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The Crystal Structures of Free Radical Salts and Complexes. IV.
(1,1'-Ethylene-2,2'-bipyridylium)²⁺–(7,7,8,8-Tetracyanoquinodimethane⁻)₂

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Crystals of $(C_{12}H_{12}N_2)^{2+}(C_{12}H_4N_4^-)_2$ are triclinic, space group $P\bar{1}$, with lattice constants $a = 7.416$, $b = 13.371$, $c = 14.625$ Å, $\alpha = 87.800°$, $\beta = 95.567°$, $\gamma = 95.200°$, $Z = 2$. The structure was solved by Patterson methods and refined by block-diagonal least-squares analysis using 4785 observed reflexions measured on a Hilger and Watts computer-controlled, four-circle diffractometer. The structure contains columns of tetracyanoquinodimethane (TCNQ) ions packed in a plane-to-plane manner. The four TCNQ ions per unit cell form two crystallographically independent centrosymmetric dimers. Within the dimers there are short interplanar spacings of 3.22 and 3.26 Å between the TCNQ ions indicating charge-transfer interaction. Between the dimers there is a gap of 3.59 Å.

Introduction

Molecular complexes containing ions and molecules of 7,7,8,8-tetracyanoquinodimethane (TCNQ) include some of the best electrically conducting organic compounds known. As a part of a series of crystal structure determinations of TCNQ complexes to elucidate the relationship between their structures and electrical properties, the crystal structure of (1,1'-ethylene-2,2'-bipyridylium)²⁺ (TCNQ⁻)₂ is reported.

Experimental

Crystal data

$(C_{12}H_{12}N_2)(C_{12}H_4N_4)_2$, M.W. 592.6,
Triclinic,
$a = 7.416 \pm 0.001$, $b = 13.371 \pm 0.001$,
$c = 14.625 \pm 0.001$ Å,

$\alpha = 87.800 \pm 0.004°$, $\beta = 95.567 \pm 0.004°$,
$\gamma = 95.200 \pm 0.005°$,
$U = 1436.8$ Å³;
$D_m = 1.36$ g.cm⁻³, $Z = 2$, $D_c = 1.37$ g.cm⁻³,
$F(000) = 612$.
Mo $K\alpha$ ($\lambda = 0.7107$ Å), $\mu = 0.94$ cm⁻¹.
Space group $P\bar{1}$ (assumed).

Purple lath-shaped crystals of the complex salt were obtained when 1 mole of 1,1'-ethylene-2,2'-bipyridylium bromide (diquat bromide) and 2 moles of LiTCNQ were dissolved in hot acetonitrile and added to an excess boiling solution of LiTCNQ in acetonitrile and allowed to cool slowly to room temperature. The space group and the unit-cell dimensions were obtained initially from oscillation and Weissenberg photographs taken with the crystals rotating about all the three crystallographic axes using Cu $K\alpha$ radiation. The

cell dimensions were subsequently refined on a Hilger and Watts computer-controlled four circle diffractometer. Intensity data for $\theta < 30°$ were collected using a $\theta/2\theta$ scan, a scintillation counter and Mo $K\alpha$ radiation. 8388 reflexions were measured of which significant counts were recorded for 4785. In view of the small size of the crystal ($0.5 \times 0.3 \times 0.3$ mm), no absorption corrections were made. The intensities were corrected for Lorentz and polarization factors.

Structure determination

A three-dimensional sharpened Patterson map was computed. Vectors typical of TCNQ were recognized round the origin and round strong peaks at (1)$x = 0.023$, $y = 0.243$, $z = 0.125$, (2) $x = 0.477$, $y = -0.245$,

$z = 0.375$ and (3) $x = 0.500$, $y = 0.000$ and $z = 0.500$. Peak 1 was taken to represent the combined vectors between a centrosymmetrically related pair of TCNQ ions (A' and A) and the peak 2 was taken to represent the combined vectors between the two crystallographically independent types of TCNQ ion (A and B). Peak 3 was taken to represent the combined vectors between the TCNQ ions A' and B. From the positions of the ions A and B so derived it was realized that peak 1 also corresponds to the vector between the second pair of centrosymmetrically related ions B and B'. The existence of strong vectors between the ions A and B suggests that the TCNQs are packed parallel to each other and the common orientation of the TCNQ ions was derived from the vector pattern round the origin. From this orientation, the interionic vectors, and the

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

The figures in parentheses indicate the standard deviations.

Temperature factor $= \exp\left[-(h^2B_{11} + k^2B_{22} + l^2B_{33} + hkB_{12} + hlB_{13} + klB_{23})\right]$.

