in charge-transfer complexes will be such as to maximize the overlap integral between the orbital from which the electron is donated and the orbital into which it is accepted on transfer of charge. This principle has received support from the studies by Chesnut & Moseley (1969), Vincent & Wright (1974) and Goldberg (1975). We have applied the principle in a very approximate way by simply comparing the sums of products of the coefficients of overlapping orbitals, one in the highest filled molecular orbital of the donor and the other in the lowest vacant molecular orbital of the acceptor, each product being modified by a function of the interatomic distance. We considered only donor–acceptor interatomic distances less than 3·50 Å and found that the sums for the two orientations of TCNE were not very sensitive to the distance function used. Using the inverse square of the distance in Å gave a ratio of the sums equal to 1·34 in favour of orientation *A* and using the negative exponent of the distance in Å gave the corresponding ratio 1·32. No significance can be attached to the numerical values of these ratios – they merely serve to justify semi-quantitatively the experimental observation that orientation *A* has a higher occupation factor than orientation *B*. Two perpendicular orientations for TCNE, with occupation factors 0·75 and 0·25, have been found previously in complexes with [3.3]paracyclophane (Bernstein & Trueblood, 1971) and hexamethylbenzene (Saheki, Yamada, Yoshioka & Nakatsu, 1976).

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The Crystal Structures of Free Radical Salts and Complexes.
XIII. The Crystal Structure and Electrical Conductivity of [1,2-Bis(1-benzyl-4-pyridinio)ethane]$^{2+}$(7,7,8,8-Tetracyanoquinodimethanide)$_5^{2-}$

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The crystal structure and electrical conductivity are reported for the 5:1 complex formed between 7,7,8,8-tetrcyanoquinodimethane (TCNQ) and 1,2-bis(1-benzyl-4-pyridyl)ethane. The complex $C_{26}H_{26}N_2$-5($C_{12}H_4N_4$) is triclinic, space group $P\bar{1}$, with $a = 8{\cdot}109\ (1)$, $b = 16{\cdot}115\ (1)$, $c = 15{\cdot}172\ (35)$ Å, $\alpha = 111{\cdot}25\ (5)$, $\beta = 109{\cdot}61\ (7)$, $\gamma = 84{\cdot}81\ (6)^\circ$, $Z = 1$. The structure was solved by the Patterson method and refined to $R = 0{\cdot}056$ for 1842 reflexions. The TCNQ's are stacked plane-to-plane in groups of five in columns along [$\bar{1}$10] with favourable overlap and interplanar separations of ~3·22 Å within each pentad. There is a similar overlap between pentads but with the direction of staggering reversed and a larger interplanar separation of 3·41 Å. This is consistent with the fairly low resistivity of 30 Ω cm along the stacking direction.

Introduction

Complex TCNQ salts of diquaternized 1,2-di(4-pyridinio)ethane, (D*X*PA)$^{2+}$, and 1,2-di(4-pyridinio)ethylene, (D*X*PE)$^{2+}$, have stoichiometries of 2:5 (Ashwell, Eley, Wallwork, Willis, Welch & Woodward, 1977), 1:3 (Rembaum, Hermann, Stewart & Gutmann, 1969), 1:4 (Ashwell, Eley, Fleming, Wallwork & Willis, 1976; Ashwell, Eley, Drew, Wallwork & Willis, 1977) and 1:5 (Ashwell, Eley, Harper, Torrance, Wallwork & Willis, 1977). The unusually high stoichiometry of 1:5 first reported for 1,2-bis(1-benzyl-4-pyridinio)ethylene, $(DBzPE)^{2+}$-$(TCNQ)_5^{2-}$, occurs again for 1,2-bis(1-benzyl-4-pyridinio)ethane, $(DBzPA)^{2+}(TCNQ)_5^{2-}$, the structure and electrical properties of which are reported here.

