Crystal Structure and Properties of the 7,7,8,8-Tetracyano-*p*-quinodimethanide Salt of the 1,1′-Bis-(*p*-cyanophenyl)-4,4′-bipyridinium Dication

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The crystal structure of [1,1′-bis-(*p*-cyanophenyl)-4,4′-bipyridinium]$^{2+}$ (7,7,8,8-tetracyano-*p*-quinodimethanide)$_4^{2-}$, CPP–TCNQ$_4$, its electrical conductivity, and the properties of the TCNQ salts of five *para*-substituted dications are reported. CPP–TCNQ$_4$ is triclinic, space group $P\bar{1}$, with a = 7.558(5), b = 13.501(4), c = 15.155(4) Å, α = 102.08(2), β = 100.60(4), γ = 98.43(4)°, U = 1 458.5 Å^3, D_m = 1.36 Mg m^{-3}, Z = 1, D_c = 1.34 Mg m^{-3}. The structure was solved by direct methods and refined to a final R of 0.048 for 2 338 observed reflections. The radical anions stack, plane-to-plane, in columns parallel to b, the mean inter-TCNQ spacings being 3.28, 3.36, and 3.00 Å between TCNQ(A)–TCNQ(A′), TCNQ(A)–TCNQ(B), and TCNQ(B)–TCNQ(B′), respectively. Adjacent columns form sheets, parallel to (001), successive sheets being interleaved along c by the CPP dications. The electrical conductivity along b, the direction of stacking, varies as $\sigma = \sigma_0 \exp(-E_a/kT)$ where $\sigma_{300\ K}$ 0.1 S cm^{-1} and E_a 0.10 eV.

Our interest in CPP–TCNQ$_4$ and the TCNQ salts, in general, of diquaternised 4,4′-bipyridyl stems partly from the recently observed [1] high conductivity of the simple salt (4,4′-bipyridinium)$^{2+}$(TCNQ)$_2^{2-}$ and partly from the low temperature metallic properties [2] of the complex salt [1,2-bis-(1-ethyl-4-pyridinium)ethane]$^{2+}$(TCNQ)$_{4\frac{1}{2}}^{2-}$(H$_2$O), (DEPA)(TCNQ)$_{4\frac{1}{2}}$-(H$_2$O). In this salt, the TCNQs stack, in a plane-to-plane manner, in infinite columns, with a short uniform spacing and an exocyclic bond to ring overlap of adjacent molecules, these being prerequisites for high conductivity. (DEPA)(TCNQ)$_{4\frac{1}{2}}$-(H$_2$O) is the most highly conductive member of an isostructural series [2] of 12 salts, formed between TCNQ and diquaternised 1,2-bis-(4-pyridyl)ethylene, 1,2-bis-(4-pyridyl)-ethane, and 1,3-bis-(4-pyridyl)propane. These have moderate to high conductivities in the range 0.05—500 S cm^{-1} at 300 K. In this work, in order to obtain other highly conductive salts and also in an attempt to elucidate the relation between cation geometry and TCNQ stacking, the properties of six TCNQ complex salts of diquaternised 4,4′-bipyridyl have been investigated. In CPP–TCNQ$_4$, reported here, the TCNQ lattice is periodically distorted, there being three types of overlap and three non-uniform interplanar spacings repeated along the TCNQ chains. CPP–TCNQ$_4$ and its *para*-substituted congeners are small band gap semiconductors with $\sigma_{300\ K}$ 0.007—0.3 S cm^{-1}.

Experimental

Crystal Data.—(C$_{24}$H$_{16}$N$_4$)$^{2+}$(C$_{12}$H$_4$N$_4$)$_4^{2-}$, CPP–TCNQ$_4$, M_r = 1177.2. Triclinic, a = 7.558(5), b = 13.501(4), c = 15.155(4) Å, α = 102.08(2), β = 100.60(4), γ = 98.43(4)°, U = 1458.5 Å^3, D_m = 1.36 Mg m^{-3}, Z = 1, D_c = 1.34 Mg m^{-3}, F(000) = 604. μ(Mo-K_α, λ = 0.710 69 Å) = 0.049 mm^{-1}. Space group $P\bar{1}$.

