

The Structure of the Benzene Ring in $C_6(CH_3)_6$.

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Since benzene itself is not crystalline at ordinary temperatures the study of the benzene nucleus or ring has had to be referred to certain of its derivatives. The most hopeful line of attack appeared to be in the direction of the fully substituted derivatives, such as C_6Cl_6 , or else by way of compounds such as naphthalene and anthracene which contain more than one ring. The results so far obtained, however, have only shown that the ring is centro-symmetrical,* a fact confirmed by the recent examination of crystalline benzene itself,† that its approximate width (given by the difference in lengths of the naphthalene and anthracene molecules) is 2.49 \AA ,‡ and that there exist in the nucleus two periodicities of about 1.28 and 2.66 \AA .§

If the ring be supposed to consist of six carbon atoms of diameter 1.54 arranged as in the diamond pattern,|| then periodicities of 1.26 and 2.52 would exist, the width of the ring itself being 2.52 . If, on the other hand, the benzene nucleus is a plane ring of six carbon atoms of diameter 1.42 , such as

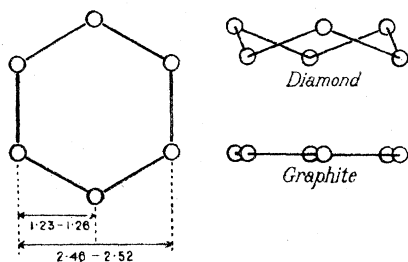


FIG. 1.

occurs in the graphite structure,¶ then the periodicities would be 1.23 and 2.46 , the width of the ring being 2.46 (fig. 1). The experimental observations (*loc. cit.*) could not definitely decide between these alternative structures, and no other criterion was found which would distinguish with certainty between a puckered and a plane ring.

One of the chief difficulties encountered in the study of these various benzene derivatives was that the unit cell invariably contained more than one

* Mark, 'Ber. Deut. Chem. Ges.,' vol. 57, p. 1820 (1924); Plummer, 'Phil. Mag.,' vol. 50, p. 1214 (1925).

† Cox, 'Nature,' vol. 122, p. 401 (1928).

‡ W. H. Bragg, 'Proc. Phys. Soc.,' vol. 34, p. 33 (1921).

§ W. H. Bragg, 'Z. Krist.,' vol. 66, p. 22 (1927).

|| W. H. and W. L. Bragg, 'X-rays and Crystal Structure,' p. 99 (4th edition, 1924).

¶ Hassel and Mark, 'Zeit. Phys.,' vol. 25, p. 317 (1924); Bernal, 'Roy. Soc. Proc.,' A, vol. 106, p. 749 (1924).

molecule, a fact which necessarily complicated any structure determination by introducing the question of relative orientations.

Hexamethylbenzene, $C_6(CH_3)_6$, proved to be free from this difficulty. The unit cell was found to be triclinic and contained one molecule only.

Experimental Investigation.

After purification the crystals melted at $164^\circ C$. Flat prisms were obtained on recrystallisation from benzene, and the measured density of these was 1.042 grs./c.c. at $18.5^\circ C$. The prisms as a rule showed only three pairs of faces (fig. 2), there being a good cleavage parallel to one of these pairs. No previous crystallographic data were available, so that all measurements were made directly on the ionisation spectrometer using a Coolidge tube with a Mo anticathode. All three crystal faces gave excellent reflections on the ionisation spectrometer; they were therefore provisionally adopted as axial planes. The tabular face of the prism was called (100), the cleavage plane (001) and the remaining side plane (010). It was found that the unit cell thus defined contained one molecule of $C_6(CH_3)_6$, and that in every case the spacings calculated agreed with the observed spacings. Well over 100 reflections were observed in five different zones, and no plane was found to have a spacing which was a multiple of that calculated. Nor were any sub-multiple spacings found, except of course in the case of higher order reflections from planes whose first orders had actually been observed. The unit cell chosen is therefore one of the infinite number of possible minimum cells, and subsequent calculations have shown that structurally the cell is a reasonable one. Mean values of the axial spacings can be calculated by using all the observed spacings and angles. These are given below and compared with those directly measured.

$(h\ k\ l).$	Mean observed spacing.	Direct measurement.	Measured angles between axial planes.
	\AA		
100	7.736	7.733	010 : 001 = $129^\circ\ 18'$
010	6.008	6.012	001 : 100 = $80^\circ\ 48'$
001	3.694	3.695	100 : 010 = $74^\circ\ 0'$

The measured angles between planes generally agreed with those calculated from the above data to within $5'$. The observed data lead to a value of

1.035 grs./c.c. for the density. The lengths of axes and the axial angles calculated from the mean observed data are (fig. 2):—

$$a = 9.010 \text{ \AA.}$$

$$\alpha = 44^\circ 27'$$

$$b = 8.926$$

$$\beta = 116^\circ 43'$$

$$c = 5.344$$

$$\gamma = 119^\circ 34'$$

$$a : b : c = 1.0095 : 1 : 0.5987.$$

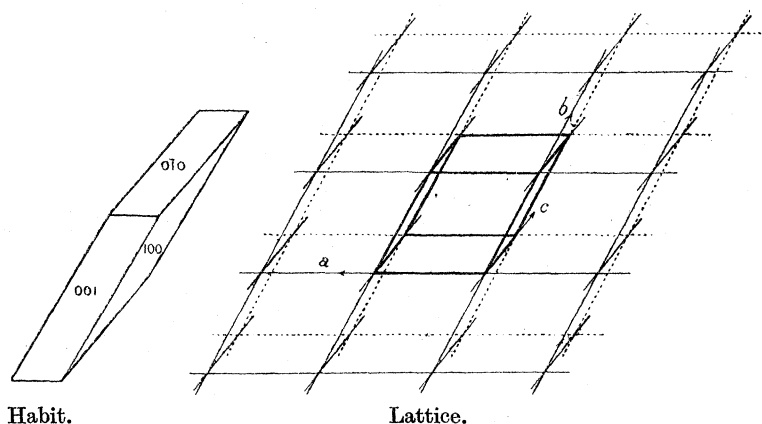


FIG. 2.

The space-group is either C_1^1 or C_i^1 , the molecule being either asymmetrical or centro-symmetrical. As far as external symmetry is concerned, the crystals appear to possess centro-symmetry, and this fact, combined with the knowledge that C_6H_6 , C_6Cl_6 and C_6Br_6 are all centro-symmetrical, would make it appear probable that $C_6(CH_3)_6$ is also centro-symmetrical. The crystals are easily deformed by slipping about any of the crystallographic axes. In this respect also they are similar to other fully-substituted benzene derivatives.

Structure Investigation.

It appears from the observations that a and b are equal to within 1 per cent. and that the angle between them is nearly $2\pi/3$. This fact at once suggested that it would be worth while to examine the $[001]$ zone for any evidence of hexagonal structure. The planes observed in that zone were divided into three groups:—

- (1) Planes $(hk0)$ lying in the acute angle between (100) and (010) , e.g., (310) (130) .

(2) Planes ($k\bar{h} + \bar{k}0$) lying in the acute angle between (0 $\bar{1}$ 0) and (1 $\bar{1}$ 0), *e.g.*, (1 $\bar{4}$ 0) (3 $\bar{4}$ 0).

(3) Planes ($\bar{h} + k\bar{h}0$) lying in the acute angle between ($\bar{1}$ 10) and ($\bar{1}$ 00), *e.g.*, ($\bar{4}$ 30) ($\bar{4}$ 10).

