

The Crystal Structures of Free Radical Salts and Complexes.

VI. [1,4-Di-(*N*-pyridinium methyl)benzene]²⁺(7,7,8,8-Tetracyanoquinodimethane)²⁻

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The 4:1 complex formed between 7,7,8,8-tetracyanoquinodimethane (TCNQ) and 1,4-di-(*N*-pyridinium methyl)benzene is triclinic, space group $P\bar{1}$ with $a = 7.5340$, $b = 14.241$, $c = 14.099$ Å, $\alpha = 104.395$, $\beta = 94.635$, $\gamma = 111.223^\circ$, $Z = 1$. The structure was solved by the Patterson method and refined to $R = 0.054$ for 3255 reflexions. TCNQ molecules and anions are packed plane-to-plane in columns parallel to b with the negative charge localized on specific TCNQ sites.

Introduction

A common feature of TCNQ salts from structures so far determined (Shibaeva & Atovmyan, 1972) is a parallel plane-to-plane stacking of TCNQ moieties in columns resulting in an electrical anisotropy (Melby, Harder, Hertler, Mahler, Benson & Mochel, 1962) usually with the highest conductivity along the stack. A thermally activated mobility has been suggested (Schegolev, 1972) to be the appropriate description of carrier transport in these systems. In *N,N'*-diethyl-4,4'-bipyridylium (TCNQ)₄ (Ashwell, Eley, Wallwork & Willis, 1974*a*), however, alternate TCNQ and cationic planes result in isotropic band model conductivities along b and c (in the plane) with a thermally activated mobility between planes. A band model conductivity has also been suggested to occur along one crystal axis in *N,N'*-di-(*n*-propyl)-4,4'-bipyridylium (TCNQ)₄ (Ashwell, Eley, Wallwork & Willis, 1974*b*).

In an attempt to elucidate the relationship between structure and electrical properties several TCNQ salts of diquaternized heterocyclic bases are at present under investigation.

Experimental

Crystal data

(C₁₈H₁₈N₂)(C₁₂H₄N₄)₄, $M_r = 1079.1$, Triclinic, $a = 7.5340$ (8), $b = 14.241$ (1), $c = 14.099$ (2) Å, $\alpha = 104.395$ (6), $\beta = 94.635$ (8), $\gamma = 111.223$ (6)[°]; $U = 1341.21$ Å³, $D_m = 1.31$ g cm⁻³, $Z = 1$, $D_c = 1.336$ g cm⁻³; $F(000) = 556$. Mo $K\alpha$ ($\lambda = 0.71069$ Å), $\mu = 0.92$ cm⁻¹. Space group $P\bar{1}$ (assumed).

Black plate-like crystals of the complex were deposited when a warm acetonitrile solution (200 ml) of TCNQ (0.2 g) and LiTCNQ (0.2 g) was added to a warm aqueous solution (10 ml) of 1,4-di-(*N*-pyridinium methyl)benzene dibromide (0.2 g), and allowed to cool slowly. The space group and cell constants were obtained initially from oscillation and Weissenberg photographs: The cell dimensions were subsequently refined on a Hilger and Watts computer-controlled, four-circle diffractometer. Intensities were collected from a

