Crystal Structure of [N,N′-di(n-propyl)-4,4′-bipyridinium]$^{2+}$ (7,7,8,8-Tetracyano-p-quinodimethanide)$_4^{2-}$

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The 4:1 complex salt formed between 7,7,8,8-tetracyano-p-quinodimethane (TCNQ) and the N,N′-di(n-propyl)-4,4′-bipyridinium dication (DPrBP) is monoclinic, space group $P2_1/c$, with $a = 13.334(1)$, $b = 25.954(3)$, $c = 7.877(1)$ Å, $\beta = 93.66(1)°$. The structure was solved by the Patterson method and refined to $R = 0.070$ for 3277 unique reflections. The TCNQ moieties stack plane-to-plane, in stoichiometric groups of four, with a favourable exocyclic bond to quinonoid ring overlap of adjacent molecules and short interplanar spacings of 3.20 and 3.23 Å between TCNQ(A)-TCNQ(A′) and TCNQ(A)-TCNQ(B) respectively. TCNQ(A) makes the closet contact to the dication and the charge is partially localised on this molecule.

Introduction

The mixed-valent radical anion salts and charge transfer complexes of TCNQ have been actively investigated for a quarter century and since 1960 approximately 3000 papers have been published on the versatile chemistry of TCNQ and on the electrical, magnetic, structural and spectral properties of its many radical ion salts and charge transfer complexes. Of particular interest to us are the TCNQ salts of diquaternised 4,4′-bipyridyl and 1,*n*-bis-(4-pyridyl)alkane. In these salts the TCNQ's stack, plane-to-plane, in a direction parallel to the length of the cation, either in columns or in stoichiometric groups [1], and the stoichiometry may be altered by varying the cation length [2]. By increasing the size of the quaternary groups and the bridge between the pyridinium rings the maximum stoichiometry obtainable for a particular cation may be progressively increased from 1:2 as in (4,4′-bipyridinium)$^{2+}$-(TCNQ)$_2^{2-}$ [3] to 1:5 as in [1,3-bis(N-propyl-4-pyridinium)propane]$^{2+}$ (TCNQ)$_5^{2-}$ [4].

TCNQ salts show a wide range of physical properties which may be related *in part* to the mean charge on the TCNQ lattice sites and *in part* to the TCNQ stacking characteristics and to the interstack coupling distances. In order to elucidate the relation between electrical conductivity and the structural features we have determined the structures of 25 bipyridinium TCNQ salts. The cations differ both in the quaternary group and in the group linking the pyridinium rings and a full analysis of the electrical and structural properties of this series shall appear separately [5]. The title complex, [N,N′-di(n-propyl)-4,4′-bipyridinium]$^{2+}$ (TCNQ)$_4^{2-}$ DPrBP-TCNQ$_4$, is a member of the series and in this paper the crystal structure is reported. The ac and dc conductivity together with some preliminary structural data have been reported previously [6].

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Experimental

Crystal data. $(C_{16}H_{22}N_2)^{2+}(C_{12}H_4N_4)_4^{2-}$, DPrBP-TCNQ$_4^{2-}$, $M_r = 1059.1$. Monoclinic, $a = 13.334(1)$, $b = 25.954(3)$, $c = 7.877(1)$ Å, $\beta = 93.66(1)°$, $U = 2720.3$ Å^3, $\varrho_m = 1.29(1)$ Mg m^{-3}, $Z = 2$, $\varrho_c = 1.293$ Mg m^{-3}, $F(000) = 1096$. μ(MoKα, $\lambda = 0.71069$ Å) = 0.089 mm^{-1}. Space group $P2_1/c$.