In spite of the equality of a and b , corresponding planes obtained by successive rotations through (approximately) $\pi/3$, such as (310) (1 $\bar{4}$ 0) ($\bar{4}$ 30), show considerable divergence of spacing, because of the obliquity of the c axis to the (001) plane. It was necessary, therefore, to compare not intensities but structure factors for each of these series of planes. The structure factors S were obtained from the observed intensities I by means of the formula

$$S \propto \sqrt{I} \div \left(\Sigma F e^{-M} \times \sqrt{\frac{0.15 + \cos^2 2\theta}{\sin 2\theta}} \right)$$

where $(0.15 + \cos^2 2\theta)$ is a measure of the polarisation factor for MoK α radiation under the conditions of the experiment.*

F is the scattering power of the atom,

e^{-M} is the temperature factor.

Now to a first approximation the effect of the hydrogen atoms must be neglected and therefore the value of Fe^{-M} taken applies to carbon atoms only. Miss Knaggs, of the Davy Faraday Laboratory, very kindly supplied me with some unpublished data concerning the temperature factors for graphite and diamond. She found that for diamond no change either of spacing or of intensity could be observed after a decrease in temperature from 15° C. to -183° C. This result agrees with previous high temperature observations by Backhurst† and low temperature observations by Ehrenburg, Ewald and Mark‡ on various planes of diamond. Similar measurements made by Backhurst on the (0001) cleavage plane of graphite showed a decrease of intensity of about 10 per cent. over a range of 900° upwards from room temperature. Miss Knaggs, however, found that not only were the absolute measurements of intensity for that plane identical, within the limits of experimental error, at 15° C. and at -183° C., but that the relative intensities of all orders up to the fourth were also the same at the two temperatures. She agreed with Backhurst in finding an abnormally large coefficient of expansion perpendicular

* Bishop, 'Phys. Rev.', vol. 28, p. 625 (1926); Kirkpatrick, 'Phys. Rev.', vol. 29, p. 632 (1927).

† 'Roy. Soc. Proc.,' A, vol. 102, p. 340 (1922).

‡ 'Z. Krist.', vol. 66, p. 547 (1928).

to the (0001) plane of graphite. These observations show that the temperature factor for carbon can safely be neglected.

A difficulty arose in the evaluation of F . It was found that when the structure factors were calculated using Ponte's* F curve, derived from measurements on diamond, the results so obtained were still slightly dependent upon the angle of deviation. This is also true of the observations on graphite recorded by Bernal (*loc. cit.*). Although other considerations have shown rigorously† that the carbon atoms in graphite all lie in the (0001) planes, yet the structure factors deduced for the various orders of reflection from that plane are *not* equal, if Ponte's F curve is adopted, but exhibit a regular falling off with increased angle of diffraction. Moreover, Ponte himself mentions that his one observation on graphite leads to a value of F_c not on his curve, and suggests that F_c may decrease more rapidly with $\sin \theta$ for graphite than for diamond. An attempt to obtain an F curve more applicable to this compound was therefore made as follows: the observations of the relative intensities of five orders of graphite (0001) are recorded by Bernal as

$$100 : 12.4 : 2.0 : 0.4 : 0.08 : 0.$$

Now according to Ponte the absolute value of F_c corresponding to the first of these is 3.4, and the structure of graphite is such that the structure factors calculated from each of the orders should be the same. Hence since

$$S_{0001} \propto \sqrt{I} \div \left(F_c \times \sqrt{\frac{1 + \cos^2 2\theta}{\sin 2\theta}} \right), \text{ approx.,}$$

we see that

$$\begin{aligned} \frac{F_c^{000n}}{F_c^{0002}} &= \sqrt{\frac{I_n}{I_2} \times \frac{1 + \cos^2 2\theta_2}{1 + \cos^2 2\theta_n} \cdot \frac{\sin 2\theta_n}{\sin 2\theta_2}}, \\ F_c^{000n} &= \frac{3.4}{10} \sqrt{I_n \times \frac{1 + \cos^2 2\theta_2}{1 + \cos^2 2\theta_n} \cdot \frac{\sin 2\theta_n}{\sin 2\theta_2}}. \end{aligned}$$

Thus the lower curve shown in fig. 3 was obtained. It is not claimed that this is necessarily a true F curve for graphitic carbon, but only that under the given experimental conditions it represents the falling off of scattering power with $\sin \theta$.

Since we do not know whether the carbon atoms in $C_6(CH_3)_6$ behave like those in diamond or in graphite, two sets of structure factors have been calculated using each of the above curves. These may be regarded as limiting

* 'Phil. Mag.,' vol. 3, p. 195 (1927).

† Ott, 'Ann. Physik,' vol. 85, p. 81 (1928).

values of the structure factors for the given planes. However, the use of the "graphite" F values practically removed the dependency on angle previously

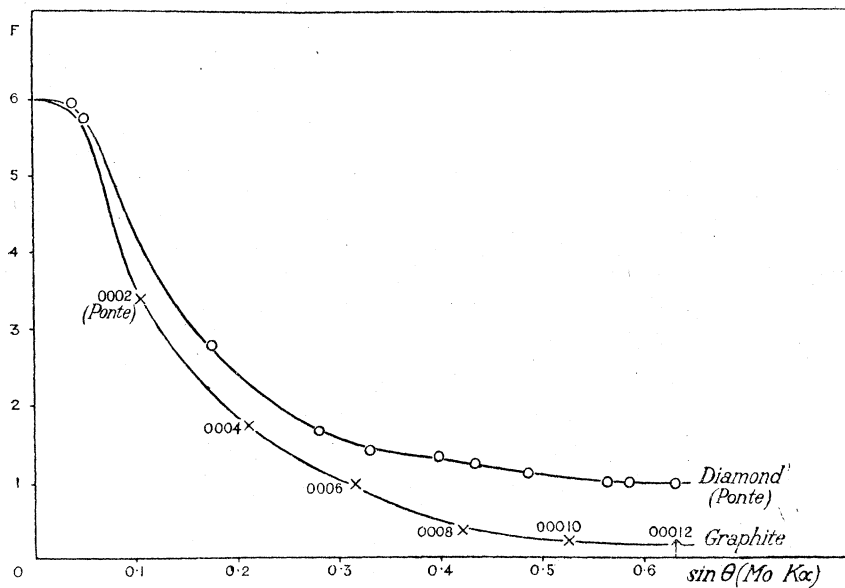


FIG. 3.— $F : \sin \theta$ (MoK α).

remarked, and therefore it is likely that they represent the variation in scattering power most closely. The series of "observed" structure factors thus obtained for each of the three groups of planes are shown graphically in fig. 4.

