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The Crystal Structures of Free Radical Salts and Complexes.

XIV. (1,1'-Dimethyl-4,4'-bipyridylium)²⁺ (7,7,8,8-Tetracyano-*p*-quinodimethanide)₃²⁻

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Abstract

(1,1'-Dimethyl-4,4'-bipyridylium)²⁺ (7,7,8,8-tetracyano-*p*-quinodimethanide)₃²⁻, C₁₂H₁₄N₂²⁺·(C₁₂H₄N₄)₃²⁻, (DMBP)²⁺(TCNQ)₃²⁻, is triclinic, space group *P*1̄ with *a* = 7.862 (3), *b* = 10.008 (4), *c* = 13.453 (4) Å, *α* = 73.84 (2), *β* = 102.36 (2), *γ* = 96.70 (2)°, *Z* = 1. The structure was refined to *R* = 0.094 for 2770 reflexions. The TCNQ's are stacked plane-to-plane in groups of three with no direct overlap between adjacent triads. Within triads there is a favourable exocyclic double bond to quinonoid ring overlap of adjacent molecules with short mean perpendicular spacings of 3.16 Å.

Introduction

The crystal structure of (DMBP)²⁺(TCNQ)₃²⁻ has been determined as part of a series of structure determinations on conducting bipyridylium–TCNQ salts. In most of these complexes the TCNQ's are stacked plane-to-plane in stoichiometric groups of three or four molecules with little or no direct overlap between adjacent groups. Such non-uniformity of spacing and

overlap gives rise to semiconducting behaviour. The conductivity of compacted pellets of (DMBP)²⁺(TCNQ)₃²⁻ is 10⁻¹ Ω⁻¹ m⁻¹ at 300 K and the activation energy is 0.25 eV.

Experimental

Crystal data

C₁₂H₁₄N₂²⁺·(C₁₂H₄N₄)₃²⁻, *M_r* = 798.8, triclinic, *a* = 7.862 (3), *b* = 10.008 (4), *c* = 13.453 (4) Å, *α* = 73.84 (2), *β* = 102.36 (2), *γ* = 96.70 (2)°, *U* = 991.16 Å³, *Z* = 1, *D_m* = 1.34, *D_c* = 1.34 Mg m⁻³, *F*(000) = 412, Mo *K*_α radiation (*λ* = 0.71069 Å), *μ* = 0.091 mm⁻¹; space group *P*1̄ (assumed).

A microcrystalline complex with majority composition (DMBP)²⁺(TCNQ)₃²⁻ was deposited when a warm acetonitrile solution (200 ml) of 1,1'-dimethyl-4,4'-bipyridylium diiodide (0.2 g) and TCNQ (0.4 g) was allowed to cool slowly to room temperature. Small crystals of (DMBP)²⁺(TCNQ)₃²⁻ were isolated from the microcrystalline products. The space group and cell dimensions were obtained initially from oscillation and Weissenberg photographs with Cu *K*_α radiation. The cell constants were subsequently refined and intensities collected on a Hilger & Watts computer-controlled four-circle diffractometer, with a *θ*/*2θ* scan, a scintil-

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lation 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 from a Patterson synthesis and refined initially by block-diagonal least squares with 2786 significant reflexions [$I > 3\sigma(I)$]. In the later stages, positional parameters of the H atoms were calculated and confirmed by a difference synthesis. Refinement of the H and non-H atoms, with isotropic and anisotropic thermal parameters respectively, and the weighting scheme $1/w = \{1 + [(|F_o| - B)/A]^2\}$, where $|F_o|$ is on the absolute scale, $A = 13$ and $B = 2$, gave a final $R = 0.094$. Sixteen weak reflexions were omitted from the final stages. Scattering factors were taken from *International Tables for X-ray Crystallography* (1974). The final positional parameters are listed in Table 1. Least-squares planes through the cation and TCNQ moieties are listed in Table 2.*

Discussion of the structure

Fig. 1 shows the structure of $(DMBP)^{2+}(TCNQ)_3^{2-}$ projected along **a** and **b**. The TCNQ's are stacked

* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34258 (30 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

plane-to-plane, in stoichiometric groups of three, with the line joining the molecular centres of each triad approximately parallel to $[120]$. There is a favourable exocyclic double bond to quinonoid ring overlap between adjacent molecules within each triad but there