The space group and unit cell parameters were obtained from oscillation and Weissenberg photographs using CuKα radiation. The parameters were

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Table 1. Final positional and thermal parameters (all $\times 10^4$). The figures in parentheses indicate standard deviations. Temperature factor = $\exp[-2\pi^2(h^2 U_{11} a^{*2} + k^2 U_{22} b^{*2} + l^2 U_{33} c^{*2} + hk U_{12} a^* b^* + hl U_{13} a^* c^* + kl U_{23} b^* c^*)]$

	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	1357(2)	614(1)	−1969(3)	430(15)	403(14)	299(13)	14(12)	−32(11)	−0(11)
C(2)	391(2)	518(1)	−2829(3)	439(15)	458(16)	266(13)	11(12)	−33(11)	−11(11)
C(3)	−455(2)	509(1)	−1977(3)	389(15)	440(15)	309(14)	−19(12)	−87(11)	−33(11)
C(4)	−423(2)	601(1)	−175(3)	401(14)	353(13)	334(14)	15(12)	−44(11)	2(11)
C(5)	538(2)	698(1)	678(3)	422(15)	436(15)	253(13)	−8(12)	−62(11)	−22(11)
C(6)	1391(2)	706(1)	−182(3)	367(14)	474(17)	318(14)	1(12)	−61(11)	−12(11)
C(7)	2231(2)	626(1)	−2866(3)	435(15)	497(16)	309(14)	−2(13)	−32(11)	7(12)
C(8)	3202(2)	714(1)	−2056(4)	473(17)	672(21)	396(16)	28(15)	40(13)	−9(14)
C(9)	2221(2)	543(1)	−4651(4)	474(17)	611(20)	411(16)	26(14)	27(13)	−16(14)
C(10)	−1301(2)	587(1)	730(3)	405(15)	400(14)	304(13)	32(12)	−36(11)	−21(11)
C(11)	−1281(2)	681(1)	2510(3)	435(16)	553(18)	351(13)	27(13)	−5(12)	−40(13)
C(12)	−2262(2)	481(1)	−73(3)	433(16)	486(17)	366(15)	35(13)	−22(12)	−8(12)
C(13)	2299(2)	1845(1)	−3920(4)	462(16)	459(17)	449(16)	−43(13)	−28(13)	0(13)
C(14)	1350(2)	1759(1)	−4847(4)	484(17)	548(18)	390(15)	−19(14)	−32(13)	9(13)
C(15)	491(2)	1743(1)	−4026(4)	479(17)	525(17)	383(15)	−14(14)	−69(12)	−1(13)
C(16)	501(2)	1817(1)	−2224(4)	448(16)	383(15)	402(15)	2(12)	−35(12)	−19(12)
C(17)	1446(2)	1905(1)	−1310(4)	504(17)	482(16)	345(14)	−52(13)	−17(12)	−34(12)
C(18)	2303(2)	1915(1)	−2114(4)	474(16)	491(17)	447(17)	−89(14)	−47(13)	−35(13)
C(19)	3187(2)	1868(1)	−4767(4)	510(18)	555(19)	542(19)	−56(15)	51(14)	19(15)
C(20)	4130(3)	1961(2)	−3859(5)	471(19)	844(27)	749(24)	−149(18)	130(17)	2(20)
C(21)	3197(3)	1814(1)	−6556(5)	569(21)	721(24)	589(20)	−29(17)	155(16)	18(18)
C(22)	−385(2)	1800(1)	−1386(4)	443(16)	421(15)	412(15)	5(12)	−38(12)	−16(12)
C(23)	−398(2)	1891(1)	414(4)	471(17)	486(17)	503(17)	−5(14)	8(13)	−59(14)
C(24)	−1333(2)	1695(1)	−2268(4)	448(17)	542(19)	540(19)	68(14)	15(14)	−94(15)
C(25)	5115(3)	827(2)	2250(5)	974(30)	710(25)	596(23)	−214(22)	−232(21)	100(19)
C(26)	4836(3)	373(1)	2955(4)	755(24)	670(22)	552(21)	−157(19)	−255(18)	4(17)
C(27)	5161(2)	240(1)	4600(4)	426(16)	529(17)	448(16)	1(13)	−93(12)	−65(13)
C(28)	5804(3)	586(2)	5457(4)	832(26)	800(26)	472(19)	−314(21)	−188(18)	−2(18)
C(29)	6066(3)	1034(2)	4717(5)	882(29)	841(28)	665(25)	−400(23)	−139(21)	−50(21)
C(30)	5907(4)	1687(2)	2364(7)	1139(39)	661(27)	1230(41)	−182(26)	401(32)	18(27)
C(31)	6727(6)	1700(2)	1422(10)	2028(71)	834(37)	2026(71)	356(41)	1336(61)	325(42)
C(32)	6861(4)	2222(2)	563(6)	1235(40)	668(27)	979(33)	132(26)	494(29)	162(24)
N(1)	2243(2)	485(1)	−6089(4)	712(20)	1081(27)	402(15)	38(18)	32(14)	−95(16)
N(2)	3992(2)	787(2)	−1472(4)	450(16)	1226(30)	653(20)	−27(17)	−67(14)	−63(19)
N(3)	−1295(2)	753(1)	3939(3)	705(20)	924(24)	386(15)	83(17)	1(13)	−79(14)
N(4)	−3053(2)	396(1)	−648(4)	485(16)	822(21)	548(16)	−11(14)	−94(13)	−54(15)
N(5)	3222(3)	1775(2)	−8009(4)	762(23)	1241(32)	620(20)	−20(21)	172(16)	−26(20)
N(6)	4889(3)	2032(2)	−3161(5)	559(21)	1459(39)	1085(31)	−272(22)	−10(19)	57(27)
N(7)	−409(2)	1962(1)	1843(4)	759(21)	799(22)	522(17)	−3(17)	41(14)	−133(15)
N(8)	−2092(2)	1607(1)	−2956(4)	477(17)	964(25)	854(23)	79(16)	−106(15)	−279(19)
N(9)	5709(2)	1157(1)	3142(4)	827(22)	582(18)	659(19)	−131(16)	24(16)	−27(15)

