

The Crystal Structures of Free Radical Salts and Complexes.

VII. [1,2-Di(*N*-ethyl-4-pyridinium)ethylene]²⁺(7,7,8,8-Tetracyanoquinodimethane)₄²⁻

BY G. J. ASHWELL, D. D. ELEY, R. J. FLEMING,* S. C. WALLWORK AND M. R. WILLIS
Department of Chemistry, University of Nottingham, Nottingham NG7 2RD, England

(Received 4 March 1976; accepted 29 April 1976)

[1,2-Di(*N*-ethyl-4-pyridinium)ethylene]²⁺(7,7,8,8-tetracyanoquinodimethane)₄²⁻, (DEPE)²⁺(TCNQ)₄²⁻, crystallizes in two forms: a metallic form (DEPE)²⁺(TCNQ)₄²⁻ I with a high electrical conductivity of 150–2200 Ω⁻¹ cm⁻¹ and a semiconducting form (DEPE)²⁺(TCNQ)₄²⁻ II with an intermediate conductivity of 10⁻³ Ω⁻¹ cm⁻¹, both measured at 300 K along the TCNQ stacking direction. Evidence of structural differences between forms I and II has been obtained from X-ray powder photographs. (DEPE)²⁺(TCNQ)₄²⁻ II is triclinic, space group *P* $\bar{1}$ with $a=7.964$, $b=15.549$, $c=16.200$ Å, $\alpha=123.46$, $\beta=125.55$, $\gamma=76.00^\circ$, $Z=1$. The structure was solved by the Patterson method and refined to $R=0.073$ for 3017 reflexions. The mean dimensions of chemically similar bonds of the two crystallographically independent TCNQ moieties indicate a delocalization of charge.

Introduction

In an attempt to elucidate the relation between crystal structure and electrical properties (Ashwell, Eley, Wallwork & Willis, 1975*a, b*) several TCNQ salts of bipyridilium cations are at present under investigation. One such complex, (DEPE)²⁺(TCNQ)₄²⁻, has two crystallographic forms with vastly differing electrical (Ashwell, Eley & Willis, 1976) and magnetic properties (Ashwell, Eley, Willis & Woodward, 1976). The electrical conductivity of (DEPE)²⁺(TCNQ)₄²⁻ I is unique for any organic material. On cooling from room temperature to 30 mK (Ashwell, Eley & Willis, 1976) the conductivity remains metallic and shows a monotonic increase, with $\sigma_{30\text{mK}}/\sigma_{\text{RT}}=3.7$. The conductivity of (DEPE)²⁺(TCNQ)₄²⁻ II, however, varies as $\exp(-E_A/kT)$ where $E_A=0.26$ eV. The present paper reports the crystal structure determination of form II.

Experimental

Crystal data

(DEPE)²⁺(TCNQ)₄²⁻ II: (C₁₆H₂₀N₂)(C₁₂H₄N₄)₄, $M_r=1057.1$, triclinic; $a=7.964$ (2), $b=15.549$ (2), $c=16.200$ (2) Å; $\alpha=123.46$ (3), $\beta=125.55$ (3), $\gamma=76.00$ (1) $^\circ$; $U=1352.5$ Å³, $Z=1$, $D_c=1.298$ g cm⁻³; $F(000)=546$; Mo $K\alpha$ ($\lambda=0.71069$ Å), $\mu=0.89$ cm⁻¹; space group *P* $\bar{1}$ (assumed.)

Black crystals of the complex were deposited when a warm acetonitrile solution (200 ml) of TCNQ (0.5 g) was added to an aqueous solution (10 ml) of 1,2-di(*N*-ethyl-4-pyridinium)ethylene diiodide (0.2 g) and allowed to cool slowly. This preparation yielded either metallic or semiconducting crystals or occasionally mixtures of

the two forms. The stoichiometry was determined by spectral analysis (Ashwell, Eley & Willis, 1975). The space group and cell constants of (DEPE)²⁺(TCNQ)₄²⁻ II were obtained initially from oscillation and Weissenberg photographs. The cell dimensions were subsequently refined on a Hilger & Watts computer-controlled, four-circle diffractometer. Intensities were collected on this diffractometer from a crystal, 0.5 × 0.5 × 0.15 mm, with a $\theta/2\theta$ scan, a scintillation counter and Mo $K\alpha$ radiation. 5923 reflexions were measured of which significant counts were recorded for 3017. The intensities were corrected for Lorentz and polarization factors but not for absorption.

