

The Crystal and Molecular Structure of Biphenyl

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Crystals of biphenyl are monoclinic with two molecules in a unit cell of dimensions

$$a = 8.12, b = 5.64, c = 9.47 \text{ \AA}; \beta = 95.4^\circ.$$

Although a very weak 030 reflexion was observed, structure analysis has been completed satisfactorily on the basis of space group $P2_1/a$. The carbon skeleton of the molecule is completely planar within the limits of experimental error, the maximum deviation from the mean molecular plane being only 0.007 Å. Hydrogen atoms are reasonably well-resolved on the ($F_o - F_c$) maps, and their positions, although they can be determined only approximately, suggest that the hydrogens also are situated on the plane of the carbon atoms, but that there are small in-plane displacements of the *ortho* hydrogen atoms from idealized positions, which reduce steric strain. The length of the central C-C bond is 1.507 Å, and the other molecular dimensions indicate that the molecular symmetry is *mmm*. All the intermolecular contacts correspond to normal van der Waals interactions.

Introduction

The molecular configuration of biphenyl in the solid state was first established more than thirty years ago by the observation that the crystals are monoclinic with two molecules in a unit cell of space group $P2_1/a$ (Hengsteberg & Mark, 1929; Clark & Pickett, 1930, 1931; Dhar, 1932). This necessitates a molecular centre of symmetry, and hence the two rings must be coplanar. A later study of the intensities of the X-ray reflexions (Dhar, 1949) was not sufficiently detailed to provide further accurate information about the molecular configuration or dimensions.

The earliest electron diffraction investigation of biphenyl vapour (Karle & Brockway, 1944) was interpreted as indicating a non-coplanar structure, although this conclusion was not based entirely on the experimental evidence, since a completely planar arrangement agreed equally well with the data. A later investigation of biphenyl vapour, together with similar studies of 3,3'-dichlorobenzidine and 3,3'-dibromobiphenyl (Bastiansen, 1949), suggested an angle of $45 \pm 10^\circ$ between the planes of the two rings.

A detailed X-ray investigation of crystalline biphenyl is obviously long overdue, especially in view of recent examples of a statistically-centrosymmetric arrangement of non-centrosymmetric molecules in space group $P2_1/a$ (Trotter, 1958; Robertson, Shearer, Sim & Watson, 1958). If such an arrangement were present in biphenyl crystals, then non-coplanar molecules could be accommodated, even in space group $P2_1/a$ with $Z=2$. The present paper describes an investigation of the crystal structure of biphenyl using X-ray diffraction methods.

During the course of the investigation the author learned that a similar study was in progress elsewhere (Hargreaves & Rizvi, 1960), but it was agreed that it

would be useful for the two studies to proceed independently, and perhaps for some comparison to be made afterwards.

Experimental

The crystals were obtained from the walls and neck of a bottle where they had been deposited by very slow sublimation. The density was measured by flotation in aqueous potassium iodide solution. The unit-cell dimensions and space group were determined from rotation and oscillation photographs of crystals rotating about the *a* and *b* axes, and $0kl$ and $h0l$ Weissenberg films.

Crystal data

Biphenyl, $C_{12}H_{10}$; M.W. = 154.2; m.pt. = 71 °C.

Monoclinic, $a = 8.12, b = 5.64, c = 9.47 \text{ \AA}, \beta = 95.4^\circ$.

Volume of the unit cell = 431.8 Å³.

Density, calculated (with $Z=2$) = 1.179 g.cm.⁻³,
measured = 1.170 g.cm.⁻³.

Absorption coefficient for X-rays, $\lambda = 1.542 \text{ \AA},$
 $\mu = 6.06 \text{ cm.}^{-1}$.

Total number of electrons per unit cell = $F(000) = 164$.

Careful examination of the Weissenberg films indicated the absence of $h0l$ reflexions when *h* is odd, and also of $0k0$ reflexions when *k* is odd, except for a very weak 030 reflexion. Since no 010, 050 or 070 reflexions could be observed, and since the 030 was extremely weak, it was felt that it might be a Renninger reflexion, and that the true space group was $P2_1/a$. Nevertheless, it was considered that it would be better to proceed without choosing initially between the three possible space groups *Pa*, $P2_1/a$ and $P2_1/a$.

