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The Crystal Structure of Bis(trimethylammonium) Tris-(7,7,8,8-tetracyanoquinodimethanide), $(TMA^+)_2(TCNQ)_3^{2-}$

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$(TMA^+)_2(TCNQ)_3^{2-}$ crystallizes in space group $C2/m$ with $a=26\cdot662$ (2), $b=9\cdot767$ (1), $c=7\cdot725$ (1) Å and $\beta=93\cdot98$ (3)° and with $Z=2$. The structure was deduced from a Patterson synthesis and refined by the block-diagonal least-squares method to an R value of 0·098 based on 1274 reflexions collected by diffractometer methods. The molecular geometries of the two independent TCNQ molecules indicate that they are in the states $TCNQ^0$ and $TCNQ^-$, respectively. $TCNQ^0$ is monomeric and two $TCNQ^-$ are stacked face-to-face to form a dimer. Overlap between $TCNQ^0$ and $TCNQ^-$ is very small. The crystals are constructed from the isolated monomers of $TCNQ^0$ and dimeric ions, $(TCNQ)_2^{2-}$. Molecular planes of all the TCNQ are parallel to the plane (010). Trimethylammonium cations are arranged in the channels formed by TCNQ molecules. The polarized crystal spectra were measured in 350–700 mμ region. The broad aspects of the spectra are similar to those of the other 2:3 complexes.

Introduction

The salts containing the anion radical of 7,7,8,8-tetracyanoquinodimethane (TCNQ) are noted among organic compounds for their high electrical conductivity. *N*-Methylphenazinium–(TCNQ) (Epstein, Etemad, Garito & Heeger, 1972) and quinolinium–$(TCNQ)_2$ (Walatka & Perlstein, 1971) are very highly conductive and they are considered to show metallic behaviour above *ca.* 200°K. Thus free electrons may exist in these crystals. The shape and size of the TCNQ units in these salts seem to be intermediate between those of $TCNQ^0$ and $TCNQ^-$ (Fritchie, 1966; Kobayashi, Marumo & Saito, 1971). In low-conductive crystals of $Cs_2(TCNQ)_3$ the excess electrons were found to be localized: $TCNQ^0$ and $TCNQ^-$ could be distinguished in the crystal (Fritchie & Arthur, 1966). However, the precise picture of the electronic states in the TCNQ radical salts does not seem to be fully understood. It may be of interest to see whether or not the excess electrons in TCNQ units are localized in $(TMA^+)_2(TCNQ)_3^{2-}$. The crystal structure of this compound was determined in order to gain a better knowledge about the charge localization in TCNQ molecules.

Experimental

The compound was prepared according to the method described by Melby, Harder, Hartler, Mahler, Benson & Mochel (1962). Trimethylamine vapour was introduced into the tetrahydrofuran solution of TCNQ. The resulting solution was allowed to stand overnight. Black crystals with a metallic lustre were collected by filtration. The TCNQ/cation ratio was determined as 1·5 from unit-cell dimensions and the density of the crystal, which was confirmed at a later stage by the crystal structure analysis. This composition does not agree with the reported value of 2.

The cell dimensions determined from higher order reflexions recorded on Weissenberg photographs were later refined by employing data obtained on a single-crystal diffractometer with Mo $K\alpha$ radiation ($\lambda=0\cdot7107$ Å). The density of the crystal was measured by flotation.

The crystal data are: $(C_3H_{10}N^+)_2(C_{12}H_4N_4)_3^{2-}$, F.W. 732·7; monoclinic, $a=26\cdot662$ (2), $b=9\cdot767$ (1), $c=7\cdot725$ (1) Å, $\beta=93\cdot98$ (3)°. Space group $C2/m$, Cm or $C2$ from systematic absences. $U=2007$ Å^3; $D_m=1\cdot195$ g cm^{-3}, $Z=2$, $D_x=1\cdot190$ g cm^{-3}. The linear absorption coefficient for Mo $K\alpha$ radiation, $\mu=0\cdot69$ cm^{-1}.

The intensity data were collected on a Rigaku automated four-circle diffractometer with Mo $K\alpha$ radiation monochromated by a graphite crystal. A crystal with a maximum dimension of about 0·3 mm was used. The ω–2θ scan technique was employed. Of the 4922 accessible reflexions with $2\theta\leq70°$, significant counts larger than 3σ were recorded for 1274 independent reflexions. Measurements of three standard reflexions were repeated every fifty reflexions. The fluctuations in the intensities of the standard reflexions were within 2–3%. The intensities were corrected for Lorentz and polarization effects, but corrections for absorption and extinction were not applied.

