

- FRITCHIE, C. J., JR & ARTHUR, P. (1966). *Acta Cryst.* **21**, 139.
- FURNAS, T. C. (1957). *Single Crystal Orienter Instruction Manual*. Milwaukee: General Electric Company.
- GANTZEL, P. K. & TRUEBLOOD, K. N. (1966). Private communication.
- GOLDSTEIN, P., SEFF, K. & TRUEBLOOD, K. N. (1968). *Acta Cryst.* **A24**, 778.
- HANSON, A. W. (1965). *Acta Cryst.* **19**, 610.
- HODGSON, L. T. & ROLLETT, J. S. (1963). *Acta Cryst.* **16**, 329.
- LONG, R. E., SPARKS, R. A. & TRUEBLOOD, K. N. (1965). *Acta Cryst.* **18**, 932.
- MILLS, O. S. & ROLLETT, J. S. (1961). In *Computing Methods and the Phase Problem in X-ray Crystal Analysis*, p. 117. Oxford: Pergamon Press.
- SCHOMAKER, V. & TRUEBLOOD, K. N. (1968). *Acta Cryst.* **B24**, 63.

*Acta Cryst.* (1968). **B24**, 778

## The Crystal Structure of Tetraphenylphosphonium Bis(tetracyanoquinodimethanide)\*

BY P. GOLDSTEIN†, K. SEFF AND K. N. TRUEBLOOD

*Department of Chemistry, University of California, Los Angeles, California 90024, U.S.A.*

(Received 17 July 1967)

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<sup>-3</sup> 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

\* Contribution no. 2111. This work was supported in part by the National Science Foundation under grants GB-2029 and G20207.

† Present address: Philips Laboratories, Briarcliff Manor, New York, U.S.A.

Table I. Observed and calculated structure factors

The running index is h; values of k and l for each group immediately precede that group. The central column is 10|F<sub>o</sub>|, the right-hand column 10|F<sub>c</sub>|. The symbols immediately following some values of F<sub>o</sub> have these meanings: U, unobserved; E, omitted from least squares because of extinction; \*, omitted from least squares because of measurement error.

Table with multiple columns containing numerical data for structure factors, including observed (F<sub>o</sub>) and calculated (F<sub>c</sub>) values, and various symbols (U, E, \*) indicating data quality.

Table I (cont.)

Table with multiple columns containing numerical data, likely representing crystallographic parameters or diffraction data. The table is organized into several vertical sections, each with its own set of column headers. The data includes various numerical values, some with subscripts or superscripts, and some with labels like 'h', 'k', 'l'.

single-crystal orienter, using Furnas & Harker's (1955) moving-crystal moving-counter technique. The crystal used was nearly regular in shape, with extreme dimensions of  $0.36 \times 0.39 \times 0.42$  mm, and its shape could be described rather well in terms of eight bounding planes; absorption corrections ( $\mu = 9.98 \text{ cm}^{-1}$ ) were made with a FORTRAN program written by Charles Burnham and modified by one of us (P.G.).

Cu  $K\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ), reasonably monochromatized by means of a  $K\beta$  filter and a pulse-height analyzer, was used throughout. Of the 4409 unique reflections in the sphere, 4206 were examined (those with  $2\theta \leq 160^\circ$ ), and significant counts were made for 3522. Sixteen of these were omitted from later refinements because of apparent measurement errors; it was not feasible to reestimate them. At a late stage of refinement the reflection (204) with the largest  $|F|$  was omitted because of apparent extinction.

The electrical resistance of a single crystal was estimated with an ohmmeter and wire brushes. Specific resistivities of  $10^3$ ,  $10^6$ , and  $2 \times 10^6$  ohm-cm in crystallographically unspecified directions were reported by Melby *et al.* (1962), and we wished, after determining the structure, to find which axis possessed the lowest resistance. We used a single crystal which approximated a parallelepiped in shape, with dimensions about 2.2 mm parallel to **b** and 0.8 and 0.25 mm normal to **b**, parallel to the side faces. Resistivities measured along two nearly normal directions in the **a-c** plane were  $1.7 \times 10^6$  and  $2.1 \times 10^6$  ohm.cm; the resistivity along **b** was  $4.5 \times 10^3$  ohm.cm, somewhat high in comparison with the results of Melby *et al.* (perhaps owing to poor electrical contacts, impurities, or lattice defects) but nevertheless low enough to identify **b** unambiguously as the longest principal axis of the ellipsoid of electrical conductance.

### Structure determination

The phosphorus position was readily deduced from a sharpened three-dimensional Patterson map, and the remaining atoms were found on successive three-dimensional electron density maps phased initially with the phosphorus atom. Full-matrix least-squares refinement based on 3505 observed reflections, with anisotropic temperature factors for the non-hydrogen atoms and isotropic temperature factors for the hydrogen atoms, eventually brought the unweighted  $R$  index to 0.043. The program used was that of Gantzel, Sparks & Trueblood (A.C.A. no. 317, modified), which minimizes  $\sum \omega(\Delta|F|)^2$ . All the hydrogen atoms were found on an intermediate three-dimensional difference Fourier synthesis. The weights used were proportional to  $1/\sigma^2(F)$ , where  $\sigma(F)$  is the estimated standard deviation of a structure factor as deduced from considerations of counting statistics and estimated errors in background measurement, in instrument stability, and in the absorption and filter corrections. The intensities of about 90% of the unobserved

reflections are calculated to be less than the minimum observable intensity ( $F_{\min}$ ), and all but one are less than  $2 F_{\min}$ .

The scattering curves were: P, Freeman & Watson (1962); N and C (valence), Hoerni & Ibers (1954); and H (bonded), Stewart, Davidson & Simpson (1965). In the last cycle of least-squares refinement, the average shifts were about 0.12 e.s.d.'s of position; no non-hydrogen coordinate shift exceeded  $0.0009 \text{ \AA}$ , or  $0.6 \sigma$ , and no hydrogen coordinate shift exceeded  $0.014 \text{ \AA}$ , or  $0.7 \sigma$ . Table 1 gives the observed and calculated structure factors.

The highest point ( $0.18 \text{ e. \AA}^{-3}$ ) on the final difference Fourier map was less than half the height of the lowest hydrogen atom found on an earlier difference map, and about 2.5 times the e.s.d. of the electron density,

Table 2. Final positional parameters and their standard deviations\*

	$x, \sigma(x)$	$y, \sigma(y)$	$z, \sigma(z)$
P	0.0	0.1284, 1	0.25
C(1)	0.03324, 4	-0.0112, 2	0.33426, 9
C(2)	0.05459, 5	-0.1453, 2	0.30811, 11
C(3)	0.07920, 6	-0.2598, 3	0.36978, 13
C(4)	0.08291, 6	-0.2426, 3	0.45758, 13
C(5)	0.06206, 6	-0.1126, 3	0.48404, 12
C(6)	0.03687, 5	0.0059, 2	0.42292, 10
C(7)	0.03101, 4	0.2690, 2	0.20598, 9
C(8)	0.00956, 6	0.4019, 2	0.14970, 12
C(9)	0.03255, 8	0.5194, 3	0.11865, 14
C(10)	0.07665, 8	0.5066, 3	0.14402, 15
C(11)	0.09793, 7	0.3764, 3	0.19969, 14
C(12)	0.07526, 5	0.2554, 2	0.23060, 11
C(13)	0.21056, 4	0.2388, 2	0.40398, 10
C(14)	0.24403, 5	0.1545, 2	0.38118, 10
C(15)	0.27466, 5	0.2450, 2	0.36110, 10
C(16)	0.27460, 5	0.4286, 2	0.36206, 10
C(17)	0.24080, 5	0.5130, 2	0.38360, 11
C(18)	0.21018, 5	0.4229, 2	0.40346, 11
C(19)	0.17946, 5	0.1458, 2	0.42622, 10
C(20)	0.14584, 5	0.2293, 2	0.44837, 11
C(21)	0.17998, 5	-0.0375, 2	0.42832, 12
C(22)	0.30634, 5	0.5244, 2	0.34330, 11
C(23)	0.30692, 5	0.7070, 2	0.34622, 12
C(24)	0.34081, 5	0.4476, 2	0.32163, 12
N(1)	0.11874, 5	0.2973, 2	0.46498, 12
N(2)	0.18111, 5	-0.1841, 2	0.43049, 13
N(3)	0.30770, 5	0.8538, 2	0.34750, 13
N(4)	0.36910, 5	0.3915, 2	0.30464, 13
H(1)	0.0521, 6	-0.150, 2	0.2411, 14
H(2)	0.0944, 7	-0.358, 3	0.3480, 14
H(3)	0.1006, 6	-0.326, 3	0.5007, 13
H(4)	0.0648, 7	-0.098, 3	0.5431, 15
H(5)	0.0232, 5	0.105, 2	0.4440, 11
H(6)	-0.0218, 7	0.415, 3	0.1310, 13
H(7)	0.0191, 7	0.621, 3	0.0824, 15
H(8)	0.0931, 7	0.594, 3	0.1232, 14
H(9)	0.1290, 7	0.363, 3	0.2173, 14
H(10)	0.0912, 6	0.169, 3	0.2690, 13
H(11)	0.2441, 5	0.036, 2	0.3791, 11
H(12)	0.2975, 5	0.187, 2	0.3474, 11
H(13)	0.2404, 5	0.639, 2	0.3830, 10
H(14)	0.1870, 5	0.479, 2	0.4159, 11

