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# The Crystal and Molecular Structure of the Organic Conductor 4,4′,5,5′-Tetramethyl-$\Delta^{2,2'}$-bis-1,3-dithiolium 7,7,8,8-Tetracyano-*p*-quinodimethanide [TMTTF–TCNQ]*

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The 1:1 charge-transfer salt of 4,4′,5,5′-tetramethyl-$\Delta^{2,2'}$-bis-1,3-dithiole and 7,7,8,8-tetracyano-*p*-quinodimethane [TMTTF–TCNQ], when grown from solution, usually crystallizes in the monoclinic system, space group $P2/c$, with crystal data: $a = 18{\cdot}82\,(2)$, $b = 3{\cdot}850\,(1)$, $c = 15{\cdot}08\,(2)$ Å, $\beta = 103{\cdot}70\,(7)^\circ$, $V = 1061{\cdot}6$ Å$^3$, $Z = 2$, $D_m = 1{\cdot}455\,(5)$, $D_c = 1{\cdot}454\,(3)$ g cm$^{-3}$. Intensities for 1391 independent reflections were collected by the $\theta$–$2\theta$ scan technique on an automated diffractometer with graphite-monochromatized Mo $K\bar{\alpha}$ radiation. The structure was solved by standard heavy-atom methods and has been refined by full-matrix least squares to a final $R$ value $[F_o \geq 1\sigma(F_o)]$ of 0·089. The final weighted $R$ and goodness-of-fit values are 0·053 and 1·3 respectively. As in other heterofulvalene–TCNQ systems, the crystal structure is dominated by homologous columns of separately stacked molecular cations and anions, with interplanar spacings of 3·53 and 3·27 Å. The interstack dihedral angle between the cation and anion planes is 55·4° and is approximately bisected by [010]. Examination of the intermolecular contacts suggests that the interchain coupling in TMTTF–TCNQ is substantially weaker than in any other member of the TTF–TCNQ family, consistent with electrical and magnetic measurements.

## Introduction

The series of nearly one-dimensional organic conductors based on the prototype TTF–TCNQ displays substantial variations in electrical conductivity. In the previous paper (Bechgaard, Kistenmacher, Bloch & Cowan, 1977) and elsewhere (Bloch, Cowan, Bechgaard, Pyle, Banks & Poehler, 1975; Phillips, Kistenmacher, Bloch & Cowan, 1976), we have argued that many of the variations among compounds arise from differences in the interactions among conducting chains of separately stacked molecular ions.

To elucidate further the role of interchain coupling, we have determined the crystal structure of one of the simplest and earliest of the substituted conducting analogs of TTF–TCNQ, a 1:1 TCNQ salt of 4,4′,5,5′-tetramethyl-$\Delta^{2,2'}$-bis-1,3-dithiole (Ferraris, Poehler, Bloch & Cowan, 1973).

We have found that unlike TTF–TCNQ itself, the tetramethyl salt forms in several distinct crystalline phases. One, the non-stoichiometric semiconductor (TMTTF)$_{1\cdot3}$(TCNQ)$_2$, is grown by vapor deposition and has been discussed elsewhere (Kistenmacher, Phillips, Cowan, Ferraris, Bloch & Poehler, 1976). From solu-

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tion, several phases have appeared (Phillips, Ferraris, Kistenmacher, Poehler, Bloch & Cowan, 1974), but we have been able to grow only one reproducibly and in crystals of sufficient quality for reliable crystallographic studies. At high temperatures, its electrical conductivity (Ferraris, Poehler, Bloch & Cowan, 1973; Carruthers, Bloch, Kistenmacher, Pyle, Phillips & Cowan, 1977) is similar to that of TTF–TCNQ, reaching a peak near 65 K of 15 to 20 times its room-temperature value of *ca* 350 $\text{ohm}^{-1}\ \text{cm}^{-1}$. In contrast to TTF–TCNQ (Etemad, 1976; Horn & Rimai, 1976), however, the resistivity of TMTTF–TCNQ rises slowly with further cooling to a single weak phase transition near 34 K, where it does not exhibit critical behavior. Together with an exceptionally narrow spin resonance line, this behavior suggests interchain couplings substantially weaker than in TTF–TCNQ (Poehler, Bohandy, Bloch & Cowan, 1976, 1977; Tomkiewicz, Schultz, Engler, Taranko & Bloch, 1976).