Structure determination

The space group $C2/m$ was assumed and this was indeed verified by the reasonable convergence of the structure at a later stage of the refinement. The trial structure was easily deduced from the three-dimen-

Table 1. *Atomic parameters*

Positional and thermal parameters of the non-hydrogen atoms (× 10^4), with their estimated standard deviations in parentheses. The B_{ij}'s are defined by:

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

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
N(1)	1763 (2)	0	777 (8)	16 (1)	333 (14)	302 (14)	0	4 (6)	0
N(2)	948 (2)	0	5368 (7)	17 (1)	162 (9)	196 (11)	0	0 (5)	0
N(3)	1764 (1)	3352 (4)	5517 (5)	14 (1)	194 (7)	348 (10)	0 (4)	3 (4)	5 (16)
N(4)	982 (1)	3196 (5)	309 (5)	21 (1)	254 (8)	213 (8)	−2 (5)	−1 (4)	6 (15)
N(5)	2702 (2)	0	7123 (7)	13 (1)	256 (11)	205 (12)	0	2 (5)	0
C(1)	451 (2)	0	−825 (7)	10 (1)	133 (9)	145 (11)	0	2 (5)	0
C(2)	456 (2)	0	1044 (7)	11 (1)	100 (8)	135 (10)	0	1 (5)	0
C(3)	−19 (2)	0	1819 (7)	11 (1)	129 (9)	157 (11)	0	2 (5)	0
C(4)	900 (2)	0	2039 (7)	12 (1)	142 (10)	129 (11)	0	1 (5)	0
C(5)	1382 (2)	0	1329 (8)	14 (1)	195 (11)	179 (13)	0	2 (6)	0
C(6)	920 (2)	0	3881 (8)	11 (1)	126 (9)	184 (12)	0	0 (5)	0
C(7)	446 (1)	3332 (4)	4175 (5)	12 (1)	110 (6)	186 (8)	0 (3)	2 (3)	2 (12)
C(8)	466 (1)	3337 (4)	5995 (5)	11 (1)	93 (5)	194 (7)	0 (3)	0 (3)	0 (12)
C(9)	3 (1)	3327 (4)	6791 (5)	13 (1)	106 (5)	154 (7)	0 (3)	1 (3)	0 (13)
C(10)	932 (1)	3354 (4)	7001 (5)	12 (1)	98 (5)	198 (8)	0 (3)	1 (4)	4 (12)
C(11)	1393 (1)	3357 (5)	6192 (5)	14 (1)	115 (6)	223 (9)	0 (4)	−1 (4)	6 (14)
C(12)	959 (1)	3269 (5)	8829 (5)	10 (1)	145 (6)	217 (8)	−1 (4)	−1 (3)	3 (14)
C(13)	2205 (2)	0	6239 (13)	13 (1)	207 (13)	336 (19)	0	−2 (7)	0
C(14)	2767 (3)	1274 (8)	8125 (8)	44 (2)	425 (17)	346 (16)	−17 (9)	5 (8)	−27 (28)

Table 1 (*cont.*)

Positional parameters of the hydrogen atoms (× 10^3)

	x	y	z	B(Å^2)	Population
H(1)	77	0	−132	2·9	
H(2)	−2	0	309	4·0	
H(3)	75	333	356	2·9	
H(4)	0	333	803	2·6	
H(5)	293	0	618	7·1	
H(6)*	193	40	718		0·5
H(7)	218	67	527		0·5
H(8)	207	86	606		0·5
H(9)	273	778	775		0·5
H(10)	292	804	795		0·5
H(11)	248	872	879		0·5
H(12)	311	878	860		0·5
H(13)	275	913	960		0·5
H(14)	318	950	871		0·5

* H(6) ~ H(14) are methyl hydrogen atoms. The mean isotropic temperatuie factor of these atoms is 8·0 Å^2.