X-ray powder photographs and powder diffractometer traces of microcrystalline specimens of the metallic and semiconducting forms were obtained on a Philips powder diffractometer using Cu $K\alpha$ radiation.

Structure determination

The structure of (DEPE)²⁺(TCNQ)₄²⁻ II was solved from a Patterson synthesis and refined by block-diagonal least squares with 3017 significant reflexions. Refinement of the positional and isotropic thermal parameters of the 41 non-H atoms, with unit weights, gave $R=0.12$. Positional parameters of the aromatic H atoms were calculated and confirmed by a difference synthesis. The atomic coordinates of the ethyl H atoms were not obvious from the difference map and all attempts to locate them failed. This is presumed to result from hindered rotation of the alkyl C atoms about the C–C and C–N single bonds. The H atom attached to the ethylene C was also not located. These H atoms were therefore not included in the refinement. Block-diagonal, least-squares refinement with anisotropic and isotropic thermal parameters for the non-H and H atoms respectively, and the weighting scheme $w=(A/|F_o|)^2$ for $A>|F_o|$, otherwise $w=1$, where $A=16$

* Present address: Department of Physics, Monash University, Clayton, Victoria, Australia.

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

The figures in parentheses indicate standard deviations. Temperature factor:

$$\exp[-2\pi^2(h^2U_{11}a^{*2} + k^2U_{22}b^{*2} + l^2U_{33}c^{*2} + 2hkU_{12}a^*b^* + 2hlU_{13}a^*c^* + 2klU_{23}b^*c^*)].$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃
C(1)	961 (6)	1275 (3)	1120 (3)	363 (20)	414 (22)	428 (22)	18 (17)	235 (18)	186 (19)
C(2)	-902 (6)	1378 (3)	204 (4)	331 (19)	483 (24)	506 (25)	60 (17)	250 (19)	262 (21)
C(3)	-971 (6)	1321 (3)	-677 (4)	305 (19)	493 (24)	481 (24)	85 (17)	208 (18)	276 (20)
C(4)	853 (6)	1176 (3)	-700 (4)	371 (20)	421 (23)	457 (23)	67 (17)	247 (18)	211 (19)
C(5)	2710 (6)	1076 (3)	224 (4)	309 (19)	515 (25)	483 (23)	65 (17)	232 (18)	264 (20)
C(6)	2778 (6)	1112 (3)	1095 (4)	303 (19)	514 (25)	447 (23)	68 (17)	180 (18)	272 (21)
C(7)	1016 (6)	1295 (3)	2011 (4)	375 (20)	460 (24)	474 (24)	23 (17)	257 (19)	207 (20)
C(8)	2832 (7)	1151 (4)	2911 (4)	542 (26)	580 (28)	580 (28)	52 (21)	369 (23)	301 (24)
C(9)	-750 (7)	1465 (4)	2080 (4)	449 (23)	607 (28)	495 (25)	25 (20)	270 (21)	247 (23)
C(10)	805 (6)	1127 (3)	-1594 (3)	339 (20)	534 (26)	439 (23)	93 (18)	226 (18)	249 (21)
C(11)	-1032 (7)	1210 (4)	-2556 (4)	510 (25)	582 (28)	530 (26)	128 (21)	348 (22)	272 (23)
C(12)	2585 (7)	990 (4)	-1642 (4)	446 (24)	757 (32)	497 (26)	133 (22)	291 (21)	340 (24)