subsequently refined on a Hilger & Watts four-circle diffractometer. Intensities were collected from a crystal $0.2 \times 0.3 \times 0.6$ mm^3 with a $\Theta/2\Theta$ scan, a scintillation counter and MoKα radiation. The intensities were corrected for Lorentz and polarisation factors but not for absorption. The structure was solved from a three-dimensional Patterson synthesis and refined by a block-diagonal least-squares method using 3277 reflections with $I > 3\sigma(I)$. Location of the propyl hydrogens was made impossible by the partial rotation of the alkyl carbon atoms. Scattering factors were taken from the International Tables of X-ray Crystallography [7] and the weighting scheme $w^{-1} = 1 + [(|F_0| - B)/A]^2$ where $A = 21.0$ and $B = 5.0$ adopted. Refinement using anisotropic thermal parameters for the non-hydrogen atoms gave the final $R = 0.070$. The final atomic coordinates of the non-hydrogen atoms are listed in Table 1 and the results of the least-squares planes calculations are in Table 2.

Results and Discussion

The structure, projected along a, is shown in Figure 1. The TCNQ's stack in stoichiometric

Table 2. Details of molecular planes. Equations to the planes where x, y and z are fractional atomic coordinates

(i) $-1.5417\,x + 25.4252\,y - 1.2324\,z - 1.6012 = 0$,
(ii) $-1.5429\,x + 25.5146\,y - 1.0583\,z - 4.7957 = 0$,
(iii) $-10.9102\,x + 11.6735\,y + 3.2262\,z + 3.8810 = 0$.

Distances from the planes (in Å).

plane (i)		plane (ii)		plane (iii)	
C(1)	−0.007	C(13)	−0.028	C(25)	−0.008
C(2)	0.005	C(14)	−0.003	C(26)	−0.007
C(3)	0.007	C(15)	0.003	C(27)	0.014
C(4)	0.013	C(16)	−0.002	C(28)	−0.007
C(5)	0.008	C(17)	−0.019	C(29)	−0.008
C(6)	0.003	C(18)	−0.041	N(9)	0.016
C(7)	0.000	C(19)	−0.016		
C(8)	−0.026	C(20)	−0.022		
C(9)	0.011	C(21)	0.032		
C(10)	0.002	C(22)	0.002		
C(11)	0.018	C(23)	0.047		
C(12)	−0.021	C(24)	−0.026		
N(1)	0.037	N(5)	0.084		
N(2)	−0.034	N(6)	−0.031		
N(3)	0.027	N(7)	0.078		
N(4)	−0.043	N(8)	−0.059		