The curves given are based on the behaviour of graphite. The crosses show the structure factors calculated on the behaviour of diamond. The difference is not great except in the case of small-spacing planes. When no reflection was found from the plane in question an arrow is drawn, the height of which represents the structure factor corresponding to the minimum observable intensity. The actual structure factor for the given plane must then lie somewhere along the arrow and cannot be greater than the height of the arrow. For the sake of comparison, similar arrows are shown for planes whose reflections were more intense than this minimum value. The height of the arrow is obviously an inverse measure of the spacing of the plane, and the ratio of the observed structure factor to the height of the arrow is a measure of the probable accuracy of the factor. The intensities used are not absolute values, but are merely the "peak" value of the intensity for each reflection, relative to that of (001). Owing to the extreme softness of the crystals it was not possible to obtain any required section, and the shape of the crystal has

undoubtedly influenced the relative intensities to a certain extent. In spite of this, a remarkable similarity is at once observable between the three groups

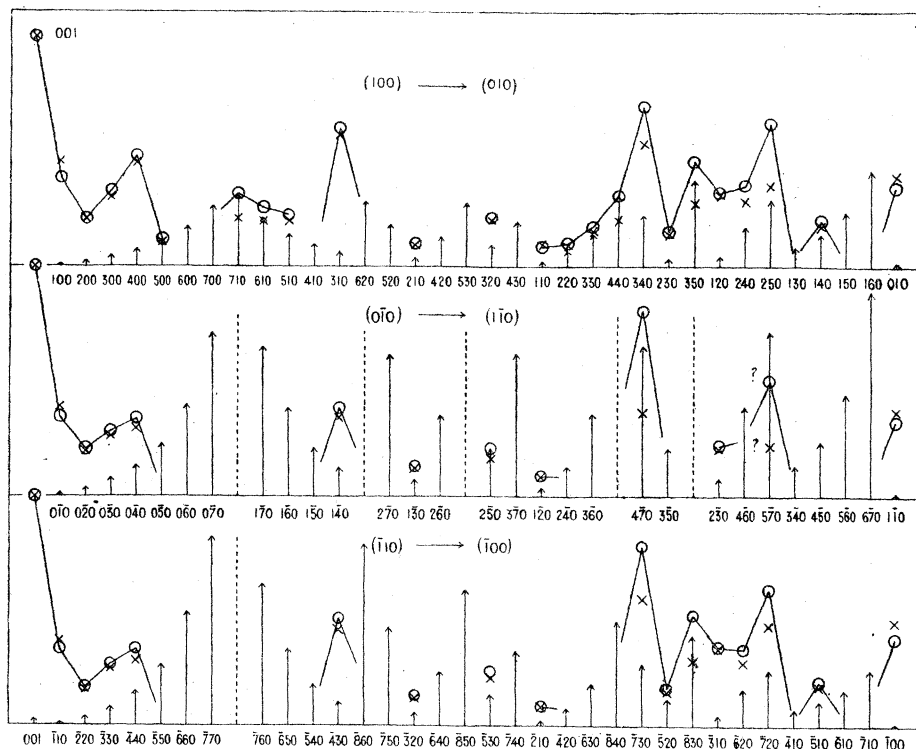


FIG. 4.

of structure factors. This indicates most clearly a hexagonal arrangement of atoms in the $[001]$ zone.

The reflections from the (001) cleavage plane were also of great interest. It was found that the intensities fell off regularly in the first four orders, no further orders being observable. The relative values were

$$100 : 9.51 : 1.87 : 0.29 : < 0.08 : < 0.08.$$

Using the "diamond" and "graphite" F values respectively, the corresponding structure factors are proportional to

$$\begin{array}{ccccccc} 2.21 : 1.93 : 1.71 : 1.10 : < 0.89 : < 1.35 \\ \downarrow \quad \downarrow \quad \downarrow \quad \downarrow \quad \downarrow \quad \downarrow \\ 2.64 : 2.45 : 2.65 : 2.52 : < 3.28 : < 7.01 \end{array}$$

It is clear that there is a marked similarity between the reflection from this plane and those from the corresponding cleavage plane of graphite. Moreover,

the structure factor obtained from the observations is larger than that for any other plane in the crystal. These two facts combine to prove that the carbon atoms, at least, all lie in or near the (001) planes. The question now arises: How near do they lie? An answer to this question is best attempted after the approximate positions of the atoms have been found.

Location of the Carbon Atoms.

It has been mentioned above that the structure factor for (001) was the largest observed. The factors for the planes (340) (470) and (730) are, however, almost as large. This is very important, because these are small-spacing planes, and therefore any deviation of the atoms away from these planes will cause a more rapid falling off of structure factor than would a similar movement away from a plane of larger spacing. In other words, the exceptionally large factors observed for these planes prove that the carbon atoms must lie at or very near their intersections with one another. There are 36 such intersections in the unit cell (fig. 5) and only 12 carbon atoms for which to find

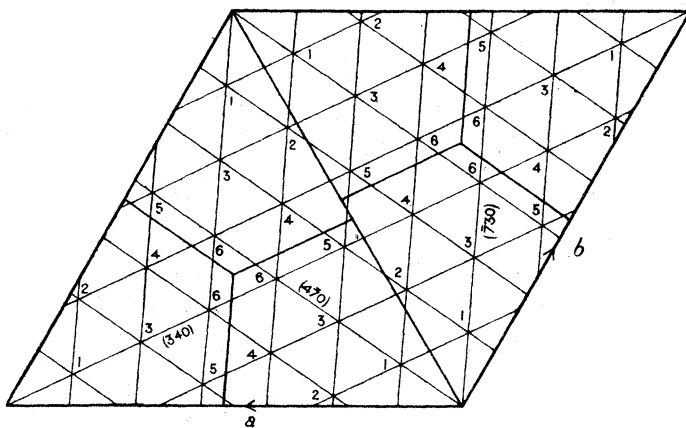


FIG. 5.

places. The problem is considerably simplified by the fact, already demonstrated, that there is a hexagonal arrangement of atoms in the [001] zone. If it can be shown which two of the positions 1—6 in one sector are occupied by carbon atoms, then the positions of the remaining ten carbon atoms automatically follow. Fifteen possibilities present themselves if only two out of six positions are to be filled. It is a simple matter to calculate structure factors for, say, the first six orders of the (100) plane for each of these possibilities. These calculations are shown graphically in fig. 6.

It will be seen that only one arrangement fulfils the necessary conditions, namely, that the second, fifth and sixth orders should all be smaller than the

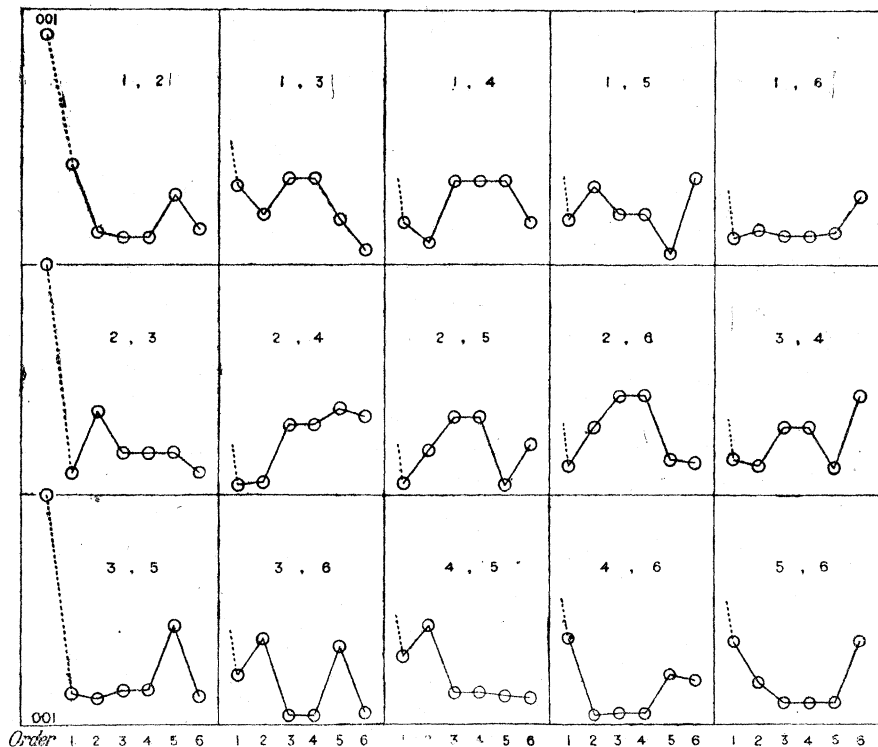


FIG. 6.

first, third and fourth (compare observed factors in fig. 4). This arrangement involves the placing of carbon atoms in the positions 1 and 3, and the ten corresponding positions obtained by rotation through $2\pi/6$ in the (001) plane, about the c axis (fig. 7).

