

chemistry of the entire molecule is determined. This absolute configuration is presented in Figs. 1 & 2.

We express our appreciation to the Robert A. Welch Foundation for their financial support and the TCU Research Foundation for the purchase of the equipment. We also thank Dr I. L. Karle for helpful discussions and encouragement.

References

- AMES, T. R., HALSALL, T. G. & JONES, E. R. H. (1951). *J. Chem. Soc.* p. 450.
 BARTON, D. H. R. & HOLNESS, N. J. (1952). *J. Chem. Soc.* p. 78.
 BEYNON, J. H. (1960). *Mass Spectrometry and Its Applications to Organic Chemistry*, pp. 345-354. Amsterdam: Elsevier.
 CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* **18**, 104.
 DOUGLAS, G. K. & LEWIS, K. G. (1966). *Austral. J. Chem.* **19**, 175.
 HALSALL, T. G., JONES, E. R. H. & MEAKINS, G. D. (1952). *J. Chem. Soc.* p. 2862.
 KARLE, J. & HAUPTMAN, H. (1956). *Acta Cryst.* **9**, 45.
 KOENIG, D. E. (1969). Biology Department, Brookhaven National Laboratory, Upton, New York.
 LEWIS, K. G. (1959). *J. Chem. Soc.* p. 73.
 LINDGREN, B. O. & SVAHN, C. M. (1966). *Acta Chem. Scand.* **20**, 1720.
 SIMONSEN, J. & ROSS, W. C. J. (1957). *The Terpenes*, Vol. V, pp. 470-478. Cambridge Univ. Press.
 STEMPLE, N. R. (1970). Ph.D. Dissertation, Texas Christian Univ.
 STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175.

Acta Cryst. (1972). **B28**, 14

The Crystal Structure of Rubidium 7,7,8,8-Tetracyanoquinodimethane, Rb-TCNQ, at -160°C

BY A. HOEKSTRA, TINY SPOELDER AND AAFJE VOS

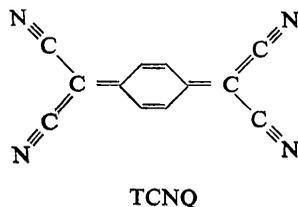
*Laboratorium voor Structuurchemie, Rijksuniversiteit Groningen,
 Zernikelaan, Paddepoel, Groningen, The Netherlands*

(Received 14 December 1970)

Crystals of Rb-TCNQ have monoclinic symmetry; the space group is $P2_1/c$, $a = 7.187$ (1), $b = 12.347$ (2), $c = 13.081$ (3) Å, $\beta = 98.88$ (2)°, $Z = 4$. Rb⁺ and TCNQ⁻ are both at general positions. The intensities were collected at -160°C on an automatic Nonius diffractometer. Approximate values for the atomic coordinates were obtained from Patterson and difference Fourier maps. Anisotropic least-squares refinement decreased the residual R to 0.066 for 5512 independent reflexions. The bond lengths in the TCNQ⁻ ion show that the ion has quinoid character; the group is not planar but has the shape of a shallow boat. The TCNQ⁻ radical-ions form charge-resonance bounded rows along the a axis. The interaction between the rows is small. Within a row interplanar spacings of 3.159 and 3.484 Å alternate. The distance of 3.159 Å is the shortest distance found so far between successive TCNQ planes. The Rb⁺ ions also form rows along the a axis with alternating distances of 3.483 and 3.726 Å between the ions. These distances are appreciably longer than twice the radius of Rb⁺ (3.0 Å). Rb⁺ is octahedrally surrounded by eight negatively charged TCNQ nitrogen atoms at distances of 2.982, 2.996, 3.004, 3.009, 3.025, 3.055, 3.057 and 3.108 Å.

Introduction

Salts of the stable TCNQ⁻ radical anion, derived from 7,7,8,8-tetracyanoquinodimethane (TCNQ), show interesting electrical and magnetic properties.



Some of these organic radical salts are among the

organic compounds with the highest electrical conductivities known, approximately 100 ohm⁻¹. cm⁻¹ at room temperature, whereas for others the conductivity is as small as 10⁻¹² ohm⁻¹. cm⁻¹ at room temperature (Acker, Harder, Hertler, Mahler, Melby, Benson & Mochel, 1960; Melby, Harder, Hertler, Mahler, Benson & Mochel, 1962). Recent measurements of the electrical conductivities and absolute magnetic susceptibilities of the crystalline M¹-TCNQ salts (M¹ = alkali cation) have revealed that phase transitions occur in all these salts except in Li-TCNQ (Vegter, Hibma & Kommandeur, 1969). Table 1 shows that especially for Rb-TCNQ the heat of transition is large. We observed that crystals of this compound do not remain single during the transition, indicating that the changes in the structure are pronounced.

Table 1. *Transition points T and heats of transition ΔH for the M^I -TCNQ salts and for Würster's blue perchlorate (TMPD·ClO₄)*

	T (°K)	ΔH (cal/mole)
*Li-TCNQ	no phase transition observed	
Na-TCNQ	348	unobservable
K-TCNQ	395	60
Rb-TCNQ	381	1010
Cs-TCNQ	210	unobservable
†ClO ₄ -TMPD	186	240

* Vegter, Hibma & Kommandeur (1969).

† see also: Nordio, Soos & McConnell (1966).

The magnetic susceptibilities of the M^I -TCNQ salts are so small (molar paramagnetic susceptibilities of the order 10^{-5} emu at room temperature), that they cannot be considered as approximately fully paramagnetic radical salts. Neither are the susceptibility data consistent with the usual relation

$$\chi_p T = (g^2 \beta^2 N_0 / 3k) [1 + \frac{1}{2} \exp(2J/kT)]^{-1}$$

for singlet ground-state dimers, each having a triplet state lying at an energy $2J$ above this ground-state (Vegter *et al.*, 1969). Therefore attempts have been made in the literature to find a theory to explain the magnetic properties. The proposed theories assume that the organic radicals are arranged in rows having little mutual interaction as is the case in Cs₂(TCNQ)₃ (Fritchie & Arthur, 1966), K-TCNQ (Anderson & Fritchie, 1963) and in Würster's blue perchlorate TMPD·ClO₄ (de Boer & Vos, 1971).

Our X-ray work on the M^I -TCNQ salts was initiated by the fact that only little structural information was available for these compounds. After some unsuccessful attempts to determine the crystal structures of Li-TCNQ and K-TCNQ, we were able to do a complete three-dimensional X-ray diffraction study of Rb-TCNQ at low temperature (-160°C).

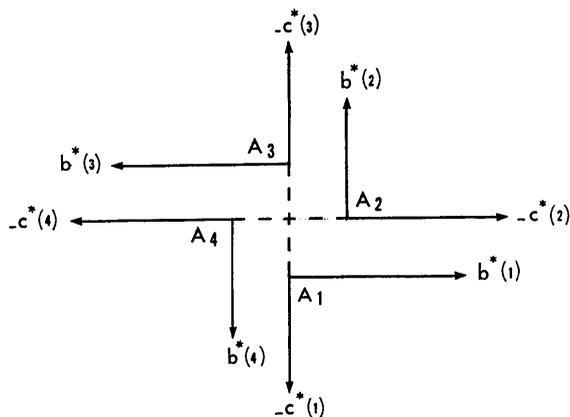


Fig. 1. Mutual orientation of the individuals in quadruplets of K-TCNQ. The locations of b^* and c^* on a non-zero layer line about the a axis are given. A_1 through A_4 are the points of intersection of the a^* axes with the layer line.

Preliminary work on Li-TCNQ and K-TCNQ

Li-TCNQ

We started to investigate Li-TCNQ as this compound has the advantage of having no transition point, so that the χ_p curve of the same modification can be studied over a large temperature range. No good crystals have been obtained so far, however. According to preliminary rotation and Weissenberg photographs the compound is tetragonal, $a=b=12.3$, $c=7.9$ Å, $Z=4$. The odd layers about the c axis are present as diffuse lines on the rotation photographs.