sional Patterson synthesis. The atomic coordinates and isotropic thermal parameters of the non-hydrogen atoms were refined by block-diagonal least-squares methods. The R value was reduced to 0·17. A difference synthesis at this stage revealed the positions of four hydrogen atoms of the TCNQ molecules and a hydrogen atom attached to TMA. It also indicated the rotational disorder of the methyl hydrogen atoms. Accordingly, the methyl group was assumed to adopt two alternative orientations with equal probability. This disorder was taken into account in the subsequent refinement. After inclusion of the hydrogen atoms the structure was refined anisotropically. The R value converged at 0·098. At the final stage of the refinement all the parameter shifts of the non-hydrogen atoms were less than one eighth of their standard deviations. The

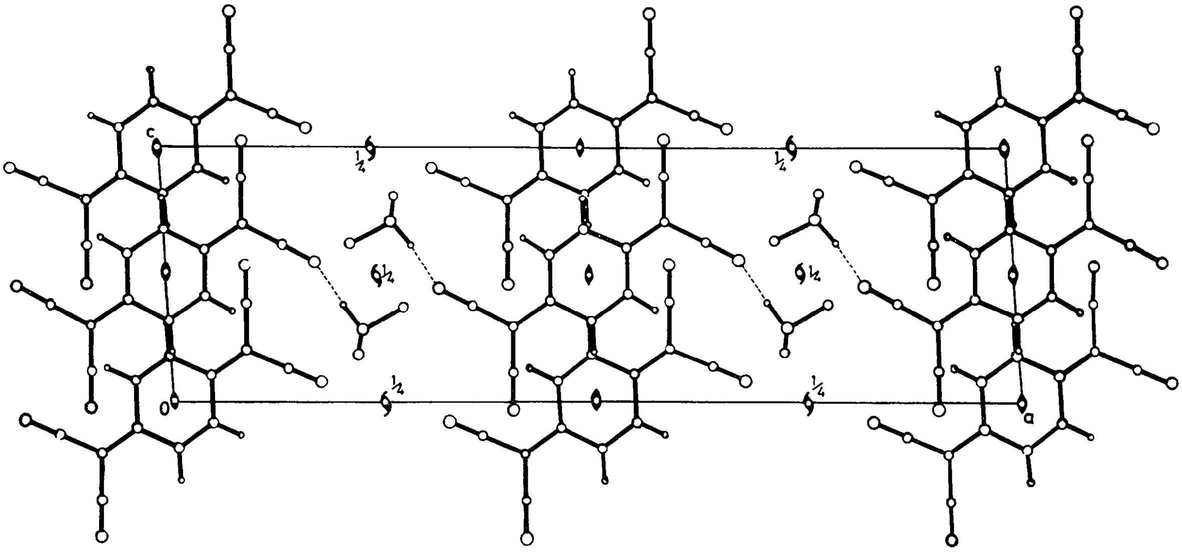


Fig. 1. A projection of the structure along the b axis.

weighting scheme adopted was: $\omega=1$ for $|F_o|\geq 7{\cdot}5$ and $\omega=0{\cdot}2$ for $|F_o|<7{\cdot}5$. The atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962). The positional and thermal parameters are listed in Table 1. The observed and calculated structure factors are compared in Table 2.

Description of the structure and discussion

A projection of the structure as viewed along the *b* axis is presented in Fig. 1. There are two crystallographically independent TCNQ molecules. The centre of gravity of one molecule lies at (000) (TCNQ 1) and that of the other lies at $(0,\frac{1}{2},\frac{1}{2})$ (TCNQ 2). TCNQ 1 and 2 are arranged on (010) with their long axis inclined at an angle of 34° with respect to the *a* axis. There is almost no overlap between TCNQ 1 and 2. TCNQ 1 is essentially a monomer. On the other hand, two TCNQ 2 molecules related by a centre of symmetry at $(0,\frac{1}{2},\frac{1}{2})$ form a dimeric pair with an interplanar distance of 3·26 Å. The interplanar distances between two TCNQ 2 molecules of two adjacent dimeric pairs is about 5·15 Å. Accordingly the structure is constructed from a mono-