	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
C(1)	-996 (3)	433 (2)	1142 (2)	125 (4)	39 (1)	37 (1)	5 (4)	29 (3)	-0 (2)
C(2)	844 (3)	281 (2)	1006 (2)	119 (4)	36 (1)	33 (1)	15 (3)	11 (3)	-6 (2)
C(3)	1819 (3)	1027 (2)	480 (2)	116 (4)	39 (1)	37 (1)	13 (4)	21 (3)	-3 (2)
C(4)	1039 (3)	1870 (2)	143 (2)	137 (4)	38 (1)	37 (1)	20 (4)	38 (3)	4 (2)
C(5)	-771 (3)	2038 (2)	307 (2)	143 (4)	37 (1)	29 (1)	32 (4)	20 (3)	-4 (2)
C(6)	-1763 (3)	1278 (2)	804 (2)	126 (4)	42 (1)	36 (1)	19 (4)	30 (3)	-5 (2)
C(7)	1652 (3)	-573 (2)	1379 (2)	130 (4)	38 (1)	42 (1)	18 (4)	13 (4)	6 (2)
C(8)	3491 (3)	-728 (2)	1281 (2)	141 (5)	42 (1)	52 (1)	27 (4)	9 (4)	20 (2)
C(9)	749 (3)	-1314 (2)	1937 (2)	156 (5)	45 (1)	46 (1)	23 (4)	6 (4)	13 (2)
C(10)	-1505 (3)	2963 (2)	38 (2)	152 (5)	45 (1)	35 (1)	54 (4)	25 (4)	8 (2)
C(11)	-529 (3)	3713 (2)	-474 (2)	186 (5)	45 (1)	35 (1)	73 (4)	38 (4)	3 (2)
C(12)	-3193 (4)	3200 (2)	310 (2)	193 (5)	49 (2)	41 (1)	62 (5)	46 (4)	4 (2)
C(13)	3794 (3)	-1940 (2)	5005 (2)	135 (4)	42 (1)	35 (1)	15 (4)	34 (3)	5 (2)
C(14)	5607 (3)	-2146 (2)	4894 (2)	132 (4)	43 (1)	32 (1)	14 (4)	18 (3)	-3 (2)
C(15)	6663 (3)	-1442 (2)	4363 (2)	126 (4)	47 (1)	39 (1)	15 (4)	34 (3)	13 (2)
C(16)	5942 (3)	-618 (2)	3947 (2)	124 (4)	46 (1)	36 (1)	4 (4)	24 (3)	-1 (2)
C(17)	4097 (3)	-426 (2)	4038 (2)	135 (4)	42 (1)	32 (1)	11 (4)	17 (3)	1 (2)
C(18)	3070 (3)	-1113 (2)	4595 (2)	114 (4)	47 (1)	36 (1)	18 (4)	35 (3)	1 (2)
C(19)	6294 (3)	-3058 (2)	5252 (2)	147 (5)	49 (1)	38 (1)	36 (4)	31 (4)	7 (2)
C(20)	8089 (3)	-3293 (2)	5155 (2)	164 (5)	53 (2)	34 (1)	46 (4)	32 (4)	-2 (2)
C(21)	5197 (3)	-3819 (2)	5685 (2)	157 (5)	51 (2)	38 (1)	55 (4)	28 (4)	4 (2)
C(22)	3332 (3)	414 (2)	3598 (2)	129 (4)	46 (1)	35 (1)	7 (4)	19 (3)	9 (2)
C(23)	4319 (3)	1111 (2)	3030 (2)	137 (4)	54 (2)	40 (1)	29 (4)	14 (4)	13 (2)
C(24)	1489 (3)	585 (2)	3665 (2)	153 (4)	49 (2)	44 (1)	20 (4)	19 (4)	24 (2)
C(25)	2231 (3)	3498 (2)	2178 (2)	159 (5)	42 (1)	37 (1)	32 (4)	23 (4)	-9 (2)
C(26)	930 (4)	2703 (2)	2278 (2)	208 (6)	42 (1)	38 (1)	13 (4)	4 (4)	-5 (2)
C(27)	-712 (4)	2860 (2)	2598 (2)	192 (6)	52 (2)	45 (1)	-34 (5)	21 (4)	-5 (2)
C(28)	-978 (3)	3809 (2)	2852 (2)	142 (5)	59 (2)	39 (1)	-6 (4)	37 (4)	3 (2)
C(29)	-1 (3)	5583 (2)	3092 (2)	151 (5)	50 (2)	46 (1)	48 (4)	56 (4)	-16 (2)
C(30)	1741 (4)	6079 (2)	3514 (2)	189 (5)	47 (1)	41 (1)	22 (4)	58 (4)	-19 (2)
C(31)	4279 (4)	6960 (2)	2770 (2)	181 (5)	44 (2)	53 (2)	-11 (4)	-2 (4)	4 (2)
C(32)	5626 (4)	7004 (2)	2188 (2)	162 (5)	55 (2)	64 (2)	-12 (5)	8 (5)	22 (3)
C(33)	5747 (4)	6188 (2)	1651 (2)	132 (5)	69 (2)	57 (2)	29 (5)	44 (4)	31 (3)
C(34)	4525 (3)	5341 (2)	1707 (2)	133 (4)	53 (2)	45 (1)	36 (4)	50 (4)	9 (2)
C(35)	3204 (3)	5322 (2)	2319 (2)	120 (4)	39 (1)	34 (1)	30 (4)	19 (3)	3 (2)
C(36)	1897 (4)	4446 (2)	2430 (1)	114 (4)	40 (1)	30 (1)	23 (3)	23 (3)	0 (2)
N(1)	4978 (3)	-874 (2)	1218 (2)	148 (5)	74 (2)	92 (2)	42 (5)	41 (5)	39 (3)
N(2)	71 (4)	-1925 (2)	2396 (2)	229 (6)	65 (2)	69 (2)	9 (5)	42 (5)	52 (3)
N(3)	276 (4)	4304 (2)	-895 (2)	259 (6)	57 (2)	51 (1)	68 (5)	82 (4)	24 (2)
N(4)	-4557 (4)	3396 (2)	536 (2)	232 (6)	69 (2)	72 (6)	98 (5)	102 (5)	9 (3)
N(5)	9535 (3)	3497 (2)	5088 (2)	186 (5)	83 (2)	51 (1)	73 (5)	52 (4)	-4 (2)
N(6)	4328 (3)	-4455 (2)	6028 (2)	199 (5)	59 (2)	57 (1)	38 (4)	71 (4)	26 (2)
N(7)	5084 (3)	1680 (2)	2573 (2)	183 (5)	79 (2)	63 (2)	15 (5)	48 (4)	54 (3)
N(8)	-2 (3)	721 (2)	3713 (2)	149 (5)	82 (2)	79 (2)	43 (5)	55 (4)	44 (3)
N(9)	310 (3)	4574 (1)	2786 (1)	140 (4)	42 (1)	31 (1)	24 (3)	35 (3)	-3 (2)
N(10)	3117 (3)	6135 (1)	2836 (1)	151 (4)	39 (1)	37 (1)	20 (3)	16 (3)	-4 (2)

