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The Crystal and Molecular Structure of an Organic Conductor from 4,4′,5,5′-Tetramethyl-$\Delta^{2,2'}$-bis-1,3-diselenole and 7,7,8,8-Tetracyano-*p*-quinodimethane [TMTSF–TCNQ]*

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This report relates the synthesis of two salts, one conducting and one insulating, and the crystal structure of the conducting salt formed from TMTSF and TCNQ. The conducting salt crystallized in the triclinic system, space group $P\bar{1}$, with cell data: $a = 3.883\,(1)$, $b = 7.645\,(5)$, $c = 18.846\,(9)$ Å, $\alpha = 77.34\,(5)$, $\beta = 89.67\,(3)$, $\gamma = 94.63\,(3)°$, $V = 543.97$ Å^3, $Z = 1$, $D_m = 1.98\,(1)$, $D_c = 1.99$ g cm^{-3}. Intensities for 2216 non-zero reflections were collected by counter methods on an automated diffractometer. The structure was solved by standard heavy-atom methods and has been refined by full-matrix least squares to a final R value of 0.107. The TMTSF cations and TCNQ anions form separate, homologous stacks in the crystal with interplanar spacings of 3.60 and 3.26 Å respectively. The planes of the molecular ions are tilted in opposite directions relative to the short a axis to form a dihedral angle of 54.9°. The intrachain stacking and molecular overlaps are close to those observed in the chemically similar salt HMTSF–TCNQ, but the interchain coupling in TMTSF–TCNQ appears to be substantially weaker. Since HMTSF–TCNQ remains conducting at low temperature whereas TMTSF–TCNQ does not, we infer that interchain interactions play a crucial role in the evolution of the metal-to-insulator transition in TMTSF–TCNQ.

Introduction

The molecular salt $\Delta^{2,2'}$-bis-1,3-dithiolium 7,7,8,8-tetracyano-*p*-quinodimethanide (TTF–TCNQ) (Ferraris, Cowan, Walatka & Perlstein, 1973; Bloch, Ferraris, Cowan & Poehler, 1973) is the prototype for a class of organic conductors whose electrical properties are subject to systematic chemical control. Its crystal structure (Kistenmacher, Phillips & Cowan, 1974) consists of nearly planar open-shell cations and anions separately stacked so as to form an array of parallel conducting chains. By chemically altering the substituent molecular ions so as to adjust ionization potentials, bandwidths, and interchain coupling, dramatic variations in electrical behavior are achieved (Bloch, Cowan & Poehler, 1974; Garito & Heeger, 1974). For example, the strongly anisotropic interchain coupling in the TCNQ salt of $\Delta^{2,2'}$-bis(4,5-trimethylene)-1,3-diselenole (HMTSF) (Bloch, Cowan, Bechgaard, Pyle, Banks & Poehler, 1975; Phillips, Kistenmacher, Bloch & Cowan, 1976) leads to the first organic material which remains a metallic conductor at low temperatures and to magnetic behavior reminiscent of a semimetal (DiSalvo, Reed, Bloch & Cowan, 1977).

Particularly interesting in this context are the TCNQ salts of 4,4′,5,5′-tetramethyl-$\Delta^{2,2'}$-bis-1,3-diselenole (TMTSF), the tetramethyl analog of HMTSF. Spectroscopic, electrochemical, and magnetic studies (Bechgaard, Cowan & Bloch, 1974) confirm that the valence π-electron systems of the TMTSF and HMTSF molecules are virtually indistinguishable. Yet, the electrical propeties of TMTSF–TCNQ (Bloch, Carruthers, Pyle, Poehler & Cowan, 1977) contrast sharply with the low-temperature semimetal HMTSF–TCNQ (Bloch, Cowan, Bechgaard, Pyle, Banks & Poehler, 1975). We find that TMTSF–TCNQ crystallizes in either of two phases, a red insulator and a black form whose conductivity rises sharply with cooling to a sharp peak below which a single metal-to-insulator transition occurs at 57 K. Since the differences between TMTSF and HMTSF are largely steric rather than electronic, we expect the differences in electrical behavior to have crystallographic antecedents. Hence the crystal structure of TMTSF has special importance for an understanding of conduction in this class of materials.

