SHIEH, H. -S. & VOET, D. (1975). *Acta Cryst.* B31, 2192–2201.

SMIT, P. H. & KANTERS, J. A. (1974). *Acta Cryst.* B30, 784–790.

SOBELL, H. M. (1971). *The Purines, Theory and Experiment (The Jerusalem Symposia on Quantum Chemistry and Biochemistry* IV), edited by E. D. BERGMAN & B. PULLMAN, pp. 124–148. New York: Academic Press.

STOUT, G. H. & JENSEN, L. H. (1968). *X-ray Structure Determination,* pp. 456–458. New York: Macmillan.

VOET, D. (1972). *J. Amer. Chem. Soc.* 94, 8213–8222.

VOET, D. (1975). *Quantum and Molecular Pharmacology (The Jerusalem Symposia on Quantum Chemistry and Biochemistry* VII), edited by E. D. BERGMAN & B. PULLMAN, pp. 429–439. Dordrecht, Holland: Reidel Publishing Co.

VOET, D. & RICH, A. (1970). *Progr. Nucl. Acid. Res. Mol. Biol.* 10, 183–265.

VOET, D. & RICH, A. (1972). *J. Amer. Chem. Soc.* 94, 5888–5891.

WOOLFSON, M. M. (1956). *Acta Cryst.* 9, 804–810.

A Neutron-Diffraction Study of the 1:1 Molecular Complex of 7,7,8,8-Tetracyanoquinodimethane with p-Terphenyl*

By G. C. LISENSKY,† C. K. JOHNSON AND H. A. LEVY‡

Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830, U.S.A.

The 1:1 complex between 7,7,8,8-tetracyanoquinodimethane (TCNQ) and deuterated p-terphenyl forms dark red crystals, space group $P\bar{1}$, with one molecule of each component in the unit cell of dimensions $a = 8\cdot0189$ (5), $b = 8\cdot8927$ (5), $c = 8\cdot0264$ (5) Å, and $\alpha = 96\cdot413$ (3), $\beta = 95\cdot861$ (9), $\gamma = 102\cdot800$ (7)°. The structure was solved by fitting the transform of terphenyl-d to neutron-diffraction intensity data and was refined by least-squares methods, using 2614 unique reflections, to a final discrepancy index $R(F^2)$ of $0\cdot042$. All bond distances were determined to a precision of $\leq 0\cdot002$ Å. The structure consists of stacks in which TCNQ and terphenyl molecules alternate on centers of symmetry along the a axis. p-Terphenyl is an overcrowded molecule showing in-plane and out-of-plane deviations from the idealized planar conformation, the largest of which is a 12° torsion between the center and each end ring. The resultant distances between overcrowded deuterium atoms, 1·972 (2) and 1·985 (2) Å, are still less than the sum of van der Waals radii. An unusual pattern of incomplete deuteration was noted.

Introduction

Two main structure types of molecular complexes with TCNQ have been observed. In 'segregated stack' structures, approximately parallel molecules of the same kind occur in infinite stacks, while in 'mixed-stack' structures, molecules of two kinds alternate. Some charge-transfer complexes with TCNQ are good organic electrical conductors; although the segregated-stack arrangement seems to characterize the best conductors, mixed-stack structure determinations help to provide further understanding of TCNQ behavior.§ The structures of a number of mixed-stack charge-transfer complexes of TCNQ and planar aromatic compounds have been determined and are listed in Table 5.

The p-terphenyl complex with TCNQ has two features which are different from those with other planar aromatic compounds whose structures have been determined. The p-terphenyl molecule is longer than the TCNQ, so that there are several ways the two could overlap. The present structure determination shows that viewed perpendicular to the TCNQ plane the quinonoid *exo* double bonds center over the middle ring of terphenyl (see Fig. 1). Secondly, p-terphenyl in a planar conformation is an overcrowded molecule because the distance between the *ortho* bay§ hydrogen atoms is less than the sum of van der Waals radii. Rietveld, Maslen & Clews (1970) found that in crystals of p-terphenyl the molecule departs only slightly from planarity and the overcrowding is relieved by in-plane deformations. Baudour (1972) concluded that the planarity, however, did not necessarily correspond to the equilibrium configura-

† Oak Ridge Associated Universities research participant from Earlham College, Richmond, Indiana 47374.

‡ Author to whom correspondence should be addressed.

§ The present compound is an insulator: the conductivity at room temperature is less than 4×10^{-11} ohm^{-1} cm^{-1}.

§ We suggest the descriptive term '*ortho* bay' to designate a pair of positions on separate rings each *ortho* to and lying on the same side of the bond between the rings. Jones & Sowden (1975) have employed the term 'bay' in a similar connection.

tion. Biphenyl, also found to be planar in crystal-structure studies by Robertson (1961), Trotter (1961), and Hargreaves & Rizvi (1962), has been shown by several investigators, most recently by Almenningen & Bastiansen (1958), to have a 42° dihedral angle between rings in the vapor phase. The present study found that when complexed with TCNQ terphenyl has both in- and out-of-plane deformations as well as a 12° twist between rings (see Fig. 2). Most studies of overcrowding have been limited by the accuracy of the
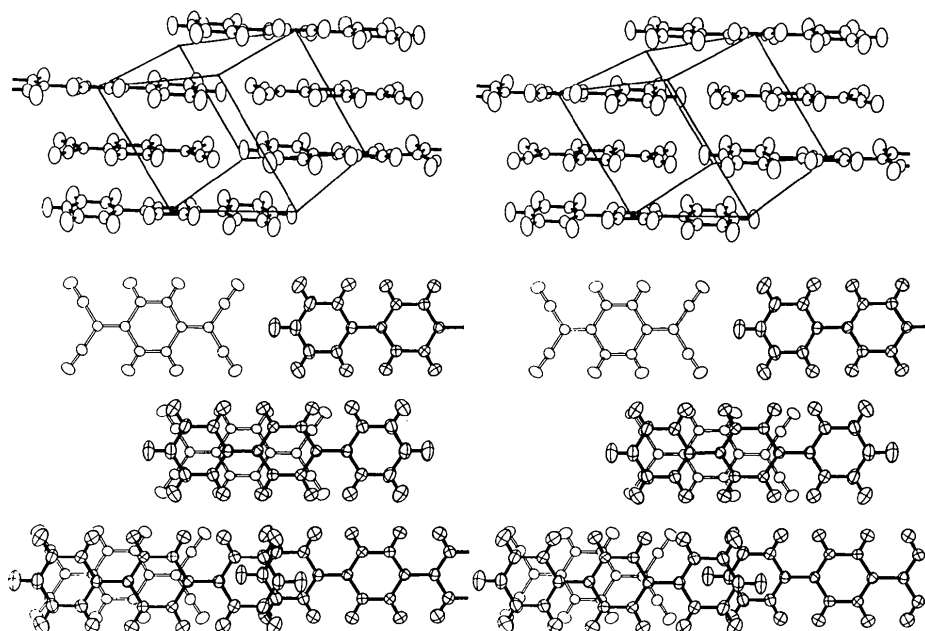

Fig. 1. Stereo drawings of the terphenyl-TCNQ structure. The top view shows the molecular packing between planes and the bottom view shows molecular overlap and in-plane packing. The bottom left drawing is a view perpendicular to the plane of the center TCNQ molecule.

