almost no difference in the bond distances and angles in the Te—O octahedra in Na_2TeO_4 compared with those reported for $KTeO_3(OH)$, in spite of the different charge and the presence of strong hydrogen bonds in the latter.

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The Crystal Structures of Free Radical Salts and Complexes. XI. The Crystal Structure and Electrical Properties of [1,2-Di(*N*-methyl-4-pyridinium)ethane]$^{2+}$(7,7,8,8-Tetracyanoquinodimethane)$_4^{2-}$

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The structure and electrical conductivity are reported for [1,2-di(*N*-methyl-4-pyridinium)ethane]$^{2+}$(7,7,8,8-tetracyanoquinodimethane)$_4^{2-}$, (DMPA)$^{2+}$(TCNQ)$_4^{2-}$. The complex is triclinic, space group $P\bar{1}$ with a = 7·6728, b = 13·4610, c = 12·9636 Å, α = 101·059, β = 91·159, γ = 90·402°, Z = 1. The structure was solved by the Patterson method and refined to R = 0·074 for 1245 reflexions. The TCNQ's are stacked plane-to-plane in isolated groups of four, each group consisting of a pair of dimers with mean interplanar spacings of 3·20 Å within each dimer and 3·39 Å between dimers.

Introduction

The radical anion salts of TCNQ are of considerable interest as electronic materials; several exhibit metallic behaviour. However, in these one-dimensional systems the metallic state is unstable and lattice distortions result in the occurrence of insulating behaviour at low temperatures. In two complexes, HMTSF(TCNQ) (Bloch, Cowan, Bechgaard, Pyle, Banks & Poehler, 1975) and (DEPE)$^{2+}$(TCNQ)$_4^{2-}$ I (Ashwell, Eley & Willis, 1976), the insulating state is suppressed and metallic conductivities have been observed for $T < 1$ K. (DEPE)$^{2+}$(TCNQ)$_4^{2-}$ I also exhibits Pauli paramagnetism (Ashwell, Eley, Willis & Woodward, 1977; Craik, 1976) and a temperature-independent thermoelectric power of $-35\ \mu V\ K^{-1}$ (Ashwell, Eley & Willis, 1976), characteristic of an organic metal. (DEPE)$^{2+}$-

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$(TCNQ)_4^{2-}$ also has an alternative, non-metallic crystal modification (Ashwell, Eley, Fleming, Wallwork & Willis, 1976).

In an attempt to find further highly conducting organic complexes the electrical, magnetic and structural properties of several TCNQ salts of *N*-substituted 1,2-di(4-pyridinium)ethylenes and 1,2-di(4-pyridinium)-ethanes are under investigation.

Experimental

Crystal data

$(C_{14}H_{18}N_2)(C_{12}H_4N_4)_4$, $M_r = 1031{\cdot}1$, triclinic, $a = 7{\cdot}6728\ (2)$, $b = 13{\cdot}4610\ (1)$, $c = 12{\cdot}9636\ (5)$ Å, $\alpha = 101{\cdot}059\ (1)$, $\beta = 91{\cdot}159\ (2)$, $\gamma = 90{\cdot}402\ (1)°$; $U = 1313{\cdot}8$ Å^3, $Z = 1$, $D_c = 1{\cdot}30$ g cm^{-3}; $F(000) = 532$. Mo $K\alpha$ ($\lambda = 0{\cdot}71069$ Å), $\mu = 0{\cdot}90$ cm^{-1}. Space group $P\bar{1}$ (assumed).

Table 1. *Final positional parameters* ($\times 10^3$)

The figures in parentheses indicate standard deviations.