## Experimental

Black crystals of TMTTF–TCNQ were obtained by slow cooling of a hot $CH_3CN$ solution containing equimolar concentrations ($5{\cdot}0 \times 10^{-3}$ *M*) of TMTTF and TCNQ. Some difficulty was experienced in finding a suitable single crystal in that many of the crystals examined by X-ray photography were twinned and/or deformed.

The crystal chosen for intensity data collection was free of these problems and had dimensions $0{\cdot}18 \times 0{\cdot}08 \times 0{\cdot}03$ mm along *b*, *a*, and $c^*$ respectively. Oscillation and Weissenberg photographs were consistent with the monoclinic space group $P2/c$ (systematic absences: $h0l$, $l = 2n + 1$). Unit-cell dimensions were obtained from a least-squares fit to the $2\theta$, $\omega$, and $\chi$ values for 14 reflections carefully centered on an automated diffractometer. The crystal density was measured by the neutral buoyancy technique in a $BaBr_2/H_2O$ solution. Complete crystal data are listed in Table 1.

A total of 3540 reflections were measured on a Syntex $P\bar{1}$ computer-controlled diffractometer equipped with a graphite monochromator and employing Mo $K\bar{\alpha}$ radiation. Intensity data (the $+h$-hemisphere to $2\theta = 45°$) were collected in the $\theta$–$2\theta$ scan mode. Individual scan speeds were determined by a rapid scan at the calculated Bragg peak, and the rate of scanning ($2\theta$) varied from $1{\cdot}0°\ \text{min}^{-1}$ (less than 100 counts during the rapid scan) to $4{\cdot}0°\ \text{min}^{-1}$ (more than 1000 counts during the rapid scan). Three standard reflections were monitored after every 100 reflection measurements and their intensities showed no unusual variations over the course of the experiment (maximum deviation of any standard from its mean intensity was about 5%).

Table 1. *Crystal data for TMTTF–TCNQ*

$a = 18{\cdot}82\ (2)$ Å
$b = 3{\cdot}850\ (1)$
$c = 15{\cdot}08\ (2)$
$\beta = 103{\cdot}70\ (7)°$
$V = 1061{\cdot}6$ Å$^3$
Space group $P2/c$

$C_{10}H_{12}S_4.C_{12}N_4H_4$
$M_r = 464{\cdot}6$
$Z = 2$
$D_m = 1{\cdot}455\ (5)\ \text{g cm}^{-3}$
$D_c = 1{\cdot}454\ (3)$
$\mu[\lambda(\text{Mo}\ K\bar{\alpha}) = 0{\cdot}71069\ \text{Å}] = 5{\cdot}4\ \text{cm}^{-1}$

The 3540 measured intensities, which included standards and systematic absences as well as symmetry-related data, were then condensed into a set of 1391 independent reflections of which 132 had net intensities less than zero. Observational variances for all reflections were based on the equation: $\sigma^2(I) = S + (B_1 + B_2)(T_S/2T_B)^2 + (pI)^2$, where $S$, $B_1$, and $B_2$ are the scan and background counts, $T_S$ and $T_B$ are the scan and individual background counting times ($T_B = T_S/4$ for all reflections) and $p$ was taken to be $0{\cdot}03$ and represents the expected error proportional to the diffracted intensity (Busing & Levy, 1957). The 132 reflections with negative intensities were assigned $F$'s of zero. The intensities and their standard deviations were corrected for Lorentz and polarization effects, but no correction for absorption effects was applied ($\mu = 5{\cdot}4\ \text{cm}^{-1}$). Wilson's (1942) method was used to place the squared structure factors on an approximate absolute scale.

## Solution and refinement of the structure

The presence of two formula units of TMTTF–TCNQ per unit cell requires that each of the molecular ions have at least $\bar{1}$ molecular symmetry, *i.e.* each of the molecular ions has its centroid coincident with one of the centers of symmetry in the space group $P2/c$. These symmetry requirements plus packing considerations allowed the approximate positioning of the cations and anions in the unit cell. Examination of a three-dimensional Patterson synthesis confirmed the approximate arrangement of the molecular ions and allowed accurate positions to be obtained for the two S atoms in the asymmetric unit. A structure factor Fourier synthesis signed by the two S atom positions revealed the remaining 13 non-hydrogen atoms.

