

The Crystal Structure of the 2:1 Complex of 7,7,8,8-Tetracyanoquinodimethan and *N,N,N',N'*-Tetramethyl-*p*-phenylenediamine, (TCNQ)₂⁻, TMPD⁺

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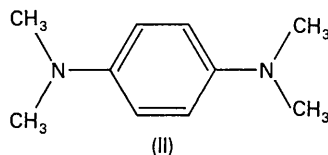
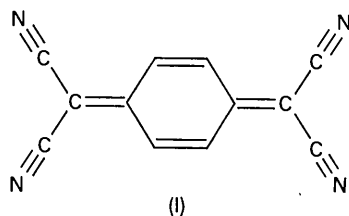
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Crystals of (TCNQ)₂⁻, TMPD⁺ are triclinic, with probable space group *P* $\bar{1}$ and $a=7.782$, $b=15.020$, $c=6.488$ Å, $\alpha=93.52$, $\beta=102.77$, $\gamma=82.97^\circ$, $Z=1$. The structure was deduced from a three-dimensional Patterson synthesis, and refined by block-diagonal least squares. It consists of columns of TCNQ ions which overlap in characteristic fashion. These columns are held together by TMPD ions. The average spacing between overlapping TCNQ ions is 3.24 Å. The bond lengths found for both ions are consistent with recently-reported data for similar complexes.

Introduction

The X-ray analysis of the ionic 1:1 complex of 7,7,8,8-tetracyanoquinodimethan (TCNQ; I) and *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (TMPD; II) (Hanson, 1965) indicates that the bond-length distribution in each of the species present differs significantly from that in the neutral molecule. [The bond-length distribution is assumed for neutral TMPD, and known for neutral TCNQ (Long, Sparks & Trueblood, 1965).] The pseudo-aromatic character of TCNQ ions bearing a formal charge of -1 has since been confirmed by studies of other complexes (Fritchie, 1966; Fritchie & Arthur, 1966).



A 2:1 complex of TCNQ and TMPD also occurs. (It was produced by the same techniques as the 1:1 complex, and was for a time confused with it.) The X-ray analysis was undertaken to see whether (as one might reasonably predict) the TCNQ ion, with a formal charge of $-\frac{1}{2}$, has a bond-length distribution intermediate between those for TCNQ⁰ and TCNQ⁻. While this work was in progress, Goldstein, Seff & Trueblood

(1968) were engaged in a study of tetraphenylphosphonium tetracyanoquinodimethanide, a complex which also contains a TCNQ ion with a formal charge of $-\frac{1}{2}$. The results of both analyses are consistent with the findings for TCNQ⁰, and for TCNQ⁻¹ in other complexes. Moreover, it is pleasant to record that the two sets of results agree very well with each other.

Experimental

Crystal data

Triclinic

$a=7.782 \pm 0.005$, $b=15.020 \pm 0.010$, $c=6.488 \pm 0.010$ Å
 $\alpha=93.52 \pm 0.05$, $\beta=102.77 \pm 0.05$, $\gamma=82.97 \pm 0.05^\circ$
 $V=733.8$ Å³, Formula (C₁₂N₄H₄)₂, C₁₀N₂H₁₆,
 F.W. 572.6, $D_m=1.28 \pm 0.02$ g.cm⁻³, $D_x=1.295 \pm 0.005$ g.cm⁻³, $Z=1$, $\mu=7.7$ cm⁻¹ (Cu $K\alpha$).

The crystal class was deduced from precession and Weissenberg photographs. The space group *P* $\bar{1}$ is consistent with the deduced structure. Molecular symmetry: centre.

The crystalline material was black, shiny, and opaque. The cell constants and relative intensities were measured at room temperature with the use of a General Electric XRD 5 spectrogoniometer and goniostat, with scintillation counter. (It was belatedly realized that the crystal decomposed slowly, with small, gradual changes in the cell constants. The derivation of the constants given above is discussed in the Appendix.) The specimen, which was cleaved from a larger sample, was a reasonably regular solid with extreme dimensions 0.3 and 0.4 mm. Copper $K\alpha$ radiation was used, and reasonable monochromatization was achieved by means of a $K\beta$ filter and a reverter (pulse-height analyser). The moving-crystal moving-counter method of Furnas (1957) was used. Of the 3279 accessible reflexions (those for which $2\theta \leq 165^\circ$) significant counts were recorded for 2595. Absorption corrections were deemed to be unnecessary, and were not made.

Structure determination

If the space group is $P\bar{1}$, the lone TMPD ion must occupy a centre of symmetry, while the two TCNQ ions may lie in general positions. A trial structure consistent with these assumptions was readily deduced by inspection of the three-dimensional Patterson synthesis. It was refined by means of Fourier syntheses, followed by seven cycles of block-diagonal least-squares analysis.

