

*The Crystalline Structure of Benzene.*

By E. G. Cox.

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In a previous communication\* the writer gave the preliminary results of an investigation on the structure of solid benzene. It may be recalled that the unit cell was found to have the following dimensions at  $-22^{\circ}\text{C.}$ ;  $a = 7.44$ ,  $b = 9.65$ ,  $c = 6.81\text{ \AA.U.}$ , while the space-group was determined as  $Q_h^{15}$  (orthorhombic bipyramidal). The unit cell contains four molecules, the molecules being centro-symmetrical.

Since the publication of these results a certain amount of information has been obtained by other investigators. Bruni and Natta† took powder photographs of benzene which confirmed the above values of the cell-dimensions; this is very satisfactory, since previous workers (Broomé and Eastman) had obtained axial ratios which did not agree particularly well with each other's or with the writer's. Mrs. Lonsdale‡ has shown that in hexamethylbenzene the benzene ring is planar, the diameter of the atoms being  $1.42\text{ \AA.U.}$  More recently§ she has examined hexachlorobenzene, and although in this case the investigation did not yield quite such definite results, it was shown that if the ring is planar then again the diameter of the atoms must be  $1.42\text{ \AA.U.}$

Since the publication of the preliminary results the writer has endeavoured to obtain further information on the structure of benzene itself by consideration of the intensities of reflections from as many lattice planes as possible. Unfortunately there are several circumstances which introduce difficulties. The vapour pressure of solid benzene is very high ( $24.4\text{ mm.}$  at  $0^{\circ}\text{C.}$  as compared with  $4.6\text{ mm.}$  for ice at the same temperature) so that even at comparatively low temperatures a small piece of frozen benzene evaporates rapidly. This consideration, together with the fact that all the manipulation must be done at a temperature below  $0^{\circ}\text{C.}$ , makes it almost impossible to carry out experiments on the ionisation spectrometer. The experimental work was carried out by the rotating-crystal method in a special camera constructed by Mr. Jenkinson and his assistant in the Davy Faraday Laboratory. By circulating methylated spirits, previously cooled in carbonic snow, the temperature inside

\* 'Nature,' vol. 122, p. 401 (1928).

† 'Rec. Trav. chim. Pays-Bas.,' vol. 48, p. 860 (1929).

‡ 'Proc. Roy. Soc.,' A, vol. 123, p. 494 (1929).

§ 'Proc. Roy. Soc.,' A, vol. 133, p. 536 (1931).

the camera could be reduced, if necessary, to  $-40^{\circ}\text{C}$ . Lower temperatures than this would have made the manipulation of the apparatus inconvenient. Although the rotating-crystal method is more rapid than the ionisation spectrometer, it was necessary to keep a crystal for some hours at least, and the simplest way of preventing evaporation was found to be to enclose the crystal in a gelatine capsule such as is used for medical purposes. These capsules when coated very lightly with shellac, were found to be reasonably transparent to X-rays, and were sufficiently impervious to benzene vapour to enable a crystal to be kept for several days.

The capsule causes a certain amount of absorption which will not be the same for all diffracted beams, but this is not a serious source of error and in any case is unavoidable. Other factors which influence the intensities of reflections are the shape of the crystal and its degree of perfection; in these experiments the crystals were in general of quite irregular shape, because they were grown by slow recrystallisation in a frozen mass of benzene. Other methods of crystallisation were not successful. With regard to the perfection of the crystal, the effects of primary and secondary extinction are unknown, although the former is probably small. The problem of the influence of crystal shape on the intensities of reflections is connected with the question of secondary extinction, but it is not clear, in the absence of experiments directed specifically to the investigation of these points, what allowance should be made for them. Taking these and various other factors into consideration, it was thought sufficient for the preliminary attempts at determining the structure to estimate the intensities by eye. To assist in this, and with a view to more accurate measurements on the radioactive photometer later, calibration spots were put on the photographs in the manner described by Astbury.\* By trial on a photograph on which the intensities of the spots had been measured accurately, it was found that with care the error in intensity estimated by eye in only one instance exceeded 20 per cent. and averaged 9 per cent. Thus it may reasonably be assumed that the average error in the structure factors obtained in this work is not much more than 5 per cent., and that the error of individual results is rarely more than 10 per cent.