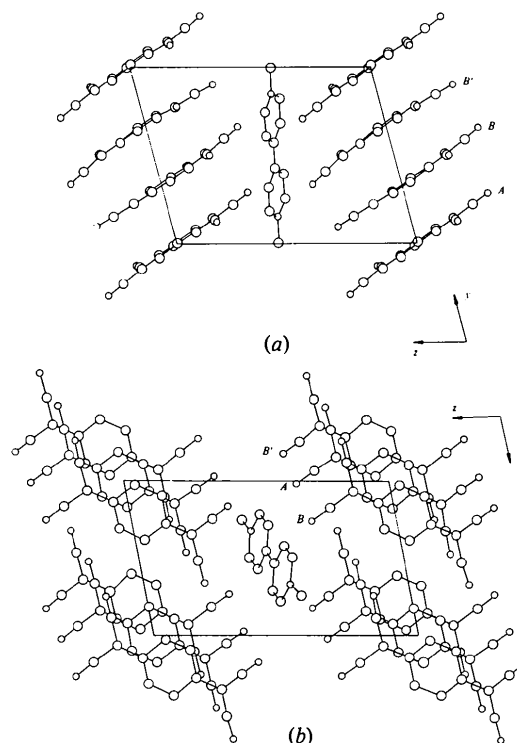


Fig. 1. Projections of $(DMBP)^{2+}(TCNQ)_3^{2-}$ along (a) the **a** axis, and (b) the **b** axis.

Table 1. Final positional parameters ($\times 10^4$, for H $\times 10^3$) of $(DMBP)^{2+}(TCNQ)_3^{2-}$

The figures in parentheses indicate e.s.d.'s.

	<i>x</i>	<i>y</i>	<i>z</i>		<i>x</i>	<i>y</i>	<i>z</i>
C(1)	757 (5)	688 (4)	-888 (3)	C(18)	-1099 (6)	2243 (4)	1434 (3)
C(2)	1777 (5)	-128 (4)	49 (3)	N(3)	1732 (6)	6645 (5)	-3792 (3)
C(3)	1029 (5)	-790 (4)	904 (3)	N(4)	6744 (6)	4982 (5)	-2276 (3)
C(4)	1534 (5)	1390 (4)	-1764 (3)	N(5)	2603 (7)	1009 (5)	3168 (3)
C(5)	558 (6)	2209 (5)	-2698 (3)	N(6)	-2553 (6)	2221 (4)	1468 (3)
C(6)	3302 (5)	1289 (5)	-1784 (3)	H(3)	489 (6)	355 (5)	-34 (4)
N(1)	-210 (6)	2893 (6)	-3457 (3)	H(4)	404 (5)	224 (4)	113 (3)
N(2)	4736 (5)	1237 (5)	-1835 (3)	H(5)	-73 (6)	366 (5)	-42 (4)
H(1)	282 (6)	-11 (5)	10 (3)	H(6)	22 (6)	488 (5)	-194 (3)
H(2)	183 (5)	-138 (4)	153 (3)	C(19)	2588 (9)	59 (6)	5831 (4)
C(7)	2805 (5)	4288 (4)	-1304 (3)	C(20)	2221 (7)	2566 (5)	5074 (4)
C(8)	3893 (5)	3491 (4)	-369 (3)	C(21)	2868 (6)	3937 (5)	4845 (6)
C(9)	3208 (5)	2847 (4)	504 (3)	C(22)	4638 (6)	4270 (4)	5113 (3)
C(10)	1416 (5)	2902 (4)	512 (3)	C(23)	5700 (6)	3169 (5)	5596 (4)
C(11)	323 (5)	3661 (4)	-433 (3)	C(24)	5007 (7)	1826 (5)	5826 (4)
C(12)	1017 (5)	4330 (4)	-1298 (3)	N(7)	3310 (5)	1537 (4)	5562 (3)
C(13)	3539 (5)	5029 (4)	-2179 (3)	H(7)	100 (6)	220 (4)	488 (3)
C(14)	2522 (6)	5919 (5)	-3080 (3)	H(8)	207 (6)	466 (5)	449 (4)
C(15)	5323 (6)	4990 (5)	-2219 (3)	H(9)	691 (7)	342 (6)	582 (4)
C(16)	702 (5)	2246 (4)	1413 (3)	H(10)	562 (7)	108 (6)	619 (4)
C(17)	1763 (6)	1552 (4)	2380 (3)				

Table 2. Details of molecular planes (x, y, z are fractional atomic coordinates; asterisks denote atoms not defining the planes; numbers in parentheses are standard deviations of atomic positions)

TCNQ(A)		
Equations to the planes (including centrosymmetrically related atoms)		
Molecule	$0.532x + 9.155y + 7.608z = 0$	
Quinonoid group	$0.432x + 9.198y + 7.590z = 0$	

Distances from the planes (Å)