\* See Figs. 1 & 2 for the identities of the atoms. The e.s.d., separated by a comma, is in the units of the least significant digit given for the corresponding parameter.

0.07 e.Å<sup>-3</sup>. A minor negative region (-0.30 e.Å<sup>-3</sup>) was found near the phosphorus atom, perhaps because no dispersion correction for P was included. No systematic indication of chemical bond electron density was observed. The final positional and thermal parameters are given in Tables 2 and 3 respectively.

The isotropic temperature factors of the hydrogen atoms are greater than those of the carbon atoms to which they are bonded by 0.6 to 3.1 Å<sup>2</sup>. For carbon temperature factors in the range 4.6 to 8.4 Å<sup>2</sup>, the rule,

$$B_H = 1.6 B_C - 2.0$$

Table 3. Thermal vibration parameters\* and their standard deviations

I. Phosphorus, carbon, and nitrogen temperature factor =  
exp  $\{- (b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl)\}$

	10 <sup>5</sup> b <sub>11</sub>	10 <sup>4</sup> b <sub>22</sub>	10 <sup>5</sup> b <sub>33</sub>	10 <sup>4</sup> b <sub>12</sub>	10 <sup>5</sup> b <sub>13</sub>	10 <sup>4</sup> b <sub>23</sub>
P	78.2, 4	151, 1	362, 2	0	140, 2	0
C(1)	85, 1	173, 3	418, 6	4, 1	125, 4	6, 2
C(2)	113, 2	213, 3	506, 7	13, 1	147, 6	1, 3
C(3)	116, 2	224, 4	703, 10	20, 1	160, 7	35, 3
C(4)	113, 2	284, 5	660, 10	14, 2	126, 7	88, 3
C(5)	151, 2	316, 5	444, 7	4, 2	140, 7	55, 3
C(6)	121, 2	234, 3	446, 7	0, 1	174, 6	8, 3
C(7)	103, 1	172, 3	450, 6	-7, 1	206, 5	-15, 2
C(8)	151, 2	186, 3	650, 9	4, 1	293, 7	33, 3
C(9)	242, 4	186, 4	752, 11	-13, 2	465, 11	21, 3
C(10)	242, 4	231, 4	791, 12	-63, 2	571, 11	-70, 4
C(11)	142, 2	317, 5	774, 11	-49, 2	388, 8	-84, 4
C(12)	104, 2	241, 3	540, 8	-16, 1	215, 6	-35, 3
C(13)	94, 1	138, 2	509, 7	-1, 1	125, 5	-15, 2
C(14)	108, 2	120, 2	572, 8	1, 1	175, 6	-22, 2
C(15)	107, 2	140, 3	556, 7	7, 1	195, 6	-16, 2
C(16)	104, 2	137, 2	510, 7	4, 1	164, 5	-5, 2
C(17)	111, 2	124, 3	652, 8	8, 1	204, 6	1, 2
C(18)	101, 2	134, 3	649, 8	9, 1	196, 6	-8, 2
C(19)	94, 1	146, 3	565, 7	-2, 1	136, 5	-21, 2
C(20)	100, 2	166, 3	604, 8	-7, 1	158, 6	-12, 2
C(21)	102, 2	159, 3	672, 9	-13, 1	188, 6	-32, 2
C(22)	117, 2	143, 3	563, 8	8, 1	227, 6	10, 2
C(23)	125, 2	155, 3	714, 9	5, 1	304, 7	16, 3
C(24)	144, 2	164, 3	682, 9	6, 1	336, 7	21, 3
N(1)	123, 2	229, 3	905, 11	5, 1	305, 7	-28, 3
N(2)	150, 2	160, 3	1078, 12	-14, 1	344, 8	-37, 3
N(3)	182, 2	154, 3	1127, 13	3, 1	511, 9	12, 3
N(4)	196, 2	230, 3	1107, 13	25, 2	625, 10	32, 3

II. Hydrogen

	B (Å <sup>2</sup> )		B (Å <sup>2</sup> )
H(1)	6.5, 5	H(8)	7.8, 5
H(2)	8.4, 6	H(9)	7.9, 6
H(3)	6.5, 5	H(10)	6.4, 5
H(4)	7.7, 6	H(11)	4.7, 4
H(5)	5.1, 4	H(12)	4.0, 4
H(6)	7.2, 5	H(13)	4.7, 4
H(7)	7.6, 5	H(14)	4.6, 4

\* See Figs. 1 & 2 for the identity of the atoms. The e.s.d., separated by a comma, is in the units of the least significant digit given for the corresponding parameter.

Table 4. Least-squares planes†

No.	Direction cosines (× 10 <sup>4</sup> ) with respect to			Description of plane	r.m.s. deviation from plane (Å × 10 <sup>3</sup> )
	a	b	c*		
1	2616	-0012	9652	C <sub>6</sub> (TCNQ ring)‡	5
2	2615	-0013	9652	C <sub>8</sub> (TCNQ quinonoid group)	15
3	2579	0015	9662	C <sub>12</sub> N <sub>4</sub> (TCNQ without hydrogens)‡	35
4	2570	0024	9664	C <sub>4</sub> N <sub>4</sub> (4 cyano groups)	26
5	2698	0261	9626	C <sub>3</sub> N <sub>2</sub> (1st C-(CN) <sub>2</sub> group)‡	4
6	2374	-0270	9710	C <sub>3</sub> N <sub>2</sub> (2nd C-(CN) <sub>2</sub> group)‡	3
7	7947	5888	1473	C <sub>6</sub> (1st TPP <sup>+</sup> phenyl group, Ph)‡	1
8	-1819	5804	7938	C <sub>6</sub> (2nd TPP <sup>+</sup> phenyl group, Ph)‡	4

† For the molecule whose coordinates are given in Table 2.

‡ See also Table 5.

holds with a mean error of  $0.3 \text{ \AA}^2$ , an amount less than the e.s.d.'s of the hydrogen temperature factors.

The direction cosines of the least-squares planes through various groups of atoms in the structure are presented in Table 4, and the deviations of some atoms from these planes are in Table 5. It is noteworthy that both  $-\text{C}(\text{CN})_2$  groups are entirely on the same side of the TCNQ ring, resulting in a 'bowing' of the plane of the molecule. The 'interplanar' spacings of the TCNQ anions therefore depend slightly on which atoms are chosen to define the plane; these spacings are given in Table 6.

