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Molecular Complexes Exhibiting Polarization Bonding. XII. The Crystal Structure of the 2:1 Complex between 9-Ethylcarbazole and Tetracyanoethylene

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The complex, $2(C_{14}H_{13}N).C_6N_4$, crystallizes as blue-black laths in the orthorhombic space group *Pbca* with $Z = 4$ and $a = 8{\cdot}941$ (2), $b = 17{\cdot}253$ (3), $c = 17{\cdot}888$ (3) Å. The structure consists of centrosymmetric groups of two carbazole donor molecules and one tetracyanoethylene acceptor molecule within which the tetracyanoethylene molecule is disordered unequally in two orientations. The mean perpendicular separation between donor and acceptor is 3·24 Å.

Experimental

Blue-black crystals of the complex were prepared by refluxing together, for ten minutes, solutions of 9-ethylcarbazole (EtCBZ) and tetracyanoethylene (TCNE), concentrating the resulting deep-blue solution by evaporation under reduced pressure and allowing it to cool. The crystals were washed with cold acetonitrile and dried *in vacuo*. The space group and unit-cell dimensions were found from oscillation and Weissenberg photographs taken with Cu $K\alpha$ radiation. A crystal of approximate dimensions $0{\cdot}2 \times 0{\cdot}5 \times 0{\cdot}6$ mm was mounted so as to rotate about its longest (*a*) axis on a Hilger & Watts, four-circle, computer-controlled diffractometer. The cell dimensions were refined and intensities were measured using a $\theta/2\theta$ scan, a scintillation counter and Mo $K\alpha$ radiation for 3814 reflections up to $\theta = 25°$. Of these, 3334 had significant intensities $[I > 3\sigma(I)]$ but only the 2142 largest values were used in the solution and refinement of the structure. The disorder in the structure, which became apparent during refinement, indicated that the computing difficulties involved in using all the significant data would not be warranted. The intensities were corrected for Lorentz and polarization factors but not for absorption. The solution and refinement of the structure were carried out on the University's ICL 1906A computer using the XRAY system of programs edited by Stewart, Kundell & Baldwin (1970).

Crystal data

$2(C_{14}H_{13}N).C_6N_4$, $M_r = 518{\cdot}6$; orthorhombic, $a = 8{\cdot}941$ (2), $b = 17{\cdot}253$ (3), $c = 17{\cdot}888$ (3) Å; $U = 2759$ (1) Å^3, $D_m = 1{\cdot}25$ (1), $D_c = 1{\cdot}248$ g cm^{-3}, $Z = 4$, $F(000) = 1088$, Mo $K\alpha$ ($\lambda = 0{\cdot}71069$ Å), $\mu = 0{\cdot}826$ cm^{-1}, space group *Pbca* from systematic absences.

The structure was solved by direct methods with the *MULTAN* program (Germain, Main & Woolfson, 1971) using 203 $|E| > 1{\cdot}86$. The $\sum_1$ relationship gave positive signs for four reflections and four further reflections were used as a starting set to be given all combinations of positive and negative signs. An *E* map based on the set of phases with the highest figure of merit gave chemically reasonable peak positions for all 20 non-hydrogen atoms in the asymmetric unit (EtCBZ