C(13)	2039 (6)	3640 (3)	1329 (4)	378 (20)	458 (24)	465 (23)	58 (17)	259 (19)	229 (20)
C(14)	103 (6)	3708 (3)	402 (4)	382 (21)	465 (24)	513 (24)	78 (18)	281 (19)	264 (20)
C(15)	-49 (6)	3699 (3)	-477 (4)	406 (21)	463 (24)	529 (25)	93 (18)	309 (20)	268 (20)
C(16)	1770 (6)	3639 (3)	-492 (4)	435 (22)	491 (25)	523 (25)	74 (19)	298 (20)	261 (21)
C(17)	3688 (6)	3555 (4)	422 (4)	383 (21)	593 (27)	526 (26)	54 (19)	273 (20)	279 (23)
C(18)	3827 (6)	3546 (3)	1293 (4)	358 (21)	522 (25)	499 (24)	31 (18)	243 (19)	253 (21)
C(19)	2182 (6)	3682 (3)	2246 (4)	395 (21)	496 (25)	483 (24)	78 (18)	262 (19)	266 (21)
C(20)	4068 (7)	3626 (4)	3184 (4)	541 (26)	608 (29)	563 (27)	105 (21)	362 (23)	323 (24)
C(21)	439 (7)	3860 (4)	2332 (4)	530 (25)	600 (28)	551 (27)	144 (21)	356 (22)	338 (24)
C(22)	1613 (7)	3678 (4)	-1368 (4)	459 (24)	635 (29)	520 (26)	49 (21)	293 (21)	308 (23)
C(23)	-317 (7)	3744 (4)	-2280 (4)	654 (29)	610 (28)	580 (28)	108 (23)	430 (25)	311 (25)
C(24)	3375 (7)	3689 (4)	-1388 (4)	552 (27)	885 (37)	587 (29)	75 (25)	366 (24)	394 (28)
C(25)	104 (7)	2881 (4)	5335 (5)	503 (26)	728 (34)	784 (35)	162 (24)	404 (26)	430 (29)
C(26)	-715 (7)	2021 (4)	5048 (5)	525 (27)	738 (34)	765 (25)	89 (24)	392 (26)	403 (29)
C(27)	476 (8)	1246 (4)	5160 (4)	689 (30)	696 (32)	505 (26)	-81 (24)	356 (24)	242 (24)
C(28)	2533 (8)	1356 (4)	5512 (5)	695 (31)	632 (32)	651 (31)	193 (25)	422 (27)	365 (27)
C(29)	3297 (7)	2236 (4)	5782 (4)	453 (24)	681 (31)	646 (30)	114 (22)	325 (23)	352 (26)
C(30)	-540 (8)	340 (4)	4885 (5)	636 (32)	820 (39)	613 (31)	204 (25)	403 (28)	344 (28)
C(31)	2262 (15)	3924 (6)	4943 (7)	2158 (89)	1045 (56)	939 (51)	-476 (56)	787 (57)	434 (45)
C(32)	2934 (8)	3979 (4)	6038 (5)	686 (32)	574 (31)	793 (36)	18 (25)	436 (29)	329 (28)
N(1)	4269 (6)	1023 (4)	3636 (4)	606 (25)	1061 (36)	679 (27)	162 (24)	368 (22)	551 (27)
N(2)	-2153 (6)	1604 (4)	2152 (4)	566 (25)	1056 (36)	786 (30)	74 (24)	451 (24)	430 (28)
N(3)	-2463 (6)	1280 (4)	-3325 (4)	614 (26)	999 (35)	625 (27)	265 (24)	331 (23)	494 (27)
N(4)	4008 (6)	891 (4)	-1683 (4)	542 (25)	1303 (43)	804 (32)	215 (26)	448 (25)	588 (32)
N(5)	5599 (6)	3581 (4)	3943 (4)	584 (25)	1029 (36)	684 (28)	181 (24)	316 (23)	528 (28)
N(6)	-991 (6)	4007 (4)	2384 (4)	604 (25)	1043 (36)	769 (29)	228 (24)	485 (24)	518 (28)
N(7)	-1907 (7)	3798 (4)	-3016 (4)	726 (28)	910 (33)	682 (27)	209 (24)	421 (24)	492 (26)
N(8)	4804 (7)	3700 (5)	-1388 (4)	696 (30)	1507 (50)	879 (34)	95 (30)	527 (28)	657 (36)
N(9)	2091 (5)	2997 (3)	5707 (3)	456 (19)	578 (23)	568 (22)	102 (17)	308 (18)	312 (19)

and $|F_o|$ is on the absolute scale, gave $R=0.073$. 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.*