Table 5. Deviations of atoms from least-squares planes\* ( $\text{\AA} \times 10^3$ )

	Plane no.					Plane no.	
	1	3	5	6		7	8
C(13)	7	<b>-26</b>	4		P	-67	123
C(14)	-3	<b>-43</b>			C(1)	1	
C(15)	-4	<b>-46</b>			C(2)	-1	
C(16)	7	<b>-32</b>		22	C(3)	-1	
C(17)	-2	<b>-34</b>			C(4)	2	
C(18)	<b>-5</b>	<b>-34</b>			C(5)	-2	
C(19)	32	2	0		C(6)	0	
C(20)	33	9	7		C(7)		2
C(21)	66	<b>32</b>	<b>-6</b>		C(8)		4
C(22)	33	<b>-8</b>		0	C(9)		<b>-5</b>
C(23)	75	<b>38</b>		5	C(10)		1
C(24)	46	<b>-1</b>		<b>-4</b>	C(11)		5
N(1)	17	<b>-2</b>	<b>-4</b>		C(12)		<b>-6</b>
N(2)	106	<b>68</b>	3		H(1)	41	
N(3)	97	<b>63</b>		<b>-3</b>	H(2)	-10	
N(4)	67	<b>15</b>		2	H(3)	-2	
H(11)	-29				H(4)	19	
H(12)	15				H(5)	55	
H(13)	-15				H(6)		8
H(14)	-42				H(7)		66
					H(8)		27
					H(9)		-15
					H(10)		4

\* Boldface deviations indicate the atoms used to define the least-squares plane. A negative deviation from a plane indicates that the atom with the coordinates given in Table 2 lies between that plane and the origin. See Figs. 1 and 2 for the identity of the atoms.

Table 6. Interplanar angles and TCNQ interplanar distances

Planes No.	Planes No.	Angle	Distances	
			Plane No.	Intra-dimer Inter-dimer
1	5	$1.6^\circ$ *	1	3.22 $\text{\AA}$ 3.35 $\text{\AA}$
1	6	$2.0^\circ$ *	2	3.21 3.36
5	6	$1.9^\circ$ *	3	3.15** 3.46
3	7	$50.8^\dagger$	4	3.10 3.52
3	8	$32.0^\dagger$		
7	8	$55.9^\ddagger$		
7	7	$123.6^\ddagger, \S$		
8	8	$124.8^\ddagger, \S$		

\* See Table 4 and Fig. 1.

† For the arrangement shown in Fig. 4.

‡ For the TPP<sup>+</sup> ion shown in Fig. 2.

\*\* Reported *incorrectly* as  $3.69 \text{ \AA}$  at the Feb. 1966 meeting of the American Crystallographic Association (abstracts, p. 39).

§ Intraionic, between equivalent phenyl planes.

### Thermal motion

The possible molecular motions of five different groups of atoms have been analyzed in terms of the rigid-body tensors of translation (T), libration (L), and screw motion (S) (Schomaker & Trueblood, 1968). The computer program used was (new) ACA No. 1. The r.m.s. discrepancy between observed and calculated  $U_{ij}$  serves as a measure of the applicability of this analysis and thus of the rigidity of a particular grouping.

Some rigid-body parameters for the eight-atom quinonoid skeleton of the TCNQ molecule are given in Table 7; the fit was excellent. The translational motion is reasonably isotropic, while libration is quite anisotropic, with the only appreciable motion corresponding to a r.m.s. amplitude of  $5.5^\circ$  about an axis ( $L1$ ) only  $3^\circ$  away from the long axis of the molecule. The close similarity of this pattern with those found for TCNQ in other crystals (Long, Sparks & Trueblood, 1965; Hanson, 1968) attests to its physical reality. When a similar analysis was tried for the entire TCNQ molecule, the r.m.s. value of  $\Delta U_{ij}$  increased more than threefold, indicating that the cyano groups are wagging appreciably and cannot properly be regarded as part of a rigid molecule. This is consistent with the situation in tetracyanoethylene (Bekoe & Trueblood, 1960), TCNQ (Long *et al.*, 1965), and Hanson's (1968) complex.

The TPP<sup>+</sup> ion was examined in some detail. A rigid-body analysis for the whole ion (PC<sub>24</sub>) gave a r.m.s.  $\Delta U_{ij}$  of  $53 \times 10^{-4} \text{ \AA}^2$ , a value whose magnitude indicates significant internal motion. The group of nine atoms consisting of the phosphorus atom and the four carbon atoms bonded to it, together with the four carbon atoms *para* to these (PC<sub>8</sub>), was tried. The r.m.s.  $\Delta U_{ij}$  was  $39 \times 10^{-4} \text{ \AA}^2$ , indicating that this group of atoms was likewise not very rigid. The indicated translational and librational amplitudes were small and not significantly anisotropic, averaging about  $0.21 \text{ \AA}$  and  $3^\circ$  respectively, and were very similar for the PC<sub>8</sub> grouping and the PC<sub>24</sub> combination. Finally, the two seven-atom rigid bodies consisting of each phenyl group and the attached phosphorus atom were investigated. (The phenyl groups alone cannot be treated because all the atoms of each lie approximately on a conic section.) For convenience in this discussion, we will refer to the ring consisting of atoms C(1) to C(6) as Ph and to that comprising atoms C(7) to C(12) as Ph'. The fit for each of these seven-atom groups was generally plausible (Table 7). The translational motion was relatively small and not significantly anisotropic, nor was there any apparent correlation with the inertial axes of the groups. For each ring the principal librational motion corresponded to an amplitude of about  $6^\circ$  about an axis not far from the direction of the P-C bond (deviating by  $18^\circ$  and  $16^\circ$  for P-Ph and P-Ph' respectively), and  $L2$  was not far from the normal to the least-squares plane (deviating by  $20^\circ$  and  $13^\circ$ ). The third eigenvalue was very small (and in fact

Table 7. *Rigid-body thermal parameters\**

TCNQ quinoid group, C(13) to C(19) and C(22)				P-Ph, phosphorus and C(1) to C(6)				P-Ph', phosphorus and C(7) to C(12)				
L [ $\times 10^{-1}(\text{°})^2$ ] 226,25				201,29				116,45				
108,13 -44,14				-98,29 77,25				107,26 -139,21				
100,18 -26,9				253,44 -150,30				234,39 -28,25				
42,9				106,52				211,25				
Principal axes of L												
	r.m.s. amplitude	Direction cosines ( $\times 10^3$ )			r.m.s. amplitude	Direction cosines ( $\times 10^3$ )			r.m.s. amplitude	Direction cosines ( $\times 10^3$ )		
L1	5.5°	851	489	-194	6.5°	496	-728	474	6.1°	566	570	-596
L2	1.9	515	-849	118	3.6	863	472	-178	4.4	091	-762	-642
L3	1.8	107	201	974	1.0	094	-497	-862	(0)†	819	-309	483
Principal axes of reduced† T												
	r.m.s. amplitude	Direction cosines ( $\times 10^3$ )			r.m.s. amplitude	Direction cosines ( $\times 10^3$ )			r.m.s. amplitude	Direction cosines ( $\times 10^3$ )		
	0.24 Å	285	226	-931	0.23 Å	400	-566	721	0.22 Å	305	930	-207
	.22	905	256	339	.21	121	-747	-654	.21	866	-181	465
	.19	315	-940	133	.17	909	349	-230	.18	395	-322	-860
Displacement of libration axes from intersecting (Å)												
Parallel to L1		0.54				10.29				‡		
Parallel to L2		-0.27				3.01				‡		
Parallel to L3		1.92				0.93				-0.61		
Effective screw translations (Å)												
Parallel to L1		-0.001				-0.010				-0.026		
Parallel to L2		0.000				0.012				0.019		
Parallel to L3		0.002				0.023				‡		
( $\Delta U^2_{ij}$ ) <sup>1/2</sup> (Å <sup>2</sup> )		0.0010				0.0019				0.0017		

\* Axes of references are a, b, c\*. E.s.d. of components of L are given after them, separated by a comma, in units of last place shown.