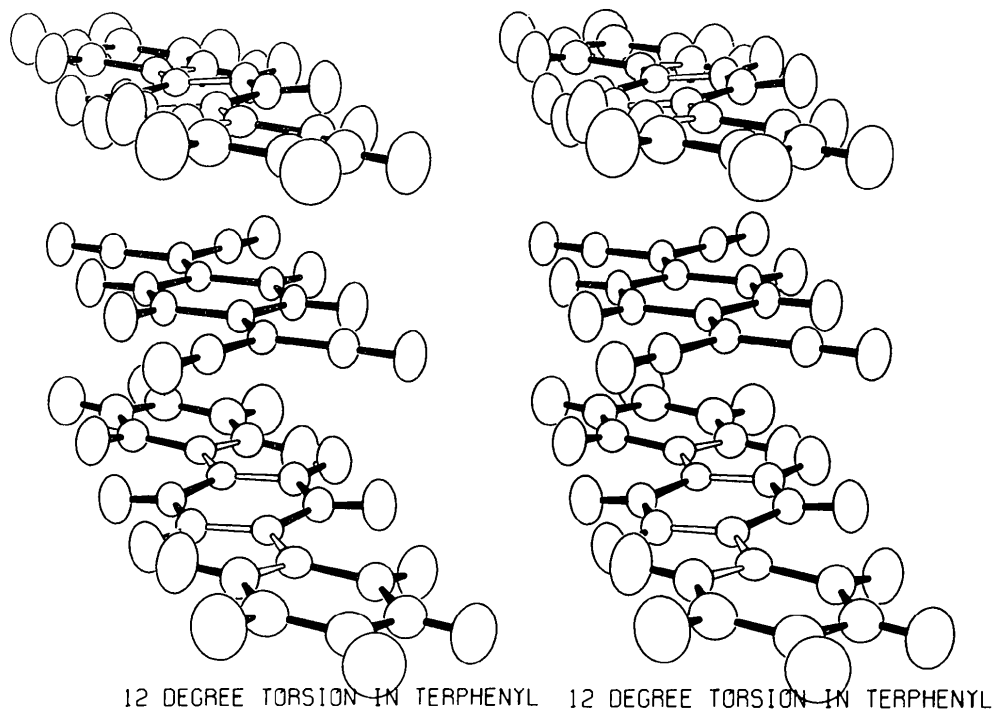12 DEGREE TORSION IN TERPHENYL   12 DEGREE TORSION IN TERPHENYL

Fig. 2. Stereo view showing the terphenyl ring twist.

hydrogen positions. Consequently, the present study was carried out using full three-dimensional neutron-diffraction data and supposedly fully deuterated ter-phenyl. The neutron-diffraction study also provides a comparison with X-ray determinations of TCNQ molecular dimensions.

Experimental

Crystals of the complex were prepared by C. R. Watson by slow cooling from the boiling point of a solution of 1 milliequivalent each of TCNQ and deuterated *p*-terphenyl in 400 ml dry acetonitrile and 40 ml of dry benzene. Crystallization in the absence of benzene yielded a large proportion of fine needle-shaped crystals unsuitable for neutron-diffraction study. Symmetry information and cell constants were initially determined from precession photographs and later refined from neutron-diffraction diffractometer data.

Crystal data

Space group $P\bar{1}$ or $P1$ (the former proved to be correct), $a = 8\cdot0189$ (5), $b = 8\cdot8927$ (5), $c = 8\cdot0264$ (5) Å, $\alpha = 96\cdot413$ (3), $\beta = 95\cdot861$ (9), $\gamma = 102\cdot800$ (7)°, at 20 ± 2°C with $\lambda = 1\cdot24592$ (5) Å based on a_0 (NaCl) = $5\cdot64085$ Å at 25°C. $D_c = 1\cdot26$ g cm^{-3} for $Z = 1$ formula unit of $(C_{18}D_{14})(C_{12}H_4N_4)$, M.W. 448·6.

Three-dimensional neutron-diffraction intensity data were collected from a dark-red 11·7 mg crystal using a computer-controlled four-circle Picker diffractom-

eter situated at the Oak Ridge 100 MW High Flux Isotope Reactor. The neutrons, obtained by reflection from a beryllium monochromator crystal, have wavelength 1·2459 Å. 2614 unique reflections were collected out to sin $\theta/\lambda = 0\cdot66$ using θ–2θ step scanning. Measurements of 12 reflections at intermediate angles were inadvertently omitted. Electronic and crystal stability were monitored by the periodic measurement of a reference reflection and no significant changes were noted. The weights used for the least-squares refinement were based on counting statistics with an added 3% variance correction: $\sigma = [\sigma_{stat} + (0\cdot03F^2)^2]^{1/2}$.

Structure determination and refinement*

The data were corrected for absorption using a polyhedral description of the crystal and a linear absorption coefficient $\mu = 0\cdot59$ cm^{-1} and were put on an approximate absolute scale by the use of a standard NaCl crystal Statistical evaluation of the derived

---

* Computer programs used in this study were: *DATALIB*, for data reduction, by H. A. Levy and R. D. Ellison; *ORESTES*, for *E*-value calculation and structure factor statistics, by W. E. Thiessen and H. A. Levy; *ORTRAN*, *ORPREP* and *ORPHEX*, for direct-methods phasing, by W. E. Thiessen and W. R. Busing; *ORFFP*, for Fourier calculations, by H. A. Levy; *ORXFLS*, for least-squares refinement, by W. R. Busing *et al.*; *ORFFE*, for function and error calculations, W. R. Busing and H. A. Levy; *ORSBA*, for segmented-body analysis, by C. K. Johnson; and *ORTEP*, for stero drawings, by C. K. Johnson.