The least-squares program was written by the author specifically for this problem, for use on the IBM/system 360 computer. It forms a 3×3 matrix for the position

parameters and a 6×6 matrix for the thermal parameters of each atom. The scale factor of observed structure amplitudes and the overall isotropic temperature factor are refined in a 2×2 matrix. Schomaker's correction (Hodgson & Rollett, 1963) is applied to the shifts of the thermal parameters. The quantity minimized is $\sum w(F_o - F_c)^2$, where $1/w = 1 + \{(V/I_0 - 5V/I_T)/8V/I_T\}^2$. I_T is the nominal minimum observable intensity, in this case 9. This weighting scheme reduces the weight slightly for very weak reflexions, and greatly for strong reflexions. It is analogous to a scheme proposed by Mills & Rollett (1961), but the substitu-

Table 1. Final parameters and estimated standard deviations of non-hydrogen atoms $\pm(x, y, z)$
Temperature factor = $\exp[-2\pi^2(U_{11}a^2h^2 + 2U_{12}a^*b^*hk + 2U_{13}a^*c^*hl + U_{22}b^{*2}k^2 + 2U_{23}b^*c^*kl + U_{33}c^{*2}l^2)]$.

B_i are the temperature factors corresponding to the principal radii of the thermal motion ellipsoids.

	x $\times 10^5$	y $\times 10^5$	z $\times 10^5$	U_{11} $\times 10^4$ (\AA^2)	U_{12} $\times 10^4$ (\AA^2)	U_{13} $\times 10^4$ (\AA^2)	U_{22} $\times 10^4$ (\AA^2)	U_{23} $\times 10^4$ (\AA^2)	U_{33} $\times 10^4$ (\AA^2)	B_1 (\AA^2)	B_2 (\AA^2)	B_3 (\AA^2)
TCNQ Molecule												
C(1)	2795 18	2288 9	25932 22	317 7	-32 5	60 5	365 7	31 6	329 7	2.45	2.61	2.94
C(2)	-16151 18	2656 9	21745 23	303 7	1 5	63 6	370 7	35 6	389 8	2.28	3.03	3.18
C(3)	-24125 18	-4974 9	18743 24	285 7	-17 5	67 6	407 7	23 6	406 8	2.24	3.20	3.28
C(4)	-14007 18	-13616 9	19422 23	337 7	-39 5	86 6	376 7	16 6	358 8	2.59	2.84	2.98
C(5)	4877 18	-13953 9	23489 24	321 7	10 5	92 6	363 7	47 6	433 8	2.32	2.99	3.53
C(6)	12925 18	-6339 9	26700 24	288 6	-10 5	65 6	382 7	30 6	406 8	2.23	3.06	3.26
C(7)	-22295 20	-21477 10	16446 26	386 7	-57 6	124 6	394 7	-1 6	479 9	2.87	3.11	3.83
C(8)	11112 18	10096 9	29120 23	337 7	-38 5	58 6	371 7	36 6	377 8	2.62	2.83	3.17
C(9)	-41078 22	-21268 11	12609 29	456 9	-119 7	141 8	436 8	-33 7	589 10	2.90	3.78	4.81
C(10)	-12482 23	-30106 11	17462 30	493 9	-109 7	186 8	411 8	-30 8	651 11	2.94	3.71	5.32
C(11)	29898 20	9982 10	33227 26	396 8	-80 6	64 6	397 7	18 6	449 8	2.93	3.45	3.76
C(12)	1580 21	18832 10	28782 26	417 8	-71 6	41 7	393 7	35 6	486 9	3.07	3.35	4.24
N(13)	-56097 21	-21185 12	9717 33	444 8	-162 7	169 9	658 10	-80 10	1029 14	3.14	5.68	8.44
N(14)	-4801 25	-37096 11	18393 36	728 12	-20 8	327 11	444 8	-6 9	1184 17	3.67	5.41	9.42
N(15)	44891 19	10135 11	36370 28	380 8	-112 7	74 7	656 9	25 8	786 11	2.89	5.69	6.38
N(16)	-5490 23	25933 10	28757 30	659 10	38 7	38 9	424 8	32 8	850 12	3.23	5.23	7.56
TMPD Molecule												
C(17)	33952 25	52447 13	5634 35	519 10	19 8	202 9	544 10	44 9	767 13	3.52	4.70	6.12
C(18)	45677 26	45473 11	16144 32	652 12	-94 8	167 9	424 8	30 8	622 11	3.23	4.73	5.25
C(19)	61818 26	43137 12	9863 34	574 11	52 8	112 9	444 9	102 9	731 13	3.02	5.10	5.92
N(20)	41549 29	41167 13	32091 34	987 15	-86 10	400 12	697 11	233 10	923 15	4.05	6.83	9.25
C(21)	24427 43	42931 22	37445 50	1146 22	-527 18	476 17	1174 21	21 16	952 20	4.01	7.94	12.17
C(22)	53129 51	33755 17	42310 48	1720 31	-62 17	376 20	646 15	284 14	908 20	3.62	8.05	13.71

tion of $|I_o|$ for $|F_o|$ results in a further (presumably beneficial) reduction in the weights of very low-angle and very high-angle reflexions.

Contributions of the hydrogen atoms to the structure factors were included in the later stages of refinement, but no attempt was made to refine their parameters. The positions of the six ring hydrogen atoms were estimated from chemical considerations, and those of the six methyl hydrogen atoms were deduced (with some idealistic adjustment) from a difference synthesis. The isotropic temperature factors were assumed to be the mean isotropic values of the adjacent carbon atoms, but the nominal values were reduced by 2.5 \AA^2 to compensate for the known shortcomings of the scattering-factor curve employed. Final bond-length and angle calculations confirm that the positions given in Table 2 are consistent with reasonable expectation. All C-H distances lie in the range $0.92\text{--}1.02 \text{ \AA}$. Bond angles involving methyl hydrogens lie in the range $105\text{--}113^\circ$; for other hydrogen atoms, the range is $119\text{--}121^\circ$.