Five cycles of full-matrix isotropic least-squares refinement, minimizing $\Sigma\, w(|F_o| - |F_c|)^2$ where $w = 4F_o^2/\sigma^2(F_o^2)$, plus one cycle of anisotropic refinement lowered the $R$ value ($\Sigma\, ||F_o| - |F_c|| / \Sigma |F_o|$) to $0{\cdot}13$. Owing to limitations in computer storage, it was found necessary to split this and later anisotropic cycles into two matrices: (1) non-hydrogen atom positional parameters and (2) an overall scale factor and the anisotropic thermal parameters.

At this point in the analysis, a difference Fourier map was computed, and in conjunction with geometrical considerations the positions of the eight independent H atoms were determined. Excluding areas coincident with the assigned H atoms, no peak on this difference map exceeded ±0·13 e Å$^{-3}$. The contributions of the H atoms, with isotropic thermal parameters equivalent to those of the atoms to which they were bonded, were included in all subsequent cycles of refinements. No attempt has been made to refine any of the H atom parameters.

Two further cycles of anisotropic refinement led to final $R$ values of 0·123 (all reflections), 0·106 (excluding zeros) and 0·089 [$F_o \geq 1\sigma(F_o)$]. The final weighted $R$ value $\{[\Sigma\, w(|F_o| - |F_c|)^2/\Sigma\, w(|F_o|)^2]^{1/2}\}$ and goodness-of-fit value $\{[\Sigma\, w(|F_o| - |F_c|)^2/(\mathrm{NO}-\mathrm{NV})]^{1/2}$, where NO = 1391 observations and NV = 136 total variables$\}$ were 0·053 and 1·3 respectively. The maximum shift/error value for any parameter in the last cycle was 0·7. The quantity $\langle w(\Delta F)^2\rangle$ showed no unusual dependence on $|F_o|$ or $(\sin\theta/\lambda)$.

The scattering factors for S, C, and N were taken from the compilation of Hanson, Herman, Lea & Skillman (1964). The scattering curve for H was that of Stewart, Davidson & Simpson (1965). Final non-hydrogen parameters are collected in Table 2, while those for the H atoms are given in Table 3.*

The structure factor and Fourier calculations were performed with the X-RAY 67 series of programs (Stewart, 1967); the least-squares refinements were carried out with an extensively modified version of *ORFLS* (Busing, Martin & Levy, 1962); the best-plane calculations were performed with the program of Pippy & Ahmed (1968); the illustrations were prepared with the aid of the computer program *ORTEP* (Johnson, 1965). All other calculations were performed with locally written programs.

## Results and discussion

### *Molecular dimensions*

Like other charge-transfer salts in this series, the crystal structure of TMTTF–TCNQ is dominated by homologous face-to-face columnar stacking of the individual TMTTF cation and TCNQ anion components, Figs. 1–4. The two molecular ions each lie on inversion centers and are therefore required to have at least $\bar{1}$ molecular symmetry.

Details of the bond lengths and angles in the TMTTF cation and the TCNQ anion are shown in Figs. 5 and 6 respectively. Average estimated standard deviations for the various types of bond lengths and angles are S–C 0·006, C–N 0·016, C–C 0·014–0·020 Å; bond angles 0·6–0·7°.

Table 3. *Hydrogen atom parameters*

The fractional coordinates have been multiplied by 10$^3$. The isotropic thermal parameters are those of the atom to which the hydrogen atom is bonded (enclosed in square brackets).

| | $x$ | $y$ | $z$ | $B$ |
|---|---|---|---|---|
| H(1)[C(5)] | 191 | 438 | 285 | 4·4 |
| H(2)[C(5)] | 138 | 312 | 314 | 4·4 |
| H(3)[C(5)] | 124 | 678 | 280 | 4·4 |
| H(4)[C(4)] | 241 | 564 | 63 | 4·2 |
| H(5)[C(4)] | 241 | 625 | 167 | 4·2 |
| H(6)[C(4)] | 270 | 275 | 134 | 4·2 |
| H(7)[C(10)] | 512 | 353 | 351 | 2·8 |
| H(8)[C(11)] | 394 | 347 | 551 | 2·9 |

