Ring twist, which is strictly defined as the H(4a)—C(4a)—C(8a)—H(8a) torsion angle {−60 (3)° [−58 (2)°]}, is also described to a good approximation by the more accurately determined C(1)—C(8a)—C(4a)—C(5) torsion angle of 69·4 (3)° [68·5 (3)°]. The latter torsion angles are slightly larger in the present structures than in any other 4α-naphthoquinol studied in the series, probably as a result of crowding of the pseudo-axial O(1) substituent.

The C(6)=C(7) bond length of 1·324 (4) Å [1·323 (4) Å] is not significantly longer than that in similarly substituted tetrahydro-1-naphthoquin-4α-ol derivatives (Greenhough & Trotter, 1981; Secco & Trotter, 1982); the increased endocyclic angles around C(6) and C(7) in the present structure follow the previously noted trend of internal-angle enlargement accompanying increased substitution at these centers. The C(5)—C(6) and C(7)—C(8) bonds are longer in the diol than in the unsubstituted tetrahydronaphthoquinol, as expected on the basis of previous trends observed in the naphthoquinols with methyl substituents at C(6) and C(7).

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References

Bucourt, R. & Hainaut, D. (1965). *Bull. Soc. Chim. Fr.* pp. 1366–1378.

Busing, W. R., Martin, K. O. & Levy, H. A. (1962). *ORFLS*. Report ORNL–TM-305. Oak Ridge National Laboratory, Tennessee.

Busing, W. R., Martin, K. O. & Levy, H. A. (1964). *ORFFE*. Report ORNL–TM-306. Oak Ridge National Laboratory, Tennessee.

Cromer, D. T. & Mann, J. B. (1968). *Acta Cryst.* **A24**, 321–324.

Greenhough, T. J. & Trotter, J. (1981). *Acta Cryst.* **B37**, 126–132.

Johnson, C. K. (1976). *ORTEP* II. Report ORNL–5138. Oak Ridge National Laboratory, Tennessee.

McDowell, C. A., Naito, A., Scheffer, J. R. & Wong, Y. F. (1981). *Tetrahedron Lett.* **22**, 4779–4782.

Main, P., Woolfson, M. M., Lessinger, L., Germain, G. & Declercq, J. P. (1980). *MULTAN* 80. *A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

Secco, A. S. & Trotter, J. (1982). *Acta Cryst.* **B38**, 2190–2196.

Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

Sutton, L. E. (1965). Editor. *Tables of Interatomic Distances and Configuration in Molecules and Ions.* Spec. Publ. No. 18. London: The Chemical Society.

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Structures of Free Radical Salts and Complexes. XV.* 1,2,4-Trimethylpyridinium 7,7,8,8-Tetracyano-*p*-quinodimethanide (1:2), $C_8H_{12}N^+.2C_{12}H_4N_4^{\frac{1}{2}-}$

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Abstract. MDMP$^+$ (TCNQ)$_2^-$, $M_r = 530{\cdot}55$, monoclinic, $P2_1/c$, $a = 13{\cdot}796$ (1), $b = 12{\cdot}889$ (1), $c = 7{\cdot}846$ (2) Å, $\beta = 92{\cdot}18$ (1)°, $U = 1394{\cdot}1$ (5) Å^3, $Z = 2$, $D_m = 1{\cdot}26$ (1), $D_c = 1{\cdot}264$ Mg m^{-3}, Cu $K\alpha$, $\lambda = 1{\cdot}5418$ Å, $\mu = 0{\cdot}656$ mm^{-1}, $F(000) = 550$. $R = 0{\cdot}0613$ for 1110 significant reflections [$I > 3\sigma(I)$]. The TCNQ's are stacked plane-to-plane, in groups of two, with no direct overlap between adjacent pairs. Within the pairs, there is a favourable exocyclic-double-bond–quinonoid-ring overlap of adjacent molecules, with short mean perpendicular distances of 3·20 (2) Å. The cation appears to occupy at random two slightly separated centrosymmetrically related positions.

Introduction. The title substance shows an interesting anomaly in the temperature dependence of the microwave conductivity, which is not shown in the d.c. conductivity measurements (Swietlik, Przybylski & Graja, 1981). As a possible aid to the explanation of this phenomenon, the room-temperature crystal structure has been determined.

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* Part XIV: Ashwell & Wallwork (1979).

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Experimental. 1474 I with $\theta_{\max} = 65°$, Enraf–Nonius CAD-4 computer-controlled four-circle diffractometer, $\omega/1{\cdot}33\theta$ scan, scintillation counter, Cu $K\alpha$, no absorption correction.