Table 2. *Comparison of observed and final calculated structure factors* (10 × *absolute scale*)

Table 2 (*cont.*)

Table 2 (*cont.*)

Table 2 (cont.)

known dimensions of TCNQ⁻ a set of trial atomic parameters for the two TCNQ ions was deduced. One cycle of block-diagonal least-squares refinement of the positional and isotropic thermal parameters of the 32 atoms with temperature factors of 3·00 and 4·50 Å² for carbon and nitrogen atoms respectively gave the value of the residual index, $R=0.616$. Using the signs of the structure factors derived from the TCNQ co-ordinates, a three-dimensional Fourier electron density distribution was computed. The Fourier map confirmed the positions of the two TCNQ's and also showed the 12 atoms of the two pyridyl groups.

At this stage it was not obvious which of the 12 atoms were the two nitrogen atoms so all were initially assumed to be carbon atoms and were given isotropic temperature factors of 3·00 Å². Two cycles of least-squares refinement improved the R value to 0·397. In the course of the least-squares refinement two atoms of the diquat ion had consistently lower temperature factors and these corresponded to high electron-density peaks in the Fourier map computed using the signs of the output structure factors. These two atoms were, therefore, taken as nitrogen atoms. The Fourier map also showed the remaining two atoms of the diquat ion linked to the atoms that had been identified as nitrogen atoms. Seven further cycles of isotropic, block-diagonal least-squares refinement of all the 46 atoms gave the value of $R=0.123$.

The weighting scheme used was $\sqrt{w}=\{1+[(|F_o|-P_2)/P_1]^2\}^{-1/2}$ where P_1 and P_2 were given values of 116 and 60 respectively on the scale of Table 2.

A difference Fourier synthesis computed with low order reflexions showed peaks in plausible positions for all the 20 hydrogen atoms. A further five cycles of anisotropic least-squares refinement of the non-hydrogen atoms, with hydrogen atoms in fixed positions with fixed isotropic temperature factors 0·5 Å² greater than the atoms to which they are attached, and excluding 198 weak reflexions, gave the final value of $R=0.057$. The atomic scattering factor curves used

Table 3. Details of molecular planes

x, y, z are orthogonal atomic coordinates in Å where x is along **a**, y is in the (a, b) plane and z is along **c***.
The figures in parentheses indicate the standard deviations.