	x	y	z
C(1)	37 (1)	119 (1)	137 (1)
C(2)	−56 (1)	129 (1)	44 (1)
C(3)	28 (1)	137 (1)	−45 (1)
C(4)	216 (1)	134 (1)	−49 (1)
C(5)	309 (1)	122 (1)	42 (1)
C(6)	225 (1)	117 (1)	132 (1)
C(7)	−52 (1)	112 (1)	226 (1)
C(8)	42 (1)	100 (1)	318 (1)
C(9)	−235 (2)	112 (1)	233 (1)
C(10)	304 (1)	141 (1)	−139 (1)
C(11)	214 (1)	150 (1)	−233 (1)
C(12)	489 (2)	136 (1)	−145 (1)
N(1)	118 (1)	88 (1)	394 (1)
N(2)	−382 (1)	111 (1)	237 (1)
N(3)	141 (1)	159 (1)	−308 (1)
N(4)	636 (1)	135 (1)	−153 (1)
C(13)	180 (1)	369 (1)	70 (1)
C(14)	83 (1)	376 (1)	−22 (1)
C(15)	163 (1)	384 (1)	−112 (1)
C(16)	348 (1)	384 (1)	−117 (1)
C(17)	447 (1)	375 (1)	−24 (1)
C(18)	365 (1)	368 (1)	66 (1)
C(19)	100 (1)	363 (1)	162 (1)
C(20)	191 (2)	360 (1)	254 (1)
C(21)	−86 (2)	363 (1)	171 (1)
C(22)	428 (1)	391 (1)	−211 (1)
C(23)	331 (2)	402 (1)	−301 (1)
C(24)	609 (2)	392 (1)	−219 (1)
N(5)	261 (1)	359 (1)	332 (1)
N(6)	−235 (1)	364 (1)	176 (1)
N(7)	255 (2)	409 (1)	−376 (1)
N(8)	760 (1)	391 (1)	−227 (1)
C(25)	587 (2)	291 (1)	480 (1)
C(26)	502 (1)	209 (1)	491 (1)
C(27)	583 (1)	135 (1)	538 (1)
C(28)	756 (1)	152 (1)	566 (1)
C(29)	840 (1)	237 (1)	552 (1)
C(30)	853 (2)	399 (1)	493 (1)
C(31)	487 (1)	41 (1)	548 (1)
N(9)	757 (1)	307 (1)	507 (1)

Table 2. *Details of molecular planes* (x, y, z *are fractional atomic coordinates; asterisks denote atoms not defining the planes*)

TCNQ(A)

Equations to the planes

Molecule	$0{\cdot}211x + 12{\cdot}882y + 1{\cdot}274z - 1{\cdot}694 = 0$
Quinonoid group	$0{\cdot}242x + 12{\cdot}883y + 1{\cdot}265z - 1{\cdot}713 = 0$

Distances from the planes (Å)

	Molecule	Quinonoid group
C(1)	0·025	0·005
C(2)	0·014	−0·007
C(3)	0·020	0·002
C(4)	0·019	0·007
C(5)	−0·009	−0·019
C(6)	0·027	0·014
C(7)	0·019	−0·004
C(8)	0·004	−0·017*
C(9)	0·007	−0·022*
C(10)	0·010	0·001
C(11)	−0·012	−0·023*
C(12)	−0·020	−0·022*
N(1)	−0·031	−0·050*
N(2)	−0·045	−0·078*
N(3)	−0·014	−0·026*
N(4)	−0·012	−0·010*

TCNQ(B)

Equations to the planes

Molecule	$0{\cdot}029x + 12{\cdot}980y + 0{\cdot}967z - 4{\cdot}894 = 0$
Quinonoid group	$0{\cdot}074x + 12{\cdot}953y + 1{\cdot}059z - 4{\cdot}870 = 0$

Distances from the planes (Å)

	Molecule	Quinonoid group
C(13)	−0·034	−0·005
C(14)	−0·026	−0·011
C(15)	−0·014	−0·003
C(16)	−0·007	0·011
C(17)	−0·043	−0·011
C(18)	−0·040	−0·003
C(19)	−0·018	0·015
C(20)	0·031	0·077*
C(21)	−0·015	0·011*
C(22)	−0·006	0·007
C(23)	0·041	0·041*
C(24)	0·000	0·020*
N(5)	0·091	0·148*
N(6)	−0·006	0·013*
N(7)	0·059	0·049*
N(8)	−0·013	0·014*

Pyridine ring

Equation to the plane

$$-2{\cdot}246x + 4{\cdot}128y + 10{\cdot}848z - 5{\cdot}073 = 0$$

Distances from the plane (Å)

C(25)	0·015	C(29)	0·010
C(26)	−0·015	N(9)	−0·012
C(27)	0·013	C(30)	0·006*
C(28)	−0·010	C(31)	−0·050*

The complex salt was deposited from an acetonitrile solution (200 ml) of TCNQ (0·4 g) and 1,2-di(*N*-methyl-4-pyridinium)ethane diiodide (0·2 g) in microcrystalline form. Small single crystals of $(DMPA)^{2+}$-$(TCNQ)_4^{2-}$ were obtained from acetone. The space group and cell constants were obtained initially from oscillation and Weissenberg photographs. The cell constants were subsequently refined on a Hilger & Watts, computer-controlled, four-circle diffractometer. Intensities were collected from a crystal 0·7 × 0·4 × 0·1 mm with a $\theta/2\theta$ scan, a scintillation counter and Mo $K\alpha$ radiation. About 2500 reflexions were measured of which significant counts $[I > 3\sigma(I)]$ were recorded for 1245. The intensities were corrected for Lorentz and polarization factors but not for absorption.

