 (14)
H(4)	−313 (17)	1452 (30)	44 (15)
H(121)^c	2643 (13)	−612 (23)	77 (13)
H(131)	2709 (31)	−2090 (56)	144 (30)
H(132)^c	2128 (20)	−2014 (38)	174 (23)
H(221)^c	−429 (13)	4280 (24)	78 (13)
H(231)	−1441 (28)	4533 (42)	114 (25)
H(232)^c	−1314 (20)	3597 (29)	147 (20)

(*a*) $\times 10^4$. (*b*) $\times 10^3$. For atoms refined anisotropically, $U_{eq} = (\frac{1}{6}\pi^2)\sum_i\sum_j \beta_{ij}\,\mathbf{a}_i.\mathbf{a}_j$. (*c*) All *z* coordinates were set to zero excepting those of H(121), H(132), H(221), and H(232); their *z* coordinates refined to 1263 (53), 1086 (85), 1097 (55), and 1294 (77), respectively ($\times 10^4$).

The systematic extinctions *hkl* ($h + k + l \neq 2n$), $0kl$ ($k \neq 2n$, $h \neq 2n$), and $h0l$ ($h \neq 2n$, $l \neq 2n$), do not distinguish the space groups *Ibam* and *Iba*2. The successfully refined model used *Ibam* symmetry; trial models employing *Iba*2 symmetry could not be refined to chemically realistic structures.

Programs used in the determination were extensively modified versions of *FORDAP* (Zalkin, 1965), *ORFLS* (Busing, Martin & Levy, 1962), and *ORFFE* (Busing, Martin & Levy, 1964). Drawings were produced with the aid of *ORTEP* (Johnson, 1965).

Discussion. The TCBTP molecule has $2/m$ symmetry, requiring all non-H atoms to be coplanar. Relatively large anisotropic thermal parameters for the ethyl-group atoms indicate that a disordered, nearly planar configuration for them might be possible. However, the lack of any large peaks in the final difference Fourier map, coupled with the relatively small data set, discouraged any detailed study of disorder in the system. The atomic labeling is indicated in Fig. 1, with important bond distances and angles listed in Table 2. Structural parameters for the ester groups are well within the range of values commonly observed for related systems.

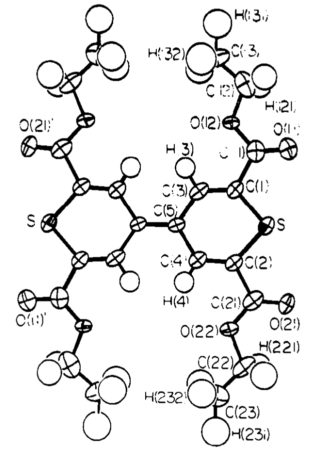


Fig. 1. Atomic labeling for TCBTP. Ellipsoids are drawn at the 50% probability level. The spheres representing the H atoms have been reduced for clarity.

Table 2. *Interatomic distances* (Å) *and angles* (°)

S–C(1)	1·728 (5)	O(12)–C(12)	1·464 (7)
S–C(2)	1·740 (5)	O(22)–C(22)	1·471 (6)
C(1)–C(3)	1·326 (7)	C(12)–C(13)	1·487 (9)
C(2)–C(4)	1·338 (6)	C(22)–C(23)	1·479 (10)
C(3)–C(5)	1·430 (7)	C(3)–H(3)	0·90 (4)
C(4)–C(5)	1·449 (6)	C(4)–H(4)	0·89 (4)
C(5)–C(5^{i})	1·405 (8)	C(12)–H(121)	1·03 (3)
C(1)–C(11)	1·505 (7)	C(13)–H(131)	0·90 (7)
C(2)–C(21)	1·492 (7)	C(13)–H(132)	0·96 (6)
C(11)–O(11)	1·190 (6)	C(22)–H(221)	0·92 (3)
C(21)–O(21)	1·203 (5)	C(23)–H(231)	1·06 (6)
C(11)–O(12)	1·328 (5)	C(23)–H(232)	1·03 (5)
C(21)–O(22)	1·316 (5)		