Table 1. *Atomic crystal coordinates and thermal parameters*

The thermal parameters are the coefficients $b_{ij} \times 10^4$ in the expression $\exp[-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + 2b_{12}hk + 2b_{13}hl + 2b_{23}kl)]$. Standard errors in parentheses are given in units of the last decimal place.

	x	y	z	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Terphenyl									
C(1)	0·0502 (1)	0·0367 (1)	−0·1530 (1)	144 (2)	101 (2)	113 (2)	42 (1)	41 (1)	25 (1)
C(2)	0·0544 (1)	−0·1115 (1)	−0·1113 (1)	100 (2)	91 (2)	106 (2)	25 (1)	21 (1)	13 (1)
C(3)	0·0029 (1)	−0·1446 (1)	0·0451 (1)	143 (2)	94 (1)	121 (2)	39 (1)	40 (1)	26 (1)
C(4)	0·1123 (1)	−0·2267 (1)	−0·2257 (1)	104 (2)	94 (1)	113 (2)	22 (1)	18 (1)	6 (1)
C(5)	0·1354 (2)	−0·2037 (1)	−0·3923 (1)	175 (2)	119 (2)	114 (2)	45 (2)	34 (2)	11 (1)
C(6)	0·1945 (2)	−0·3093 (2)	−0·4980 (2)	205 (3)	143 (2)	128 (2)	43 (2)	50 (2)	−9 (2)
C(7)	0·2308 (2)	−0·4418 (2)	−0·4403 (2)	192 (3)	122 (2)	166 (2)	42 (2)	47 (2)	−24 (2)
C(8)	0·2072 (2)	−0·4672 (1)	−0·2765 (2)	183 (3)	102 (2)	185 (2)	47 (2)	45 (2)	4 (2)
C(9)	0·1489 (2)	−0·3612 (1)	−0·1700 (2)	153 (2)	101 (2)	146 (2)	43 (1)	35 (2)	16 (1)
D(1)	0·0931 (2)	0·0705 (2)	−0·2700 (2)	298 (4)	145 (2)	152 (3)	79 (2)	104 (2)	52 (2)
D(3)	0·0002 (2)	−0·2583 (2)	0·0824 (2)	307 (4)	127 (2)	195 (3)	91 (2)	102 (3)	61 (2)
D(5)	0·1067 (3)	−0·1025 (2)	0·4405 (2)	381 (6)	189 (3)	157 (3)	131 (3)	82 (3)	52 (2)
D(6)	0·2110 (3)	−0·2900 (2)	−0·6265 (2)	403 (5)	230 (3)	155 (3)	109 (4)	105 (3)	15 (2)
D(7)	0·2760 (3)	−0·5236 (2)	−0·5227 (2)	367 (6)	185 (3)	242 (4)	111 (3)	108 (4)	−40 (3)
D(8)	0·2370 (3)	−0·5690 (2)	−0·2296 (2)	360 (5)	146 (3)	287 (4)	125 (3)	99 (4)	44 (3)
D(9)	0·1376 (3)	−0·3825 (2)	−0·0414 (2)	323 (5)	164 (3)	180 (4)	118 (3)	85 (3)	57 (2)
TCNQ									
C(1′)	0·5336 (1)	0·0365 (1)	−0·1615 (1)	140 (2)	81 (1)	97 (2)	38 (1)	34 (1)	28 (1)
C(2′)	0·5557 (1)	−0·1089 (1)	−0·1104 (1)	117 (2)	73 (1)	95 (2)	31 (1)	23 (1)	17 (1)
C(3′)	0·5194 (1)	−0·1409 (1)	0·0563 (1)	147 (2)	76 (1)	102 (2)	43 (1)	33 (1)	27 (1)
C(4′)	0·6114 (1)	−0·2144 (1)	−0·2174 (1)	126 (2)	82 (1)	100 (2)	36 (1)	28 (1)	20 (1)
C(5′)	0·6493 (2)	−0·1860 (1)	−0·3825 (1)	163 (2)	104 (1)	108 (2)	48 (1)	44 (2)	27 (1)
C(6′)	0·6349 (2)	−0·3592 (1)	−0·1719 (1)	163 (2)	84 (1)	121 (2)	48 (1)	41 (2)	23 (1)
N(1)	0·6810 (1)	−0·1675 (1)	−0·5162 (1)	266 (2)	168 (2)	130 (1)	80 (2)	80 (1)	52 (1)
N(2)	0·6560 (1)	−0·4771 (1)	−0·1405 (1)	267 (2)	104 (1)	190 (2)	86 (1)	60 (2)	50 (1)
H(1)	0·5592 (4)	0·0611 (3)	−0·2869 (3)	279 (6)	145 (4)	129 (4)	77 (4)	75 (4)	52 (3)
H(3)	0·5341 (4)	−0·2502 (3)	0·0968 (3)	290 (6)	117 (3)	180 (4)	99 (4)	78 (4)	50 (3)

structure factors showed a centric distribution indicating the space group to be $P\bar{1}$. There was also found to be a systematic alternation in average intensities for even and odd index h: the average E^2 for odd h is 0·484, while that for even h is 1·535.

A brief attempt to solve the structure using direct methods was unsuccessful. On the suspicion that the problem was caused by an unusually large number of aberrant relationships due to the alignment of benzene-shaped rings, the program *ORTRAN* of Thiessen & Busing (1974) was used to fit to the experimental data the transform calculated from an assumed planar terphenyl molecule with 120° angles, single C–C bond lengths of 1·5 Å, aromatic bond lengths of 1·4 Å, and

C–D bond lengths of 1·1 Å. The terphenyl molecule in the orientation so derived was located on the crystallographic center of symmetry at the cell origin. The TCNQ molecule was assumed to be parallel and was translated to the center of symmetry half a unit cell away along x. The fractional coordinates of the atoms derived in this manner were then refined by the method of least squares. The discrepancy index $R(F^2) = \sum(F_o^2 - F_c^2)/\sum F_o^2$ refined to 0·376 after several cycles. Isotropic temperature factors for each atom brought the R value down to 0·192. Since the strong reflections seemed to suffer from extinction, an isotropic extinction coefficient (Zachariasen, 1968) was added and refined by least squares [final value of $r^* = 0·0330$ (9)

Table 2. *Results of the segmented-body thermal-motion analysis*

The axial systems are described in the text.

	R.m.s. Amplitude	Principal axis direction cosines		
C(1′), C(2′), C(3′), C(4′) of TCNQ				
T	0·1929 Å	0·1430	−0·1101	0·9836
	0·1683	0·9197	−0·3523	−0·1732
	0·1569	0·3655	0·9294	0·0509
L	4·336°	0·9985	−0·0479	−0·0251
	1·090	−0·0116	0·2637	−0·9646
	0·823	0·0528	0·9634	0·2627
Center ring of terphenyl				
T	0·1847 Å	0·6830	0·0528	0·7285
	0·1797	−0·2884	−0·8968	0·3354
	0·1708	0·6711	−0·4392	−0·5973
L	5·938°	0·9990	−0·0244	−0·0384
	1·654	−0·0426	−0·2075	−0·9773
	0·288	0·0159	0·9779	−0·2083
End ring of terphenyl				
T	0·1870 Å	0·7229	0·0	0·6909
	0·1870	−0·1021	−0·9890	0·1068
L	0·1694	0·6833	−0·1478	−0·7150
	5·086°	0·9980	−0·0209	−0·0603
	2·666	0·0635	0·4112	0·9093
	2·073	0·0058	−0·9113	0·4117

Table 3. *Bond distances* (Å), *as observed and as corrected according to segmented-body thermal-motion analysis*

Standard errors are given in parentheses in units of the last decimal place for the uncorrected bond lengths.