A number of important deductions can be made even from this approximate result :—

- (1) *The molecule exists in the crystal as a separate entity.*
- (2) *The benzene carbon atoms are arranged in ring formation.*
- (3) *The ring is hexagonal or pseudo-hexagonal in shape.*

These facts have been believed by chemists for a long time and nearly all the models which have been suggested have conformed to these rules ; but so far no aromatic substance except the one under investigation has had a simple enough structure for the positions of the separate atoms to be found *without*

any previous hypotheses as to the shape or size of the molecule. The above reasoning, in fact, supplies a definite proof, from an X-ray point of view, that

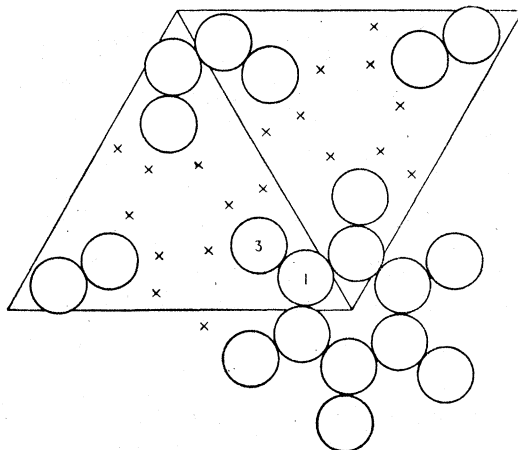


FIG. 7.

the chemist's conception of the benzene ring is a true representation of the facts.

The mean distance from centre to centre of adjacent carbon atoms in the molecule is 1.48 \AA . (The slight difference between a and b and the deviation of γ from 120° of course involves a slight variation in the distances from one intersection to another.) This distance is a mean of the carbon diameters in diamond (1.54) and in graphite (1.42). We must now see whether the carbon atom positions and the consequent diameters can be found more exactly.

The carbon atoms have been placed at such of the intersections of (340) (470) (730) and (001) that they actually lie along the lines

$$\left. \begin{aligned} 3x/a + 4y/b &= 0 \\ 4x/a - 7y/b &= 0 \\ -7x/a + 3y/b &= 0 \end{aligned} \right\} \quad (\text{A})$$

at distances of about 1.48 and 2.96 from the origin. Three kinds of variation from these positions are now to be investigated:—

- (1) A motion away from or towards the origin along the lines A, *i.e.*, a variation in the atomic diameters and consequently in the size of the ring.
- (2) A variation in the directions along which the atoms lie, *i.e.*, a rotation of the ring as a whole in the (001) plane.
- (3) Shifts of the atoms perpendicular to the (001) plane, *i.e.*, a puckering of the benzene ring and side-chain carbon atoms.

The effect of each kind of variation upon the structure factors is best shown graphically.

Result of Variation in Atomic Diameters.

The co-ordinates of the points of intersection at which the carbon atoms lie are :—

Aromatic : $(\mp \frac{7}{37}a \pm \frac{4}{37}b \ 0) (\pm \frac{3}{37}a \pm \frac{7}{37}b \ 0) (\mp \frac{4}{37}a \pm \frac{3}{37}b \ 0)$

Aliphatic or side-chain : $(\pm \frac{14}{37}a \pm \frac{8}{37}b \ 0) (\pm \frac{6}{37}a \pm \frac{14}{37}b \ 0) (\mp \frac{8}{37}a \frac{6}{37} \pm b \ 0)$

Their exact distances from the origin are 1.488, 1.472, 1.472, 2.976, 2.944, 2.944. For purposes of calculation it is much easier to leave the distances in these proportions than to make them exactly equal. The effect of this approximation upon the structure factors is negligible at the present stage. Fig. 8 (a) is a composite curve showing the "observed" structure factors obtained by taking the mean of the three curves given in fig. 4. Where no reflection was observed, the arrow given is that corresponding to the smallest of the three arrows, and the structure factor must be understood to be less than that amount. The structure factors for the planes (100) \rightarrow (010) [or (0 $\bar{1}$ 0) \rightarrow (1 $\bar{1}$ 0), or (1 $\bar{1}$ 0) \rightarrow ($\bar{1}$ 00)] have been calculated on the assumption that the atoms lie in the above initial positions and the resulting curve is shown in fig. 8 (b). The (001) values are also shown in each case, and for the sake of comparison the calculated and observed structure factors have been made to correspond for this one plane, since the observations are entirely relative. The following curves (c)–(h) show typical results of variation in the distance of the atoms from the origin. Actually a considerably larger parameter range was tested in order to obtain definite limits for the possible values of the radii. The agreement is clearly much better when the diameter of the aromatic carbon atom is less than 1.48 (e) (f) than when it is greater (c) (d). If, however, the diameter is decreased too much obvious discrepancies begin to appear. As suggestions have recently been made* that the diameter of carbon in organic compounds may be as small as 1.30, curves (g) and (h) have been given, in the first of which the aromatic carbon diameter is 1.42 and the aliphatic 1.30, and in the second the diameters of both aromatic and aliphatic carbon atoms are 1.30. The agreement in the first case is distinctly poor, and the second is quite out of the question. The best agreement is obtained when the diameter of aromatic carbon is 1.42 ± 0.03 Å. and that of the side-chain (aliphatic) carbon 1.54 ± 0.12 Å. Thus *the aromatic carbon atom is of the same*

* Hendricks, 'Z. Krist.', vol. 68, p. 189 (1928).