The intensities of the $0kl$ and $h0l$ reflexions were recorded on Weissenberg exposures of the equatorial

layers for crystals rotating about the a and b crystal axes, using Cu $K\alpha$ radiation, with multiple-film technique to correlate strong and weak reflexions. The intensities were estimated visually, the range being about 100,000 to 1. The crystals had fairly uniform cross-sections and no absorption corrections were applied. The structure amplitudes were derived by the usual formulae for a mosaic crystal, the absolute scale being established later by correlation with the calculated structure factors. 62 independent $0kl$ reflexions and 85 independent $h0l$ reflexions were observed, representing 82% and 84% respectively of the possible numbers observable with Cu $K\alpha$ radiation.

Structure analysis

The determination of the complete structure proceeded by examining initially the projection down the b -axis. The very strong $20\bar{1}$ reflexion suggested that all the atoms must be situated very close to this plane. Much more detailed information about the atomic positions, however, could be deduced from the additional observation that the $40\bar{2}$ reflexion was too weak to be observed. These two pieces of information taken together suggested that carbon atoms 1, 1', 4 and 4' were situated exactly on the $(20\bar{1})$ plane, and that the other eight carbon atoms were displaced from this plane by one-sixth of the $20\bar{1}$ spacing, so that their contribution to the $40\bar{2}$ reflexion exactly cancelled the contribution of the first four atoms. Further consideration of the high-order reflexions corresponding to the 1.2 and 2.1 Å, spacings of the six-membered rings indicated that the 4-4' axis was exactly perpendicular to the b -axis, and established coordinates for all the carbon atoms in the molecule. These atomic parameters indicated that this projection at least must be centrosymmetrical or nearly so. Structure factors were calculated for all the $h0l$ reflexions using the scattering factor for carbon of Berghuis *et al.* (1955), with $B=4.8 \text{ \AA}^2$ for all the atoms and the discrepancy factor was 24.2%.

The b -axis projection indicated that the space group was probably either $P2_1/a$ or $P2/a$, so that the molecule must be situated on a centre of symmetry in either of these space groups, and hence must be planar, or on a two-fold axis in space group $P2/a$, in which case measurements on the projection indicated an angle of about 60° between the planes of the two rings.

In order to decide between these various possibilities it was necessary to consider the projection along the a -axis. When a centrosymmetrical molecule was placed on a centre of symmetry in space group $P2/a$, all the $0k0$ reflexions with k odd had high F_c values. When a molecule with a two-fold symmetry axis was placed on the space-group two-fold axis, that is in the special position $(0, y, \frac{1}{2})$, and y was taken as $\frac{1}{2}$, excellent agreement between F_o and F_c was obtained for all $0kl$ reflexions with k even, and $0k0$ reflexions with k odd had zero F_c values for this particular arrange-

ment. It was felt that this was very promising, since small atomic shifts during further refinement might explain the observation of the weak 030 reflexion. However when structure factors were calculated for the $0kl$ reflexions with k odd, it was noted that the agreement was very poor, particularly for the $0k1$ reflexions, so poor in fact that this structure was quite obviously incorrect.

Structure factors were then calculated for the remaining possibility—a centrosymmetrical, planar molecule at $(0, 0, 0)$ in space group $P2_1/a$ —and excellent agreement was obtained between observed and calculated structure factors, the R value for all the $0kl$ reflexions being 16.5%.

It was now apparent that the space group was $P2_1/a$, or very close to $P2_1/a$, and that the molecule was planar, or very nearly planar, and that the structure factor agreement was good enough to indicate that there was no possibility of a statistical arrangement of molecules with a 45° angle between the planes of the rings. It was considered that any small deviation from $P2_1/a$ would become apparent (as strongly anisotropic thermal parameters) during the course of refinement.