At a late stage in refinement a small correction for extinction was applied to the fourteen most intense reflexions. The correction did not exceed 22% of F_o for any reflexions, and was of no importance to the refinement.

Table 2. *Hydrogen parameters (not refined)*

	<i>x</i> × 10 ⁴	<i>y</i> × 10 ⁴	<i>z</i> × 10 ⁴	<i>B</i> (\AA^2)
H(2)	-2363	862	2070	0.2
H(3)	-3734	-453	1586	0.2
H(5)	1239	-1989	2450	0.2
H(6)	2626	-684	2957	0.2
H(17)	2213	5414	979	2.0
H(19)	7024	3806	1682	2.0
H(21 <i>a</i>)	2357	3920	4900	5.6
H(21 <i>b</i>)	2238	4875	4225	5.6
H(21 <i>c</i>)	1470	4230	2445	5.6
H(22 <i>a</i>)	4850	3129	5290	5.6
H(22 <i>b</i>)	5615	2897	3145	5.6
H(22 <i>c</i>)	6400	3557	4950	5.6

The scattering factor curves of Freeman (1959) were used throughout. A factor of 0.8 was applied to all parameter shifts in all cycles except the last. In the last cycle, no coordinate shift exceeded 0.0006 \AA , or 0.4 e.s.d.'s of position. The final parameters for all atoms are given in Tables 1 and 2.

Thermal motion and correction of bond lengths

The thermal motion ellipsoids of the individual atoms are illustrated in Fig. 1. The molecular motion has been

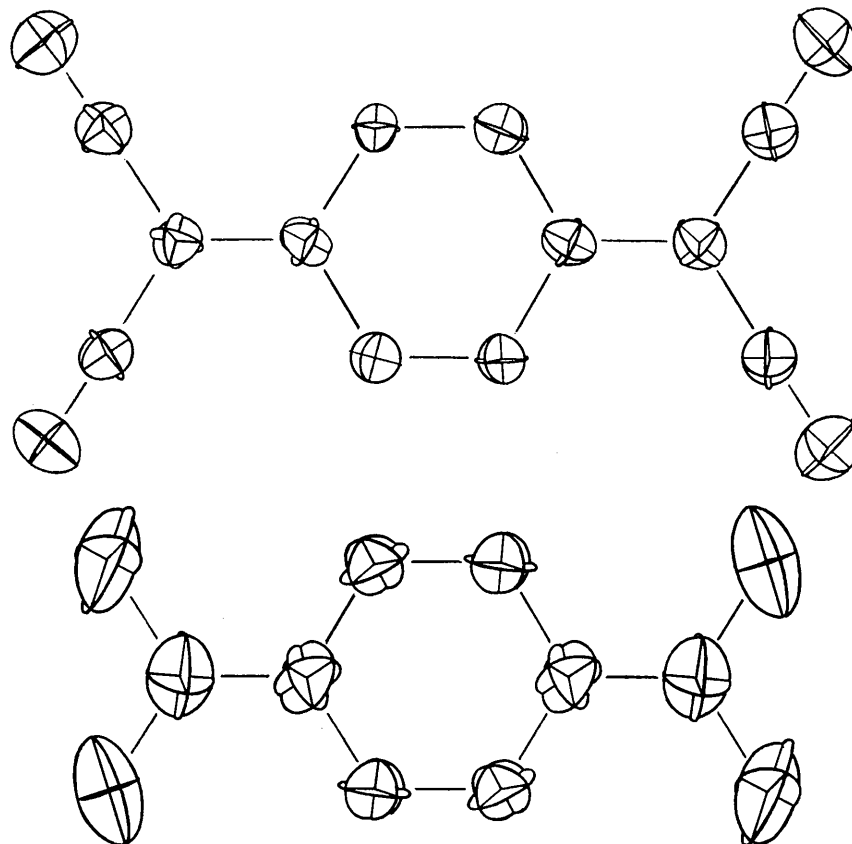


Fig. 1. The thermal motion ellipsoids.

Table 3. Rigid-body thermal parameters

(a) TCNQ, 8 innermost atoms only

$$T = \begin{pmatrix} 301 & 26 & 0 \\ & 362 & 21 \\ & & 314 \end{pmatrix} \times 10^{-4} \text{ \AA}^2 \quad L = \begin{pmatrix} 92 & 66 & 8 \\ & 148 & 20 \\ & & 37 \end{pmatrix} \times 10^{-1} (^\circ)^2$$

$$\sigma(T) = \begin{pmatrix} 4 & 3 & 4 \\ & 3 & 4 \\ & & 8 \end{pmatrix} \times 10^{-4} \text{ \AA}^2 \quad \sigma(L) = \begin{pmatrix} 11 & 8 & 6 \\ & 16 & 8 \\ & & 4 \end{pmatrix} \times 10^{-1} (^\circ)^2$$

Unique origin† -0.660 -0.488 1.512
 Centre of gravity -0.866 -0.895 1.435 \AA

Principal axes of T:	Direction cosines ($\times 10^4$)				Comment
Eigenvalue					
0.0377 \AA ²	3054	9048	2967	—	inclined at 16° to long axis of molecule
0.0311	4267	1486	-8921		
0.0289	8513	-3990	3407		

Principal axes of L	Direction cosines ($\times 10^4$)				Comment
Eigenvalue					
19.5 (°) ²	5462	8274	1306	—	inclined at 1° to long axis of molecule
4.9	8171	-4920	-3005		
3.3	1842	-2706	9449		

r.m.s. discrepancy between obs. and calc. U_{ij} : $6 \times 10^{-4} \text{ \AA}^2$.