Two cations can only be accommodated in a unit cell of space group $P2_1/c$ if they have molecular centres of symmetry coincident with two crystallographic centres of symmetry of the cell. The 1,2,4-trimethylpyridinium cation cannot have a centre of symmetry so, if the space group is correct, an apparent centre of symmetry must be generated by each cation occupying, at random, two centrosymmetrically related positions (with an occupation factor of $\frac{1}{2}$ at each position). There is no comparable problem with the arrangement of the TCNQ moieties, provided the single negative charge is equally shared, on average, between the two TCNQ's of each formula unit, thereby giving four indistinguishable $\mathrm{TCNQ}^{\frac{1}{2}-}$ ions in the four general positions of the cell. On this basis, the TCNQ ions were located by means of Patterson synthesis and, after some refinement, an $(F_o - F_c)$ Fourier synthesis gave the partially resolved positions of the disordered pair of cations. On further refinement, with constraints on the cation dimensions, the two centrosymmetrically-related disordered positions for the cation were found to have slightly displaced molecular centres. Least-squares refinement of a cation, assumed to have an occupation factor of 0·5, in one of these positions, was then carried out, together with the one TCNQ in the asymmetric unit: 1110 significant reflections $[I > 3\sigma(I)]$, dimensions of cation constrained, as shown in Fig. 2(*b*), C and N of TCNQ anisotropic, rest isotropic, $1/w = \{1 + [(|F_o| - 30)/50]^2\}$, $|F_o|$ 4·93 times absolute scale; scattering factors from *International Tables for X-ray Crystallography* (1974); H from Fourier difference map, calculated positions, $U = 0{\cdot}05$ Å^2, not refined; H of 4-methyl group not included; final $R = 0{\cdot}0613$.

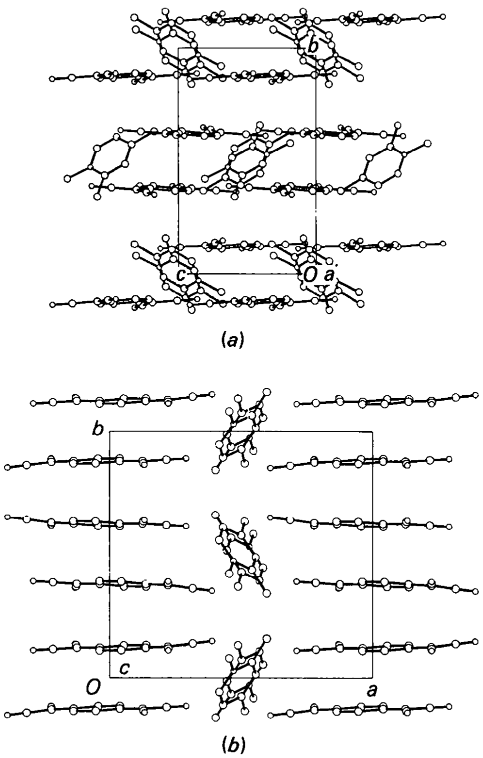
The possiblity that the structure might really be non-centrosymmetric, and have one, non-disordered cation position, was investigated by attempting refinement in space group Pc. Although a slightly lower R factor was obtained, the molecules became very distorted, so the disordered centrosymmetric structure seems more probable. Calculations were carried out with *CRYSTALS* (Carruthers & Rollett, 1975).

Discussion. Positional parameters are given in Table 1.* Fig. 1 shows the structure of $\mathrm{MDMP}^+(\mathrm{TCNQ})_2^-$, projected along **a** and **c**. The TCNQ's are stacked plane-to-plane, in centrosymmetrically related pairs, approximately perpendicular to **b**.

Table 1. *Final fractional atomic coordinates and isotropic* [C(13) *to* N(5)] *or equivalent isotropic* [C(1) *to* N(4)] *thermal parameters, with e.s.d.'s in parentheses*