This elucidation of the structure has been described in some detail to stress that there is no doubt about the planar configuration of the molecule.

Further refinement proceeded by computing $(F_o - F_c)$ syntheses, and altering the positional and isotropic temperature parameters of the carbon atoms to minimize the slopes and difference electron-densities at the atomic centres. One cycle reduced the discrepancy factors to 16.5% for the $h0l$ zone and 14.8% for the $0kl$ zone. A second set of difference syntheses was computed but no further changes in carbon-atom positional parameters were indicated. There were, however, significant well-resolved maxima corresponding to hydrogen atoms, and it was possible to obtain approximate values for the coordinates of all the hydrogen atoms in the molecule. The measured structure factors are compared in Table 2 with the values calculated for the carbon atoms only. Inclusion of hydrogen atom contributions would reduce the discrepancy factors slightly. Final electron-density projections, computed with measured structure amplitudes and calculated signs, are shown in Figs. 1 and 2. Fig. 1 also shows the second $h0l$ difference synthesis, to illustrate the resolution of the hydrogen atoms.

Coordinates and molecular dimensions

The final positional and temperature parameters of the carbon and hydrogen atoms are listed in Table 1, x, y, z being coordinates referred to the principal crystallographic axes and expressed as fractions of the unit-cell edges. Deviations of the atoms from the best plane through their centres are included in Table 1.

The bond lengths and valency angles in the molecule, calculated from the coordinates of Table 1, are shown in Fig. 3(a). On the basis of the standard

Table 1. *Final positional and temperature parameters, and deviations from the mean molecular plane*

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å ²)	Δ (Å)
C ₁	0.0357	-0.0007	0.0764	4.0	-0.002
C ₂	-0.0042	0.1738	0.1690	4.8	-0.007
C ₃	0.0648	0.1723	0.3130	5.4	-0.001
C ₄	0.1719	-0.0040	0.3607	5.4	+0.007
C ₅	0.2103	-0.1795	0.2672	5.4	0
C ₆	0.1416	-0.1770	0.1253	4.8	-0.006
H ₂	-0.091	0.308	0.150	—	-0.10
H ₃	0.033	0.314	0.385	—	+0.01
H ₄	0.222	-0.005	0.468	—	0
H ₅	0.284	-0.308	0.297	—	-0.01
H ₆	0.197	-0.317	0.057	—	+0.13

deviations of the atomic positions, described below, the molecular symmetry does not deviate significantly from *mmm*, and the mean values of the C-C bond distances and of the valency angles are shown in Fig. 3(b). None of the differences between the C-H distances are significant, and the mean value of 1.06 Å is included in Fig. 3(b).

Standard deviations

The estimated standard deviations of the atomic coordinates, calculated from Cruickshank's (1949) formulae, are $\sigma(x) = \sigma(y) = \sigma(z) = 0.016$ Å for carbon, and $\sigma(x) = \sigma(y) = \sigma(z) = 0.12$ Å for hydrogen. The corresponding standard deviations of the measured bond distances are 0.023 Å for C-C bonds (0.032 Å for the central bond) and 0.12 Å for C-H bonds.

Discussion

The appearance of the very weak 030 reflexion on the photographic records for the *Ok*l zone had suggested initially that the true space group might be *P2/a* or *Pa*. As described above, the agreement between *F_o* and *F_c* values for *Ok*l reflexions with *k* odd was very poor for the only plausible trial structure in space group *P2/a*, so that this space group was apparently incorrect. Refinement then proceeded satisfactorily on the basis of space group *P2₁/a*, with the biphenyl molecules situated on centres of symmetry, and hence having