Molecule A (TCNQ⁻)
Equation to the plane:
$-0.2496\,x-0.4889\,y-0.8359\,z+1.6141=0$

	Distance from the plane (Å)
C(1)	0·158 (2)
C(2)	0·074 (2)
C(3)	0·063 (2)
C(4)	0·089 (2)
C(5)	0·123 (2)
C(6)	0·181 (2)
C(7)	0·007 (2)
C(8)	−0·120 (3)
C(9)	−0·037 (3)
C(10)	0·007 (2)
C(11)	−0·023 (2)
C(12)	−0·154 (3)
N(1)	−0·229 (3)
N(2)	−0·084 (3)
N(3)	−0·033 (3)
N(4)	−0·295 (3)

Molecule B (TCNQ⁻)
Equation to the plane:
$-0.1707\,x-0.5238\,y-0.8346\,z+5.0689=0$

	Distance from the plane (Å)
C(13)	−0·169 (2)
C(14)	−0·124 (2)
C(15)	−0·090 (2)
C(16)	−0·052 (2)
C(17)	−0·059 (2)
C(18)	−0·140 (2)
C(19)	−0·028 (3)
C(20)	0·021 (2)
C(21)	0·101 (3)
C(22)	0·003 (2)
C(23)	0·095 (3)
C(24)	0·040 (3)
N(5)	0·058 (3)
N(6)	0·225 (3)
N(7)	0·168 (3)
N(8)	0·078 (3)

Pyridinium rings of the diquat ion
Ring (1)
Equation to the plane:
$-0.3347\,x+0.1730\,y-0.9263\,z+2.4231=0$

	Distance from the plane (Å)
C(25)	0·002 (2)
C(26)	−0·020 (3)
C(27)	0·016 (3)
C(28)	0·011 (2)
N(9)	−0·015 (2)
C(36)	0·015 (2)

Ring (2)
Equation to the plane:
$-0.5915\,x+0.3640\,y-0.7145\,z+0.6376=0$

	Distance from the plane (Å)
N(10)	−0·002 (2)
C(31)	0·009 (3)
C(32)	−0·006 (3)
C(33)	−0·004 (3)
C(34)	0·007 (3)
C(35)	−0·003 (2)

throughout were those of Cromer & Waber (1965) for the carbon and nitrogen atoms and that quoted in *International Tables for X-ray Crystallography* (1962) for the hydrogen atoms. The final positional and anisotropic thermal parameters of non-hydrogen atoms, together with their standard deviations, are listed in Table 1. The final calculated structure factors are compared with the observed values in Table 2. Least-squares planes were calculated through each of the TCNQ ions and through the pyridyl groups of the

diquat ion and the results are summarized in Table 3.

The anisotropic thermal parameters, B_{ij}, were used in an analysis of the rigid-body translational and librational motions of the molecules based on the theory of rigid-body motions (Cruickshank, 1956). The results for the two TCNQ moieties and the diquat ion are given in Table 4. The observed U_{ij} values and the differences between the observed U_{ij}s and those calculated on the basis of rigid-body motion are listed in Table 5. The bond lengths both uncorrected and cor-

Table 4. *Rigid-body thermal parameters*

(a) Molecule A (TCNQ)

$$\mathbf{T} = \begin{pmatrix} 327 & -4 & 16 \\ & 345 & -29 \\ & & 283 \end{pmatrix} \times 10^{-4}\ \text{Å}^2 \qquad \boldsymbol{\omega} = \begin{pmatrix} 78 & -88 & 35 \\ & 224 & -76 \\ & & 68 \end{pmatrix} \times 10^{-1}\ (\text{deg})^2$$

$$\sigma(\mathbf{T}) = \begin{pmatrix} 18 & 15 & 18 \\ & 16 & 17 \\ & & 21 \end{pmatrix} \times 10^{-4}\ \text{Å}^2 \qquad \sigma(\boldsymbol{\omega}) = \begin{pmatrix} 8 & 18 & 11 \\ & 28 & 12 \\ & & 7 \end{pmatrix} \times 10^{-1}\ (\text{deg})^2$$

Principal axes: | | Direction cosines* | | | Comments |
		x	y	z	
T	0·0359 Å²	0·2968	−0·8711	0·3914	inclined at 10° to long axis of the molecule
	0·0328	0·9283	0·3593	0·0959	
	0·0269	0·2242	−0·3349	−0·9152	
ω	29·6 (deg)²	−0·3978	0·8502	−0·3448	inclined at 4° to long axis of the molecule
	3·8	−0·5635	0·0700	0·8232	
	3·6	−0·7244	−0·5216	−0·4508	

(b) Molecule B (TCNQ)

$$\mathbf{T} = \begin{pmatrix} 323 & -19 & 21 \\ & 407 & -22 \\ & & 304 \end{pmatrix} \times 10^{-4}\ \text{Å}^2 \qquad \boldsymbol{\omega} = \begin{pmatrix} 66 & -79 & 40 \\ & 170 & -85 \\ & & 77 \end{pmatrix} \times 10^{-1}\ (\text{deg})^2$$

$$\sigma(\mathbf{T}) = \begin{pmatrix} 18 & 15 & 18 \\ & 16 & 17 \\ & & 21 \end{pmatrix} \times 10^{-4}\ \text{Å}^2 \qquad \sigma(\boldsymbol{\omega}) = \begin{pmatrix} 7 & 16 & 11 \\ & 27 & 14 \\ & & 9 \end{pmatrix} \times 10^{-1}\ (\text{deg})^2$$

