water molecules were not located, the hydrogen-bonding network cannot be explicitly described; however, Table 3 lists inter- and intramolecular oxygen–oxygen distances of less than 3·00 Å.

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The Ion Radical Salt of 1-Methyl-3-propylimidazolium with 7,7,8,8-Tetracyano-*p*-quinodimethane: MPI⁺.TCNQ⁻

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Abstract. $C_7H_{13}N_2^+.C_{12}H_4N_4^-$, $M_r = 329.39$, triclinic, $P\bar{1}$, $a = 10.982$ (2), $b = 14.337$ (2), $c = 8.750$ (1) Å, $\alpha = 91.37$ (1), $\beta = 139.09$ (1), $\gamma = 94.40$ (1)°, $V = 892.3$ (2) Å³ at 295 K, $Z = 2$, $F(000) = 346$, $D_x = 1.226$ (1), $D_m = 1.211$ (1) Mg m⁻³ (by flotation), graphite-monochromated Cu $K\alpha$ radiation, $\mu = 0.573$ mm⁻¹. The structure was solved by combined direct and Patterson methods and refined to $R = 0.042$ for 2464 counter reflexions. The interplanar distance between TCNQ anions is 3·13 (1) Å.

Introduction. The family of tetracyanoquinodimethane (TCNQ) salts and charge-transfer complexes is of interest, as several of the best-known one-dimensional organic metals are its members. Although the ion radical salt of 1-methyl-3-propylimidazolium (MPI) and TCNQ with stoichiometry 1:1 is not a good conductor ($\sigma_{300K} = 3.1 \times 10^{-5}$ Ω⁻¹ m⁻¹ for a powder sample; Šorm, Nešpůrek, Procházka & Koropecký, 1982), the arrangement of TCNQ anions relative to that of MPI cations is worthy of study.

The molecular formula of the title compound was confirmed by elemental analysis. The cell parameters and intensities (θ–2θ scan) were measured on a Syntex $P2_1$ automated diffractometer (Cu $K\alpha$) under conditions described by Langer & Huml (1978). In the range up to $2\theta = 127°$, 2941 independent reflexions were measured, 2465 of which were observed ($I > 1.96\sigma_I$). The data were corrected for the Lorentz–polarization factor (for formula see Langer, Huml & Zachová, 1979), but not for absorption.

The first attempt to solve the structure was made using *MULTAN* 78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978), but a chicken-wire-like structure resulted, where the TCNQ anion might be placed in seven overlying positions, although the orientation was still the same. As the E statistics indicated a centrosymmetric structure, the Patterson function was calculated and the highest peak (origin removed) was regarded as an overlap of 16 parallel vectors between centrosymmetrically related TCNQ anions and, therefore, the translation vector for TCNQ

with the orientation found in the E map. Two subsequent difference syntheses revealed the whole MPI cation.

The structure was refined by the least-squares method in the block-diagonal approximation using the modified program NRC-10 (Ahmed, Hall, Pippy & Huber, 1966). The function minimized was $\sum w\Delta^2$, where $w = [\sigma_F^2 + (0.02F_o)^2]^{-1}$ and $\Delta = ||F_o| - |F_c||$. Scattering factors were taken from *International*

Tables for X-ray Crystallography (1974); the H atoms were considered as a spherical approximation to the bonded atoms. Unobserved reflexions were eliminated from the refinement and so was the reflexion $1\bar{1}1$ due to extinction. The refinement of all non-H (anisotropic) and H atoms (isotropic) was stopped when the shifts of all parameters were $<0.05\sigma$. The final agreement factors are: $R_1 = \sum \Delta / \sum |F_o| = 0.042$, $R_2 = [\sum \Delta^2 / \sum |F_o|^2]^{1/2} = 0.071$, $R_{w2} = [\sum w\Delta^2/$

Table 1. *Final positional parameters* ($\times 10^4$) *and B_{eq} values* (Å^2) *of the non-H atoms with e.s.d.'s in parentheses*

	x	y	z	B_{eq}
C(1)	1342 (2)	8249 (1)	2102 (2)	3.2 (1)
C(2)	546 (2)	8722 (1)	2567 (2)	3.5 (1)
C(3)	785 (2)	9680 (1)	2916 (2)	3.6 (1)
C(4)	1838 (2)	10248 (1)	2818 (2)	3.3 (1)
C(5)	2627 (2)	9776 (1)	2345 (2)	3.4 (1)
C(6)	2397 (2)	8818 (1)	2014 (2)	3.4 (1)
C(7)	1147 (2)	7250 (1)	1818 (2)	3.4 (1)
C(8)	2076 (2)	11246 (1)	3170 (2)	3.8 (1)
C(9)	36 (2)	6672 (1)	1802 (3)	4.0 (1)
C(10)	2079 (2)	6774 (1)	1580 (3)	4.0 (1)
C(11)	1380 (2)	11729 (1)	3763 (3)	4.6 (1)
C(12)	3106 (2)	11829 (1)	3067 (2)	4.1 (1)
N(13)	−872 (2)	6188 (1)	1768 (3)	6.0 (2)
N(14)	2841 (2)	6368 (1)	1402 (3)	5.7 (1)
N(15)	857 (2)	12142 (1)	4280 (3)	6.9 (2)
N(16)	3926 (2)	12325 (1)	2989 (3)	5.7 (1)
N(01)	2995 (2)	4952 (1)	5620 (2)	3.6 (1)
C(02)	4014 (2)	5797 (1)	6734 (3)	3.7 (1)
N(03)	3964 (2)	6082 (1)	8131 (2)	3.6 (1)
C(04)	2864 (2)	5396 (1)	7891 (3)	4.1 (1)
C(05)	2268 (2)	4694 (1)	6338 (3)	4.0 (1)
C(06)	2668 (3)	4393 (1)	3892 (3)	5.5 (2)
C(07)	4876 (2)	7001 (1)	9608 (3)	4.5 (1)
C(08)	3645 (3)	7744 (1)	8279 (4)	6.1 (2)
C(09)	4599 (4)	8701 (1)	9735 (4)	8.2 (2)