Experimental

Crystal data

$C_{26}H_{26}N_2.5(C_{12}H_4N_4)$, $M_r = 1387{\cdot}4$, triclinic, $a = 8{\cdot}109\,(1)$, $b = 16{\cdot}115\,(1)$, $c = 15{\cdot}172\,(35)$ Å, $\alpha = 111{\cdot}25\,(5)$, $\beta = 109{\cdot}61\,(7)$, $\gamma = 84{\cdot}81\,(6)°$, $U = 1739{\cdot}5$ Å^3, $Z = 1$, $D_c = 1{\cdot}32$ g cm^{-3}; $F(000) = 716$. Mo $K\alpha$ ($\lambda = 0{\cdot}71069$ Å), $\mu = 0{\cdot}90$ cm^{-1}. Space group $P\bar{1}$ (assumed).

Black plate-like crystals of the complex were deposited when a warm aqueous solution (10 ml) of 1,2-bis(1-benzyl-4-pyridinio)ethane dichloride (0·2 g) was added to a warm acetonitrile solution (200 ml) of LiTCNQ (0·2 g) and TCNQ (0·3 g) and allowed to cool slowly. The space group and unit-cell dimensions were obtained initially from oscillation and Weissenberg photographs, using Cu $K\alpha$ radiation. The cell constants were subsequently refined on a Hilger & Watts computer-controlled, four-circle diffractometer. Intensities were collected using a $\theta/2\theta$ scan, a scintillation counter and Mo $K\alpha$ radiation. The intensities were corrected for Lorentz and polarization factors but not for absorption.

Structure determination

The structure was solved by means of a Patterson synthesis and refined by block-diagonal least-squares calculations using 1842 significant reflexions $[I > 3\sigma(I)]$. Positional parameters of the H atoms were calculated from the coordinates of the C atoms and confirmed by a difference synthesis. The H atoms were given isotropic temperature factors of 0·05 Å^2 and were included in the last few cycles of refinement in fixed calculated positions. Block-diagonal least-squares refinement of the non-hydrogen atoms with anisotropic thermal parameters and the weighting scheme $1/w = \{[(|F_o| - A)/B]^2 + 1\}$ where $|F_o|$ is on the absolute scale, $A = 13$ and $B = 10$ gave $R = 0{\cdot}056$. Scattering factors were taken from *International Tables for X-ray Crystallography* (1974). The calculations were performed using the Oxford *CRYSTALS* program (Carruthers & Rollett, 1975). The final positional parameters are listed in Table 1.* Least-squares planes were calculated for each of the TCNQ moieties and the

Table 1. *Final positional parameters (with standard deviations in parentheses) all* $\times 10^4$