† Because the eigenvalue of L3 was negative for P-Ph' (see text), the reduced T corresponding to equation (20) of Schomaker & Trueblood (1968) is without significance. The values given here for each group of atoms correspond to the origin which symmetrizes S; the reduced T calculated in this fashion normally differs only slightly from that calculated by equation (20).

‡ These quantities for P-Ph' are not meaningful because the eigenvalue of L3 was negative.

Table 8. *Bond lengths\*(Å)*

TPP+	Distance		TCNQ	Distance	
	Uncorr.	Corr.†		Uncorr.	Corr.†
P—C(1)	1.792	1.796	C(13)—C(14)	1.431	1.436
C(1)—C(2)	1.396	1.403	C(14)—C(15)	1.354	1.355
C(2)—C(3)	1.375	1.378	C(15)—C(16)	1.426	1.431
C(3)—C(4)	1.372	1.382	C(16)—C(17)	1.430	1.435
C(4)—C(5)	1.365	1.370	C(17)—C(18)	1.350	1.352
C(5)—C(6)	1.398	1.401	C(18)—C(13)	1.430	1.435
C(6)—C(1)	1.387	1.396	C(13)—C(19)	1.394	1.395
			C(19)—C(20)	1.427	1.433
C(2)—H(1)	1.05		C(19)—C(21)	1.424	1.430
C(3)—H(2)	1.04		C(16)—C(22)	1.396	1.397
C(4)—H(3)	0.99		C(22)—C(23)	1.419	1.425
C(5)—H(4)	0.92		C(22)—C(24)	1.425	1.430
C(6)—H(5)	1.01		C(20)—N(1)	1.143	1.17‡
			C(21)—N(2)	1.140	1.17‡
P—C(7)	1.791	1.796	C(23)—N(3)	1.140	1.17‡
C(7)—C(8)	1.398	1.406	C(24)—N(4)	1.141	1.17‡
C(8)—C(9)	1.379	1.383			
C(9)—C(10)	1.379	1.389	C(14)—H(11)	0.92	
C(10)—C(11)	1.376	1.383	C(15)—H(12)	0.97	
C(11)—C(12)	1.390	1.394	C(17)—H(13)	0.98	
C(12)—C(7)	1.385	1.395	C(18)—H(14)	0.96	
C(8)—H(6)	0.99				
C(9)—H(7)	0.99				
C(10)—H(8)	0.99				
C(11)—H(9)	0.98				
C(12)—H(10)	0.95				

\* Estimated standard deviations average: P—C, 0.003 Å; C—C and C—N, 0.003–0.004 Å; C—H, 0.02 Å (not including an expected error arising from the use of a spherically symmetric form factor); angles involving heavy atoms, 0.2–0.3°; H—C—C, 1.5°.

† The shape parameters ( $q^2$ ) used in calculating bond-length corrections were as follows: aromatic C, 0.08; aliphatic C, 0.096; cyano C, 0.07; N, 0.046; P, 0.13.

‡ Corrected on the assumption of riding motion (see text).

for P-Ph' it was slightly, although not significantly, negative, presumably reflecting experimental errors in the *B*'s or partial inadequacy of the rigid-body model). The primary motion of the phenyl groups – libra-

tion about the P-C bond – was expected, but the secondary motion about an axis nearly normal to the rings was not. The latter may reflect an in-plane wag of the phenyl groups about the phosphorus atom.

Table 9. Results of molecular-orbital calculations\*

Bond	Observed bond lengths (Å)			$\pi$ -bond order†		Changes in bond length (Å)‡	
	TCNQ	(TCNQ) <sub>2</sub> <sup>-</sup>	TCNQ-§	TCNQ	TCNQ <sup>-</sup>	Observed	Predicted
<i>a</i>	1.346(4)	1.354(2)	1.356(10)	0.82	0.77	+0.014(5)	+0.014
<i>b</i>	1.448(3)	1.434(2)	1.425(7)	0.45	0.51	-0.026(5)	-0.016
<i>c</i>	1.374(4)	1.396(2)	1.401(8)	0.65	0.56	+0.035(5)	+0.024
<i>d</i>	1.440(3)	1.428(3)	1.417(4)	0.41	0.45	-0.023(5)	-0.011
<i>e</i>	-	1.17 (1)	-	0.88	0.85	-	+0.003

Effective  $\pi$ -system charge (e<sup>-</sup>)

	TCNQ	TCNQ <sup>-</sup>
C(13), C(16)	+0.07	+0.01
C(14), C(15), C(17), C(18)	+0.02	-0.02
C(19), C(22)	+0.01	-0.13
C(20), C(21), C(23), C(24)	+0.16	+0.14
N(1), N(2), N(3), N(4)	-0.22	-0.31

\* The significance of bonds *a*, *b*, *c*, *d*, *e* is shown in Fig. 1. E.s.d.'s are in parentheses, in units of the last place shown. The values for (TCNQ)<sub>2</sub><sup>-</sup> are averages of those found here with those of Hanson (1968).

† The  $\pi$ -bond orders are those predicted by Hückel (LCAO) M.O. calculations (Long, Sparks & Trueblood, 1965).

‡ Changes in bond length are calculated per unit molecular charge added. The 'observed' changes were calculated from the values in the first three columns, taking the e.s.d.'s into account and assuming that bond lengths vary linearly with the average charge over this small range. The predicted changes were calculated using the empirical value 0.27 Å/unit  $\pi$ -bond order in the bond-order range 0.40 to 0.92 (Cruickshank & Sparks, 1960).

§ Values for TCNQ<sup>-</sup> are uncorrected for libration and are averages of the results of Fritchie & Arthur (1966), Fritchie (1966*b*) and Hanson (1965).

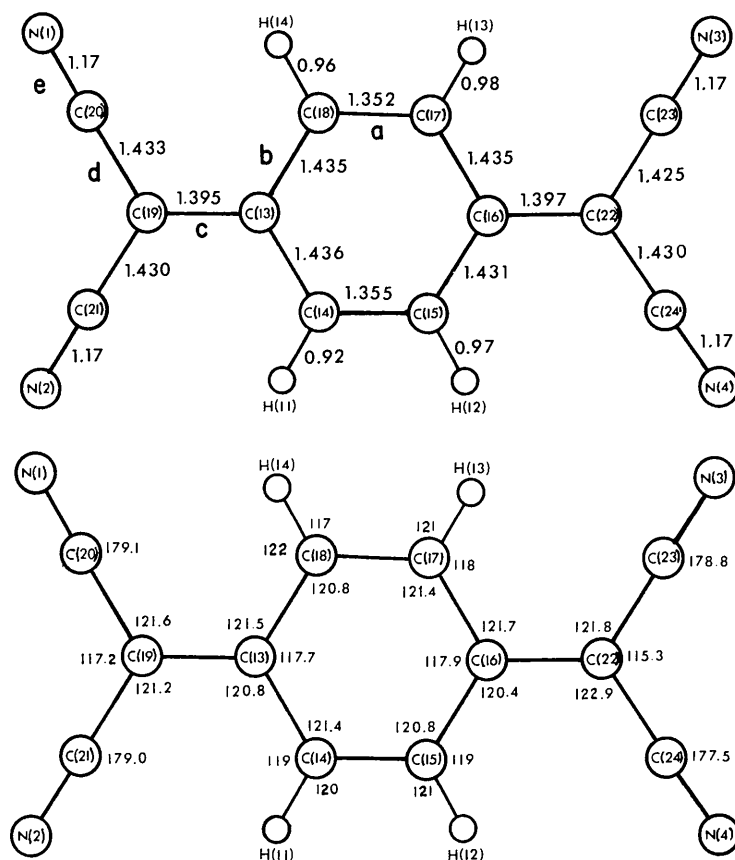


Fig. 1. Unique molecular dimensions of (TCNQ)<sub>2</sub><sup>-</sup> (corrected for libration).



