Table 5. *Intermolecular contacts* (Å) *less than* 3·8 Å

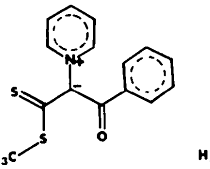
Standard deviations are in parentheses.

Symmetry code

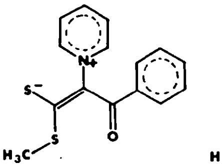
(i) $-1+x,\quad y,\quad z$
(ii) $1-x,\quad \frac{1}{2}+y,\quad \frac{1}{2}-z$
(iii) $1-x,\quad -\frac{1}{2}+y,\quad \frac{1}{2}-z$
(iv) $1-x,\quad -y,\quad -z$
(v) $1-x,\quad -y,\quad 1-z$
(vi) $x,\quad \frac{1}{2}-y,\quad \frac{1}{2}+z$
(vii) $-1+x,\quad \frac{1}{2}-y,\quad -\frac{1}{2}+z$

C(1)···C(11)^{i}	3·596 (5)	S(4)···C(18)^{iii}	3·487 (4)
C(1)···C(12)^{i}	3·623 (5)	S(4)···C(19)^{iii}	3·638 (4)
C(1)···C(17)^{vii}	3·552 (6)	O(7)···C(9)^{v}	3·395 (5)
C(1)···C(18)^{i}	3·582 (6)	O(7)···C(10)^{v}	3·717 (6)
S(2)···C(9)^{v}	3·772 (3)	O(7)···C(11)^{ii}	3·759 (5)
S(2)···C(17)^{i}	3·487 (5)	O(7)···C(12)^{vi}	3·769 (5)
S(2)···C(18)^{i}	3·781 (5)	O(7)···C(13)^{vi}	3·163 (5)
S(4)···C(12)^{iv}	3·740 (4)		

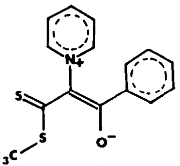
From these data, three possible canonical forms of the title compound can be drawn: the pyridinium ylide structure (I) has sufficient negative charge on the central C(5) atom, but structures (II) and (III) may also make some contribution.



(I)



(II)



(III)

Intermolecular interatomic distances, less than 3·8 Å, are listed in Table 5, the shortest of which is O(7)···C(13) of 3·16 Å.

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The 1:1 Salt from 2,2′,6,6′-Tetramethyl-$\Delta^{4,4'}$-bithiopyran (TMBTP) and 7,7,8,8-Tetracyano-*p*-quinodimethane (TCNQ)

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Abstract. TMBTP–TCNQ, $C_{26}H_{20}N_4S_2$, triclinic, $P\bar{1}$, $a = 7{\cdot}209$ (1), $b = 8{\cdot}404$ (1), $c = 10{\cdot}139$ (2) Å, $\alpha = 107{\cdot}21$ (1), $\beta = 97{\cdot}33$ (1), $\gamma = 102{\cdot}70$ (1)°, $V = 560{\cdot}1$ Å^3, $D_m = 1{\cdot}35 \pm 0{\cdot}01$, $D_c = 1{\cdot}342$ Mg m^{-3}. Full-matrix least-squares refinement with all atoms anisotropic based on 1752 reflections led a final R of 0·037 and weighted R of 0·048. The TMBTP molecular ion is nearly planar except for the H atoms, while the TCNQ is slightly twisted about its long axis. The bond distances and angles observed for the TCNQ molecular ions are very close to literature values for TCNQ$^-$. The molecular ions occur in an alternating (mixed) stack; least-squares planes of TMBTP and TCNQ are not quite parallel, deviating by 5·3°. The average distance from atoms of TMBTP to the plane of TCNQ is 3·4 Å.