	Molecule	Quinonoid group
C(1)	-0.005 (4)	-0.008 (4)
C(2)	0.015 (4)	-0.004 (4)
C(3)	0.019 (4)	0.004 (4)
C(4)	0.012 (4)	0.006 (4)
C(5)	0.000 (5)	0.008 (5)*
C(6)	-0.001 (4)	-0.025 (4)*
N(1)	0.007 (5)	0.028 (5)*
N(2)	-0.012 (4)	-0.051 (4)*

TCNQ(B)

Equations to the planes

Molecule	$0.266x + 9.293y + 7.467z - 3.162 = 0$
Quinonoid group	$0.277x + 9.312y + 7.397z - 3.118 = 0$

Distances from the planes (Å)

	Molecule	Quinonoid group
C(7)	-0.077 (4)	-0.013 (4)
C(8)	-0.090 (4)	-0.033 (4)
C(9)	-0.056 (4)	-0.006 (4)
C(10)	-0.046 (4)	0.002 (4)
C(11)	-0.075 (4)	-0.020 (4)
C(12)	-0.081 (4)	-0.019 (4)
C(13)	-0.022 (4)	0.051 (4)
C(14)	0.106 (5)	0.185 (5)*
C(15)	-0.041 (5)	0.034 (5)*
C(16)	-0.002 (4)	0.038 (4)
C(17)	0.104 (4)	0.136 (4)*
C(18)	-0.036 (4)	0.001 (4)*
N(3)	0.228 (5)	0.313 (5)*
N(4)	-0.052 (5)	0.025 (5)*
N(5)	0.210 (5)	0.237 (5)*
N(6)	-0.070 (5)	-0.035 (5)*

Cation

Equation to the plane

$$-2.624x + 3.492y + 13.315z - 7.074 = 0$$

Distances from the plane (Å)

C(19)	0.032 (6)*	C(23)	-0.012 (5)
C(20)	-0.004 (5)	C(24)	0.008 (5)
C(21)	-0.001 (6)	N(7)	0.000 (6)
C(22)	0.008 (4)		

is no direct overlap between the triads and they are held together sideways by van der Waals forces. In this way layers of TCNQ's are formed parallel to (001) interleaved by layers of cations. The short intermolecular contacts within the arrays are listed in Table 3. Within the triads the dihedral angle and mean perpendicular separation between TCNQ(A) and TCNQ(B) are 2.4°

Table 3. Short intermolecular contacts ($<3.4 \text{ \AA}$)

The figures in parentheses indicate e.s.d.'s.

Intra-triad			
C(1 ^l)-C(10 ^l)	3.218 (6)	C(3 ^l)-C(16 ^l)	3.344 (6)
C(1 ^l)-C(11 ^l)	3.268 (6)	C(3 ^l)-C(17 ^l)	3.399 (6)
C(1 ^l)-C(16 ^{ll})	3.234 (6)	C(4 ^l)-C(7 ^l)	3.138 (6)
C(1 ^l)-C(18 ^{ll})	3.269 (6)	C(4 ^l)-C(8 ^l)	3.343 (6)
C(2 ^l)-C(9 ^l)	3.231 (6)	C(4 ^l)-C(12 ^l)	3.260 (6)
C(2 ^l)-C(10 ^l)	3.315 (6)	C(5 ^l)-C(7 ^l)	3.295 (6)
C(2 ^l)-C(18 ^{ll})	3.222 (6)	C(5 ^l)-C(12 ^l)	3.152 (6)
C(3 ^l)-C(10 ^{ll})	3.393 (5)	C(6 ^l)-C(7 ^l)	3.321 (7)
C(3 ^l)-C(11 ^{ll})	3.130 (6)	C(6 ^l)-C(8 ^l)	3.226 (7)
Inter-triad			
C(2 ^l)-N(2 ^{ll})	3.305 (5)	C(12 ^l)-C(18 ^v)	3.377 (6)
C(3 ^l)-N(2 ^{ll})	3.332 (5)	C(13 ^l)-N(6 ^v)	3.372 (7)
C(9 ^l)-N(6 ^{lv})	3.372 (6)	C(14 ^l)-N(6 ^v)	3.222 (7)
C(11 ^l)-C(11 ^{lv})	3.333 (6)		
TCNQ(A)-cation		TCNQ(B)-cation	
N(1 ^l)-C(23 ^{vl})	3.208 (6)	N(3 ^l)-C(19 ^{vll})	3.321 (7)
N(1 ^l)-C(20 ^{vll})	3.128 (8)	N(3 ^l)-C(20 ^v)	3.282 (7)
N(2 ^l)-C(24 ^{vll})	3.085 (7)	N(4 ^l)-C(21 ^{lv})	3.391 (7)
N(2 ^l)-N(7 ^{vll})	3.379 (5)	N(5 ^l)-C(24 ^v)	3.380 (7)
		N(5 ^l)-N(7 ^l)	3.327 (6)