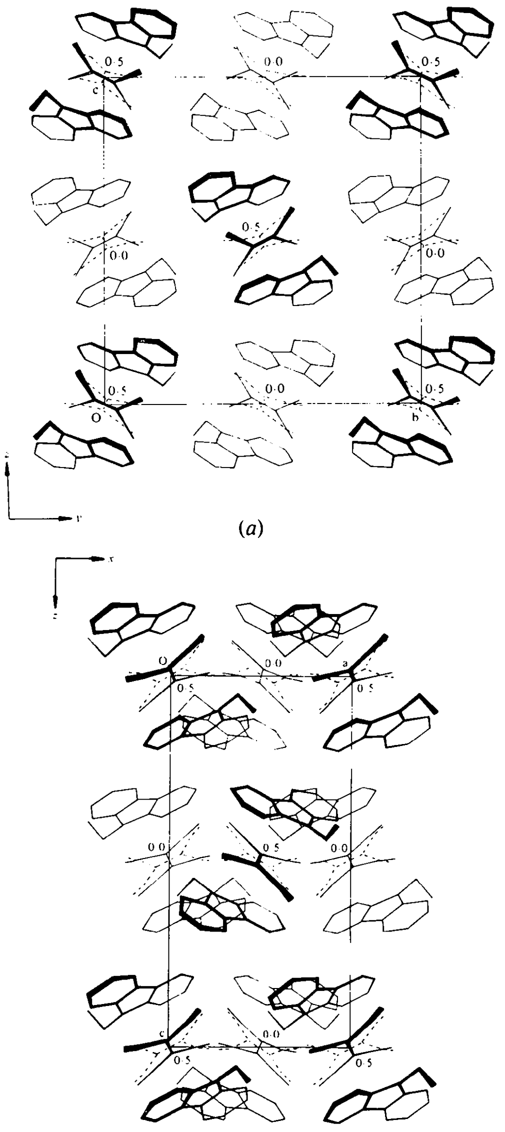
+ $\frac{1}{2}$TCNE) with TCNE, as expected, lying across a centre of symmetry.

Block-diagonal least-squares refinement of the atomic positions with initially isotropic thermal parameters and later anisotropic thermal parameters for non-hydrogen atoms and isotropic thermal parameters for H atoms (the positions of which were found by means of a difference Fourier synthesis and then refined) led to an R of 0·093. This gave a rather distorted TCNE with thermal parameters for the central pair of C atoms about ten times those for the rest of the structure. Recalculation of atomic positions for a regular TCNE, followed by full-matrix refinement of these atoms with the carbazole atoms fixed, and by a difference Fourier calculation, showed evidence of a second central C=C group approximately perpendicular to the first. It then became clear that the TCNE is disordered in this structure with some molecules at right angles to the others, though still in the same plane. This is reasonable since the N atoms form an approximate square which can then pack almost equally well in four orientations corresponding to two crystallographically different orientations of the molecule. The atomic positions, anisotropic thermal parameters and occupation factors corresponding to both disordered positions for the TCNE molecules were then refined by full-matrix calculations, assuming each atomic position to have an initial occupation factor of 0·5 and keeping the atoms of carbazole fixed. Then, the positions and anisotropic thermal parameters of the non-hydrogen atoms of the carbazole molecule were refined by block-diagonal least-squares calculations, keeping all the parameters for TCNE and the H atoms fixed. Finally the thermal and occupation parameters of the TCNE molecules were refined by full-matrix calculations. The R value fell to 0·052. During the later stages of the refinement of each type of molecule a weighting scheme was used in the form $w = (A/|F_o|)^2$ for $|F_o| > A$, otherwise $w = 1$, with $A = 20$ and $|F_o|$ on the absolute scale. The atomic scattering factors used throughout were taken from *International Tables for X-ray Crystallography* (1962).

Table 1. *Final positional* (×10⁴) *and population parameters for non-hydrogen atoms*

Figures in parentheses indicate standard deviations in final digits.