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Introduction. The synthesis and initial electrical characterization of a new class of highly conducting salts of 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ) and the parent and 2,2′,6,6′-tetramethyl derivatives of $\Delta^{4,4'}$-bithiopyran (BTP), an organosulfur donor iso-π-electronic to the extensively studied tetrathiafulvalene (TTF), were recently reported (Sandman, Epstein, Holmes & Fisher, 1977). This paper reports the structure determination of the semiconducting TMBTP–TCNQ, and is the first complete structure determination of a 1:1 mixed-stack example of a 14-π-electron organochalcogen–TCNQ salt. Lattice constants have been reported for the mixed-stack 1:1 TCNQ salts of the tetra-*n*-propyl (Coleman, Yamagishi, Garito, Heeger, Dahm, Miles & Wilson, 1975) and octamethylene (Tanaka, Tanaka, Kawai, Takobe & Maki, 1976) derivatives of TTF, and the structure of a 1:2 mixed-stack TCNQ salt of tetraethyl-TTF has been recently reported (Galigné, Fabre & Giral, 1977). The structure of 1:1 mixed-stack TCNQ salts of tetramethyl-*p*-phenylenediamine (TMPD) (Hanson, 1965), dimethyldihydrophenazine (Goldberg & Shmueli, 1973), and methyldihydrophenazine (Morosin, 1976) are also known. The structural work on segregated-stack derivatives of TTF–TCNQ has been reviewed (Stucky, Schultz & Williams, 1977). Lattice constants consistent with a segregated-stack structure have been reported for the 1:1 TCNQ salt of 2,2′,6,6′-tetraphenyl-BTP (Alizon, Blanc, Gallice, Robert, Fabre, Strezelecka, Rivory & Weyl, 1976).

Crystals of TMBTP–TCNQ suitable for X-ray analysis were obtained by mixing a dry dimethylformamide (5 ml) solution of twice-gradient-sublimed TCNQ (30·2 mg, 0·15 mmol) with a dimethylformamide (1 ml) solution of twice-gradient-sublimed TMBTP (37·8 mg, 0·15 mmol) at room temperature in a glove box under nitrogen. The solution was stored in a refrigerator at 273 K overnight. Dark purple crystals with highly reflective faces (16 mg) were isolated by suction filtration.

The crystal used for data collection measured 0·1 × 0·15 × 0·3 mm and was mounted with its longest dimension coaxial with the φ axis of an Enraf–Nonius CAD-4 diffractometer. The data were collected by Molecular Structure Corporation, College Station, Texas 77840. The cell parameters were obtained from a least-squares refinement of diffractometer settings for 25 reflections. 2403 reflections were collected up to a 2θ(Cu $K\alpha$) of 150°; from these, a set of 2307 independent reflections was obtained.

Three standard reflections were monitored periodically during the data collection; no significant changes in intensity were observed. The variance of each intensity was calculated from the expression $\sigma^2(I) = S^2 + (C + R^2B) + (0{\cdot}05I)^2$, where S is the scan rate, C is the peak count, R is the ratio of scan time to background time, and B is the total background count. The intensities were corrected for Lorentz and polarization effects, but not for absorption [μ(Cu $K\alpha$) = 2·25 mm^{-1}]. Wilson's (1942) method was used to put the data on an approximately absolute scale. A data set including the 1752 reflections with $F > \sigma(F)$ was used in all subsquent calculations.

Table 1. *Final atomic parameters* (×10^4)

Estimated standard deviations are in parentheses.

	x	y	z
S	2104 (1)	1455 (1)	1500·3 (5)
C(*B*1)	2620 (4)	−642 (3)	2998 (2)
C(*B*2)	3011 (3)	1203 (2)	3043 (2)
C(*B*3)	4005 (3)	2564 (2)	4219 (2)
C(*B*4)	4482 (2)	4344 (2)	4345 (2)
C(*B*5)	3892 (3)	4772 (2)	3133 (2)
C(*B*6)	2859 (3)	3647 (2)	1857 (2)
C(*B*7)	2282 (5)	4182 (3)	621 (3)
H(*B*3)	4424 (27)	2239 (23)	5071 (18)
H(*B*5)	4267 (29)	5984 (25)	3164 (19)
H(11)	3096 (41)	−600 (29)	3947 (28)
H(12)	3417 (47)	−1224 (30)	2363 (30)
H(13)	1190 (36)	−1191 (31)	2642 (28)
H(71)	2685 (52)	5465 (32)	774 (30)
H(72)	3159 (43)	4002 (49)	38 (39)
H(73)	1058 (48)	3768 (41)	149 (33)
C(*T*1)	2871 (3)	7956 (2)	8606 (2)
C(*T*2)	2050 (3)	8045 (2)	7290 (2)
C(*T*3)	2302 (3)	9707 (3)	7162 (2)
C(*T*4)	871 (3)	4848 (3)	6246 (2)
C(*T*5)	1029 (3)	6522 (2)	6145 (2)
C(*T*6)	110 (3)	6611 (2)	4857 (2)
N(1)	3520 (3)	7855 (2)	9666 (2)
N(2)	2494 (3)	11031 (2)	7022 (2)
H(*T*4)	1501 (29)	4767 (24)	7105 (20)
H(*T*6)	171 (27)	7808 (25)	4738 (18)

Patterson and Fourier methods yielded positional parameters for all of the non-hydrogen atoms. After two cycles of least-squares refinement, a difference Fourier synthesis was used to locate the H atoms, which were added to the parameter list. The refinement proceeded without difficulty to a final R value $(=\sum||F_o| - |F_c||/\sum|F_o|)$ of 0·037 and a final weighted R value $[=(\sum w||F_o| - |F_c||^2/\sum w|F_o|^2)^{1/2}]$ of 0·048. The weight used in the refinement was $[\sigma^2(F)]^{-1}$; the quantity minimized was $\sum w(|F_o| - |F_c|)^2$.