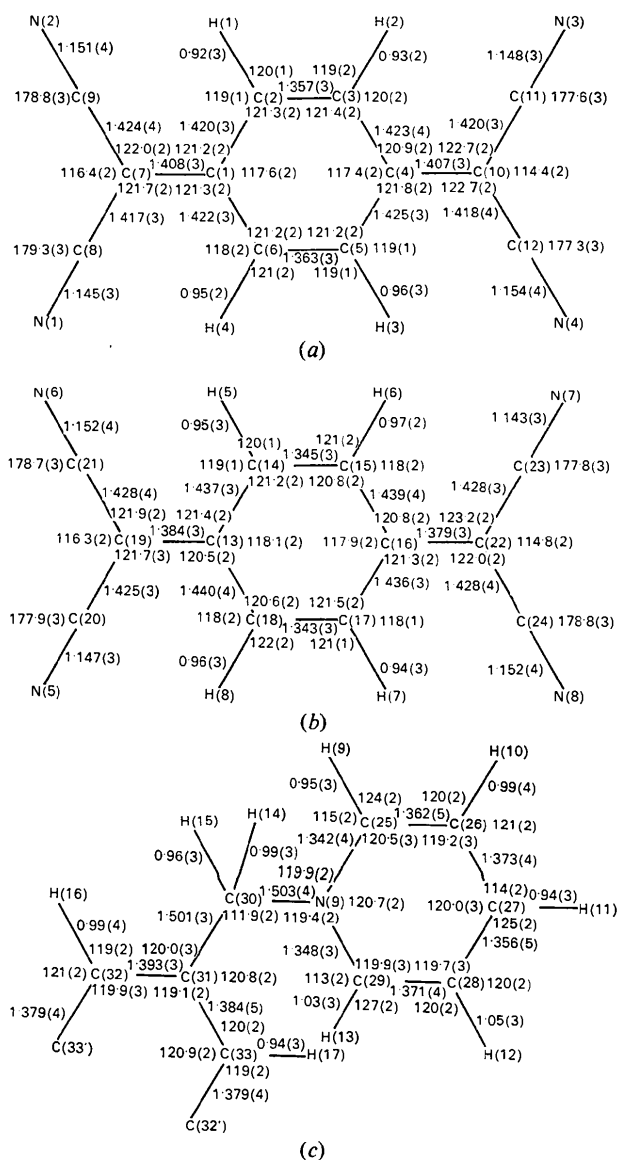


Fig. 1. Bond lengths (Å), angles ([°]) and their e.s.d.'s of (a) TCNQ(A), (b) TCNQ(B) and (c) the cation.

crystal of dimensions $0.8 \times 0.5 \times 0.02$ mm with a $\theta/2\theta$ scan, a scintillation counter and Mo $K\alpha$ radiation. 4701 reflexions were measured of which significant counts were recorded for 3255. The intensities were corrected for Lorentz and polarisation factors but not for absorption.

Structure determination

The structure was solved from a Patterson synthesis and refined by block-diagonal least-squares calculations with 2032 reflexions with counts greater than 200. Refinement of positional and isotropic thermal parameters of the 42 non-hydrogen atoms, with unit weights, gave $R=0.106$.

Positional parameters of the 17 hydrogen atoms were calculated and confirmed by a difference synthesis. Block-diagonal least-squares refinement with anisotropic and isotropic thermal parameters for the non-

hydrogen and hydrogen atoms respectively, and the weighting scheme $1/w = 1.0 + (|F_o| - B)/A$ where $A = 11.0$, $B = 6.0$ and $|F_o|$ is on the absolute scale gave $R = 0.043$. Further refinement with all 3255 significant reflexions and $A = 9.5$, $B = 5.0$ gave the final $R = 0.054$. Four weak reflexions were omitted from the last cycles of refinement. Scattering factors were taken from *International Tables for X-ray Crystallography* (1962). The final positional and thermal parameters are listed in Tables 1 and 2. Least-squares planes were calculated through the cation and TCNQ moieties and the results are summarized in Table 3.*

* The table of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30843 (45 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester, CH1 1NZ, England.

Table 1. Final positional and thermal parameters (all $\times 10^4$) for non-hydrogen atoms

The figures in parentheses indicate standard deviations. Temperature factor = $\exp[-2\pi^2(h^2U_{11}a^{*2} + k^2U_{22}b^{*2} + l^2U_{33}c^{*2} + hkU_{12}a^*b^* + hlU_{13}a^*c^* + klU_{23}b^*c^*)]$.