Black needles and elongated plates of CPP–TCNQ$_4$ were obtained when a hot aqueous acetonitrile solution (200 cm^3) of 1,1′-bis-(*p*-cyanophenyl)-4,4′-bipyridinium di-iodide (0.3 g) and 7,7,8,8-tetracyano-*p*-quinodimethane (0.4 g) was allowed to cool slowly to room temperature. The electronic absorption spectrum of the crystals, dissolved in acetonitrile, showed maxima at 842, 824, 762, 745, 728, 679, 666, 436, 420, and 395 nm with A_{395}/A_{842} = 2.1 characteristic of a TCNQ$^-$: TCNQ ratio of 1 : 1 and a stoicheiometry of 1 : 4 (Found: C, 73.2; H, 2.9; N, 23.7. C$_{72}$H$_{32}$N$_{20}$ requires C, 73.45; H, 2.75; N, 23.8%).

The unit cell parameters were obtained initially from precession and Weissenberg photographs and were subsequently refined on an Enraf–Nonius CAD4 four-circle diffractometer. Intensities were collected, in the range $1.5° < \theta < 25.0°$, from a crystal of approximate dimensions 0.25 × 0.15 × 0.10 mm, using Mo-K_α radiation and of the 3 799 unique reflections measured 2 338 had significant counts [$I > 2\sigma(I)$]. Lorentz and polarisation factors were applied but no absorption correction was made.

Multisolution direct methods using SHELX [3] enabled the positions of all non-hydrogen atoms to be readily located. The hydrogens were included in positions calculated from the molecular geometry (C–H 1.08 Å). Common isotropic temperature factors were applied to the hydrogens and refined to final values of U = 0.080(4), 0.071(4), and 0.062(5) Å^2 for the cation, TCNQ(A), and TCNQ(B) respectively. Scattering factors were taken from ref. 4 and the weighting scheme $w = [\sigma^2(F_o) + 0.002\,35(F_o)^2]^{-1}$ adopted. Full matrix refinement with anisotropic temperature factors for the non-hydrogen atoms gave the final R = 0.048 and R_w = 0.053. The final difference map showed no peaks greater than 0.18 eÅ^{-3}. The final atomic co-ordinates are listed in Table 1 [5] and the results of the least-squares-planes calculations are in Table 2. Lists of structure factors, thermal parameters, and hydrogen atomic co-ordinates are in Supplementary Publication No. SUP 23718 (17 pp.).†

Results and Discussion

A general view of the structure of CPP–TCNQ$_4$ is shown in Figure 1. The TCNQs stack in a plane-to-plane manner, in columns parallel to b, with mean interplanar spacings of 3.28, 3.36, and 3.00 Å respectively between TCNQ(A)–TCNQ(A′),

† See Instructions for Authors in *J. Chem. Soc., Perkin Trans. 2*, 1983, Issue 1.

Table 1. Final fractional positional parameters ($\times 10^4$) and equivalent isotropic temperature factors ($\times 10^3$) with e.s.d.s in parentheses. The U_{eq} values were calculated from ref. 5