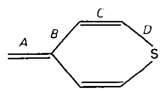
C(1)–S–C(2)	99·0 (2)	C(21)–O(22)–C(22)	117·4 (5)
C(3)–C(1)–S	126·5 (4)	O(12)–C(12)–C(13)	105·1 (5)
C(4)–C(2)–S	125·8 (4)	O(22)–C(22)–C(23)	107·9 (5)
C(5)–C(3)–C(1)	126·8 (5)	C(5)–C(3)–H(3)	124 (3)
C(5)–C(4)–C(2)	126·1 (5)	C(5)–C(4)–H(4)	117 (3)
C(4)–C(5)–C(3)	115·7 (4)	H(121)–C(12)–H(121^{ii})	112 (4)
C(1)–C(11)–O(11)	123·6 (5)	H(131)–C(12)–H(132)	115 (4)
C(2)–C(21)–O(21)	122·2 (4)	H(132)–C(13)–H(132^{ii})	101 (6)
C(1)–C(11)–O(12)	111·4 (5)	H(221)–C(22)–H(221^{ii})	109 (4)
C(2)–C(21)–O(22)	112·4 (4)	H(231)–C(23)–H(232)	104 (3)
C(11)–O(12)–C(12)	117·2 (4)	H(232)–C(23)–H(232^{ii})	118 (5)

Symmetry code: (i) $\bar{x},\bar{y},0$; (ii) $x,y,\bar{z}$.

The present structure provides a base of structural information which can be used for comparisons with the BTP moiety in oxidized forms. Table 3 gives a summary of bond distances which are particularly sensitive to changes in oxidation state. As is often the case in such comparisons, the differences noted between neutral and oxidized species are barely significant. The data currently available, however, are remarkably consistent, indicating that the differences are real.

The central 'double' bond (*A*) is actually longer than the 'single' bond (*B*) in the oxidized examples of BTP and TMBTP. In the neutral species, the situation is reversed, with the 'single' bond being the longer of the

Table 3. *Comparison of bond distances* (Å) *for 4-thiapyranylidene*



Values are symmetry-averaged where possible.

	Neutral		Oxidized	
	TCBTP[a]	φ_4BTP[b]	BTP[c]	TMBTP[d]
A	1·405 (8)	1·389 (7)	1·429 (6)	1·435 (3)
B	1·439 (7)	1·441 (5)	1·418 (1)	1·421 (1)
C	1·332 (8)	1·339 (5)	1·351 (11)	1·360 (4)
D	1·732 (5)	1·745 (3)	1·702 (8)	1·710 (4)

(*a*) This study. (*b*) Tetraphenylbithiapyranylidene (Luss & Smith, 1980). (*c*) In BTP–TCNQ (2:3) (Sandman *et al.*, 1980). (*d*) In TMBTP.TCNQ (Darocha *et al.*, 1979).

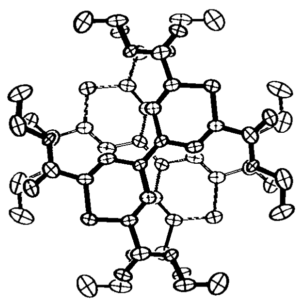


Fig. 2. Projection looking along the *c* axis. Ellipsoids are drawn at the 50% probability level.

two. In the oxidized and neutral examples, both the (*A*) and (*B*) bond distances resemble aromatic C—C distances, pointing to a considerable degree of electron delocalization in these bonds. The ring 'double' bond (*C*) is much shorter in the neutral species, at the upper end of the range usually reported for C double bonds. Oxidation of the system lengthens this bond while shortening the adjacent C—S bond. These changes tend to confirm the expectation that the bonding in BTP donors becomes more 'aromatic' upon the loss of an electron.

The relatively long central double bonds observed in neutral BTP derivatives are not limited to these compounds, but may be a general feature of centrosymmetric molecules in which a formal double bond is tetrasubstituted by conjugated double bonds with H substituents. The central double bond in heptafulvalene (Thomas & Coppens, 1972) is 1·379 Å, and the double bond between rings in 3,3″,5,5″-tetra-*tert*-butyl-*p*-terpheno-*p*-quinone is 1·417 Å (Jorgensen & West, 1981).

The TCBTP molecules crystallize in uniform stacks (interplanar distance, 3·394 Å) along the *c* axis. Interplanar contacts are minimized by a staggering of adjacent molecules by about 88°; there are no S—S contacts. The shortest interplanar contact for non-H atoms is between C(11) and O(12) $(x,\bar{y},\frac{1}{2})$ at 3·396 (2) Å. Additional short contacts are C(4)—C(4) $(\bar{x},y,\frac{1}{2})$ 3·404 (2), C(21)—O(22) $(\bar{x},y,\frac{1}{2})$ 3·408 (2), and C(3)—C(3) $(x,\bar{y},\frac{1}{2})$ 3·424 (2) Å. A view of two adjacent molecules seen down **c** is given in Fig. 2.

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