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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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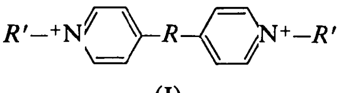
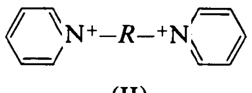
Abstract. $(\mathrm{DPB})^{2+}(\mathrm{TCNQ})_4^{2-}$, $M_r = 1031{\cdot}07$, triclinic, $P\bar{1}$, $a = 7{\cdot}75\ (1)$, $b = 13{\cdot}21\ (2)$, $c = 15{\cdot}49\ (5)$ Å, $\alpha = 101{\cdot}84\ (3)$, $\beta = 122{\cdot}39\ (2)$, $\gamma = 87{\cdot}64\ (4)°$, $U = 1306\ (10)$ Å^3, $Z = 1$, $D_m = 1{\cdot}30\ (1)$, $D_c = 1{\cdot}31$ 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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block-diagonal least squares, 1489 significant intensities $I > 3\sigma(I)$, anisotropic, H from Fourier difference synthesis, isotropic; $1/w = 1 + [(|F_o| - 15{\cdot}8)/11]^2$, $|F_o|$ 0·931 times absolute scale; scattering factors from *International Tables for X-ray Crystallography* (1974); final $R = 0{\cdot}055$; *CRYSTALS* (Carruthers & Rollett, 1975).

Table 1. *Final fractional atomic coordinates* ($\times 10^4$, $\times 10^3$ *for* H) *and isotropic or equivalent isotropic thermal parameters* (Å^2 $\times 10^3$, $\times 10^2$ *for* H)

The standard deviations in parentheses are in units of the least significant digit. $U_{eq} = \frac{1}{3}\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j$.

	x	y	z	U_{eq} or U_{iso}
C(1)	2665 (9)	1227 (5)	1122 (5)	42 (4)
C(2)	795 (10)	1274 (5)	173 (5)	46 (4)
C(3)	757 (10)	1298 (5)	−698 (6)	46 (4)
C(4)	2609 (9)	1275 (5)	−695 (5)	42 (4)
C(5)	4482 (10)	1247 (5)	258 (5)	44 (4)
C(6)	4516 (10)	1204 (5)	1132 (6)	43 (4)
C(7)	2701 (9)	1152 (5)	2020 (5)	44 (4)
C(8)	4549 (11)	1053 (5)	2957 (6)	52 (5)
C(9)	904 (12)	1195 (5)	2069 (5)	56 (4)
C(10)	2552 (9)	1294 (5)	−1613 (5)	43 (4)
C(11)	712 (12)	1291 (6)	−2572 (6)	58 (5)
C(12)	4386 (11)	1295 (5)	−1630 (5)	49 (4)
N(1)	6017 (10)	952 (5)	3705 (5)	75 (4)
N(2)	−507 (10)	1240 (5)	2118 (5)	82 (4)
N(3)	−764 (10)	1289 (6)	−3369 (6)	87 (4)
N(4)	5825 (9)	1309 (5)	−1640 (5)	65 (4)
C(13)	3317 (10)	3688 (5)	499 (5)	46 (4)
C(14)	1398 (10)	3788 (5)	−421 (5)	45 (4)
C(15)	1299 (11)	3821 (5)	−1311 (6)	48 (4)
C(16)	3048 (10)	3778 (5)	−1376 (5)	44 (4)
C(17)	4952 (10)	3690 (5)	−460 (6)	45 (4)
C(18)	5102 (10)	3641 (5)	441 (6)	42 (4)
C(19)	3464 (9)	3652 (5)	1430 (5)	46 (4)
C(20)	5329 (11)	3592 (5)	2359 (6)	50 (4)
C(21)	1691 (12)	3710 (5)	1493 (5)	55 (5)
C(22)	2925 (10)	3838 (6)	−2293 (6)	55 (4)
C(23)	1030 (13)	3950 (6)	−3204 (6)	65 (5)
C(24)	4657 (12)	3805 (5)	−2375 (6)	56 (5)
N(5)	6845 (10)	3554 (5)	3104 (5)	69 (4)
N(6)	289 (10)	3742 (5)	1563 (5)	75 (4)
N(7)	−510 (11)	4059 (7)	−3920 (6)	103 (5)
N(8)	6075 (10)	3781 (5)	−2428 (5)	73 (4)
C(25)	4709 (13)	2143 (6)	5305 (6)	64 (5)
C(26)	4197 (14)	1392 (7)	5638 (7)	73 (5)
C(27)	2211 (16)	1304 (8)	5385 (8)	84 (7)
C(28)	845 (14)	1964 (9)	4853 (8)	90 (6)
C(29)	1412 (12)	2712 (8)	4523 (7)	71 (5)
C(30)	4015 (15)	3570 (7)	4424 (7)	68 (6)
C(31)	4685 (14)	4600 (6)	5197 (6)	62 (5)
N(9)	3350 (9)	2776 (4)	4764 (4)	57 (3)
H(1)	−47 (10)	133 (5)	20 (5)	3 (2)
H(2)	−52 (9)	139 (4)	−134 (4)	0 (2)
H(3)	580 (9)	125 (4)	34 (4)	0 (2)
H(4)	573 (10)	114 (5)	171 (5)	3 (2)
H(5)	32 (11)	391 (5)	−31 (5)	4 (2)
H(6)	7 (10)	388 (4)	−187 (5)	1 (2)
H(7)	620 (9)	370 (4)	−41 (4)	1 (2)
H(8)	645 (9)	366 (4)	111 (4)	1 (2)
H(9)	603 (10)	229 (5)	550 (5)	2 (2)
H(10)	539 (13)	95 (7)	608 (7)	9 (3)
H(11)	194 (12)	75 (6)	567 (6)	6 (3)
H(12)	−72 (13)	191 (6)	446 (6)	7 (3)
H(13)	42 (12)	320 (6)	402 (6)	6 (3)
H(14)	251 (12)	364 (6)	367 (6)	6 (2)
H(15)	448 (13)	336 (7)	399 (7)	7 (3)
H(16)	593 (7)	452 (4)	596 (4)	0 (1)
H(17)	340 (12)	471 (6)	514 (6)	6 (3)