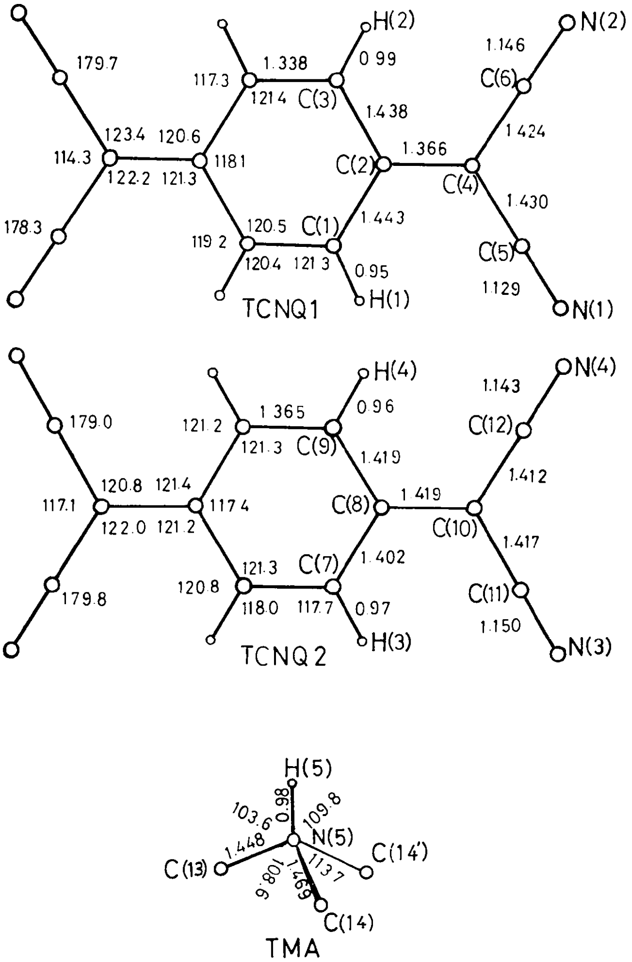


Fig. 2. Bond lengths (Å) and angles (°). Estimated standard deviations for C–C(N) and C(N)–H bonds are about 0·007 and 0·05 Å, respectively. Those for C–C(N)–C(N) and C–C(N)–H angles are 0·05 and 4·0°, respectively.

Table 2. *Observed and calculated structure factors* (× 10)

Table 3. *Interatomic distances*

Symmetry code

None	$x,\ \ y,z$	ii	$0{\cdot}5-x,0{\cdot}5-y,1-z$
i	$x,1-y,z$		

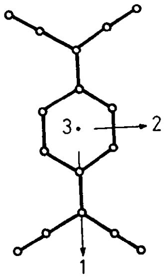
N(2)····C(14)	3·373 (8) Å
N(3)····N(3^{i})	3·220 (8)
C(7)····C(7^{i})	3·258 (6)
C(8)····C(8^{i})	3·249 (6)
C(9)····C(9^{i})	3·269 (6)
C(10)···C(10^{i})	3·215 (6)
C(11)···C(11^{i})	3·215 (6)
C(12)···C(12)	3·382 (7)
N(3)····N(5^{ii})	3·031 (8)
N(3)····C(14^{ii})	3·179 (7)
N(3)····H(5^{ii})	2·27 (5)

meric unit of TCNQ 1 and dimeric pairs of TCNQ 2 and TMA^+ ions. The cations are arranged in the channels formed by TCNQ molecules. The closest approach between the cation and TCNQ occurs between the nitrogen atom of the cation and a nitrogen atom of TCNQ 2. The N···N distance is 3·031 Å. Other important contacts are listed in Table 3.

The bond lengths and angles of TCNQ 1 and 2 and TMA^+ are shown in Fig. 2, and are not corrected for thermal vibration. Thermal ellipsoids are illustrated in Fig. 3. The molecular motion has been analysed in terms of the rigid-body vibration using the approach described by Cruickshank (1956). The translation (**T**) and the libration (**ω**) tensors are listed in Table 4. The translational motion is nearly isotropic, whereas the libration is markedly anisotropic. The smallest amplitude of translation of TCNQ 1 is parallel to the molecular plane. On the other hand, the direction of the smallest amplitude of TCNQ 2 is perpendicular to the molecular plane. The difference in the directions of the smallest molecular translation is certainly related to the fact that TCNQ 1 and 2 occur as monomeric units and dimeric pairs respectively in the crystal.

