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The Crystal and Molecular Structure of the Organic Conductor 2,3,6,7-Tetramethyl-1,4,5,8-tetraselenafulvalenium 2,5-Dimethyl-7,7,8,8-tetracyano-*p*-quinodimethanide (TMTSF–DMTCNQ)

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The crystal and molecular structure of the highly conducting 1:1 charge-transfer salt 2,3,6,7-tetramethyl-1,4,5,8-tetraselenafulvalenium 2,5-dimethyl-7,7,8,8-tetracyano-*p*-quinodimethanide (TMTSF–DMTCNQ) was determined from diffractometer data. The unit cell is triclinic, space group $P\bar{1}$: $a = 3.938$ (1), $b = 8.085$ (3), $c = 18.956$ (9) Å, $\alpha = 97.31$ (3), $\beta = 98.12$ (4), $\gamma = 91.37$ (3)°, $V = 592.0$ Å³, $Z = 1$, $D_c = 1.841$, $D_m = 1.818$ (5) g cm⁻³ (by flotation). Full-matrix least-squares refinement gave a final $R = 0.039$ for 2348 observed reflections measured by the ω -scan technique on a four-circle diffractometer with graphite-monochromatized Mo $K\alpha$ radiation. The TMTSF cations and DMTCNQ anions form segregated, homologous stacks in the crystal with interplanar spacings of 3.64 and 3.31 Å respectively. The planes of the ions are tilted in opposite directions relative to the short a axis. Their normals make an angle of 45.8°. The interesting Se–N distance is 3.48 Å, which is the longest distance reported so far for this class of materials. Another important feature is the low symmetry of the DMTCNQ molecules, which modifies the stacking mode of the acceptor columns and may produce lower electron mobility.

Introduction

Since the discovery of the highly conducting organic compound tetrathiafulvalenium 7,7,8,8-tetracyano-*p*-quinodimethanide (TTF–TCNQ) (Ferraris, Cowan, Walatka & Perlstein, 1973; Coleman, Cohen, Sandman, Yamagishi, Garito & Heeger, 1973), extensive interest and research efforts have been focused on organic conductors. These are a narrow class of organic charge-transfer complexes consisting of planar π -electron donors and acceptors and most examples reported are based on the prototype TTF–TCNQ. Their structures are all dominated by segregated stacks of donor and acceptor molecules, but the spatial arrangements of these stacks can be quite different even for chemically closely related materials (Kistenmacher, Phillips & Cowan, 1974; Schultz, Stucky, Craven, Schaffman & Salamon, 1976; Greene, Mayerle, Schumaker, Castro, Chaikin, Etemad &

LaPlaca, 1976; Phillips, Kistenmacher, Bloch & Cowan, 1976; Bechgaard, Kistenmacher, Bloch & Cowan, 1977; Phillips, Kistenmacher, Bloch, Ferraris & Cowan, 1977).

The changes made in these systems by modifying the constituent molecules have to some extent elucidated

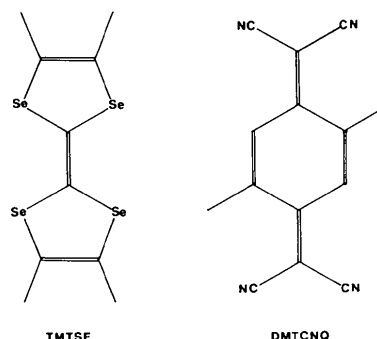


Fig. 1. Donor and acceptor molecules.

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the effects of variations in the degree of charge-transfer and interstack/intrastack distances on the physical properties of these materials. It is thus important to analyse in detail the crystal structures of new compounds in this series.

We report the crystal structure of TMTSF-DMTCNQ (Fig. 1), which is probably the most one-dimensional Se-containing organic conductor.

The details of the synthesis and some physical data, including conductivity as well as crystal data ($a = 3.94$, $b = 8.12$, $c = 18.9$ Å, $\alpha = \beta = 97.5$, $\gamma = 91.4^\circ$), based on Weissenberg and precession photographs were published as a preliminary report (Andersen, Jacobsen, Rindorf, Soling & Bechgaard, 1975).