K-TCNQ

According to Anderson & Fritchie (1963) the compound is monoclinic, space group $P2_1/n$, $a=7.10$ (1), $b=17.80$ (3), $c=17.88$ (3) Å, $\beta=94.9$ (3)°, $Z=8$ indicating that there are two independent TCNQ units on general positions in the cell. We could verify the conclusions concerning the lattice parameters and space group, but found that the approximate tetragonal geometry in the bc plane gives rise to twinning with the formation of quadruplets around a . In Fig. 1 the relationship between the four individuals is given. It can be concluded that the approximate tetragonal symmetry observed by Anderson & Fritchie (AF) for the reflexions $0kl$ is partly due to the quadruplet formation.

The preliminary structure determination by AF shows that both the K^+ ions and the TCNQ groups are stacked in rows along the a axis. From the available experimental crystallographic evidence it is not certain whether or not there is a bimolecular association of TCNQ groups in the rows, as has been suggested by Vegter, Hibma & Kommandeur (1969).

Experimental work on Rb-TCNQ

Preparation and crystal data

Crystals of Rb-TCNQ were prepared by a diffusion process of RbI and TCNQ in acetonitrile by Vegter, Hibma & Kommandeur (1969), in the Laboratory for Physical Chemistry at Groningen. Use was made of the crystal growth apparatus described by Pott & Kommandeur (1967). The two parts of the apparatus were filled with a 0.09 M solution of RbI in acetonitrile and a 0.03 M solution of TCNQ in acetonitrile. Needles as long as 0.5 cm along the a axis were obtained.

The cell dimensions were determined from zero layer line Weissenberg photographs superimposed with NaCl reflexion spots for calibration purposes. Small crystals with dimensions of $0.1 \times 0.1 \times 0.1$ mm were used. During the exposure the crystals were cooled by a stream of cold nitrogen gas, obtained by evaporating liquid nitrogen. In this way a temperature of -160°C was achieved (measured with a copper-constantan thermocouple). The cell dimensions were calculated by a least-squares program from the $\sin^2 \theta/\lambda^2$ values of 62 reflexions [$\lambda(\text{Cu } K\alpha_2)=1.54434$ Å, $\lambda(\text{Cu } K\alpha_1)=1.54050$ Å, $a(\text{NaCl})=5.64006$ Å at 21°C].

In Table 2 the values obtained are given with the standard deviations as calculated by the least-squares program. The symmetry relations between the reflexions and the systematic absences observed on Weissenberg and precession photographs ($h0l$ absent for l odd, $0k0$ absent for k odd) are characteristic for the well known space group $P2_1/c$ (No. 14 in *International Tables for X-ray Crystallography*, 1959). Preliminary values for the cell dimensions at room temperature are $a=7.30$ (2), $b=12.40$ (4), $c=13.13$ (4) Å, $\beta=98.8$ (2°).

Table 2. *Crystal data of Rb-TCNQ at -160°C*

Monoclinic	Formula: $\text{C}_{12}\text{N}_4\text{H}_4\text{Rb}$;
$a=7.187 \pm 0.001$ Å	F.W. 290
$b=12.347 \pm 0.002$	$D_c=1.68$ g.cm $^{-3}$
$c=13.081 \pm 0.003$	$D_m=1.6$ g.cm $^{-3}$ (20°C)
$\beta=98.88 \pm 0.02^{\circ}$	$Z=4$
$V=1147$ Å 3	$\mu=45.5$ cm $^{-1}$ (Mo $K\alpha$)
Space group $P2_1/c$	$\mu=62.3$ cm $^{-1}$ (Cu $K\alpha$)

Structure factors

A crystal with dimensions of $0.31 \times 0.16 \times 0.16$ mm was used for the intensity measurements; it was mounted on the tip of a glass fibre and aligned along the monoclinic b axis. We collected the intensities on a three-circle automatic Nonius diffractometer, using the moving-counter moving-crystal method and Zr-filtered Mo radiation (Furnas, 1957). The crystal was again cooled down to -160°C by a cold stream of nitrogen gas. A cooling system designed by van Bolhuis (1971) was used.

All independent reflexions with $k < 4$ were measured up to $\theta=42^{\circ}$; for $k > 4$ only reflexions with $0 < \theta < 37^{\circ}$ were considered. Deviations from linearity of the (scintillation) counting equipment were kept below 1% by the use of attenuation filters; every two hours a reference reflexion was measured accurately. Corrections were made for intensity changes in the primary beam, for the Lorentz and polarization effects and for absorption. The latter corrections were calculated according to the Busing & Levy (1957) scheme: $6 \times 6 \times 6$ volume fragments and 6 accurately located bounding planes were taken into account. Reflexions with a negative net intensity were given zero weight. For the other reflexions the weight w_c was calculated from the relation $w_c = [\sigma_c(F)]^{-2}$, $\sigma_c(F)$ being the standard deviation in F due to counting statistics and errors in the filter factors (only for reflexions measured with an attenuation filter). For the structure determination 5512 reflexions with $w_c > 0$ were available.

Determination of the structure

The peaks in the Patterson synthesis indicated the Rb^+ ions lying approximately midway between two successive inversion centres in the x direction, for instance approximately at $(\frac{1}{4}, \frac{1}{2}, 0)$, $(\frac{3}{4}, \frac{1}{2}, 0)$, $(\frac{1}{4}, 0, \frac{1}{2})$ and $(\frac{3}{4}, 0, \frac{1}{2})$. The vector model for this case is strongly similar to the

vector model obtained for a location of the Rb atoms on inversion centres, for instance on $(0, \frac{1}{2}, 0)$, $(\frac{1}{2}, \frac{1}{2}, 0)$, $(0, 0, \frac{1}{2})$ and $(\frac{1}{2}, 0, \frac{1}{2})$. For the latter model some of the peaks are expected to be higher and sharper than for the former. From the heights and shapes of the peaks it was decided to place the independent Rb atom at $(0.25, 0.52, 0.01)$. Its position was refined by isotropic least-squares techniques. The reflexions with both h and $k+l$ even, having a large contribution of the Rb atoms, were used: $R=29.8\%$. The positions of the 'heavy' atoms of the TCNQ group could be selected from four images of the TCNQ group in a $[F_o - F_c(\text{Rb})]$ map of the reflexions with h and $k+l$ both even.

The least-squares refinement of the structure was done on a TR-4 computer with a program working in block-diagonal approximation (Cruickshank, 1961*b*). For the 'heavy' atoms (Rb^+ , C, N,) the scattering factors of Doyle & Turner (1968) were used and for hydrogen the f curve of Stewart, Davidson & Simpson (1965) was taken. After anisotropic refinement of the 'heavy' atoms, a difference Fourier synthesis of 3000 reflexions with $\sin \theta/\lambda < 0.68$ Å $^{-1}$ showed four positive areas at the positions expected for the four hydrogen atoms. In addition to these maxima there appeared to be diffraction ripples around the Rb atom. In the last few cycles of the least-squares refinement the hydrogen atoms were fixed at 1.08 Å from the respective carbon atoms. The valence angles were obtained from geometrical considerations and their temperature factors were assumed to be isotropic and were refined by the least-squares program. In the final stages of the refinement all 5512 reflexions were used with $w = [w_c^{-1} + p|F_o|^2]^{-1}$; the constant $p = 36 \times 10^{-4}$ was chosen such as to make $\langle w(F_o - F_c)^2 \rangle$ as equal as possible for different values of $\sin \theta/\lambda$ and $|F|$. The obtained values for $\langle w(F_o - F_c)^2 \rangle$ at the end of the refinement are given in Table 3. The weighted residual $R = [\sum w(F_o - F_c)^2 / \sum wF_c^2]^{1/2}$ was 6.57% for all reflexions. In the last cycle the shifts in the atomic positions were smaller than 0.1σ .

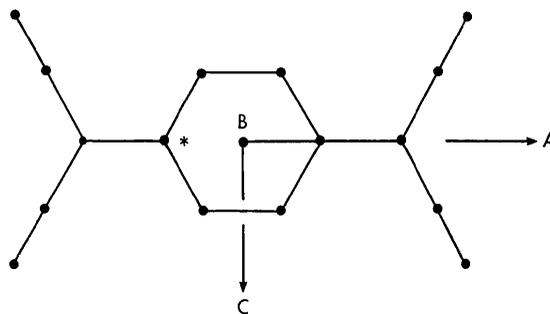


Fig. 2. Molecular axes. A and C lie in the least-squares plane of the quinoid skeleton, B is perpendicular to this plane. * is the projection along B of the point of intersection of the libration axes. The direction cosines (in units 10^{-4}) relative to a^* , b and c are: 4030, -6591 and 6350 for A , 9074, 3794 and -1804 for B and 1235, -6515 and -7486 for C .