groups of four with a favourable exocyclic bond to quinonoid ring overlap of adjacent molecules. The TCNQ's are not quite planar. The $-C(CN)_2$ groups are rotated slightly out of the molecular plane with maximum deviations of 0.043 Å for TCNQ(A) and 0.084 Å for TCNQ(B). The mean perpendicular spacing between the molecular planes is 3.23 Å whereas for the symmetry related planes TCNQ(A)-TCNQ(A′) the spacing is 3.20 Å. If only the quinonoid groups are considered then the mean perpendicular spacings are 3.22 Å each, the differences between the molecular and quinonoid interplanar spacings being caused by the $-C(CN)_2$ out-of-plane distortions which result in slightly different tilts for the mean planes.

Between molecules TCNQ(B)-TCNQ(B′) in adjacent tetrads there is no direct plane-to-plane overlap and all intermolecular contacts are greater than the sum of the van der Waals radii, the closest being C(16)−N(7′) = 3.456(4) Å. The dihedral angle between these planes is 21.1° and this unusual tilt is caused *in part* by the "zig-zag" packing arrangement of the dications and *in part* by the strong electrostatic interaction between the TCNQ and DPrBP moieties. The arrangement gives rise to only weakly interacting TCNQ tetrads, in sheets parallel to the *bc* plane, and interleaved along *a* by the dications.

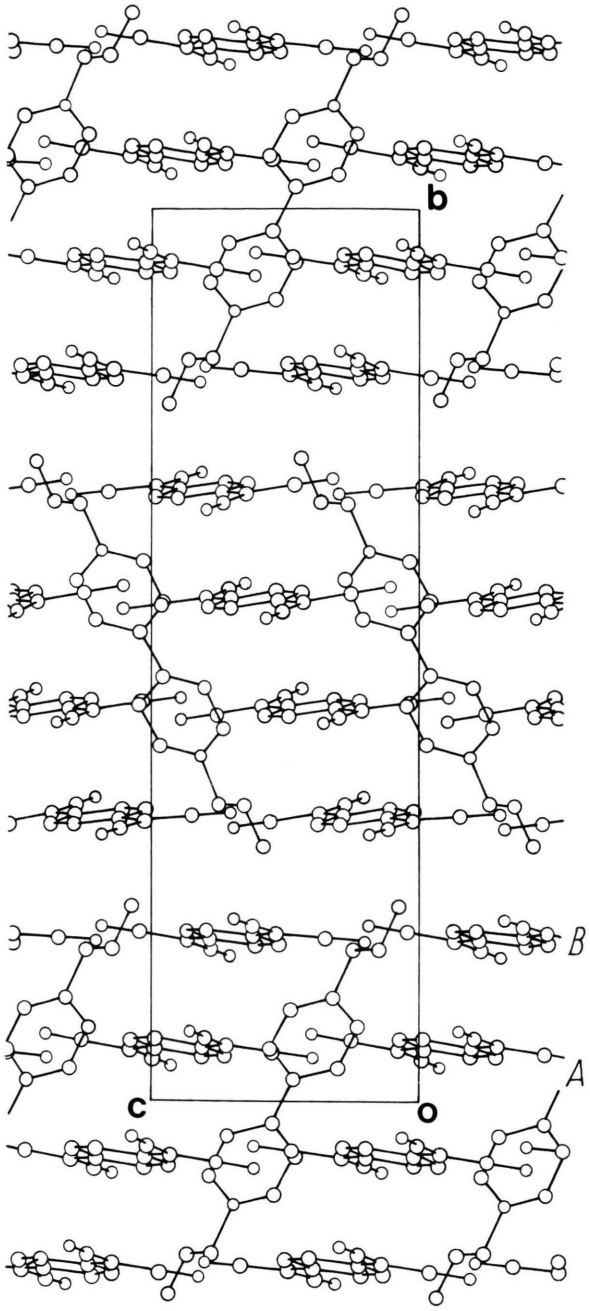


Fig. 1. Projection along *a* showing the "zig-zag" arrangement of cations and the isolated TCNQ tetrads.