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 4. The averaged bond lengths of molecules *A* and *B* are identical within experimental error. They are

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31854 (29 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

intermediate between those observed for TCNQ (Long, Sparks & Trueblood, 1965) and the radical anion TCNQ⁻ and agree well with the dimensions previously published for TCNQ^{1/2-}. These facts suggest delocalization of negative charge, but this cannot be stated

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

The figures in parentheses indicate standard deviations.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i>
H(1)	-218 (6)	155 (3)	25 (4)	23 (12)
H(2)	-211 (6)	147 (3)	-124 (4)	15 (11)
H(3)	397 (6)	101 (3)	23 (4)	23 (11)
H(4)	405 (6)	104 (3)	172 (3)	14 (10)
H(5)	-125 (7)	378 (4)	40 (4)	52 (15)
H(6)	-124 (8)	382 (4)	-101 (4)	10 (10)
H(7)	492 (7)	352 (4)	39 (4)	34 (14)
H(8)	516 (7)	349 (4)	190 (4)	39 (14)
H(9)	-63 (8)	351 (4)	527 (5)	84 (17)
H(10)	-232 (9)	195 (5)	475 (5)	80 (20)
H(11)	347 (9)	83 (4)	559 (5)	65 (18)
H(12)	468 (6)	241 (3)	608 (4)	30 (12)

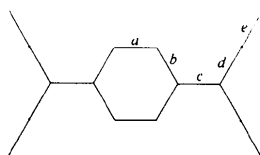
with certainty in view of the rather large standard deviations of the individual dimensions.

Table 3. *Details of molecular planes*

x, y, z are fractional atomic coordinates.

Molecule <i>A</i>		Molecule <i>B</i>	
Equation to the plane: $1.1044x + 12.8633y$ $- 0.6324z - 1.6449 = 0$		Equation to the plane: $0.5534x + 12.8142y$ $- 0.16483z - 4.8346 = 0$	
Distances from the plane (Å)		Distances from the plane (Å)	
C(1)	0.030	C(13)	-0.080
C(2)	0.015	C(14)	-0.084
C(3)	-0.010	C(15)	-0.089
C(4)	0.006	C(16)	-0.065
C(5)	0.024	C(17)	-0.082
C(6)	0.024	C(18)	-0.100
C(7)	0.006	C(19)	-0.033
C(8)	-0.035	C(20)	-0.016
C(9)	0.025	C(21)	0.098
C(10)	-0.005	C(22)	-0.009
C(11)	-0.041	C(23)	-0.017
C(12)	0.017	C(24)	0.102
N(1)	-0.087	N(5)	-0.001
N(2)	0.044	N(6)	0.206
N(3)	-0.061	N(7)	-0.024
N(4)	0.050	N(8)	0.195
Pyridinium ring			
Equation to the plane: $-2.4299x - 2.1807y$ $+ 14.0351z - 6.8343 = 0$			
Distances from the plane (Å)			
C(25)	-0.001	C(28)	-0.009
C(26)	-0.016	C(29)	-0.008
C(27)	0.021	N(9)	0.013

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



Bond	<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>	<i>e</i>
TCNQ *	1.346	1.448	1.374	1.440	1.138
TCNQ †	1.362	1.424	1.413	1.417	1.149
TCNQ ^{1/2} ‡	1.355	1.433	1.396	1.424	1.145
$\Delta(T^- - T^0)$	0.016	-0.024	0.039	-0.023	0.011
TCNQ(<i>A</i>)	1.350	1.426	1.394	1.426	1.144
TCNQ(<i>B</i>)	1.353	1.432	1.386	1.419	1.148
$\Delta(B-A)$	0.003	0.006	-0.008	-0.007	0.004

* Long, Sparks & Trueblood (1965)

† Chasseau, Gaultier & Hauw (1972); Chasseau, Gaultier, Hauw & Schvoerer (1972); Fritchier (1966); Hanson (1965); Hoekstra, Spoedler & Vos (1972); Kistenmacher, Phillips & Cowan (1974); Konno & Saito (1974); Sundaresan & Wallwork (1972a).