	x	y	z	U_{eq} (Å^2)
C(1)	5 215(4)	3 043(2)	−1 379(2)	41(2)
C(2)	3 376(4)	3 146(2)	−1 305(2)	42(2)
C(3)	3 015(4)	3 575(2)	−489(2)	42(2)
C(4)	4 420(4)	3 922(2)	343(2)	41(2)
C(5)	6 265(4)	3 816(2)	265(2)	44(2)
C(6)	6 631(4)	3 398(2)	−555(2)	46(2)
C(7)	5 581(4)	2 612(3)	−2 230(2)	45(2)
C(8)	7 407(5)	2 528(3)	−2 347(2)	55(2)
C(9)	4 163(5)	2 177(3)	−3 045(2)	45(2)
C(10)	4 063(4)	4 362(3)	1 187(2)	43(2)
C(11)	2 253(5)	4 481(2)	1 285(2)	51(2)
C(12)	5 484(5)	4 732(3)	2 014(2)	53(2)
C(13)	2 367(4)	643(2)	−1 184(2)	43(2)
C(14)	522(4)	738(2)	−1 126(2)	44(2)
C(15)	140(4)	1 159(2)	−306(2)	45(2)
C(16)	1 528(4)	1 531(2)	519(2)	41(2)
C(17)	3 372(4)	1 443(2)	460(2)	44(2)
C(18)	3 769(4)	1 018(2)	−359(2)	46(2)
C(19)	2 747(4)	176(2)	−2 025(2)	44(2)
C(20)	4 561(6)	79(3)	−2 118(2)	55(2)
C(21)	1 318(5)	−260(3)	−2 823(2)	49(2)
C(22)	1 116(4)	1 958(2)	1 362(2)	45(2)
C(23)	−713(5)	2 039(3)	1 433(2)	48(2)
C(24)	2 492(5)	2 362(3)	2 190(2)	49(2)
C(25)	12 748(5)	5 345(3)	4 055(2)	53(2)
C(26)	11 565(4)	4 501(2)	4 236(2)	41(2)
C(27)	10 029(4)	3 962(2)	3 549(2)	45(2)
C(28)	8 865(4)	3 180(2)	3 728(2)	45(2)
C(29)	9 229(4)	2 961(2)	4 587(2)	39(2)
C(30)	10 733(4)	3 491(2)	5 271(2)	44(2)
C(31)	11 907(4)	4 268(2)	5 084(2)	46(2)
C(32)	8 639(4)	1 467(2)	5 231(2)	45(2)
C(33)	7 501(4)	640(2)	5 340(2)	45(2)
C(34)	5 614(4)	456(2)	4 959(2)	37(1)
C(35)	4 975(4)	1 162(2)	4 496(2)	44(2)
C(36)	6 142(4)	1 993(3)	4 411(2)	44(2)
N(1)	3 017(4)	1 804(2)	−3 692(2)	60(2)
N(2)	8 851(5)	2 455(3)	−2 449(2)	84(2)
N(3)	797(5)	4 569(3)	1 348(2)	74(2)
N(4)	6 637(5)	5 029(3)	2 664(2)	76(2)
N(5)	137(4)	−632(2)	−3 449(2)	64(2)
N(6)	6 029(5)	1(3)	−2 187(2)	80(2)
N(7)	−2 199(4)	2 095(3)	1 479(2)	65(2)
N(8)	3 603(4)	2 711(3)	2 859(2)	70(2)
N(9)	13 635(5)	6 031(3)	3 927(2)	73(2)
N(10)	7 985(3)	2 129(2)	4 760(2)	39(1)

TCNQ(A)–TCNQ(B), and TCNQ(B)–TCNQ(B′). The corresponding overlaps are shown in Figure 2. Adjacent columns form sheets parallel to the *ab* plane, successive sheets being interleaved along *c* by the CPP dications. Similar packing has been observed for other TCNQ salts of diquaternised 4,4′-bipyridyl, 1,2-bis-(4-pyridyl)ethylene, and 1,2-bis-(4-pyridyl)-ethane. For a review of their electrical and structural properties, see ref. 6.

The bond lengths and angles of the CPP dication are listed in Table 3. The cation shows no abnormal dimensions, the bond lengths and angles being in close agreement with values reported previously [7,8] in, for example, [1,1′-dimethyl-4,4′-bipyridinium]$^{2+}$(TCNQ)$_3^{2-}$ and [1,1′-diethyl-4,4′-bipyridinium]$^{2+}$(TCNQ)$_4^{2-}$. The CPP dication is not planar, the angle between the mean planes of the cyanophenyl and pyridinium rings being 38.8°. For distances out of the mean planes see Table 2.