Terphenyl	Uncorrected	Corrected	TCNQ	Uncorrected	Corrected
C(1)–C(3*)	1·387 (1)	1·388	C(1′)–C(3′*)	1·352 (1)	1·353
C(1)–C(2)	1·402 (1)	1·408	C(1′)–C(2′)	1·442 (1)	1·446
C(2)–C(3)	1·403 (1)	1·409	C(2′)–C(3′)	1·443 (1)	1·446
C(2)–C(4)	1·482 (1)	1·483	C(2′)–C(4′)	1·379 (1)	1·379
C(4)–C(5)	1·400 (1)	1·406	C(4′)–C(5′)	1·427 (1)	1·435
C(4)–C(9)	1·401 (1)	1·407	C(4′)–C(6′)	1·423 (1)	1·430
C(5)–C(6)	1·388 (2)	1·390	C(5′)–N(1)	1·149 (1)	1·155
C(8)–C(9)	1·391 (2)	1·394	C(6′)–N(1)	1·149 (1)	1·155
C(6)–C(7)	1·391 (2)	1·397	C(1′)–H(1)	1·083 (2)	1·107
C(7)–C(8)	1·383 (2)	1·388	C(3′)–H(3)	1·086 (2)	1·110
C(1)–D(1)	1·084 (2)	1·102			
C(3)–D(3)	1·083 (2)	1·103			
C(5)–D(5)	1·079 (2)	1·108			
C(9)–D(9)	1·079 (2)	1·106			
C(6)–D(6)	1·082 (2)	1·105			
C(8)–D(8)	1·082 (2)	1·106			
C(7)–D(7)	1·075 (2)	1·104			

* The designated atom inverted through the center of symmetry.

mm]. The coherent scattering amplitudes used were from the February 1972 MIT (Shull, 1972) compilation: carbon 0·6648 (3) $\times 10^{-12}$ cm, protium $-0·3740$ (3) $\times 10^{-12}$ cm, deuterium 0·6672 (7) $\times 10^{-12}$ cm, and nitrogen 0·940 $\times 10^{-12}$ cm. The coherent scattering amplitude for each deuterium atom was also allowed to vary in the refinement. These coefficients refined to significantly smaller values, showing that the terphenyl molecule was neither fully nor uniformly deuterated. This is discussed in a later section. The final value of $R(F^2)$ was 0·042 and the standard error of fit σ_1 was 1·089. The largest parameter shift in the last refinement cycle was less than 1% of its standard error.*

At a point near the end of the refinement the coherent scattering amplitude for each protium and nitrogen atom was also released for refinement. The values for the two nitrogen atoms changed less than 1%, and of those for the protium, one became more negative and the other less negative. Consequently, they were fixed at their accepted values.

A difference synthesis using all data had no peaks of magnitude greater than 0·065 $\times 10^{-12}$ cm Å^{-3}, the highest at atom locations being 0·046 at D(7), 0·045 at N(1), and $-0·061$ at H(3) (see Fig. 3 for atom numbering). An examination was made for evidence of curvilinear thermal motion by evaluating the contracted third cumulants using the method of Johnson (1970*a,b*) with a modified least-squares refinement program *JFLS*. Although the agreement index improved, $R(F^2)$ =0·0408 and $\sigma_1 = 1·016$, no structurally significant conclusions were evident, even involving the overcrowded deuterium atoms.

The final atomic positional and thermal parameters, together with their standard errors estimated from the inverse matrix, are given in Table 1.

Comparison of the final atomic positions of terphenyl with those located using the terphenyl transform shows that the carbon positions were located within an average of 0·09 Å along the *a* axis and 0·05 Å along the *b* and *c* axes, and that the deuterium positions were located within an average of 0·2 Å along the three crystal axes. This is quite a good fit considering the simple model used and the distortions the terphenyl molecule was found to have. The program *ORTRAN* is designed to use the transform to aid in phase determination by direct methods. This was done retrospectively to see whether the same result could have been found. With the *p*-terphenyl transform, some 500 important Σ_2 relationships with Hauptman *D* (Fisher, Hancock & Hauptman, 1970) greater than 5 were predicted to have phase sums of π. Similarly, 6 of 10 Σ_1 phase sums were predicted as π. A phase refinement incorporating these new predictions correctly phased 139 out of the 150 strongest *E* values.

Crystal structure

p-Terphenyl-TCNQ is a mixed-stack charge-transfer complex. Both TCNQ and terphenyl are located on centers of symmetry, the centers being $\frac{1}{2}$ unit cell apart along the *a* axis (top view, Fig. 1). The molecules have their long axes nearly parallel along [011]; the major principal axes of inertia of the two molecules differ by only $\frac{1}{2}°$.

The center and end rings of the terphenyl molecule are not coplanar. In order to compare their orientations, orthonormal basis vectors u_1, v_1, and w_1 for the end ring and u_2, v_2, and w_2 for the center ring are defined, as illustrated in the following diagram, in terms of interatomic vectors q_1 and q_3 together with vectors q_2 and q_4 which link the indicated bond midpoints.

$$u_1\|q_1, \quad w_1\|u_1 \times q_2, \quad v_1\|w_1 \times u_1,$$
$$u_2\|q_3, \quad w_2\|u_2 \times q_4, \quad v_2\|w_2 \times u_2.$$

(I)
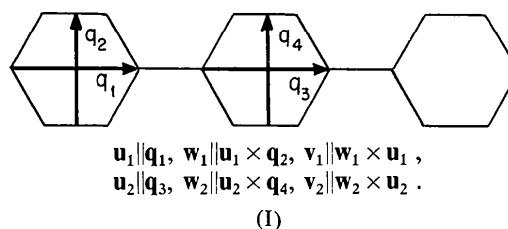
The angle between u_1 and u_2 is 1·88°, between v_1 and v_2 11·81°, and between w_1 and w_2 11·96°. This corresponds roughly to a slight bend of the long axis and a 12° dihedral angle between rings (see Fig. 2). Because of the center of symmetry, the end rings are parallel, twisted the same way with respect to the center ring.

Neither the center nor end ring planes of terphenyl are parallel to the plane of the TCNQ molecule. Comparing the above axial systems with a TCNQ coordinate system with basis vectors along the eigenvectors of the second moment matrix about the molecular center, the angles between the axes are 0·95, 6·38, and 6·40° for the center ring, and 1·18, 5·50, and 5·57° for the end rings. Both rings are inclined with respect to the TCNQ molecule, the center ring a little more so than the end rings, although in opposite sense.