Experimental

As TMTSF-DMTCNQ is fairly soluble and tends to produce supersaturated solutions, the normal crystal-growth techniques utilizing diffusion or slow cooling are of little value. Instead it turned out that an evaporation technique produced satisfactory crystals: 0.05 mmol of TMTSF and DMTCNQ, respectively, were placed in a 50 ml volumetric flask and were dissolved in 45 ml of a 1:1 mixture of CH_3CN and CH_2Cl_2 . The flask was placed in a thermostatted bath at 40°C protected from light. Approximately 90% of the solvent was allowed to evaporate, and the black, prismatic crystals formed were harvested and washed with *n*-pentane.

A single crystal, $0.425 \times 0.200 \times 0.175$ mm, giving Weissenberg photographs of a satisfactory quality, was selected for data collection. The unit-cell dimensions and reflection intensities were measured with a four-circle diffractometer (CAD-4). Graphite-monochromatized radiation was used [$\lambda(\text{Mo } K\alpha) = 0.71073$ Å]. The crystal data are given in Table 1.

Space group $P\bar{1}$ rather than $P1$ was indicated by intensity statistics and confirmed by the refinement. All reflections in the interval $0.05 < \sin \theta/\lambda < 0.70$ Å⁻¹ were ω -scanned. The width of the scan was $(1.8 + 0.35 \tan \theta)^\circ$ and the width of the variable horizontal detector aperture was $(4.0 + \tan \theta)$ mm.

The stability of the crystal and the measuring system were controlled by remeasuring three reflections every 4 h of exposure time. A unique set of 3408 net intensities were calculated from the 7742 observations by averaging symmetry-equivalent reflections. (Agree-

ment among equivalent reflections: $R = 0.03$.) The 2348 averaged net intensities having $I > 2\sigma(I)$ corrected for the Lp effect were used in the subsequent calculations. No corrections were made for absorption, extinction or anomalous dispersion.

Solution and refinement

The approximate sites of all non-hydrogen atoms were found by conventional heavy-atom procedures. H atoms, except those attached to C(5), appeared on a difference Fourier map.

The structure was refined by full-matrix least-squares calculations minimizing $\sum w(\Delta F)^2$, where $\Delta F = |F_o| - |F_c|$. During the final stages of refinement, a weight function was applied: $w = xy$. If $\sin \theta > 0.487$, $x = (0.487/\sin \theta)^2$, otherwise $x = (\sin \theta/0.487)^2$. If $|F_o| < 38.5$, $y = 1$, otherwise $y = (38.5/F_o)^2$. This weighting scheme was chosen to make $w(\Delta F)^2$ approximately independent of $|F_o|$ and $\sin \theta$. All Se, C and N atoms were refined with anisotropic thermal parameters, while the H atoms were given the isotropic thermal parameters equivalent to those of the atoms to which they are bonded. To obtain convergence, it was necessary to fix H(C5)2 and H(C5)3 at chemically reasonable positions. The average shift/error in the final least-squares refinement was 0.06 and the R value ($\sum |F_o| - |F_c| / \sum |F_o|$) was 0.039. The final weighted R value $\{[\sum w(|F_o| - |F_c|)^2 / \sum wF_o^2]^{1/2}\}$ was 0.043. The final fractional atomic coordinates are given in Tables 2 and 3.*

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33321 (43 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. Fractional atomic coordinates ($\times 10^4$) for the non-hydrogen atoms

The e.s.d.'s are given in parentheses in units of the last decimal place.

	<i>x</i>	<i>y</i>	<i>z</i>
Se(1)	1643 (1)	2609 (0.5)	9750 (0.2)
Se(2)	902 (1)	-961 (0.5)	8840 (0.2)
N(1)	6748 (12)	9830 (5)	5893 (3)
N(2)	7681 (13)	6307 (6)	7307 (3)
C(1)	2484 (12)	2394 (6)	8784 (3)
C(2)	2224 (12)	891 (6)	8403 (2)
C(3)	517 (11)	322 (5)	9719 (2)
C(4)	2854 (19)	467 (9)	7636 (3)
C(5)	3504 (17)	3997 (7)	8527 (3)
C(6)	5776 (10)	8527 (5)	5965 (2)
C(7)	6252 (11)	6493 (5)	6756 (2)
C(8)	4691 (10)	6907 (5)	6079 (2)
C(9)	2354 (9)	5918 (4)	5563 (2)
C(10)	1026 (10)	6598 (4)	4923 (2)
C(11)	1215 (9)	4234 (4)	5626 (2)
C(12)	2421 (12)	3382 (5)	6272 (2)