Table 2. Details of molecular planes. Asterisks denote atoms not defining the plane

TCNQ(A)

Equation to the plane

$$0.0665X + 0.9804Y - 0.1855Z - 5.0906 = 0$$

Distances from the plane (in Å)

C(1)	0.000(3)	C(9)	−0.106(4)*
C(2)	−0.006(3)	C(10)	0.064(4)*
C(3)	0.008(3)	C(11)	0.006(4)*
C(4)	−0.005(3)	C(12)	0.027(4)*
C(5)	−0.001(3)	N(1)	−0.232(3)*
C(6)	0.003(3)	N(2)	0.107(4)*
C(7)	0.006(4)*	N(3)	0.007(4)*
C(8)	0.006(4)*	N(4)	0.053(4)*

TCNQ(B)

Equation to the plane

$$0.0553X + 0.9790Y - 0.1964Z - 1.7103 = 0$$

Distances from the plane (in Å)

C(13)	−0.004(3)	C(21)	−0.147(4)*
C(14)	0.004(3)	C(22)	−0.015(3)*
C(15)	−0.002(3)	C(23)	−0.033(4)*
C(16)	−0.001(3)	C(24)	0.025(4)*
C(17)	0.001(3)	N(5)	−0.270(3)*
C(18)	0.002(3)	N(6)	−0.028(4)*
C(19)	−0.044(3)*	N(7)	−0.053(4)*
C(20)	−0.033(4)*	N(8)	0.087(4)*

Cation

Equations to the planes

(i) $0.7266X - 0.5963Y - 0.3413Z - 0.0842 = 0$

(ii) $0.3802X - 0.3540Y - 0.8545Z + 4.6604 = 0$

Distances from the plane (in Å)

	Plane (i)		Plane (ii)
C(25)	−0.055(4)*	C(32)	−0.004(3)
C(26)	0.002(3)	C(33)	−0.010(3)
C(27)	−0.005(3)	C(34)	0.011(3)
C(28)	0.005(3)	C(35)	0.002(3)
C(29)	−0.001(3)	C(36)	−0.015(3)
C(30)	−0.002(3)	N(10)	0.017(3)
C(31)	0.002(3)		
N(9)	−0.152(3)*		

The dimensions of the crystallographically independent types of TCNQ moiety (Tables 4 and 5) are intermediate between those of neutral TCNQ [11] and those of the radical anion [12–14] in, for example, Na$^+$TCNQ$^-$, K$^+$TCNQ$^-$, and Rb$^+$TCNQ$^-$. By applying the method of Flandrois and Chasseau [15] to the mean bond lengths of TCNQ(A) and TCNQ(B) the charges on each may be estimated as 0.3e and 0.6e, respectively. In Table 6, these results are compared with the data obtained for [1,1′-dimethyl-4,4′-bipyridinium]$^{2+}$-(TCNQ)$_3^{2-}$, [1,1′-diethyl-4,4′-bipyridinium]$^{2+}$(TCNQ)$_4^{2-}$, [1,1′-di-n-propyl-4,4′-bipyridinium]$^{2+}$(TCNQ)$_4^{2-}$, and [1,1′-dibenzyl-4,4′-bipyridinium]$^{2+}$(TCNQ)$_4^{2-}$. For each of the salts there is indication of the negative charge being partially localised on specific sites within the TCNQ lattice but, in view of the sensitivity of the calculation to minor changes in the bond lengths, this indication can only be tentative. However, it is of interest to note that, in each case, the TCNQ moiety on which the charge is localised makes the closest contact with the cation and that this contact is to the α-position of the pyridinium ring. In CPP·TCNQ$_4$ the closest non-hydrogen TCNQ to cation contacts are N(5)–C(32)′ = 3.062(5) Å,