‡ Ashwell, Eley, Wallwork & Willis (1975a); Ashwell, Diaconu, Eley, Wallwork & Willis (1976); Chasseau, Gaultier, Hauw & Jaud (1973a, b); Goldstein, Seff & Trueblood (1968); Hanson (1968); Kobayashi, Marumo & Saito (1971); McPhail, Semeniuk & Chesnut (1971); Sundaresan & Wallwork (1972b).

Fig. 2 shows three views of the structure projected along each of the crystal axes. The TCNQ molecules are stacked plane-to-plane in groups of four with no direct overlap between adjacent tetrads. This gives rise to a series of two-dimensional arrays of TCNQ molecules in the *ab* plane separated by sheets of 1,2-di(*N*-ethyl-4-pyridinium)methylene cations. In the congeners, *N,N'*-diethyl-4,4'-bipyridylium(TCNQ)₄ (Ashwell, Eley, Wallwork & Willis, 1975a, b) and *N,N'*-di(*n*-propyl)-4,4'-bipyridylium(TCNQ)₄ (Ashwell, Diaconu, Eley, Wallwork & Willis, 1976) similar structures have been observed.

Two types of TCNQ overlap (Fig. 3) are observed with interplanar separations of 3.32 and 3.15 Å between the quinonoid rings *AA'* and *AB* respectively. However, when the whole molecule is considered, the

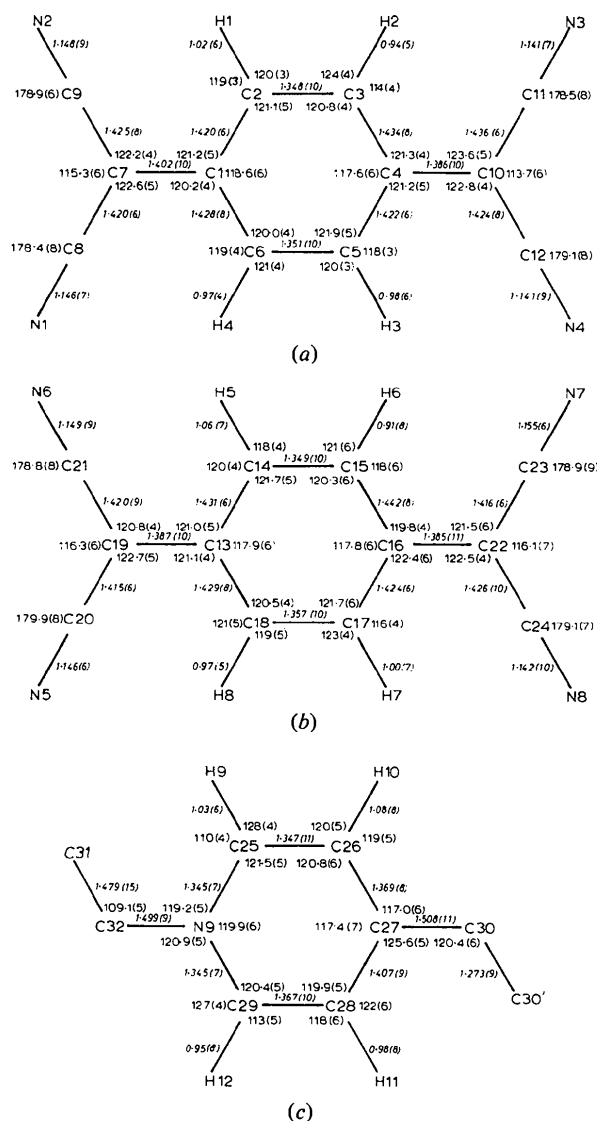


Fig. 1. Bond lengths, bond angles and their e.s.d.'s of (a) TCNQ(*A*), (b) TCNQ(*B*) and (c) the cation.