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

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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 34536 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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. Both molecules are required to be centrosymmetric; their structures and dimensions are summarized in Fig. 1. The structural parameters for the TCNQ are well within the range of typical reported values (Herbstein, 1971). The present values agree very closely with those for TCNQ having a formal negative charge, such as in K^+TCNQ^- (Konno, Ishii & Saito, 1977) and the noncentrosymmetric TCNQ in Rb_2TCNQ_3 (van der Wal & van Bodegom, 1978), to cite two recent examples. The molecular parameters of the present structure differ from those of neutral TCNQ (Long, Sparks & Trueblood, 1965) by as much as 17σ. The least-squares planes of the $C(CN)_2$ residues are twisted about the long axis of the molecule by 3·9° with respect to the plane of the quinoid ring. A similar twist of 3·4° was reported for K^+TCNQ^- (Konno, Ishii & Saito, 1977).

The structural parameters determined for TMBTP are more difficult to evaluate because relatively few comparative data are available. The 4-thiopyranylidene moiety also occurs in the ion-radical salt BTP_2TCNQ_3 (Lee, Titus & Sandman, 1979) and the neutral molecules 2-(4-thiopyranylidene)-1,3-dithiole (TPDT) (Sandman, Fisher, Holmes & Epstein, 1977; Schramm, Titus & Sandman, 1979) and 2,2′,6,6′-tetraethoxycarbonyl-$\Delta^{4,4'}$-bithiopyran (TCBTP) (Sandman, Holmes & Warner, 1979; Darocha, Titus, Sandman & Warner, 1979). Table 2 lists average bond distances and angles for the four systems. Since both TMBTP and BTP were investigated in ion-radical salts with TCNQ, it is not surprising to find that their molecular structures are very similar, but both show significant variations from the corresponding moieties in neutral TCBTP and TPDT. The bridging C=C bond in the TMBTP cation is 1·435 (3) Å, which seems long. The corresponding bond in the non-stoichiometric TCNQ salt of TMTTF is 1·385 (14) Å (Kistenmacher, Phillips, Cowan, Ferraris, Bloch & Poehler, 1976) and in the corresponding salt of TTF it is 1·369 (4) Å (Kistenmacher, Phillips & Cowan, 1974). However, in BTP_2TCNQ_3 the bridging carbon distance, 1·429 (6) Å, does not deviate significantly from the present example. We note that the central double bond in TTF derivatives is tetrasulfur substituted while that in BTP derivatives is substituted by four trigonal C—H groups. The anion-radical of biphenyl, which is iso-π-electronic to a BTP cation, has a central bond length of 1·435 (6) Å (Noordik, Beurskens, van den Hark & Smits, 1979).

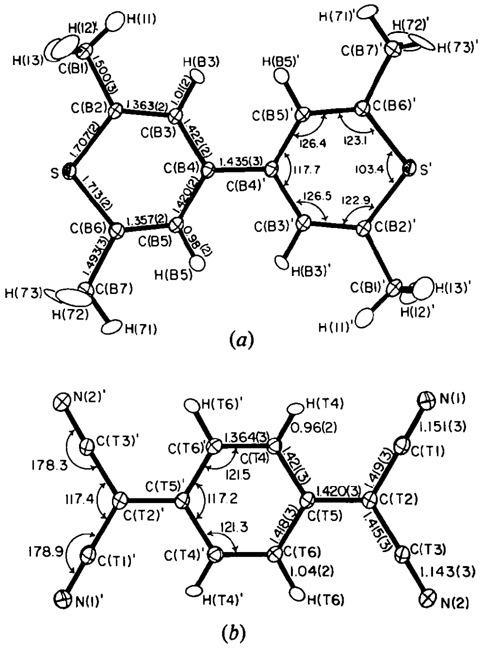
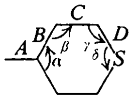


Fig. 1. Structural parameters (Å and degrees) (*a*) for the TMBTP cations and (*b*) for the TCNQ anion. Ellipsoids are drawn at the 10% probability level. Estimated standard deviations for the angles are 0·1 to 0·2°.