Table 2. *Measured and calculated structure factors*

<i>h k l</i>	<i>F_o</i>	<i>F_c</i>	<i>h k l</i>	<i>F_o</i>	<i>F_c</i>	<i>h k l</i>	<i>F_o</i>	<i>F_c</i>	<i>h k l</i>	<i>F_o</i>	<i>F_c</i>
0 0 1	23.6	+21.6	4 0 $\bar{5}$	4.2	+5.5	8 0 $\bar{2}$	2.1	+3.3	0 3 1	0.5	-0.7
2	33.7	-34.5	4	15.4	+13.8	$\bar{1}$	3.7	+4.2	2	1.3	-1.2
3	9.2	+7.6	3	1.3	+0.4	0	0.7	-0.9	3	1.4	+0.5
4	18.8	-20.5	$\bar{2}$	<0.5	0	1	<0.7	+1.9	4	0.5	-0.4
5	18.3	-16.1	$\bar{1}$	<0.5	+0.2	2	0.6	-1.5	5	1.1	-1.1
6	2.0	+2.2	0	10.3	+7.5	3	8.8	-9.5	6	<0.5	+1.1
7	0.8	+0.4	1	10.7	+10.4	4	3.2	-2.8	7	0.7	+1.3
8	<0.7	-0.4	2	6.2	-8.2	5	2.0	+2.0	8	0.9	-0.2
9	2.7	-2.6	3	5.9	-6.2	6	<0.4	+0.1	9	<0.5	-0.5
10	1.9	-1.3	4	1.2	-0.9	7	<0.3	+1.5	10	0.3	-0.2
11	1.9	+1.7	5	2.4	-1.6	10,0, $\bar{4}$	1.8	+1.7	11	<0.2	-0.1
12	<0.4	+0.9	6	<0.7	-0.2	$\bar{3}$	<0.4	0	0 4 0	4.7	+4.3
2,0, $\bar{12}$	1.2	+2.1	7	3.1	-4.5	0	0.7	+1.0	1	1.9	+0.9
$\bar{11}$	0.5	-0.1	8	3.3	-2.4	$\bar{1}$	<0.4	-0.7	2	5.8	+4.7
$\bar{10}$	1.9	+1.7	9	1.5	+1.1	0	0.9	-0.7	3	3.3	+4.3
9	<0.7	-0.2	10	<0.4	-0.6	1	<0.4	-0.5	4	2.5	-3.3
$\bar{8}$	10.4	-11.2	6,0, $\bar{10}$	2.8	-3.7	2	1.4	-3.0	5	0.4	-0.5
7	4.8	-4.9	9	2.3	-3.2	0 1 1	<0.3	-0.7	6	3.4	-2.7
$\bar{6}$	0.6	-0.2	8	<0.6	+0.9	2	8.0	+9.2	7	4.3	-4.9
5	6.5	-9.7	7	1.1	-1.1	3	1.2	+2.3	8	0.3	-0.3
4	5.7	+7.8	6	1.8	+2.7	4	5.5	+3.1	9	0.3	-0.4
$\bar{3}$	2.3	-0.4	5	6.7	+8.3	5	8.9	+8.5	10	0.3	-0.4
$\bar{2}$	4.2	+5.3	4	1.1	+0.8	6	3.6	-4.9	0 5 1	1.4	+1.0
$\bar{1}$	75.4	+68.5	3	2.8	-6.7	7	9.4	-11.4	2	1.2	-1.3
0	19.7	+17.2	2	1.7	-3.5	8	0.7	-0.3	3	0.4	-0.4
1	21.1	-21.2	$\bar{1}$	9.2	+9.6	9	4.1	+4.3	4	<0.5	-0.3
2	8.2	+8.3	0	9.2	+8.5	10	0.4	+0.8	5	1.2	-1.7
3	20.9	-18.9	1	2.3	-2.3	11	<0.4	+0.9	6	1.5	+1.0
4	26.2	-21.4	2	0.8	+3.2	12	0.8	+1.0	7	2.3	+2.6
5	4.1	+4.0	3	1.7	-2.8	0 2 0	5.8	-4.7	8	0.3	+0.1
6	8.5	+8.8	4	11.7	-12.0	1	2.8	-1.9	0 6 0	9.0	+9.4
7	<0.6	+0.3	5	2.6	-2.3	2	20.8	+19.7	1	2.6	+2.2
8	6.2	-6.9	6	1.8	+0.7	3	12.0	+12.3	2	1.2	-1.9
9	3.4	-2.6	7	1.4	-0.9	4	6.3	-7.1	3	<0.5	+0.4
10	1.7	+1.0	8	1.2	+1.7	5	1.9	+2.4	4	2.2	-2.5
11	0.5	-0.3	9	0.5	+0.7	6	2.1	-4.9	5	1.7	-2.2
4,0, $\bar{11}$	0.7	+1.5	8 0 $\bar{8}$	1.0	-1.4	7	11.6	-11.2	6	<0.3	+0.1
$\bar{10}$	<0.6	+0.1	7	0.4	+0.7	8	1.7	-1.0	0 7 1	<0.3	+0.1
9	9.5	-10.2	6	1.1	+1.7	9	<0.5	-0.1	2	<0.3	+0.4
8	5.8	-6.7	5	<0.6	+0.5	10	0.6	-0.6	3	<0.2	+0.3
7	2.2	+3.8	4	2.6	+0.6	11	1.5	+1.6			
6	2.5	-2.4	3	1.6	-0.3						