Principal axes: | | Direction cosines* | | | Comments |
		x	y	z	
T	0·0417 Å²	0·2425	−0·9437	0·2252	inclined at 18° to long axis of the molecule
	0·0327	0·8366	0·3209	0·4440	
	0·0290	0·4913	−0·0807	−0·8673	
ω	26·0 (deg)²	−0·4146	0·7884	−0·4545	inclined at 1° to long axis of the molecule
	3·1	−0·6355	0·1066	0·7647	
	2·1	−0·6513	−0·6059	−0·4569	

(c) Diquat ion

$$\mathbf{T} = \begin{pmatrix} 310 & 38 & 39 \\ & 356 & -13 \\ & & 333 \end{pmatrix} \times 10^{-4}\ \text{Å}^2 \qquad \boldsymbol{\omega} = \begin{pmatrix} 56 & 15 & 12 \\ & 116 & -41 \\ & & 86 \end{pmatrix} \times 10^{-1}\ (\text{deg})^2$$

$$\sigma(\mathbf{T}) = \begin{pmatrix} 14 & 12 & 15 \\ & 13 & 13 \\ & & 20 \end{pmatrix} \times 10^{-4}\ \text{Å}^2 \qquad \sigma(\boldsymbol{\omega}) = \begin{pmatrix} 16 & 13 & 9 \\ & 21 & 10 \\ & & 8 \end{pmatrix} \times 10^{-1}\ (\text{deg})^2$$

Principal axes: | | Direction cosines* | | |
		x	y	z
T	0·0380 Å²	−0·5702	−0·7808	−0·2556
	0·0356	−0·2983	0·4867	−0·8211
	0·0264	−0·7655	0·3919	0·5103
ω	14·5 (deg)²	−0·0654	−0·8251	0·5612
	7·5	−0·6857	−0·3715	−0·6259
	3·8	−0·7250	0·4258	0·5414

* All positions and directions in the above Table are referred to a set of orthogonal axes in which the x axis is parallel to a, the y axis lies in the (a, b) plane and the z axis is parallel to c.*

rected for the effects of molecular librations (Busing & Levy, 1964) are given in Table 6. The corrections are barely significant, being of the order of 1 to 2 standard deviations.

Table 5. U_{ij} (Å²) × 10⁴ relative to the orthogonal axes detailed in Table 4

The first line for each atom gives the U_{ij} values derived from the B_{ij} values and the second line gives the differences between these and the values calculated from rigid-body parameters.

(a) Molecule A (TCNQ)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	337	351	393	−17	40	11
	−8	−26	3	−12	5	−10
C(2)	324	321	358	12	−1	−17
	−22	−30	55	7	−15	6
C(3)	311	347	394	4	20	−4
	−30	−48	5	−14	−32	−24
C(4)	360	346	395	18	63	31
	2	−39	28	9	10	9
C(5)	377	335	312	53	27	−12
	30	−20	9	48	17	9
C(6)	333	378	387	17	48	−14
	4	−12	−22	13	18	−33
C(7)	353	342	447	10	−10	41
	−45	−32	84	−20	−13	44
C(8)	386	386	558	21	−38	115
	−24	−76	−1	−61	−50	60
C(9)	430	410	488	13	−38	77
	−64	7	32	−22	−67	11
C(10)	393	407	376	97	32	15
	−7	31	12	66	30	17
C(11)	471	409	374	147	66	25
	−23	7	−85	113	38	−41
C(12)	492	441	444	116	82	31
	68	−22	−103	19	44	−21
N(1)	390	673	981	27	0	220
	−36	76	93	−114	−43	52
N(2)	629	602	739	−55	19	276
	13	123	87	−108	−78	83
N(3)	658	521	544	117	162	133
	53	46	−128	73	66	−64
N(4)	561	622	769	191	199	67
	89	14	−69	1	72	−98

The r.m.s. difference is 0·0051 Å². The estimated standard deviation of U_{ij}^{obs} is 0·0022 Å².
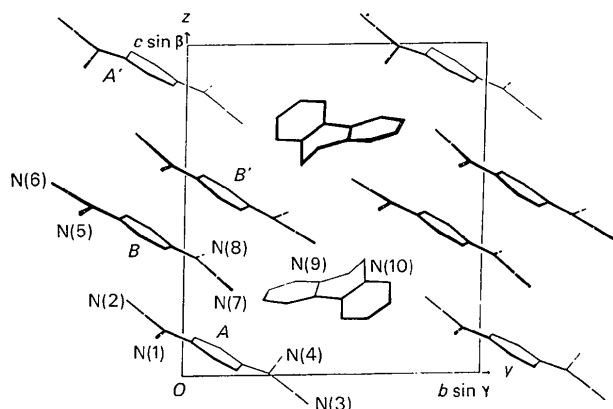
Fig. 1. The molecular arrangement, viewed along the *a* axis.

Table 5 (cont.)