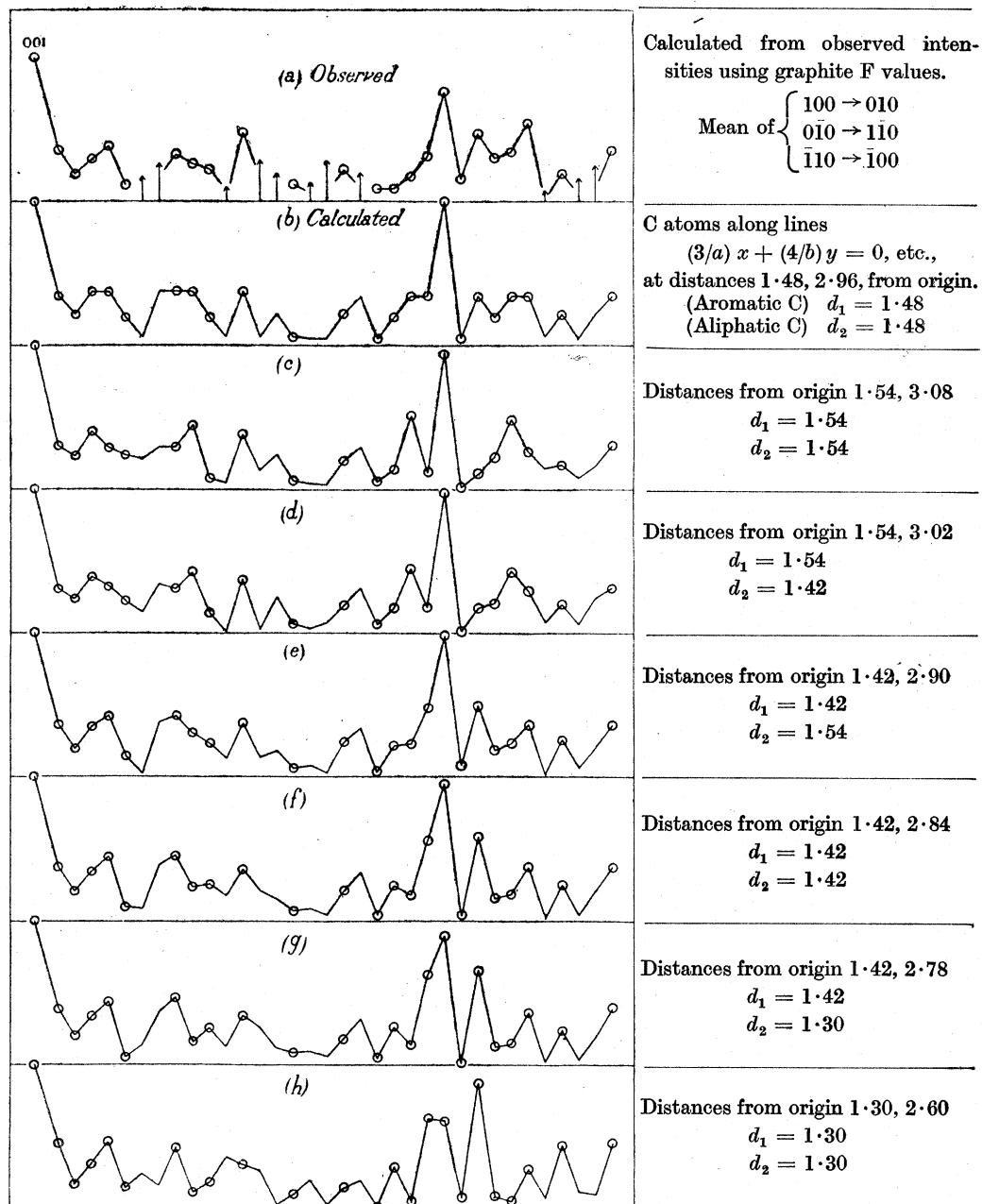


FIG. 8.

size as that in graphite. The carbon atom in the methyl group will be considered more fully at a later stage.

Result of Rotation of Ring in the (001) Plane.

The angle between the a axis and the line $\frac{7}{a}x - \frac{3}{b}y = 0$ is 94° . The line $\frac{2}{a}x - \frac{1}{b}y = 0$ makes an angle of $89^\circ 46'$ with a . Thus by turning the whole system of atoms in an anti-clockwise direction through $4^\circ 14'$, the molecule is brought into a "symmetrical" position, in which the a , b and $[1\bar{1}0]$ directions bisect the sides of the benzene ring. As fig. 9 (a) shows, this has a disastrous

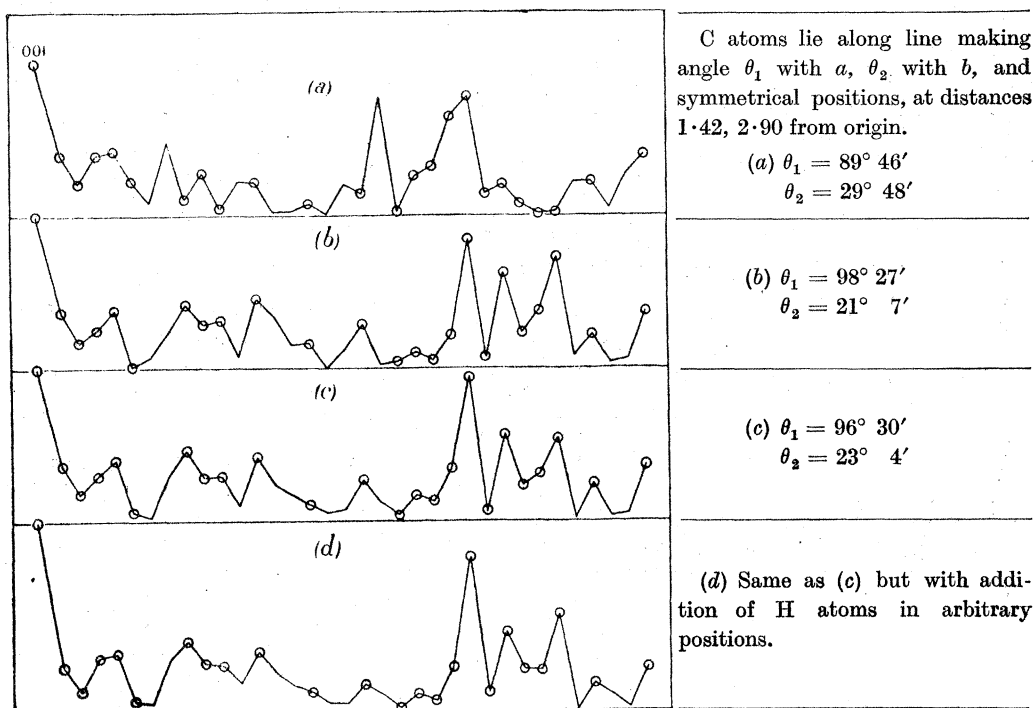


FIG. 9.

effect upon the calculated structure factors. Thus the factors for (430) (340) become equal, as do also those for (310) (130); whereas observation has shown that the structure factor of (430) is small and that of (340) very large, and similarly that of (310) is fairly large and that of (130) very small. The calculated curve has been given on a basis of 1.42, 1.54 as the aromatic and aliphatic carbon diameters respectively. but the same result would apply for any other

figures ; it is simply the effect of placing the ring symmetrically with respect to the *a* and *b* axes.

An almost equal rotation (of $4^{\circ} 27'$) in a clockwise direction from its initial situation will bring the ring into such a position that one of its sides is perpendicularly bisected by the *projection* of the *c* axis upon the (001) plane. It will be seen from fig. 9 (*b*) that in some respects the agreement with observation is improved by this movement, the factors for (310) and (250), for example, being increased. In other respects, however, the agreement is not so good. Fig. 9 (*c*) shows the result of a clockwise rotation of only $2^{\circ} 30'$, the atoms being still left at distances of 1.42, 2.90 from the origin, and this curve combines the best features of both 8 (*e*) and 9 (*b*). At this stage it was thought advisable to consider the possible effect of the neglected H atoms upon the structure factor calculations. There are 18 H atoms in the unit cell. Since their scattering power is small compared with that of the carbon atoms, the arguments used above in limiting the positions of the latter cannot be held to apply to the H atoms. They are not necessarily in or even near the (001) plane and they may not be arranged trigonally or hexagonally about the centre of the ring. In fact it does not seem feasible to attempt their exact location. An estimate of their importance may, however, be gained by placing them arbitrarily in any reasonable positions (say, by distributing them evenly about the unoccupied space in the cell) and then calculating the effect upon the structure factor curve. For example, fig. 9 (*d*) shows the result of placing all the atoms in the (001) plane and one-third of the way between nearest C atoms in neighbouring molecules (see small crosses in fig. 7). It is clear that no great errors are introduced by the neglect of the H atoms, since their arbitrary insertion in reasonable positions in the structure causes scarcely any disturbance of the agreement previously attained. Naturally, it would be possible to find positions for the H atoms which would materially upset the agreement, but such positions are special cases and the very closeness of the agreement shows that they are unlikely. Thus in fig. 9 (*d*) the factor for (001) is relatively too large, but that is because (for convenience' sake) the H atoms were given a very special position with regard to that one plane.