	x	y	z
C(1)	1470 (10)	149 (4)	862 (5)
C(2)	−240 (10)	−23 (4)	862 (5)
C(3)	−1632 (9)	−157 (4)	37 (5)
C(4)	2920 (10)	288 (4)	1703 (5)
C(5)	4650 (10)	471 (5)	1739 (6)
C(6)	2803 (9)	244 (4)	2614 (6)
N(1)	6010 (10)	623 (5)	1750 (5)
N(2)	2736 (9)	212 (5)	3341 (5)
C(7)	8856 (9)	2084 (4)	10429 (5)
C(8)	7220 (10)	1917 (4)	10495 (5)
C(9)	5760 (10)	1765 (4)	9693 (5)
C(10)	5800 (10)	1767 (4)	8765 (5)
C(11)	7470 (10)	1936 (4)	8706 (5)
C(12)	8930 (10)	2093 (4)	9509 (5)
C(13)	10380 (10)	2228 (4)	11248 (5)
C(14)	12060 (10)	2392 (5)	11224 (5)
C(15)	10429 (9)	2220 (4)	12192 (6)
C(16)	4290 (10)	1600 (4)	7927 (5)
C(17)	2630 (10)	1442 (5)	7969 (5)
C(18)	4234 (9)	1610 (5)	6987 (6)
N(3)	13420 (9)	2523 (4)	11224 (5)
N(4)	10502 (9)	2207 (5)	12946 (5)
N(5)	1283 (9)	1312 (4)	7997 (5)
N(6)	4197 (9)	1620 (5)	6238 (5)
C(19)	−4058 (9)	3965 (4)	−73 (5)
C(20)	−5763 (9)	3793 (4)	−60 (5)
C(21)	−7179 (9)	3645 (4)	−886 (5)
C(22)	−7061 (9)	3629 (4)	−1811 (5)
C(23)	−5358 (9)	3805 (4)	−1813 (5)
C(24)	−3926 (8)	3980 (4)	−995 (5)
C(25)	−2613 (9)	4118 (4)	760 (5)
C(26)	−920 (10)	4290 (4)	756 (5)
C(27)	−2675 (9)	4096 (4)	1679 (6)
C(28)	−8525 (9)	3465 (4)	−2658 (5)
C(29)	−10210 (10)	3268 (5)	−2654 (6)
C(30)	−8410 (10)	3452 (5)	−3580 (6)
N(7)	459 (9)	4423 (4)	769 (5)
N(8)	−2753 (9)	4085 (5)	2415 (5)
N(9)	−11520 (10)	3097 (5)	−2645 (6)
N(10)	−8314 (9)	3431 (5)	−4312 (5)
C(31)	9310 (20)	70 (10)	4940 (20)
C(32)	8370 (20)	896 (7)	4736 (9)
C(33)	8960 (10)	1384 (8)	4320 (9)
C(34)	8050 (10)	2070 (7)	4124 (6)
C(35)	5960 (10)	1805 (7)	4722 (7)
C(36)	6840 (20)	1127 (8)	4943 (8)
C(37)	5550 (10)	3062 (6)	4165 (5)
C(38)	6319 (9)	3912 (5)	5017 (4)
C(39)	7520 (10)	4439 (6)	4977 (6)
C(40)	8250 (10)	5191 (6)	5794 (8)
C(41)	7820 (10)	5426 (6)	6620 (7)
C(42)	6620 (10)	4933 (7)	6661 (7)
C(43)	5860 (10)	4185 (6)	5864 (7)
N(11)	6531 (9)	2297 (4)	4341 (4)

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33775 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

planar portions of the cation; the results are summarized in Table 2.

Table 2. *Details of molecular planes* (*x*,*y*,*z* *are fractional atomic coordinates; asterisks denote atoms not defining the plane*)

TCNQ(*A*)

Equations to the planes

Molecule $1{\cdot}599x - 14{\cdot}682y - 0{\cdot}321z + 0{\cdot}000 = 0$

Quinonoid group $1{\cdot}450x - 14{\cdot}848y + 0{\cdot}028z + 0{\cdot}000 = 0$

Distances from the plane (Å)

	Molecule	Quinonoid group		Molecule	Quinonoid group
C(1)	−0·01	−0·01	C(5)	0·00	−0·02*
C(2)	−0·03	0·00	C(6)	0·01	0·05*
C(3)	−0·03	0·00	N(1)	−0·01	−0·05*
C(4)	−0·01	0·00	N(2)	0·02	0·09*

TCNQ(*B*)

Equations to the planes

Molecule $1{\cdot}511x - 14{\cdot}792y - 0{\cdot}081z + 1{\cdot}808 = 0$

Quinonoid group $1{\cdot}521x - 14{\cdot}823y + 0{\cdot}024z + 1{\cdot}713 = 0$

Distances from the plane (Å)

	Molecule	Quinonoid group		Molecule	Quinonoid group
C(7)	−0·02	−0·01	C(15)	0·00	0·04*
C(8)	−0·02	−0·01	C(16)	0·03	0·01
C(9)	−0·01	0·00	C(17)	0·01	−0·01*
C(10)	0·00	0·00	C(18)	0·01	−0·01*
C(11)	0·00	0·00	N(3)	0·01	0·04*
C(12)	−0·02	−0·01	N(4)	0·03	0·07*
C(13)	−0·01	0·02	N(5)	0·00	−0·02*
C(14)	0·00	0·03*	N(6)	0·00	−0·04*

TCNQ(*C*)