(b) TCNQ, all atoms.

$$T = \begin{pmatrix} 300 & 44 & 7 \\ & 364 & 20 \\ & & 279 \end{pmatrix} \times 10^{-4} \text{ \AA}^2 \quad L = \begin{pmatrix} 130 & 123 & 20 \\ & 222 & 37 \\ & & 56 \end{pmatrix} \times 10^{-1} (^\circ)^2$$

$$\sigma(T) = \begin{pmatrix} 11 & 9 & 12 \\ & 9 & 10 \\ & & 14 \end{pmatrix} \times 10^{-4} \text{ \AA}^2 \quad \sigma(L) = \begin{pmatrix} 6 & 13 & 4 \\ & 16 & 6 \\ & & 3 \end{pmatrix} \times 10^{-1} (^\circ)^2$$

Unique origin† -0.595 -0.456 1.631
 Centre of gravity -0.863 -0.891 1.450 \AA

Principal axes of T:	Direction cosines ($\times 10^4$)				Comment
Eigenvalue					
0.0390 \AA ²	4417	8780	1846	—	inclined at 6° to long axis of molecule
0.0280	7826	-2765	-5577		
0.0273	4386	-3908	8093		

Principal axes of L	Direction cosines ($\times 10^4$)				Comment
Eigenvalue					
31.5 (°) ²	5599	8129	1604	—	inclined at 2° to long axis of molecule
5.3	5166	-1913	-8346		
4.1	6478	-5501	5270		

r.m.s. discrepancy between obs. and calc. U_{ij} : $31 \times 10^{-4} \text{ \AA}^2$.

(c) TMPD, 8 atoms.

$$T = \begin{pmatrix} 471 & -31 & -47 \\ & 308 & -60 \\ & & 56 \end{pmatrix} \times 10^{-4} \text{ \AA}^2 \quad L = \begin{pmatrix} 310 & 24 & -157 \\ & 371 & -184 \\ & & 500 \end{pmatrix} \times 10^{-1} (^\circ)^2$$

$$\sigma(T) = \begin{pmatrix} 10 & 10 & 10 \\ & 13 & 12 \\ & & 13 \end{pmatrix} \times 10^{-4} \text{ \AA}^2 \quad \sigma(L) = \begin{pmatrix} 28 & 14 & 24 \\ & 28 & 26 \\ & & 38 \end{pmatrix} \times 10^{-1} (^\circ)^2$$

Centre of libration and centre of gravity coincident with symmetry centre.

Principal axes of T:	Direction cosines ($\times 10^4$)				Comment
Eigenvalue					
0.0587 \AA ²	3345	1611	-9285	—	inclined at 10° to c
0.0467	9165	-2851	2807		
0.0285	2195	9449	2430		

Principal axes of L	Direction cosines ($\times 10^4$)				Comment
Eigenvalue					
68.6 (°) ²	3625	4904	-7926	—	inclined at 7° to long axis of molecule
31.5	6867	-7155	-1286		
18.1	6302	4976	5961		

r.m.s. discrepancy between obs. and calc. U_{ij} : $18 \times 10^{-4} \text{ \AA}^2$.

All positions and directions in this 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***.

† The 'unique origin' mentioned in (a) and (b) is the origin which symmetrizes **S**.

analysed in terms of the rigid-body modes of translation (**T**), libration (**L**), and screw (**S**) motion, using the approach described by Schomaker & Trueblood (1968). The procedures were carried out in Professor Trueblood's laboratory by Dr Karl Seff, using the program MGTLs (Gantzel & Trueblood, 1966).

It is of course unrealistic to expect that either molecule will behave strictly as a rigid body. For the first analysis of TCNQ, only the innermost eight atoms were considered. (Results of this and other analyses are summarized in Table 3.) The r.m.s. deviation between observed and derived thermal parameters is 0.0006 \AA^2 , a quantity which is of about the same magnitude as the e.s.d.'s given in Table 1. Also, the indicated modes of motion are physically reasonable. Although the translation tensor **T** is not markedly anisotropic, the direction of greatest vibration is quite close to that of the long axis of the molecule. The libration tensor **L** is much more anisotropic, and the axis of greatest libration corresponds quite precisely to the long axis – that is, the axis of least moment of inertia – of the molecule. The appropriate bond lengths and angles have been corrected by the method of Cruickshank (1956, 1961) using the arbitrarily assigned shape parameters given in Table 5.

A second analysis was carried out, treating the entire molecule as a rigid body. The agreement between observed and derived parameters is still reasonable, and the modes of motion are similar to those indicated for the first analysis. However, the amplitude of libration about the long axis is somewhat greater. This analysis has been used in correcting the remaining bond angles and C–C bond lengths. (The difference between the corrections indicated by the two analyses is trivial, amounting to no more than 0.001 \AA for any bond.) The cyano groups undoubtedly suffer non-rigid thermal motion, and the C–N distances have been corrected by the method of Busing & Levy (1964), assuming 'riding' motion. The corrections are quite large, and may not be reliable.