The final parameters are listed in Tables 4 and 5, with (in parentheses) their standard deviations as calculated by the least-squares program. The observed and calculated intensities are compared in Table 6.

Table 3. $\langle w(F_o - F_c)^2 \rangle$ as a function of F and $\sin \theta / \lambda$

The average values are taken for the reflexions considered in each group.

Nr.	Nr. = number of reflexions in a group.		Nr. $\langle (\sin \theta / \lambda)^2 \rangle$ $\langle w(F_o - F_c)^2 \rangle$		
	$\langle F_o \rangle$	$\langle w(F_o - F_c)^2 \rangle$			
454	3.9	0.2	32	0.0146	7.8
2316	11.0	0.8	142	0.0483	3.4
1399	21.8	0.6	191	0.0938	1.7
668	32.7	0.8	239	0.1407	1.0
286	44.4	1.0	273	0.1874	0.7
164	55.4	1.2	293	0.2333	0.8
75	66.7	1.9	325	0.2797	0.5
69	78.0	1.6	351	0.3272	0.5
31	88.8	2.6	374	0.3739	0.6
19	99.2	1.4	383	0.4205	0.5
5	111.4	2.1	388	0.4665	0.6
4	121.9	2.3	449	0.5123	0.6
9	136.3	3.2	419	0.5590	0.6
5	145.3	2.6	464	0.6054	0.6
6	156.1	4.9	468	0.6530	0.6
0			404	0.6981	0.6
0			90	0.7444	0.8
0			81	0.7935	0.6
1	204.1	6.1	107	0.8390	0.8
1	212.4	0.1	39	0.8744	0.9

Thermal motion

The anisotropic thermal parameters (Table 5) of the 16 heavy atoms of the TCNQ molecule were used in an analysis of the rigid-body translational and librational motion (Cruickshank, 1956, 1961*a*). The point of intersection of the axes of libration was varied (Pawley, 1963). The results are listed in Table 7(*a*). From the unrealistically low values of ω_{22} and ω_{33} it must be

concluded that not too much physical significance can be attached to the values of T and ω and to the position of the point of intersection of the libration axes. No libration corrections have therefore been applied to the bond lengths given in Fig. 8.

Table 4. Final atomic coordinates ($\times 10^5$) and parameters B for the hydrogen atoms

Standard deviations ($\times 10^5$) are in parentheses. The positions of the hydrogen atoms were not refined. For numbering of atoms, see Fig. 3.

	x/a	y/b	z/c	$B(H)$
Rb	24054 (4)	51076 (2)	-356 (2)	
N(1)	6351 (42)	7669 (25)	-31757 (24)	
C(2)	9150 (43)	10142 (26)	-23211 (25)	
C(3)	12569 (42)	12945 (24)	-12526 (24)	
C(4)	5798 (42)	23139 (25)	-9822 (24)	
N(5)	375 (42)	31447 (24)	-7480 (25)	
C(6)	20745 (39)	5429 (24)	-4921 (24)	
C(7)	22672 (42)	7965 (24)	5826 (24)	
C(8)	30444 (40)	636 (24)	13162 (23)	
C(9)	36758 (40)	-9710 (24)	10267 (24)	
C(10)	34708 (42)	-12232 (24)	-439 (23)	
C(11)	26899 (42)	-4912 (26)	-7775 (24)	
N(12)	54551 (40)	-36453 (23)	12813 (22)	
C(13)	50235 (43)	-27861 (25)	15044 (24)	
C(14)	44799 (43)	-17369 (24)	17775 (23)	
C(15)	46719 (42)	-15192 (24)	28484 (24)	
N(16)	48386 (42)	-13428 (23)	37247 (22)	
H(17)	18059	15683	8219	0.1 (6) Å ²
H(18)	31851	2776	21213	1.1 (8)
H(19)	39301	19961	-2841	2.1 (9)
H(20)	25498	-7042	-15830	1.4 (8)

Although only qualitative aspects of the thermal motion can be discussed, it is noticeable that the longest principle axis of libration nearly coincides with the molecular axis A (Fig. 2) for which the moment of inertia is smallest. The translation appears to be smallest along

Table 5. Final thermal parameters

The temperature factor is of the form

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

All values are multiplied by 10^4 and standard deviations are given in parentheses.

	U_{11}	U_{22}	U_{33}	$2U_{12}$	$2U_{23}$	$2U_{13}$
Rb	122 (1)	144 (1)	134 (1)	6 (2)	-6 (3)	7 (2)
N(1)	215 (13)	204 (14)	149 (13)	22 (22)	-41 (22)	-12 (22)
C(2)	138 (12)	130 (13)	140 (14)	50 (20)	37 (22)	-14 (21)
C(3)	137 (12)	88 (12)	111 (13)	21 (19)	-24 (20)	-35 (20)
C(4)	137 (12)	126 (13)	107 (13)	-29 (20)	26 (21)	-28 (20)
N(5)	204 (13)	164 (13)	210 (15)	19 (21)	-61 (23)	-5 (22)
C(6)	104 (11)	99 (12)	105 (12)	-9 (19)	-42 (20)	-5 (19)
C(7)	160 (13)	92 (12)	104 (12)	5 (20)	-11 (20)	46 (20)
C(8)	147 (11)	100 (12)	101 (11)	-12 (20)	-28 (20)	39 (18)
C(9)	111 (11)	106 (12)	101 (12)	-17 (19)	-8 (20)	21 (19)
C(10)	157 (12)	93 (12)	80 (12)	39 (19)	-23 (19)	18 (20)
C(11)	136 (12)	130 (13)	91 (12)	16 (20)	-17 (20)	17 (20)
N(12)	206 (13)	138 (12)	135 (12)	44 (20)	-15 (20)	-11 (20)
C(13)	158 (13)	129 (13)	82 (12)	-31 (20)	16 (20)	-18 (20)
C(14)	171 (13)	97 (12)	80 (12)	-1 (20)	-17 (20)	26 (20)
C(15)	158 (13)	88 (12)	97 (12)	-8 (19)	18 (20)	24 (20)
N(16)	259 (14)	148 (13)	111 (12)	31 (21)	19 (20)	34 (21)

Table 6. Comparison of observed and calculated intensities

The running index is h; values of k and l for each group immediately precede that group. The value for |F_o|² is given first, the second value is |F_c|²

Table with columns for h, k, l, |F_o|², and |F_c|². The table contains multiple rows of data, each representing a different set of Miller indices (h, k, l) and their corresponding observed and calculated intensities. The data is organized into several groups, with the running index h being the primary key for each group. The values for |F_o|² and |F_c|² are listed in columns, with the observed intensity |F_o|² appearing first and the calculated intensity |F_c|² appearing second for each group. The table is dense with numerical data and includes various sub-headers and group labels such as '0, 0, L', '1, 0, L', '2, 0, L', etc., indicating different crystallographic directions or symmetry groups. The values range from 0 to over 1000, with some groups showing a high degree of agreement between observed and calculated values, while others show significant discrepancies. The table is a comprehensive comparison of experimental data with theoretical calculations for the crystal structure of Rb-TCNQ at -160°C.

Table 6 (cont.)

Table with multiple columns of numerical data, likely representing coordinates or parameters for different TCNQ groups. The table is organized into several sections with headers like '1.7.1', '1.7.2', etc., and contains numerous rows of values.

the B axis, which is reasonable in view of the packing of the molecules to be discussed in the next section.

compared in Table 7(b). We see that the thermal motion in Rb-TCNQ, studied at -160°C, is relatively small. Our rather inaccurate thermal parameters do

Table 6 (cont.)