Equations to the planes

Molecule $1{\cdot}591x - 14{\cdot}828y + 0{\cdot}117z + 6{\cdot}505 = 0$

Quinonoid group $1{\cdot}527x - 14{\cdot}880y + 0{\cdot}213z + 6{\cdot}524 = 0$

Distances from the plane (Å)

	Molecule	Quinonoid group		Molecule	Quinonoid group
C(19)	−0·02	0·00	C(27)	0·03	0·06*
C(20)	−0·04	0·00	C(28)	−0·02	0·01
C(21)	−0·05	−0·02	C(29)	0·01	0·05*
C(22)	−0·02	0·01	C(30)	0·01	0·03*
C(23)	−0·01	0·00	N(7)	0·03	0·03*
C(24)	−0·03	−0·02	N(8)	0·04	0·08*
C(25)	−0·01	0·01	N(9)	0·05	0·10*
C(26)	0·01	0·02*	N(10)	0·05	0·06*

Pyridinium ring

Equation to the plane

$$2{\cdot}047x + 5{\cdot}399y + 9{\cdot}364z - 6{\cdot}631 = 0$$

Distances from the plane (Å)

C(32)	0·00	C(34)	0·00	C(36)	0·01
C(33)	0·00	C(35)	−0·01	N(11)	0·01

Aromatic ring

Equation to the plane

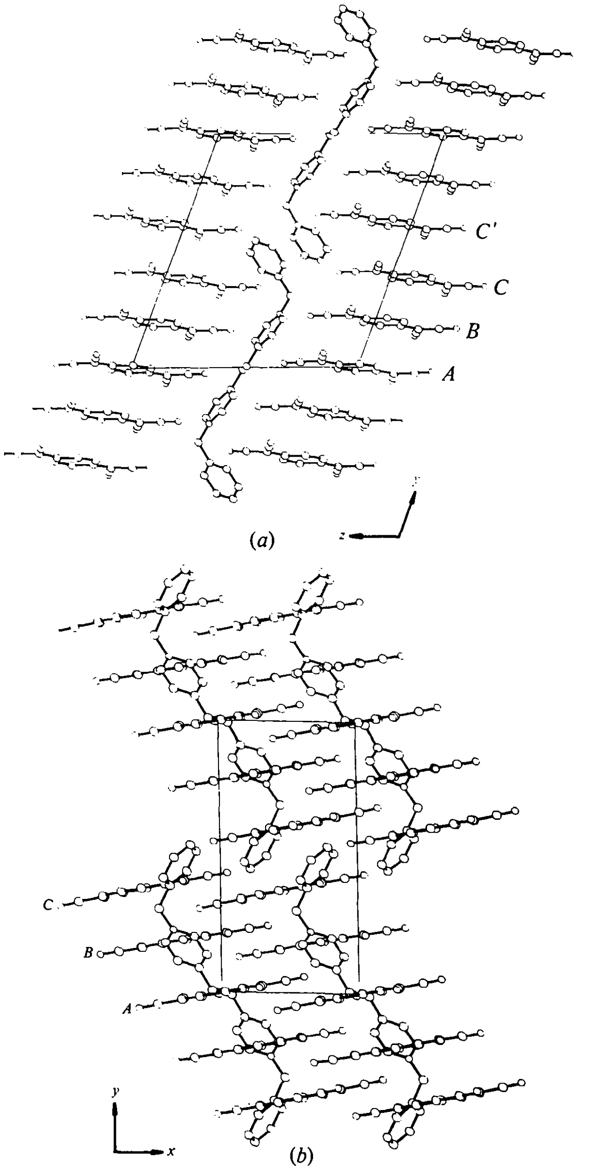
$$-4{\cdot}711x + 10{\cdot}753y - 5{\cdot}701z + 1{\cdot}614 = 0$$

Distances from the plane (Å)

C(38)	−0·02	C(40)	0·01	C(42)	0·00
C(39)	0·01	C(41)	−0·01	C(43)	0·01

Discussion

The structure of (DBzPA)(TCNQ)$_5$ projected along *a* and *c* is shown in Fig. 1. The TCNQ's are stacked plane-to-plane in columns in the (001) plane diagonally between the positive direction of *b* and the negative direction of *a*, *i.e.* along $[\bar{1}10]$. Along *c* two-dimensional arrays of TCNQ's and cations alternate.