Result of Puckering the Ring.

That the carbon atoms must lie very near, if not in, the (001) plane, is proved not only by the large structure factor and "normal" intensity decrease for the various orders of that plane, but also by the fact that the observed structure factors for planes in general are almost independent of their last index "*l*."

Thus fig. 10 (a) shows the observed structure factors for the set of planes (hll) and in fig. 10 (b) are given the observed factors for the corresponding planes $(h\bar{l}0)$. The similarity is most marked.

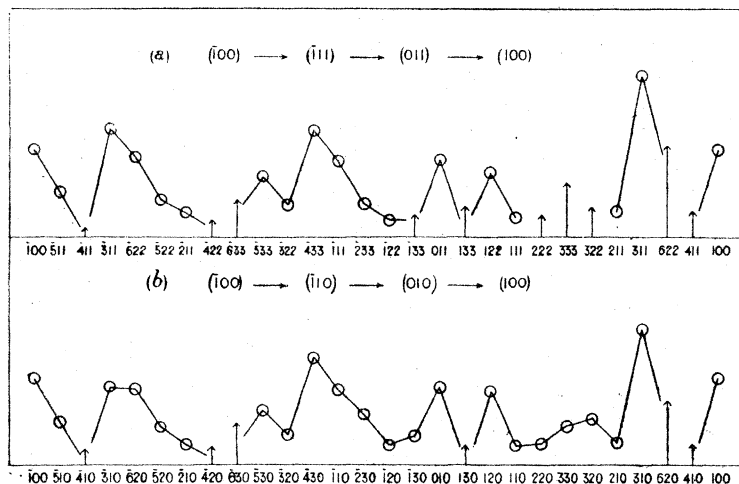


FIG. 10.

The structure factors are calculated from the assumed positions (x, y, z) of the atoms of scattering power A according to the formula

$$S = \sum A \cos 2\pi \left(\frac{h}{a}x + \frac{k}{b}y + \frac{l}{c}z \right).$$

Since this expression has to be very nearly independent of l , z must be zero or very near zero for all the atoms. Any puckering of the ring is bound to be shown up most clearly in the smaller spacing planes having high values of l . It will also, however, disturb the hexagonal structure in the $[001]$ zone, as can be seen from fig. 11.

This shows the projections *along the c axis* on to the (001) plane of various

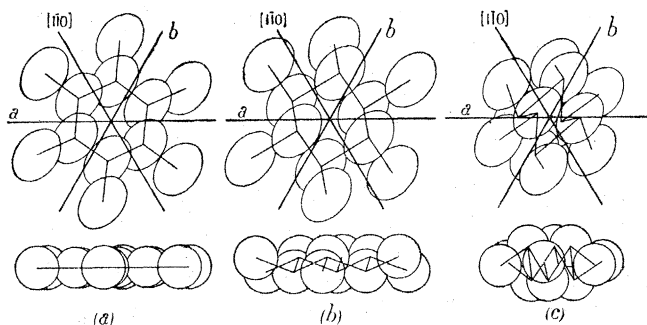


FIG. 11.

types of molecule. The spherical atoms of course project into ellipses, the ratio of the minor to the major axis being equal to the ratio of the (001) spacing to the length of the c axis. In each case the length of the minor axis is the same as the diameter of the actual atom. Only this oblique projection can show the effect on the [001] zone of movements of the atoms perpendicular to the (001) plane. The plane molecule of course retains its hexagonal configuration after projection (fig. 11 (a)). The greater the puckering, the greater the departure from hexagonal symmetry in the projection. Fig. 11 (b) shows the appearance of the "diamond" type of benzene ring after projection. Fig. 11 (d) represents the projection of the model suggested by Morse* in which the aromatic carbon atoms would lie at distances of ± 0.611 and the side-chain carbon atoms at ∓ 0.06 Å. from the (001) plane.

In order to introduce both effects, *i.e.*, the effect on the hexagonal symmetry in the [001] zone and the effect on planes having high values of l , a selection of the observed structure factors has been given in fig. 12 (a). In fig. 12 (b) the corresponding calculated structure factors are shown for the arrangement of carbon atoms (neglecting the hydrogens) which was found to give the best agreement for all planes in the [001] zone (see fig. 9 (c)). The co-ordinates of these atoms are shown in Table I. They lie along lines making angles of θ_1 with $+a$ and θ_2 with $+b$, at distances of 1.42 and 2.90 Å. from the origin.

Table I.

θ_1 .	θ_2 .	Aromatic carbons.	Side-chain carbons.
° ' ''	° ' ''		
+ 96 30	- 23 4	A (+ 0.64 + 1.62 0)	G (+ 1.31 + 3.31 0)
+156 30	+ 36 56	B (- 0.98 + 0.65 0)	H (- 2.00 + 1.33 0)
-143 30	+ 96 56	C (- 1.62 - 0.97 0)	J (- 3.31 - 1.98 0)
- 83 30	+156 56	D (- 0.64 - 1.62 0)	K (- 1.31 - 3.31 0)
- 23 30	-143 4	E (+ 0.98 - 0.65 0)	L (+ 2.00 - 1.33 0)
+ 36 30	- 83 4	F (+ 1.62 + 0.97 0)	M (+ 3.31 + 1.98 0)

Fig. 12 (c) shows the result of leaving atoms G-M in the (001) plane, but of shifting A, C, E through 0.255 Å. perpendicular to (001) on the $+c$ side and B, D, F by the same amount in the negative direction. This has the effect of puckering the ring to just the extent required for the "diamond" structure. The projection of the c axis on the (001) plane makes an angle of only about 9° with the b axis, and therefore atoms lying outside the (001) plane are in projecting moved nearly parallel to (100). Hence the structure factors for the

* Morse, 'Proc. Nat. Acad. Sci.' vol. 13, p. 789 (1927).