The bond distances of TCNQ 1 and 2 corrected for thermal vibrations are compared with those observed in other 2:3 compounds in Table 5. The values were averaged by assuming a D_{2h} symmetry. Significance tests on the differences in the bond lengths between TCNQ 1 and 2 were carried out (Cruickshank & Robertson, 1953). A multivariance significance test gave a value of $T^2=120$, which indicates the difference is highly significant for four degrees of freedom. As discerned from Table 5, TCNQ 1 and TCNQ 2 occur as $TCNQ^0$ and $TCNQ^-$, respectively. The dimeric pairs

Table 4. *Rigid-body thermal parameters*



TCNQ 1

Principal axes of the molecule in the form $L\mathbf{a}+M\mathbf{b}+N\mathbf{c}$

	L	*M*	*N*
1	0·0324	0·0	0·0735
2	−0·0191	0·0	0·1070
3	0·0	0·1024	0·0

Molecular vibrational tensors

$$\mathbf{T}\times10^4 \begin{pmatrix} 493 & 60 & 0 \\ & 330 & 0 \\ & & 482 \end{pmatrix} \text{Å}^2 \qquad \boldsymbol{\omega}\times10 \begin{pmatrix} 308 & 74 & 0 \\ & 51 & 0 \\ & & 51 \end{pmatrix} \text{deg}^2$$

Principal axes of the **T** and **ω** tensors relative to the molecular axes

R.m.s. amplitude	Direction cosines		
0·18 Å	−0·313	0·950	0·0
0·22	0·0	0·0	−1·0
0·23	0·950	0·313	0·0
1·8°	−0·257	0·966	0·0
2·3	0·0	0·0	−1·0
5·7	0·966	0·257	0·0

TCNQ 2

Principal axes of the molecule in the form: $L\mathbf{a}+M\mathbf{b}+N\mathbf{c}$

	L	*M*	*N*
1	0·0329	0·0	0·0703
2	−0·0181	0·0	0·1091
3	0·0	0·1024	0·0

Molecular vibrational tensors

$$\mathbf{T}\times10^4 \begin{pmatrix} 490 & 72 & 0 \\ & 457 & 0 \\ & & 380 \end{pmatrix} \text{Å}^2 \qquad \boldsymbol{\omega}\times10 \begin{pmatrix} 381 & -27 & 0 \\ & 27 & 0 \\ & & 59 \end{pmatrix} \text{deg}^2$$

Principal axes of the **T** and **ω** tensors relative to the molecular axes

R.m.s. amplitudes	Direction cosines		
0·19 Å	0·0	0·0	1·0
0·20	0·9264	−0·781	0·0
0·23	0·781	0·624	0·0
1·6°	0·075	0·997	0·0
2·4	0·0	−1·0	−1·0
6·2	0·997	−0·075	0·0

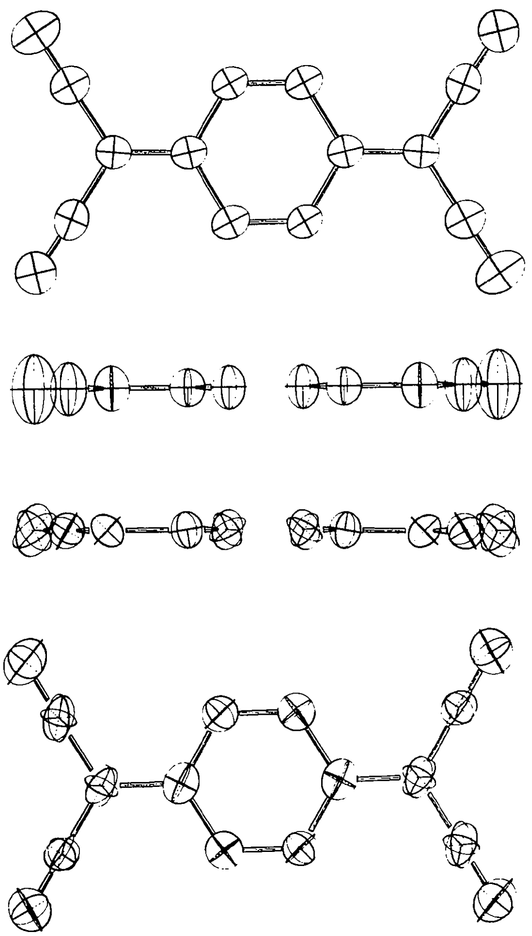


Fig. 3. Ellipsoids of thermal motion. TCNQ 1: above, TCNQ 2: below.

of TCNQ have also been recognized in crystals of tetraphenylphosphonium–TCNQ (Goldstein, Seff & Trueblood, 1968) and Rb–TCNQ I(Hoekstra, Spoelder & Vos, 1972); however, the structure containing isolated TCNQ^0 and (TCNQ)$_2^{2-}$ has not hitherto been reported.