In the usual complexing of TCNQ with the planar aromatic molecules listed in Table 5, one of the quinonoid *exo* double bonds of TCNQ is found to be approximately centered over an aromatic ring. (An exception is TCNQ with benzene, where the center of the benzene molecule is over a quinonoid *endo* double bond.) The dimensions of terphenyl and the packing of the terphenyl and TCNQ molecules are such that both quinonoid *exo* double bonds of TCNQ have an aromatic ring above and below. The sequence of stacking approximately perpendicluar to the molecular planes is: center ring, TCNQ *exo* double bond, end ring, end ring, TCNQ *exo* double bond, and center ring. These relationships can be found in Fig. 1. The

shortest intermolecular contact within a layer is 2·634 Å and that between layers is 3·156 Å.

Charge transfer complexes are considered by Mulliken (1952) to involve bonding between components by transfer of π electron density from the donor to the acceptor. This tendency for maximum π bond overlap should produce parallel molecules; consequently, deviations of a terphenyl ring from being parallel with TCNQ are not likely to be caused by bonding with TCNQ.

Thermal motion

A segmented-body thermal-motion analysis was performed using the program ORSBA by Johnson (1970a). Four segments were used to describe the TCNQ molecule. Segment one is comprised of C(1'), C(2'), C(3'), and C(4'); the hydrogen atoms make up segment two; and the two cyanide groups are segments three and four. Segments two, three, and four ride as rigid bodies on segment one. For segments one and two the origin is at the center of the molecule and a coordinate system u, v, w is defined in terms of interatomic vectors q_1 and q_2 as illustrated.

$$u \| q_1, \quad w \| u \times q_2, \quad v \| w \times u .$$

(II)
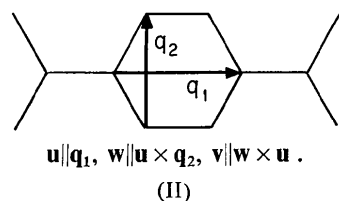
Segment one was given full translational and librational freedom, but no correlation between the two since this is forbidden by the center of symmetry. The principal r.m.s. amplitudes and directions are listed in Table 2. Note that translation and libration are essentially along and about the segment axes. The libration about u is greatest, with an r.m.s. amplitude of 4·3°. For segment two, in-plane C–H bond stretching is approximately by translations along u and v and these were fixed with r.m.s. amplitudes of 0·077 Å; this value is taken from spectroscopic normal coordinate analyses of benzene (Cyvin, 1968). The in-plane bending of the C–H bonds, approximated by libration about w, and out-of-plane bending, approximated by translation along w, were found to have r.m.s. amplitudes of 2·66° and 0·166 Å. Out-of-plane motion for the cyanide group –C(5')≡N(1) is approximated by libration about an axis through C(4') in-plane and perpendicular to the C(4')–C(5') bond. This r.m.s. amplitude of libration is 3·46°. The corresponding amplitude for –C(6')≡N(2) is 2·55°. In-plane motion was approximated by libration about an axis through C(4') and perpendicular to the plane of C(4'), C(5'), and C(6'). These r.m.s. amplitudes are 3·44° for –C(5')≡N(1) and 3·16° for –C(6')≡N(2). For the TCNQ moiety this segmented-body analysis gave an r.m.s. ΔU_{ij} residual of 0·0009 Å². Bond distances corrected for libration are given in Table 3.

The motions of the middle and end terphenyl rings were treated as independent. The axial systems for the center and end rings were set up in an analogous manner to the previously described coordinate system of TCNQ segment one. The origin of the middle ring was taken at its center of symmetry, while the origin of the end ring was taken at C(2), since a preliminary analysis showed the reaction center for the end ring to be close to C(2). The end rings were given full freedom for rigid-body motion, but the center ring may only have translational and librational motion because of the symmetry center. However, screw motion for the end rings is of small amplitude. The principal r.m.s. amplitudes of libration and translation are listed in Table 2. The translation is almost isotropic. Libration is greatest about u, having r.m.s. amplitudes of 5·9 and 5·1° respectively for the center and end rings, smaller about w, and only the end rings have appreciable libration about v. In a model similar to that for the TCNQ, the deuterium atoms ride as a rigid body about the center or end ring. Fixed translational amplitudes of 0·066 Å along u and v were assumed to represent the C–D bond stretch; this value is taken from spectroscopic normal coordinate analyses of C_6D_6 (Cyvin, 1968). The deuterium atoms have r.m.s. libration amplitudes of 2·12 and 2·03° about w (with the origin at the respective ring center), and r.m.s. translational amplitudes of 0·137 Å and 0·195 Å along w. The r.m.s. ΔU_{ij} residuals for the center and end ring calculations are 0·0005 and 0·0012 Å². Bond distances corrected for libration are listed in Table 3.

The internal motion of the hydrogen atoms calculated using our model of hydrogen atoms riding as a rigid body around the carbon ring is compared in Table 4 with that calculated for other compounds by

Table 4. *R.m.s. amplitude in Å of hydrogen-atom internal motion in various compounds*

Values from references a and b were refined as extra parameters during least squares, benzene values were determined spectroscopically, and the remainer were determined from segmented-body analyses.

	Bond stretch	In-plane bend	Out-of-plane bend
Protium atoms			
Pyrene[a]	0·07	0·13	0·17
Trichlorobenzene[b]	0·08	0·11	0·14
Benzene[c]	0·07	0·11	0·14
3-endo-Phenyl-2-endo-norbornol[c]	0·08	0·13	0·19
TCNQ[d]	0·08[e]	0·12	0·17
Deuterium atoms			
Naphthalene[a]	0·07	0·09	0·15
Anthracene[a]	0·05	0·10	0·13
End ring of terphenyl[d]	0·07[e]	0·09	0·20
Center ring of terphenyl[d]	0·07[e]	0·09	0·14

(a) Pawley (1971); (b) Hazell, Lehman & Pawley (1972); (c) Johnson (1970a); (d) present study; (e) not refined.

other methods. In the table the r.m.s. amplitude of the in-plane libration has been converted to ångströms by changing degrees to radians and multiplying by the distance from the libration origin. The internal motions of both protium and deuterium atoms in the present model agree well with those derived from the other methods.
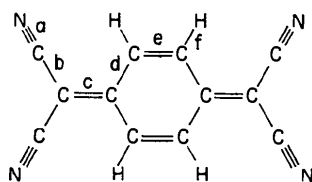
Molecular structure

The atoms of the TCNQ molecule have a maximum deviation of 0·015 Å from the least-squares best plane, and the ring carbon and hydrogen atoms are coplanar to within 0·006 Å. The intramolecular distances agree well with other TCNQ mixed-stack charge-transfer complexes (see Table 5). There seems to be no systematic difference between X-ray and neutron results. The present analysis does not yield the large libration correction of 0·03 Å given by some previous investigators (Goldberg & Shmueli, 1973*a,b,c*) for the length of the C–N bond. Note in Fig. 3 that the chemically equivalent molecular dimensions of TCNQ in the present study are in excellent agreement.