The geometrical structure factors were calculated from the intensities by the relation

$$I_{hkl} = F_{hkl}^2 f_0^2 L$$

where

$$I_{hkl} = \text{corrected intensity of reflection from } (hkl),$$

\* 'Proc. Roy. Soc.,' A, vol. 123, p. 575 (1929).

and

$F_{hkl}$  = geometrical structure factor for  $(hkl)$ ,  
 $f_{\theta}$  = scattering power (effective atomic number) of the carbon atom for angle  $\theta$  where  $\theta$  is the glancing angle for  $(hkl)$ ,  
 $L$  = the Lorentz factor,  $\frac{1 + \cos^2 2\theta}{\sin 2\theta}$ .

In the above formula a constant has been omitted, since the intensities, being relative only, are expressed in terms of a purely arbitrary unit. To obtain  $f_{\theta}$ , an  $f$ -curve for graphitic carbon was constructed, using the data given by Bernal\* and by Ponte.† As the work of Brindley and others has shown, the curve thus obtained is probably not very accurate, but it was considered sufficiently so for the present purpose. The corrected intensity  $I_{hkl}$  is the intensity estimated from the photograph multiplied by a factor to correct for oblique incidence and for the angular position of the reflecting plane.‡ Although this factor was usually not much different from unity, it was less than 0.5 for some planes and so could not be neglected.

In the following table the corrected intensities and corresponding geometrical structure factors are given for most of the more important lattice planes. The values given are in nearly all cases the mean of several estimations ; the scale for both intensity and structure factor is arbitrary, but the values of the structure factors given are of the same order as the absolute values. On the

Table I.

$hkl$ .	I.	$F_{hkl}$ .	$hkl$ .	I.	$F_{hkl}$ .
002	50	2.3	132	1	0.8
004	6	6.3	133	10	3.8
020	100	1.5	200	67	2.2
021	18	1.0	202	32	3.6
022	8	1.4	210	12	1.1
023	<1	<1.2	211	54	2.9
024	10	10.4	212	16	2.8
040	76	6.0	213	12	3.7
041	<1	<1.1	220	<1	<0.4
042	2.5	2.2	221	13	2.3
102	67	3.2	222	<1	<0.8
111	200	2.7	223	<1	<2.0
112	12	1.5	240	<1	<0.9
113	8	3.0	302	27	6.6
121	12	1.4	323	11	11.5
122	21	2.6	331	11	3.4
123	1	1.3	332	6	6.3
131	16	2.2	400	17	7.2

\* 'Proc. Roy. Soc.,' A, vol. 106, p. 749 (1924).  
† 'Phil. Mag.,' vol. 3, p. 195 (1927).  
‡ Cox and Shaw, 'Proc. Roy. Soc.,' A, vol. 127, p. 71 (1930).

scale of intensities adopted, the least intensity observable has the value 1, so that when the intensity is given as less than 1, it indicates that the reflection was not observed. It is not possible to estimate really big intensities very accurately, so that the errors in values greater than 50 are likely to be appreciably greater than in the smaller values.

The data of the above table, although of limited accuracy, are sufficient to indicate the main outlines of the structure of crystalline benzene. In attempting to determine the structure it was not thought advisable to try the Fourier series method at this stage, particularly as no absolute intensity measurements were available. The structure factors for the more important planes were calculated for various possible structures and compared with the experimental figures. As is usual in work of this kind the scattering power of the hydrogen atoms was neglected. The symmetry of  $Q_h^{15}$  is such that the calculations are not very involved, although laborious. The arrangement of the molecules may be called pseudo-face-centred, since if the centre of one molecule is taken at the corner of the unit cell, the centres of the other three are at the face centres, although their orientation is different. Also, owing to the arrangement of the two-fold screw axes of  $Q_h^{15}$ , if the orientation of the first molecule relative to the crystal axes is defined by three direction cosines, then the orientations of the other molecules are given by the same direction cosines with various changes of sign. Thus if a definite molecular structure is assumed, by varying the three cosines to cover all possible values, the complete range of possibilities for structures involving that model may be investigated. This has been done fairly completely for the case of the flat hexagonal model for the benzene molecule as follows. Let six atoms of radius  $r$  be arranged with their centres at the corners of a regular hexagon, and for reference purposes take the centre of the hexagon as origin, with axes  $Oz$  perpendicular to the plane of the ring,  $Oy$  passing through the centre of one of the atoms and  $Ox$  at right angles to the other two. Then if the direction cosines of  $Ox$  and  $Oy$  relative to the crystal axes  $OX$ ,  $OY$  and  $OZ$  are respectively  $l_1$ ,  $m_1$  and  $n_1$  and  $l_2$ ,  $m_2$  and  $n_2$ , it can be shown that the geometrical structure factor of the plane  $(hkl)$ , considering only one molecule, is