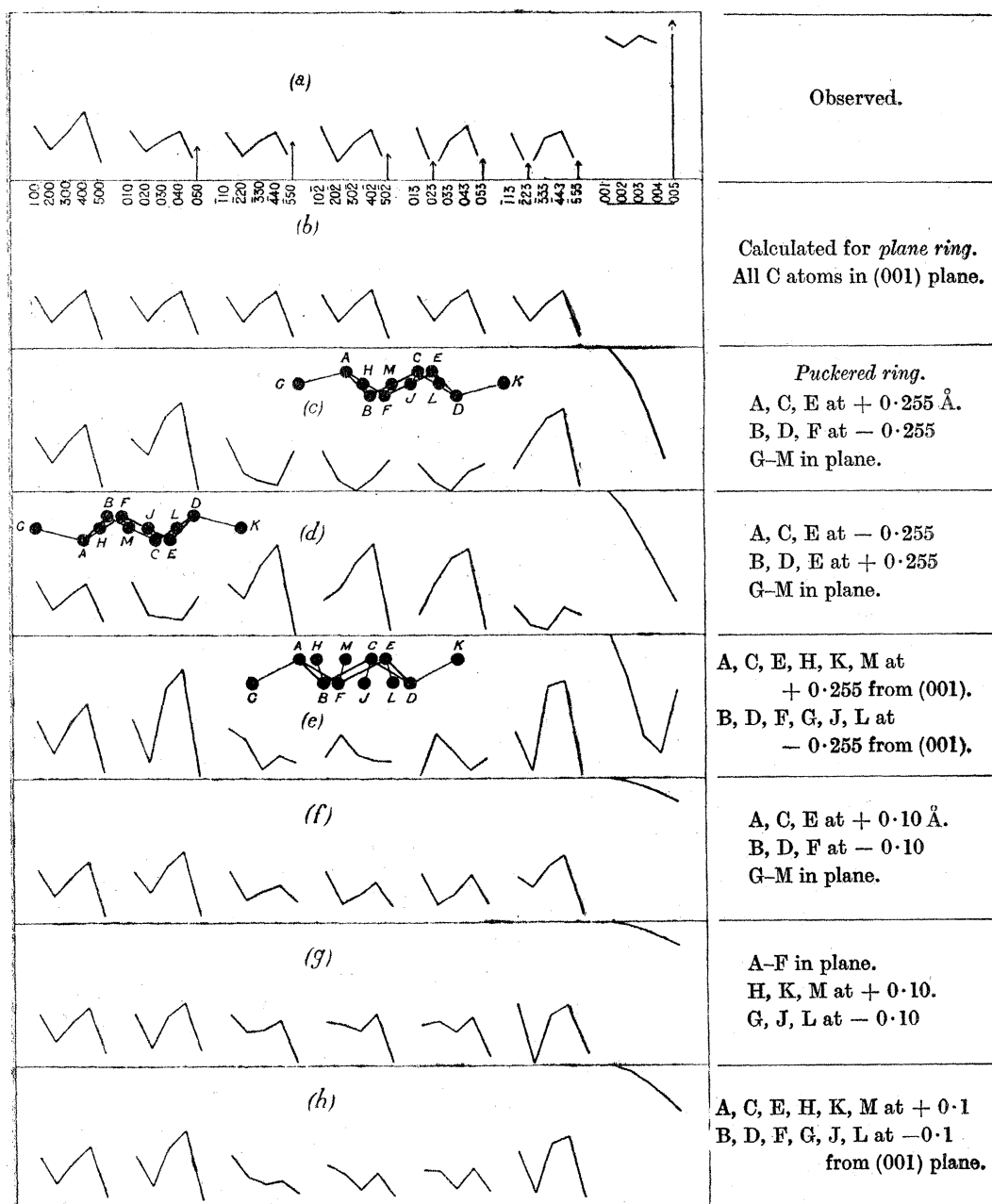


FIG. 12.

various orders of (100) are not much affected by puckering. Those of (010) and (1 $\bar{1}$ 0) are affected almost equally by movements in opposite directions. This is seen by comparing (c) and (d), the latter being obtained by an inversion of the ring, so that A, C, E are at a perpendicular distance of -0.255 Å. from (001), and B, D, F at $+0.255$. In both cases the agreement is completely spoilt. The hexagonal structure in the [001] zone is lost and the structure factors are now markedly dependent upon the value of l . The effect of shifting the side-chain C atoms, G-M, perpendicular to the (001) plane is to accentuate the disagreement even further (fig. 12 (e)). The calculations illustrated in (f) (g) and (h) show, in fact, that neither the nuclear nor the side-chain carbon atoms can be as much as 0.1 Å. from the (001) plane. Variations of the first two co-ordinates of the atomic positions do not alter this result, in fact small movements of the atoms *parallel* to the (001) plane do not appreciably affect curves (c)–(h).

Thus the "diamond" type of benzene ring is shown to be wholly inadmissible.

Other models, such as that of Morse, in which the carbon atoms are even further from the (001) plane, can be dismissed simply by a consideration of the structure factors for that plane only, irrespective of their position relative to the [001] zone. The relative values of the structure factors are shown in Table II.

Table II.

	001	002	003	004	005	006	100	010	1 $\bar{1}$ 0
Observed { Diamond F values using { Graphite F values	100 100	87.5 92.8	77.5 100.3	49.9 95.3	<40.4 <124	<61.2 <268	45.3 38.2	39.0 34.3	37.2 32.8
Calculated for carbons only— Plane ring (Table I)	100	100	100	100	100	100	35.2	34.5	34.2
Diamond type ring { G-M in (001) A, C, E ± 0.255 { G-M at ∓ 0.255 B, D, F ∓ 0.255 { G-M at ± 0.765	100 100 100	86.4 71.3 -17.9	66.5 28.4 -39.3	44.1 -17.8 26.2	23.1 -61.8 35.5	7.5 -94.5 -68.5	36.4 40.4 39.5 58.8 64.8	34.6 35.7 41.3 35.8 44.1 75.1	35.3 34.1 34.9 41.3 76.8 40.7
Morse ring { Aromatic carbons at 0.865 from origin, ± 0.611 from (001), aliphatics at 1.90, and ∓ 0.06 Å }	100	32.8	- 3.1	25.7	88.8	120.9	91.9 91.9	86.6 86.6	84.5 84.5

The very compactness of the Morse model is also a drawback, since that is bound to lead to a structure factor for (100) which is much too large compared with that for (001). The figures in the last three columns of Table II are

obtained on the assumption that the atoms lie along the directions given in Table I (first and second columns), but the result is not changed much by a rotation of the ring into any other position.

The conclusions are that :—

- (1) *Only a plane ring can account both qualitatively and quantitatively for the hexagonal structure of the [001] zone, for the lack of dependence upon l and for the relative values of the structure factors observed for (001) and a large number of other planes.*
- (2) *The diameter of the aromatic carbon atom is 1.42 ± 0.03 Å., that is, the ring is similar to that occurring in graphite, not only in structure but also in dimensions.*

Structure and Position of the Methyl Groups.

It has already been shown in fig. 12 (g) that the side-chain carbon atoms cannot even be as much as 0.10 Å. away from the (001) plane, and that they are therefore co-planar with the ring itself. In order to complete the structure determination it is necessary to consider whether the methyl group scatters as a whole or not. Fig. 13 (a) shows the result of placing the atoms as in Table

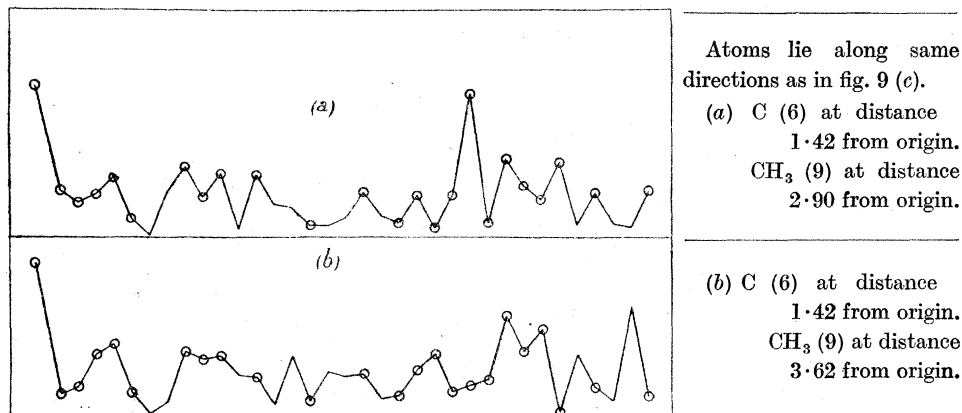


FIG. 13.