The structure was solved from a Patterson synthesis and refined by block-diagonal least squares with all the significant reflexions. In the later stages, positional parameters of the H atoms were calculated and confirmed by a difference synthesis. These atoms were included in the subsequent refinement in fixed calculated positions with constant isotropic thermal parameters of 0·05 Å^2. Block-diagonal, least-squares refinement of the non-hydrogen atoms with anisotropic thermal parameters and the weighting scheme $1/w = \{1 + [(|F_o| - A)/B]^2\}$, where $|F_o|$ is on the absolute scale, $A = 13$ and $B = 10$, gave a final $R = 0·074$. Scattering factors were taken from *International Tables for X-ray Crystallography* (1974). The final positional parameters are listed in Table 1. Least-squares planes were calculated through the cation and TCNQ moieties and are listed in Table 2.*

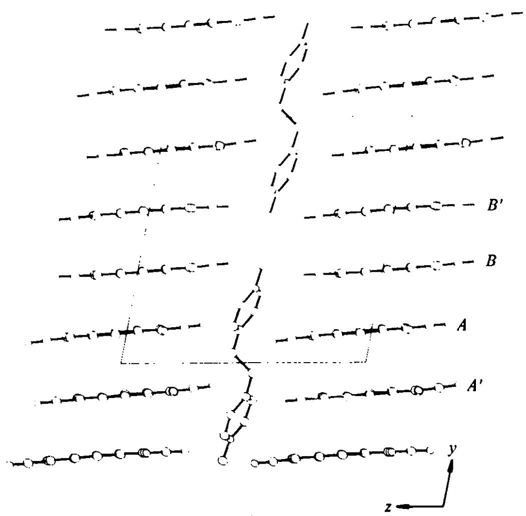
Discussion

Description of the structure

Fig. 1 shows the structure projected along **a** and **c**. The TCNQ molecules are stacked plane-to-plane in groups of four with no direct overlap between adjacent tetrads. The tetrads are held together by van der Waals forces with the closest contacts between stacks C(3)···N(4) = 3·30 along x and C(23)···N(6) = 3·35 Å along y (Table 3). A similar packing arrangement has been observed in 1,2-di(*N*-ethyl-4-pyridinium)-ethylene$(TCNQ)_4$ (Ashwell, Eley, Fleming, Wallwork & Willis, 1976), a congener of $(DMPA)^{2+}(TCNQ)_4^{2-}$.

Within the tetrads two types of overlap are observed (Fig. 2) with intermolecular separations of 3·39 (3·43) and 3·20 (3·17) Å between TCNQ(*A*)–TCNQ(*A′*) and TCNQ(*A*)–TCNQ(*B*) respectively. The tetrads are therefore better considered as pairs of partially interacting dimers. The angle between the planes through TCNQ(*A*) and TCNQ(*B*) is 1·9 (1·6)°. The figures in parentheses indicate the corresponding distances and angle between the quinonoid groups of the TCNQ's.

The dimensions of the two crystallographically independent TCNQ moieties are shown in Fig. 3. They are identical within experimental error. From these



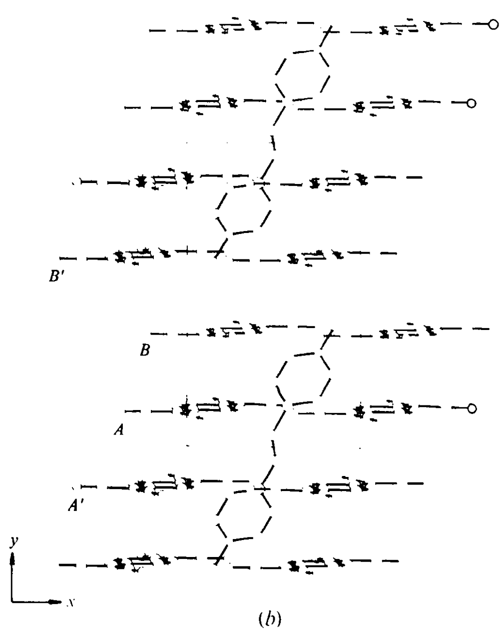


Fig. 1. The crystal structure of 1,2-di(*N*-methyl-4-pyridinium)-ethane$(TCNQ)_4$ projected (*a*) along **a** and (*b*) along **c**.

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32531 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 3. *Short intermolecular contacts* (Å)

The figures in parentheses indicate standard deviations.