	x	y	z	Population
C(1)	3752 (2)	1494 (1)	1203 (1)	1·000
C(2)	4528 (2)	2191 (1)	1132 (1)	1·000
C(3)	5895 (2)	2248 (1)	1491 (1)	1·000
C(4)	6480 (2)	1635 (1)	1908 (1)	1·000
C(5)	5716 (2)	942 (1)	1978 (1)	1·000
C(6)	4325 (2)	871 (1)	1627 (1)	1·000
C(7)	2019 (2)	548 (1)	1165 (1)	1·000
C(8)	724 (2)	115 (1)	1058 (1)	1·000
C(9)	659 (2)	−608 (1)	1385 (1)	1·000
C(10)	1830 (2)	−900 (1)	1813 (1)	1·000
C(11)	3115 (2)	−472 (1)	1923 (1)	1·000
C(12)	3220 (2)	263 (1)	1601 (1)	1·000
C(13)	1352 (2)	1798 (1)	513 (1)	1·000
C(14)	391 (3)	2263 (1)	1038 (1)	1·000
C(15)	5996 (3)	−673 (2)	653 (2)	0·609 (10)
C(16)	4904 (3)	−356 (2)	160 (1)	0·597 (7)
C(17)	6375 (3)	845 (1)	25 (2)	0·619 (10)
C(18)	5654 (5)	53 (3)	174 (2)	0·363 (7)
C(19)	6283 (5)	−525 (2)	667 (3)	0·400 (11)
C(20)	6615 (4)	692 (2)	16 (2)	0·376 (10)
N(1)	2374 (2)	1282 (1)	909 (1)	1·000
N(2)	6812 (3)	−924 (2)	1074 (2)	0·622 (17)
N(3)	7425 (3)	1172 (1)	105 (1)	0·611 (10)
N(4)	6862 (5)	997 (3)	994 (3)	0·374 (17)
N(5)	7293 (5)	1312 (2)	−15 (2)	0·366 (10)



(*a*)

(*b*)

Fig. 1. Projections of the structure (*a*) along the *a* axis, (*b*) along the *b* axis. The TCNE molecules are shown in orientation *A* by full lines and in orientation *B* by broken lines. Numbers indicate *x* or *y* for the centres of the groups of three molecules.

The final positional and occupation parameters are shown in Table 1.* The structure is illustrated in Fig. 1, the overlap of molecules in Fig. 2 and the bond lengths and angles are shown in Fig. 3. Least-squares planes have been calculated for each molecule and the details are given in Table 2. Table 3 shows close intermolecular contacts.

Description and discussion of the structure

The molecules of EtCBZ and TCNE occur in groups of three such that each TCNE is sandwiched between two centrosymmetrically-related EtCBZ molecules. The mean plane of EtCBZ makes an angle of 4·5° with the mean plane of TCNE(*A*) and 2·7° with TCNE(*B*) (Table 2), all the molecular planes being approximately parallel to $(\bar{1}12)$ and symmetry-related planes. The mean separation between EtCBZ and TCNE planes is 3·24 Å for both TCNE(*A*) and TCNE(*B*). There is good overlap between TCNE, in either orientation, and the EtCBZ on either side of it within the sandwich (Fig. 2), but no direct overlap between EtCBZ molecules in adjacent sandwiches. This correlates well with the low electrical conductivity observed for this complex. The centres of the sandwiches form a lattice centred on all faces but the sandwiches are best regarded as forming pleated sheets whose average plane corresponds to (010) but whose pleats are alternately parallel to (021) and $(02\bar{1})$ [see Fig. 1(*a*)]. The most significant faces on well-formed crystals are (021), (010), $(02\bar{1})$ and $(0\bar{1}0)$ and the crystals are elongated along *a*. The electrical conductivity at room temperature between the main crystal faces (and therefore from sheet to sheet of the structure) is $1{\cdot}8 \times 10^{-16}\ \Omega^{-1}\ \mathrm{cm}^{-1}$ and the conductivity across the breadth of the crystal (parallel to *c*, therefore in the sheet perpendicular to the folds of the pleats) is $1{\cdot}1 \times 10^{-15}\ \Omega^{-1}\ \mathrm{cm}^{-1}$. The energy of activation for both directions is 0·65 eV.

Table 2. *Details of molecular planes*

Δ indicates distances from the mean plane in Å. A prime indicates a centrosymmetrically related atom.