	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	1137 (3)	1640 (2)	646 (2)	305 (11)	390 (12)	452 (13)	90 (9)	43 (9)	167 (10)
C(2)	-203 (3)	1257 (2)	-267 (2)	284 (11)	458 (13)	521 (13)	135 (9)	85 (9)	161 (11)
C(3)	132 (3)	713 (2)	-1121 (2)	296 (11)	479 (13)	482 (13)	103 (9)	4 (9)	147 (11)
C(4)	1860 (3)	524 (2)	-1143 (2)	296 (10)	385 (12)	468 (13)	101 (9)	76 (9)	155 (10)
C(5)	3210 (3)	912 (2)	-229 (2)	305 (11)	432 (12)	520 (13)	143 (9)	85 (9)	179 (10)
C(6)	2865 (3)	1453 (2)	630 (2)	318 (11)	428 (12)	454 (13)	127 (9)	46 (9)	161 (10)
C(7)	785 (3)	2206 (2)	1531 (2)	320 (11)	456 (12)	441 (12)	132 (9)	71 (9)	172 (10)
C(8)	2108 (3)	2588 (2)	2448 (2)	429 (13)	513 (14)	473 (13)	181 (11)	121 (10)	178 (11)
C(9)	-891 (3)	2447 (2)	1550 (2)	415 (12)	492 (13)	453 (13)	153 (10)	116 (10)	193 (11)
C(10)	2197 (3)	-35 (2)	-2035 (2)	348 (11)	447 (13)	461 (13)	145 (10)	66 (9)	133 (10)
C(11)	914 (3)	-386 (2)	-2963 (2)	437 (13)	563 (15)	516 (14)	199 (11)	116 (11)	120 (12)
C(12)	3919 (3)	-219 (2)	-2095 (2)	461 (13)	484 (13)	457 (13)	187 (11)	87 (10)	140 (11)
C(13)	2960 (3)	4641 (2)	1498 (2)	339 (11)	428 (12)	525 (14)	126 (9)	128 (10)	204 (11)
C(14)	1603 (3)	4247 (2)	574 (2)	331 (11)	492 (13)	539 (14)	189 (10)	129 (10)	225 (11)
C(15)	1949 (3)	3716 (2)	-272 (2)	325 (11)	499 (13)	495 (13)	153 (10)	87 (10)	226 (11)
C(16)	3695 (3)	3522 (2)	-276 (2)	310 (11)	417 (12)	513 (13)	129 (9)	125 (9)	224 (10)
C(17)	5035 (3)	3902 (2)	651 (2)	288 (11)	475 (13)	560 (14)	149 (9)	103 (10)	208 (11)
C(18)	4702 (3)	4441 (2)	1496 (2)	306 (11)	479 (13)	501 (13)	115 (10)	68 (10)	165 (11)
C(19)	2637 (3)	5215 (2)	2304 (2)	393 (12)	499 (14)	549 (14)	157 (10)	138 (11)	177 (11)
C(20)	4028 (4)	5659 (2)	3270 (2)	538 (15)	591 (16)	562 (15)	226 (12)	184 (12)	130 (12)
C(21)	904 (4)	5405 (2)	2398 (2)	517 (14)	575 (15)	605 (16)	243 (12)	187 (12)	164 (13)
C(22)	4060 (3)	2985 (2)	-1145 (2)	328 (11)	467 (13)	508 (13)	149 (10)	129 (10)	212 (11)
C(23)	2766 (3)	2591 (2)	-2083 (2)	411 (12)	601 (15)	523 (14)	241 (11)	165 (11)	206 (12)
C(24)	5795 (3)	2797 (2)	-1175 (2)	397 (12)	544 (14)	539 (14)	186 (11)	137 (11)	223 (12)
C(25)	8097 (4)	2068 (2)	5484 (2)	418 (14)	730 (18)	629 (17)	151 (13)	24 (12)	211 (14)
C(26)	7220 (4)	1580 (3)	6139 (2)	600 (18)	929 (23)	651 (18)	206 (16)	-1 (14)	391 (17)
C(27)	5238 (4)	1214 (2)	6036 (2)	616 (17)	774 (20)	660 (18)	153 (15)	151 (14)	343 (16)
C(28)	4176 (4)	1333 (2)	5285 (2)	454 (14)	734 (18)	675 (18)	204 (13)	133 (13)	243 (14)
C(29)	5094 (4)	1830 (2)	4637 (2)	512 (15)	603 (16)	521 (15)	237 (12)	19 (11)	129 (12)
C(30)	8034 (4)	2750 (2)	4044 (2)	746 (18)	557 (16)	503 (15)	150 (14)	233 (13)	134 (13)
C(31)	9051 (3)	3918 (2)	4535 (2)	446 (13)	530 (14)	434 (13)	151 (11)	125 (10)	134 (11)
C(32)	11024 (4)	4358 (2)	4943 (2)	490 (14)	597 (16)	736 (18)	250 (13)	186 (13)	208 (14)
C(33)	8050 (3)	4570 (2)	4597 (2)	384 (13)	642 (16)	645 (17)	134 (12)	58 (11)	211 (13)
N(1)	3191 (3)	2903 (12)	3184 (2)	619 (14)	824 (17)	520 (13)	278 (12)	-3 (11)	157 (12)
N(2)	-2232 (3)	2656 (2)	1557 (2)	472 (12)	851 (17)	746 (15)	353 (12)	196 (11)	309 (13)
N(3)	-76 (4)	-681 (2)	-3729 (2)	662 (16)	988 (20)	537 (14)	313 (14)	-32 (12)	89 (13)
N(4)	5295 (3)	-386 (2)	-2186 (2)	521 (13)	823 (17)	705 (15)	374 (12)	133 (11)	180 (13)
N(5)	5177 (4)	6042 (2)	3989 (2)	717 (17)	960 (20)	620 (15)	339 (15)	59 (13)	32 (14)
N(6)	-484 (4)	5570 (2)	2412 (2)	612 (15)	916 (19)	903 (19)	433 (14)	232 (13)	194 (15)
N(7)	1772 (3)	2262 (2)	-2847 (2)	605 (14)	943 (19)	605 (15)	363 (13)	90 (11)	214 (13)
N(8)	7189 (3)	2642 (2)	-1216 (2)	458 (12)	890 (17)	818 (17)	351 (12)	206 (12)	296 (14)
N(9)	7040 (3)	2187 (2)	4745 (1)	501 (11)	457 (11)	416 (11)	128 (9)	72 (9)	79 (9)