Symmetry code

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

Table 4. Comparison of mean bond lengths (Å) in TCNQ⁰, TCNQ⁻ and (DMBP)²⁺(TCNQ)₃²⁻, all uncorrected for libration

	a	b	c	d	e
TCNQ ^{-*}	1.363	1.422	1.420	1.417	1.145
TCNQ ^{0†}	1.344	1.442	1.373	1.435	1.138
$\Delta(T^- - T^0)$	0.009	-0.024	0.041	-0.020	0.009
TCNQ(A)	1.372	1.423	1.415	1.413	1.151
TCNQ(B)	1.361	1.430	1.405	1.426	1.143
$\Delta(A - B)$	0.011	-0.007	0.010	-0.013	0.008

* Hoekstra, Spoelder & Vos (1972); Konno & Saito (1974); Konno, Ishii & Saito (1977). Only simple TCNQ salts of alkali metals in their low-temperature forms have been included in this mean in order to avoid examples where ionization may be incomplete.

† Long, Sparks & Trueblood (1965).

and 3.16 \AA respectively. The molecules, however, are not quite planar; the $\text{C}=\text{C}(\text{CN})_2$ groups are slightly rotated out of the plane of the quinonoid ring of molecule A, and molecule B is slightly bowed in a direction away from molecule A. This causes a different

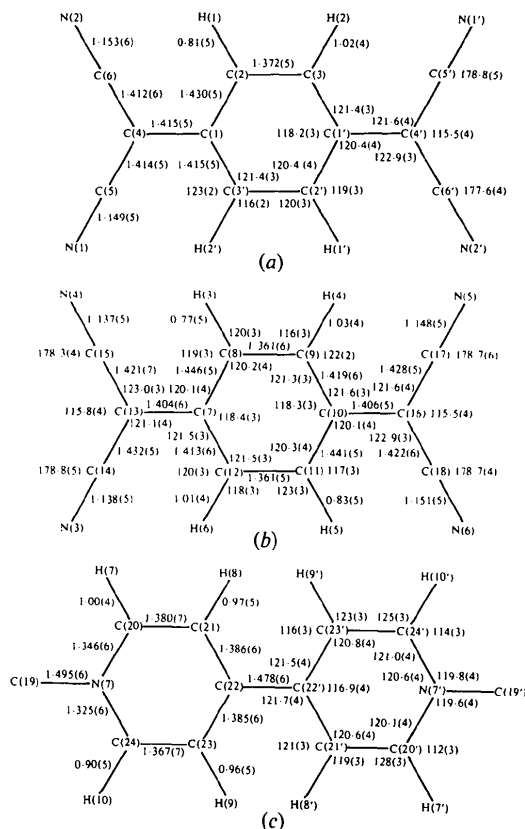


Fig. 2. Molecular dimensions (Å and deg) of (a) TCNQ(A), (b) TCNQ(B) and (c) the (DMBP)²⁺ cation. Figures in parentheses indicate e.s.d.'s.

average tilt with a dihedral angle of 1.8° and a mean perpendicular separation of 3.12 Å when the planes of only the quinonoid groups are considered.

The dimensions of the crystallographically independent types of TCNQ moiety are shown in Fig. 2. From a comparison of the mean bond lengths of TCNQ(A) and TCNQ(B) with those of TCNQ⁰ and TCNQ⁻

(Table 4) it is possible to obtain some indication of the charge distribution within the complex. The dimensions of TCNQ(A) are generally similar to those of TCNQ⁻ whereas those of TCNQ(B) are intermediate between those of TCNQ⁰ and TCNQ⁻. By applying the method of Flandrois & Chasseau (1977) the charges may be estimated as 0.96 e on TCNQ(A) and 0.61 e on TCNQ(B). This indicates partial electron localization on TCNQ(A) within the triads and is consistent with the fact that TCNQ(A) generally makes closer contacts with the cation than TCNQ(B), Table 3.

The dimensions of the (DMBP)²⁺ cation (Fig. 2c) are in reasonable agreement with the values previously reported in (1,1'-diethyl-4,4'-bipyridylium)²⁺ (TCNQ)₄⁻ (Ashwell, Eley, Wallwork & Willis, 1975) and 1,1'-dimethyl-4,4'-bipyridylium dihalides (Russell & Wallwork, 1972).

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