Table 2. *Final positional parameters* ($\times 10^3$) *and B_{iso} values* (Å^2) *of the H atoms with e.s.d.'s in parentheses*

|	x	y	z	B_{iso}
H(2)	−16 (2)	834 (1)	266 (2)	3.5 (3)
H(3)	24 (2)	999 (1)	322 (2)	4.3 (3)
H(5)	335 (2)	1016 (1)	228 (2)	3.8 (3)
H(6)	298 (2)	850 (1)	174 (2)	3.6 (3)
H(02)	470 (2)	616 (1)	658 (3)	4.9 (4)
H(04)	264 (2)	547 (1)	876 (3)	5.0 (4)
H(05)	151 (2)	410 (1)	572 (3)	4.5 (3)
H(061)	357 (4)	394 (2)	464 (5)	13.0 (9)
H(062)	143 (3)	404 (2)	277 (4)	12.1 (8)
H(063)	287 (3)	478 (2)	318 (3)	8.1 (5)
H(071)	605 (2)	717 (1)	1019 (3)	5.5 (4)
H(072)	521 (2)	692 (1)	1099 (3)	5.9 (4)
H(081)	338 (3)	777 (2)	689 (4)	9.0 (6)
H(082)	251 (3)	753 (1)	774 (3)	7.5 (5)
H(091)	569 (3)	887 (2)	1006 (4)	11.0 (7)
H(092)	508 (3)	871 (2)	1129 (4)	10.7 (7)
H(093)	378 (3)	914 (2)	879 (4)	9.4 (6)

(a)

(b)
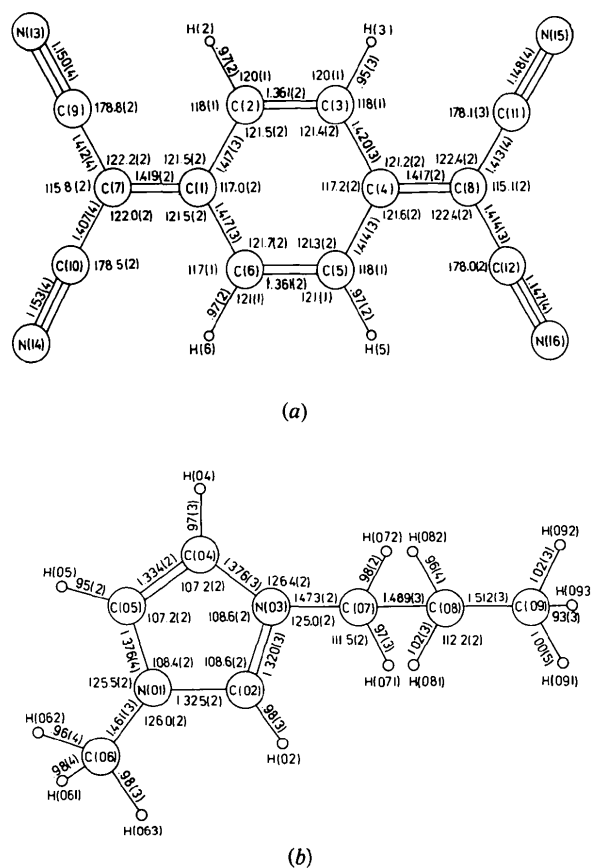
Fig. 1. Numbering scheme with bond distances (Å), valency angles (°) and their respective e.s.d.'s. (*a*) TCNQ anion; (*b*) MPI cation: only angles not including H atoms are given.