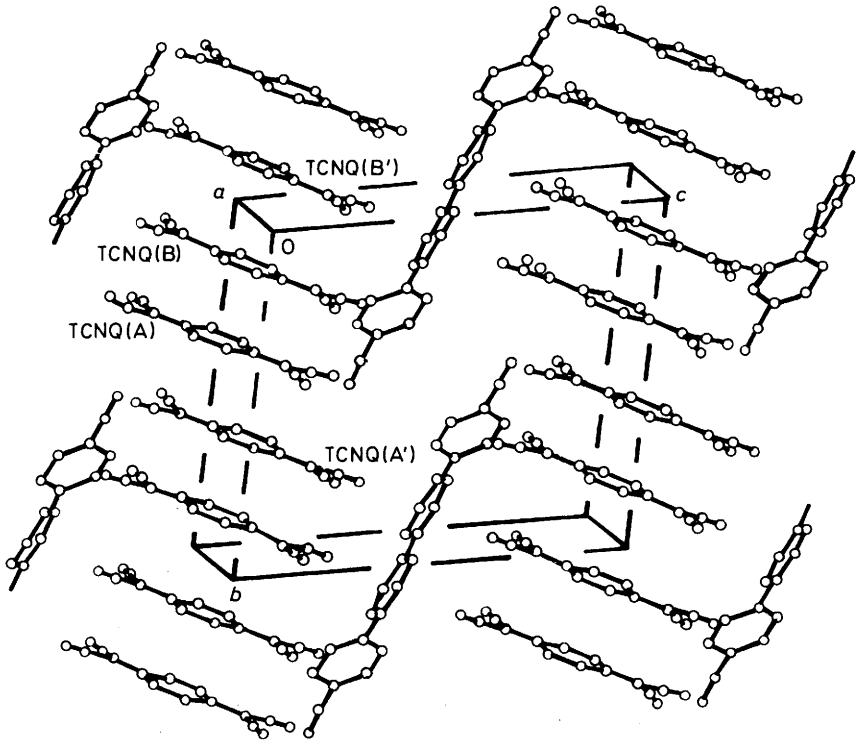


Figure 1. A general view of the structure of CPP–$TCNQ_4$

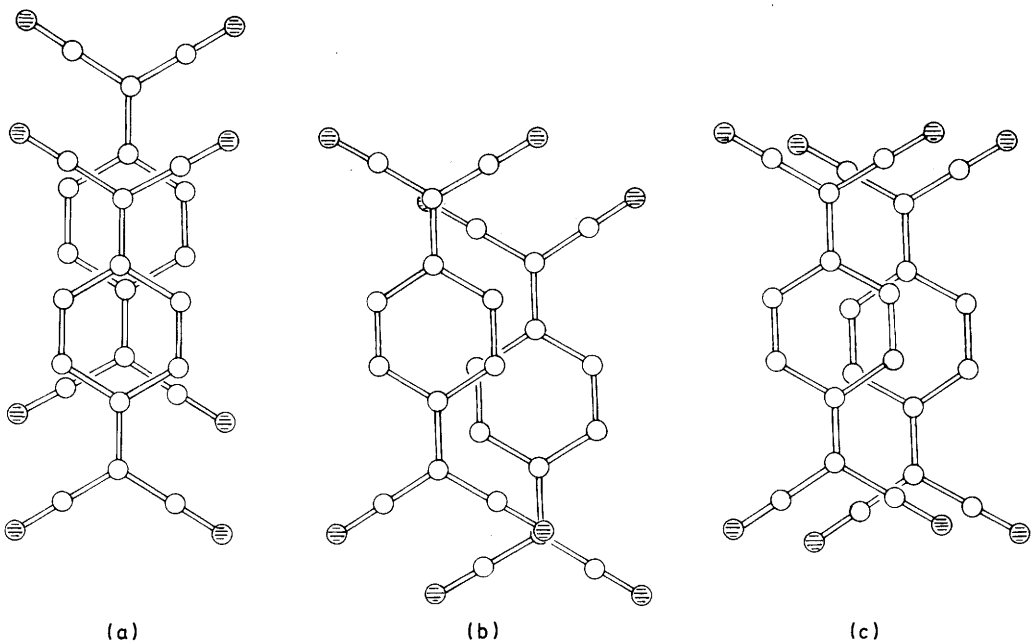
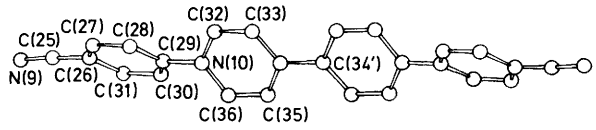


Figure 2. TCNQ molecular overlaps: (a) TCNQ(A)-TCNQ(A'), (b) TCNQ(B)–TCNQ(B'), and (c) TCNQ(A)–TCNQ(B)

N(8)–C(36) = 3.162(5) Å, and N(5)–N(10') = 3.201(5) Å for TCNQ(B) and N(1)–C(32'') = 3.329(5) Å for TCNQ(A) (*cf.* van der Waals' distances of 3.0 and 3.2 Å for N–N and C–N, respectively). The cation charge, obtained by summing the charges on the TCNQs within the stoicheiometric unit, does not differ significantly from 2+.