Based on its color, electrical conductivity and preliminary structural information, the red form of TMTSF–TCNQ probably comprises donor and acceptor molecules alternating within a stack. The structure of the black, conducting form is the subject of this paper.

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Experimental

Syntheses

(*a*) *TMTSF:TCNQ* (*black*). 10^{-5} mol of TMTSF (Bechgaard, Cowan & Bloch, 1974; Bechgaard, Cowan, Bloch & Kenriksen, 1975) and 10^{-5} mol of TCNQ were placed one in each arm of an H-shaped diffusion tube holding approximately 10 ml of solvent. The arm holding the TMTSF was filled with methylene chloride and the rest of the tube with acetonitrile. The connection between the two arms was then seeded with a small amount (3–4 crystals) of black material obtained by rapid cooling methods. After about one week, large, well formed crystals formed. After harvesting, they were washed with methylene chloride and stored under argon. Yield 90–100%. Calculated $C_{22}H_{16}N_4Se_4$:C 40·52, H 2·46, N 8·59%; found: C 40·33, H 2·33, N 8·44%.

(*b*) *TMTSF:TCNQ* (*red*). The red form was obtained under very similar conditions to those which produced the black material, but without seeding, in methylene chloride or ethyl acetate. The red form was also obtained by recrystallization of either black or red material from hot acetonitrile. Calculated $C_{22}H_{16}N_4Se_4$: C 40·52, H 2·46, N 8·59%; found: C 40·76, H 2·54, N 8·55%.

Collection and reduction of the X-ray diffraction data

The black crystals grow in a prismatic habit with a as the prism axis. In all instances, the (001) face was well developed. Preliminary Weissenberg photographs indicated that the crystal system was triclinic, space group $P1$ or $P\bar{1}$. Unit-cell dimensions and their associated standard deviations were derived on the basis of a least-squares fit to the 2θ, ω and χ setting angles for 15 carefully centered reflections measured on a Syntex $P\bar{1}$ automated diffractometer. The crystal density was measured by neutral buoyancy methods in a mixture of carbon tetrachloride and bromoform; the measured density indicated one formula unit per unit cell. Complete crystal data are given in Table 1.

The 2692 reflections in the $+h$-hemisphere to $2\theta = 55°$ were measured on the diffractometer with graphite-monochromatized Mo radiation. The crystal used in data collection had dimensions 0·22 × 0·12 × 0·06 mm. Intensity data were collected in the θ–2θ scan mode; individual scan speeds were determined by a rapid scan at the calculated Bragg peak, and the rate of scanning (2θ) ranged from 1·0° $\min^{-1}$ (less than 100 counts during the rapid scan) to 12·0° $\min^{-1}$ (more than 1000 counts during the rapid scan). Three standards were measured after every 100 reflections, and their intensities showed no unusual variations over the course of the experiment (the maximum deviation of any standard from its mean intensity was about 4%). The 2692 measured intensities, which included standards as well as some symmetry-related data, were then reduced to a set of 2216 reflections with $I > 0$. These 2216 non-zero intensities were used as the basis for the structural solution and refinement and were assigned observational variances based on the equations: $\sigma^2(I) = S + (B_1 + B_2)(T_S/2T_B)^2 + (pI)^2$, where S, B_1 and B_2 are the scan and individual extremum background counts, T_S and T_B are the scan and individual background counting times ($T_B = \frac{1}{4}T_S$ for all reflections), and p was taken to be equal to 0·04 and represents the expected error proportional to the diffracted intensity (Busing & Levy, 1957). The non-zero intensities and their derived variances were corrected for Lorentz and polarization effects and approximately placed on an absolute scale by the method of Wilson (1942).

Table 1. *Crystal data for TMTSF–TCNQ*

$a = 3{\cdot}883\ (1)$ Å
$b = 7{\cdot}645\ (5)$
$c = 18{\cdot}846\ (9)$
$\alpha = 77{\cdot}34\ (5)°$
$\beta = 89{\cdot}67\ (3)$
$\gamma = 94{\cdot}63\ (3)$
$V = 543{\cdot}97$ Å^3

$Se_4C_{10}H_{12}.N_4C_{12}H_4$
Space group $P\bar{1}$
$D_m = 1{\cdot}98\ (1)$ g cm^{-3}
$D_c = 1{\cdot}99$
$Z = 1$