(*a*)

(*b*)

Fig. 1. Projections of the structure (*a*) along *a*, (*b*) along *c*.

Within the columns, the TCNQ's are grouped in fives with a favourable exocyclic double bond to quinonoid-ring overlap of adjacent molecules (Fig. 2). Within pentads the double bond to ring staggering of molecules is in the same direction. Between pentads, *i.e.* between TCNQ(*C*) and TCNQ(*C*′), the direction of staggering is reversed but the type of overlap remains the same. A similar stacking arrangement has also been found in the related complex, 1,2-bis(1-benzyl-4-pyridinio)ethylene(TCNQ)$_5$ (Ashwell, Eley, Harper, Torrance, Wallwork & Willis, 1977).

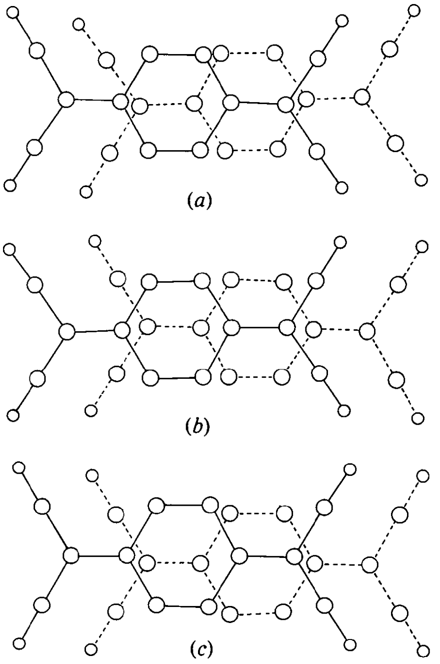


Fig. 2. Overlap of adjacent TCNQ moieties (*a*) TCNQ(*A*) and TCNQ(*B*), (*b*) TCNQ(*B*) and TCNQ(*C*), (*c*) TCNQ(*C*) and TCNQ(*C*′).

Table 3. *Short intermolecular contacts* (Å)

The figures in parentheses indicate standard deviations.

TCNQ–TCNQ Intrapentad	
C(1^{i})–C(13^{ii})	3·277 (9)
C(2^{i})–C(12^{iii})	3·312 (9)
C(3^{i})–C(8^{ii})	3·273 (9)
C(3^{i})–C(14^{iii})	3·396 (9)
C(4^{i})–C(10^{iii})	3·272 (9)
C(6^{i})–C(11^{iii})	3·338 (9)
C(7^{i})–C(25^{iv})	3·304 (9)
C(8^{i})–C(27^{iv})	3·308 (9)
C(9^{i})–C(20^{iv})	3·323 (9)
C(10^{i})–C(19^{iv})	3·328 (9)
C(11^{i})–C(24^{iv})	3·305 (9)
C(12^{i})–C(26^{iv})	3·346 (9)
C(16^{i})–C(22^{iv})	3·279 (9)
C(17^{i})–C(21^{iv})	3·330 (9)
C(18^{i})–C(22^{iv})	3·373 (9)
C(18^{i})–C(23^{iv})	3·328 (9)

TCNQ–TCNQ Interpentad	
C(9^{i})–N(3^{v})	3·315 (9)
C(12^{i})–N(5^{vi})	3·302 (9)
C(20^{i})–C(24^{vii})	3·383 (8)
N(7^{i})–N(7^{viii})	3·344 (8)

TCNQ–cation	
N(2^{i})–C(35^{i})	3·387 (11)
N(4^{i})–C(34^{ix})	3·151 (11)
N(6^{i})–C(35^{i})	3·197 (11)
N(6^{i})–C(36^{i})	3·233 (13)

Superscripts indicate equivalent positions as follows:

(i) x,y,z
(ii) $x-1, y, z-1$
(iii) $1-x, y, 1-z$
(iv) $1+x, y, 1+z$
(v) $x-1, y, z$
(vi) $x+1, y, z$
(vii) $-1-x, 1-y, \bar{z}$
(viii) $\bar{x}, 1-y, \bar{z}$
(ix) $x, y, z+1$.