Discussion. The final positional and isotropic thermal parameters, together with their e.s.d.'s, are listed in Table 1.* Bond lengths and angles are given in Fig. 1. Two views of the structure are shown in Fig. 2.

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* Lists of structure factors, anisotropic thermal parameters, details of least-squares molecular planes and Table 3 and Fig. 3 have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38131 (24 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

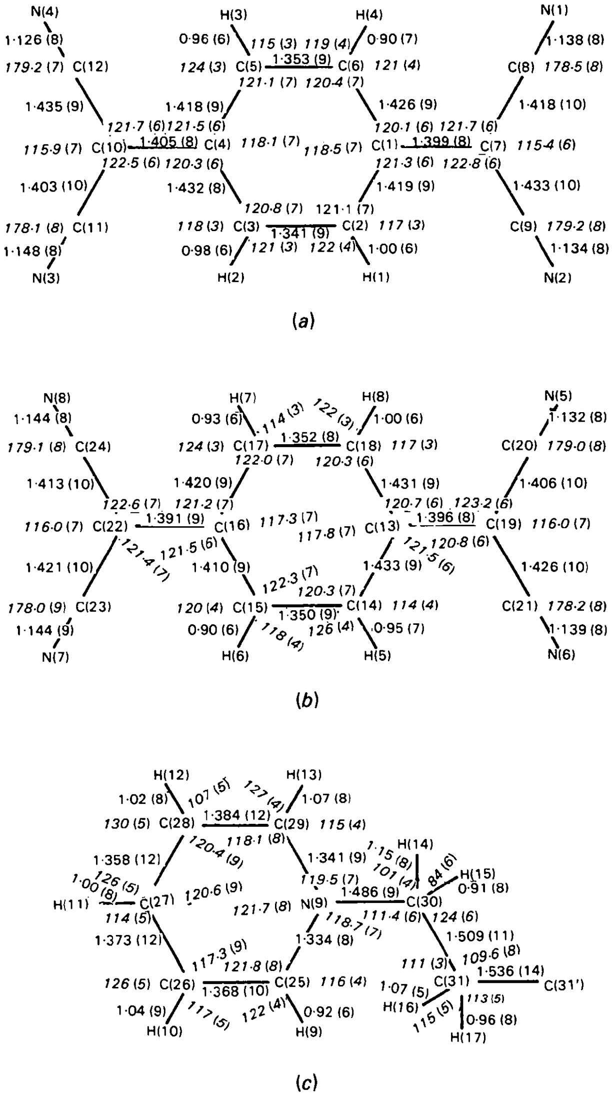

Fig. 1. Bond lengths (Å) and angles (°): (*a*) TCNQ(*A*), (*b*) TCNQ(*B*) and (*c*) the asymmetric half of the (DPB)$^{2+}$ cation. Figures in parentheses indicate e.s.d.'s. Further angles, not shown in (*c*), are: C(31)–C(30)–H(14) = 109 (4), N(9)–C(30)–H(15) = 119 (6), C(31')–C(31)–H(16) = 111 (3) and C(30)–C(31)–H(17) = 97 (5).

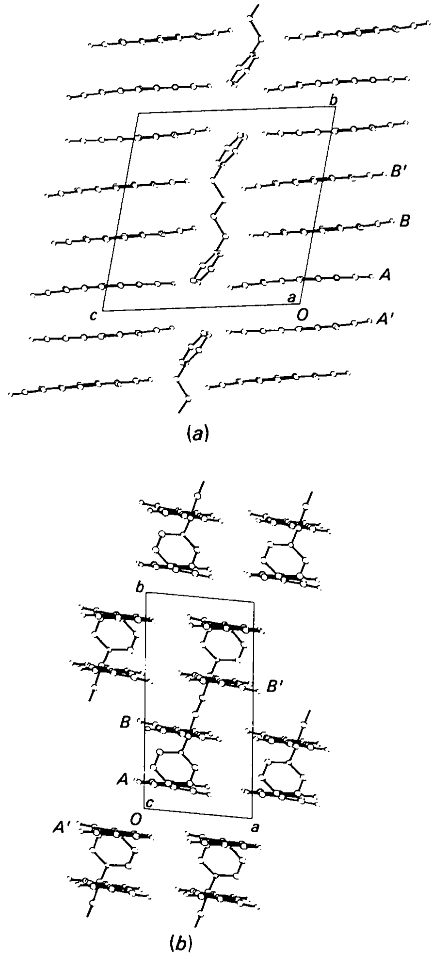

Fig. 2. Projections of the structure along (*a*) the *a* axis and (*b*) the *c* axis.