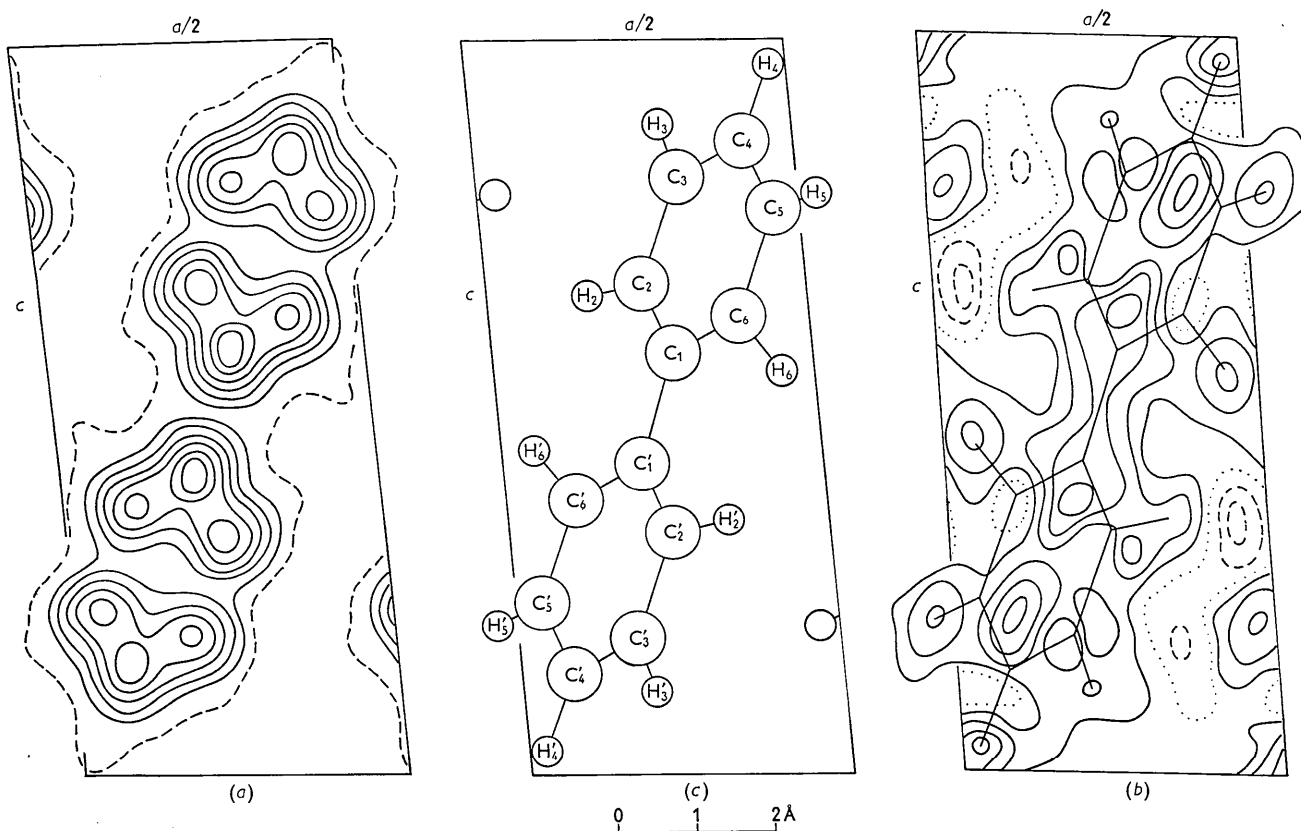


Fig. 1. (a) Electron-density projection along the b -axis; contours at intervals of $1 \text{ e.}\text{\AA}^{-2}$, with the one-electron line broken. (b) Projection of the structure onto (010). (c) $(F_0 - F_c)$ synthesis, showing hydrogen atoms; contours at intervals of $0.2 \text{ e.}\text{\AA}^{-2}$, negative contours broken, zero contour dotted.

coplanar rings. If then the true space group were Pa , it would have to correspond quite closely to $P2_1/a$, the two rings in each molecule would have to be nearly coplanar, and the deviations from the space group of higher symmetry and from planar molecules would be detectable as strongly anisotropic thermal parameters for atoms C_2, C_3, C_5 and C_6 , and as very elongated hydrogen atom peaks. Neither of these effects is in fact observed. The peaks within the six-membered rings on the $h0l$ ($F_0 - F_c$) maps (Fig. 1(c)) could probably be removed by introducing anisotropic temperature factors for the carbon atoms, but this thermal