(b) Molecule B (TCNQ)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(13)	359	376	373	2	53	34
	18	−75	−1	8	5	5
C(14)	359	383	344	2	17	−2
	22	−32	29	14	−2	13
C(15)	332	420	418	1	51	19
	7	−35	23	12	20	−10
C(16)	337	417	386	−26	28	6
	2	−29	−7	−6	−7	−25
C(17)	370	379	343	−8	12	14
	32	−34	27	4	−9	30
C(18)	298	423	385	8	57	18
	−35	−36	6	7	11	−9
C(19)	384	441	404	47	42	46
	6	6	53	39	23	43
C(20)	426	477	368	75	53	0
	31	−40	−94	17	19	−58
C(21)	405	458	408	96	37	30
	−31	−4	−55	95	6	−40
C(22)	353	413	379	−24	12	54
	−26	−20	26	−32	−7	52
C(23)	370	488	425	22	−8	76
	−69	17	−26	12	−49	3
C(24)	416	448	472	−1	−6	130
	25	−69	7	−56	−37	71
N(5)	467	744	549	120	90	−3
	48	90	−115	−1	17	−172
N(6)	512	535	608	39	122	145
	9	3	−76	50	72	−51
N(7)	493	723	677	−51	40	287
	−18	163	40	−73	−49	83
N(8)	384	752	847	20	48	242
	−21	95	164	−88	−13	65

The r.m.s. difference is 0·0051 Å². The estimated standard deviation of U_{ij}^{obs} is 0·0020 Å².

(c) Diquat ion

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(25)	422	371	396	51	28	−32
	−33	9	−16	−2	−9	0
C(26)	577	375	409	0	−26	−10
	−19	5	−88	18	0	7
C(27)	548	463	487	−124	12	−10
	26	2	−74	−14	67	−70
C(28)	385	531	420	−60	61	14
	17	21	−112	−10	41	−61
C(29)	377	445	491	89	111	−65
	12	−24	16	−4	−1	−71
C(30)	492	419	434	29	124	−79
	2	7	41	−44	37	−27
C(31)	521	398	569	−68	−63	36
	8	4	100	−22	−28	34
C(32)	466	498	683	−87	−55	128
	0	−9	104	24	−28	39
C(33)	344	630	616	2	48	170
	−34	52	49	39	−41	71
C(34)	337	476	478	45	85	58
	−14	1	41	7	−16	34
C(35)	316	354	365	43	16	24
	2	−17	15	10	−26	30
C(36)	299	361	319	25	33	10
	−30	4	−26	−9	−2	23
N(9)	365	377	330	28	65	−5
	46	−41	−75	7	19	−22
N(10)	410	350	397	20	6	−8
	18	−14	25	0	−13	12

The r.m.s. difference is 0·0037 Å². The estimated standard deviation of U_{ij}^{obs} is 0·0014 Å².

Description and discussion of the structure

Fig. 1 shows a general view of the structure in which the four TCNQ ions are packed in a plane-to-plane manner to form a column along the [101] axis which
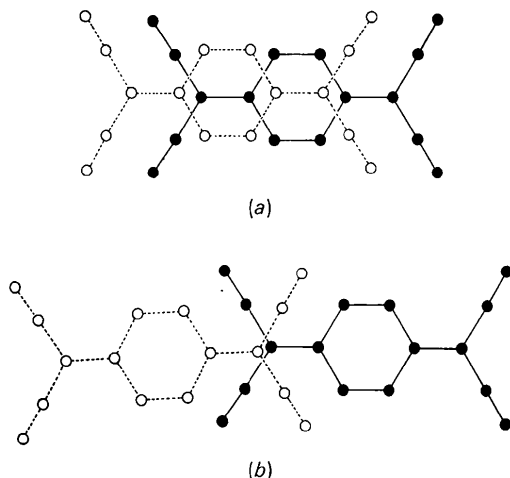

(a)

(b)

Fig. 2. Nearest neighbour overlap of TCNQ ions. (a) A (—) and A' ($\cdots$), B (—) and B' ($\cdots$), (b) A (—) and B ($\cdots$).
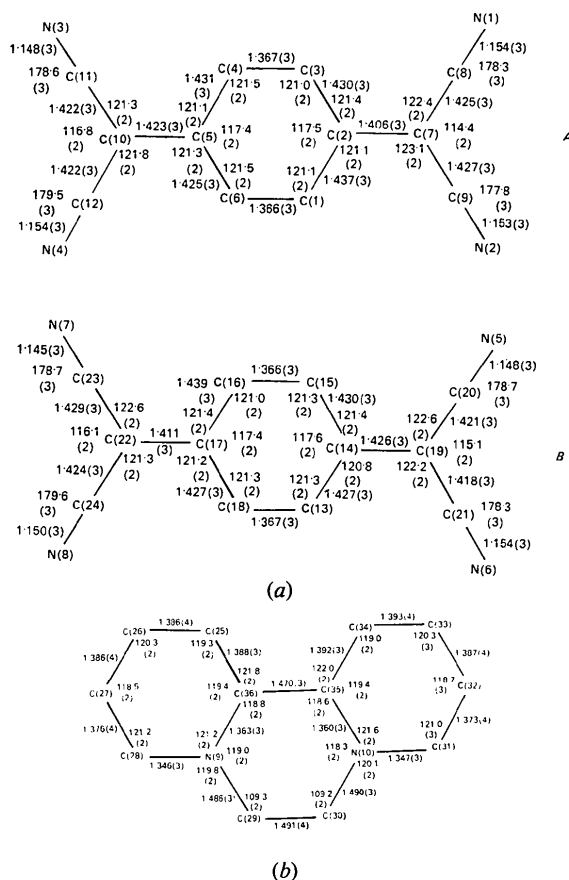