(*a*) All non-H atoms of carbazole

Equation to the plane:

$$-3{\cdot}8771x + 6{\cdot}5693y + 14{\cdot}5131z - 1{\cdot}2967 = 0$$

	Δ		Δ
C(1)	−0·025	C(7)	−0·028
C(2)	0·030	C(8)	0·033
C(3)	0·058	C(9)	0·058
C(4)	0·033	C(10)	0·034
C(5)	−0·024	C(11)	−0·025
C(6)	−0·041	C(12)	−0·048
		N(1)	−0·056

(*b*) Non-H atoms of the pyrrole ring of carbazole

Equation to the plane:

$$-3{\cdot}8924x + 6{\cdot}5371y + 14{\cdot}5116z - 1{\cdot}2492 = 0$$

C(1)	0·012	C(7)	0·014
C(6)	−0·003	C(12)	−0·007
		N(1)	−0·016

(*c*) Non-H atoms of the first benzenoid ring of carbazole

Equation to the plane:

$$-4{\cdot}0582x + 6{\cdot}0322y + 14{\cdot}5564z - 1{\cdot}1321 = 0$$

C(1)	−0·003	C(4)	0·001
C(2)	0·000	C(5)	−0·004
C(3)	0·001	C(6)	0·006

(*d*) Non-H atoms of the second benzenoid ring of carbazole

Equation to the plane:

$$-3{\cdot}5912x + 6{\cdot}9765y + 14{\cdot}6165z - 1{\cdot}3642 = 0$$

C(7)	−0·004	C(10)	0·001
C(8)	0·002	C(11)	−0·002
C(9)	−0·001	C(12)	0·004

(*e*) TCNE(*A*)

Equation to the plane:

$$-4{\cdot}2771x + 7{\cdot}2780y + 13{\cdot}6556z + 2{\cdot}1385 = 0$$

C(15)	−0·024	C(15′)	0·024
C(16)	0·001	C(16′)	−0·001
C(17)	0·061	C(17′)	−0·061
N(2)	0·020	N(2′)	−0·020
N(3)	−0·041	N(3′)	0·041

(*f*) TCNE(*B*)

Equation to the plane:

$$-3{\cdot}8665x + 7{\cdot}2886y + 14{\cdot}1513z + 1{\cdot}9333 = 0$$

C(18)	0·032	C(18′)	−0·032
C(19)	0·066	C(19′)	−0·066
C(20)	−0·094	C(20′)	0·094
N(4)	−0·039	N(4′)	0·040
N(5)	0·048	N(5′)	−0·048

Distances of TCNE atoms from the carbazole plane (*a*)

C(15)	−3·116	C(15′)	−3·335
C(16)	−3·199	C(16′)	−3·271
C(17)	−3·177	C(17′)	−3·294
N(2)	−2·985	N(2′)	−3·485
N(3)	−3·253	N(3′)	−3·218
C(18)	−3·202	C(18′)	−3·269
C(19)	−3·109	C(19′)	−3·362
C(20)	−3·381	C(20′)	−3·090
N(4)	−3·169	N(4′)	−3·301
N(5)	−3·284	N(5′)	−3·186

Dihedral angles (°)

Planes	Angle	Planes	Angle
(*b*) and (*c*)	2·00	(*a*) and (*e*)	4·47
(*b*) and (*d*)	2·48	(*a*) and (*f*)	2·66

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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 33774 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The bond lengths and angles of the carbazole unit are, in general, in good agreement with those reported for carbazole itself (Kurahashi, Fukuyo & Shimada, 1969) apart from N(1)–C(1), C(10)–C(11) and C(6)–C(12), all of which appear to be significantly shorter than expected, and the angles C(2)–C(3)–C(4), which is smaller, and C(3)–C(4)–C(5) and C(7)–C(8)–C(9), which are larger, than expected. These differences may be partly real (due to the introduction of the ethyl group) and partly errors due to the difficulty of refining a disordered structure. The disorder, and particularly the incomplete resolution of the CN groups of the two half-weight molecules of TCNE, means that the TCNE atomic positions are inaccurately determined and no valid comparison can be made with previously published dimensions.