The innermost eight atoms of the TMPD molecule were analysed as a rigid body. For this molecule, **T** is quite anisotropic, but the eigenvectors are not simply related to the molecular axes. The direction of greatest vibration is in fact quite close to **c**; that is, the molecule moves most freely along the tunnel which lies between adjacent columns of TCNQ. The axis of greatest libration, however, is again quite close to the long axis of the molecule. The appropriate bond lengths and angles have been corrected as before.

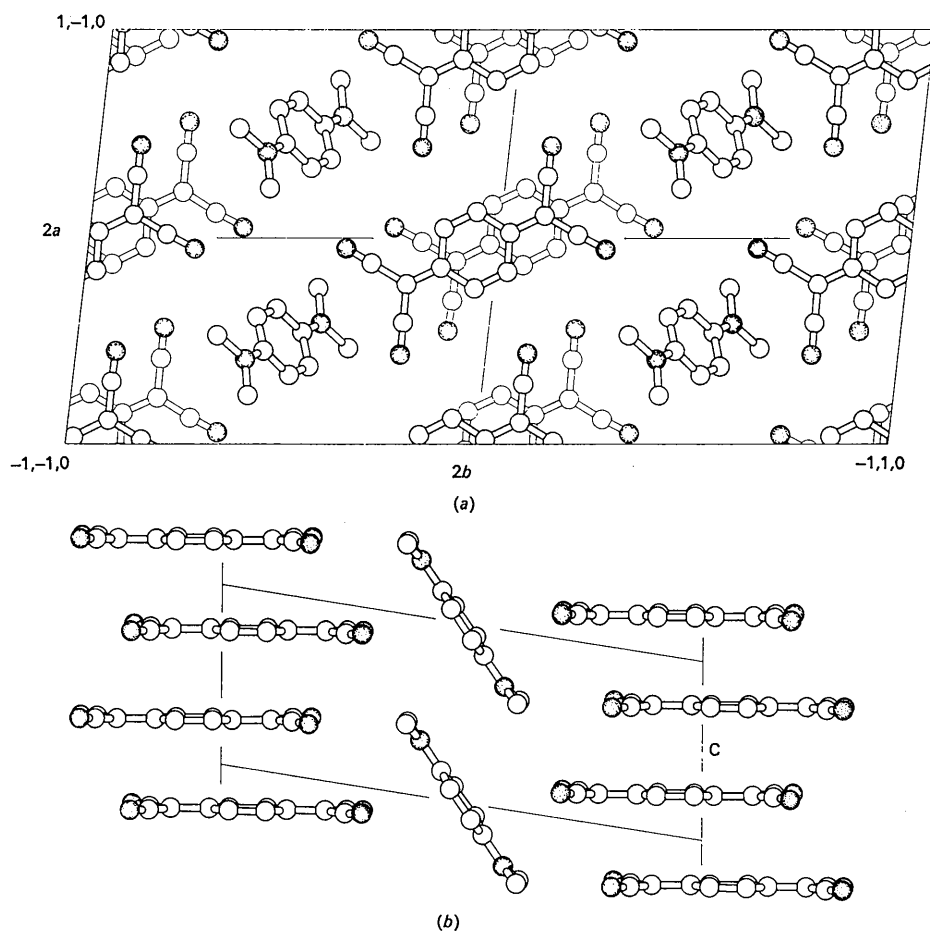


Fig. 2. (a) The structure viewed along *c*. (b) The structure viewed along the normal to the plane (110).

Table 4. Observed and calculated structure factors For unobserved reflexions (indicated by an asterisk) mod F₀ is the estimated threshold value.

Table with multiple columns for different reflections (e.g., 1 0 0, 1 1 0, 2 0 0, etc.) and rows for observed and calculated structure factors. The table is organized into several groups based on the reflection indices.

Table 4 (cont.)

L	FD	FC	L	FD	FC	L	FD	FC	L	FD	FC	L	FD	FC	L	FD	FC	L	FD	FC	L	FD	FC	L	FD	FC	L	FD	FC	L	FD	FC	L	FD	FC	L	FD	FC	
H ^a	7 _a	K ^a	14																																				
	-3	21	-17																																				
H ^a	7 _a	K ^a	15																																				
	-1	25	22																																				
H ^a	8 _a	K ^a	0																																				
	0	13	18																																				
	1	13	9																																				
	3	7 _a	3																																				
	-1	8 _a	7																																				
	-2	40	-167																																				
	-3	58	-65																																				
	-4	30	31																																				
	-5	15	13																																				
	-6	11	-10																																				
H ^a	8 _a	K ^a	1																																				
	0	16	21																																				
	1	8 _a	0																																				
	2	48	-51																																				
	3	17	-17																																				
	-1	11	15																																				
	-2	10	-16																																				
	-3	9	13																																				
	-4	72	71																																				
	-4	43	49																																				
	-6	10	-11																																				

Table 5. Summary of bond lengths

The shape parameters (q^2) used in calculating bond-length corrections are as follows: Atoms 1-6, 0.08; atoms 7-8, 0.096; atoms 9-12, 0.07; atoms 17-20, 0.08.