AA' and AB spacings are changed to 3.29 and 3.24 Å respectively by CN out-of-plane distortions which cause a slightly different average tilt. The dihedral angle between molecules A and B is 4.07° (3.75° between quinonoid rings). Between tetrads short contacts of 3.298 and 3.333 Å occur between atoms C(2)–N(4) and C(5)–N(2) respectively along x and 3.389, 3.378 and 3.388 Å between atoms C(13)–N(7), C(14)–C(23) and C(19)–N(7) respectively along y . In addition several short contacts occur between the cation and TCNQ moieties (Table 5).

The dimensions of the pyridinium ring (Fig. 1) are in agreement with values reported previously (Ashwell,

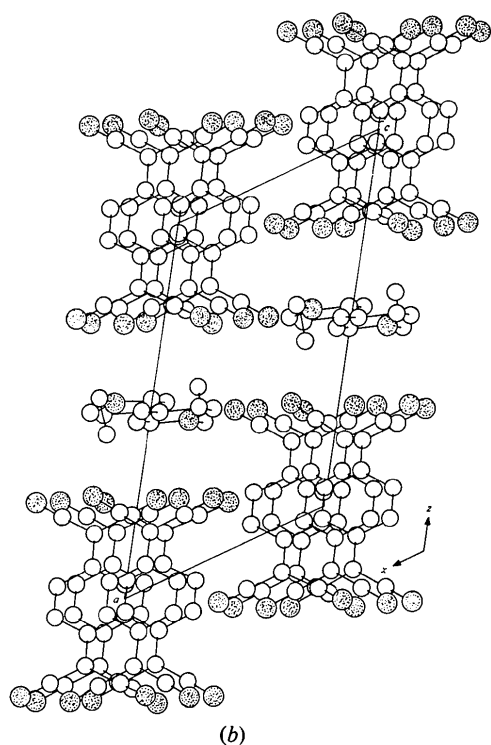
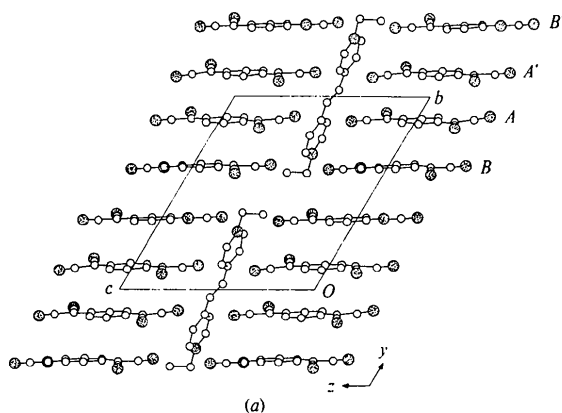


Fig. 2. Projection of the structure of $(\text{DEPE})_2^+(\text{TCNQ})_4^-$ along (a) the a axis, (b) the b axis.

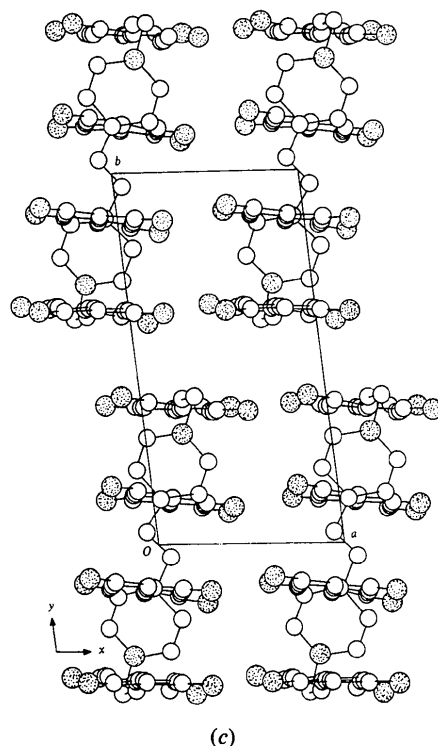


Fig. 2 (cont.) (c) Projection of the structure along the c axis.