Table 1. Crystal data

$\text{C}_{10}\text{H}_{12}\text{Se}_4\text{-C}_{14}\text{H}_8\text{N}_4$, space group $P\bar{1}$
$a = 3.938$ (1), $b = 8.085$ (3), $c = 18.956$ (9) Å
$\alpha = 97.31$ (3), $\beta = 98.12$ (4), $\gamma = 91.37$ (3) $^\circ$
$V = 592.00$ Å ³ , $Z = 1$, $t = 22^\circ\text{C}$
D_m (floatation) = 1.818 (5), $D_c = 1.841$ g cm ⁻³

Table 3. *Fractional atomic coordinates ($\times 10^3$) and thermal parameters ($\times 10^2$) for H*

	x	y	z	$U (\text{\AA}^2)$
H(C4)1	404 (17)	142 (9)	744 (4)	5.4
H(C4)2	453 (9)	-37 (10)	758 (4)	5.4
H(C4)3	135 (20)	-5 (9)	735 (4)	5.4
H(C5)1	260	393	803	5.3
H(C5)2	260	489	879	5.3
H(C5)3	556 (20)	404 (9)	847 (4)	5.3
H(C10)	188 (12)	769 (6)	488 (3)	2.6
H(C12)1	477 (16)	332 (7)	634 (3)	3.3
H(C12)2	191 (14)	400 (7)	668 (3)	3.3
H(C12)3	114 (14)	242 (7)	625 (3)	3.3

The atomic scattering factors for non-hydrogen atoms were those of Cromer & Mann (1968), and for H those of Stewart, Davidson & Simpson (1965).

The structure analysis was performed with the XRAY 72 system of programs (Stewart, Kruger, Ammon, Dickinson & Hall, 1972). The illustrations were made by means of the ORTEP II program (Johnson, 1965). For other calculations, locally written programs were used.

Results and discussion

The cation TMTSF and the anion DMTCNQ are shown in Figs. 2 and 3 projected on their least-squares molecular planes, with the numbering of the atoms, and

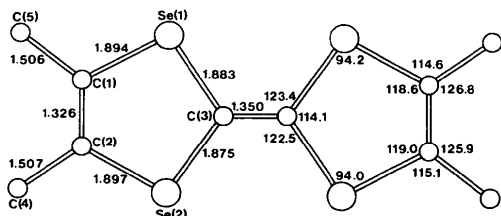


Fig. 2. TMTSF. The e.s.d.'s of bond lengths are: C-C 0.006–0.008 Å, and Se-C 0.005 Å. The e.s.d.'s of the angles are 0.2–0.3°.

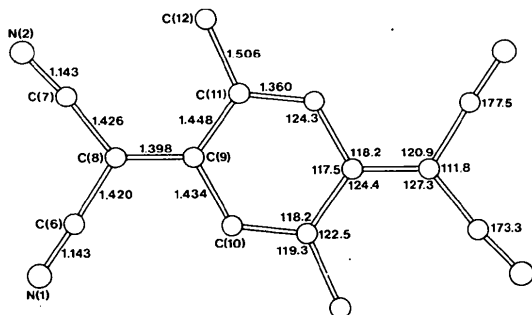


Fig. 3. DMTCNQ. The e.s.d.'s of bond lengths are about 0.006 Å. The e.s.d.'s of the angles are about 0.3°.

the interatomic distances and angles. Atoms marked with a prime in the text are related through a centre of symmetry to the corresponding unprimed atoms.

TMTSF is centrosymmetric and has approximate $mmm (D_{2h})$ molecular symmetry. The TMTSF cation in TMTSF-TCNQ is described in detail by Bechgaard, Kistenmacher, Bloch & Cowan (1977). The bond lengths and angles found here are in good agreement with their results. TMTSF is slightly chair-shaped with an angle of 2.3° between the central plane Se(1)–C(3)–Se(2)–Se(1')–C(3')–Se(2)' and the plane Se(1)–Se(2)–C(1)–C(2). Distances to the atoms from the molecular plane and from the central plane are listed in Table 4.