Bond		l uncorrected (Å)	l corrected (Å)		Mean l and $\sigma(l)$ (Å)	l and $\sigma(l)$ G.S.T.* (Å)	l and $\sigma(l)$ H* (Å)
C(2)	C(3)	1.353	1.354	(a)	1.354 (2)	1.354 (3)	—
C(5)	C(6)	1.353	1.355				
C(1)	C(2)	1.434	1.437				
C(3)	C(4)	1.431	1.435	(b)	1.434 (2)	1.434 (3)	—
C(4)	C(5)	1.430	1.433				
C(6)	C(1)	1.430	1.433				
C(1)	C(8)	1.391	1.392	(c)	1.395 (2)	1.396 (2)	—
C(4)	C(7)	1.397	1.398				
C(7)	C(9)	1.424	1.428				
C(7)	C(10)	1.419	1.422	(d)	1.427 (3)	1.430 (4)	—
C(8)	C(11)	1.425	1.429				
C(8)	C(12)	1.425	1.428				
C(9)	N(13)	1.141	1.171				
C(10)	N(14)	1.141	1.176		1.172 (15)†	1.141 (2)	—
C(11)	N(15)	1.142	1.169				
C(12)	N(16)	1.139	1.170				
C(17)	C(18)	1.405	1.418		1.418 (3)	—	1.416 (6)
C(18)	C(19)	1.403	1.417				
C(17)	C(19')	1.357	1.367		1.367 (3)	—	1.374 (10)
C(18)	N(20)	1.368	1.373		1.373 (3)	—	1.365 (7)
N(20)	C(21)	1.440	1.455		1.458 (15)†	—	1.474 (7)
N(20)	C(22)	1.439	1.462				

* G.S.T.: Goldstein, Seff & Trueblood (1968).

H.: Hanson (1965).

† E.s.d. arbitrarily increased because of uncertainty in correction for thermal motion.

An attempt to treat the entire molecule as a rigid body failed (yielding a *negative* minor-axis libration amplitude) presumably because of non-rigidity of the N(CH₃)₂ groups. The thermal motion of the CH₃ groups is quite intense, and the nature of the non-

rigidity cannot be specified with confidence. The N-CH₃ distances have been corrected by the method of Busing & Levy assuming riding motion. The assumption may well be unwarranted, and the 'corrected' distances unreliable.

Assessment of results

The agreement between observed and calculated structure amplitudes is reasonable (Table 4) and there can be no doubt of the essential correctness of the structure. The agreement residual ($R = \sum ||F_o| - |F_c|| / \sum |F_o|$) is 0.049, for observed reflexions only. (This figure assumes the corrected values of the reflexions believed to suffer from extinction.) A three-dimensional difference synthesis indicates that the residual electron density does not exceed the limits $\pm 0.2 \text{ e.}\text{\AA}^{-3}$. The e.s.d. of coordinates of non-hydrogen atoms ranges from 0.0015 to 0.0040 \AA , depending on type and thermal motion. (However, the thermal motion is such that systematic errors in the positions of the methyl carbon atoms and cyano nitrogen atoms undoubtedly exceed the e.s.d.'s.)

It must be emphasized that the analysis does not unequivocally demonstrate the existence of the species $\text{TCNQ}^{\pm-}$; the observed structure might be merely a superposition of TCNQ^0 and TCNQ^- . Such superposition could result from disorder, or from the use of the wrong space group ($P\bar{1}$ instead of, possible, $P1$). All that can be said is that the observed structure is consistent with what one might expect for $\text{TCNQ}^{\pm-}$.

Discussion

The architecture of the complex is illustrated in Fig. 2. Stacks of overlapping $\text{TCNQ}^{\pm-}$ ions are held together by half as many non-overlapping TMPD^+ ions. The TCNQ ions lie in planes which are very nearly (within 3°) normal to c , and Fig. 2(a) therefore gives a good impression of the manner in which they overlap. This overlap configuration is very similar to that found by Goldstein, Seff & Trueblood (1968) for tetraphenylphosphonium, TCNQ and by Fritchie (1966) for *N*-methylphenazinium, TCNQ . It also resembles that found for unlike ions in the 1:1 complex (Hanson, 1965). The interplanar spacings of adjacent TCNQ ions range from 3.23 and 3.25 \AA to 3.25 and 3.23 \AA , depending on whether all or only the central ring of the ion is used to define the mean plane. It is thus clear that no dimerization occurs; each ion is attracted equally to its nearest neighbours, with a mean interplanar spacing of 3.24 \AA . This is unlike the situation for the tetraphenylphosphonium salt, where definite dimers are observed.

There are no unusually short intermolecular contacts, other than those between overlapping TCNQ ions. Minimum distances for non-overlapping ions are: C-C, 3.84 \AA ; C-N, 3.39 \AA ; N-N, 3.59 \AA .

The molecular geometry is summarized in Fig. 3. Differences between chemically equivalent bonds are not significant for either molecule, a fact which suggests that the quoted e.s.d.'s are realistic. The 6-ring of the TMPD ion is planar, but both the nitrogen atoms and the methyl carbon atoms lie somewhat out of the plane. The configuration of the nitrogen atom is slightly pyramidal; this atom lies 0.062 \AA from the plane of

the adjacent carbon atoms. The 6-ring of the TCNQ ion is strictly planar, and the molecule as a whole is approximately so.