$$U_{\rm eq} = \tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$ or U(iso)(Å^2)
C(1)	0·1361 (3)	0·3779 (3)	0·2074 (5)	0·048 (2)
C(2)	0·0443 (3)	0·3877 (3)	0·2823 (5)	0·051 (2)
C(3)	−0·0390 (3)	0·3888 (3)	0·1866 (5)	0·051 (2)
C(4)	−0·0383 (3)	0·3785 (3)	0·0048 (5)	0·045 (1)
C(5)	0·0540 (3)	0·3686 (3)	−0·0713 (5)	0·048 (2)
C(6)	0·1375 (3)	0·3679 (3)	0·0250 (5)	0·050 (2)
C(7)	0·2217 (3)	0·3741 (3)	0·3074 (6)	0·053 (2)
C(8)	0·3146 (4)	0·3608 (4)	0·2354 (6)	0·068 (2)
C(9)	0·2225 (3)	0·3820 (4)	0·4895 (7)	0·060 (2)
C(10)	−0·1246 (3)	0·3781 (3)	−0·0934 (5)	0·049 (2)
C(11)	−0·2159 (4)	0·3841 (4)	−0·0171 (6)	0·064 (1)
C(12)	−0·1277 (3)	0·3690 (4)	−0·2746 (7)	0·056 (2)
N(1)	0·3889 (3)	0·3510 (5)	0·1789 (6)	0·100 (2)
N(2)	0·2229 (3)	0·3883 (4)	0·6337 (6)	0·086 (2)
N(3)	−0·2899 (3)	0·3888 (4)	0·0432 (6)	0·098 (2)
N(4)	−0·1315 (3)	0·3632 (3)	−0·4200 (6)	0·075 (2)
C(13)	0·4607 (7)	−0·0641 (7)	−0·040 (1)	0·072 (3)
C(14)	0·4454 (9)	−0·0138 (9)	0·111 (1)	0·088 (4)
C(15)	0·5007 (8)	0·0738 (7)	0·159 (1)	0·080 (3)
C(16)	0·403 (1)	−0·159 (1)	−0·093 (2)	0·136 (6)
C(17)	0·487 (1)	0·132 (1)	0·322 (2)	0·146 (6)
C(18)	0·5690 (9)	0·1069 (9)	0·050 (1)	0·092 (4)
C(19)	0·5829 (7)	0·0554 (7)	−0·095 (1)	0·070 (3)
C(20)	0·5459 (9)	−0·0795 (9)	−0·310 (1)	0·090 (3)
N(5)	0·5300 (5)	−0·0287 (6)	−0·1426 (8)	0·052 (2)



(*a*)

(*b*)

Fig. 1. The structure projected along (*a*) the *a* axis, (*b*) the *c* axis.

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* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, details of least-squares planes and Table 3 and Fig. 3 have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38130 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

There is a favourable exocyclic-double-bond to quinonoid-ring overlap between adjacent molecules within each pair, but there is no direct overlap between the pairs, and they are held together sideways by van der Waals forces. In this way, sheets of only slightly interacting pairs of TCNQ's are formed, parallel to (100), interleaved by disordered layers of cations, each cation bridging a pair of TCNQ's. The short intermolecular contacts within the arrays are listed in Table 2. Within a pair, the mean perpendicular separation between the two TCNQ's is 3·20 (2) Å. The molecules, however, are not quite planar; the $C{=}C(CN)_2$ groups are tilted out of the plane of the quinonoid ring, both in the same direction. Each makes an angle of 2·1 (3)° with the ring, and a dihedral angle of 4·1 (3)° with the other. Because of this, slightly different least-squares planes are obtained when the quinonoid ring atoms only are considered. These give an interplanar separation within a pair of 3·18 (1) Å. Between adjacent (not quite parallel) pairs the mean perpendicular spacing is about 3·6 Å and there is also appreciable sideways separation of adjacent TCNQ's [Fig. 3(*b*)].*

The dimensions of the TCNQ moiety both corrected and uncorrected for librational motion are shown in Fig. 2(*a*). They are in close agreement with previous $TCNQ^{\frac{1}{2}-}$ dimensions (Table 3).* This agreement indicates total charge delocalization within the pairs of TCNQ's consistent with the short separation.

The constraints imposed on the dimensions of the cation (bond lengths constrained within 0·01 Å and angles within 1°) are shown in italics in Fig. 2(*b*). They were based on typical dimensions of related molecules.