Table 3. *Valency angles* (°), *and their e.s.d.'s, including* H *atoms for the* MPI *cation*

N(01)−C(02)−H(02)	127 (1)	C(08)−C(07)−H(071)	111 (1)
N(03)−C(02)−H(02)	124 (1)	C(08)−C(07)−H(072)	112 (1)
N(03)−C(04)−H(04)	122 (1)	H(071)−C(07)−H(072)	106 (2)
C(05)−C(04)−H(04)	131 (1)	C(07)−C(08)−H(081)	106 (2)
C(04)−C(05)−H(05)	134 (1)	C(07)−C(08)−H(082)	106 (2)
N(01)−C(05)−H(05)	119 (1)	C(09)−C(08)−H(081)	109 (2)
N(01)−C(06)−H(061)	111 (2)	C(09)−C(08)−H(082)	113 (2)
N(01)−C(06)−H(062)	108 (2)	H(081)−C(08)−H(082)	111 (2)
N(01)−C(06)−H(063)	112 (2)	C(08)−C(09)−H(091)	106 (2)
H(061)−C(06)−H(062)	108 (3)	C(08)−C(09)−H(092)	114 (2)
H(061)−C(06)−H(063)	104 (3)	C(08)−C(09)−H(093)	108 (2)
H(062)−C(06)−H(063)	114 (3)	H(091)−C(09)−H(092)	109 (3)
N(03)−C(07)−H(071)	108 (1)	H(091)−C(09)−H(093)	106 (3)
N(03)−C(07)−H(072)	108 (1)	H(092)−C(09)−H(093)	113 (3)

$\sum w|F_o|^2]^{1/2} = 0.050$, $S = [\sum w\Delta^2/(m-n)]^{1/2} = 0.91$, where m is the number of reflexions used in the refinement (2464) and n is the number of refined parameters (294). The residual electron density on the final difference map did not exceed ± 0.40 e Å^{-3}. The coordinates of all non-H atoms with B_{eq} values (Hamilton, 1959) are given in Table 1 and coordinates of H atoms with B_{iso} values are given in Table 2.*

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36207 (33 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 4. Weighted mean planes

Equations are referred to a Cartesian coordinate system defined by $X \parallel a$, Y in the ab plane, $Z \parallel c^*$. Deviations from planes (Å × 10^3) marked with a dagger indicate the plane-defining atoms.

(I) $-0.1413X + 0.1344Y - 0.9808Z - 0.5087 = 0$ ($\chi^2 = 13.7$)
(II) $-0.4197X + 0.5250Y - 0.7404Z - 1.5473 = 0$ ($\chi^2 = 5.0$)

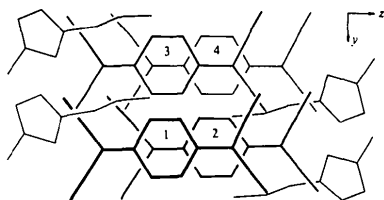| (I)		(II)	
C(1)	1 (1)†	N(01)	0 (2)†
C(2)	2 (2)†	C(02)	2 (2)†
C(3)	−2 (2)†	N(03)	−2 (2)†
C(4)	−1 (1)†	C(04)	3 (2)†
C(5)	3 (1)†	C(05)	−1 (2)†
C(6)	−3 (2)†	C(06)	18 (2)
C(7)	−42 (2)	C(07)	43 (2)
C(8)	3 (2)	H(02)	8 (19)
C(9)	18 (2)	H(04)	8 (19)
C(10)	−173 (2)	H(05)	−15 (18)
C(11)	−70 (2)		
C(12)	13 (2)		
N(13)	74 (2)		
N(14)	−291 (2)		
N(15)	−148 (2)		
N(16)	26 (2)		
H(2)	−13 (14)		
H(3)	3 (15)		
H(5)	0 (14)		
H(6)	−31 (14)		

Fig. 2. The crystal packing of TCNQ anions. Projection perpendicular to the mean plane (I) in Table 4.
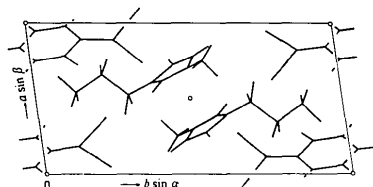

Fig. 3. Projection of the structure along c.

Table 5. Characteristics of the relative positions of TCNQ anions

δx is the interplanar spacing; δy and δz are the shifts of the centre of mass in the directions y and z (for orientation of axes and for numbers of TCNQ anions see Fig. 2).

Anions	δx (Å)	δy (Å)	δz (Å)
TCNQ (1–2), (3–4)	3·13 (1)	0·15 (1)	2·10 (1)
TCNQ (1–3), (2–4)	6·28 (1)	−3·53 (1)	−0·14 (1)
TCNQ (2–3)	3·15 (1)	−3·68 (1)	−1·96 (1)

Discussion. The numbering scheme, bond distances, valency angles and their e.s.d.'s are given in Fig. 1 and Table 3. For the deviations of the atoms from the weighted mean planes through the six-membered ring of TCNQ (plane I) and the imidazole ring (plane II) see Table 4. The χ^2 values show the significant non-planarity of the six-membered ring (and deviations of remaining atoms from it indicate the non-planarity of the whole TCNQ anion), whereas the imidazole ring can be considered planar. The angle between planes (I) and (II) is 31·12 (1)°.

The magnitude of the charge transfer for the TCNQ anion as calculated by the method of Flandrois & Chasseau (1977) is 1·00e.

The crystal packing can be seen in Fig. 2 and Fig. 3. The interplanar spacings and shifts of the centre of mass in directions y and z are given in Table 5. The explanation of poor electrical conductivity is apparent from the arrangement of TCNQ anions.

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