Description and discussion of the structure

The dimensions of the two crystallographically independent types of TCNQ moiety are shown in Fig. 1 and the average lengths of chemically similar bonds in

Table 2. Final positional and thermal parameters (all $\times 10^3$) for hydrogen atoms

The figures in parentheses indicate standard deviations.

	x/a	y/b	z/c	U
H(1)	-129 (3)	140 (2)	-28 (2)	22 (6)
H(2)	-77 (3)	49 (2)	-170 (2)	22 (6)
H(3)	440 (3)	81 (2)	-22 (2)	19 (6)
H(4)	375 (3)	168 (2)	124 (2)	19 (6)
H(5)	49 (3)	442 (2)	55 (2)	23 (6)
H(6)	106 (3)	349 (2)	-90 (2)	27 (7)
H(7)	613 (3)	373 (2)	66 (2)	23 (6)
H(8)	558 (4)	468 (2)	212 (2)	31 (7)
H(9)	946 (4)	235 (2)	551 (2)	57 (9)
H(10)	801 (5)	149 (3)	668 (2)	63 (10)
H(11)	473 (4)	85 (2)	649 (2)	48 (9)
H(12)	266 (5)	103 (3)	519 (2)	66 (10)
H(13)	445 (4)	197 (2)	404 (2)	42 (8)
H(14)	706 (4)	259 (2)	345 (2)	49 (9)
H(15)	894 (4)	243 (2)	387 (2)	40 (8)
H(16)	1175 (4)	389 (2)	487 (2)	45 (8)
H(17)	674 (4)	429 (2)	430 (2)	39 (8)

Table 3. Details of molecular planes

x, y, z are fractional atomic coordinates.