The dimensions of the cation, listed in Table 3, are in close agreement with values reported previously for other 4,4′-bipyridinium salts of TCNQ [8–10], the halides [11, 12] and chlorometallate anions [13, 14]. The C(30)−C(31) distance of the

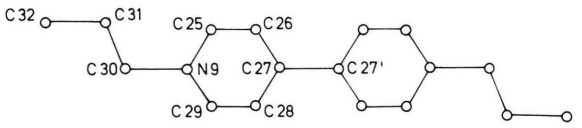
Table 3. Bond distances (Å) and angles (°) of the DPrBP dication.

(a) Bond distances (e.s.d.'s are 0.006 Å)

C(25)–N(9)	1.335	C(28)–C(29)	1.356
C(25)–C(26)	1.364	C(29)–N(9)	1.339
C(26)–C(27)	1.384	C(30)–N(9)	1.536
C(27)–C(27′)	1.472	C(30)–C(31)	1.360
C(27)–C(28)	1.387	C(31)–C(32)	1.530

(b) Bond angles (e.s.d.'s are 0.4°)

C(26)–C(25)–N(9)	120.5	C(28)–C(29)–N(9)	121.1
C(25)–C(26)–C(27)	121.3	C(31)–C(30)–N(9)	113.9
C(26)–C(27)–C(27′)	122.0	C(30)–C(31)–C(32)	112.6
C(26)–C(27)–C(28)	116.2	C(25)–N(9)–C(29)	119.9
C(28)–C(27)–C(27′)	121.9	C(25)–N(9)–C(30)	118.4
C(27)–C(28)–C(29)	120.9	C(29)–N(9)–C(30)	121.6



propyl quaternary group is shorter than expected and is probably due to incomplete refinement resulting from some freedom of rotation about the carbon-carbon single bonds. The pyridinium rings are coplanar and the maximum out of plane distance is 0.016 Å for the quaternary nitrogen. The dihedral angles between the plane through the dication and the planes through TCNQ(A) and TCNQ(B) are 61.5 and 60.9° respectively.

The dimensions of the crystallographically independent types of TCNQ moiety and the mean lengths of the chemically similar bonds are listed in Tables 4 and 5. The mean lengths are intermediate between those of neutral TCNQ [15] and those of the radical anion [16–18], and both molecules show some quinonoid character. The average length of

Table 4. Bond distances (Å) and angles (°) of TCNQ(A) and TCNQ(B).

(a) Bond distances (e.s.d.'s are 0.004 Å)

C(1)–C(2)	1.438	C(13)–C(14)	1.437
C(1)–C(6)	1.426	C(13)–C(18)	1.434
C(1)–C(7)	1.401	C(13)–C(19)	1.397
C(2)–C(3)	1.349	C(14)–C(15)	1.351
C(3)–C(4)	1.437	C(15)–C(16)	1.432
C(4)–C(5)	1.431	C(16)–C(17)	1.429
C(4)–C(10)	1.409	C(16)–C(22)	1.390
C(5)–C(6)	1.361	C(17)–C(18)	1.342
C(7)–C(8)	1.425	C(19)–C(20)	1.427
C(7)–C(9)	1.422	C(19)–C(21)	1.417
C(8)–N(2)	1.138	C(20)–N(6)	1.136
C(9)–N(1)	1.145	C(21)–N(5)	1.152
C(10)–C(11)	1.422	C(22)–C(23)	1.439
C(10)–C(12)	1.419	C(22)–C(24)	1.429
C(11)–N(3)	1.142	C(23)–N(7)	1.142
C(12)–N(4)	1.142	C(24)–N(8)	1.140

(b) Bond angles (e.s.d.'s are 0.3°)