Although the center and end rings of terphenyl are

Table 5. *Average bond distances in Å of TCNQ with assumed mmm symmetry found in mixed-stack charge-transfer complexes with planar aromatic compounds*

Values in italics are corrected for libration.

a	b	c	d	e	f	
X-ray diffraction structures						
1·138	1·435	1·373	1·442	1·344	0·90	TCNQ
1·140	*1·440*	*1·374*	*1·448*	*1·346*		(Long, Sparks & Trueblood, 1965)
1·160	1·412	1·406	1·414	1·373		*N,N,N',N'*-Tetramethyl-*p*-phenylene-diamine (TMPD) (Hanson, 1965)
1·130	1·425	1·370	1·460	1·355		Anthracene
1·135	*1·430*	*1·370*	*1·465*	*1·355*		(Williams & Wallwork, 1968)
1·152	1·445	1·391	1·462	1·358		Hexamethylbenzene (Colton & Henn, 1970)
1·142	1·431	1·384	1·428	1·344	1·07	*N,N'*-Dimethyldihydrophenazine
1·175	*1·435*	*1·387*	*1·439*	*1·347*		(Goldberg & Schmueli, 1973*a*)
1·133	1·432	1·361	1·430	1·344	0·98	Dibenzo-*p*-dioxin (Goldberg &
1·164	*1·439*	*1·363*	*1·436*	*1·346*		Shmueli, 1973*b*)
1·145	1·436	1·364	1·436	1·340	0·96	Phenazine (Goldberg & Shmueli, 1973*c*)
1·173	*1·443*	*1·365*	*1·442*	*1·341*		
1·139	1·438	1·371	1·438	1·345		Benzidine (Yakushi, Ikemoto & Kuroda, 1974)
1·140	1·435	1·373	1·442	1·347		Average (excluding TMPD)
0·007	0·006	0·011	0·014	0·006		Standard deviation about mean
Neutron diffraction structures						
1·150	1·426	1·384	1·449	1·351	1·009	Benzene (Johnson, Reed, Hall &
1·156	*1·433*	*1·385*	*1·450*	*1·351*	*1·113*	Raaen, 1974)
1·150	1·428	1·383	1·446	1·356	1·088	Hexamethylbenzene (Johnson,
1·151	*1·435*	*1·383*	*1·449*	*1·356*	*1·113*	Reed, Hall & Raaen, 1974)
1·149	1·425	1·379	1·442	1·352	1·084	*p*-Terphenyl
1·155	*1·432*	*1·379*	*1·446*	*1·353*	*1·108*	(present study)
1·150	1·426	1·382	1·446	1·353	1·087	Average
1·154	*1·433*	*1·382*	*1·448*	*1·353*	*1·111*	

Table 6. *Distances between bay hydrogen atoms in Å for hypothetical conformations of p-terphenyl*

Conformation	D(1)–D(5)	Change	D(3)–D(9)	Change
Planar, all angles 120°	1·802 (2)		1·803 (2)	
		0·106 (3)		0·116 (3)
Planar, observed angles	1·908 (2)		1·919 (2)	
		0·049 (1)		0·052 (1)
Observed ring twist, but no deuterium bend	1·957 (2)		1·971 (2)	
		0·015 (1)		0·014 (1)
Observed conformation	1·972 (2)		1·985 (2)	

not coplanar, as discussed in a previous section, the carbon atoms of each ring are coplanar within the precision of the structure determination. The only deuterium atoms more than three standard errors out of the least-squares best planes of their carbon rings are the *ortho* bay deuterium atoms; the distances are D(1) 0·037 (4), D(5) −0·017 (4), D(9) 0·041 (4), and D(3) −0·028 (4) Å. These displacements are in the same direction as those resulting from the twist between the rings. The bond angles of the molecule also deviate from the ideal 120° in such a way as to increase the distance between *ortho* bay deuterium atoms. Table 6
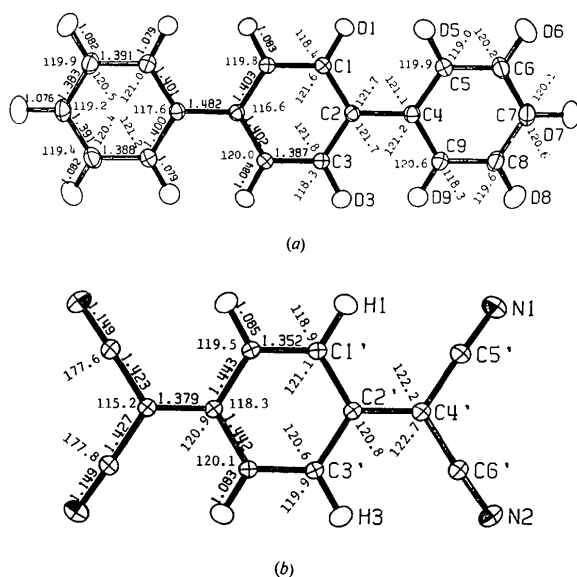

(a)

(b)

Fig. 3. The atom-numbering scheme and bond distances and angles uncorrected for libration. Note the close argeement between chemically equivalent dimensions. Standard errors for angles are 0·1° except for C(8)–C(9)–D(9), C(5)–C(6)–D(9), C(6)–C(7)–D(7), and C(9)–C(7)–D(7) which are 0·2°; those for bond distances are 0·001 Å except for C–H distances and C(5)–C(6), C(6)–C(7), C(7)–C(8), and C(8)–C(9) which are 0·002 Å.
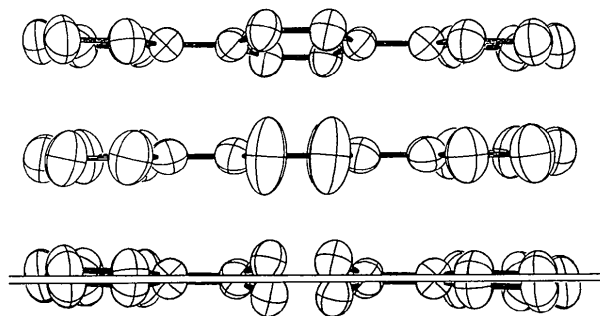

Fig. 4. Comparison of terphenyl thermal ellipsoids. Top: *p*-terphenyl from the present study with TCNQ. Middle: *p*-terphenyl from Rietveld, Maslen & Clews (1970). Bottom: composite of the top molecule superimposed upon itself after a 180° rotation. Note the similarity of the thermal ellipsoids of this disordered structure and those of the middle drawing. All three views show 80% probability ellipsoids.

summarizes the overcrowded D–D distances for a series of hypothetical conformations, starting from an idealized planar molecule having 120° angles and experimental bond lengths and ending with the observed conformation. The change in distance between the *ortho* bay deuterium atoms is listed for each successive deformation; the significant increase in each case suggests that all the deformations may well be caused by overcrowding. In Table 6 the first two calculations were performed by projecting the bond vectors of one bay onto the vector from C(2) to C(4) and finding the length of the resultant. The third calculation was carried out by projecting all C–D bond vectors onto the plane of that carbon atom, C(2), and C(4), keeping the bond lengths the same as before projection, and finding the distance between the ends of these new vectors.