5 289 289	0 724 734	8 1350	12 -10 130 14	6 178 231	-1 43 91	1 -17.L	1 188 127 -10	12 24	-8 210 146 -11	629 801	7 29 74	5.18.L	+4 1272 1039	1 44	-11 171	1	
4 7 104	2 818 1518	10 55	5 -8 38 18	9 15 34	1 35	-10 886 617	5 214 213	-4 266 182	-4 45	5 -10 775 524	8 139 117	-2 571 576	-4 454 584	2 642 1176	1 170.L		
8 210 248	4 11 11 649	615 -7	22 299	5.16.L	2 41 30 -10 992 617	5 214 213	-4 266 182	-4 45	5 -10 775 524	8 139 117	-2 571 576	-4 454 584	2 642 1176	1 170.L			
W 231 213	4 77 146 13	441 592	-6 243 250		3 240 224	-8 588 924	8 135 177	-5 108 114	-2 129 92	-6 342 342		3.18.L	-3 480 480	1 132 14	6 275 374		
7.15.L	4 432 522		22 299		-3 488 055	-12 32 96	4 172 88	-8 588 924	8 135 177	-5 108 114	-2 129 92	-6 342 342		3.18.L	-3 480 480	1 132 14	6 275 374
-10 324 303	10 102 146	-13 289 216	-2 10	-11 437 552	6 157 81	-1 384 311	11 121 96	-3 185 202	0 67 185	-4 29 82	-9 380 497	1 630 543	1 86 21	4.19.L	-4 96 96		
-9 339 289	11 96 46	-11 36	0 12	-1 138 198	5 117 81	-1 172 188	4 74 138	-4 31 8	-1 168 9	1 612 188	2 1 612 188	4 174 138	4 320 990	-4 48 12	2 41 6		
+4 366 681	12 171 110	225 134	1 133 192	-8 92 142	7 331 158	-1 142 152	5 117 81	-1 168 9	1 612 188	2 1 612 188	4 174 138	4 320 990	-4 48 12	2 41 6			
+4 136 1303	13 90 42	-9 2	3 2 49	-6 76 1	-7 702 76	-8 22 14	-1 114 35	-12 74 76	2 149 151	5 246 159	1 1033 1452	-7 262 250	3 1731 1714	5 320 990	-4 48 12	2 41 6	
+4 976 937	14 272 228	-7 35	71 4	4 53 15	-4 30 81	-7 433 475	2 1492 1347	-10 408 389	5 335 228	7 17.L	2 12 12	-2 137 42	-7 111 94	4 275 374			
-10 77 16 480	271 48 346	376 5	756 824	-3 518 457	-8 56 123	3 177 81	-9 71 0	7 269 262	3 269 262	7.17.L	3 424 445	-1 1024 804	4.18.L	2.19.L	-1 35 35		
-2 392 392	17 22 159	-4 351 392	6 47 137	-2 17 44	-4 290 244	4 2180 2078	8 400 992	8 292 249	-3 86 0	5 256 276	2 53 55	-4 224 76	-8 59 8	1 41 3			
-1 144 121	-3 137 53	7 807 825	-1 610 524	-3 454 309	6 590 497	-9 428 384	4 542 196	-2 812 708	6 22 38	3 240 240	-2 320 342	-7 94 76	3 253 272	-4 96 15			
0 497 433	1.18.L	-2 346 250	8 20 14	3 45 52	-1 650 448	6 50 50	-4 110 1592	4 542 196	-2 812 708	6 22 38	3 240 240	-2 320 342	-7 94 76	3 253 272	-4 96 15		
3 423 407	-1 14 3	9 289 428	1 949 784	2 92 108	1 487 576	6 50 50	-4 110 1592	4 542 196	-2 812 708	6 22 38	3 240 240	-2 320 342	-7 94 76	3 253 272	-4 96 15		
3 10 18 14	92 7	0 950 615	11 276 210	1 1022 1149	1 487 576	6 50 50	-4 110 1592	4 542 196	-2 812 708	6 22 38	3 240 240	-2 320 342	-7 94 76	3 253 272	-4 96 15		
4 154 149	-13 784 751	-1 14 3	9 289 428	1 949 784	2 92 108	1 487 576	6 50 50	-4 110 1592	4 542 196	-2 812 708	6 22 38	3 240 240	-2 320 342	-7 94 76	3 253 272	-4 96 15	
5 10 30 -11	440 435	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	
6 324 256	-10 6	3 4 536 515	1.16.L	7 328 408	8 174 7	9 328 408	10 174 7	11 328 408	12 174 7	13 328 408	14 174 7	15 328 408	16 174 7	17 328 408	18 174 7	19 328 408	
8.15.L	-9 48 79	6 312 302	-13 119 18	8 134 7	9 328 408	10 174 7	11 328 408	12 174 7	13 328 408	14 174 7	15 328 408	16 174 7	17 328 408	18 174 7	19 328 408	20 174 7	
-7 146 59	-5 467 350	8 121 146	-11 46 50	0 52 104	2 88 88	-12 10 4	1 72 10	-4 812 692	4 137 189	-8 77 180	-7 81 37	3 22 138	4 50 11	9 16	4 38 76		
+6 39 4	-8 88 151	10 75	16 100 276	249 8.16.L	6 157 73	-2 286 199	6 492 772	1 94 92	9 145 3	-2 432 433	-3 98 108	11 114 76	3.19.L	0 11 2	-2 24 4		
-9 231 94	-3 1030 1046	11 12	12 8 93 144	-10 41 70	8 157 73	-2 286 199	6 492 772	1 94 92	9 145 3	-2 432 433	-3 98 108	11 114 76	3.19.L	0 11 2	-2 24 4		
-4 51 9	-2 59 152	12 202 190	-7 31 4	-10 41 70	8 157 73	-2 286 199	6 492 772	1 94 92	9 145 3	-2 432 433	-3 98 108	11 114 76	3.19.L	0 11 2	-2 24 4		
-3 77 232	-1 1689 1822	13 225 306	-5 37 92	-10 41 70	8 157 73	-2 286 199	6 492 772	1 94 92	9 145 3	-2 432 433	-3 98 108	11 114 76	3.19.L	0 11 2	-2 24 4		
-2 251 92	0 13 46	-4 290 207	-6 22 24	-4 290 207	-6 22 24	-4 290 207	-6 22 24	-4 290 207	-6 22 24	-4 290 207	-6 22 24	-4 290 207	-6 22 24	-4 290 207	-6 22 24		
-1 228 144	1 1544 1632	3.16.L	-2 632 592	-5 412 433	-1 89 89	0 67 89	4 146 146	12 372 193	1 128 48	2 7 85 14	149 14	-7 78 2	3 27 7				
-2 139 139	3 1183 1150		-1 110 21	-5 137 36	13 156 158	-1 92 132	4 146 146	12 372 193	1 128 48	2 7 85 14	149 14	-7 78 2	3 27 7				
0 137 91	1 115 114	-11 908 488	-1 110 21	-5 137 36	13 156 158	-1 92 132	4 146 146	12 372 193	1 128 48	2 7 85 14	149 14	-7 78 2	3 27 7				
0.16.L	2 482 481	-11 908 488	2 243 154	-2 139 152	16 38	7 2 148	-2 111 146 123	4.17.L	1.18.L	6 32 32	7 1 68	-7 219 257	7 445 511 10	1 6			

not reveal deviations from the rigid body behaviour as observed in $\text{TMPD}(\text{TCNQ})_2$ and in tetraphenylphosphonium- $(\text{TCNQ})_2$ at room temperature. In the latter compounds, as well as in tetracyanoethylene, the $\text{C}\equiv\text{N}$ groups clearly suffer non-rigid thermal motion (Hanson, 1968; Goldstein, Seff & Trueblood, 1968; Bekoe & Trueblood 1960). For all TCNQ groups in Table 7(b) the libration is largest around the axis with the smallest moment of inertia.

Description of the structure

Packing

The structure in [100] and [010] projection is given in Figs. 3 and 4. It is easily seen that both the TCNQ groups and the Rb atoms are arranged in rows along the a axis. Similar rows have not only been observed in many other TCNQ salts and in TCNQ itself (Fritchie & Arthur, 1966; Fritchie, 1966; Williams & Wallwork, 1968; Long, Sparks & Trueblood, 1965), but also in organic radical salts with positive organic groups, such as Würster's blue perchlorate $\text{TMPD}\cdot\text{ClO}_4$ (de Boer & Vos, 1971). Wallwork (1961) noticed that strong intermolecular interaction between two different molecules, like TMPD and chloranil, also results in a characteristic plane-to-plane packing; in this case the components alternate.