(a)

(b)

Fig. 3. Bond lengths (Å) corrected for libration and bond angles (°), with their standard deviations in parentheses, for (a) the two independent TCNQ ions and (b) the diquat ion.

Table 6. *Bond lengths before and after libration correction*

(a) Molecule A (TCNQ)

	Length (Å)		
	Uncorrected	Corrected	σ (Å)
C(1)—C(2)	1·431	1·437	0·003
C(1)—C(6)	1·364	1·366	0·003
C(2)—C(3)	1·425	1·430	0·003
C(2)—C(7)	1·404	1·406	0·003
C(3)—C(4)	1·366	1·367	0·003
C(4)—C(5)	1·425	1·431	0·003
C(5)—C(6)	1·419	1·425	0·003
C(5)—C(10)	1·422	1·423	0·003
C(7)—C(8)	1·420	1·425	0·003
C(7)—C(9)	1·422	1·427	0·003
C(8)—N(1)	1·150	1·154	0·004
C(9)—N(2)	1·149	1·153	0·004
C(10)-C(11)	1·417	1·422	0·004
C(10)-C(12)	1·416	1·422	0·004
C(11)-N(3)	1·144	1·148	0·004
C(12)-N(4)	1·149	1·154	0·004

(b) Molecule B (TCNQ)

C(13)-C(14)	1·422	1·427	0·003
C(13)-C(18)	1·366	1·367	0·003
C(14)-C(15)	1·426	1·430	0·003
C(14)-C(19)	1·425	1·426	0·003
C(15)-C(16)	1·365	1·366	0·003
C(16)-C(17)	1·434	1·439	0·003
C(17)-C(18)	1·422	1·427	0·003
C(17)-C(22)	1·409	1·411	0·003
C(19)-C(20)	1·417	1·421	0·004
C(19)-C(21)	1·413	1·418	0·004
C(20)-N(5)	1·144	1·148	0·004
C(21)-N(6)	1·150	1·154	0·004
C(22)-C(23)	1·424	1·429	0·003
C(22)-C(24)	1·419	1·424	0·003
C(23)-N(7)	1·142	1·145	0·004
C(24)-N(8)	1·146	1·150	0·004

(c) Diquat ion

C(25)-C(26)	1·383	1·386	0·004
C(25)-C(36)	1·384	1·388	0·004
C(26)-C(27)	1·382	1·386	0·004
C(27)-C(28)	1·373	1·376	0·004
C(28)-N(9)	1·342	1·346	0·003
C(29)-C(30)	1·487	1·491	0·004
C(29)-N(9)	1·482	1·486	0·003
C(30)-N(10)	1·485	1·490	0·003
C(31)-C(32)	1·369	1·373	0·004
C(31)-N(10)	1·344	1·347	0·004
C(32)-C(33)	1·383	1·387	0·004
C(33)-C(34)	1·390	1·393	0·004
C(34)-C(35)	1·387	1·392	0·003
C(35)-C(36)	1·466	1·470	0·003
C(35)-N(10)	1·356	1·360	0·003
C(36)-N(9)	1·358	1·363	0·003

is 15·742 Å long. The dihedral angle between the two crystallographically independent TCNQ ions is 4·9°. The interplanar spacings between A' and A and B' and B are 3·22 and 3·26 Å respectively, indicating that the two pairs of centrosymmetrically related TCNQ ions tend to form two dimers. The mean separation between the two crystallographically independent ions A and B is 3·59 Å suggesting that here there is no appreciable molecular interaction.

Fig. 2 shows the three types of overlap A' on A, B' on B and B on A. The overlaps of A' on A and B' on B within the dimers are typical overlaps characteristic

of TCNQ salts and complexes. The overlap of B on A involves a large shift of centres parallel to the long molecular axis.

