

The Crystal Structure of Quinolinium Bis-(7,7,8,8-tetracyanoquinodimethanide), $Q^+(TCNQ)_2^-$

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Crystals of $Q^+(TCNQ)_2^-$ are monoclinic, with space group $C2/c$ and $a=28.468$, $b=3.838$, $c=25.704$ Å and $\beta=113.6^\circ$. There are four formula units in the unit cell. The structure was deduced from Patterson syntheses and refined by the block-diagonal least-squares method to an R value of 0.120 for 1274 observed reflexions. The structure consists of columns of monadic units of TCNQ parallel to the b axis. The TCNQ molecules are stacked in a fashion characteristic of the structures of TCNQ salts. The average spacing between the TCNQ molecules in the column is 3.22 Å. The shape and size of the TCNQ units seem to be intermediate between those of $TCNQ^0$ and $TCNQ^-$. Quinolinium cations are arranged in the channels formed by the TCNQ columns. The structure is disordered, with quinolinium cations adopting either of the alternative orientations with equal probability. They also form a stack parallel to the b axis with the much wider spacing of 3.50 Å. The estimation of molecular interaction energy for the system $(TCNQ)_2^-$ has revealed that the geometrical relationship of the two TCNQ units is determined primarily by the charge-transfer interaction and in part by interactions between the non-bonded atoms.

Introduction

The salts containing the anion radical $TCNQ^-$ are noted among organic compounds for their high electrical conductivity (Melby, Harder, Hertler, Mahler, Benson & Mochel, 1962; Siemons, Bierstedt & Kepler, 1963): the quinolinium salt shows an electrical conductivity as high as $100 \Omega^{-1} \text{cm}^{-1}$ at 300°K , for a single crystal in the direction of the highest conductivity.

X-ray studies of several TCNQ salts (Kobayashi, Ohashi, Marumo & Saito, 1970; Goldstein, Seff & Trueblood, 1968; Hanson, 1968; Fritchie, 1966; Fritchie & Arthur, 1966) have revealed that the planar TCNQ molecules are stacked face-to-face to form columns in most of these structures. The infinite columns hitherto reported are constructed from tetradic, triadic, diadic and monadic units of TCNQ molecules. The modes of nearest-neighbour overlapping of TCNQ molecules can be classified into two types. The first is direct and the second is such that the centre of one molecule falls over the centre of a quinomethane double-bond of the other. The interplanar distances are generally short, ranging from 3.22 to 3.32 Å.

In order to contribute to a better knowledge of the relation between the structures of these salts and their electric properties, the crystal structure of quinolinium bis-(7,7,8,8-tetracyanoquinodimethanide), $Q^+(TCNQ)_2^-$ has been determined.

Experimental

Crystal data

Quinolinium bis(7,7,8,8-tetracyanoquinodimethanide), $(C_9NH_8)^+ (C_{12}N_4H_4)_2^-$; F.W. 538.
Monoclinic

$$\begin{aligned} a &= 28.468 \pm 0.009, \quad b = 3.838 \pm 0.001, \\ c &= 25.704 \pm 0.007 \text{ \AA} \\ \beta &= 113.64 \pm 0.03^\circ, \quad U = 2572.8 \text{ \AA}^3 \\ D_m &= 1.398 \text{ g.cm}^{-3} \\ Z &= 4. \\ D_x &= 1.393 \text{ g.cm}^{-3} \\ F(000) &= 1108. \\ \mu(\text{Cu } K\alpha, \lambda = 1.5418 \text{ \AA}) &= 7.20 \text{ cm}^{-1}. \end{aligned}$$

Space group: $C2/c$ (No. 15) or Cc (No. 9) from the systematic absences: hkl absent when $h+k$ odd, $h0l$ absent when l odd.

The opaque black crystals of $Q^+(TCNQ)_2^-$ were kindly supplied by Dr T. Kondow. They are monoclinic needles elongated along the b axis. The unit-cell dimensions were determined from higher-order reflexions recorded on Weissenberg photographs. A specimen of length 0.30 mm was cut from a longer crystal with a cross section of 0.17×0.02 mm. Integrated Weissenberg intensity data were collected with $\text{Cu } K\alpha$ radiation around the b axis up to the third layer. The intensities of 1274 independent reflexions were estimated visually with a standard film strip. No absorption correction was applied, since the crystal used was sufficiently small.