Molecule A	Molecule B
Equation to the plane: $1.3764x + 11.8581y$ $-6.8388z - 1.6926 = 0$	Equation to the plane: $1.2000x + 11.9626y$ $-7.1458z - 4.8803 = 0$
Distance from the plane	Distance from the plane
C(1) -0.034 Å	C(13) -0.044 Å
C(2) -0.047	C(14) -0.017
C(3) -0.062	C(15) -0.007
C(4) -0.033	C(16) -0.027
C(5) -0.013	C(17) -0.074
C(6) -0.006	C(18) -0.073
C(7) -0.015	C(19) -0.015
C(8) -0.007	C(20) 0.036
C(9) 0.027	C(21) -0.019
C(10) -0.041	C(22) -0.004
C(11) 0.001	C(23) 0.039
C(12) 0.020	C(24) 0.000
N(1) 0.012	N(5) 0.119
N(2) 0.085	N(6) 0.001
N(3) 0.040	N(7) 0.073
N(4) 0.074	N(8) 0.011
Pyridinium ring	Xylyl ring (including centrosymmetrically related atoms)
Equation to the plane: $-2.4011x + 11.4165y$ $+ 5.2751z - 3.3098 = 0$	Equation to the plane: $-1.0854x - 2.4236y$ $+ 7.8410z - 1.6233 = 0$
Distance from the plane	Distance from the plane
C(25) -0.000 Å	C(31) 0.000 Å
C(26) -0.001	C(32) -0.000
C(27) 0.003	C(33) -0.000
C(28) -0.004	
C(29) 0.002	
N(9) -0.000	

Table 4. The dimensions of molecule A compare well with the published data for TCNQ⁻, whereas those of molecule B are intermediate between the dimensions

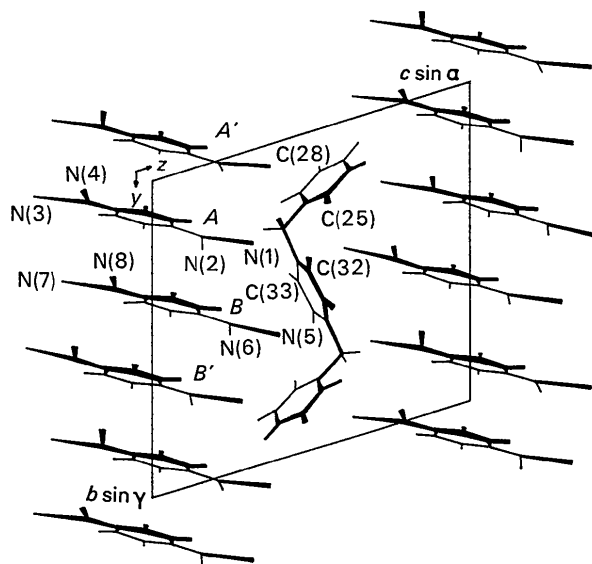


Fig. 2. Crystal structure of 1,4-di-(*N*-pyridinium methyl)-benzene (TCNQ)₄ projected along the x axis.

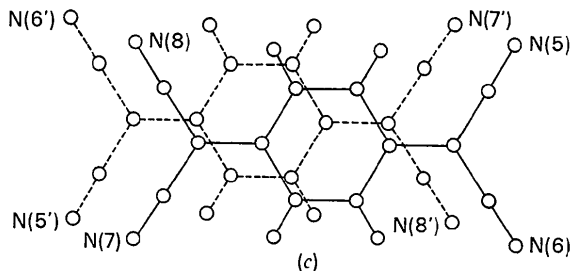
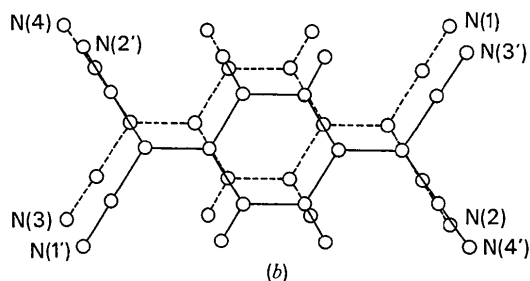
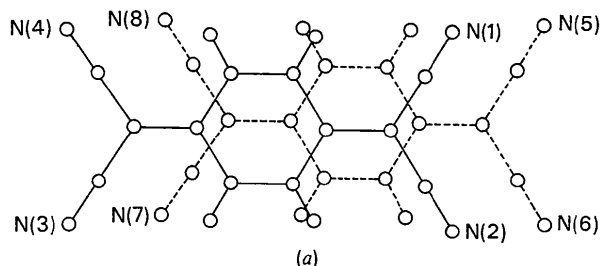


Fig. 3. Types of TCNQ molecular overlap. (a) Molecule A on B. (b) Molecule A on A'. (c) Molecule B on B'.

