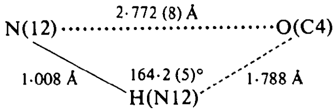
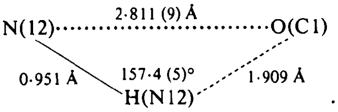
are presented in Fig. 3. The molecules are linked in infinite chains by a system of hydrogen bonds:



where O(C4) denotes the O atom of a molecule at $x + 1$, y, z. There is another hydrogen bond between the N(12) and O(C1) atoms:



The existence of bifurcated hydrogen bonding was assumed between the N(12), N(1) and O(C11) atoms. The angle N(1)—H(N12)—N(12) is 93·3 (4)°. As the distance of 2·917 (9) Å between N(1) and N(12) is too large, and the free electron pair of N(1) is involved in a conjugated double-bond system, we had to discount this possibility.

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The Structure of Tetraphenyldithiapyranylidene*

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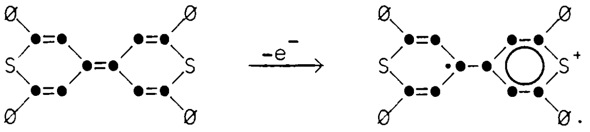
Abstract. $C_{34}H_{24}S_2$, $M_r = 496{\cdot}7$, monoclinic, $I2/a$, $a = 25{\cdot}090\,(4)$, $b = 5{\cdot}537\,(3)$, $c = 18{\cdot}067\,(4)$ Å, $\beta = 100{\cdot}17\,(2)°$, $V = 2471\,(2)$ Å^3, $Z = 4$, $D_m = 1{\cdot}34$, $D_c = 1{\cdot}335$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, μ(Mo $K\alpha$) = 0·24 mm^{-1}, $F(000) = 1040$. The structure was solved from diffractometer data by direct methods and refined by block-diagonal least squares to $R = 0{\cdot}055$. The centrosymmetric molecules are only approximately planar. The C(3)—C(3′) bond joining the thiapyranylidene rings is 1·389 Å, and the chemically unique bonds in the rings average 1·745 for S—C(1), 1·339 for C(1)—C(2), and 1·441 Å for C(2)—C(3). These distances are consistent with a hybrid molecule composed of contributions of 50% from the uncharged species and 50% from charge-separated canonical structures involving an aromatic sextet.

Introduction. The title compound (φ_4DTP) can be oxidized to form a radical cation having an aromatic sextet (Perlstein, 1977):



Such a material can function as a donor molecule in highly conducting organic charge-transfer salts. Ion-radical salts of φ_4DTP with TCNQ (Alizon *et al.*, 1977; Isett, Reynolds, Schneider & Perlstein, 1979*a*) and with iodide (Isett, Reynolds, Schneider & Perlstein, 1979*b*) have been prepared and the electrical properties investigated. We have recently completed studies of the crystal structures of two highly conducting iodide salts, $\varphi_4DTP(I_3)_{0\cdot36}(I_5)_{0\cdot40}$ (DTPI1) and $\varphi_4DTP(I_3)_{0\cdot72}$ (DTPI2) (Luss & Smith, 1980), and report here the structure of φ_4DTP for comparison with the oxidized φ_4DTP ions.

Gold, prismatic crystals elongated along b were produced on cooling and evaporating a heated 6:1 THF:acetonitrile solution. Precession photographs showed systematic absences for hkl, $h + k + l$ odd, and $h0l$, h odd, which were consistent with space groups Ia and $I2/a$. The structure was successfully solved in $I2/a$.

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

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Data were collected at Molecular Structure Corp. (MSC) in College Station, Texas, on an Enraf–Nonius CAD-4 diffractometer with graphite-monochromated Mo $K\alpha$ radiation. The cell parameters were determined by least-squares refinement of the settings for 25 reflections ($11 < 2\theta < 27°$). Intensities were measured ($2\theta < 45°$) by the θ–2θ scan technique at a variable scan rate of 4 to 40° min^{-1} (2θ) and were corrected for Lorentz and polarization effects but not for absorption. Of the 1605 intensities measured, 1322 had $I > \sigma(I)$ and were considered observed. Unobserved reflections were excluded from further calculations.