The bond lengths and angles were corrected (Cruickshank, 1956, 1961) for the effects of thermal motion indicated by the rigid body analyses. (The C-N cyano bonds were corrected by the method of Busing & Levy (1964), assuming 'riding' motion.) The molecular geometry is given in Fig.1, Fig.2, and Table 8. Hanson (1968) shows the excellent agreement of his and our  $(\text{TCNQ})_2^-$  determinations as well as a comparison of TCNQ bond lengths as a function of formal charge (Table 9). The addition of the single electron to a

TCNQ molecule increases the double-bond lengths and decreases the single-bond lengths by the amounts shown in Table 9; the usually imprecisely determined  $-\text{C}\equiv\text{N}$  is not included. The  $(\text{TCNQ})_2^-$  bond lengths do not differ significantly from the average of those for TCNQ and  $\text{TCNQ}^-$ . We must emphasize, as Hanson does, that this study does not demonstrate unequivocally that all TCNQ molecules are equivalent, either as  $(\text{TCNQ})_2^-$  dimers or as anions with super-orbitals. TCNQ and  $\text{TCNQ}^-$  molecules may alternate or be

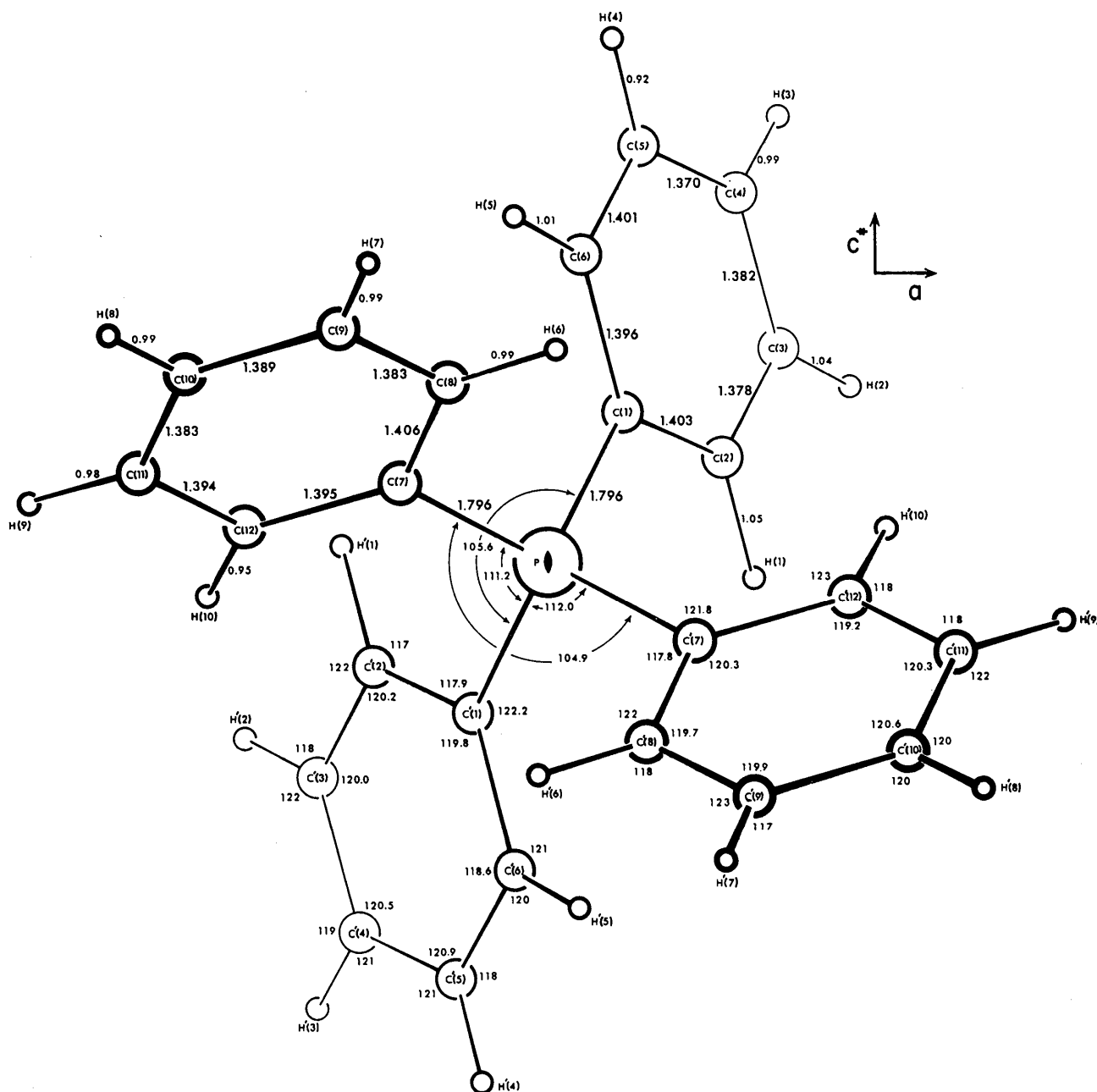


Fig. 2. Molecular dimensions of TPP<sup>+</sup> (corrected for libration).

in disorder, so that the assumed inversion center is only approximate or statistical.

Molecular orbital calculations were made by the LCAO (Hückel) method using the same parameters as earlier (Long, Sparks & Trueblood, 1965). The lowest anti-bonding molecular orbital, which is half filled by the excess electron in TCNQ<sup>-</sup>, is depicted in Fig. 3. The wave function is centrosymmetric (*gerade*) and has a mirror plane normal to the plane of the molecule, parallel to the long molecular axis. This orbital has nodes at all double-bond positions and no node at any single-bond position; predicted bond length changes (Table 9) per unit charge added per molecule are in qualitative agreement with the observed changes. Although the calculation is an approximate one, it shows that the energy level of the new orbital is only slightly anti-bonding, consistent with the ease with which TCNQ forms anions. Its energy (about +0.04 eV) lies far be-

low that of the next lowest anti-bonding orbital. Meneff & Pao (1962) calculated the energy of this orbital to be +0.24 eV; for this sort of calculation, the difference from our result is scarcely significant. Our results are in qualitative agreement with the SCF-LCAO calculations of Lowitz (1967).

The tetraphenylphosphonium ion phenyl groups are not significantly non-planar (Table 5). The average of the 12 unique C-C bond distances is 1.390 Å (corrected for libration), in agreement with the distance of 1.389 Å (corrected) in the tetraphenylarsonium ion (Palenik, 1966), 1.381 Å (uncorrected) in the triphenylmethylphosphonium ion (Fritchie, 1966*a*), 1.389 Å (corrected) in [3.3]paracyclophane (Gantzel & Trueblood, 1965), and 1.392 Å in benzene (Cox, Cruickshank & Smith, 1958). The standard deviation of the C-C bonds from their mean is 0.011 Å, essentially the same as that reported by Palenik (1966) for the tetra-

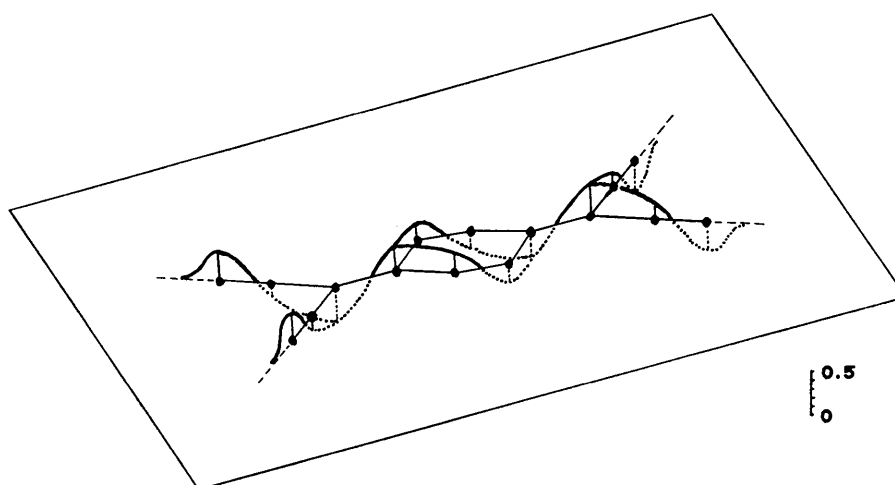


Fig. 3. The wave function for the orbital occupied by an electron added to a TCNQ molecule. A normalized-amplitude scale is given.