The bond lengths for both ions are compared in Table 5 with corresponding values found in other structures. Because of the difficulties of correcting for non-rigid thermal motion, and the differing techniques used in doing so, the comparison is probably meaningless for the distances N-CH₃ and C-N. Otherwise, the agreement is reasonable for TMPD^+ (confirming the pseudo-quinonoidal character of the ring) and excellent for $\text{TCNQ}^{\pm-}$.

For $\text{TCNQ}^{\pm-}$ the 'best' C-C bond lengths (obtained by averaging the results of both analyses) are compared in Table 6 with corresponding values for TCNQ^0 and TCNQ^{-1} . The dependence of bond-length distribution on formal charge seems now to be well-documented.

Appendix

It is now known that the crystals decompose slowly, with resultant changes in the unit-cell constants. The existence of the phenomenon was not apparent until after completion of the analysis, and it then became

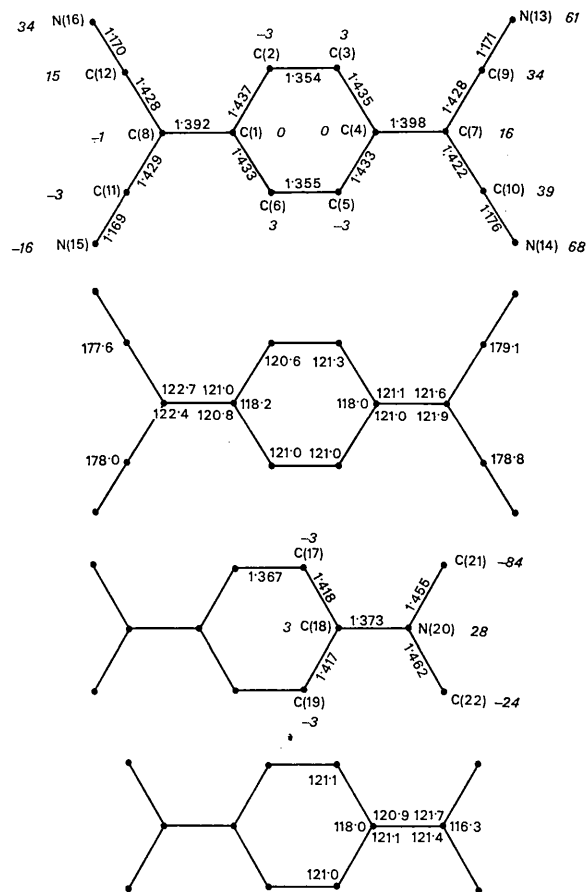


Fig. 3. Bond lengths (\AA) and angles ($^\circ$). The italicized numbers are the distances ($\text{\AA} \times 1000$) of the atoms from the mean plane of the appropriate six-membered ring.

Table 6. Bond lengths and their e.s.d.'s for TCNQ with varying formal charge

Bond	TCNQ ⁻				TCNQ ³⁻	TCNQ ⁰ L.S. & T.
	H.	F&A.	F.	Mean		
a	1.373 (9)	1.355 (4)	1.341 (6)	1.356	1.354 (2)	1.346 (4)
b	1.414 (6)	1.427 (3)	1.434 (5)	1.425	1.434 (2)	1.448 (3)
c	1.406 (8)	1.410 (4)	1.388 (6)	1.401	1.396 (2)	1.374 (4)
d	1.412 (6)	1.419 (3)	1.420 (5)	1.417	1.428 (3)	1.440 (3)
		H.	Hanson (1965)			
		F. & A.	Fritchie & Arthur (1966)			
		F.	Fritchie (1966)			
		L.S. & T.	Long, Sparks & Trueblood (1965)			

Values for TCNQ³⁻ are the mean of those found by Goldstein, Seff & Trueblood (1968) and the present author.

necessary to decide just what were the cell constants appropriate to the observed intensity data.

The specimen used had been in existence for some months before it came into the author's hands. Before commencement of data collection, its cell constants were measured on the XRD 5. On completion of data collection (process which took about six weeks) a^* , b^* , and c^* were redetermined. This was done in order to check, and if possible to improve the accuracy of, a , b , and c by using higher-angle off-axis reflexions. α^* , β^* , and γ^* were assumed to have been measured with adequate precision, however, and were not re-measured. This omission was subsequently regretted. Original and revised values of a , b and c are shown in Table 7; the differences are probably a little too great to explain as experimental error. About six months later, re-examination revealed that, while the $hk0$ net was pretty much as before, all reflexions of high l had become very weak, and $\alpha_1\alpha_2$ resolution had been lost, so that c was indeterminate.

Table 7. Cell constants at different stages of decomposition

Constant	C	A	B
a (Å)	7.793	7.780	7.783
b (Å)	15.072	15.024	15.015
c (Å)	6.458	6.482	6.494
α (°)	93.62	93.52	—
β (°)	102.64	102.77	—
γ (°)	82.89	82.97	—

A Specimen before data collection (June 1965).

B Specimen after data collection (July 1965).

C New specimen (August 1966).

Much later still, a new sample of material was made available to the author. The cell constants were re-measured, with the results shown in Table 7. It seems clear that for this material there is continuous decomposition with accompanying changes in cell constants (particularly in c) and ultimate destruction of the lattice.