The columnar arrangement of TCNQs in CPP–$TCNQ_4$ gives rise to electrical anisotropy with the highest conductivity in a direction parallel to the stack. In this direction, the conductivity varies as $\sigma = \sigma_0 \exp(-E_a/kT)$ where $\sigma_{300\,K}$ = 0.1 S cm^{-1} and E_a = 0.10 eV. The conductivity was determined by a four-probe technique in the temperature range 300—150 K. CPP–$TCNQ_4$ is a small band gap semiconductor, the gap arising from the periodic distortion of the TCNQ lattice. Metallic behaviour has not been observed in either CPP–$TCNQ_4$ or its *para*-substituted congeners (Table 7), the conductivities being in the range 0.007—0.3 S cm^{-1} at 300 K. In contrast, the congeneric salts of diquatern-

Table 3. Bond distances (Å) and angles (°), with the standard deviations in parentheses, of the CPP dication



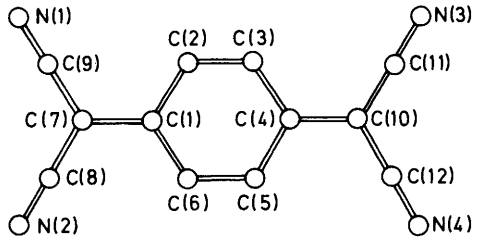
(a) Distances

C(25)–C(26)	1.448(5)	C(30)–C(31)	1.383(5)
C(25)–N(9)	1.134(5)	C(32)–C(33)	1.364(5)
C(26)–C(27)	1.397(5)	C(32)–N(10)	1.349(5)
C(26)–C(31)	1.374(5)	C(33)–C(34)	1.401(5)
C(27)–C(28)	1.378(5)	C(34)–C(34′)	1.471(5)
C(28)–C(29)	1.382(5)	C(34)–C(35)	1.387(5)
C(29)–C(30)	1.377(4)	C(35)–C(36)	1.366(5)
C(29)–N(10)	1.456(4)	C(36)–N(10)	1.366(4)

(b) Angles

C(26)–C(25)–N(9)	177.4(4)	C(33)–C(32)–N(10)	121.2(3)
C(25)–C(26)–C(27)	118.8(3)	C(32)–C(33)–C(34)	120.5(3)
C(25)–C(26)–C(31)	120.3(3)	C(33)–C(34)–C(34′)	120.9(3)
C(27)–C(26)–C(31)	120.8(3)	C(33)–C(34)–C(35)	117.0(3)
C(26)–C(27)–C(28)	119.0(3)	C(35)–C(34)–C(34′)	122.2(3)
C(27)–C(28)–C(29)	119.2(3)	C(34)–C(35)–C(36)	121.2(3)
C(28)–C(29)–C(30)	122.2(3)	C(35)–C(36)–N(10)	120.3(3)
C(28)–C(29)–N(10)	118.3(2)	C(29)–N(10)–C(32)	120.7(3)
C(30)–C(29)–N(10)	119.5(3)	C(29)–N(10)–C(36)	119.7(3)
C(29)–C(30)–C(31)	118.3(3)	C(32)–N(10)–C(36)	119.6(3)
C(26)–C(31)–C(30)	120.4(3)		

Table 4. Bond distances (Å) and angles (°), with the standard deviations in parentheses, of TCNQ(A)