In Rb-TCNQ the non-bonded distances between the heavy atoms of successive TCNQ rows are all more than 0.24 \AA longer than the sum of the van der Waals radii, indicating that there is little interaction between the TCNQ rows. The same holds for the TMPD rows in $\text{TMPD}\cdot\text{ClO}_4$ and in $\text{TMPD}\cdot\text{I}$ (de Boer, Vos & Huml, 1968).

The surroundings of the Rb⁺ ions

The distances between the Rb⁺ ions in the a direction are alternately 3.483 and 3.726 \AA , and thus appreciably larger than twice the non-bonded radius of Rb⁺ (1.5 \AA ; Pauling, 1960). Each Rb⁺ ion is surrounded by a distorted cube consisting of eight slightly negatively charged (see Table 8) nitrogen atoms at distances of 2.982 , 2.996 , 3.004 , 3.009 , 3.025 , 3.055 , 3.057 and 3.108 \AA from the positive ion. All these

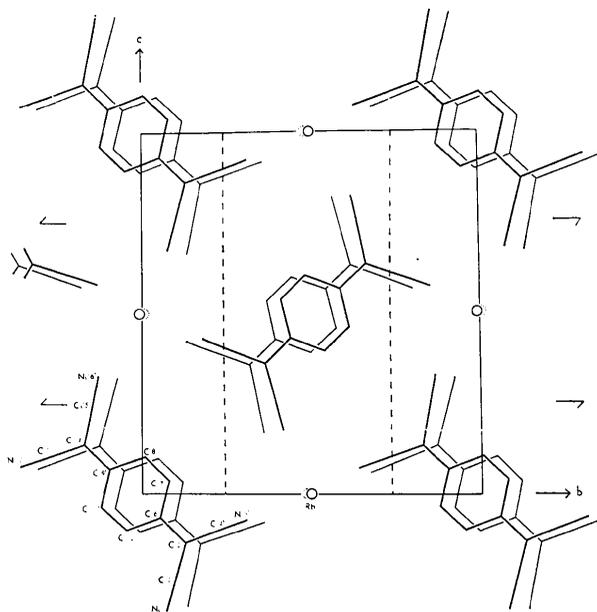


Fig. 3. Projection of the Rb-TCNQ structure along the a axis onto the plane (100). The centres of the molecules and the Rb atoms lie approximately at heights $\frac{1}{4}$ and $\frac{3}{4}$, the terminal nitrogen atoms are approximately at heights 0 and $\frac{1}{2}$ (see Fig. 4).

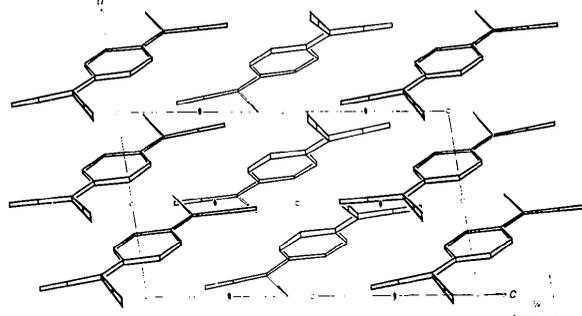


Fig. 4. Projection of the Rb-TCNQ structure along the b axis. Molecules with centres at height $y \approx 1$ are given by thick lines, those lying at $y \approx \frac{1}{2}$ are indicated by thin lines. The Rb atoms coincide with the centres of the molecules in the present projection and are not shown.

distances are not much different from the sum of the relevant van der Waals radii [$r(\text{Rb}^+) = 1.5$, $r(\text{N}) = 1.5$ Å; Pauling, 1960].

Comparison of the surroundings of the positive ions in Rb-TCNQ and in $\text{Cs}_2(\text{TCNQ})_3$ shows that there are noticeable differences. Fig. 3 illustrates that in Rb-TCNQ four rows, each with two molecules, are involved in the coordination of the Rb^+ ion, so that each nitrogen atom of the coordination cube belongs to a different TCNQ molecule. According to the preliminary model of Anderson & Fritchie (1963) the same holds for K-TCNQ. In $\text{Cs}_2(\text{TCNQ})_3$, on the other hand, only four TCNQ molecules are involved in the cube surrounding the Cs^+ ion (Fritchie & Arthur, 1966); in this case the two cyano groups at the same

end of a TCNQ molecule are coordinated to the same Cs^+ ion, as is seen from Fig. 5. Moreover Fig. 5 shows that in Rb-TCNQ and in K-TCNQ the cubes share sides, whereas in $\text{Cs}_2(\text{TCNQ})_3$ successive cubes have edges in common. No explanation has been given yet for these differences.

The TCNQ rows

The arrangement of the TCNQ groups within a row is schematically shown in Fig. 6; some interesting distances have been added. The TCNQ units are stacked in a plane-to-plane manner. A very interesting feature of the row is that a very short interplanar distance (distance between neighbouring 'best benzene planes') of 3.159 Å alternates with a larger distance of 3.484 Å. These interplanar distances may be compared with distances in similar compounds. Both in TCNQ itself (Long, Sparks & Trueblood, 1965) and in *N*-methylphenazinium-TCNQ (Fritchie, 1966) the groups in a row are equally spaced, with observed distances of 3.45 Å for TCNQ and of 3.26 Å for the phenazinium salt. A recent structure determination of triethylammonium-(TCNQ)₂ has shown that the TCNQ row in this compound contains the distance-sequence 3.32, 3.30, 3.24 Å (Kobayashi, Ohashi, Marumo & Saito, 1970).

The above values show that the distance of 3.159 Å in Rb-TCNQ is the shortest interplanar TCNQ distance observed so far, whereas it is also considerably shorter than the distance of 3.4 Å which is often found between neighbouring aromatic rings. It must thus be concluded that there is a strong interaction between the groups A_1 and B_1 in Fig. 6. A spectroscopical study by Boyd & Phillips (1965) has shown that also in solution strong interaction between TCNQ groups can be present. The authors assume a dimerization of

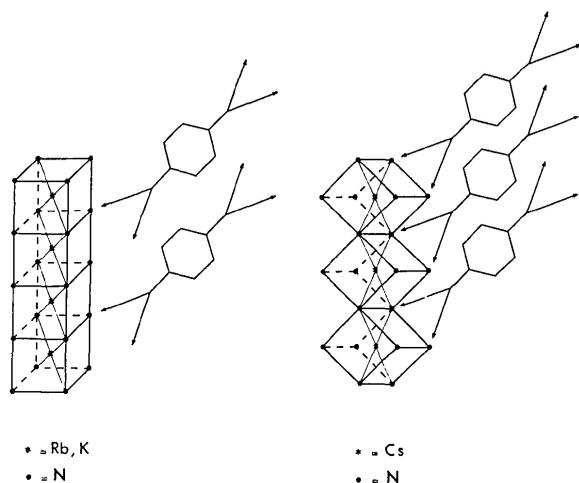


Fig. 5 Surroundings of the metal cations in Rb-TCNQ and K-TCNQ, and in $\text{Cs}_2(\text{TCNQ})_3$.

Table 7. Thermal motion in a number of TCNQ groups

T_{ij} is in 10^{-4} Å², ω_{ij} in deg²

(a) Rigid body motion of TCNQ in Rb-TCNQ at -160°C .

The direction cosines, $\cos A$, $\cos B$ and $\cos C$ (in units 10^{-4}) of the principle axes of T and ω refer to the molecular axes A , B and C respectively (Fig. 2). The point of intersection of the libration axes lies at $A = -1.004$, $B = -0.058$, $C = -0.074$ Å

	Value	$\cos A$	$\cos B$	$\cos C$		Value	$\cos A$	$\cos B$	$\cos C$
T_{11}	128	-2467	-3575	9007	ω_{11}	8.7	9990	228	-366
T_{22}	112	-9510	-896	-2961	ω_{22}	1.1	-330	-1422	-9893
T_{33}	84	-1683	9351	2771	ω_{33}	0	-278	9896	-1413

(b) Comparison of the thermal motion in different TCNQ compounds

$\omega^{\perp} = \omega$ along A , $\langle \omega^{\perp} \rangle = [\omega(B) + \omega(C)]/2$, $D = \langle [U_{ij}(\text{obs}) - U_{ij}(\text{rigid body})]^2 \rangle^{1/2}$.
Average values of the standard deviations in $U_{ij}(\text{obs})$ are given in parentheses.