anisotropy is not particularly marked. Further, the maxima corresponding to hydrogen atoms, far from being elongated, are particularly well-resolved circular peaks (Fig. 1(c)). It can be concluded then, on the basis of the satisfactory refinement, the absence of marked thermal anisotropy, and the resolved hydrogen atoms, that the true space group of biphenyl crystals is $P2_1/a$. The 030 reflexion is possibly a Renninger reflexion, although insufficient data have been recorded to determine the reflexions from which it is derived.

All the carbon atoms in the molecule lie on one plane, the maximum deviation from the mean molec-

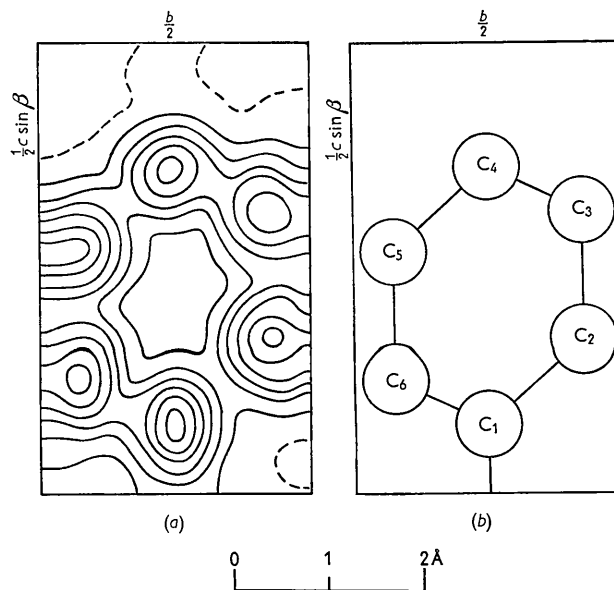


Fig. 2. (a) Electron-density projection along the a -axis; contours at intervals of $1 \text{ e.}\text{\AA}^{-2}$, with the one-electron line broken. (b) Projection of the structure along $[100]$.

ular plane being 0.007 Å and the root-mean-square deviation 0.005 Å, in comparison with an estimated standard deviation in atomic position of 0.016 Å. The