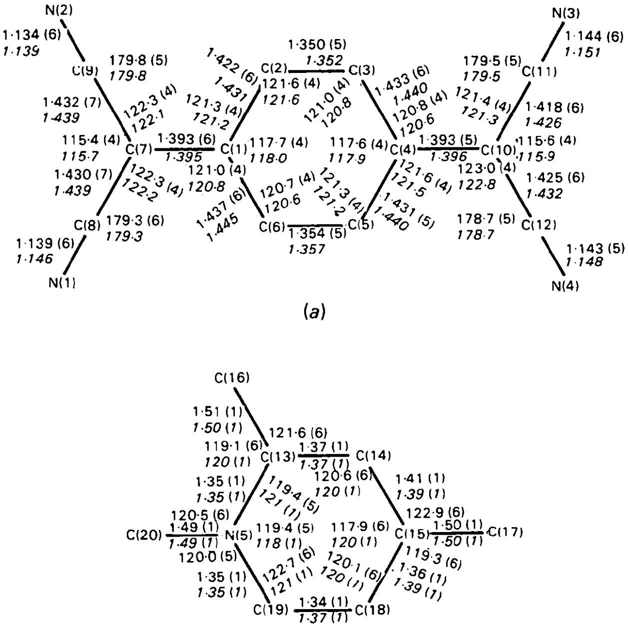

Fig. 2. Dimensions of (*a*) TCNQ, uncorrected and corrected (in italics) for librational motion of the whole molecule, (*b*) the cation, showing the constrained dimensions (in italics) and the values after refinement with these constraints. Figures in parentheses are e.s.d.'s. Additional angular constraints applied to the cation (which limit both exocyclic bond angles and non-planarity) were: angles C(16)C(13)C(18), C(17)C(15)N(5), C(20)N(5)C(15) all 180 (1)°.

The dimensions after refinement with these constraints applied are also shown. They should not be taken to be a good representation of the natural dimensions of the cation but (by the fact that there are no major changes from the constrained dimensions) as an indication that the constraints must have been reasonably appropriate.

The occurrence of TCNQ's in segregated pairs is consistent with the intermediate value of the d.c. conductivity exhibited by this salt (Swietlik, Przybylski & Graja, 1981). Conductivities in different directions in the crystal have not been reported, but it may be predicted that similar intermediate values would be expected along **b** and **c** (within the sheets of TCNQ) and a lower value along **a** (across the cation sheets). The disorder of the cations may provide a possible clue to the anomaly in the microwave conductivity, but it is not clear why the d.c. conductivity is not similarly affected.

We thank the Lebanese University, Faculty of Sciences (II), for a scholarship (to PJR), Dr M. J. Begley, for assistance with the diffractometry, Professor T. J. King for assistance with the computing and the SERC for contributing towards the cost of the diffractometer.

Table 2. *Short intermolecular distances* (Å)

Within a pair of TCNQ's, symmetry:* $-x,-y+1,-z$			
C(1)···C(10)	3·271 (6)	C(4)···C(4)	3·306 (8)
C(1)···C(12)	3·307 (6)	C(4)···C(5)	3·308 (6)
C(2)···C(12)	3·341 (6)	C(6)···C(10)	3·323 (6)
C(3)···C(5)	3·259 (6)	C(6)···C(11)	3·376 (6)
Between pairs, symmetry: $x,-y+\frac{1}{2},z+\frac{1}{2}$			
C(2)···C(5)	3·499 (6)	C(10)···N(4)	3·398 (6)
C(4)···N(4)	3·431 (6)	C(11)···N(4)	3·469 (6)
C(9)···C(6)	3·443 (6)		
Sideways, symmetry: $x,y,z\pm 1$			
C(2)···N(4)	3·445 (6)	C(5)···N(2)	3·356 (6)
C(3)···N(4)	3·401 (6)	C(6)···N(2)	3·340 (6)
With cation, (see symmetry code below)			
C(14)···N(1^{i})	3·269 (16)	C(17)···N(3^{v})	3·483 (18)
C(14)···N(2^{ii})	3·481 (14)	C(19)···N(1^{ii})	3·378 (12)
C(15)···N(1^{i})	3·469 (13)	C(19)···N(2^{i})	3·460 (11)
C(16)···N(3^{iii})	3·380 (13)	C(19)···N(3^{vi})	3·470 (9)
C(17)···N(1)	3·313 (18)	C(20)···N(1^{vii})	3·190 (10)
C(17)···N(1^{iv})	3·166 (13)	C(20)···N(2^{i})	3·455 (13)

* Symmetry operation shown acts on the second atom in each contact. Symmetry code for cation interactions: None x,y,z; (i) $-x+1,y-\frac{1}{2},-z+\frac{1}{2}$; (ii) $x,-y+\frac{1}{2},z-\frac{1}{2}$; (iii) $-x,-y,-z$; (iv) $x,-y+\frac{1}{2},z+\frac{1}{2}$; (v) $x+1,-y+\frac{1}{2},z+\frac{1}{2}$; (vi) $x+1,-y+\frac{1}{2},z-\frac{1}{2}$; (vii) $-x+1,y-\frac{1}{2},-z-\frac{1}{2}$.

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* Fig. 3 and Table 3 have been deposited.

References

ASHWELL, G. J., ELEY, D. D., WALLWORK, S. C. & WILLIS, M. R. (1975). *Proc. R. Soc. London Ser. A*, **343**, 461–475.