Compound	$\langle T_{ij} \rangle$	ω^{\perp}	$\langle \omega^{\perp} \rangle$	D	
TPP-(TCNQ) ₂	—	—	—	>30 (9)	Goldstein <i>et al.</i> , (1968)
Anthracene-TCNQ	610	34.8	7.7	40 (?)	Williams & Wallwork (1968)
Cu-complex-TCNQ†	339	25.3	3.1	29 (33)	Williams & Wallwork (1967)
TCNQ	392	29.7	3.4	21 (10)	Long <i>et al.</i> (1965)
TMPD-(TCNQ) ₂	314	31.5	4.7	31 (7)	Hanson, (1968)
Rb-TCNQ (-160°C)	108	8.7	0.5	18 (12)	Present study

* Tetraphenylphosphonium-(TCNQ)₂

† Copper-(8-hydroxyquinolino)₂-TCNQ

TCNQ groups in water and report a change in free energy (ΔF°) of -4.64 kcal per mole dimer.

It is noticeable that the groups A_1 and B_1 (or A_2 and B_2) in the present compound do not coincide looking along the normal to the 'benzene' planes. Fig. 7 shows that there is a shift of 0.84 \AA of A_1 relative to B_1 such that the centre of A_1 approximately lies below the centre of the quinodimethane double bond of B_1 . According to some authors (Fritchie, 1966) the observed configuration is a stable one for a TCNQ self-complex, but recent SCMO calculations performed by Jonkman (1970) in Groningen have failed to confirm this conclusion. From Figs. 6 and 7 it is seen that the intermolecular distances between B_1 and A_2 are longer than between B_1 and A_1 , and that also the shift of the groups relative to each other is larger, *viz.* 2.2 \AA . In this case the shift is such that six atoms lie approximately on top of each other.

Shifts as reported for Rb-TCNQ have also been observed in $[(\text{C}_6\text{H}_5\text{CH}_3)_2\text{Cr}]^+(\text{TCNQ})^-$ (Shibaeva, Atovmyan & Rozenberg, 1969) and in $\text{Cs}_2(\text{TCNQ})_3$ (Fritchie & Arthur, 1966). In the former compound all TCNQ groups in a row lie at approximately equal interplanar distances; the shift is as observed for A_1 and B_1 . In $\text{Cs}_2(\text{TCNQ})_3$ the rows consist of $\text{TCNQ}^-(P)$ and $\text{TCNQ}^{\circ}(Q)$ units in the sequence $-P-P-Q-P-P-Q$ etc. The shift between two P units resembles that between A_1 and B_1 in Rb-TCNQ, whereas the shift between P and Q is similar to that between B_1 and A_2 . It is noteworthy that the interplanar distance between the two P groups, 3.26 \AA , is larger than the corresponding distance between A_1 and B_1 , whereas the distance between P and Q , 3.22 \AA , is shorter.

In many TCNQ compounds shifts are observed which are different from those discussed above. Very often a longitudinal slipping (displacement along the axis A in Fig. 2) of one fourth the molecular length is found. This is, for instance, the case in N -methylphenazinium-TCNQ (Fritchie, 1966), $\text{TMPD}-(\text{TCNQ})_2$ (Hanson, 1968) and in triethylammonium- $(\text{TCNQ})_2$ (Kobayashi *et al.*, 1970). According to Fritchie (1966) it is not impossible that intercolumnar interaction dictates the kind of shift in a compound, but no proof is available yet for this assumption.

Individual TCNQ groups within a row

The molecular geometry is summarized in Fig. 8. The standard deviations in the bond lengths and bond angles were obtained from the standard deviations in the coordinates calculated by the least-squares program (Table 4). They amount to 0.004 \AA and 0.27° respectively. Differences between chemically equivalent bonds are not significant, which suggests that the standard deviations calculated by the least-squares program are realistic. The deviations from the best plane through the quinodimethane group are given in the lower part of Fig. 8; it is clearly seen that the molecule is not planar. Both $-\text{C}(\text{CN})_2$ groups lie entirely on the same side of the quinoid skeleton of the TCNQ molecule, so

that the molecule has the shape of a shallow boat as has been indicated in Fig. 6. The same effect has been recognized in tetraphenylphosphonium- $(\text{TCNQ})_2$ (Goldstein, Seff & Trueblood, 1968).

Results of theoretical SCMO-CI calculations by Jonkman & Kommandeur (1971) are given in Table 8. These calculations, as well as the earlier SCF-LCAO-MO calculations by Lowitz (1967), show that the length of the bond c adjacent to the 'benzene' ring is especially sensitive to the amount of charge on the molecule,

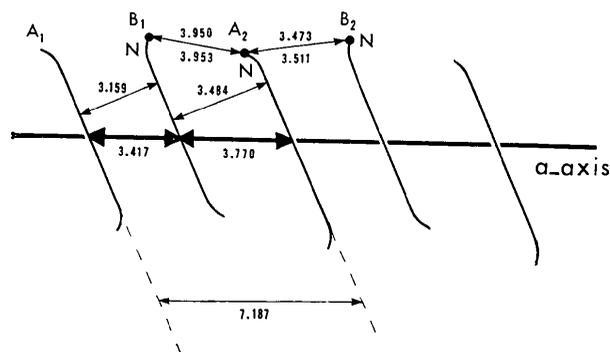


Fig. 6. Row of TCNQ groups in Rb-TCNQ. Interesting distances have been added; the two numbers between the nitrogen atoms represent two independent distances present between nitrogen atoms of adjacent molecules (see Fig. 7). The individual TCNQ groups show slight deviations from planarity (see Fig. 8).

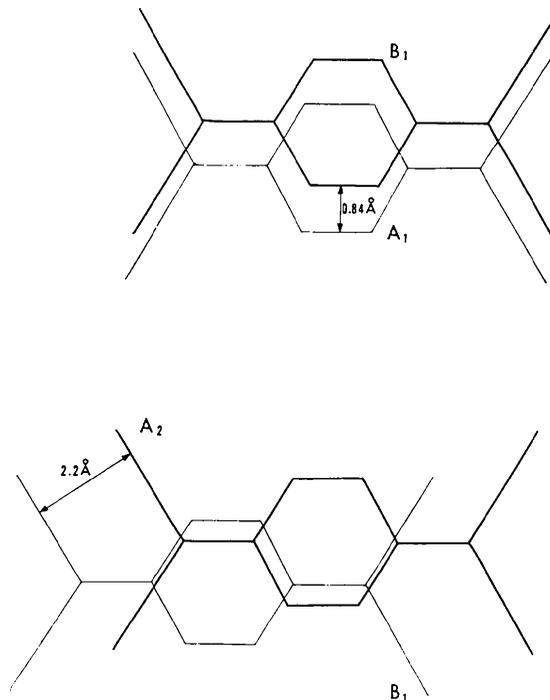


Fig. 7. TCNQ groups projected along the normal to the benzene planes. For numbering of groups see Fig. 6.

whereas the length of the CN bonds depends only slightly on this charge. In Table 9 the bond lengths in the TCNQ group of Rb-TCNQ are compared with the observed bond lengths in eleven other TCNQ compounds. It appears that the lengths of the bonds in Rb-TCNQ agree reasonably well with the bond lengths observed for the other TCNQ groups with an assumed negative charge. Significant differences only occur with bond *a* of compound IV and with the bonds *a* and *c* of VI. Moreover Tables 8 and 9 show that the agreement with the observed values is generally better than with the theoretical values for TCNQ⁻. This may

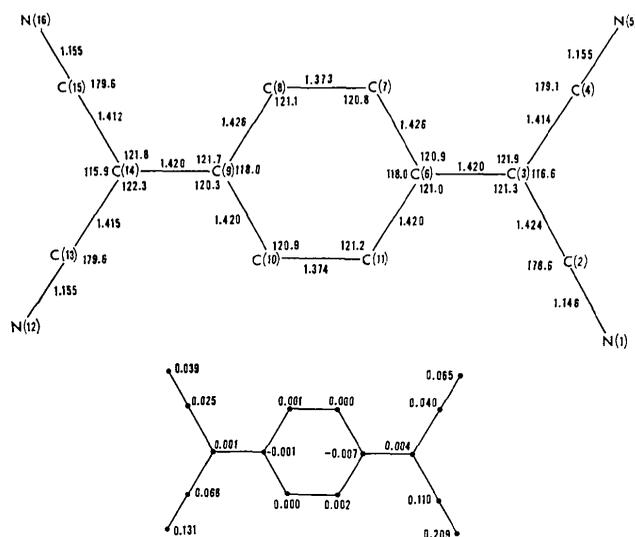


Fig. 8. Molecular geometry of TCNQ⁻ in Rb-TCNQ at -160°C. The bond lengths (Å) and angles (°), given above, have not been corrected for libration (see text). The deviations (Å) from the best plane through the quinodimethane skeleton are given below. The equation of the plane referred to the axes *X*, *Y*, *Z* parallel to *a*², *b* and *c* is: $0.9072X + 0.3798Y - 0.1808Z = 1.7421$.