Determination of the structure

The trial structure was easily deduced from the Patterson maps. The space group $C2/c$ was assumed and this was verified by the reasonable convergence of the structure at a later stage of the refinement. In the space group $C2/c$ the general position is eightfold. There

are only four quinolinium cations in the unit cell so the centre of gravity of a quinolinium cation must lie on one of the fourfold special positions. In the trial structure the quinolinium cations were assumed to have a centre of symmetry, either of the two alternative orientations being taken with equal probability. All the atoms except the hydrogen atoms came out clearly on three-dimensional electron density maps, the phases of which were calculated on the basis of the trial structure. Isotropic refinement was carried out by the block-diagonal least-squares method, with the use of the program written by T. Ashida and the resultant R value was 0.173. Anisotropic refinements were then carried out. The calculated positions of all the hydrogen atoms were included, but not refined. Temperature factors of the hydrogen atoms were

assumed to be isotropic and the value 3.0 \AA^2 was assigned. The weighting scheme adopted was: $w=1$ for $F_o \geq 5.0$ and $w=0.30$ for $F_o < 5.0$. The final R value was 0.120.

The possibility of the space group Cc was also considered. The trial model based on the space group Cc converged to an R value of 0.115. However, the estimated standard deviations of the atoms were twice as large as those of the atoms in the structure based on the space group $C2/c$ and, moreover, some of the thermal parameters, especially B_{22} , of certain atoms became unusually small or even negative. Thus the space group Cc was rejected.

The final positional and thermal parameters are given in Table 1. The observed and calculated structure factors are compared in Table 2.

Table 1. Final parameters and estimated standard deviations of non-hydrogen atoms

Temperature factor = $\exp [-(h^2 B_{11} + k^2 B_{22} + l^2 B_{33} + hk B_{12} + hl B_{13} + kl B_{23})]$.

	x $\times 10^4$	y $\times 10^4$	z $\times 10^4$	B_{11} $\times 10^5$	B_{22} $\times 10^3$	B_{33} $\times 10^5$	B_{12} $\times 10^4$	B_{13} $\times 10^5$	B_{23} $\times 10^4$
TCNQ									
C(1)	228	-1843	1339	92	37	123	-6	42	9
	3	26	4	14	8	17	9	13	10
C(2)	434	-763	940	124	35	81	-7	62	-11
	3	24	3	15	8	15	10	13	10
C(3)	872	1076	1093	124	36	112	2	59	-10
	3	25	3	15	8	17	10	13	10
C(4)	1149	2147	1682	102	53	110	14	67	23
	3	27	4	14	9	16	10	13	11
C(5)	941	1153	2091	115	30	100	11	41	-2
	3	24	3	15	8	16	9	13	10
C(6)	498	-788	1920	110	37	86	2	35	-1
	3	24	3	15	8	15	10	12	10
C(7)	-221	-3746	1168	83	33	69	2	19	12
	3	24	3	13	7	14	9	11	10
C(8)	1593	4072	1837	89	37	174	-5	58	4
	3	25	4	15	9	20	9	14	12
C(9)	-491	-4819	594	101	55	131	6	48	3
	3	27	4	14	8	18	10	13	11
C(10)	1789	5325	1443	48	53	165	1	28	8
	3	26	4	12	8	19	10	13	11
C(11)	1876	5147	2416	109	56	168	-6	66	8
	3	28	4	16	9	21	11	16	12
C(12)	-443	-4748	1561	126	53	93	-10	19	-25
	3	27	4	16	9	16	10	13	10
N(1)	-707	-5916	150	158	87	154	-16	67	-13
	3	26	3	15	9	16	11	13	11
N(2)	1936	6435	1118	158	98	253	13	130	37
	3	29	4	16	10	22	11	15	13
N(3)	2092	5949	2888	169	107	202	-10	-1	-33
	3	29	4	17	11	20	13	15	14
N(4)	-628	-5725	1855	117	130	87	-20	5	-1
	3	28	3	13	11	14	12	11	12
Quinolinium									
C(1')	3117	4505	46	156	44	286	17	155	16
	4	28	5	18	9	27	11	20	13
C(2')	3379	4457	636	113	84	253	-22	28	5
	4	33	5	18	12	28	13	18	16
C(3')	3159	3170	975	172	94	202	19	7	-21
	4	37	5	22	13	24	14	19	16
C(4')	2607	3206	-181	143	60	163	0	51	2
	4	31	4	18	10	21	11	15	13
C,N	2675	1904	762	171	86	182	11	135	-16
	3	29	4	17	10	18	11	16	13