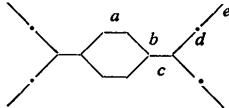
of TCNQ[°] (Long, Sparks & Trueblood, 1965) and TCNQ^{1/2-}. However, when compared with the published data (Table 5) for caesium₂(TCNQ)₃ (Fritchie & Arthur, 1966), trimethylammonium₂(TCNQ)₃ (Kobayashi, Ohashi, Marumo & Saito, 1970), morpholinium₂(TCNQ)₃ (Sundaresan & Wallwork, 1972*a*), and triethylammonium(TCNQ)₂ (Kobayashi *et al.*, 1970) which also contain TCNQ[°] but adjacent to TCNQ⁻, molecule *B* compares favourably with the neutral moiety. A better indication of the localization of charge is obtained by comparing the differences in dimensions between molecules *A* and *B* with those between TCNQ⁻ and TCNQ[°] (Table 4). They are in consistent directions and of similar magnitudes to those between ion and molecule.

Fig. 2 shows a general view of the structure in which TCNQ ions and molecules are stacked in a plane-to-plane manner along *y* giving isolated columns of TCNQ and cations. Within the TCNQ columns the

sequence is TCNQ[°] TCNQ[°] TCNQ⁻ TCNQ⁻ TCNQ[°] TCNQ[°] A similar arrangement has only been observed once before, in triethylammonium (TCNQ)₂ (Kobayashi *et al.*, 1970).

Three types of TCNQ overlap (Fig. 3) are observed in the structure. Between the radical anion *A* and the molecule *B* the overlap is similar to that found in the majority of complexes where the quinonoid double bond of one molecule is placed directly above the ring of the second. The overlaps *AA'* and *BB'*, although similar to others previously published, have not been observed before. Interplanar separations of 3.21, 3.31 and 3.48 Å occur respectively between the quinonoid rings *AB*, *AA'* and *BB'* with a dihedral angle of 0.67° between the rings *A* and *B*. The molecules, however, are not quite planar: the C-(CN)₂ groups are twisted slightly out of the planes of the quinonoid rings and the C-C≡N groups are non-linear. This causes a different average molecular tilt with separations of 3.22,

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



Bond	<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>	<i>e</i>
*TCNQ ⁻	1.362	1.424	1.413	1.417	1.149
†TCNQ [°]	1.346 (4)	1.448 (3)	1.374 (4)	1.440 (3)	1.138 (3)
‡TCNQ ^{1/2-}	1.355	1.433	1.396	1.424	1.145
$\Delta(T^- - T^\circ)$	0.016	-0.024	0.039	-0.023	0.011
Molecule <i>A</i>	1.360	1.423	1.408	1.420	1.150
Molecule <i>B</i>	1.344	1.438	1.382	1.427	1.149
$\Delta(A-B)$	0.016	-0.015	0.026	-0.007	0.001

* Chasseau, Gaultier & Hauw (1972); Chasseau, Gaultier, Hauw & Schvoerer (1972); Fritchie (1966); Hanson (1965); Hoekstra, Spoedler & Vos (1972); Kistenmacher, Phillips & Cowan (1974); Konno & Saito (1974); Sundaresan & Wallwork (1972*b*); Sundaresan & Wallwork (1972*c*).

† Long, Sparks & Trueblood (1965).

‡ Ashwell, Eley, Wallwork & Willis (1974*a*); Chasseau, Gaultier, Hauw & Jaud (1973*a*); Chasseau, Gaultier, Hauw & Jaud (1973*b*); Goldstein, Seff & Trueblood (1968); Hanson (1968); Kobayashi, Marumo & Saito (1971); McPhail, Semeniuk & Chesnut (1971); Sundaresan & Wallwork (1972*d*).