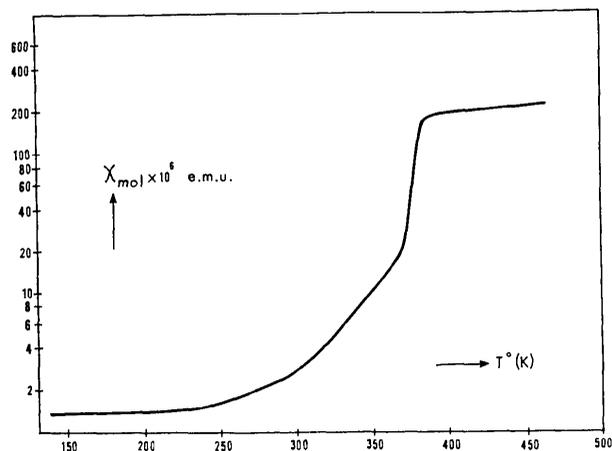
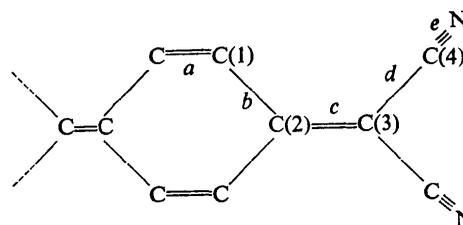


Fig. 9. Temperature dependence of the molar paramagnetic susceptibility χ_p of Rb-TCNQ as measured by Vegter & Kommandeur (1971)

indicate that either the parameters used in the theoretical work are not fit for bond length calculations (they were chosen such as to get the best possible agreement with the UV-VIS spectrum and with the spin densities of the TCNQ⁻ ion) or that the bond lengths are influenced significantly by the relatively strong intermolecular interaction. Until more detailed studies have been done, it cannot be decided whether or not the bond lengths in the TCNQ groups of Rb-TCNQ show significant differences from the bond lengths expected for free TCNQ⁻.

Table 8. Calculated values for charges, bond orders and bond lengths for free TCNQ, TCNQ⁻ and TCNQ²⁻ groups

To obtain the C-C bond lengths the relation $R(C-C) = 1.506 - 0.17p$ was used (de Boer & Vos, 1971). For TCNQ⁻ both the charges and the spin densities are given.



Charge	C(1)	C(2)	C(3)	C(4)	N
TCNQ	0.99	0.95	1.03	0.80	1.22
TCNQ ⁻¹	1.04	0.95	1.28	0.74	1.36
Spin density	0.06	0.11	0.17	0.01	0.04
TCNQ ⁻²	1.09	0.98	1.42	0.73	1.48

Bond order <i>P</i>	<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>	<i>e</i>
TCNQ	0.92	0.29	0.85	0.25	0.94
TCNQ ⁻¹	0.83	0.43	0.65	0.34	0.89
TCNQ ⁻²	0.73	0.57	0.42	0.47	0.81

Bond length <i>R</i>	<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>
TCNQ	1.350	1.457	1.361	1.464
TCNQ ⁻¹	1.365	1.433	1.395	1.448
TCNQ ⁻²	1.382	1.409	1.435	1.426

The spin densities and charges listed in Table 8 appear to offer a possible explanation for the shallow boat shape of the TCNQ⁻ ions. In view of these results one does expect that the quinoid groups of *A*₁ and *B*₁ (Fig. 6) attract each other because of their relatively high spin densities, whereas the C≡N groups are pushed apart because of their high electrical charges.

The magnetic susceptibilities of organic radical compounds

As mentioned in the introduction the theories proposed so far to describe the magnetic behaviour of organic radical compounds assume the organic radicals to be arranged in rows. In these rows the distances between the radicals can be either equal (regular rows) or alternately different (irregular rows). The present

structure determination shows that in Rb-TCNQ (see Fig. 9) and other organic radical compounds at low temperature, some type of spin-coupling between the radicals has to be assumed. At the moment there are two different views concerning this spin-coupling. Fedders & Kommandeur (1970) neglect exchange interaction between the electrons and have developed a narrow band model for the electronic energies on the basis of a one-electron theory. Spin-coupling occurs owing to the fact that many of the electrons have to be placed in the same band(s). McConnell and coworkers (Thomas, Keller & McConnell, 1963) state that 'exchange interaction' plays an essential part [according to Soos & Hughes (1967) the exchange integral J is phenomenologically defined and includes important charge-transfer and phonon effects]. Their many-electron theory, which is based on the Hamiltonian for the linear Heissenberg antiferromagnet, again gives a band model, which in this case describes the different spin states (Soos, 1965).

Although the dependence of the magnetic susceptibility on the temperature is not the same for both theories, it will be difficult to judge from $\chi(T)$ curves alone which theory is right for a particular compound as both theories work with one (for regular rows) or two (for irregular rows) parameters which can be

adjusted to the experimental $\chi(T)$ values. Therefore in addition to their magnetic behaviour, other physical properties of the organic radical compounds have to be studied, and the structures of a number of these compounds have to be determined accurately. Further work is in progress in the laboratories of Physical Chemistry and Structural Chemistry in Groningen. Vegter & Kommandeur (1971) have added another adjustable parameter to the narrow band model by extending this theory to cases where the distances between the organic radicals change with temperature. Starting from our structural parameters this extended theory has given a good description of the paramagnetic behaviour of Rb-TCNQ. It seems not impossible, however, to obtain equally good agreement between theory and experiment with the Heissenberg antiferromagnet, if in this case also variations in the intermolecular distances with temperature are taken into account.

The authors are very grateful to Professor J. Kommandeur, Drs J. H. Vegter, Dr G. R. Anderson, Mr H. Th. Jonkman and Dr J. L. de Boer for valuable discussions and for their continued interest in this research. Further we thank Mr F. van Bolhuis, Drs J. H. Noordik and Mr C. Th. Kiers for assistance

Table 9. Observed bond lengths in twelve TCNQ compounds*

The numbering is given in Table 8. Average values for chemically equivalent bonds are listed with, in parentheses, the largest deviation from this value. After the code number of each compound its standard deviation, referring to the individual bonds, is given in parentheses.