Solution and refinement of the structure

Intensity statistics were consistent with a centric distribution, and all calculations were carried out with the space group assumed to be $P\bar{1}$. The successful solution and refinement of the structure (see below) suggest that this choice was correct. The positions of the two independent Se atoms were derived from a three-dimensional Patterson synthesis, and a subsequent Fourier map ($R = \Sigma\, ||F_o| - |F_c|| / \Sigma |F_o| = 0{\cdot}32$) allowed the positioning of the remaining 14 non-hydrogen atoms in the asymmetric unit. Three cycles of full-matrix, isotropic least squares, minimizing $\Sigma\, w(|F_o| - |F_c|)^2$ where $w = 4F_o^2/\sigma^2(F_o^2)$, reduced the R value to 0·14.

At this stage a difference Fourier map was computed and an attempt made to locate the H atoms. While the map had positive regions in the expected positions of the quininoid H atoms of the TCNQ anion, the density in the space occupied by the methyl H atoms on the TMTSF cation did not allow a clear definition of the individual H atoms. In light of this, we have made no attempt to include contributions from the scattering of the H atoms in our calculations.

An attempt was then made to refine a fully anisotropic model. After two cycles, however, it became evident that some of the C atoms, especially those on the TMTSF cation, had temperature factors which were non-positive definite. This was very probably a direct result of the small size and relatively poor quality of the data crystal. It was then decided to continue the refinement with only the Se atoms anisotropic, while restraining the other non-hydrogen atoms to isotropic thermal parameters. Three cycles of refinement in this mode quickly led to convergence (all shift/error values less than 0·6) and a final R value of 0·107. The final weighted value $\{[\Sigma w(|F_o| - |F_c|)^2/\Sigma\, w|F_o|^2]^{1/2}\}$ and goodness-of-fit $\{[\Sigma\, w(|F_o| - |F_c|)^2/(\mathrm{NO} - \mathrm{NV})]^{1/2}$ where NO = 2216 non-zero observations and NV = 71 variables$\}$ were 0·089 and 2·2 respectively.

Neutral scattering curves for all atoms were taken from the compilation of Hanson, Herman, Lea & Skillman (1964). In the final cycle of refinement, the real part of the Se scattering curve was corrected for anomalous dispersion effects (Cromer & Liberman, 1970). Final atomic parameters are collected in Table 2.*

The crystallographic computations were performed with the following programs: structure factor Fourier, X-RAY 67 (Stewart, 1967); least-squares refinements, a highly-modified version of *ORFLS* (Busing, Martin & Levy, 1962); illustrations, *ORTEP* (Johnson, 1965). Calculations not cited were performed with locally written programs.

Table 2. *Final atomic parameters*

Estimated standard deviations are enclosed in parentheses. The fractional coordinates and anisotropic thermal parameters have been multiplied by 10^4.

	x	y	z	B
Se(1)	2732 (2)	−2966 (1)	291 (1)	*
Se(2)	3404 (2)	94 (1)	1177 (1)	*
N(1)	5055 (26)	5466 (14)	4005 (6)	4·4 (2)
N(2)	4376 (26)	1363 (14)	2766 (6)	4·4 (2)
C(1)	1157 (25)	−3496 (13)	1268 (5)	2·6 (2)
C(2)	1402 (24)	−2229 (12)	1658 (5)	2·5 (2)
C(3)	4218 (23)	−569 (12)	285 (5)	2·3 (2)
C(4)	271 (32)	−2378 (16)	2442 (7)	4·1 (2)
C(5)	−250 (32)	−5417 (16)	1569 (7)	4·1 (2)
C(6)	5315 (25)	1772 (13)	3276 (5)	2·7 (2)
C(7)	5679 (25)	4042 (13)	3973 (5)	2·7 (2)
C(8)	6469 (24)	2286 (12)	3919 (5)	2·4 (2)
C(9)	8183 (24)	1164 (12)	4457 (5)	2·2 (2)
C(10)	8896 (24)	−609 (12)	4368 (5)	2·4 (2)
C(11)	9324 (25)	1724 (13)	5100 (5)	2·6 (2)

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

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Se(1)	352 (7)	94 (2)	27 (0·4)	8 (3)	−2 (1)	−12 (0·6)
Se(2)	345 (7)	111 (2)	23 (0·4)	14 (3)	3 (1)	−12 (0·6)

Results and discussion

Molecular dimensions

Drawings of the TMTSF cation and the TCNQ anion, along with interatomic distances and angles, are presented in Figs. 1 and 2 respectively. Each of the molecular ions is crystallographically required to have at least $\bar{1}$ (C_i) molecular symmetry, and in fact each has approximately *mmm* (D_{2h}) molecular symmetry. Estimated standard deviations are in the range 0·007 Å (Se—C), 0·01–0·02 Å (C—C, C—N), and 0·4–1·2° for the bond angles.