The mode of overlap of TCNQ$^-$ in a dimeric pair is ring-ring type as illustrated in Fig. 4. Large inter-radical interactions in (TCNQ)$_2^{2-}$ may be expected in the present structure, since the repulsive energy between nonbonding atoms will be considerable in this configuration. Modified ring-ring overlap has been reported in crystals of Cs$_2$(TCNQ)$_3$ and (morpholinium)$_2$ (TCNQ)$_3$ (Sundaresan & Wallwork, 1972*a*). In Fig. 5, log *R* (*R*: electric resistance) of some TCNQ salts of known crystal structure is plotted against activation energy. It can be seen that the columnar structures of TCNQ seem to be closely related to the TCNQ/cation ratios and to have a bearing on the electric conductivity. The highly conductive compounds usually have columnar structures of monadic units of TCNQ (*N*-methylphenazinium–TCNQ, Fritchie, 1966; quinolinium–TCNQ$_2$, Kobayashi, Marumo & Saito, 1971; ditoluene chromium–TCNQ$_2$, Shibaeva, Atovmyan & Orfanova, 1969). In the 1:2 compounds, the shape and size of the TCNQ units are intermediate between TCNQ^0 and TCNQ$^-$. In many of the intermediate conductive salts with a TCNQ/cation ratio of 2, tetradic units are observed (triethylammonium–TCNQ$_2$, Kobayashi, Ohashi, Marumo & Saito, 1970; methylphenylphosphonium–TCNQ$_2$ and its arsonium analogue, McPhail, Semeniuk & Chesnut, 1971; *N*-(n-propyl)-quinolinium–TCNQ$_2$, Sundaresan & Wallwork, 1972*b*). The 2:3 compounds such as Cs$_2$(TCNQ)$_3$ and (morpholinium)$_2$ (TCNQ)$_3$(Sundaresan & Wallwork, 1972*a*) have triadic units of TCNQ and are mostly poorly conductive. Although having the same TCNQ/cation ratio, the present structure consists of monomeric and dimeric units of TCNQ instead of triadic units. Since no columnar structure of TCNQ exists in the crystal, the compound is expected to be poorly conductive, in agreement with our preliminary observation ($\varrho \geq 10^4$ Ω cm). In the 2:3 compound, excess charge is localized. In Cs$_2$(TCNQ)$_3$ and (morpholinium)$_2$(TCNQ)$_3$, which contain triadic units of TCNQ, excess charge is localized on the end TCNQ molecules of the triad. In the present structure the excess charge is on (TCNQ)$_2$. As for the tetrad units, it is not certain whether or not charge localization actually occurs. In methyltriphenylphosphonium(TCNQ)$_2$ and methyltriphenylarsonium (TCNQ)$_2$ charge localization was not observed. On the other hand, the geometries of TCNQ in the tetradic units of *N*,*N'*-dibenzyl-4,4'-bipyridinium(TCNQ)$_4$ (Sundaresan & Wallwork, 1972*c*) tend towards the interpretation of charge localization. Though less significant, there was also an indication of charge localization in the tetradic units in triethylammonium (TCNQ)$_2$ (Kobayashi *et al.*, 1970).

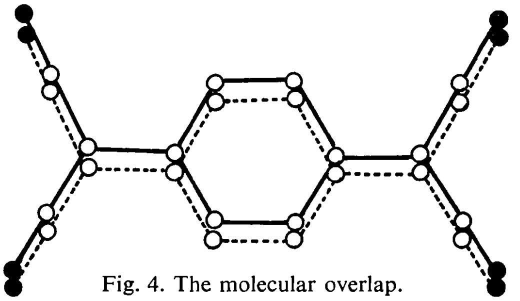
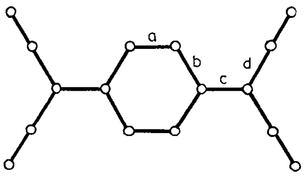


Fig. 4. The molecular overlap.