Chemically equivalent molecular dimensions for terphenyl also agree well, except for the C(6)–C(7), C(7)–C(8) pair (Fig. 3). The average C–D and ring C–C bond distances, ± the standard deviations about the mean, are 1·081 ± 0·003 and 1·394 ± 0·008 Å uncorrected for thermal motion, and 1·105 ± 0·002 and 1·399 ± 0·009 Å when corrected for thermal motion.

The crystal structure of molecular *p*-terphenyl determined by Rietveld *et al.* (1970) has an angle of 24′ between normals to the rings, and only in-plane bond-angle distortions were noted. The center drawing of Fig. 4 shows the thermal ellipsoids found in that structure analysis. The range of amplitudes was explained as an electron excess on C(2) and C(4), an electron deficit on the other carbon atoms, and an unusually large libration of r.m.s. amplitude 16·3° for the center ring about the long axis.

An alternate interpretation is presented in Fig. 4. The unusual thermal ellipsoid pattern could arise from static disorder of terphenyl molecules in the conformation found in the present study. Superimposing the top molecule in Fig. 4 upon its image rotated 180° about an axis perpendicular to the page gives the bottom representation. The composite thermal ellipsoids of this disordered construction are very similar to those in the center drawing.

The disorder depicted in Fig. 4 is in agreement with the calculations of Baudour, Delugeard & Sanquer (1974) who compared the results of Rietveld *et al.* for *p*-terphenyl with those of the phenyl isocyanate dimer $(C_{14}H_{10}N_2O_2)$ having a four-membered center ring. The molecular packing and thermal motion in these two almost isostructural crystals were similar except for the much larger libration about the long axis of terphenyl. The absence of low-frequency internal modes in spectroscopic measurements on terphenyl led Baudour *et al.* to the hypothesis that the differences indicated static disorder. They proposed an equilibrium position for terphenyl with the end ring twisted 5·7° and the center ring twisted 14·6° from the reported planar configuration but did not indicate whether the torsion angle between the rings is the sum or difference.

In Fig. 4 the orientation of the center ring of the top drawing is 15° from that of the middle drawing, which makes the end ring about 3° from the view direction because of the 12° dihedral angle.

Table 7. *Non-uniform deuteration of terphenyl*

	Coherent scattering amplitude of D after least-squares refinement	Average fraction deuteration
D(5)	0·591 (4) × 10⁻¹² cm	0·927 (4)
D(9)	0·585 (4)	0·921 (4)
D(1)	0·631 (4)	0·965 (4)
D(3)	0·636 (4)	0·970 (4)
D(6)	0·628 (5)	0·962 (5)
D(8)	0·640 (5)	0·974 (5)
D(7)	0·633 (5)	0·967 (5)

Incomplete deuteration of terphenyl

The refined values of the scattering amplitude for deuterium (Table 7) indicate that the terphenyl molecule is incompletely and also non-uniformly deuterated. The individual values fall into two distinct groups, yielding average fractional deuteration values of 0·924 for the *ortho* positions of the end rings and 0·968 for all other positions (internal estimates of the standard deviations of the mean are 0·003 and 0·002 respectively). The corresponding overall fractional deuteration is 0·955.

The deuterated *p*-terphenyl used in the preparation was reported by the supplier* to have been prepared by platinum-catalyzed isotopic exchange with D_2O at elevated temperature and pressure. It is not unexpected that the sterically hindered *ortho* bay positions should have a slower exchange rate, and therefore show a less nearly complete degree of deuteration if the reaction is stopped short of saturation. However, a small but significantly higher degree of exchange appears, despite steric hindrance, at the *ortho* bay positions on the center ring compared with those on the end rings. This observation is reminiscent of the enhanced reactivity of center ring positions in electrophilic aromatic substitution reactions in strong-acid media, where the effect is ascribed to activation of the center ring positions by the attached end rings. However, the analogy

---

* Merck, Sharp, and Dohme of Canada, Lot No. 63CD249.

Table 8. *Mass spectrum of deuterated terphenyl*

Mass	Number of D	Fractional deuteration Obs.ᵃ	Fractional deuteration Calc.ᵇ	Mass	Number of D	Fractional deuteration Obs.ᵃ
244	14	0·707	0·565	238	8	0·005
243	13	0·187	0·329	237	7	0·003
242	12	0·045	0·089	236	6	0·002
241	11	0·021	0·015	235	5	0·001
240	10	0·018	0·002	234	4	0·001
239	9	0·01				

(*a*) Corrected for the natural abundance of C^{13} of 1·1 %. (*b*) For independent exchange probability of 0·96.

is not close, and implication of a common explanation is questionable.

A mass spectral analysis of the deuterated starting material yielded the value 0·961 for the overall fractional deuteration, a value in reasonable agreement with 0·955 from neutron diffraction. However, the distribution among mass numbers (Table 8) is anomalous compared with the expected distribution for independent equal or nearly equal exchange probabilities at the several sites. There is an excess of $C_{18}D_{14}$ and of species with fewer than 11 deuterium atoms and a deficit of the intermediate species with 11, 12, or 13 deuterium atoms. A possible explanation is that the time or intimacy of exposure of terphenyl to the exchange reaction was variable, resulting in a product that is a mixture of portions having different probabilities of exchange. Qualitative considerations indicate that such a model could reproduce the observed distribution of masses.