The TMTSF cation is expected to be aromatic if its formal charge approaches +1, and the average Se—C bond length at 1·89 (1) Å is in good agreement with the average value of 1·899 (5) Å found by Hope, Knobler & McCullough (1970) in dibenzoselenophene where the Se—C bonds are expected to be highly aromatic. These same authors tabulate average Se—C bond lengths of 1·92 (2) Å for aromatic Se-containing systems and 1·98 (2) Å for non-aromatic Se—C systems.

The two formal C—C double bonds in the selenofulvalene system, C(3)—C(3)′ and C(1)—C(2), Fig. 1, are equivalent, within the e.s.d.'s, with bond lengths of 1·33 (2) and 1·34 (1) Å respectively. These values closely approach the reported mean distance (Kennard *et al.*, 1972) for an isolated C—C double bond, 1·337 (6) Å, and may suggest that π-electron delocalization in the TMTSF cation may not be complete.

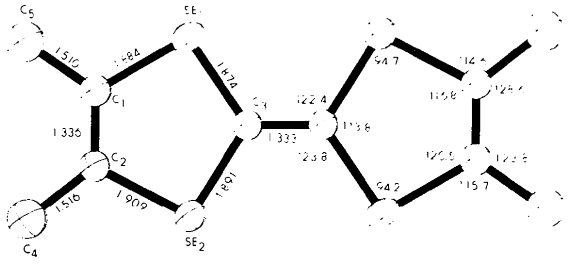

Fig. 1. Interatomic distances and angles in the TMTSF cation. Thermal ellipsoids are drawn at the 50% probability level; only the Se atoms have been refined anisotropically.

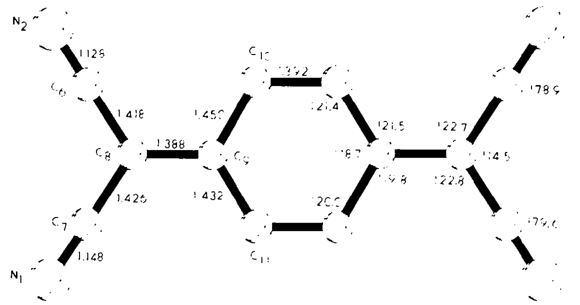

Fig. 2. Interatomic distances and angles on the TCNQ anion. Thermal ellipsoids are drawn at the 50% probability level; all atoms have isotropic thermal parameters.

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32050 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

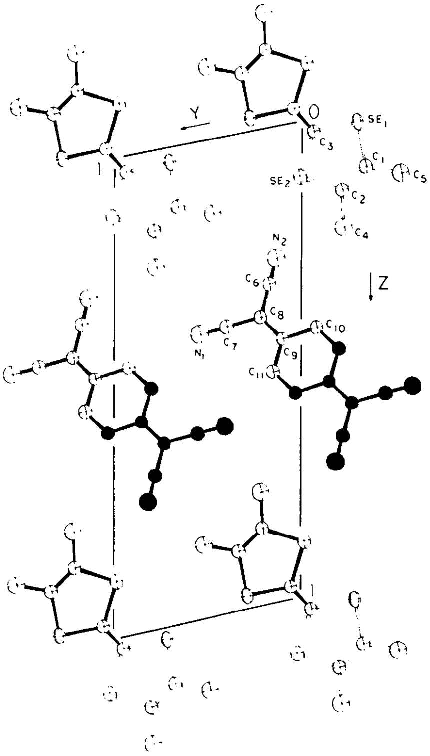

Fig. 3. A view normal to the *bc* plane of the crystal packing in TMTSF–TCNQ. The TMTSF cations have their centroids at $x = \frac{1}{2}$, while the TCNQ anions have their centroids at $x = 1$.