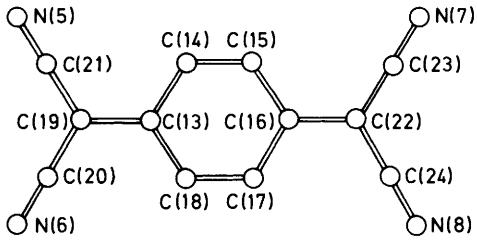
(a) Distances

C(1)–C(2)	1.439(5)	C(7)–C(8)	1.441(5)
C(1)–C(6)	1.429(5)	C(7)–C(9)	1.430(4)
C(1)–C(7)	1.394(5)	C(8)–N(2)	1.145(5)
C(2)–C(3)	1.345(5)	C(9)–N(1)	1.148(4)
C(3)–C(4)	1.432(4)	C(10)–C(11)	1.431(6)
C(4)–C(5)	1.446(5)	C(10)–C(12)	1.435(4)
C(4)–C(10)	1.385(5)	C(11)–N(3)	1.143(6)
C(5)–C(6)	1.348(5)	C(12)–N(4)	1.143(4)

(b) Angles

C(2)–C(1)–C(6)	117.7(3)	C(1)–C(7)–C(8)	122.6(3)
C(2)–C(1)–C(7)	120.5(3)	C(1)–C(7)–C(9)	122.5(3)
C(6)–C(1)–C(7)	121.8(3)	C(8)–C(7)–C(9)	114.8(3)
C(1)–C(2)–C(3)	120.9(3)	C(7)–C(8)–N(2)	179.3(3)
C(2)–C(3)–C(4)	121.9(3)	C(7)–C(9)–N(1)	178.2(4)
C(3)–C(4)–C(5)	117.0(3)	C(4)–C(10)–C(11)	121.9(3)
C(3)–C(4)–C(10)	122.3(3)	C(4)–C(10)–C(12)	122.1(3)
C(5)–C(4)–C(10)	120.6(3)	C(11)–C(10)–C(12)	116.0(3)
C(4)–C(5)–C(6)	121.1(3)	C(10)–C(11)–N(3)	178.9(3)
C(1)–C(6)–C(5)	121.4(3)	C(10)–C(12)–N(4)	178.9(5)

Table 5. Bond distances (Å) and angles (°), with the standard deviations in parentheses, of TCNQ(B)



(a) Distances

C(13)–C(14)	1.436(5)	C(19)–C(20)	1.426(6)
C(13)–C(18)	1.426(4)	C(19)–C(21)	1.418(4)
C(13)–C(19)	1.398(5)	C(20)–N(6)	1.151(6)
C(14)–C(15)	1.355(5)	C(21)–N(5)	1.143(4)
C(15)–C(16)	1.420(4)	C(22)–C(23)	1.424(5)
C(16)–C(17)	1.433(5)	C(22)–C(24)	1.421(4)
C(16)–C(22)	1.397(5)	C(23)–N(7)	1.150(5)
C(17)–C(18)	1.360(5)	C(24)–N(8)	1.151(5)

(b) Angles

C(14)–C(13)–C(18)	117.9(3)	C(13)–C(19)–C(20)	122.2(3)
C(14)–C(13)–C(19)	120.3(3)	C(13)–C(19)–C(21)	121.0(3)
C(18)–C(13)–C(19)	121.8(3)	C(20)–C(19)–C(21)	116.7(3)
C(13)–C(14)–C(15)	120.5(3)	C(19)–C(20)–N(6)	179.6(3)
C(14)–C(15)–C(16)	121.9(3)	C(19)–C(21)–N(5)	177.6(4)
C(15)–C(16)–C(17)	117.6(3)	C(16)–C(22)–C(23)	121.6(3)
C(15)–C(16)–C(22)	121.4(3)	C(16)–C(22)–C(24)	122.3(3)
C(17)–C(16)–C(22)	121.0(3)	C(23)–C(22)–C(24)	116.1(3)
C(16)–C(17)–C(18)	120.9(3)	C(22)–C(23)–N(7)	179.1(3)
C(13)–C(18)–C(17)	121.2(3)	C(22)–C(24)–N(8)	178.5(4)

ised 1,2-bis-(4-pyridyl)ethylene (DRPE), 1,2-bis-(4-pyridyl)-ethane (DRPA), and 1,3-bis-(4-pyridyl)propane (DRPP) are highly conductive [2] and a few sample-dependent crystals have shown metallic properties to below 10 K. These salts, quaternised with H, CH_3, CH_3CH_2, and $CH_3CH_2CH_2$, are isostructural [2] and attempts have been made to prepare other members of the series by using diquaternised 4,4′-bipyridyl as the counterion.