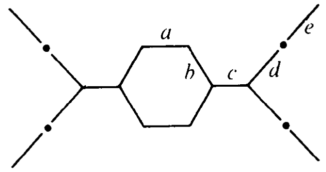
Within the columns, the mean interplanar spacings between molecules *AB*, *BC* and *CC*′ are 3·23 (3·25), 3·21 (3·24) and 3·41 (3·36) Å respectively. The dihedral angles between *AB* and *BC* are 1·0 (0·5) and 1·2 (0·8)°. The figures in parentheses indicate the mean distances and angles between the quinonoid groups and differ because of the slight out-of-plane distortions of the $C{=}C(CN)_2$ groups. Other short intermolecular contacts are listed in Table 3.

The dimensions of the three crystallographically independent types of TCNQ moiety are shown in Fig. 3 and the averaged lengths of chemically similar bonds are summarized in Table 4. Although the dimensions of TCNQ(*A*), TCNQ(*B*) and TCNQ(*C*) are generally similar and intermediate between those of TCNQ^0 and TCNQ$^-$, there is a tendency for the dimensions of TCNQ(*A*) and TCNQ(*C*) to be nearer to TCNQ^0 than are the dimensions of TCNQ(*B*) for the bonds *b*, *c* and *d* which are those more sensitive to the extent of charge. This suggests that the negative charge may be partly localized on *B* but this suggestion can only be tentative in view of the rather large standard deviations of the individual dimensions.

The dimensions of the cation are in agreement with values reported for 1,2-bis(1-benzyl-4-pyridinio)-ethylene(TCNQ)$_5$ (Ashwell, Eley, Harper, Torrance, Wallwork & Willis, 1977). The C(31)–C(31′) distance and C(31′)–C(31)–C(32) angle are clearly erroneous. This is presumably due to incomplete resolution of C(31). The dihedral angle between the pyridine and benzene rings of the cation is 105·2°. The angles that

Table 4. *Comparison of the mean bond lengths* (Å) *uncorrected for libration*

The figures in parentheses indicate standard deviations.



Bond	*a*	*b*	*c*	*d*	*e*
TCNQ$^{0(i)}$	1·346	1·448	1·374	1·440	1·138
TCNQ$^{-(ii)}$	1·362	1·424	1·413	1·417	1·149
TCNQ(*A*)	1·339 (9)	1·428 (9)	1·378 (9)	1·440 (9)	1·142 (9)
TCNQ(*B*)	1·346 (9)	1·426 (9)	1·395 (9)	1·423 (9)	1·137 (9)
TCNQ(*C*)	1·346 (9)	1·439 (9)	1·374 (9)	1·427 (9)	1·139 (9)

References: (i) Long, Sparks & Trueblood (1965). (ii) Ashwell, Eley, Wallwork & Willis (1975) and references therein.