Intra-tetrad		Inter-tetrad	
C(1^{i})–C(19^{i})	3·27 (1)	C(3^{i})–N(4^{ii})	3·30 (1)
C(1^{i})–C(21^{i})	3·38 (1)	C(6^{i})–N(2^{iii})	3·30 (1)
C(2^{i})–C(21^{i})	3·28 (1)	C(18^{i})–N(6^{iii})	3·36 (1)
C(3^{i})–C(13^{i})	3·38 (1)	C(23^{i})–N(6^{iv})	3·35 (1)
C(3^{i})–C(14^{i})	3·20 (1)		
C(4^{i})–C(13^{i})	3·25 (1)		
C(4^{i})–C(14^{i})	3·38 (1)	TCNQ–cation	
C(4^{i})–C(18^{i})	3·40 (1)	N(1^{i})–C(29^{ii})	3·39 (1)
C(5^{i})–C(18^{i})	3·30 (1)	N(3^{i})–C(28^{v})	3·34 (1)
C(6^{i})–C(20^{i})	3·37 (1)	N(3^{i})–C(29^{v})	3·22 (2)
C(10^{i})–C(16^{i})	3·25 (1)	N(5^{i})–C(25^{i})	3·35 (2)
C(10^{i})–C(17^{i})	3·38 (1)	N(7^{i})–C(30^{vi})	3·35 (2)
C(11^{i})–C(15^{i})	3·27 (1)	N(8^{i})–C(29^{vii})	3·27 (1)
C(11^{i})–C(16^{i})	3·37 (1)		
C(12^{i})–C(17^{i})	3·31 (1)		

Superscripts indicate equivalent positions as follows:

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

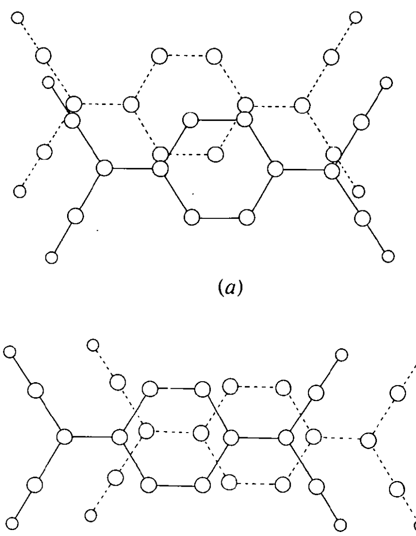


Fig. 2. Molecular overlap. (*a*) TCNQ(*A*) TCNQ(*A*′) and (*b*) TCNQ(*A*) - TCNQ(*B*).

dimensions no indication of the degree of delocalization of the negative charge is obtainable owing to the large standard deviations of the bond lengths. However, favourable overlap and a short intermolecular separation of 3·20 Å between TCNQ(*A*) and TCNQ(*B*) suggest that the charge is delocalized, at