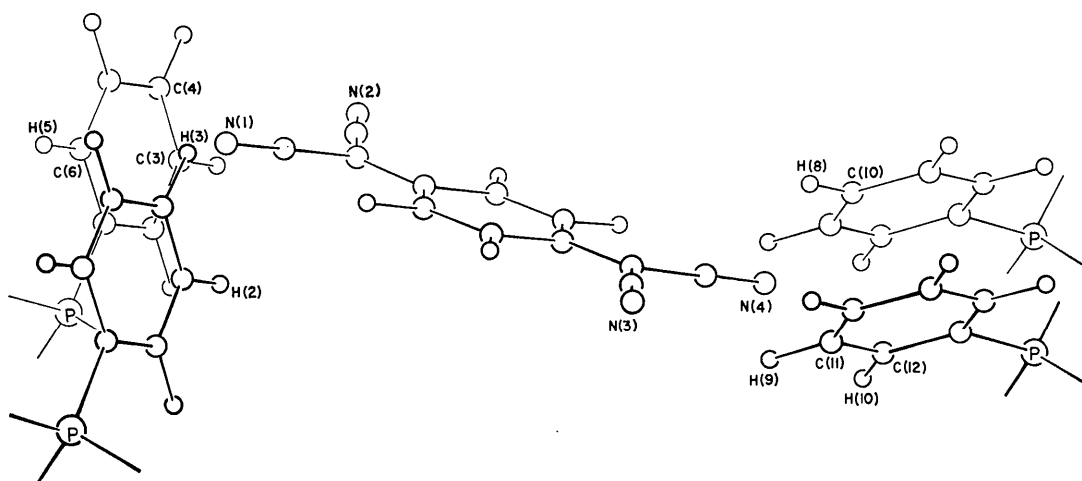


Fig. 4. Part of the TPP<sup>+</sup> environment of a TCNQ molecule. Labeled atoms (except P) participate in close interionic approaches

phenylarsonium ion. This value is significantly greater than the standard deviation of an individual C-C bond, as estimated from the inverse of the matrix of the normal equations, about 0.004 Å, which appears to be generously large when the agreement of chemically equivalent TCNQ bond lengths is considered. The small distortions of the phenyl ring therefore seem significant. Each ring shows approximately the same pattern of distortion (Fig. 2); the average difference between bonds related by the 4 molecular symmetry operation is 0.006 Å, with the ring bonds furthest from the phosphorus atom shorter than those nearest by an average of 0.019 Å. This discrepancy is greater than the 0.008 Å that might be ascribed to positional errors arising from the net shift of bonding electrons to re-

gions between carbon atoms (O'Connell, Rae & Maslen, 1966). It is possible that the effect of non-rigid thermal motion, which would be greatest for the peripheral atoms, may be responsible for this discrepancy; it is present in the tetraphenylarsonium ion (Palenik, 1966), although only to about half as great an extent, the difference between the C-C bonds nearest and furthest from the arsenic atom averaging 0.009 Å.

The P-C bond length of 1.796 Å agrees well with 1.799 Å (uncorrected for libration) found by Fritchie (1966*a*) in the triphenylmethylphosphonium ion and with 1.791 Å (uncorrected) reported by Mani, Ahmed & Barnes (1965, 1966) in two *P,P*-diphenylcyclotriposphazatriene structures. The TPP<sup>+</sup> ion nearly has the 4 axis reported by Khotsyanova & Struckhov

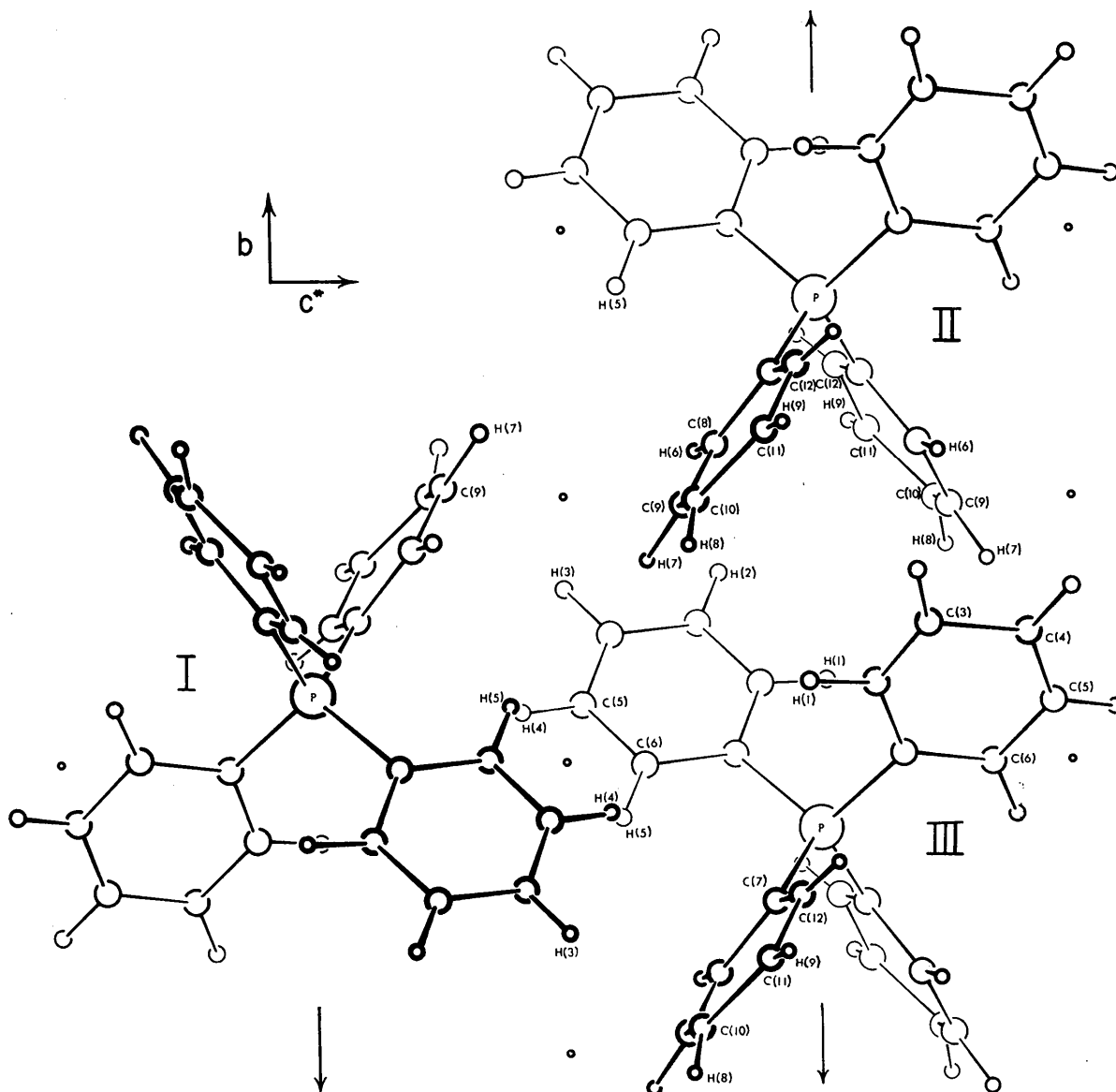


Fig. 5. Arrangement of TPP<sup>+</sup> ions within a layer of these ions. Labeled atoms participate in close interionic approaches.