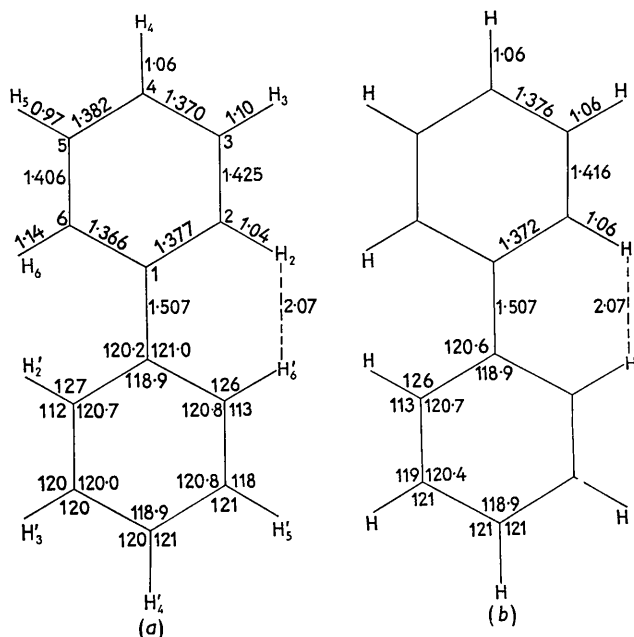


Fig. 3. (a) Measured bond lengths (Å) and valency angles (degrees) in biphenyl. (b) Mean distances and angles.

maximum deviation of the hydrogen atoms from the carbon atom plane is 0.13 Å and the r.m.s. deviation 0.07 Å, and, in comparison with the e.s.d. of 0.12 Å for hydrogen atoms, these deviations cannot be considered significant. The largest deviations are for the *ortho* hydrogen atoms, but, since H₂ and H₆' are displaced in the same directions, these displacements would not reduce the strain which one would expect in a regular planar model, even if they were large enough to be significant.

When one examines the valency angles however (Fig. 3), there is a definite indication of in-plane displacements of H₂, H₂', H₆, H₆' (the *ortho* hydrogen atoms), the deviations from 120° of the valency angles involving these hydrogen atoms being in directions which suggest an increase in the distances H₂-H₆' and H₂'-H₆ over those which would pertain in an ideal model with 120° valency angles. The H₂-H₆' distance in a regular model is 1.80 Å, while the distance calculated from the coordinates of Table 1 is 2.07 Å. Now the hydrogen atom positions have been determined only rather approximately, and on the usual standard deviation criterion, the increase from 1.80 Å to 2.07 Å is only possibly significant. Nevertheless, this increase is probably a real effect, since the steric strain which would pertain in a regular model with a H...H non-bonded distance of 1.80 Å would be considerably relieved by the increase to 2.07 Å, this relief having been achieved without sacrificing planarity.

The bond distances and valency angles in the molecule (Fig. 3(a)) indicate no significant deviation from symmetry *mmm*, and mean distances and angles are shown in Fig. 3(b). The central bond has length 1.507 Å with a standard deviation of 0.032 Å. This distance is close to those reported in perylene (Donaldson, Robertson & White, 1953) and quatterylene (Shrivastava & Speakman, 1960). Within the six-membered ring, the e.s.d. of the mean C-C distances is 0.016 Å, so that bonds 2-3 and 5-6 are possibly longer than the others. These variations in C-C bond length within the ring are in the opposite directions to those which would be predicted by resonance theory.

Intermolecular distances

All the intermolecular distances correspond to normal van der Waals interactions. The shorter contacts are illustrated in Fig. 4, and all the separations are quite large, some of the space being filled of course by the hydrogen atoms. In the *b* direction the shortest contact is 3.88 Å.