The TCNE molecules in orientations *A* and *B* have average occupation factors of 0·62 and 0·38 respectively, and an attempt has been made to explain this difference semi-quantitatively on the basis of Mulliken's (1956) 'overlap and orientation principle'. This postulates that the relative orientations of donor and acceptor

Table 3. *Close intermolecular contacts* (Å)

The figures in parentheses are standard deviations in the last digit.

(*a*) TCNE to 9-ethylcarbazole (<3·4 Å, within the same sandwich)

TCNE *A*		TCNE *B*	
C(15$^{\mathrm{i}}$)···C(12$^{\mathrm{i}}$)	3·373 (3)	C(18$^{\mathrm{i}}$)···C(6$^{\mathrm{i}}$)	3·177 (5)
C(16$^{\mathrm{i}}$)···C(12$^{\mathrm{i}}$)	3·155 (3)	C(18$^{\mathrm{i}}$)···C(12$^{\mathrm{i}}$)	3·344 (5)
C(17$^{\mathrm{i}}$)···C(1$^{\mathrm{i}}$)	3·308 (2)	C(18$^{\mathrm{ii}}$)···C(7$^{\mathrm{i}}$)	3·309 (5)
C(17$^{\mathrm{i}}$)···C(6$^{\mathrm{i}}$)	3·379 (3)	C(18$^{\mathrm{ii}}$)···C(12$^{\mathrm{i}}$)	3·369 (5)
C(15$^{\mathrm{ii}}$)···N(1$^{\mathrm{i}}$)	3·308 (3)	C(19$^{\mathrm{ii}}$)···N(1$^{\mathrm{i}}$)	3·322 (5)
C(16$^{\mathrm{ii}}$)···C(1$^{\mathrm{i}}$)	3·343 (3)	C(20$^{\mathrm{ii}}$)···C(7$^{\mathrm{i}}$)	3·239 (4)
C(16$^{\mathrm{ii}}$)···C(6$^{\mathrm{i}}$)	3·385 (3)	C(20$^{\mathrm{ii}}$)···C(8$^{\mathrm{i}}$)	3·325 (4)
N(3$^{\mathrm{i}}$)···C(3$^{\mathrm{i}}$)	3·373 (3)	C(20$^{\mathrm{ii}}$)···C(12$^{\mathrm{i}}$)	3·336 (5)
N(3$^{\mathrm{ii}}$)···C(9$^{\mathrm{i}}$)	3·295 (3)	N(5$^{\mathrm{i}}$)···C(3$^{\mathrm{i}}$)	3·369 (5)
		N(5$^{\mathrm{ii}}$)···C(9$^{\mathrm{i}}$)	3·268 (5)
		N(5$^{\mathrm{ii}}$)···C(10$^{\mathrm{i}}$)	3·382 (5)

(*b*) TCNE to 9-ethylcarbazole (<3·6 Å, between different sandwiches)

N(2$^{\mathrm{iii}}$)···C(9$^{\mathrm{i}}$)	3·454 (3)	N(5$^{\mathrm{v}}$)···C(13$^{\mathrm{i}}$)	3·477 (5)
N(4$^{\mathrm{iii}}$)···C(9$^{\mathrm{i}}$)	3·461 (5)	N(5$^{\mathrm{v}}$)···C(14$^{\mathrm{i}}$)	3·486 (5)
N(4$^{\mathrm{iv}}$)···C(14$^{\mathrm{i}}$)	3·591 (5)		

(*c*) Between two 9-ethylcarbazole molecules (<3·6 Å, in different sandwiches)

C(7$^{\mathrm{vi}}$)···C(5$^{\mathrm{i}}$)	3·577 (2)	C(12$^{\mathrm{vi}}$)···C(5$^{\mathrm{i}}$)	3·552 (2)

Superscripts indicate symmetrically equivalent positions as follows:

(i)	x,y,z	(iv)	$\frac{1}{2}-x, \frac{1}{2}+y, z$
(ii)	$1-x, -y, -z$	(v)	$x-\frac{1}{2}, \frac{1}{2}-y, -z$
(iii)	$x-1, y, z$	(vi)	$\frac{1}{2}+x, y, \frac{1}{2}-z$.