None of the 1,1′-diaryl-4,4′-bipyridinium salts is isostructural with the highly conductive series above. In the DRPE–DRPA–DRPP series, the radical anions stack in infinite columns, with a short uniform spacing and an exocyclic bond to ring overlap, the cations being arranged in channels among the TCNQ stacks.[16] The channels show no long-range order and can accommodate cations which vary in size from 1,2-bis(4-pyridinium)ethane ($C_{12}H_{14}N_2$) to 1,3-bis-(n-propyl-4-pyridinium)propane ($C_{19}H_{28}N_2$). This adaptability combined with the fact that the related 4,4′-bipyridinium salts are not also isostructural, leads us to suggest that the 1,1′-diaryl-4,4′-bipyridinium dications are too rigid to be accommodated within the narrow, disordered, cation channels. In CPP–$TCNQ_4$ the cation lattice is ordered and steric and electrostatic effects dictate the molecular packing.

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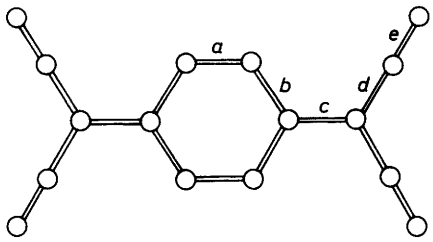
Table 6. Mean TCNQ bond lengths (Å), estimated charge on each of the TCNQs within the asymmetric unit, and closest non-hydrogen TCNQ to cation contacts (Å) in CPP–$TCNQ_4$ and related salts



Complex salt	TCNQ moiety	*a*	*b*	*c*	*d*	*e*	Charge	Closest contacts *	Ref.
1,1′-Dimethyl-4,4′-bipyridinium$(TCNQ)_3$	½A	1.372	1.423	1.415	1.413	1.151	0.95	3.085	7
	B	1.361	1.430	1.405	1.426	1.143	0.65	3.282	
1,1′-Diethyl-4,4′-bipyridinium$(TCNQ)_4$	A	1.351	1.431	1.410	1.424	1.143	0.73	3.231	8
	B	1.353	1.436	1.388	1.422	1.145	0.37	3.347	
1,1′-Di-n-propyl-4,4′-bipyridinium$(TCNQ)_4$	A	1.355	1.434	1.405	1.422	1.142	0.65	3.205	9
	B	1.346	1.433	1.394	1.428	1.142	0.44	3.322	
1,1′-Dibenzyl-4,4′-bipyridinium$(TCNQ)_4$	A	1.359	1.425	1.404	1.421	1.147	0.71	3.276	10
	B	1.350	1.433	1.384	1.432	1.139	0.26	3.338	
1,1′-Bis-(*p*-cyanophenyl)-4,4′-bipyridinium$(TCNQ)_4$	B	1.357	1.429	1.398	1.422	1.149	0.58	3.062	This
	A	1.346	1.437	1.389	1.434	1.145	0.29	3.329	work

* All are N–C contacts to the α-position of the pyridinium ring.

Table 7. Electrical properties of the complex TCNQ salts of 1,1′-diphenyl-4,4′-bipyridinium and its *para*-substituted congeners. With the exception of CPP–$TCNQ_4$ all measurements were carried out on compacted pellets of microcrystalline samples

Cation	$\sigma_{300\ K}$/ S cm^{-1}
1,1′-Diphenyl-4,4′-bipyridinium	0.07
1,1′-Bis-(*p*-methylphenyl)-4,4′-bipyridinium	0.2
1,1′-Bis-(*p*-fluorophenyl)-4,4′-bipyridinium	0.06
1,1′-Bis-(*p*-iodophenyl)-4,4′-bipyridinium	0.3
1,1′-Bis-(*p*-thiocyanophenyl)-4,4′-bipyridinium	0.007
1,1′-Bis-(*p*-cyanophenyl)-4,4′-bipyridinium	0.1 *

* Single crystal (*b* axis value).

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