I, but of taking the scattering power of the side-chain group as 9, as compared with 6 for that of the aromatic carbon. The agreement is not quite as good as before; nor is it materially improved by slight variations in the positions of the atoms. If the hydrogen atoms had actually given up their electrons to the carbon of the methyl group, this arrangement should have given a better agreement with experiment, since the whole of the scattering material in the

cell would be accounted for. Fig. 13 (b) shows the result of placing a group of scattering power 9 along the line joining the origin to each aromatic carbon atom but at a distance of 3.62 from the origin (fig. 14). In such positions methyl groups of neighbouring molecules would touch one another in the (001) plane.

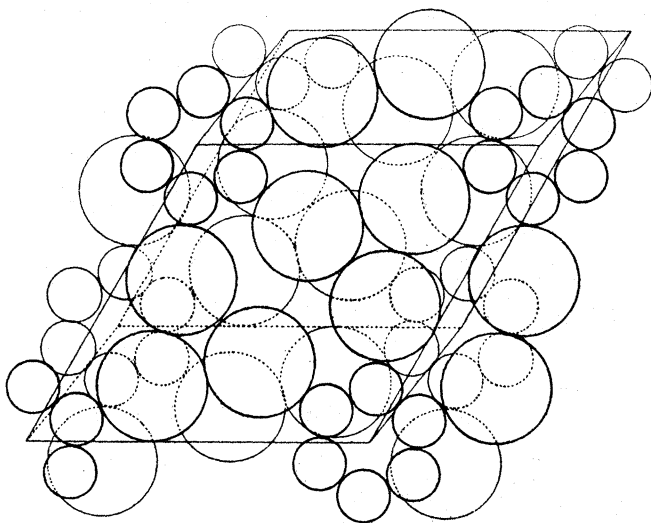


FIG. 14.—Orthogonal projection of unit cell on to (001) plane.

This arrangement, in which the methyl group, of diameter 3.0 Å., is considered to scatter spherically as a whole, is even more out of the question. It is quite clear that there cannot be anything like a spherical distribution of electrons in the methyl group. The group as a whole extends over such a volume that its "diameter" may be said to be about 3.0 Å., but it does not scatter like a single atom of the same diameter, such as Br or I. In scattering power it is heavily weighted at the end nearer to the benzene ring by its carbon atom, which appears to retain its own electronic system more or less unchanged. The hydrogen atoms do not appear to give up their single electrons to the carbon atom, but these probably form a kind of atmosphere enveloping the H nuclei. In fact the methyl group acts towards X-rays like an electronic shuttlecock, whereas single atoms behave rather like tennis balls. The carbon atom of the methyl group lies in the plane of the benzene ring so that, as in graphite, *three of the valencies of the aromatic carbon atom are co-planar*. The X-ray results can offer no direct evidence as to the behaviour of the fourth valency, except that it must be so disposed as to give the ring as a whole a centre of symmetry. This last condition quite eliminates the Kekulé static

model, with its three double bonds. The radius of the side-chain (aliphatic) carbon atom in the structure giving the best agreement with experiment (Table I, fig. 9 (c)) is 1.54 ± 0.12 Å. It appears, therefore, to resemble the carbon atom in diamond rather than that in graphite. The evidence in favour of this suggestion, however, is incomplete, since in this compound we cannot trace the directions of the three remaining valencies.

Concluding Remarks.

It is difficult to see exactly why this crystal should have been triclinic instead of, say, monoclinic like C_6Cl_6 or orthorhombic like benzene itself. The slight asymmetry in the (001) plane must be due to a certain lack of symmetry of the benzene ring together with a possible variation in the orientation of the attached methyl groups. This lack of symmetry, other than centro-symmetry, falls into line with previous observations (Mark, Cox, Bragg, *loc. cit.*) upon benzene and its fully-substituted derivatives. The displacement of successive (001) planes with respect to one another, illustrated in figs. 2 and 14, is, however, rather unexpected. A displacement certainly occurs in graphite also, but it is a symmetrical displacement. The centre of each hexagon of atoms lies vertically above an atom in the neighbouring (0001) plane. The displacement in the case of $C_6(CH_3)_6$ seems quite arbitrary. Two facts emerge from fig. 14, however, which may help to elucidate the problem. One is that the orthogonal projection of the c axis upon the (001) plane is almost perpendicular to one pair of sides of the benzene ring; and the other that the methyl groups (considered now as a whole, since it is only their volume that is in question) in one (001) plane lie more or less beneath the gaps in the plane above. Possibly if the exact shape and orientation of the methyl groups could be determined the problem of the crystal system would resolve itself into a question of the most convenient "packing." The (001) cleavage is readily explained since the cleavage planes are merely layers of flat molecules. Although very good, the cleavage is not, of course, as remarkable as the graphite cleavage, since the connection between the (001) planes is not between carbon and carbon, but between methyl and methyl, or carbon and methyl. The easy distortion of the crystals by slipping about the crystallographic axes may be caused by the rolling of methyl groups upon one another.

The writer had no available photographic apparatus when this investigation was undertaken, but Sir William Bragg was kind enough to allow photographs to be taken at the Davy Faraday Laboratory. Laue photographs taken by

sending the X-ray pencil along the c axis, like the ionisation spectrometer measurements, did not show the hexagonal structure directly. Only when the variation in spacing caused by the obliquity of the c axis to the (001) plane is allowed for, by calculation of the structure factors, does this hexagonal structure become revealed. A rotation photograph taken with the c axis as axis of rotation helped to confirm the size of the unit cell and the relative importance of some of the small-spacing planes. I am indebted to Dr. A. Müller for taking these photographs.

My thanks are also due to Prof. Ingold, F.R.S., who kindly supplied me with the material used in this investigation, to the Council of Bedford College, London, for a scholarship enabling me to work in the Physics Laboratories of the University of Leeds, and to the Royal Society for a grant covering the cost of some of the apparatus employed.

Summary.

The selected minimum cell of $C_6(CH_3)_6$ has dimensions

$$\begin{array}{ll} a = 9.010 \text{ \AA.} & \alpha = 44^\circ 27' \\ b = 8.926 & \beta = 116^\circ 43' \\ c = 5.344 & \gamma = 119^\circ 34' \end{array}$$

and contains one molecule, which is probably centro-symmetrical. The structure factors for a large number of planes have been calculated from the observed intensities and are found to obey the following rules:—

1. The factors in the [001] zone repeat themselves closely throughout the series of planes (100)→(010), (010)→(1 $\bar{1}$ 0) and (1 $\bar{1}$ 0)→($\bar{1}$ 00). They, therefore, indicate a hexagonal structure in the zone.

2. The factors are almost independent of the last index l , which shows that the carbon atoms at least must all lie within 0.1 Å. of the (001) cleavage plane.

It is shown from the relative values of the factors that a unique structure can be assigned to the molecule, which exists as a separate entity and has a ring form.

The benzene ring is similar in shape and size to the six-carbon ring in graphite, the aromatic carbon atoms having a diameter of 1.42 Å. Three of the valencies of aromatic carbon are co-planar, the ring itself and all the side-chain carbon atoms lying in one plane.

The methyl group does not scatter like a single atom but is heavily weighted in scattering power at the end nearer to the benzene ring.

The puckered or "diamond" type of benzene ring and the more compact model suggested by J. K. Morse are shown to be wholly inadmissible.