$$\begin{aligned} F = 2 \cos 2\pi r \left\{ \sqrt{3} \left( l_1 \frac{h}{a} + m_1 \frac{k}{b} + n_1 \frac{l}{c} \right) + \left( l_2 \frac{h}{a} + m_2 \frac{k}{b} + n_2 \frac{l}{c} \right) \right\} \\ + 2 \cos 2\pi r \left\{ \sqrt{3} \left( l_1 \frac{h}{a} + m_1 \frac{k}{b} + n_1 \frac{l}{c} \right) - \left( l_2 \frac{h}{a} + m_2 \frac{k}{b} + n_2 \frac{l}{c} \right) \right\} \\ + 2 \cos 4\pi r \left( l_2 \frac{h}{a} + m_2 \frac{k}{b} + n_2 \frac{l}{c} \right), \end{aligned}$$

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where  $a$ ,  $b$  and  $c$  are the lengths of the primitive translations. For purposes of calculation the above may be expressed as a product of cosines if necessary. For each of the other three molecules in the unit cell the same expression holds with appropriate changes in the signs of the direction cosines. The structure factor  $F_{hkl}$  for the whole cell is obtained by addition of the four separate  $F$ 's, allowance being made for their relative phases. Thus if  $h$ ,  $k$  and  $l$  are all odd or all even, all four are in phase, while in any other case two molecules are  $180^\circ$  out of phase with the other two.

In this way the structure factors for several important planes were calculated for a large number of possible values of  $l_1$ ,  $m_1$  and  $l_2$ , taking  $r$  as  $0.71 \text{ \AA.U.}$  By interpolation practically the whole range of values for the various direction cosines was covered. In no case was a really good agreement with experiment found. The most satisfactory structure seems to be with the plane of the ring approximately parallel with the  $b$ -axis and making an angle of about  $40^\circ$  with  $(100)$ . A projection of this arrangement on  $(010)$  is shown in fig. 1. The shaded

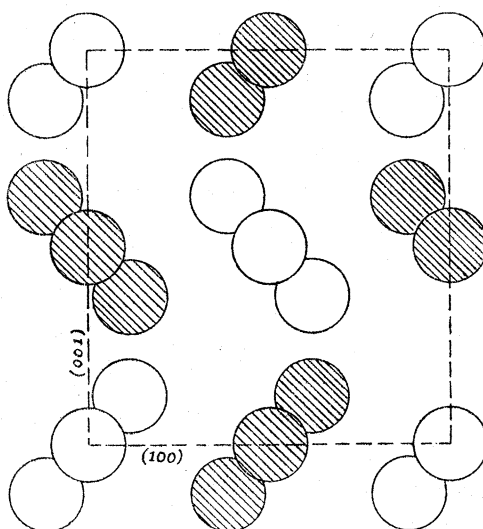


FIG. 1.

molecules lie at a depth  $b/2$  below the others. This can only be an approximate structure in any case; for example, if it were exact, in addition to the space-group halvings, all planes  $(hko)$  and  $(okl)$  for which  $k$  and  $l$  respectively were odd, would be halved. Reference to Table I, shows that although this is not so, yet the structure factors for all the planes in question are less than  $1.2$ , that is, very small. This indicates that the proposed structure is probably

reasonably close to the truth. Neglecting planes with intensities greater than 50 for reasons previously mentioned, the agreement between observed and calculated structure factors is fair. The comparison is given for some of the principal planes in Table II.

Table II.

<i>hkl.</i>	F (calculated).	F (observed).
004	7.3	6.3
400	6.8	7.2
220	0.8	<0.4
022	3.2	1.4
024	10.7	10.4
222	1.5	<0.8
202	3.6	8.0

Some calculated factors differ considerably from the observed values, but on the whole the divergence is less for this structure than for any other so far examined. By making slight adjustments in the direction cosines some improvements in the agreement can be made, but since it is very laborious to investigate all possible adjustments it was considered advisable to wait until more reliable values of the intensities are available.