in Fig. 2. This type of overlapping has been observed in various TCNQ salts such as *N*-methylphenazinium (TCNQ) (Fritchie, 1966), TEA⁺(TCNQ)₂⁻ (Kobayashi, Ohashi, Marumo & Saito, 1970) and TMPD⁺(TCNQ)₂^{-*} (Hanson, 1968). Bond lengths and angles of the TCNQ molecule and the quinolinium ion are shown in Fig. 3. The bond lengths of the TCNQ molecule averaged by assuming *D*_{2h} symmetry are also shown, in brackets. Most of them are intermediate between the values reported for TCNQ⁻ and TCNQ⁰ (Kobayashi, Ohashi, Marumo & Saito, 1970; Goldstein, Seff & Trueblood, 1968; Hanson, 1968; Fritchie, 1966; Fritchie & Arthur, 1966; Long, Sparks & Trueblood, 1965; Anderson & Fritchie, 1963). Thus the column appears to consist of TCNQ⁻ and TCNQ⁰ in a random arrangement, or simply of TCNQ^{-1/2}. Bond distances and angles observed for the quinolinium cation are in agreement with the values reported for the 8-hydroxyquinoline molecule of the molecular complex of 8-hydroxyquinoline and chloranil (Prout & Wheeler, 1967). The ellipsoids of thermal vibration are shown in Fig. 4. For TCNQ and Q⁺ the motion appears to be simply a rigid-body libration about the centre of gravity, chiefly in the molecular plane.

Some remarks on the intermolecular arrangement in the system (TCNQ)₂⁻

It is certain that the lattice energy of these anion radical salts arises mainly from the electrostatic interaction between the positive ions and the anion radicals. However, the existence of the columnar structure of TCNQ molecules seems to be a characteristic feature of the TCNQ salts. Further, as pointed out by Fritchie (1969), a fairly constant geometrical relationship was shown to exist between TCNQ molecules in a number of TCNQ salts, and this constancy was interpreted as indicating that the charge transfer force is predominant in these anion radical salts. In order to explore various molecular interactions, the system (TCNQ)₂⁻, which consists of two TCNQ molecules (TCNQ_a and TCNQ_b) and an electron, was studied. The ground-state wave function may be written as

$$\Psi = \Psi_1(\text{TCNQ}_a^-, \text{TCNQ}_b^0) + \Psi_2(\text{TCNQ}_a^0, \text{TCNQ}_b^-),$$

* TMPD: *N,N,N',N'*-Tetramethyl-*p*-phenylenediamine.

where $\Psi_1(\text{TCNQ}_a^-, \text{TCNQ}_b^0)$, for example, is a wave function associated with the electronic configuration where the excess electron is in the lowest vacant orbital of TCNQ_a⁻, both molecules being in the unexcited state. The expression for Ψ is reasonable because the energies of other electronic configurations are more than about 4eV higher than those of Ψ_1 and Ψ_2

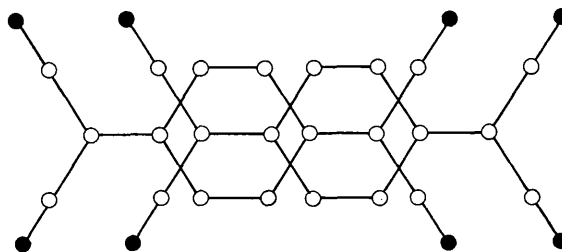


Fig. 2. Nearest-neighbour packing of TCNQ.

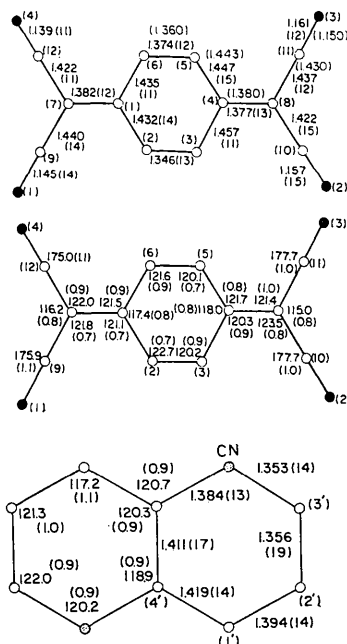


Fig. 3. Bond lengths (Å) and bond angles (degrees), with their standard deviations. The mean bond lengths of TCNQ averaged by assuming *D*_{2h} symmetry are shown in brackets.