Table 2. *Final heavy-atom parameters* (×10$^4$)

Estimated standard deviations are enclosed in parentheses. The anisotropic thermal ellipsoid is defined by the equation:
$\exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl)]$.

| | $x$ | $y$ | $z$ | $B_{11}$ | $B_{22}$ | $B_{33}$ | $B_{12}$ | $B_{13}$ | $B_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| S(1) | 276 (0·8) | 1759 (5) | 1416 (1) | 27 (0·6) | 650 (17) | 27 (0·8) | −7 (3) | 6 (0·6) | −17 (4) |
| S(2) | 1111 (0·8) | 1716 (5) | 10 (1) | 23 (0·6) | 590 (16) | 33 (0·9) | −6 (3) | 8 (0·6) | −11 (4) |
| N(1) | 3951 (3) | −920 (16) | 2237 (3) | 46 (2) | 984 (70) | 37 (3) | −28 (11) | 7 (2) | −33 (12) |
| N(2) | 2716 (3) | −756 (15) | 4302 (3) | 33 (2) | 819 (66) | 59 (4) | −30 (10) | 14 (2) | 2 (12) |
| C(1) | 1165 (3) | 3284 (16) | 1731 (3) | 33 (2) | 302 (47) | 30 (3) | 12 (10) | 4 (2) | 19 (12) |
| C(2) | 1568 (3) | 3229 (18) | 1092 (4) | 24 (2) | 420 (52) | 42 (3) | −22 (10) | −0 (2) | −1 (13) |
| C(3) | 294 (3) | 744 (15) | 293 (3) | 27 (2) | 393 (60) | 28 (3) | 12 (9) | 6 (2) | 10 (11) |
| C(4) | 2325 (3) | 4533 (19) | 1179 (4) | 26 (2) | 672 (70) | 64 (4) | −30 (11) | 10 (3) | −11 (15) |
| C(5) | 1426 (4) | 4550 (19) | 2703 (4) | 49 (3) | 566 (69) | 37 (4) | −0 (12) | −2 (3) | −17 (13) |
| C(6) | 3936 (3) | 15 (18) | 2953 (4) | 28 (2) | 506 (58) | 33 (3) | −14 (10) | 3 (2) | 0 (13) |
| C(7) | 3239 (3) | 63 (17) | 4104 (4) | 24 (2) | 388 (52) | 36 (3) | −22 (10) | 4 (2) | −24 (12) |
| C(8) | 3888 (3) | 1054 (16) | 3841 (3) | 25 (2) | 459 (62) | 27 (3) | 9 (10) | 2 (2) | −1 (12) |
| C(9) | 4444 (3) | 3038 (15) | 4406 (3) | 26 (2) | 313 (44) | 26 (3) | 21 (9) | 5 (2) | 23 (12) |
| C(10) | 5080 (3) | 4105 (16) | 4130 (3) | 24 (2) | 611 (66) | 26 (3) | −1 (10) | 11 (2) | 2 (12) |
| C(11) | 4388 (3) | 4073 (16) | 5313 (4) | 19 (2) | 636 (67) | 31 (3) | −9 (10) | 10 (2) | 2 (12) |

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32053 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