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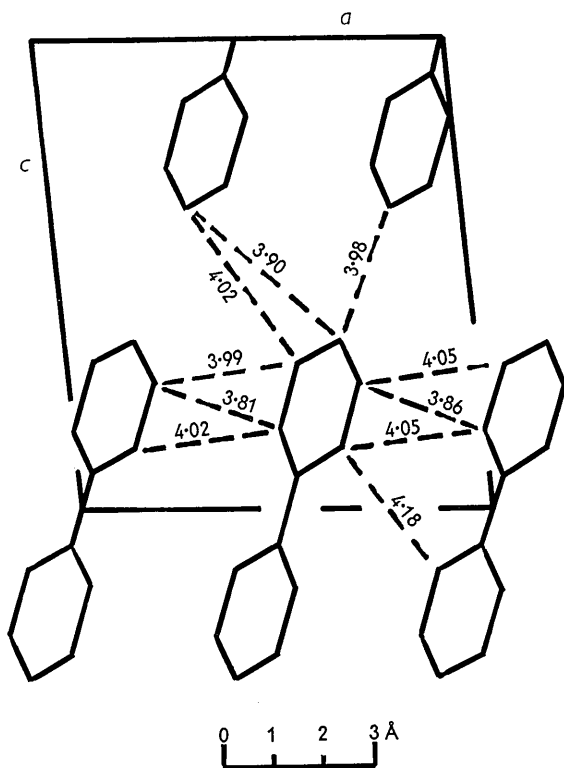


Fig. 4. Projection of the structure along [010], showing the shorter intermolecular contacts (Å).

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X-ray Diffraction Study of Indium Phosphate Dihydrate and Isostructural Thallic Compounds

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The isostructural crystals, $\text{InPO}_4 \cdot 2\text{H}_2\text{O}$, $\text{TIPO}_4 \cdot 2\text{H}_2\text{O}$, and $\text{TlAsO}_4 \cdot 2\text{H}_2\text{O}$ have been studied by means of single crystal X-ray diffraction techniques. Structural parameters are given for the indium compound, which was chosen to represent the group. For this crystal, the cell, containing eight formula weights, has dimensions $a = 10.36$, $b = 8.84$, $c = 10.19$ Å. The space group is $Pbca(D_{2h}^{15})$. The structure is a complex three-dimensional net, in which two sets of water oxygens are very differently situated. The framework of the net is built up of indium, phosphate groups and one set of water oxygens. The second set of water oxygens lie in otherwise unoccupied channels of the framework. The number and lengths of the bonds formed in each case strongly suggest that one has the nature of an $(\text{OH})^-$ and the other of an $(\text{OH}_3)^+$ group. These laboratory grown crystals are isostructural with the minerals, strengite ($\text{FePO}_4 \cdot 2\text{H}_2\text{O}$) and scorodite, ($\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$).

Introduction

Under suitable conditions of preparation, the orthophosphates of indium and of trivalent thallium may be crystallized either as anhydrides or as dihydrates. The structure of InPO_4 and its isotype, TIPO_4 , has been described in an earlier paper (Mooney, 1956). An X-ray analysis of the hydrated crystals was undertaken as a continuation of a series of structure studies of the phosphates of trivalent elements. Early stages in the examination of these two crystals, and also of a third, $\text{TlAsO}_4 \cdot 2\text{H}_2\text{O}$, showed, as expected, that the atomic arrangement in all three is essentially the same. The indium compound was selected as the most favorable case for detailed structure determination.

Preparation of the crystals

The addition of phosphate ion to an aqueous solution of indium nitrate results in the immediate precipitation of a voluminous white amorphous product, described in chemical literature as a basic salt of indefinite composition. It is highly insoluble except in

acids. A simple method proved successful in promoting the growth of single crystals suitable for X-ray diffraction. Precipitates were dissolved in nitric acid solution and crystallized out by very slow dilution or neutralization at temperatures of about 75 °C. The crystals, of composition $\text{InPO}_4 \cdot 2\text{H}_2\text{O}$, generally appear as short, stout bipyramidal prisms, the largest of which have dimensions of a few tenth millimeters. Crystals of thallic phosphate dihydrate and thallic arsenate dihydrate were grown in the same way. The crystals of the arsenate were inferior to the other two in size and perfection of form.

X-ray diffraction methods

For $\text{InPO}_4 \cdot 2\text{H}_2\text{O}$, a complete set of diffraction data within the $\text{Cu } K\alpha$ range was collected. For the other two crystals, observations were limited to zero and first layers about the three axial directions. All of the data was photographically recorded on three-film packs by means of an integrating Weissenberg instrument. The intensities were measured by means of a