C(2)–C(1)–C(6)	117.7	C(14)–C(13)–C(18)	118.1
C(2)–C(1)–C(7)	121.0	C(14)–C(13)–C(19)	120.6
C(6)–C(1)–C(7)	121.3	C(18)–C(13)–C(19)	121.3
C(1)–C(2)–C(3)	121.4	C(13)–C(14)–C(15)	120.5
C(2)–C(3)–C(4)	121.0	C(14)–C(15)–C(16)	121.1
C(3)–C(4)–C(5)	117.5	C(15)–C(16)–C(17)	118.2
C(3)–C(4)–C(10)	121.5	C(15)–C(16)–C(22)	120.8
C(5)–C(4)–C(10)	121.0	C(17)–C(16)–C(22)	121.0
C(4)–C(5)–C(6)	121.4	C(16)–C(17)–C(18)	121.0
C(1)–C(6)–C(5)	120.9	C(13)–C(18)–C(17)	121.1
C(1)–C(7)–C(8)	122.6	C(13)–C(19)–C(20)	121.0
C(1)–C(7)–C(9)	122.7	C(13)–C(19)–C(21)	122.2
C(8)–C(7)–C(9)	114.7	C(20)–C(19)–C(21)	116.8
C(7)–C(8)–N(2)	177.2	C(19)–C(20)–N(6)	178.8
C(7)–C(9)–N(1)	177.7	C(19)–C(21)–N(5)	178.7
C(4)–C(10)–C(11)	122.0	C(16)–C(22)–C(23)	121.8
C(4)–C(10)–C(12)	122.4	C(16)–C(22)–C(24)	121.8
C(11)–C(10)–C(12)	115.6	C(23)–C(22)–C(24)	116.4
C(10)–C(11)–N(3)	177.9	C(22)–C(23)–N(7)	179.8
C(10)–C(12)–N(4)	176.9	C(22)–C(24)–N(8)	179.1

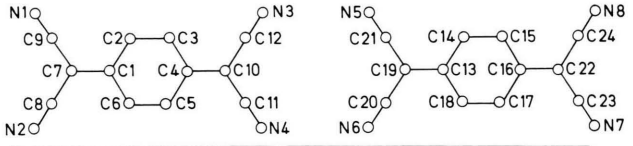


Table 5. Mean lengths of the chemically similar bonds of TCNQ(A) and TCNQ(B).

TCNQ(A)					
(a)	C(2)–C(3),	C(5)–C(6)			1.355 Å
(b)	C(1)–C(2),	C(1)–C(6),	C(3) –C(4),	C(4) –C(5)	1.433 Å
(c)	C(1)–C(7),	C(4)–C(10)			1.405 Å
(d)	C(7)–C(8),	C(7)–C(9),	C(10)–C(11),	C(10)–C(12)	1.422 Å
(e)	C(8)–N(2),	C(9)–N(1),	C(11)–N(3),	C(12)–N(4)	1.142 Å
TCNQ(B)					
(a)	C(14)–C(15),	C(17)–C(18)			1.346 Å
(b)	C(13)–C(14),	C(13)–C(18),	C(15)–C(16),	C(16)–C(17)	1.433 Å
(c)	C(13)–C(19),	C(16)–C(22)			1.394 Å
(d)	C(19)–C(20),	C(19)–C(21),	C(22)–C(23),	C(22)–C(24)	1.428 Å
(e)	C(20)–N(6),	C(21)–N(5),	C(23)–N(7),	C(24)–N(8)	1.142 Å

the exocyclic bond is slightly shorter and the adjacent bonds longer in TCNQ(B) which suggests that the charge may be partially localised on TCNQ(A). By applying the method of Flandrois and Chasseau [19] to the mean bond lengths of TCNQ(A) and TCNQ(B) the charges on each may be estimated as 0.65 e and 0.44 e, respectively. The method is sensitive to relatively minor changes in the averaged bond lengths but it may be noted that the result is consistent with the fact that TCNQ(A) also makes the closest contact with the dication. The closest non-hydrogen cation to TCNQ contacts are C(25)–N(2) = 3.207(5) Å for TCNQ(A) and C(29)–N(8) = 3.322(5) Å for TCNQ(B), the contacts being to the α-position of the pyridinium ring. Similar results have been obtained for the corresponding methyl, ethyl, benzyl and cyanophenyl quaternary analogues [10].

Acknowledgements

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