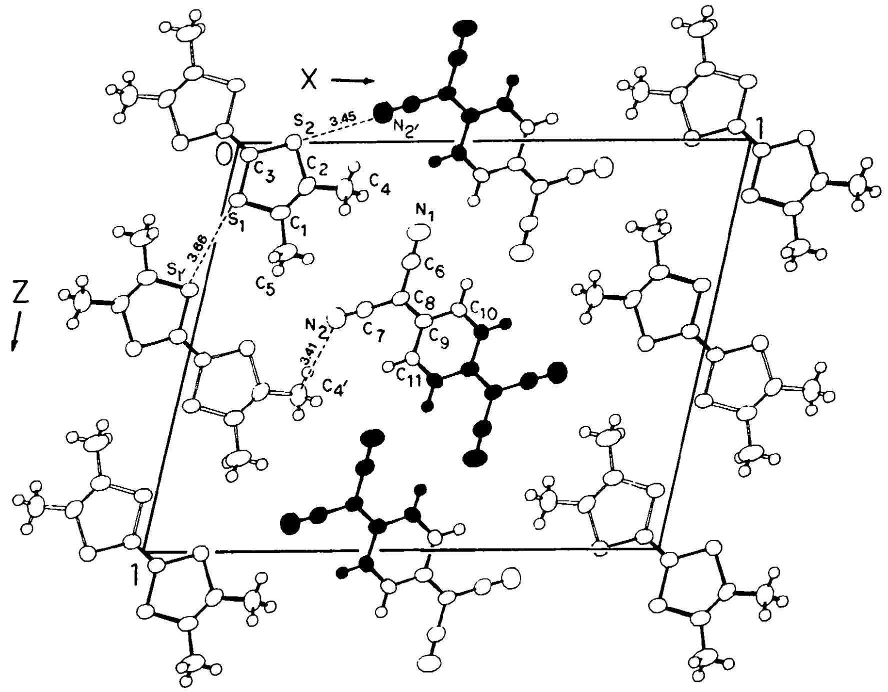

Fig. 1. Crystal packing in TMTTF–TCNQ as viewed along the *b* axis. The labeled molecular ions have their coordinates as given in Table 2.

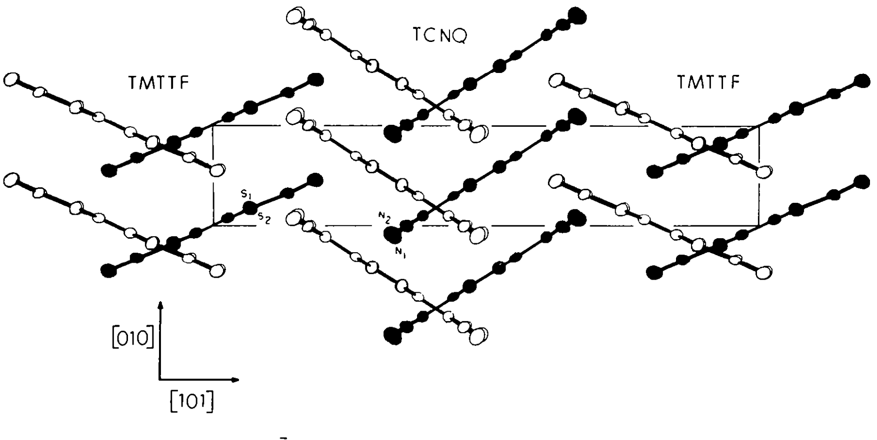

Fig. 2. A view of the crystal packing in the (10$\bar{1}$) plane. The labeled molecular ions have their coordinates as given in Table 2.

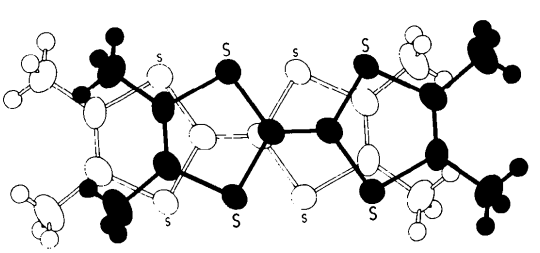

Fig. 3. The molecular overlap in columns of TMTTF cations. The view direction is normal to the mean molecular plane.

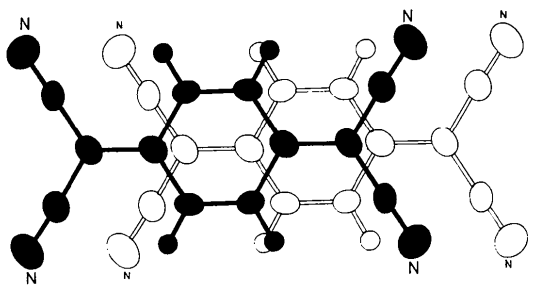

Fig. 4. The molecular overlap in the column of TCNQ anions. The view direction is normal to the mean molecular plane.