Table 5. Average TCNQ bond lengths (in Å) in complex salts where the charge is localized

		<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>	<i>e</i>
(1) Caesium ₂ ⁺ (TCNQ) ₃ ²⁻	TCNQ ⁻	1.355	1.427	1.410	1.419	1.152
	TCNQ [°]	1.341	1.444	1.371	1.429	1.140
(2) Trimethylammonium ₂ ⁺ (TCNQ) ₃ ²⁻	TCNQ ⁻	1.365	1.411	1.419	1.415	1.147
	TCNQ [°]	1.338	1.441	1.366	1.427	1.138
(3) Morpholinium ₂ ⁺ (TCNQ) ₃ ²⁻	TCNQ ⁻	1.355	1.419	1.415	1.414	1.145
	TCNQ [°]	1.348	1.431	1.391	1.426	1.141
(4) Triethylammonium ⁺ (TCNQ) ₂ ⁻	TCNQ ⁻	1.377	1.433	1.409	1.408	1.159
	TCNQ [°]	1.345	1.444	1.387	1.422	1.152
Mean of (1) to (4)	TCNQ ⁻	1.363	1.423	1.413	1.414	1.151
	TCNQ [°]	1.343	1.440	1.379	1.426	1.143
(5) 1,4-di-(N-pyridinium methyl)-benzene ²⁺ (TCNQ) ₂ ²⁻	TCNQ ⁻	1.360	1.423	1.408	1.420	1.150
	TCNQ [°]	1.344	1.438	1.382	1.427	1.149

(1) Fritchie & Arthur (1965); (2) Kobayashi, Danno & Saito (1973); (3) Sundaresan & Wallwork (1972*a*); (4) Kobayashi, Ohashi, Marumo & Saito (1970); (5) this work.

3.39 and 3.40 Å respectively between AB , AA' and BB' and a dihedral angle of 2.0° between A and B . From either set of separations a pairing of TCNQ° and TCNQ^- is indicated. Short intermolecular contacts are listed in Table 6.

Table 6. Short intermolecular contacts (in Å)

(a) Molecule A to molecule B

$C(1^i)-C(15^i)$	3.393 (4)	$C(7^i)-C(13^i)$	3.269 (3)
$C(1^i)-C(16^i)$	3.315 (3)	$C(7^i)-C(14^i)$	3.382 (4)
$C(2^i)-C(15^i)$	3.286 (3)	$C(8^i)-C(13^i)$	3.387 (4)
$C(3^i)-C(23^i)$	3.365 (4)	$C(8^i)-C(18^i)$	3.321 (4)
$C(4^i)-C(22^i)$	3.291 (3)	$C(9^i)-C(14^i)$	3.268 (4)
$C(4^i)-C(23^i)$	3.393 (4)	$C(11^i)-N(4^i)$	3.392 (4)
$C(5^i)-C(22^i)$	3.385 (4)	$C(12^i)-N(3^i)$	3.390 (4)
$C(5^i)-C(24^i)$	3.346 (4)		
$C(6^i)-C(16^i)$	3.372 (4)		
$C(6^i)-C(17^i)$	3.263 (3)		

(b) Molecule A to molecule A'

$C(1^i)-C(3^{ii})$	3.390 (4)	$C(3^i)-C(6^{ii})$	3.371 (3)
$C(1^i)-C(4^{ii})$	3.373 (3)	$C(7^i)-C(10^{ii})$	3.381 (3)
$C(2^i)-C(5^{ii})$	3.380 (3)		

(c) Other intermolecular contacts

$N(1^i)-C(29^i)$	3.356 (5)	$N(6^i)-C(18^{iv})$	3.376 (3)
$N(3^i)-C(28^{ii})$	3.321 (4)	$N(7^i)-C(25^v)$	3.369 (4)
$N(5^i)-C(29^{iii})$	3.251 (4)	$N(7^i)-C(26^v)$	3.295 (4)
$N(5^i)-C(33^{iii})$	3.280 (4)	$N(8^i)-C(15^{vi})$	3.349 (3)

Superscripts indicate equivalent positions as follows:

(i)	x	y	z
(ii)	$-x$	$-y$	$-z$
(iii)	$1-x$	$1-y$	$1-z$
(iv)	$x-1$	y	z
(v)	$x-1$	y	$z-1$
(vi)	$x+1$	y	z

The cation shows no abnormal dimensions. The angle between the mean planes of the pyridyl and xyllyl rings is 72.8° . The angles that these planes make with $\text{TCNQ}(A)$ are 57.5 and 52.0° and with $\text{TCNQ}(B)$ are 58.1 and 50.8 respectively.