Charge transfer between TMBTP and TCNQ appears to be accompanied by a general delocalization of the molecular orbitals of the two species, resulting in lengthening of double bonds, and shortening of single bonds. The bridging C=C bond in TMBTP provides a particularly good example of this behavior. This bond in neutral TCBTP is still quite long for a carbon–carbon double bond, 1·405 (9) Å (Darocha, Titus, Sandman & Warner, 1979). The magnitude of the central-double-bond lengthening on electron transfer in BTP derivatives is thus *ca* 0·03 Å.

Table 2. *Comparison of bond distances* (Å) *and angles* (°) *for* 4-*thiopyranylidene*

Values are symmetry averaged where possible.



	TMBTP[(a)]	BTP[(b)]	TCBTP[(c)]	TPDT[(d)]
A	1·435 (3)	1·429 (6)	1·405 (9)	–
B	1·421 (1)	1·418 (19)	1·440 (7)	1·453 (6)
C	1·360 (4)	1·351 (11)	1·332 (8)	1·316 (1)
D	1·710 (4)	1·702 (8)	1·734 (5)	1·737 (4)
α	117·7 (2)	117·0 (11)	115·7 (5)	116·6 (2)
β	126·4 (2)	126·0 (11)	126·4 (6)	125·7 (6)
γ	123·0 (1)	124·9 (11)	126·2 (5)	125·6 (5)
δ	103·36 (9)	101·2 (10)	99·0 (3)	100·0 (2)

(*a*) This study. (*b*) In BTP_2TCNQ_3 (Lee, Titus & Sandman, 1979). (*c*) Neutral molecule (Darocha, Titus, Sandman & Warner, 1979). (*d*) Neutral molecule (Schramm, Titus & Sandman, 1979).

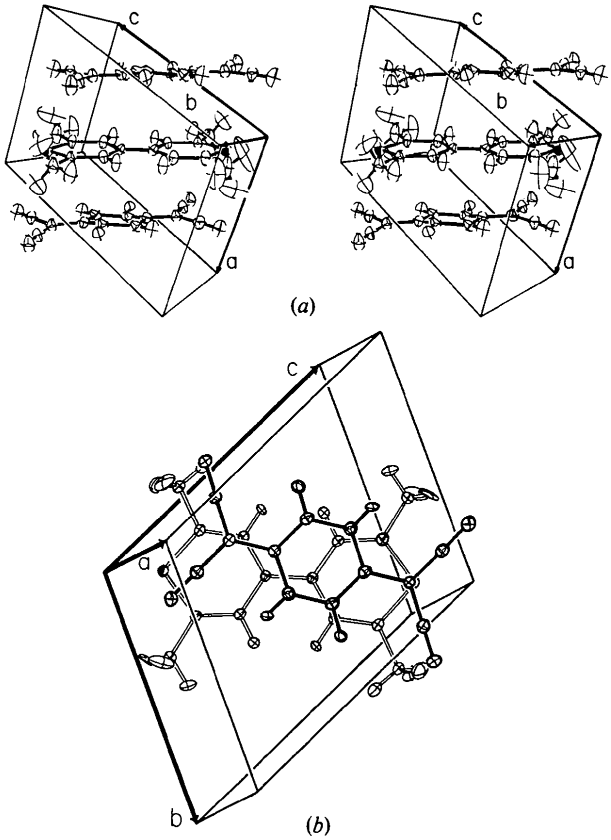


Fig. 2. (a) Stereoview of the unit cell. Ellipsoids are drawn at the 30% probability level. (b) Projection perpendicular to the TMBTP plane. Ellipsoids are drawn at the 10% probability level.

Both molecules are nearly planar, although C(*B*1) and C(*B*7) deviate 0·056 and 0·045 Å, respectively, from the least-squares plane of TMBTP, and C(*T*4) deviates 0·062 Å from the least-squares plane of TCNQ. Except for the H atoms, no other atom deviates from its plane by more than 0·018 Å. The rather large deviations of the ring H atoms from the planes (up to 0·12 Å) suggests that the uncertainties in their positions are higher than estimated. The molecular planes are not quite parallel, with the TMBTP rotated 5·3° (with respect to a plane parallel to the TCNQ quinoid plane) about its long axis. The average distance of TMBTP atoms from the TCNQ plane is 3·4 Å; the shortest interplanar contact between non-hydrogen atoms is C(*B*3)···C(*T*5), 3·375 (3) Å. A stereoview of the unit cell and a projection perpendicular to the TMBTP plane are given in Fig. 2.

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