Table 5. *Comparison of mean bond lengths*



(TMA$^+$)$_2$(TCNQ)$_3^{2-}$	*a*	*b*	*c*	*d*
TCNQ 1	1·340	1·449 1·444	1·368	1·436 1·427
mean	1·340 (8)	1·447 (5)	1·368 (7)	1·433 (6)
TCNQ 2	1·367	1·427 1·410	1·421	1·425 1·420
mean	1·367 (6)	1·419 (4)	1·421 (6)	1·423 (5)
Δr	0·027	−0·028	0·053	−0·010
(Morp)$_2$(TCNQ)$_3$				
TCNQ^0	1·348 (3)	1·431 (3)	1·391 (3)	1·426 (3)
TCNQ$^-$	1·355 (3)	1·419 (3)	1·416 (3)	1·414 (3)
Δr	0·007	−0·012	0·024	−0·012
Cs$_2$(TCNQ)$_3$				
TCNQ^0	1·341 (5)	1·444 (4)	1·371 (5)	1·428 (4)
TCNQ$^-$	1·355 (4)	1·427 (3)	1·410 (4)	1·419 (3)
Δr	0·014	−0·017	0·039	−0·009

Polarized absorption spectra of single crystals

Polarized absorption spectra of single crystals of this compound are of interest in view of its characteristic structure involving TCNQ^0 and $(\mathrm{TCNQ})_2^{2-}$. Very thin plates with well formed {100} were obtained. The spectra were measured with a microspectrophotometer in the 350–690 mμ region and the results are presented in Fig. 6.

The peak intensities of the *b* and *c* polarized spectra around 16 kK and 27 kK are approximately equal to those observed in other 2:3 compounds (Iida, 1969). A broad band at about 26·5 kK is completely polarized along the *c* axis, indicating that the transition moment lies in the molecular plane. Neutral TCNQ in acetonitrile shows a band at about 27 kK (Boyd & Phillips, 1965; Rembaum, Hermann, Stewart & Gutmann 1969). Therefore, this *c*-polarized band at 26·5 kK may be due to the non-interacting TCNQ^0 and $(\mathrm{TCNQ})_2^{2-}$. A peak at 24·1 kK, whose transition moment is in the molecular plane, agrees well with that observed for monomeric TCNQ^- in an aqueous solution. Accordingly the electronic state of $(\mathrm{TCNQ})_2^{2-}$ in this crystal may be a mixture of monomeric and dimeric states. The crystalline spectra of other 2:3 compounds do not show the strong peak at 24 kK present in the case of this compound (Iida, 1969). A weak shoulder around 23·0 kK was also observed in $\mathrm{Cs_2(TCNQ)_3}$. A peak at 16·4 kK may be compared with that observed in simple salts such as Na(TCNQ) and K(TCNQ) and $\mathrm{Cs_2(TCNQ)_3}$ (Iida, 1969). In the latter case, this peak was ascribed to the shifted band of TCNQ^- monomer. The inter-radical charge-transfer spectrum appears at 15·4 kK, in agreement with the dimer spectrum in an aqueous solution (Boyd & Phillips, 1965). This band is polarized along the *b* and *c* axes, indicating that it possesses characteristics of charge transfer and local excitation. A weak shoulder at 18·5 kK may be ascribed to charge transfer in view of the polarization character.

All the calculations were carried out on HITAC 5020 of the Computer Centre at this University.

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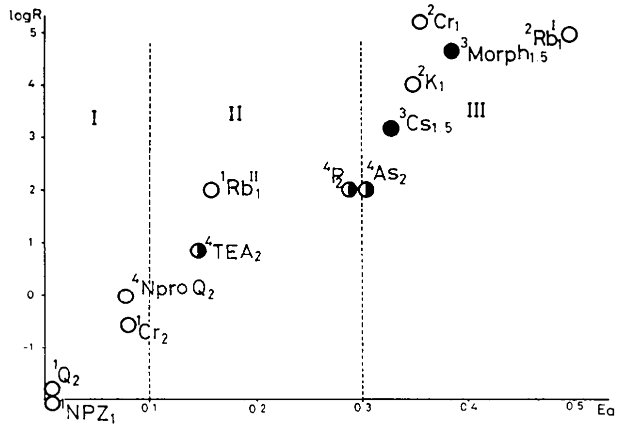