The structure was solved by direct methods at MSC using their structure-determination programs. An E map calculated using the phase set with the best combined figure of merit gave all the nonhydrogen atom positions. H atom positions were determined from a subsequent difference electron density map. Refinement (carried out at our laboratories) was by block-diagonal least squares (Ahmed, 1970) with 9 × 9 and 4 × 4 blocks, respectively, for atoms with anisotropic or isotropic thermal parameters. The quantity minimized was $\sum w(F_o - KF_c)^2$ with the final weighting defined by $w^{-1} = \sigma^2(F_o) + (0{\cdot}02F_o)^2 + 2{\cdot}0$. Atomic scattering factors and anomalous-scattering factors for S were obtained from *International Tables for X-ray Crystallography* (1974).

Refinement with isotropic temperature factors for hydrogens and anisotropic temperature factors for all other atoms converged to $R = 0{\cdot}055$ and $R_w = 0{\cdot}067$. All parameter shifts on the final cycle were $<0{\cdot}2\sigma$. The final scale factor, K, was 1·474 (6). Residual density in the difference electron density map was between −0·22 and +0·23 e Å^{-3} except for two peaks (+0·53 and −0·52 e Å^{-3}) about 1 Å on either side of the S atom position. The final atomic parameters are given in Table 1, with estimated standard deviations in parentheses.*

Discussion. The molecules possess crystallographic $\bar{1}$ symmetry compared to crystallographic 222 symmetry for both DTPI1 and DTPI2. Atomic labeling and bond lengths and angles are given in Fig. 1, which shows the excellent consistency for chemically equivalent pairs of bonds and angles. The distances are consistent with a hybrid molecule composed of contributions of 50% from the uncharged species

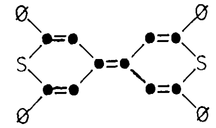

Table 1. *Fractional atomic coordinates* (×10^3 *for hydrogen and* ×10^4 *for other atoms*)

For nonhydrogen atoms the thermal parameters are isotropic equivalents of the anisotropic thermal parameters (Hamilton, 1959). Equivalent positions in *I*2/*a* are (0,0,0; $\frac{1}{2}\frac{1}{2}\frac{1}{2}$) ± ($x,y,z$; $\frac{1}{2}-x,y,\bar{z}$).

	x	y	z	$B_{\rm iso}$ (Å^2)
S	2893·0 (4)	2116 (2)	6092·9 (7)	5·9
C(1)	2279 (1)	1855 (6)	6410 (2)	3·0
C(2)	2198 (1)	189 (6)	6918 (2)	3·1
C(3)	2577 (1)	−1603 (6)	7271 (2)	3·0
C(4)	3125 (1)	−1390 (6)	7143 (2)	3·4
C(5)	3314 (1)	115 (6)	6673 (2)	3·1
C(6)	3887 (1)	178 (6)	6569 (2)	3·2
C(7)	4078 (2)	1932 (7)	6143 (3)	5·3
C(8)	4609 (2)	1952 (9)	6042 (3)	6·3
C(9)	4965 (1)	264 (8)	6363 (2)	5·2
C(10)	4786 (2)	−1499 (9)	6773 (3)	6·0
C(11)	4255 (2)	−1563 (8)	6869 (3)	5·4
C(12)	1857 (1)	3563 (6)	6057 (2)	3·1
C(13)	1318 (1)	3227 (7)	6103 (2)	4·9
C(14)	928 (2)	4803 (8)	5766 (3)	5·6
C(15)	1057 (2)	6742 (7)	5365 (2)	4·8
C(16)	1587 (2)	7115 (7)	5314 (2)	4·5
C(17)	1982 (1)	5557 (6)	5654 (2)	3·7
H(2)	185 (1)	24 (6)	707 (2)	4·6 (8)
H(4)	338 (1)	−234 (7)	743 (2)	5·5 (9)
H(7)	384 (1)	303 (7)	597 (2)	6·7 (10)
H(8)	471 (2)	311 (8)	575 (2)	7·7 (11)
H(9)	532 (1)	24 (7)	630 (2)	5·8 (9)
H(10)	501 (2)	−254 (8)	699 (2)	8·0 (11)
H(11)	414 (2)	−272 (8)	710 (2)	7·1 (10)
H(13)	121 (2)	182 (8)	639 (2)	7·0 (10)
H(14)	57 (2)	445 (9)	579 (2)	8·1 (11)
H(15)	79 (1)	767 (6)	514 (2)	4·4 (8)
H(16)	170 (1)	842 (7)	503 (2)	6·2 (10)
H(17)	233 (1)	586 (6)	565 (2)	3·6 (7)