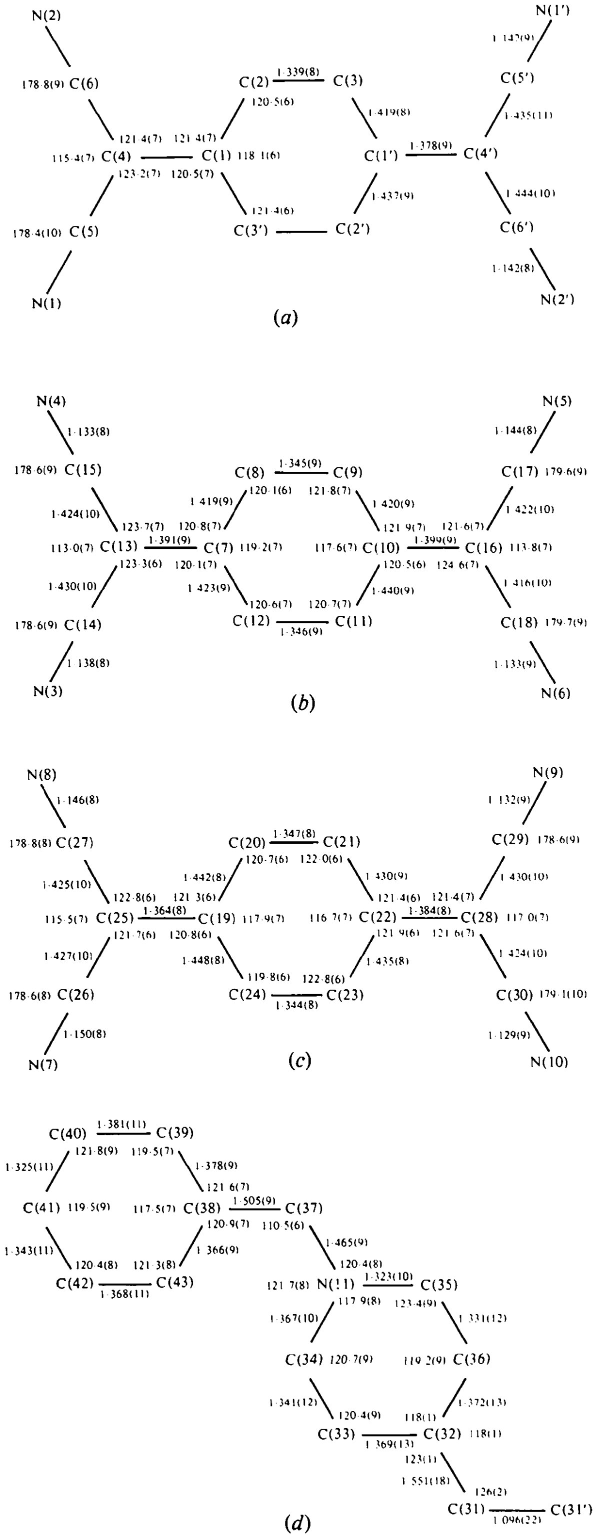


Fig. 3. Bond lengths (Å) and angles (°) in (*a*) TCNQ(*A*), (*b*) TCNQ(*B*), (*c*) TCNQ(*C*) and (*d*) the cation, with standard deviations in parentheses.

these planes make with TCNQ(*A*) are 58·7 and 47·5°, with TCNQ(*B*) are 59·1 and 47·3° and with TCNQ(*C*) are 60·3 and 46·2° respectively.

The single-crystal resistivities of (DBzPA)(TCNQ)$_5$ after degassing at ~50°C, measured under vacuum at 300 K along the long (**a**), intermediate (~**b**) and short (~**c**) crystal axes are 70, 30 and 300 Ω cm respectively. After degassing at ~80°C, and subsequent cooling to room temperature, these values increase to ~200, 300 and 700 Ω cm. Such changes in resistivity may be due to decomposition, crystal fracture, or possibly to loss of solvent from the lattice and are being investigated further.

The single-crystal resistivities of (DBzPA)(TCNQ)$_5$ measured after degassing at ~50°C are consistent with values of 1–10, 10–20 and 60–80 Ω cm obtained for 1,2-bis(1-benzyl-4-pyridinio)ethylene(TCNQ)$_5$, (DBzPE)(TCNQ)$_5$, and 18, 25 and 1500 Ω cm for [1,2-bis(1-ethyl-4-pyridinio)ethane]$_2$(TCNQ)$_5$, (DEPA)$_2$-(TCNQ)$_5$, measured under the same conditions. The structures of these complexes (Ashwell, Eley, Harper, Torrance, Wallwork & Willis, 1977; Ashwell, Eley, Wallwork, Willis, Welch & Woodward, 1977) are similar in so far as the TCNQ's are stacked plane-to-plane, in groups of five, in columns with good overlap between adjacent anions, though the stacking in (DEPA)$_2$(TCNQ)$_5$ differs in detail from that of the other two structures.

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