The preceding discussion has so far been confined to structures involving a flat ring. The only serious alternative is a puckered ring, in which the atoms, of diameter approximately 1.54 Å.U., are formed into a ring in such a way that the tetrahedral angle is everywhere conserved. A formula, similar to the one given above for the flat ring can be derived to give the structure factor for any given plane in terms of the orientation of the molecule, so that the possibilities of this model can also be investigated. Actually it has not been found necessary to do this, as considerations of a general character show that the puckered ring is not likely to give satisfaction.

In the first place, it is found that the structure factor for (020) calculated for the structure proposed above, is much too big, even allowing for uncertainty in the experimental value. Now the molecules are arranged so that they take up the greatest possible space in the direction of the *b*-axis; this has the effect of making  $F_{020}$  as small as possible. Consequently a puckered ring, which even with larger atoms would take up less room than the flat ring, would make the value of  $F_{020}$  even further from the experimental value. In fact the open character of the structure in the direction of the *b*-axis would be increased



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considerably if the molecule were puckered ; this would almost certainly show as a cleavage parallel to (010). Among the large number of crystals handled during this work no sign of cleavage has been observed, the crystals actually being rather hard and compact compared with most crystalline aromatic substances.

The flat-ring structure is quite loosely knit ; the average distance from centre to centre of carbon atoms in neighbouring molecules is about  $3.8 \text{ \AA.U.}$ , compared with  $3.5 \text{ \AA.U.}$ , which is the distance most usually found to occur in other organic substances. The puckered ring is smaller than the flat one in two directions and larger in one, so that on the whole the gaps between the carbon rings would be increased by introducing the puckered molecule. It seems unlikely that such large gaps should occur, especially as the crystals are not particularly soft. The structure factors for (200) and (002) as well as (020) would be made far too big with a puckered ring model.

At present the balance of evidence is thus in favour of a flat ring for benzene ; also it is evident from what has been said that the agreement between the proposed structure and the experimental results could be improved by giving the carbon atom a diameter greater than it has in graphite and hexamethylbenzene. It may be, however, that a more accurate  $f$ -curve for carbon would make a larger atom unnecessary ; it is interesting to note that with the present data, the tendency is for  $F$  (calculated) to be greater than  $F$  (observed) for planes of large spacing, and for the reverse to be true for planes of small spacing.

It is intended to take further photographs under carefully controlled conditions in order to obtain more accurate intensity measurements. It is hoped also to investigate the optical properties of single crystals of benzene and if possible to relate them to the structure. A preliminary examination has shown that benzene, like anthracene and naphthalene, has very high birefringence.

*Summary.*

Previous work on the crystalline structure of benzene has now been extended ; by consideration of the intensities of the X-ray reflections from a number of lattice-planes, it has been found possible to decide on the arrangement of the molecules in the lattice, and in addition, it is found that the experimental results are strongly in favour of a flat-ring molecule. These conclusions are definite, but it is proposed to carry out further experiments to determine the finer details of the structure.

The experimental work on which this paper is based was carried out in the Davy Faraday Laboratory. The writer wishes to record his gratitude to Sir William Bragg, who suggested the work, for his continued interest, and to the Managers of the Royal Institution for providing facilities for the research. He wishes to acknowledge the interest taken in the work by his late colleagues in the Davy Faraday Laboratory, particularly Mr. W. T. Astbury.

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*The Flow of a Compressible Liquid in the Neighbourhood of the Throat of a Constriction in a Circular Wind Channel.*

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As a result of earlier work by G. I. Taylor on the two-dimensional motion of a compressible fluid,\* it appears evident that the elastic property of a fluid places a limitation upon the maximum velocity which can exist in a field in order that a certain type of irrotational motion may continue to be possible. So far a complete solution of the equation of motion of a compressible fluid in any particular problem has eluded the workers on this subject; and the greatest theoretical advance came when Taylor used the idea of expanding the velocity potential in a power series about the point of maximum velocity.

In a report to the Aeronautical Research Committee, Taylor† discusses by this means the irrotational flow of a non-viscous, compressible fluid past convex surfaces. He works out in detail the flow through a throat in a parallel walled channel, the constriction being formed by two circular arcs of radii  $R$  so related to the minimum distance  $2h$  between them that

$$\frac{h}{R} = \frac{1}{4}.$$

The arrangement is similar to that shown in fig. 1, if the axis of  $\varpi$  is replaced by  $y$  and the figure is regarded as representing two-dimensional conditions. It was first pointed out by Reynolds that there are two types of motion possible

\* 'Aero. Res. Ctee., Rep. & Mem.,' No. 1196 (1928).

† 'Aero. Res. Ctee.,' No. T2904 (1930).