One question which must be considered is: what set of cell constants is appropriate to the observed structure, column 2, 3, or something in between? Fortunately the difference between these sets is not too great, so that the question is slightly academic. The author's

choice was for the arithmetic mean for a , b , and c , and α , β , and γ from column 2. (Regrettably, no other values are available for the angles; however, a tentative extrapolation from columns 1 and 2 suggests that the angles do not change appreciably in any case.) Another question is: is it valid to assume that the observed intensity data represent a single structure? Here the only appeal is to the fact that the structure refined smoothly to give a physically reasonable result.

Finally, one may speculate on the nature of the decomposition. The very intense thermal motion of the TMPD ions indicates that they are held somewhat loosely. It has moreover been demonstrated that the direction of greatest vibration of the ion is quite close to c . It seems possible therefore that TMPD molecules may be able to escape along the tunnels between adjacent columns of TCNQ, leaving some vacancies. Formation of such vacancies would involve the conversion of neighbouring TCNQ ion pairs to neutral-molecule pairs (which require a larger separation) with a consequent increase in c . Total loss of TMPD molecules should lead to a value for $c/2$ of 3.45 Å, the observed intermolecular separation for neutral TCNQ (Long, Sparks & Trueblood, 1965). Of course, the structure would collapse long before this point was reached.

The specimen material was prepared by Mr I.E. Scheffler in the Division of Pure Chemistry. The analyses of thermal motion were carried out by Dr Karl Seff of the Department of Chemistry, University of California, Los Angeles. Professor Trueblood contributed much useful discussion and was kind enough to review the first draft of the paper. Programs used in the analysis, but not identified in the text, are those of Dr F.R. Ahmed, Dr S.R. Hall, Dr J.A. Bevan, and Mrs M.E. Pippy. The generous assistance of these people, and the continued encouragement of Dr W.H. Barnes, are gratefully acknowledged.

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The Crystal Structure of Tetraphenylphosphonium Bis(tetracyanoquinodimethanide)*

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Tetraphenylphosphonium bis(tetracyanoquinodimethanide), $(C_6H_5)_4P^+ \cdot (C_{12}N_4H_4)_2^-$ or $TPP(TCNQ)_2$, forms monoclinic crystals with $a_0 = 33.005$, $b_0 = 7.766$, $c_0 = 15.961$ Å, $\beta = 109.31^\circ$, and four molecules in the unit cell, probably in space group $C 2/c$. The structure has been refined by full-matrix least-squares methods, and the final molecular geometry includes small corrections for molecular libration. The TPP^+ ion lies on the twofold axis and nearly has $\bar{4}$ symmetry. Dimer pairs of TCNQ molecules are found about an inversion center, sharing a single negative charge and overlapping in a fashion characteristic of other TCNQ-complex structures. These pairs stack in planes normal to a^* which alternate with planes of TPP^+ ions. Intramolecular bond distances are normal, with the $(TCNQ)_2^-$ distances intermediate between those of TCNQ and $TCNQ^-$. The effect of charge on bond length is in qualitative agreement with the results of a simple molecular orbital calculation. The principal axis of electrical conductance is b , parallel to the twofold and 2_1 axes, parallel to the planes of the $(TCNQ)_2^-$ ions, and parallel to the layers of $(TCNQ)_2^-$ dimers.

Introduction

Several molecular complexes of TCNQ exhibit the largest specific conductances (Melby, Harder, Hertler, Mahler, Benson & Mochel, 1962) of any organic molecular crystals known. Furthermore, recent investigations (Hanson, 1968; Fritchie, 1966*b*; Fritchie & Arthur, 1966; Hanson, 1965; Long, Sparks & Trueblood, 1965; Anderson & Fritchie, 1963) have shown a small but significant dependence of the molecular geometry of TCNQ on its formal charge. When we began this work, no structural studies of TCNQ complexes had been reported, and we hoped that a precise determination of the structure of one of these complexes would suggest correlations of the anisotropic conductivity with the molecular arrangement and that knowledge of the precise molecular geometry of $(TCNQ)_2^-$ might aid in identifying the molecular orbital occupied by the odd electron.

Our results permit identification of a reasonable conduction path in the crystalline salt formed by the TPP

cation with the dimeric TCNQ anion, $(TCNQ)_2^-$. In addition we find that the bond-length distribution for the present TCNQ ion, with its formal charge of $-\frac{1}{2}$, is intermediate between those of TCNQ and $TCNQ^-$, in excellent agreement with the concurrent work of Hanson (1968).

Experimental

Crystals were supplied by Dr L. R. Melby; they are black, shiny, and opaque. The space group, $C2/c$, was assigned on the basis of Weissenberg photographs, from a diffractometer check of some of the expected extinctions (hkl , $h+k$ odd; $h0l$, l odd), and from an indication of centricity by the Howells-Phillips-Rogers (Howells, Phillips & Rogers, 1950) test. Fifteen weak diffraction maxima violated the $h0l$, $l=2n$ condition, but all of them could be attributed to double reflection under the experimental conditions used – a monoclinic crystal mounted about b for the 0-layer intensities (Zachariasen, 1965). The unit-cell dimensions are: $a_0 = 33.005 \pm 0.003$, $b_0 = 7.766 \pm 0.002$, $c_0 = 15.961 \pm 0.002$ Å, and $\beta = 109.31 \pm .02^\circ$. The measured density of 1.285 agrees well with the value of 1.286 g.cm⁻³ calculated for a four-molecule unit cell. The cell constants and relative intensities were measured at about 22°C, with a Picker diffractometer and a General Electric

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