The TMTTF cation is not quite as planar as one might expect considering its quasi-aromatic ring system. The crystallographically unique half of the molecular ion is in an envelope conformation with a dihedral angle between the planes S(1)–S(2)–C(3) and S(1)–S(2)–C(1)–C(2) (Table 4) of 2·2 (6)°. Comparable degrees of non-planarity are found in TTF–TCNQ, TMTSF–TCNQ, and $(\mathrm{TMTTF})_{1\cdot3}$-$(\mathrm{TCNQ})_2$ with dihedral angles of 2·2 (2), 1·7 (7) and 1·4 (5)° respectively. The TCNQ anion is approximately planar (Table 4), with the benzenoid ring being very planar and the malononitrile groups twisting slightly (1°) out of the benzenoid plane.

Qualitatively, we expect the cation charge to be larger for TMTTF–TCNQ than for TTF–TCNQ, since the inductive effect of the methyl groups should lower the group ionization potential of the heterofulvalene ring system. Electrochemical (Bechgaard, Cowan & Bloch, 1976) and HeI photoelectron spectral data (Gleiter *et al.*, 1975) support this conclusion. Unfortunately, the crystallographic molecular dimensions yield little further information on the degree of charge transfer because of their apparent sensitivity to local environment. For example, the TMTTF cation in Fig. 5 is significantly skewed, particularly with respect to the S–C bond lengths, in a way that clearly follows the molecular environment (Fig. 1). The dimensions in the TCNQ anion (Fig. 6), on the other hand, are typical, and we also make no attempt to deduce molecular charge from them.

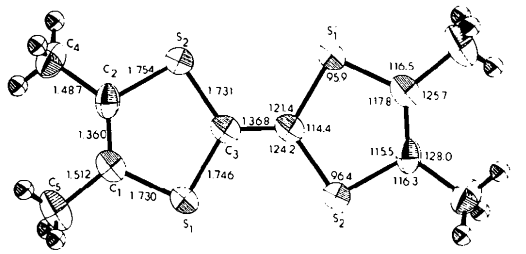

Fig. 5. Molecular dimensions and thermal ellipsoids for the TMTTF cation. The thermal ellipsoids are drawn at the 50% probability level.

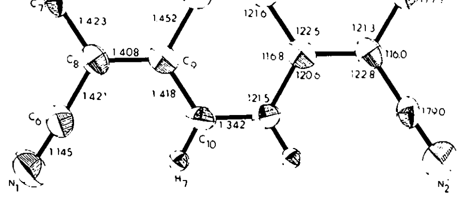

Fig. 6. Molecular dimensions and thermal ellipsoids for the TCNQ anion. The thermal ellipsoids are drawn at the 50% probability level.

*Intrachain stacking*

The longitudinal axes of both the cations and the anions are approximately aligned along the $(10\bar{1})$ plane, and the major component of tilt with respect to **b** is contained in this plane. The tilt of the individual molecules within $(10\bar{1})$ is in the same direction, with the TCNQ molecular plane being tilted approximately 9° more than TMTTF (Figs. 1 and 2). Along **a** and **c**, the tilts alternate, much as in TTF–TCNQ.

The molecular overlap in the cation column is illustrated in Fig. 3. As in other members of the TTF–TCNQ family, the stacking interaction is nominally of the 'ring double bond' type (Herbstein, 1971) with the bridging C(3)–C(3′) bond of one cation lying approximately over the centroid of the dithiolium ring of an adjacent cation. The perpendicular stacking distance between vicinal molecular planes is 3·53 Å, comparable with values we have observed in other methylated dithiolium and diselenolium salts of TCNQ:

Table 4. *Some least-squares planes and deviations* (Å)

In each of the equations of the planes *X*, *Y* and *Z* are coordinates (Å) referred to the orthogonal axes *a*, *b* and *c**. Atoms indicated by an asterisk were given zero weight in calculating the plane; all other atoms were equally weighted.