Table 3. *Least-squares planes*

		Direction cosines with respect to				
		<i>a</i>	<i>b</i>	<i>c</i>		
	TCNQ	-0.5132	0.8392	0.0410		
	Quinolinium	-0.4074	0.9113	0.2180		
Deviation (Å)						
TCNQ	C(1)	-0.004	C(2)	0.001	C(3)	-0.030
	C(5)	-0.001	C(6)	0.002	C(7)	0.021
	C(9)	0.010	C(10)	0.035	C(11)	-0.046
	N(1)	-0.074	N(2)	0.143	N(3)	-0.055
Quinolinium	C(1')	-0.005	C(2')	0.004	C(3')	-0.001
			C,N	-0.001	C(4')	0.003

(Lowitz, 1967). Using the approximation, $\langle \Psi_1 | H | \Psi_2 \rangle = -kS_{12}$, the stabilization energy of the ground state can be given as

$$W_N = -kS_{12},$$

where $S_{12} = \int \Psi_1 \Psi_2 dr$. The constant k is about 20eV when Slater atomic orbitals are employed (Kuroda, Amano, Ikemoto & Akamatu, 1967). S_{12} was calculated using the formula proposed by Mulliken, Rieke, Orloff & Orloff (1949) under the following conditions.

(i) The molecular plane and the long axis of TCNQa are parallel to those of TCNQb.

(ii) The intermolecular distance is fixed at 3.22 Å which is the value observed for $Q^+(\text{TCNQ})_2^-$.

The result of this calculation revealed that the direct-overlap configuration (hereafter called configuration *A*) is most stable, the energy of which is about 12 kcal.mole⁻¹. The next most stable is the configuration where the centre of one molecule falls over the centre of one quinodimethane double bond of the other, the stabilization energy being about 7 kcal.mole⁻¹ (hereafter called configuration *B*).

In fact, both configurations are found in the structures of TCNQ salts; for example, configuration *A* is found in $\text{Cs}_2(\text{TCNQ})_3$ (Fritchie & Arthur, 1966) and

configuration *B* is found in the present structure and most of the other TCNQ-salt structures. The fact that configuration *B* is more frequently observed in actual structures would indicate that configuration *B* is more stable than configuration *A*. Clearly the repulsive interaction between two molecules tends to make configuration *B* more stable than *A*. Thus the interactions between non-bonded atoms were considered. The interaction energy can be given by

$$U = \sum_i \sum_j \frac{a_{ij} \exp(-b_{ij}r_{ij})}{r_{ij}d_{ij}} - \sum_i \sum_j \frac{c_{ij}}{r_{ij}^6} - \sum_i \frac{\alpha_i}{2} E_i^2,$$

where a_{ij} , b_{ij} , ... are constants associated with the i th atom of TCNQ and the j th atom of TCNQ⁻, r_{ij} is the interatomic distance, α_i the probability of the i th atom and E_i is the electric field on the i th atom of TCNQ⁰. The first term of U represents the repulsive energy, the second term the van der Waals energy and the third term is the energy of interaction between TCNQ⁻ and the dipole moments of the atoms of TCNQ⁰ induced by TCNQ⁻. The first two terms of the potential function were used by Giglio (1969) for the analysis of the crystal structure of dimethylglyoxime and the constants a_{ij} , etc. are given in his paper. The results of a calculation with slightly modified versions of the