Fig. 3 (a) and Table 6 show the dimensions of the two crystallographically independent TCNQ ions. The bond lengths of the two TCNQ's agree very well between themselves and reasonably with the previously published dimensions for TCNQ⁻. The ions A and B are both not quite planar and have bowed configurations, the C=C–(CN)$_2$ groups being bent away from their centrosymmetrically related ions A' and B'. The C=C–(CN)$_2$ groups C(5)C(10)C(11)C(12)N(3)N(4) and C(14)C(19)C(20)C(21)N(5)N(6) are bent more noticeably from the planes of the quinonoid rings, the average dihedral angle between the mean planes through the C=C–(CN)$_2$ groups and the respective quinonoid rings being 9° in each case. The large bend of these C=C–(CN)$_2$ groups may also be related to the lengthening of the bonds C(5)–C(10) and C(14)–C(19) compared with C(2)–C(7) and C(17)–C(22). Nevertheless, these bonds differ in length from their respective means by less than 3 standard deviations.

Table 7. *Short intermolecular contacts*

(*a*) Molecule A to molecule A'

C(1^i)—C(2^{ii})	3·334 Å
C(1^i)—C(3^{ii})	3·109
C(2^i)—C(2^{ii})	3·175
C(2^i)—C(3^{ii})	3·243
C(4^i)—C(7^{ii})	3·279
C(4^i)—C(9^{ii})	3·282
C(5^i)—C(7^{ii})	3·189
C(5^i)—C(8^{ii})	3·360
C(6^i)—C(7^{ii})	3·373
C(6^i)—C(8^{ii})	3·274

(*b*) Molecule B to molecule B'

C(13^i)-C(22^v)	3·400
C(13^i)-C(23^v)	3·260
C(14^i)-C(22^v)	3·251
C(14^i)-C(23^v)	3·378
C(15^i)-C(22^v)	3·331
C(15^i)-C(24^v)	3·274
C(16^i)-C(17^v)	3·313
C(16^i)-C(18^v)	3·195
C(17^i)-C(17^v)	3·201
C(17^i)-C(18^v)	3·370

(*c*) Other intermolecular contacts

C(1^i)—N(1^{iii})	3·329
C(4^i)—C(26^i)	3·367
C(5^i)—C(26^i)	3·160
C(6^i)—C(26^i)	3·326
C(11^i)-N(3^{iv})	3·365
C(12^i)-C(33^{iv})	3·395
C(14^i)-C(31^{vi})	3·396
C(16^i)-N(8^{vii})	3·398
C(25^i)-N(7^i)	3·362
C(26^i)-N(8^i)	3·380
C(27^i)-N(7^{iii})	3·362
C(28^i)-N(6^{viii})	3·299
C(28^i)-N(5^v)	3·123
C(29^i)-N(5^{ix})	3·271
C(29^i)-N(3^{iv})	3·198
C(30^i)-N(2^x)	3·347
C(30^i)-N(5^{ix})	3·049
C(32^i)-N(1^x)	3·178

Table 7 (*cont.*)

C(33^i)-N(3^{xi})	3·375
C(33^i)-N(4^{iv})	3·274
C(34^i)-N(4^{vii})	3·324
C(35^i)-N(6^v)	3·138
C(35^i)-N(3^{iv})	3·219
C(36^i)-N(3^{iv})	3·152
N(3^i)—N(9^{iv})	3·107
N(3^i)—N(3^{iv})	3·348
N(5^i)—N(9^v)	3·373
N(6^i)—N(10^v)	3·357

Superscripts indicate the following equivalent positions:

i	x	y z	v	$1-x$	$\bar{y}$ $1-z$	xi	$x-1$	$1+y$ z
ii	$\bar{x}$	$\bar{y}$ $\bar{z}$	vi	x	$1-y$ z	x	x	$1+y$ z
iii	$x-1$	y z	vii	$1+x$	y z	xi	$1-x$	$1-y$ $\bar{z}$
iv	x	$1-y$ $\bar{z}$	viii	$\bar{x}$	$\bar{y}$ $1-z$			

The short interionic contacts are listed in Table 7. Though there are some short contacts between the TCNQs and the cation, it is difficult to interpret which of these contacts are attractive and which are repulsive in character. If we assume that the negative charge concentrates mainly on the nitrogen atoms of TCNQ, then the contact N(3)···N(9) = 3·107 Å may be considered as the attractive force between the two charged ions. The contacts C(35)···N(3) = 3·219 Å and C(36)···N(3) = 3·152 Å follow as a direct consequence of the N(3)···N(9) contact. The other close contacts C(28)···N(5) = 3·123 Å, C(28)···N(6) = 3·299 Å and C(35)···N(6) = 3·138 Å are probably unavoidable in view of the way the ions are packed and, if so, result in repulsive forces. In particular the close contact C(30)···N(5) = 3·049 Å is probably due to packing the non-planar cation with the planar TCNQ ions.

Fig. 3(b) shows the dimensions of the diquat ion. The bond lengths and the bond angles are in good agreement with the values reported for the ion in the crystal structure of diquat dibromide (Derry & Hamor, 1969). The ion is not planar. The two pyridinium rings are each nearly planar, but the dihedral angle between their mean planes is 22·0°, due essentially to a rotation of one ring with respect to the other about the central bond.

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