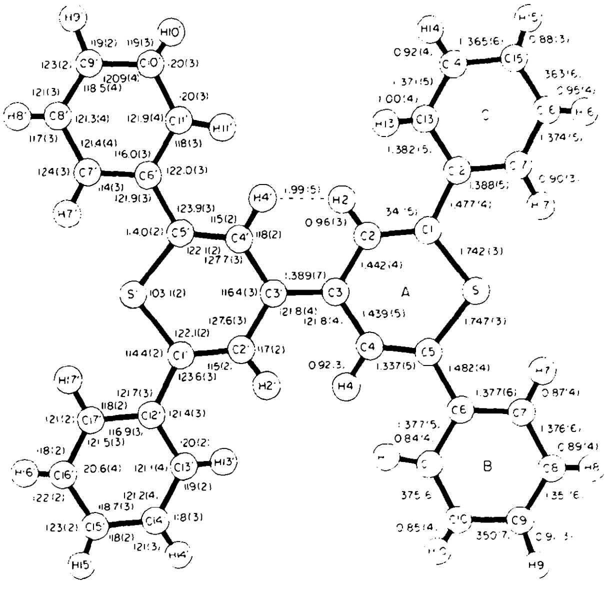

Fig. 1. Atomic labeling and bond lengths (Å) and angles (°) with e.s.d.'s given in parentheses.

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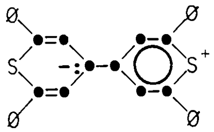
* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34994 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Comparison of bond lengths with expected values and with similar bonds in the radical-cation polyiodide salts*

	Bond numbers		Bond lengths (Å)			
	Observed[a]	Predicted	Predicted[a]	φ_4DTP[b]	DTPI1[c]	DTPI2[c]
S–C(1) S–C(5)	*d*	1·13	*d*	1·742 1·747	1·729	1·715
C(1)–C(2) C(4)–C(5)	2·0	1·79	1·35	1·341 1·337	1·360	1·366
C(3)–C(3′)	1·5	1·50	1·39	1·389	1·447	1·442
C(2)–C(3) C(3)–C(4)	1·2	1·21	1·44	1·442 1·439	1·417	1·422
C(1)–C(12) C(5)–C(6)	1·0	1·00	1·48	1·477 1·482	1·465	1·482

(*a*) Burke-Laing & Laing (1976). (*b*) This study. (*c*) Luss & Smith (1980). (*d*) Reliable bond-length bond-number curves are not available. The bonds here compare very favorably with those found in TTT_2I_3 [av. = 1·738 (3) Å] where a bond number of 1·13 is expected (Smith & Luss, 1977).

and 50% from the twelve canonical structures of the form



in which charges have separated to form an aromatic sextet in one of the thiapyranylidene rings. A bond-length bond-number curve (Burke-Laing & Laing, 1976) was used to obtain observed bond numbers for the C–C bonds. These are compared in Table 2 with bond numbers expected for a 50/50 combination of the above structures, the ratio having been selected to give reasonable agreement between observed and predicted values. Also in Table 2, the predicted and observed bond lengths are compared and show very good agreement. The comparable bond lengths for the oxidized φ_4DTP species in the polyiodide complexes are also listed and show the much greater contribution of the aromatic sextet form in these structures in which the φ_4DTP moiety has a charge of about +0·74.

The thiapyranylidene ring is only approximately planar with maximum and r.m.s. deviations of 0·070 and 0·050 Å, respectively, but can be considered to be creased about a line between S and C(3) forming two planes which enclose a dihedral angle of 9·3°. Planes fitted to the two thiapyranylidene rings of a molecule are necessarily parallel but are separated by 0·28 Å. Both the crease and the plane displacement help to relieve overcrowding between the H(2) and H(4′) atoms. In the oxidized polyiodides DTPI1 and DTPI2 (Luss & Smith, 1980), the thiapyranylidene rings, which are related by twofold symmetry, are not parallel but are twisted relative to each other by 20·7 and 20·9°, respectively. Both phenyl rings in φ_4DTP are twisted about the C–C bond to the thiapyranylidene rings, describing dihedral angles of 8·2° between rings *A* and *B* (Fig. 1) and 12·5° between rings *A* and *C*. The comparable angles are 26·1° in DTPI1 and 26·5° in DTPI2.