(*a*) *TMTTF molecular plane*

$(-0\cdot2776X + 0\cdot9171Y - 0\cdot2862Z = 0\ \text{Å})$

| | | | |
|---|---|---|---|
| S(1) | ±0·024 | C(3) | ±0·015 |
| S(2) | ±0·022 | C(4) | ±0·008 |
| C(1) | ∓0·003 | C(5) | ∓0·004 |
| C(2) | ∓0·029 | | |

(*b*) *TMTTF central plane*

$(-0\cdot2868X + 0\cdot911Y - 0\cdot2961Z = 0\ \text{Å})$

| | | | |
|---|---|---|---|
| S(1) | ∓0·001 | C(3) | ±0·005 |
| S(2) | ∓0·001 | C(4)* | ∓0·056 |
| C(1)* | ∓0·050 | C(5)* | ∓0·069 |
| C(2)* | ∓0·071 | | |

(*c*) *TMTTF exterior plane*

$(-0\cdot2587X + 0\cdot9268Y - 0\cdot2724Z = 0\cdot0638\ \text{Å})$

| | | | |
|---|---|---|---|
| S(1) | −0·005 | C(3)* | −0·031 |
| S(2) | 0·005 | C(4)* | 0·060 |
| C(1) | 0·010 | C(5)* | 0·037 |
| C(2) | −0·010 | | |

(*d*) *TCNQ molecular plane*

$(-0\cdot3691X + 0\cdot8461Y - 0\cdot3848Z = -4\cdot0018\ \text{Å})$

| | | | |
|---|---|---|---|
| N(1) | ∓0·008 | C(8) | ∓0·013 |
| N(2) | ±0·013 | C(9) | ±0·003 |
| C(6) | ∓0·002 | C(10) | ±0·028 |
| C(7) | ±0·002 | C(11) | ∓0·012 |

(*e*) *TCNQ benzenoid ring*

$(-0\cdot3776X + 0\cdot8489Y - 0\cdot3699Z = -3\cdot9540\ \text{Å})$

| | | | |
|---|---|---|---|
| N(1)* | ∓0·065 | C(8)* | ∓0·028 |
| N(2)* | ±0·026 | C(9) | ∓0·004 |
| C(6)* | ∓0·040 | C(10) | ±0·005 |
| C(7)* | ±0·003 | C(11) | ±0·005 |

Table 5. *Electronically significant interchain contacts*

| | Contact | Number of contacts per molecular pair | Distance, Å | Van der Waals distance, Å |
|---|---|---|---|---|
| TMTTF–TCNQ[1] | S–N | 2 | 3·45 | 3·35 |
| | S–S | 2 | 3·66 | 3·70 |
| TTF–TCNQ[2] | S–N | 2 | 3·20 | 3·35 |
| | S–N | 2 | 3·25 | 3·35 |
| | N–C | 2 | 3·29 | 3·10 |
| TMTSF–TCNQ[3] | Se–N | 2 | 3·4 | 3·5 |
| | Se–Se | 2 | 4·10 | 4·0 |
| HMTSF–TCNQ[4] | Se–N | 4 | 3·1 | 3·5 |

References: (1) This study. (2) Kistenmacher, Philips & Cowan (1974). (3) Bechgaard, Kistenmacher, Bloch & Cowan (1977). (4) Philips, Kistenmacher, Bloch & Cowan (1976).

3·59 Å in $(\mathrm{TMTTF})_{1\cdot 3}(\mathrm{TCNQ})_2$ (Kistenmacher, Phillips, Cowan, Ferraris, Bloch & Poehler, 1976); 3·60 Å in TMTSF–TCNQ, the Se analogue of the present complex (Bechgaard, Kistenmacher, Bloch & Cowan, 1977). The stacking distances in the methylated derivatives are all measurably larger than in TTF–TCNQ, 3·47 Å (Kistenmacher, Phillips & Cowan, 1974). The slight increase in the stacking distance, as well as a small longitudinal shift of adjacent molecular planes within the stacks, is probably due to the presence of the bulky, exocyclic methyl substituents (Kistenmacher, Phillips, Cowan, Ferraris, Bloch & Poehler, 1976).

The molecular overlap in the TCNQ anionic column, illustrated in Fig. 4, is essentially identical with those found in all charge-transfer salts of this type that we have studied. There is, however, a noticeable variance in the stacking distance in the range of materials we have investigated: 3·27 Å in the present system, 3·24 Å in $(\mathrm{TMTTF})_{1\cdot 3}(\mathrm{TCNQ})_2$, 3·26 Å in TMTSF–TCNQ and 3·17 Å in TTF–TCNQ. As in the cation column, the TCNQ stacking distance is measurably larger than the unmethylated TTF–TCNQ. This result cannot be as simply related to the chemical modification as in the cation column. It is possible that the enlarged stacking distances in the methylated cation–TCNQ salts result from the alteration in intercolumn interactions or different degrees of charge transfer.