Table 2. *Intermolecular contacts* (*in* Å) *less than* 3·4 Å

(Standard deviations are all about 0·009 Å.)

TCNQ(*A*) to TCNQ(*B*) within the dimer		Other TCNQ–TCNQ sideways between stacks		TCNQ–cation	
C(1^{i})–C(19^{i})	3·177	C(2^{i})–N(4^{ii})	3·343	N(1^{i})–C(25^{i})	3·257
C(1^{i})–C(20^{i})	3·397	C(3^{i})–N(4^{ii})	3·282	N(1^{i})–C(28^{iv})	3·356
C(1^{i})–C(21^{i})	3·339	C(5^{i})–C(5^{iii})	3·395	N(2^{i})–C(29^{i})	3·347
C(2^{i})–C(21^{i})	3·315	C(5^{i})–N(2^{iv})	3·378	N(3^{i})–C(25^{vi})	3·273
C(3^{i})–C(13^{i})	3·393	C(6^{i})–N(2^{iv})	3·301	N(3^{i})–C(26^{vi})	3·354
C(3^{i})–C(14^{i})	3·252	C(8^{i})–N(4^{iii})	3·288	N(5^{i})–C(29^{iv})	3·308
C(4^{i})–C(13^{i})	3·244	C(19^{i})–N(8^{vii})	3·773	N(7^{i})–C(31^{viii})	3·313
C(4^{i})–C(18^{i})	3·346			N(8^{i})–C(25^{ix})	3·350
C(5^{i})–C(13^{i})	3·314				
C(5^{i})–C(18^{i})	3·151				
C(6^{i})–C(19^{i})	3·304				
C(6^{i})–C(20^{i})	3·223				
C(10^{i})–C(16^{i})	3·243				
C(10^{i})–C(17^{i})	3·357				
C(12^{i})–C(17^{i})	3·224				