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References

- ASHWELL, G. J., ELEY, D. D., WALLWORK, S. C. & WILLIS, M. R. (1974a). *Proc. Roy. Soc.* In the press.
- ASHWELL, G. J., ELEY, D. D., WALLWORK, S. C. & WILLIS, M. R. (1974b). To be published.
- CHASSEAU, D., GAULTIER, J. & HAUW, C. (1972). *C.R. Acad. Sci. Paris*, **C274**, 1434-1437.
- CHASSEAU, D., GAULTIER, J., HAUW, C. & JAUD, J. (1973a). *C.R. Acad. Sci. Paris*, **C276**, 661-664.
- CHASSEAU, D., GAULTIER, J., HAUW, C. & JAUD, J. (1973b). *C.R. Acad. Sci. Paris*, **C276**, 751-753.
- CHASSEAU, D., GAULTIER, J., HAUW, C. & SCHVOERER, M. (1972). *C.R. Acad. Sci. Paris*, **C275**, 1491-1493.
- FRITCHIE, C. J. (1966). *Acta Cryst.* **20**, 892-898.
- FRITCHIE, C. J. & ARTHUR, P. (1966). *Acta Cryst.* **21**, 139-145.
- GOLDSTEIN, P., SEFF, K. & TRUEBLOOD, K. N. (1968). *Acta Cryst.* **B24**, 778-791.
- HANSON, A. W. (1965). *Acta Cryst.* **19**, 610-613.
- HANSON, A. W. (1968). *Acta Cryst.* **B24**, 768-778.
- HOEKSTRA, A., SPOEDLER, T. & VOS, A. (1972). *Acta Cryst.* **B28**, 14-25.
- International Tables for X-ray Crystallography* (1962). Vol. III, pp. 202-207. Birmingham: Kynoch Press.
- KISTENMACHER, T. J., PHILLIPS, T. E. & COWAN, D. O. (1974). *Acta Cryst.* **B30**, 763-768.
- KOBAYASHI, H., DANNO, T. & SAITO, Y. (1973). *Acta Cryst.* **B29**, 2693-2699.
- KOBAYASHI, H., MARUMO, F. & SAITO, Y. (1971). *Acta Cryst.* **B27**, 373-378.
- KOBAYASHI, H., OHASHI, Y., MARUMO, F. & SAITO, Y. (1970). *Acta Cryst.* **B26**, 459-467.
- KONNO, M. & SAITO, Y. (1974). *Acta Cryst.* **B30**, 1294-1299.
- LONG, R. E., SPARKS, R. A. & TRUEBLOOD, K. N. (1965). *Acta Cryst.* **18**, 932-939.
- MCPHAIL, A. T., SEMENIUK, G. M. & CHESNUT, D. B. (1971). *J. Chem. Soc. (A)*, pp. 2174-2180.
- MELBY, L. R., HARDER, R. J., HERTLER, W. R., MAHLER, W., BENSON, R. E. & MOCHEL, W. E. (1962). *J. Amer. Chem. Soc.* **84**, 3374-3387.
- SCHEGOLEV, I. F. (1972). *Phys. Stat. Sol.* **12**, 9-45.
- SHIBAeva, R. P. & ATOVMyAN, L. O. (1972). *Zh. Strukt. Khim.* **13**, 546-566.
- SUNDARESAN, T. & WALLWORK, S. C. (1972a). *Acta Cryst.* **B28**, 491-497.
- SUNDARESAN, T. & WALLWORK, S. C. (1972b). *Acta Cryst.* **B28**, 3065-3074.
- SUNDARESAN, T. & WALLWORK, S. C. (1972c). *Acta Cryst.* **B28**, 3507-3511.
- SUNDARESAN, T. & WALLWORK, S. C. (1972d). *Acta Cryst.* **B28**, 1163-1169.