## *Interchain coupling*

As shown in Fig. 1, the interactions between the molecular stacks of TTF–TCNQ (Kistenmacher, Phillips & Cowan, 1974) appear to be weakened substantially by methylation of the cation. Indeed, the rotation of the stacks to accommodate the methyl groups completely eliminates the *c*-axis coupling in TTF–TCNQ *via* the N(1)···C(5) contact of 3·29 Å. Further, in place of the four short S···N contacts along the TTF–TCNQ *a* axis (two each of 3·20 and 3·25 Å), there remain only the two much weaker 3·45 Å contacts between N(2′) $(x, -y, -\frac{1}{2}+z)$ and S(2). Some compensation may be gained from the S(1)···S(1′) $(-x, y, \frac{1}{2}-z)$ contact of 3·66 Å along **c**, which is slightly shorter than the van der Waals separation of 3·7 Å (Pauling, 1960). The shortest remaining contacts [N(1)···C(11′)$(x, -y, -\frac{1}{2}+z)$ = 3·42 and N(2)···C(4′)$\mathrm{H}_3(x, -y, \frac{1}{2}+z)$ = 3·41 Å along **c**; N(1)···C(4)$\mathrm{H}_3(x, -1+y, z)$ and N(2)···C(5)$\mathrm{H}_3(x, -1+y, z)$ in the $(10\bar{1})$ plane] are not expected to be electronically significant.

The apparent weakness of the interchain coupling suggests that TMTTF–TCNQ may be the most 'one-dimensional' of the stoichiometric members of the TTF–TCNQ family that we have studied. For comparison, the electronically important interchain contacts for the series are listed in Table 5. In order of increasing interchain coupling, our structural studies suggest that these compounds rank as follows: TMTTF–TCNQ < TTF–TCNQ ~ TMTSF–TCNQ < HMTSF–TCNQ. This trend is consistent with electrical (Carruthers, Bloch & Cowan, 1976; Carruthers, Bloch, Kistenmacher, Pyle, Phillips & Cowan, 1977), magnetic (DiSalvo, Reed, Bloch & Cowan, 1977), and spin-resonance data (Poehler, Bohandy, Bloch & Cowan, 1976, 1977).

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# The Crystal Structure of Onitin, a Phenolic Illudoid Sesquiterpene from the Fern *Onychium auratum*

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Onitin monomethyl ether (6-hydroxyethyl-4-methoxy-2,2,5,7-tetramethyl-1-indanone), $C_{16}H_{22}O_3$, crystallizes in the space group *Pbca*, with $a = 16{\cdot}14$ (1), $b = 16{\cdot}95$ (1), $c = 10{\cdot}59$ (1) Å and $Z = 8$. Its structure has been determined by the symbolic addition method from visually estimated Weissenberg data, and refined by least squares to an $R$ of 0·075 for 1266 observed reflexions. The 1-indanone skeleton deviates significantly from planarity. There is considerable distortion of valence angles in the region of the *gem*-dimethyl. Rotational disorder is observed in the hydroxyethyl part of the molecule: the OH group is statistically distributed over two of the three possible orientational sites. This is attributed to the fact that O–H $\cdots$ O bond formation occurs for both these configurations. The crystal structure is stabilized by these intermolecular hydrogen bonds spiralling around the $2_1$ axes along **c**.

## Introduction

A new class of illudoid sesquiterpenes, collectively called pterosins, has come to be known after the first report of their isolation by Yoshihira, Fukuoka, Kuroyanagi & Natori (1971) from *Pteridium aquilinum*, a fern known for its radiomimetic and carcinogenic properties (Evans, 1968; Price & Pamukcu, 1968; Hirono, Shibuya, Fushimi & Haga, 1970). More members of this class have since been discovered, all from closely related ferns (Fukuoka, Kuroyanagi, Toyama, Yoshihira & Natori, 1972; Hayashi, Nishizawa & Sakan, 1973; Hasegawa & Akabori, 1974). The pterosins have a 1-indanone type