Table 5. Short intermolecular contacts (Å)

(a) TCNQ to cation		(b) TCNQ to TCNQ (intratetrad)	
N(1 ⁱ)–C(29 ⁱ)	3.389 (9)	C(1 ⁱ)–C(19 ⁱ)	3.232 (7)
N(3 ⁱ)–C(28 ⁱⁱ)	3.276 (7)	C(2 ⁱ)–C(19 ⁱ)	3.398 (6)
N(3 ⁱ)–C(29 ⁱⁱⁱ)	3.157 (6)	C(2 ⁱ)–C(21 ⁱ)	3.311 (5)
N(5 ⁱ)–C(25 ⁱⁱⁱ)	3.247 (7)	C(3 ⁱ)–C(7 ^v)	3.391 (6)
N(7 ⁱ)–C(25 ^{iv})	3.377 (11)	C(3 ⁱ)–C(8 ^v)	3.354 (5)
N(7 ⁱ)–C(26 ^v)	3.317 (8)	C(3 ⁱ)–C(13 ⁱ)	3.392 (6)
N(8 ⁱ)–C(29 ^v)	3.324 (8)	C(3 ⁱ)–C(14 ⁱ)	3.195 (7)
		C(4 ⁱ)–C(13 ⁱ)	3.260 (5)
		C(4 ⁱ)–C(14 ⁱ)	3.377 (6)
(c) TCNQ to TCNQ (intertetrad)		C(5 ⁱ)–C(18 ⁱ)	3.328 (7)
C(2 ⁱ)–N(4 ^{vi})	3.298 (5)	C(6 ⁱ)–C(20 ⁱ)	3.331 (5)
C(5 ⁱ)–N(2 ^{vi})	3.333 (5)	C(10 ⁱ)–C(16 ⁱ)	3.347 (7)
C(13 ⁱ)–N(7 ^{vii})	3.389 (6)	C(11 ⁱ)–C(15 ⁱ)	3.311 (5)
C(14 ⁱ)–C(23 ^{vii})	3.378 (6)	C(12 ⁱ)–C(17 ⁱ)	3.382 (6)
C(19 ⁱ)–N(7 ^{vii})	3.388 (7)		

Superscripts indicate equivalent positions as follows:

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

Eley, Wallwork & Willis, 1975*a, b*; Ashwell, Diaconu, Eley, Wallwork & Willis, 1976). The angles between the plane through the pyridinium ring and the planes through TCNQ(A) and TCNQ(B) are 64.4 and 64.6° respectively.

X-ray powder photographs of microcrystalline samples of the highly conducting and semiconducting forms of $(\text{DEPE})_2^+(\text{TCNQ})_4^-$ show significant differences, indicating a difference in the crystal structures. 2θ values of the major reflexions of $(\text{DEPE})_2^+$

Table 6. Powder diffraction data for the two forms of $(\text{DEPE})^{2+} (\text{TCNQ})_4^{2-}$

$\lambda = 1.5418 \text{ \AA}$; estimated error in $2\theta = \pm 0.1^\circ$; vw = very weak; w = weak; m = medium; s = strong; vs = very strong.

Form I, metallic		Form II, semiconducting	
2θ	Intensity	2θ	Intensity
6.7	<i>m</i>	6.8	<i>mw</i>
7.2	<i>w</i>	7.8	<i>m</i>
8.2	<i>m</i>	11.4	<i>mw</i>
11.3	<i>m</i>	13.7	<i>s</i>
13.15	<i>w</i>	14.6	<i>s</i>
14.0	<i>vs</i>	15.95	<i>m</i>
14.55	<i>s</i>	18.2	<i>mw</i>
16.4	<i>w</i>	19.6	<i>ms</i>
17.7	<i>w</i>	20.85	<i>m</i>
19.1	<i>vw</i>	21.2	<i>w</i>
20.1	<i>m</i>	23.55	<i>mw</i>
21.0	<i>w</i>	24.4	<i>ms</i>
22.65	<i>w</i>	25.4	<i>ms</i>
23.45	<i>mw</i>	26.1	<i>w</i>
24.9	<i>ms</i>	26.55	<i>ms</i>
25.7	<i>w</i>	27.6	<i>vs</i>
27.0	<i>vs</i>	29.25	<i>w</i>
28.2	<i>m</i>	30.3	<i>vw</i>
29.2	<i>mw</i>	31.2	<i>mw</i>
30.0	<i>vw</i>	32.4	<i>m</i>
30.95	<i>w</i>	33.9	<i>mw</i>
32.9	<i>m</i>	34.9	<i>mw</i>
34.35	<i>mw</i>	36.8	<i>vw</i>
36.05	<i>mw</i>	37.7	<i>vw</i>
37.55	<i>m</i>	38.7	<i>m</i>