(1956) in tetraphenylphosphonium iodide. Examination of the tetrahedron formed by the four *para* carbon atoms in TPP<sup>+</sup> shows that the ion (Fig. 2) is somewhat elongated along the twofold axis; these C...C distances nearly normal to **b** are 6.97 and 7.08 Å whereas the other four sides have unique distances of 7.65 and 7.67 Å.

Some of the close interactions between TPP<sup>+</sup> and (TCNQ)<sub>2</sub><sup>-</sup> are shown in Fig. 4, and some interionic distances are given in Table 10. It is not clear that any of these approach distances are related to the variations noted in the phenyl C-C distances. The shortest

N...H contact (2.6 Å) involves the nitrogen atom whose cyano group participates in conduction.

The packing of the TPP<sup>+</sup> cations is illustrated in Fig. 5, and the closest approach distances between atoms on neighboring cations are included in Table 10. These are all reasonable van der Waals contacts.

### Discussion

The structure within one unit cell is illustrated in Fig. 6 as viewed along **b**. The alternate rows of TPP<sup>+</sup> and (TCNQ)<sub>2</sub><sup>-</sup> ions extend in the **b** and **c** directions to form

Table 10. *Some non-bonded interatomic distances\**

(a) Nitrogen atoms of TCNQ to TPP <sup>+</sup>			
N(1) ... H(3)	3.1 Å	N(4) ... H(10)	3.0 Å
... H(8)	3.0	N(1) ... C(6)	3.42
N(2) ... H(2)	3.0	N(2) ... C(3)	3.23
N(3) ... H(9)	2.6	... C(4)	3.44
N(4) ... H(1)	2.9	N(3) ... C(11)	3.44
... H(8)	2.7	N(4) ... C(10)	3.44
(b) Between TCNQ molecules related by the symmetry center			
†C(13)...C(13)	3.30 Å	C(15)...C(20)	3.30 Å
...C(14)	3.36	C(16)...C(19)	3.27
C(14)...C(18)	3.32	...C(21)	3.29
C(15)...C(19)	3.34	C(17)...C(21)	3.27
(c) Between TCNQ molecules related by the screw axis			
C(14)...C(22)	3.56 Å	C(16)...N(3)	3.59 Å
...C(23)	3.48	C(21)...N(4)	3.57
C(15)...C(23)	3.52	N(2) ... N(4)	3.61
...N(3)	3.63		
(d) Between coplanar TCNQ's related by the <b>b</b> translation			
N(2) ... H(13)	2.7 Å	N(3) ... H(11)	2.7 Å
... H(14)	2.6	... H(12)	2.6
(e) Between equivalent phenyl groups within TPP <sup>+</sup>			
C(1)...C(1)	2.85 Å	C(7)...C(7)	2.84 Å
...C(2)	3.21	...C(8)	3.19
...C(6)	3.44	C(8)...C(8)	3.46
C(2)...C(2)	3.46	C(7)...H(6)	2.9
C(1)...H(1)	2.9		
(f) Between non-equivalent phenyl groups within TPP <sup>+</sup>			
C(1) ... C(7)	2.97 Å	C(1) ... C(7)‡	2.96 Å
... C(12)	3.24	C(6) ... C(7)‡	3.22
C(2) ... C(12)	3.50	... C(8)‡	3.46
C(1) ... H(10)	2.8	C(7)‡...H(5)	2.8
C(2) ... H(10)	2.9	C(8)‡...H(5)	2.8
H(1) ... H(10)	2.8	H(5) ... H(6)‡	2.7
(g) Between different TPP <sup>+</sup> ions			
I-II§		II-III	
C(9)...H(7)	3.3	C(3)...H(6)	3.2
H(5) ... H(7)	3.1	C(5)...H(7)	3.3
H(7) ... H(7)	3.1	C(9)...H(1)	3.2
I-III		C(10)...H(2)	3.3
C(10)...H(3)	3.0	C(11)...H(2)	3.2
C(11)...H(3)	3.2	H(1) ... H(7)	3.0
...H(4)	3.2	H(2) ... H(6)	3.1
C(12)...H(4)	3.1		
H(3) ... H(8)	2.9		
H(4) ... H(5)	3.0		

\* The distances shown in each section are the shortest for that approach.

† This distance only occurs once per dimer; others occur twice.

‡ These atoms are in Ph' related by the 2-fold axis to those in Table 2.

§ See Fig. 5.

layers of like ions. These layers stack alternately normal to  $a^*$  to give the structure.

A view of a portion of the TCNQ layer seen normal to the TCNQ plane (Fig. 7) shows the overlap (characteristic of TCNQ in its complexes) of TCNQ ions within the dimer (ions III & V) as well as the secondary overlap of TCNQ ions (I & II) in adjacent dimers. The motif repeats parallel to  $b$ , the major axis of the conduction ellipsoid.

If some close contact among TCNQ ions is necessary for conduction, presumably by the transfer of an electron from one molecule to another, then one or both of the two kinds of contact must be involved. The close approach (3.45 Å) of the cyano group [C(23)-N(3)] of one TCNQ to the ring of another TCNQ in another dimer appears to be involved because only this contact, together with the body of the TCNQ ions themselves, provides a path (I to II to III to IV) parallel to the principal axis of conduction and extending throughout the crystal.

The intimate characteristic overlap does not participate in conduction even though paths which involve both kinds of TCNQ contacts can be traced from V to III to II or IV. Our measurements show that the conductivity is much lower in directions perpendicular to  $b$  than along  $b$ ; if these second paths were operative, one of the two remaining axes would exhibit a higher conductance than it does.

Presumably, since conduction takes place along the polar  $2_1$  axis, the opposite charges of the cyano group of one molecule and the quinonoid ring of another lower the barrier for electron migration and thus facilitate the conduction. Table 9 shows the shift of  $\pi$ -electron density from the central ring in both TCNQ and TCNQ<sup>-</sup>. Perhaps, if TCNQ and TCNQ<sup>-</sup> coexist in the structure, the similarity of their geometries may allow this electron transfer to occur easily and rapidly as in the CrO<sub>4</sub><sup>2-</sup>, CrO<sub>4</sub><sup>-</sup> system, by electron tunnelling or resonance. Furthermore an examination of the path I

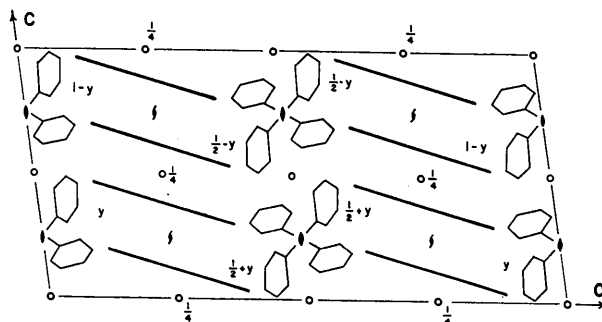


Fig. 6. The structure of one unit cell viewed along  $b$ . TCNQ molecules, seen edgewise, are represented by straight lines. The heights along the  $b$  axis are shown in terms of the  $y$  positions given in Table 2; each position shown applies to the TCNQ and to the two phenyl groups nearest it.