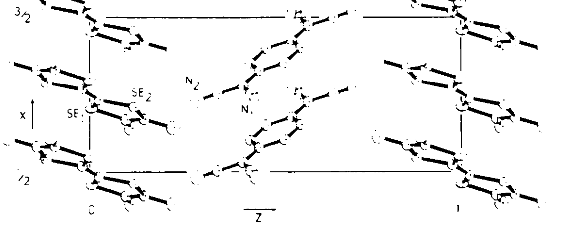

Fig. 4. A view along **b*** of the crystal packing in TMTSF–TCNQ.

The two halves of the heteronuclear fulvalene ring system are slightly distorted in *anti*-envelope conformations giving rise to an overall chair conformation for the molecular ion. This type of distortion in the heterofulvalene ring system has been observed in neutral TTF (Cooper, Kenney, Edmonds, Nagel, Wudl & Coppens, 1971), TTF–TCNQ and other systems we have studied (Kistenmacher, Phillips, Cowan, Ferraris, Bloch & Poehler, 1976; Phillips, Kistenmacher, Bloch, Ferraris & Cowan, 1977).

The dimensions of the TCNQ anion, Fig. 2, are, in general, in good agreement with results of other crystal structure analyses of cation–TCNQ salts (Herbstein, 1971).

Intrachain stacking

Consistent with its high conductivity, the structure of black TMTSF–TCNQ contains homologous columns of cations and anions, Figs. 3 and 4. The molecular overlaps within these columns are illustrated in Figs. 5 and 6. In each instance, the molecular overlap is of the 'ring double bond' type. The stacking in the TMTSF column is very similar to that in the TTF column of TTF–TCNQ except for a slight shift of the adjacent ions along the long molecular axis. This shift is probably a result of the substitution of the exocyclic methyl groups in TMTSF for the protons in TTF. The interplanar stacking distance, 3·59 Å, is 0·12 Å longer than observed in TTF–TCNQ and is again consistent with the bulkiness of the exocyclic methyl groups. The contacts within these columns are dominated by Se···Se interactions at 3·883 Å, the length of the *a* axis. These contacts are approximately 0·1 Å less than twice the van der Waals radius (2·0 Å) for Se.

The stacking in the TCNQ column, Fig. 6, is similar to that found in many cation–TCNQ salts. The interplanar stacking distance, 3·26 Å, is 0·09 Å larger than found in TTF–TCNQ, but comparable to those found in NMP–TCNQ (3·26 Å, Fritchie, 1966) and quinolinium–TCNQ (3·22 Å, Kobayashi, Marumo & Saito, 1971). Close contacts within the TCNQ column are

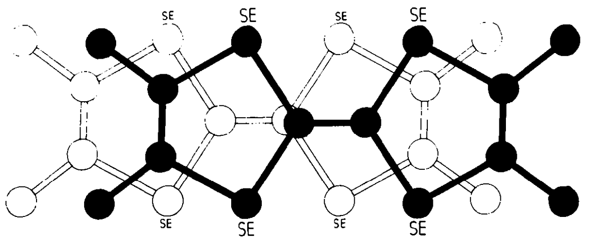

Fig. 5. Molecular overlap in the columnar stacking of the TMTSF cations. The view direction is normal to the least-squares molecular plane. The two molecular ions are related by the symmetry transform [1 + *x*, *y*, *z*].

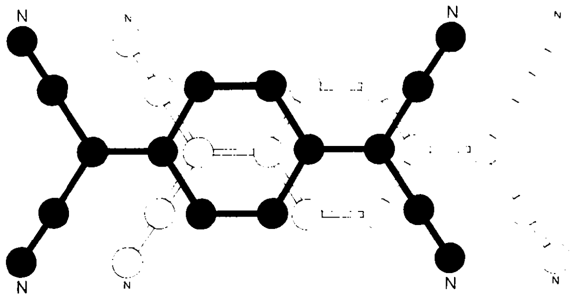

Fig. 6. Molecular overlap in the columnar stacking of the TCNQ anions. The view direction is normal to the least-squares molecular plane. The two molecular ions are related by the symmetry transform [1 + *x*, *y*, *z*].

C(7)···C(11) 3·365 (10); C(8)···C(9) 3·354 (10); C(9)···C(9) 3·332 (10); C(10)···C(11) 3·327 (10) Å.