Symmetry code
(i) x,y,z;
(ii) $x-1,y,z$;
(iii) $1-x,-y,-z$;
(iv) $1+x,y,z$;
(v) $1-x,-y,1-z$;
(vi) $x-1,y,z-1$;
(vii) $1-x,1-y,-z$;
(viii) $x-1,y,z-1$;
(ix) $x,y,z-1$

The TCNQ moieties are stacked in the (001) plane, roughly along [110], the diagonal between $+x$ and $+y$, and the cation is elongated along a line parallel to this at $z=0\cdot5$. However, there is only good overlap between TCNQ(*A*) and TCNQ(*B*), as shown in Fig. 3,* and the perpendicular separation between TCNQ's is $AB=$ 3·19 (2) [3·14 (1)], $AA'=3\cdot21$ (2) [3·28 (1)], $BB'=$ 3·32 (2) [3·38 (1)] Å, so the four TCNQ's associated with each cation occur as the dimers *AB* and *A'B'*, with slight interaction between pairs of dimers at *B* and *B'*. The separations in square brackets are between the planes defined by the quinonoid groups of the TCNQ's only and they differ from the values for the whole molecules because of slight out-of-plane distortions of the $C(CN)_2$ groups. The dihedral angle between the planes of molecules *A* and *B* is 2·0 (4) [2·6 (4)]°. Intermolecular contacts less than 3·400 Å between non-hydrogen atoms are in Table 2; there are a number of short contacts within dimers and sideways between TCNQ stacks, and also between TCNQ's and the cation. The shortest contacts between non-hydrogen atoms of centrosymmetrically related pairs of TCNQ's are 3·402 (9) Å between C(3) and C(9′) and 3·469 (9) Å between C(2) and C(2′), both from *A* to *A'*, and 3·451 (9) Å between C(17) and C(17′), from *B* to *B'*.

The averaged lengths of chemically similar bonds are compared in Table 3* with typical dimensions for TCNQ^{0}, TCNQ^{-} and TCNQ$^{1/2-}$ (Ashwell, Eley, Wallwork & Willis, 1975). The dimensions of *A* and *B* do not differ significantly from each other or from TCNQ$^{1/2-}$ suggesting that the charge is equally shared with 1/2– on each TCNQ. By the method of Flandrois & Chasseau (1977), the charges on *A* and *B* appear to be 0·68 and 0·58 e, respectively. It is unlikely, however, that there is a total of more than 1 e on the two TCNQ's and these values are probably both approximations to 0·5, being slightly greater because of the only moderate accuracy of the bond lengths.

The dimensions of the cation agree well with corresponding dimensions in the related 1,1′-(*p*-phenylenedimethylene)dipyridinium cation (Ashwell *et al.*, 1975). The plane of the pyridine ring makes dihedral angles of 132·5 (4) [132·1 (4)°] and 133·3 (4) [133·3 (4)°] with the planes of TCNQ's *A* and *B* (or their quinonoid rings).

The fact that the TCNQ moieties occur in pairs which are stacked in an interrupted way along **b** but have moderately close sideways contacts along **a** is consistent with the anisotropy of electrical conductivity (Drew, Eley, Willis & Waclawek, 1982) in which σ_b is slightly larger than σ_a, and σ_c (across the sheets of cations) is about ten times smaller.

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* See deposition footnote.