DMTCNQ is centrosymmetric and approximately planar with $2/m (C_{2h})$ molecular symmetry. A comparison of the interatomic distances in the DMTCNQ anion with those in the TCNQ anion in TTF-TCNQ (Kistenmacher, Phillips & Cowan, 1974) shows a very slight elongation of the C(9)–C(11) bond from 1.433 (3) Å in TCNQ to 1.448 (5) Å in DMTCNQ. The two methyl groups produce a distortion of the regular shape of the ring, and the angles around C(7), C(8) and C(9) differ by up to 6° from the corresponding angles in TCNQ. The ring in DMTCNQ is planar with an angle of 2.3° between the ring and the plane N(1)–C(6)–C(8)–C(7)–N(2). Distances to the atoms from the plane of the benzenoid rings are listed in Table 4.

Table 4. *Distances from the best planes ($\text{\AA} \times 10^3$)*

Atoms marked with an asterisk do not define the planes.

TMTSF molecular plane

Se(1) \pm 43	C(3) \pm 18
Se(2) \pm 23	C(4) \mp 5
C(1) \mp 7	C(5) \mp 20
C(2) \pm 4	

TMTSF central plane

Se(1) \mp 1	C(3) \pm 4
Se(2) \mp 1	C(4)* \mp 84
C(1)* \mp 79	C(5)* \mp 120
C(2)* \mp 59	

DMTCNQ benzenoid ring

C(6)* \pm 72	C(11) \mp 0.2
C(7)* \mp 3	C(12)* \mp 0.4
C(8)* \pm 23	N(1)* \pm 126
C(9) \pm 0.5	N(2)* \mp 10
C(10) \mp 0.3	H(C10)* \pm 37

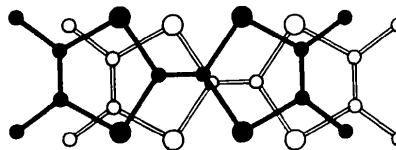


Fig. 4. TMTSF stacking, viewed along the normal to the molecular plane.

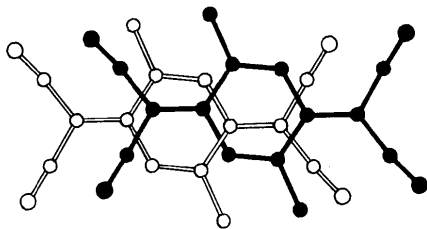


Fig. 5. DMTCNQ stacking, viewed along the normal to the molecular plane.

The molecular stacking within the two separate columns of TMTSF and DMTCNQ is shown in Figs. 4 and 5. The stackings in the TMTSF columns and in the DMTCNQ columns are of the type describable as 'double bond over the ring'. In the TMTSF-TCNQ structure (Bechgaard, Kistenmacher, Bloch & Cowan, 1977) it was found that in the projection on the molecular plane of two adjacent ions in the TMTSF stacks, C(3) and C(3)' from the two TMTSF ions fall approximately on a line, and in the projection on the molecular plane of two adjacent ions in the TCNQ stacks, C(8), C(9), C(8)' and C(9)' from the two TCNQ ions fall approximately on a line. In the present investigation these 'linearities' are distorted as shown in the figures. This is most pronounced in the acceptor columns, where the low symmetry of the DMTCNQ molecule and the resulting asymmetric intrastack overlap (Fig. 5) also seem to have important consequences for the transport properties. In molecular crystals consisting of approximately planar molecules some of the softest lattice modes correspond to in-plane rotations of the molecules (libronic motion). This motion efficiently modulates the overlap integral so that strong electron-libron coupling is expected (Gutfreund & Weger, 1977). In most conducting compounds based on unsubstituted TCNQ, however, the symmetry of the overlap forbids first-order coupling (Merrifield & Suna, 1976); but even the second-order coupling is believed to be strong enough to dominate the high-temperature resistivity (Gutfreund & Weger, 1977). In TMTSF-DMTCNQ first-order coupling is allowed and hence the electron mobility may be quite low on the acceptor stacks as indicated by the unusual thermopower observed (Jacobsen, Mortensen, Andersen & Bechgaard, 1978).

The interplanar distances are 3.64 (2) Å in the TMTSF columns and 3.31 (2) Å in the DMTCNQ columns. They are the longest reported for any conducting material belonging to the TTF-TCNQ family, but this seems to have only a minor effect on the overlap integral, t_{ij} , as optical measurements indicate the order of magnitude normally seen for this type of compound (Jacobsen, Mortensen, Andersen & Bechgaard, 1978).