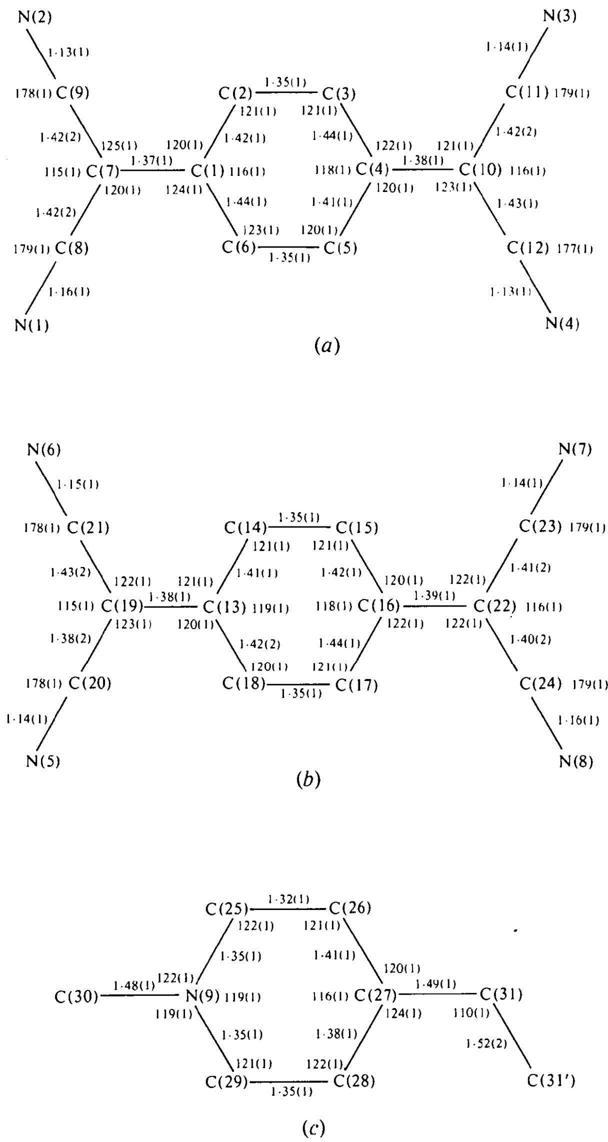


Fig. 3. Bond distances, angles and their standard deviations of (*a*) TCNQ(*A*), (*b*) TCNQ(*B*) and (*c*) the cation.

least within each dimer, so that the TCNQ's are indistinguishable with a net charge of $\frac{1}{2}-$ on each.

The dimensions of the cation (Fig. 3) are in close agreement with values reported for 1,2-di(*N*-ethyl-4-pyridinium)ethylene(TCNQ)$_4$ (Ashwell, Eley, Fleming, Wallwork & Willis, 1976) and *N*,*N*′-diethyl-4,4′-bipyridylium(TCNQ)$_4$ (Ashwell, Eley, Wallwork & Willis, 1975). The angles between the plane through the cation and the planes through TCNQ(*A*) and TCNQ(*B*) are 57·4 (57·5) and 58·2 (57·9)° respectively. The figures in parentheses indicate the angles between the cation plane and the planes through the quinonoid groups.

Electrical properties

The electrical conductivity at 300 K and activation energy of single crystals (short axis) are $2 \times 10^{-3}\ \Omega^{-1}$ cm^{-1} and 0·3 eV respectively. This corresponds to the TCNQ stacking direction (b axis) of the structure. The data are consistent with values reported previously for N,N-diethyl-4,4′-bipyridylium(TCNQ)$_4$ (Ashwell, Eley, Wallwork & Willis, 1975) and 1,2-di(N-ethyl-4-pyridinium)ethylene(TCNQ)$_4$ (Ashwell, Eley, Fleming, Wallwork & Willis, 1976) which are also homosoric.

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The Crystal Structures of Free Radical Salts and Complexes. XII. The Crystal Structure and Electrical Properties of [1,3-Di(N-pyridinium)propane]$^{2+}$(7,7,8,8-Tetracyanoquinodimethane)$_4^{2-}$

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The structure and electrical properties of [1,3-di(N-pyridinium)propane]$^{2+}$(7,7,8,8-tetracyanoquinodimethane)$_4^{2-}$, (DPP)$^{2+}$(TCNQ)$_4^{2-}$, are reported. The complex is monoclinic, space group $P2_1$, with a = 7·737, b = 25·289, c = 13·059 Å, β = 92·771°, Z = 2. The TCNQ's are stacked plane-to-plane in isolated groups of four in the (001) plane separated along **c** by layers of cations. Within the tetrads the mean intermolecular separations are 3·20, 3·25 and 3·18 Å. The electrical properties are discussed in terms of the crystal structure.

Introduction

The crystal structures of TCNQ complexes fall into three distinct groups (Dahm, Horn, Johnson, Miles & Wilson, 1975), *i.e.* homosoric, heterosoric and nonsoric with characteristic high, intermediate and low conductivities respectively. The complex salts of bipyridinium cations generally have homosoric structures in which the TCNQ's are stacked plane-to-plane in isolated triads (Ashwell & Wallwork, 1975) or tetrads (Ashwell, Eley, Wallwork & Willis, 1975; Ashwell, Eley, Fleming, Wallwork & Willis, 1976; Ashwell, Eley, Drew, Wallwork & Willis, 1977). In this paper we report the electrical conductivity and crystal structure of [1,3-di(N-pyridinium)propane]$^{2+}$(TCNQ)$_4^{2-}$, which is also homosoric.

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Experimental

Crystal data

$(C_{13}H_{16}N_2)(C_{12}H_4N_4)_4$, M_r = 1017·1, monoclinic, a = 7·737 (2), b = 25·289 (9), c = 13·059 (3) Å, β = 92·771 (6)°, U = 2552·1 Å^3, D_m = 1·31 (1), Z = 2, D_c = 1·324 g cm^{-3}; $F(000)$ = 524. Mo $K\alpha$ (λ = 0·71069 Å), μ = 0·91 cm^{-1}. Space group $P2_1$.

Black crystals of the complex were deposited when a warm acetonitrile solution (200 ml) of TCNQ (0·2 g) and LiTCNQ (0·2 g) was added to an aqueous solution