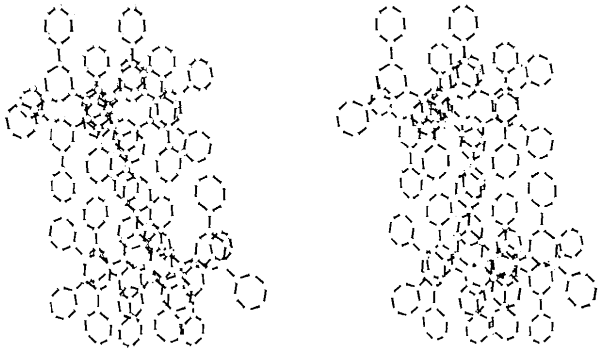


Fig. 2. (001) stereoscopic view (Johnson, 1971) of the molecular packing. The *b* axis is horizontal, left to right, and *a* is vertical, top to bottom. Atom C(1) has been drawn larger for identification.

The molecular packing is shown in Fig. 2. The molecules pack plane-to-plane in columns along *b*. Adjacent columns in the *a* and *c* directions are related by the *a* and *c* glides. Because the molecule is not planar, excluding phenyls, the plane-to-plane separation is not well defined; however, the distance between planes fitted to the molecules (excluding phenyls) is 3·5 Å.

We thank Mrs E. D. Schneider for providing the crystals, Dr J. H. Perlstein for suggesting the problem, and Dr B. A. Frenz and Dr J. M. Troup of Molecular Structure Corp. for the use of their equipment for data collection and initial structure solution.

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cis-9-Ethyl-9-methylthioxanthene 10-Oxide

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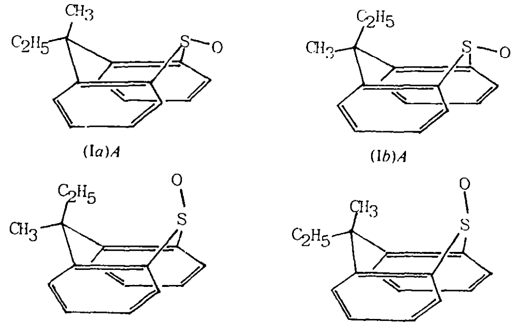
Abstract. $C_{16}H_{16}OS$, orthorhombic, *Pnam*, $Z = 4$, $M_r = 256{\cdot}35$, $a = 11{\cdot}249\,(1)$, $b = 9{\cdot}693\,(1)$, $c = 11{\cdot}797\,(2)$ Å, $V = 1286{\cdot}3\,(2)$ Å^3, $D_x = 1{\cdot}322$ Mg m^{-3}, $\lambda(\mathrm{Cu}\ K\alpha) = 1{\cdot}5418$ Å, $\mu(\mathrm{Cu}\ K\alpha) = 2{\cdot}027$ mm^{-1}, final $R = 0{\cdot}063$. In the *cis* isomer of the title compound, the 9-ethyl and 10-oxide groups have a *cis* relation, and both are in a 'boat-equatorial' conformation with respect to the central ring. The two halves of the molecule are related by a mirror plane.

Introduction. Single crystals of the title compound (I) were obtained through the courtesy of Dr Andrew L. Ternay Jr of the Chemistry Department of the University of Texas at Arlington. The crystals are transparent prisms. The unit-cell parameters were obtained from a least-squares analysis of 15 reflections with 2θ values in the range of 20–65°. The space group, $Pna2_1$ or *Pnam*, was deduced from systematic absences (0*kl* absent with $k + l$ odd, *h*0*l* absent with *h* odd). The intensity data were collected on a Syntex $P2_1$ automatic diffractometer with a crystal approximately $0{\cdot}54 \times 0{\cdot}18 \times 0{\cdot}11$ mm. The crystal was mounted with the *a* axis approximately along the φ axis of the diffractometer. A $\theta/2\theta$ scanning mode with graphite-monochromated Cu $K\alpha$ radiation was used to measure 1128 independent reflections with 2θ values below 130°; of these, 1006 reflections were considered as observed by the criterion $I > 3{\cdot}0\sigma(I)$, where $\sigma(I)$ was determined from counting statistics. The intensity data were reduced to structure amplitudes by the application of Lorentz and polarization factors, and no absorption corrections were applied.



(Ia)*A* (Ib)*A*

(Ia)*B* (I) (Ib)*B*

The structure was determined by the application of direct methods with the weighted multisolution tangent-refinement program *MULTAN* (Germain, Main & Woolfson, 1971). The correct space group was proved to be *Pnam* by the structure determination, and the normalized structure factors were also shown to have centrosymmetric distributions. The ratios between $\langle E \rangle$, $\langle E^2 \rangle$, and $\langle E^2 - 1 \rangle$ are 0·815, 1·000, and 0·922, respectively. The *E* map showed the positions of all non-hydrogen atoms. The refinement was carried out by the full-matrix least-squares method (Busing, Martin

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