References

ALMENNINGEN, A. & BASTIANSEN, O. (1958). *Kgl. Norske Vidensk. Selskabs Skrifter*, No. 4, 1.
BAUDOUR, J. L. (1972). *Acta Cryst.* B28, 1649–1656.
BAUDOUR, J. L., DELUGEARD, Y. & SANQUER, M. (1974). *Acta Cryst.* B30, 691–696.
COLTON, R. H. & HENN, D. E. (1970). *J. Chem. Soc. (B)*, pp. 1532–1535.
CYVIN, S. J. (1968). *Molecular Vibrations and Mean Square Amplitudes.* Oslo: Universitetsforlaget.
FISHER, J. E., HANCOCK, J. H. & HAUPTMAN, H. (1970). *Computer Program for the Calculation of the Crystal Structure Invariants Based on Certain Conditional Distributions,* NRL Report 7157, Naval Research Laboratory, Washington, D. C.
GOLDBERG, I. & SHMUELI, U. (1973*a*). *Acta Cryst.* B29, 421–431.
GOLDBERG, I. & SHMUELI, U. (1973*b*). *Acta Cryst.* B29, 432–440.
GOLDBERG, I. & SHMUELI, U. (1973*c*). *Acta Cryst.* B29, 440–448.
HANSON, A. W. (1965). *Acta Cryst.* 19, 610–613.
HARGREAVES, A. & RIZVI, S. H. (1962). *Acta Cryst.* 15, 365–373.
HAZELL, R. G., LEHMANN, M. S. & PAWLEY, G. S. (1972). *Acta Cryst.* B28, 1388–1394.
JOHNSON, C. K. (1970*a*). *Thermal Neutron Diffraction,* pp. 132–160. Edited by B. T. M. WILLIS. Oxford Univ. Press.
JOHNSON, C. K. (1970*b*). Chemistry Division Annual Report, ORNL-4581, pp. 133–134. Oak Ridge National Laboratory, Oak Ridge, Tennessee.
JOHNSON, C. K., REED, H. L., HALL, R. F. & RAAEN, V. F. (1974). *Amer. Cryst. Assoc. Spring Meeting Abstracts,* p. 135. A more complete account to be published.

JONES, D. W. & SOWDEN, J. M. (1975). *Acta Cryst.* A31, S126.

LONG, R. E., SPARKS, R. A. & TRUEBLOOD, K. N. (1965). *Acta Cryst.* 18, 932–939.

MULLIKEN, R. S. (1952). *J. Amer. Chem. Soc.* 74, 811–824.

PAWLEY, G. S. (1971). *Acta Cryst.* A27, 80–81.

RIETVELD, H. M., MASLEN, E. N. & CLEWS, C. J. B. (1970). *Acta Cryst.* B26, 693–706.

ROBERTSON, G. B. (1961). *Nature, Lond.* 191, 593.

SHULL, C. G. (1972). Private communication.

THIESSEN, W. E. & BUSING, W. R. (1974). *Acta Cryst.* A30, 814–821.

TROTTER, J. (1961). *Acta Cryst.* 14, 1135–1140.

WILLIAMS, R. M. & WALLWORK, S. C. (1968). *Acta Cryst.* B24, 168–174.

YAKUSHI, K., IKEMOTO, I. & KURODA, H. (1974). *Acta Cryst.* B30, 835–837.

ZACHARIASEN, W. H. (1968). *Acta Cryst.* A24, 212–216.

The Crystal Structure of N,N,N,N',N',N'-Hexamethylisopropylenediamine Diiodide–Silver Iodide(I)

BY M. M. THACKERAY AND J. COETZER

National Physical Research Laboratory, CSIR, P.O. Box 395, Pretoria 0001, South Africa

Crystals of $Ag_{11}I_{13}C_9H_{24}N_2$ are orthorhombic, space group *Ibam*, with $a=13\cdot84$ (2), $b=15\cdot65$ (2), $c=20\cdot69$ (2) Å, $D_c=4\cdot44$ g cm^{-3} for $Z=4$. The structure was solved by direct methods with 1084 independent reflexions and refined to $R=0\cdot080$. A three-dimensional lattice of face-sharing I tetrahedra permits the conduction of Ag^+ ions through the structure. The Ag^+ ions are situated in the I tetrahedral sites and are extensively disordered. Holes in the I lattice contain the amine chains which are disordered about three mutually perpendicular diad axes.

Introduction

Several quaternary amine iodide salts, when reacted with silver iodide, have been found to produce solid electrolytes with high electrical conductivities. Owens (1970) has studied the tetraalkylammonium iodide–silver iodide system. In particular tetramethylammonium iodide–silver iodide shows a maximum conductivity of $0\cdot04$ (Ω cm)$^{-1}$ corresponding to a phase containing approximately 87 mol % AgI and 13 mol % $(CH_3)_4NI$. Geller & Lind (1970) have reported the crystal structure of this phase which has the formula $[(CH_3)_4N]_2Ag_{13}I_{15}$. The results of conductivity measurements made on the hexamethylethylenediamine diiodide–silver iodide and hexamethylisopropylenediamine diiodide–silver iodide systems have recently been reported (Coetzer & Thackeray, 1976a). The former system shows a maximum conductivity of $0\cdot11$ (Ω cm)$^{-1}$ corresponding to an electrolyte in which the AgI concentration is 97 mol %. We have been able to isolate three phases of this system with AgI concentrations of 67, 86 and 89 mol %, respectively. The structures of these phases have been reported (Coetzer & Thackeray, 1975a, b; Coetzer, Kruger & Thackeray, 1976). The structure reported here is the first phase to be isolated from the hexamethylisopropylenediamine diiodide–silver iodide system.

Experimental

Irregularly shaped crystals were obtained from a reaction mixture of 93 mol % AgI and 7 mol % hexamethyliso-propylenediamine diiodide. The preparation of the reaction mixture is described elsewhere (Coetzer & Thackeray, 1976b). A $0\cdot08 \times 0\cdot10 \times 0\cdot10$ mm crystal was selected for data collection. The cell data are: $a=13\cdot84$ (2), $b=15\cdot65$ (2), $c=20\cdot69$ (2) Å, $D_c=4\cdot44$ g cm^{-3}, $Z=4$, $\mu=136\cdot2$ cm^{-1}, F.W. 2996·8. Formula $Ag_{11}I_{13}C_9H_{24}N_2$. Space group *Ibam*.

The cell parameters were determined from the least-squares refinement of the angular settings of 25 high-order reflexions. 1084 independent reflexions were collected over the range $3° \leq \theta \leq 22°$ on a Philips PW1100 diffractometer in the ω–2θ mode with Mo $K\alpha$ ($\lambda = 0\cdot7107$ Å) radiation. A scan speed of $0\cdot04° \theta$ s^{-1} and a scan width of $1\cdot2° \theta$ were used. Reflexion conditions: hkl $h+k+l=2n$, $0kl$ $k=2n$ ($l=2n$) and $h0l$ $h=2n$ ($l=2n$) indicated the two possible space groups *Ibam* and *Iba*2. The background was counted for half the scan time on each side of a reflexion. 375 reflexions were considered to be unobserved according to the criterion $I < 1\cdot65\sigma(I)$, where $\sigma(I)=[(0\cdot02S)^2+S+B]^{1/2}$, $S=$scan count and $B=$background count. Three strong reflexions measured periodically throughout the data collection indicated no crystal decomposition. Lorentz and polarization factors were applied but no absorption corrections were made.

Solution of the structure

All computations for solving and refining the structure were executed with the X-RAY system (Stewart, Kruger, Ammon, Dickinson & Hall, 1972). The structure