Fig. 5. A diagram showing the relation between the electric conductivity and the columnar structure of TCNQ anion radical salts. The TCNQ salts are distinguished by their cations. Superscripts and subscripts stand for the number of TCNQ molecules forming a repeating unit and TCNQ/cation ratios, respectively. Open or closed circles indicate that the localization of excess charge was or was not observed from molecular geometries. A half-closed circle shows that the charge localization is ambiguous.
NPZ: *N*-methylphenazinium, Q: quinolinium, NproQ: *N*-(n-propyl)-quinolinium, TEA: triethylammonium, Cr: ditoluene chromium, P: methyltriphenylphosphonium, As: methyltriphenylarsonium: Morph: morpholinium. I: highly conductive, II: intermediately conductive, III: poorly conductive. [$^2\mathrm{Rb}_1^{\mathrm{I}}$ RbTCNQ(phase II), Shirotani & Kobayashi (1973); $^2\mathrm{Cr}_1$, Shibaeva, Atovmyan & Rozenberg (1969); $^2\mathrm{K}_1$, Anderson & Fritchie (1963).]

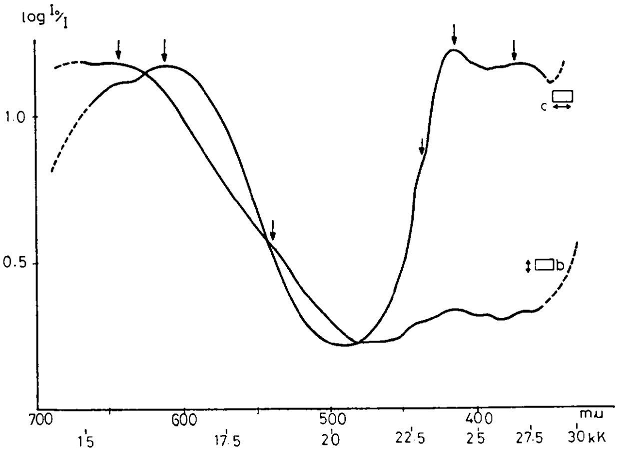

Fig. 6. Polarized absorption spectra of a single crystal.

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Crystal Packing of Amides: X-ray Structure Analysis of Optically Active Dilactylamide

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Crystals of optically active dilactylamide are hexagonal, space group $P6_522$ ($P6_122$), $a=b=8{\cdot}246\pm0{\cdot}005$, $c=22{\cdot}607\pm0{\cdot}015$ Å. The structure has been solved assuming that the molecules are held together in an infinite chain by hydrogen bonds and calculating all the possible helical conformations obeying the space-group symmetry. On the basis of packing criteria a unique solution was derived. The model was refined by least-squares methods to an R value of 0·045 for the 492 independent reflexions collected on a Siemens automatic diffractometer.

Introduction

The molecular packing modes of primary amides have been extensively reviewed by Rabinovich (1969), Leiserowitz & Rabinovich (1969) and Leiserowitz & Schmidt (1969). These authors have pointed out the role of the NH···O lone-pair geometry in the packing arrangement of primary amides and, by analysing different structures, have shown some possible modes of deformation of the ideal arrangement of the hydrogen-bond system. The purpose of this paper is to show the way in which the general criteria of the NH···O lone-pair geometry, combined with the lattice symmetry, can be usefully applied to obtain a straightforward solution of the crystal structure of an amide, the optically active dilactylamide. Preliminary data on this compound have been already reported (Martuscelli, Mazzarella, Palumbo & Pedone, 1969).

Experimental

Optically active dilactylamide, $O[CH(CH_3)CONH_2]_2$, was prepared according to the procedure described by Vièles (1935). Crystals were grown from a warm saturated aqueous solution by slow cooling. They are colourless prismatic, with hexagonal section, elongated along the c axis.

Crystals are hexagonal, space group $P6_522$ ($P6_122$) from systematic absences ($00l$ absent for $l\neq6n$) and the symmetry relationship of the reciprocal lattice ($I_{hkl}=I_{khl}$). Precise lattice constants were obtained from a least-squares refinement of the setting angles of 14 high angle reflexions on a Siemens AED automatic diffractometer with Cu $K\alpha$ radiation ($\lambda=1{\cdot}5418$ Å). A summary of the crystal data is given in Table 1. For the intensity measurements, the θ–2θ scan technique was employed. A standard reflexion was measured at regular intervals to monitor crystal stability. Its intensity remained essentially constant throughout the run. A total of 492 independent reflexions ($\theta_{\max}=65°$) with intensity values larger than $2{\cdot}5\sigma(I)$, was collected. Their intensities were corrected for Lorentz and polarization effects in the usual way.

Structure determination

The space-group symmetry requires a dyad axis, through the oxygen atom, to be present in the molecule.