		I(4)	II(9)	III(6)	IV(4)	V(13)
TCNQ ⁰	<i>a</i>	1.436 (–)	1.355 (–)	1.365 (–)	1.341 (–)	1.345 (8)
	<i>b</i>	1.448 (2)	1.460 (–)	1.443 (5)	1.445 (5)	1.444 (14)
	<i>c</i>	1.374 (–)	1.370 (–)	1.377 (–)	1.371 (–)	1.387 (5)
	<i>d</i>	1.441 (1)	1.425 (–)	1.438 (1)	1.429 (2)	1.422 (34)
	<i>e</i>	1.140 (1)	1.130 (–)	1.142 (1)	1.140 (11)	1.152 (35)
		IV(4)	V(13)	VI(6)	VII(6)	VIII(4)
TCNQ ⁻¹	<i>a</i>	1.355 (2)	1.377 (2)	1.341 (–)	1.373 (–)	1.373 (1)
	<i>b</i>	1.427 (4)	1.433 (35)	1.434 (6)	1.414 (–)	1.423 (3)
	<i>c</i>	1.410 (9)	1.409 (4)	1.388 (–)	1.406 (–)	1.420 (0)
	<i>d</i>	1.419 (3)	1.408 (24)	1.420 (1)	1.412 (–)	1.416 (8)
	<i>e</i>	1.152 (3)	1.159 (31)	1.155 (1)	1.160 (–)	1.153 (7)
		IX(4)	X(4)	XI(13)	XII ^A (5)	XII ^B (5)
TCNQ ^{-1/2}	<i>a</i>	1.355 (1)	1.353 (3)	1.360 (14)	1.358 (6)	1.352 (2)
	<i>b</i>	1.435 (2)	1.434 (3)	1.443 (14)	1.430 (6)	1.434 (7)
	<i>c</i>	1.395 (3)	1.396 (1)	1.380 (3)	1.400 (1)	1.388 (5)
	<i>d</i>	1.427 (5)	1.430 (5)	1.430 (10)	1.424 (2)	1.424 (9)
	<i>e</i>	1.171 (5)	(1.17)	1.150 (11)	1.148 (7)	1.148 (8)

* I = TCNQ (Long & Sparks, 1965),
 II = Anthracene-TCNQ (Williams & Wallwork, 1968),
 III = Cu-complex-TCNQ (Williams & Wallwork, 1967),
 IV = Cs₂(TCNQ)₃ (Fritchie & Arthur, 1966),
 V = TEA(TCNQ)₂ (Kobayashi *et al.*, 1970),
 VI = *N*-methylphenazinium TCNQ (Fritchie, 1966),
 VII = TMPD-TCNQ (Hanson, 1956),
 VIII = Rb-TCNQ (Present study),
 IX = TMPD-(TCNQ)₂ (Hanson, 1968),
 X = TPP-(TCNQ)₂ (Goldstein, Seff & Trueblood, 1968).
 XI = Quinolinium-(TCNQ)₂
 XII = Methyltriphenylphosphonium-(TCNQ)₂

during the experimental work. The calculations were done at the Computing Centre of the University of Groningen.

References

- ACKER, D. S., HARDER, R. J., HERTLER, W. R., MELBY, L. R., BENSON, R. E., MAHLER, W. & MOCHEL, W. E. (1960). *J. Amer. Chem. Soc.* **82**, 6408.
- ANDERSON, G. R. & FRITCHIE, C. J. JR (1963). Second National Meeting, Society for Applied Spectroscopy, San Diego, October 14–18, Paper 111, pp. 67–68.
- BEKOE, D. A. & TRUEBLOOD, K. N. (1960). *Z. Kristallogr.* **113**, 1.
- BOER, J. L. DE & VOS, A. (1972). *Acta Cryst.* In the press.
- BOER, J. L. DE, VOS, A. & HUML, K. (1968). *Acta Cryst.* **B24**, 542.
- BOLHUIS, F. VAN (1971). *J. Appl. Cryst.* **4**, 263.
- BOYD, R. H. & PHILLIPS, W. D. (1965). *J. Chem. Phys.* **43**, 2927.
- BUSING, W. R. & LEVY, H. A. (1957). *Acta Cryst.* **10**, 180.
- CRUICKSHANK, D. W. J. (1956). *Acta Cryst.* **9**, 747.
- CRUICKSHANK, D. W. J. (1961a). *Acta Cryst.* **14**, 896.
- CRUICKSHANK, D. W. J. (1961b). *Computing Methods and the Phase Problem in X-ray Crystal Analysis*. London: Pergamon Press.
- DOYLE, P. A. & TURNER, P. S. (1968). *Acta Cryst.* **A24**, 390.
- FEDDERS, P. A. & KOMMANDEUR, J. (1970). *J. Chem. Phys.* **52**, 2014.
- FRITCHIE, C. J. JR (1966). *Acta Cryst.* **20**, 892.
- FRITCHIE, C. J. JR & ARTHUR, P. JR (1966). *Acta Cryst.* **21**, 139.
- FURNAS, T. C. (1957). *Single Crystal Orienter Instruction Manual*. Milwaukee: General Electric Company.
- GOLDSTEIN, P., SEFF, K. & TRUEBLOOD, K. N. (1968). *Acta Cryst.* **B24**, 778.
- HANSON, A. W. (1965). *Acta Cryst.* **19**, 610.
- HANSON, A. W. (1968). *Acta Cryst.* **B24**, 768.
- International Tables for X-ray Crystallography* (1959). Vol. I. Birmingham: Kynoch Press.
- JONKMAN, H. TH. (1970). Private communication.
- JONKMAN, H. TH. & KOMMANDEUR, J. (1971). *J. Chem. Phys.* To be published.
- KOBAYASHI, H., MARUMO, F. & SAITO, Y. (1971). *Acta Cryst.* **B27**, 373.
- KOBAYASHI, H., OHASHI, Y., MARUMO, F. & SAITO, Y. (1970). *Acta Cryst.* **B26**, 459.
- LONG, R. E., SPARKS, R. A. & TRUEBLOOD, K. N. (1965). *Acta Cryst.* **18**, 932.
- LOWITZ, D. A. (1967). *J. Chem. Phys.* **46**, 4698.
- MCPHAIL, A. T., SEMENIUK, G. M. & CHESNUT, D. B. (1971). *J. Chem. Soc. (A)*, p. 2174.
- MELBY, L. R., HARDER, R. J., HERTLER, W. R., MAHLER, W., BENSON, R. E. & MOCHEL, W. E. (1962). *J. Amer. Chem. Soc.* **84**, 3374.
- NORDIO, P. L., SOOS, Z. G. & MCCONNELL, H. M. (1966). *Ann. Rev. Phys. Chem.* **17**, 237.
- PAULING, L. (1960). *The Nature of the Chemical Bond*, 3rd ed. p. 260. Ithaca: Cornell Univ. Press.
- PAWLEY, G. S. (1963). *Acta Cryst.* **16**, 1204.
- POTT, G. T. & KOMMANDEUR, J. (1967). *Mol. Phys.* **13**, 373.
- SHIBAeva, R. P., ATOVMYAN, L. O. & ROZENBERG, L. P. (1969). *Chem. Commun.* p. 649.
- SOOS, Z. G. (1965). *J. Chem. Phys.* **43**, 1121.
- SOOS, Z. G. & HUGHES, R. C. (1967). *J. Chem. Phys.* **46**, 253.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175.
- THOMAS, D. D., KELLER, H. & MCCONNELL, H. M. (1963). *J. Chem. Phys.* **39**, 2321.
- VEGTER, J. G., HIBMA, T. & KOMMANDEUR, J. (1969). *Chem. Phys. Letts.* **3**, 427.
- VEGTER, J. G. & KOMMANDEUR, J. (1971). *J. Chem. Phys.* To be published.
- WALLWORK, S. C. (1961). *J. Chem. Soc.* p. 494.
- WILLIAMS, R. M. & WALLWORK, S. C. (1967). *Acta Cryst.* **23**, 448.
- WILLIAMS, R. M. & WALLWORK, S. C. (1968). *Acta Cryst.* **B24**, 168.

Acta Cryst. (1972). **B28**, 25

Structure de l'*o*-Cresol

PAR CLAUDETTE BOIS

Université Paris VI, Laboratoire de Chimie Systématique, 8, rue Cuvier, Paris 5ème, France

(Reçu le 1 février 1971)

Crystals of *o*-cresol are trigonal, with nine molecules in a unit cell of dimensions $a=16.43$, $c=5.94$ Å, space group either $P3_1$ or $P3_2$ (enantiomorphic). The structure has been determined from three dimensional single crystal X-ray data, registered at -50°C . The positions of molecules approximately given by Patterson methods and steric considerations were refined by least-squares analysis. All hydrogen atoms were located in a difference map. Least-squares anisotropic refinement was carried out, giving the final R value of 0.08. The molecules are linked by hydrogen bonds to form three chains parallel to the c direction.

Introduction

Notre travail s'intègre dans l'étude des xylénols et des crésols entreprise au laboratoire. La structure cristal-

line des diméthyl-2,3, -2,5 et -2,6 phénols a été élucidée (Gillier-Pandraud, 1965, 1966; Brusset, Gillier-Pandraud & Viossat, 1967), celle des diméthyl-3,5 et -3,4 phénols est actuellement en cours de détermination.