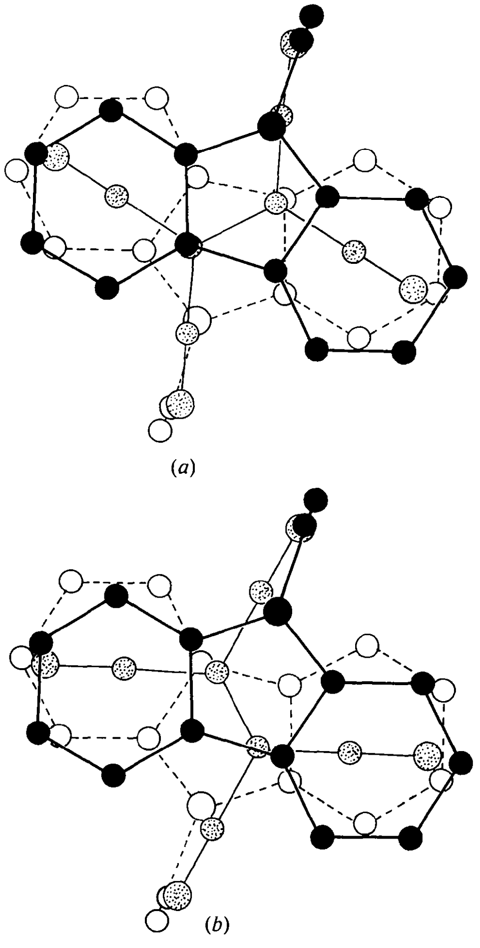

Fig. 2. Overlap within the group of three molecules, with (*a*) TCNE in orientation *A*, (*b*) TCNE in orientation *B*.

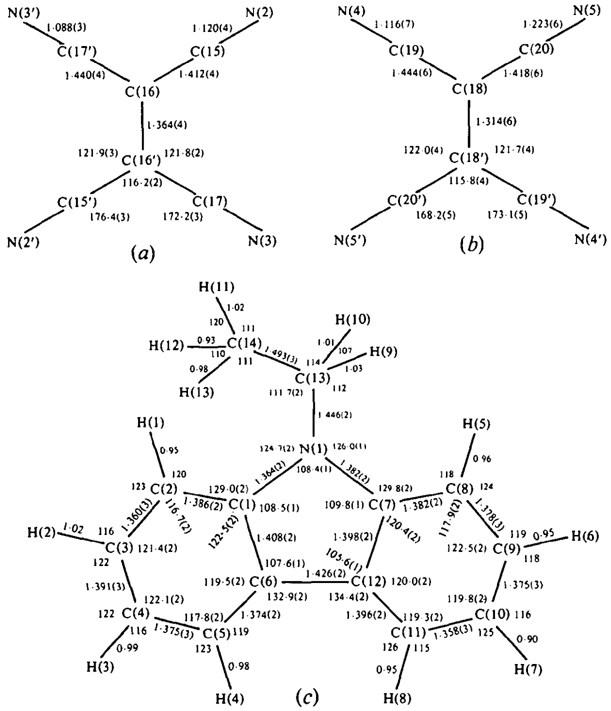

Fig. 3. Bond lengths (Å) and angles (°) for (*a*) TCNE in orientation *A*, (*b*) TCNE in orientation *B*, (*c*) 9-ethylcarbazole. For bonds involving H, $\sigma \simeq 0{\cdot}03$ Å for lengths and 2–4° for angles.

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)°, $Z = 1$. 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,