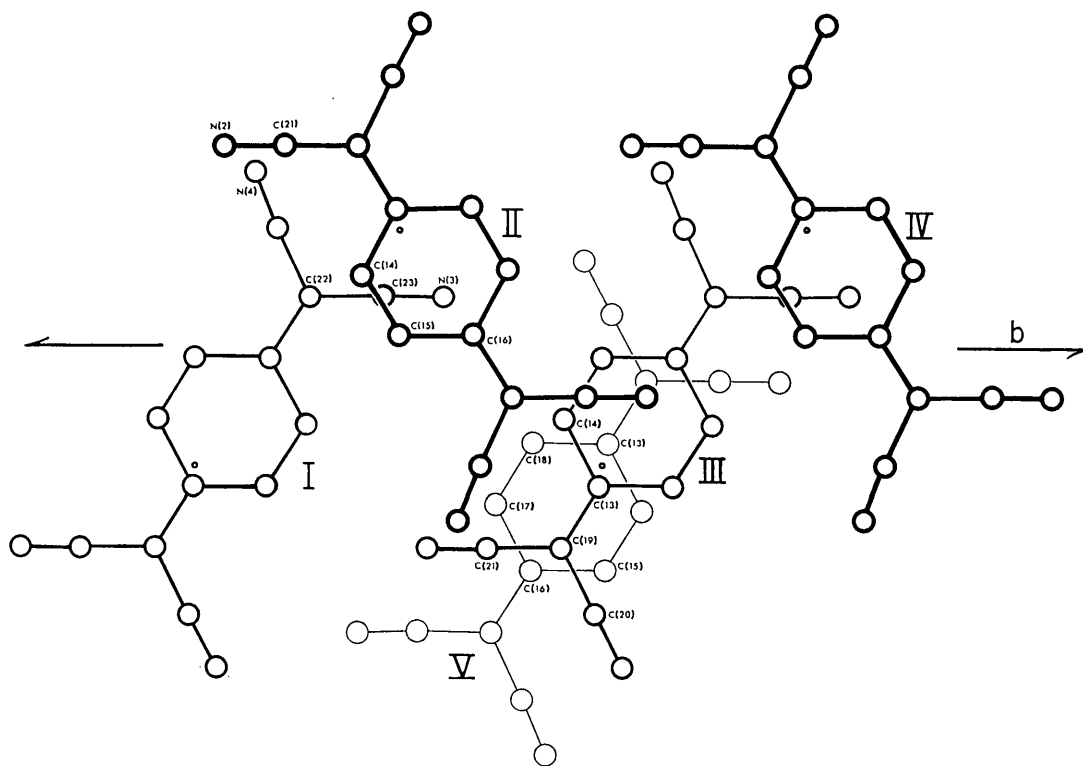


Fig. 7. The TCNQ arrangement viewed along a direction which is normal to the TCNQ molecular plane and parallel to the layer of TCNQ molecules.

to II to III in Fig. 7 shows that the polarity effect aids conduction only from left to right; in the opposite direction the resistance should be greater, perhaps so much so that each junction, and the whole path, would be a diode. In this structure the center of symmetry insures that for each path conductive in one direction, another conducts in the opposite direction, so that no rectification is observed.

Repulsive interactions due to close contacts between members of adjacent dimer pairs along the normal to the planes of the TCNQ ions explain the deviations from the TCNQ plane shown by three of the four cyano groups. The C(23)–N(3) group lies over and bends away from the ring of a TCNQ ion in another dimer pair, approaching the plane with distances of 3.44 and 3.46 Å respectively. The C(21)–N(2) group approaches the N(4) atom of a TCNQ ion in another dimer pair with distances of 3.57 and 3.61 Å respectively, such that both members of the interaction bend away from their planes. The observation that a cyano group approaches a quinonoid ring about 0.15 Å more closely than two cyano groups approach each other is consistent with the proposed polar attraction of a cyano group to the ring and with the proposed conductivity model.

This investigation was supported in part by the National Science Foundation, Grant GB2029; the diffractometer used was purchased with the help of another National Science Foundation grant, G20207. We are grateful to Dr L. R. Melby of the Central Research Department, E. I. du Pont de Nemours, Inc., for the sample used in this work. We are indebted to Dr C. A. Fritchie of Tulane University in New Orleans and to Dr A. W. Hanson of the National Research Council in Ottawa, Canada for preprints and valuable discussions, and to the UCLA Computing Facility for their cooperation.

*Note added in proof:* – It is noteworthy that within any overlapping dimer pair (such as III and V in Fig. 7), the relative displacement of the molecules is such as, for a given repulsive energy, to maximize the overlap of the orbitals for the extra electron (depicted in Fig. 3). Although a slightly greater orbital overlap at the same interplanar distance would result if the molecules were exactly superimposed, this eclipsed arrangement presumably does not occur because the increase in the repulsive energy arising from the closer van der Waals approach of each atom of one molecule to the corresponding atom of the other molecule more than offsets the increase in overlap energy. The staggered arrange-

ment may thus be rationalized without considering competition with charge-transfer interactions (Prout & Wallwork, 1966).

#### References

- ANDERSON, G. R. & FRITCHIE, C. J., JR (1963). Society for Applied Spectroscopy, San Diego, California.
- BEKOE, D. A. & TRUEBLOOD, K. N. (1960). *Z. Kristallogr.* **113**, 1.
- BUSING, W. R. & LEVY, H. A. (1964). *Acta Cryst.* **17**, 142.
- COX, E. G., CRUICKSHANK, D. W. J. & SMITH, J. A. S. (1958). *Proc. Roy. Soc. A* **247**, 1.
- CRUICKSHANK, D. W. J. (1956). *Acta Cryst.* **9**, 747, 754.
- CRUICKSHANK, D. W. J. (1961). *Acta Cryst.* **14**, 896.
- CRUICKSHANK, D. W. J. & SPARKS, R. A. (1960). *Proc. Roy. Soc. A* **258**, 270.
- FREEMAN, A. J. & WATSON, R. E. (1962). In *International Tables for X-ray Crystallography*, Vol. III. Birmingham: Kynoch Press.
- FRITCHIE, C. J., JR (1966a). *Acta Cryst.* **20**, 107.
- FRITCHIE, C. J., JR (1966b). *Acta Cryst.* **20**, 892.
- FRITCHIE, C. J., JR & ARTHUR, P., JR (1966). *Acta Cryst.* **21**, 139.
- FURNAS, T. C. & HARKER, D. (1955). *Rev. Sci. Instrum.* **26**, 449.
- GANTZEL, P. K. & TRUEBLOOD, K. N. (1965). *Acta Cryst.* **18**, 958.
- HANSON, A. W. (1965). *Acta Cryst.* **19**, 610.
- HANSON, A. W. (1968). *Acta Cryst.* **B24**, 768.
- HOERNI, J. A. & IBERS, J. A. (1954). *Acta Cryst.* **7**, 744.
- HOWELLS, E. R., PHILLIPS, D. C. & ROGERS, D. (1950). *Acta Cryst.* **3**, 210.
- KHOTSYANOVA, T. L. & STRUCHKOV, JU. T. (1956). *Kristallografiya*, **1**, 669.
- LONG, R. E., SPARKS, R. A. & TRUEBLOOD, K. N. (1965). *Acta Cryst.* **18**, 932.
- LOWITZ, D. A. (1967). *J. Chem. Phys.* **46**, 4698.
- MANI, N. V., AHMED, F. R. & BARNES, W. H. (1965). *Acta Cryst.* **19**, 693.
- MANI, N. V., AHMED, F. R. & BARNES, W. H. (1966). *Acta Cryst.* **21**, 375.
- MELBY, L. R., HARDER, R. J., HERTLER, W. R., MAHLER, W., BENSON, R. E. & MOCHEL, W. E. (1962). *J. Amer. Chem. Soc.* **84**, 3374.
- MENEFFEE, E. & PAO, Y. H. (1962). *Organic Semiconductors*, p. 49. J. J. Brophy & J. W. Buttrey, Eds. New York: Macmillan.
- O'CONNELL, A. M., RAE, A. I. M. & MASLEN, E. N. (1966). *Acta Cryst.* **21**, 208.
- PALENIK, G. J. (1966). *Acta Cryst.* **20**, 471.
- PROUT, C. K. & WALLWORK, S. C. (1966). *Acta Cryst.* **21**, 449.
- SCHOMAKER, V. & TRUEBLOOD, K. N. (1968). *Acta Cryst.* **B24**, 63.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3178.
- ZACHARIASEN, W. H. (1965). *Acta Cryst.* **18**, 705.