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Distortion of the Hexamethylenetetramine Cage System by Protonation: X-ray Structure of 1,3,5,7-Tetraazaadamantan-1-ium Bromide,* $[(CH_2)_6N_4H]Br$

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Abstract. $M_r = 221{\cdot}11$, rhombohedral, $R3m$, $a = 8{\cdot}986\ (1)$, $c = 9{\cdot}276\ (1)$ Å (hexagonal axes, obverse setting), $U = 648{\cdot}7$ Å^3, $Z = 3$, $D_m = 1{\cdot}704$, $D_x = 1{\cdot}698$ g cm^{-3}, μ(Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å) = $46{\cdot}5$ cm^{-1}. Final $R = 0{\cdot}016$ for 210 unique data. The protonated hexamethylenetetramine cage retains its idealized $3m$ symmetry in the crystal, and the three equivalent C—N bonds involving the quaternary N atom are significantly longer than the remaining C—N bonds in the saturated heterocycle. These structural features provide an insight into the mechanism of acid hydrolysis of hexamethylenetetramine in aqueous solution.

Introduction. Crystallographic studies (Hanic & Šubrtová, 1969; Mak, Ladd & Povey, 1979, and references cited therein; Hon, Mak & Trotter, 1982, and references cited therein; Shao, Wang, Zheng & Tang, 1982) have shown that quaternization of one N atom of hexamethylenetetramine $[(CH_2)_6N_4]$, as in adduct and salt formation, profoundly distorts its highly symmetric cage structure. In all cases the endocyclic C—N$_{\text{quaternary}}$ bonds and adjacent C—N$_{\text{tertiary}}$ bonds are significantly lengthened and shortened, respectively, relative to the remaining bonds in the hexamethylenetetramine cage system. These results have an important bearing on the mechanisms of the Delépine and Sommelet reactions in organic synthesis (Blažević, Kolbah, Belin, Šunjić & Kajfež, 1979). As hexamethylenetetramine generally behaves as a monoacidic base and readily undergoes various acid-catalyzed fragmentation processes (Walker, 1964; Blažević *et al.*, 1979), we decided to investigate the effect of protonation on its molecular geometry through an X-ray analysis of 1,3,5,7-tetraazaadamantan-1-ium bromide, $[(CH_2)_6N_4H]Br$.

Experimental. Prepared by mixing an aqueous solution of $(CH_2)_6N_4$ and 47% HBr in 1:1 molar ratio, slow evaporation in air at room temperature, D_m measured by flotation in *n*-hexane/CCl$_4$, transparent prisms elongated along **c**, preliminary Weissenberg and precession photographs indicated rhombohedral symmetry, single crystal, approximately $0{\cdot}12 \times 0{\cdot}20 \times 0{\cdot}25$ mm, least squares, 20 high-angle reflections, Nicolet $R3m$ automated four-circle diffractometer, graphite-monochromatized Mo $K\alpha$, 565 total, 210 unique with $I > 1{\cdot}5\sigma(I)$, $0° < 2\theta < 55°$, ω–2θ scan technique, variable scan speeds between 2·5 and 8° min^{-1}, no absorption correction.

Symmetry considerations show that both the $[(CH_2)_6N_4H]^+$ and Br^- ions are located in sites of $3m$ symmetry. With the Br atom arbitrarily fixed at the origin, trial coordinates for the two C and two N atoms were deduced from the known molecular dimensions of $(CH_2)_6N_4$ (Becka & Cruickshank, 1963) and a reasonable estimate of the N—H···Br ionic separation. These five atoms were refined anisotropically to $R = 0{\cdot}027$, and the highest peaks in the resulting difference Fourier map corresponded to H atoms of the methylene groups. In subsequent calculations, the methylene H atoms were generated on the basis of sp^3 hybridization of their respective C atoms, and were allowed to ride on them with U_{iso} fixed at $0{\cdot}05$ Å^2. $R_w = 0{\cdot}021$, $S = 0{\cdot}840$; maximum parameter shift to error ratio in final cycle was $-0{\cdot}042$, average ratio was $0{\cdot}013$, final difference

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* Adamantane is tricyclo[3.3.1.1^{3,7}]decane.

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