We note that the TMTSF and TCNQ stacking distances reported here are close to the 3·6 (1) and 3·2 (1) Å cation and anion stacking distances observed in HMTSF–TCNQ (Phillips, Kistenmacher, Bloch & Cowan, 1976). Since the pattern of molecular overlaps is essentially identical, we infer that the electrical differences between TMTSF–TCNQ and HMTSF–TCNQ derive largely from interchain rather than intrachain interactions.

Interchain coupling

Black TMTSF–TCNQ is the first heterofulvalene–TCNQ salt which contains only one cation–anion molecular pair per unit cell. Indeed, its structural motif is similar to that of NMP–TCNQ (Fritchie, 1966) both in cell dimensions and space-group symmetry. On the other hand, the cations and anions are not coplanar as in NMP–TCNQ, but form a dihedral angle of 54·9°, close to the 58·5° angle in TTF–TCNQ (Kistenmacher, Phillips & Cowan, 1974).

The arrangement of short interchain contacts in TMTSF–TCNQ differs substantially from both the NMP and TTF salts. As shown in Fig. 3, these intrachain contacts are as follows. (i) The cations and anions align themselves in a head-to-tail arrangement along the (012) plane. Within the plane, the contacts are mainly between the exocyclic methyl groups of the TMTSF cation and the terminal cyano groups of the TCNQ anions: C(4)···N(2) $[x,y,z]$, 3·34 (1) Å; C(4)···N(1) $[-1+x,\ -1+y,\ z]$, 3·57 (1) Å; C(5)···N(2) $[-1+x,\ -1+y,\ z]$, 3·49 (1) Å; C(5)···N(2) $[x,\ -1+y,\ z]$, 3·56 (1) Å. (ii) Anions of different columns interact *via* contacts of the type N(1)···C(10) $[x,\ 1+y,\ z]$, 3·45 (1) Å, and N(1)···C(11) $[1-x,\ 1-y,\ 1-z]$, 3·54 (1) Å. (iii) Cations of different columns are separated by the Se···Se contacts Se(1)···Se(1) $[-x,\ -1-y,\ -z]$, 3·979 (7) Å; Se(1)···Se(1) $[1-x,\ -1-y,\ -z]$, 4·042 (7) Å. (iv) Coupling between cations and anions along the z axis is achieved *via* the short Se(2)···N(2) $[x,y,z]$, 3·36 (1) Å, contact.

Of these sets of contacts, (i) cannot be important either for interchain charge transfer or Coulomb interactions. We also doubt that (ii) is important owing to the comparatively large C···N distances involved and to the low spin and charge densities on C(10) and C(11) (Lowitz, 1967). The Se···Se distances (iii) are comparable with twice the 2·0 Å van der Waals radius of Se. On the other hand, the Se···N contacts (iv) are substantially shorter than van der Waals separations, much like the 3·203 (3) Å and 3·249 (3) Å S···N contacts in TTF–TCNQ. We note, however, that TMTSF–TCNQ contains only two such contacts per molecular pair, in contrast to the four in TTF–TCNQ. Certainly this represents a much weaker coupling than do the four 3·10 (3) Å Se···N contacts in HMTSF–TCNQ, where the geometry is more favorable to interchain π-bonding (Phillips, Kistenmacher, Bloch & Cowan, 1976).

In summary, black TMTSF–TCNQ has the structural characteristics of a highly anisotropic organic conductor. The molecular stacking along the conducting chains is typical for materials of this class, but the interchain coupling apparently is considerably weaker than that of its semimetallic sister compound HMTSF–TCNQ. The relative simplicity of the TMTSF–TCNQ structure, which contains only one molecular pair per unit cell, may be responsible for the occurrence of a single metal-to-insulator phase transition at 57 K in place of the multiple phase transitions between 34 and 59 K in TTF–TCNQ (see, for example, Comès, Shapiro, Shirane, Garito & Heeger, 1975; Bak & Emery, 1976).

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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 θ–2θ 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 $(\mathrm{TMTTF})_{1\cdot3}(\mathrm{TCNQ})_2$, is grown by vapor deposition and has been discussed elsewhere (Kistenmacher, Phillips, Cowan, Ferraris, Bloch & Poehler, 1976). From solu-

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