ASHWELL, G. J. & WALLWORK, S. C. (1979). *Acta Cryst.* B**35**, 1648–1651.

CARRUTHERS, J. R. & ROLLETT, J. S. (1975). Private communication.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

SWIETLIK, R., PRZYBYLSKI, M. & GRAJA, A. (1981). 3rd Conf. Electrical and Related Properties of Organic Solids, Wdzydze, Poland, 18–23 June.

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Structures of Free Radical Salts and Complexes. XVI.* 1,1′-Tetramethylenedipyridinium 7,7,8,8-Tetracyano-*p*-quinodimethanide (1:4), $C_{14}H_{18}N_2^{2+}.4C_{12}H_4N_4^{\frac{1}{2}-}$

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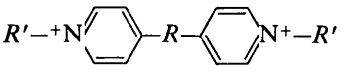
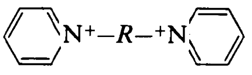
Abstract. $(DPB)^{2+}(TCNQ)_4^{2-}$, $M_r = 1031{\cdot}07$, triclinic, $P\bar{1}$, $a = 7{\cdot}75\,(1)$, $b = 13{\cdot}21\,(2)$, $c = 15{\cdot}49\,(5)$ Å, $\alpha = 101{\cdot}84\,(3)$, $\beta = 122{\cdot}39\,(2)$, $\gamma = 87{\cdot}64\,(4)°$, $U = 1306\,(10)$ Å^3, $Z = 1$, $D_m = 1{\cdot}30\,(1)$, $D_c = 1{\cdot}31$ Mg m^{-3}, Mo $K\alpha$ radiation, $\lambda = 0{\cdot}71069$ Å, $\mu = 0{\cdot}0904$ mm^{-1}, $F(000) = 532$. $R = 0{\cdot}055$ for 1489 reflexions [$I > 3\sigma(I)$]. The TCNQ's are stacked, plane-to-plane, roughly along [110] in tetrads, each consisting of two only partially overlapping pairs of molecules. Within each pair however, there is a favourable exocyclic-double-bond to quinonoid-ring overlap of adjacent TCNQ$^{1/2-}$ with a short perpendicular spacing of 3·19 (2) Å. Sheets of such tetrads in the (001) plane alternate with sheets of DPB cations orientated approximately parallel to [110]. The structure is consistent with the observed anisotropy of electrical conductivity.

Introduction. TCNQ forms many electrically conducting salts and complexes because of the readiness with which it forms the radical anion TCNQ$^-$. In most of these materials, TCNQ forms either a continuous or an interrupted stack along the direction in the crystal of high conductivity. There are a number of factors that influence the nature of this stack and hence the magnitude of the electrical conductivity, amongst the most important of which are the size of the cation and the separation of the positive charges of the cations in the crystal lattice. Cations based on hydrocarbon nuclei terminated at both ends by quaternized pyridinium groups permit the formation of structures in which the sizes of the cations and the separations of the positive charges can be varied in a controlled way. Representative TCNQ salts of two series of cations of this type have already been studied at Nottingham: one in which the pyridinium groups are attached to the central nucleus by their 4-positions and the nitrogen atoms face outwards and are quaternized by further hydrocarbon groups (type I) and the second in which the nitrogen atoms of the two pyridinium ions face inwards and are directly attached to the central hydrocarbon nucleus (type II).


(I)


(II)

A number of structures of TCNQ salts of cations of type I have been reported but, so far, only two of cations of type II [(*a*) where *R* is $CH_2C_6H_4CH_2$ (Ashwell, Wallwork, Baker & Berthier, 1975) and (*b*) where *R* is $(CH_2)_3$ (Ashwell *et al.*, 1977)]. The present structure determination extends this type II series, having a cation in which *R* is $(CH_2)_4$.

Experimental. Black crystals from addition of aqueous solution (10 ml) of 1,1′-tetramethylenedipyridinium diiodide (0·2 g) to nearly-boiling acetonitrile solution (180 ml) of TCNQ (0·4 g), mixture allowed to cool slowly in a Dewar flask over 3 d. Hilger & Watts computer-controlled, four-circle diffractometer, 2700 unique *I* with $\theta_{max} = 25°$, Mo $K\alpha$, $\theta/2\theta$ scan, scintillation counter, no absorption correction (small crystal, maximum dimension 0·5 mm); D_m by flotation in chloroform–xylene; three-dimensional Patterson map,

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* Part XV: Rizkallah, Wallwork & Graja (1983).

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