$(\text{TCNQ})_4^{2-}$ I and II are listed in Table 6. The crystal structure determination of the highly conducting form is part of our current programme in this field.

We thank the S.R.C. for contributing to the cost of the diffractometer and the Director of the Cripps Computing Centre of Nottingham University for computing facilities.

References

- ASHWELL, G. J., DIACONU, I., ELEY, D. D., WALLWORK, S. C. & WILLIS, M. R. (1976). To be published.
 ASHWELL, G. J., ELEY, D. D., WALLWORK, S. C. & WILLIS, M. R. (1975a). *Proc. Roy. Soc. A* **343**, 461–475.
 ASHWELL, G. J., ELEY, D. D., WALLWORK, S. C. & WILLIS, M. R. (1975b). *Acta Cryst.* **A31**, S205.
 ASHWELL, G. J., ELEY, D. D. & WILLIS, M. R. (1975). *J. Chem. Soc. Faraday II*, **71**, 1227–1232.
 ASHWELL, G. J., ELEY, D. D. & WILLIS, M. R. (1976). *Nature, Lond.* **259**, 201–202.

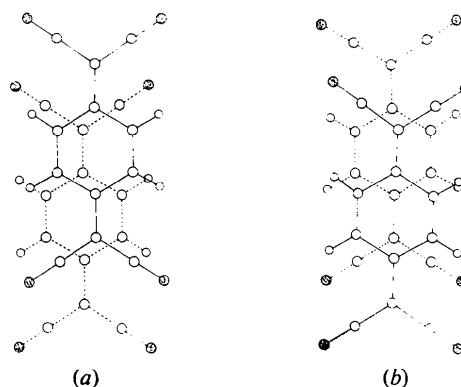


Fig. 3. Types of TCNQ overlap. (a) Molecules *A* and *A'*. (b) Molecules *A* and *B*.

- ASHWELL, G. J., ELEY, D. D., WILLIS, M. R. & WOODWARD, J. (1976). To be published.
 CHASSEAU, D., GAULTIER, J. & HAUW, C. (1972). *C.R. Acad. Sci. Paris, Sér. C*, **274**, 1434–1437.
 CHASSEAU, D., GAULTIER, J., HAUW, C. & JAUD, J. (1973a). *C.R. Acad. Sci. Paris, Sér. C*, **276**, 661–664.
 CHASSEAU, D., GAULTIER, J., HAUW, C. & JAUD, J. (1973b). *C.R. Acad. Sci. Paris, Sér. C*, **276**, 751–753.
 CHASSEAU, D., GAULTIER, J., HAUW, C. & SCHVOERER, M. (1972). *C.R. Acad. Sci. Paris, Sér. C*, **275**, 1491–1493.
 FRITCHIE, C. J. (1966). *Acta Cryst.* **20**, 892–898.
 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. D. (1974). *Acta Cryst.* **B30**, 763–768.
 KOBAYASHI, H., MARUMO, F. & SAITO, Y. (1971). *Acta Cryst.* **B27**, 373–378.
 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.
 SUNDARESAN, T. & WALLWORK, S. C. (1972a). *Acta Cryst.* **B28**, 3507–3511.
 SUNDARESAN, T. & WALLWORK, S. C. (1972b). *Acta Cryst.* **B28**, 1163–1169.