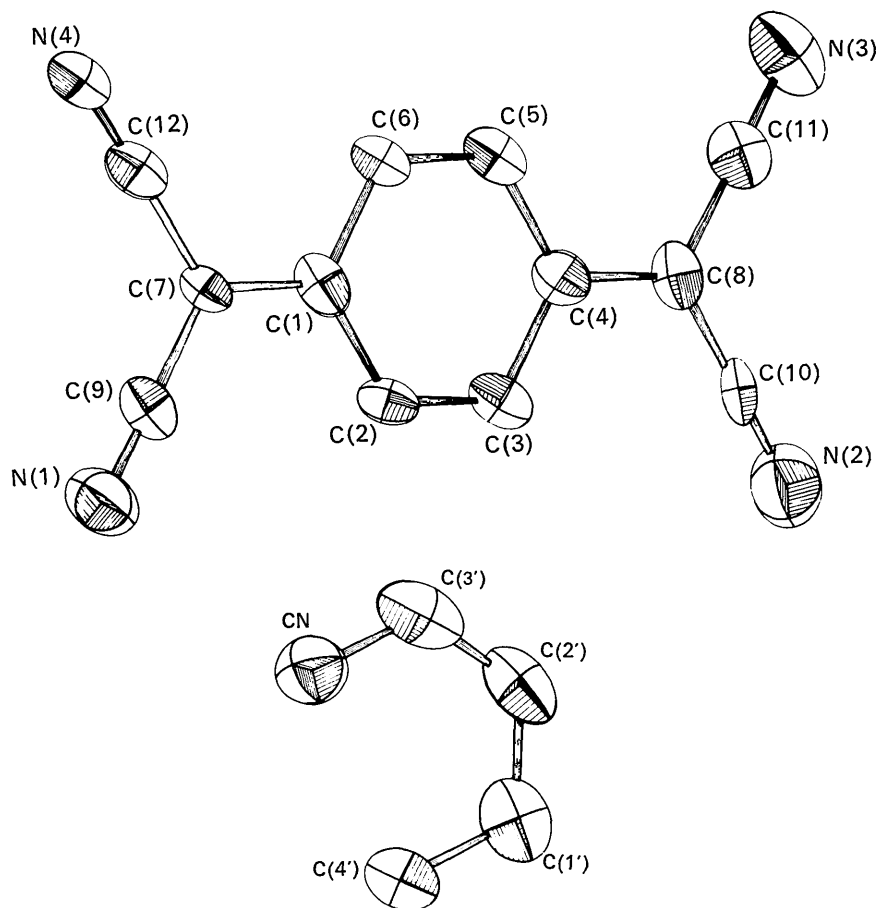


Fig. 4. The thermal motion ellipsoids drawn using the program *ORTEP* (Johnson, 1965).

constants used by Giglio show that configuration *B* is more stable than configuration *A*, in accordance with the experimental evidence. Although the result obtained here is sensitive to the choice of the various parameters, in particular those of repulsive energy, it is certain that the interactions between non-bonded atoms are important in the determination of the geometrical relationship between adjacent TCNQ molecules (Goldstein, Seff & Trueblood, 1968).

As mentioned above, TCNQ molecules are stacked face-to-face to form columns of monadic units of TCNQ. The same monadic unit has also been found in crystals of *N*-methylphenazinium(TCNQ). This fact seems to be closely related to the fact that the cations are planar (aromatic in both cases). It is noteworthy that both salts are among the best electrically conductive organic compounds hitherto reported.

The calculations were performed on the HITAC 5020E computer at the Computer Centre of this University with a universal crystallographic computation program system, *UNICS*, and on the FACOM 270-30 computer at this Institute.

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The Family 24L of ZnS Polytypes

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Twelve new ZnS polytypes of the family 24L have been found in two ZnS needles. Row lines of the X-ray oscillation photographs are shown. Observed and calculated intensities are compared.

Crystals of ZnS were grown from chemically pure ZnS powder in a quartz tube by outgassing for one hour at 650°C and then introducing H₂S at 1 atm pressure and increasing the temperature to 1280°C. This temperature was maintained for 20 hours. Two needle-shaped crystals with a hollow core along the axis containing polytypes of the family 24L were found in one batch.

Specimen 232/51 contains 9 wide (>0.1 mm) polytypic regions, six of which are new polytypes and specimen 232/56 contains 8 wide polytypic regions, six of which are new polytypes. A list of the polytypes found in these two specimens is given in Table 1.

The polytypic regions were photographed by the X-ray oscillation method using Cu K α radiation. The

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Table 1. *A list of the polytypes found in specimens 232/51 and 232/56*

Specimen No.	New polytypes	Other polytypes
232/51	72R (17 7) ₃	24L (21 3)*
	72R (22 2) ₃	72R (14 5 2 3) ₃ *
	72R (9 7 4 4) ₃	36R (7 5) ₃ †
	72R (17 3 2 2) ₃	3C
	72R (7 3 3 5 3 3) ₃	
	72R (8 6 3 2 2 3) ₃	
	72R (7 7 7 3) ₃	24L (7 7 5 5)*
232/56	24L (9 7 3 5)	24L (6 5 3 5 3 2)*
	72R (5 5 3 5 3 3) ₃	
	24L (6 5 3 3 3 4)	
	24L (7 3 3 7 2 2)	
	72R (7 5 4 2 3 3) ₃	

* Previously reported (Kiflawi & Mardix, 1969).

† Previously reported (Mardix, Kiflawi & Kalman, 1969).