Figs. 6 and 7 show the crystal packing. The normals to the planes of the molecular ions make an angle of

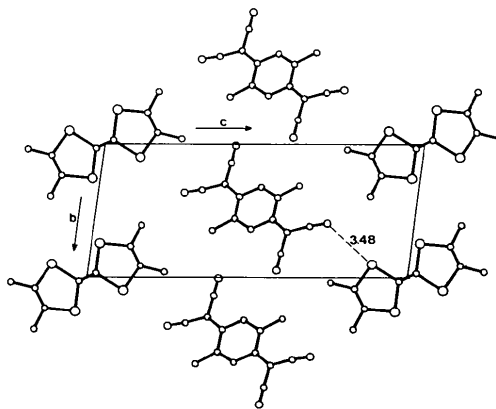


Fig. 6. Crystal packing in TMTSF-DMTCNQ, viewed along a^* .

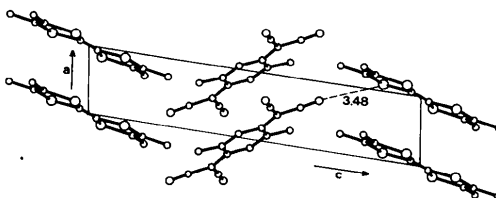


Fig. 7. Crystal packing in TMTSF-DMTCNQ, viewed along b^* .

45.8°, the molecules being tilted in opposite directions to the short a axis. Using the van der Waals radii of Bondi (1964) for C, N and Se, the following expected contact distances are obtained: N...Se 3.45 Å, Se...Se 3.80 Å; the shortest intermolecular distances found in TMTSF-DMTCNQ are in the TMTSF stack, Se(1)(x, y, z)...Se(1)(1 + x, y, z) 3.938 Å (= a), and between the TMTSF and DMTCNQ stacks, N(2)...Se(2) 3.481 (5) Å. The latter distance is believed to be important for inter-stack interactions, *i.e.* the longer the distance, the more one-dimensional is the material (Phillips, Kistenmacher, Bloch, Ferraris & Cowan, 1977). Since the distance in this case is even longer than the sum of the van der Waals radii, TMTSF-DMTCNQ is expected to be the most one-dimensional organic conductor based on a tetraselenafulvalene known. This point of view is supported by spin-resonance data, where a narrow (~70 G) ESR signal was observed (Tomkiewicz, Andersen & Taranko, 1978) and also by anisotropy measurements, where the room-temperature conductivity was found to be 200–300 times less in both transverse directions compared to the highly conducting a direction (Jacobsen, Mortensen, Andersen & Bechgaard, 1978).

Conclusion

TMTSF-DMTCNQ has the longest inter- and intra-stack distances of any material belonging to this class,

and this together with the low symmetry of the DMTCNQ molecule apparently has important consequences for the electronic behaviour of the compound.

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Molecular Configurations of the *N*-Hydro-*N'*-methylphenaziniumyl Cation (HMP⁺)*

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N-Hydro-*N'*-methylphenazinium perchlorate, C₁₃H₁₂N₂·ClO₄ (HMP–ClO₄), crystallizes in space group *Pcab* with *a* = 17.286 (4), *b* = 17.964 (3), *c* = 8.0852 (9) Å and *Z* = 8. HMP⁺ ions stack in columns along the *c* axis, with such stacks forming layers separated by the ClO₄⁻ ion along the *a* axis. The molecular configuration of the ion involves a small twist, forming a propeller. The previous communication on MP–TCNQ (II), *N*-methylphenazinium 7,7,8,8-tetracyanoquinodimethane, is shown to be actually on HMP–TCNQ, C₁₃H₁₂N₂·C₁₂H₄N₄.

Introduction

A sufficient number of cation radical salts of substituted phenazine have been studied so that a systematic comparison of the solid-state properties is becoming possible (Soos, Keller, Moroni & Nöthe, 1977). The close similarity of such 15- π -electron

phenazine radicals with the organic conductor MP–TCNQ,† in which MP⁺ is the diamagnetic, 14- π -electron cation *N*-methylphenazinium, together with the apparent different crystal phases of MP–TCNQ reported (Morosin, 1975, 1976; Fritchie, 1966; Kobayashi, 1975), suggested a need for clarification (Soos, 1976) and resulted in establishing MP–TCNQ (II)

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† Many authors employ the acronym NMP–TCNQ for this material rather than MP–TCNQ.