

## The Structure of Organic Crystals

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VI. *The Structure of Organic Crystals.* By. PROF. SIR W. H. BRAGG, K.B.E., M.A., F.R.S.

(PRESIDENTIAL ADDRESS, DELIVERED NOVEMBER 11, 1921).

## SUMMARY.

For many reasons the structure of crystals of organic substances invites examination by the methods of X-ray analysis; but their molecular complexity would seem to throw great difficulties in the way. It is possible, however, that the difficulties in the case of aromatic compounds may be surmounted by adopting a certain hypothesis, viz., that the benzene or naphthalene ring is an actual structure, having definite size and form, and that it is built as a whole into the organic substances in which it occurs. Reasons can be given why this is *a priori* probable.

The examination of certain organic crystals has been made. The results are in general agreement with the hypothesis, and lead to various deductions of interest.

THE structure of organic crystals offers a very inviting field of research by the methods of X-ray analysis. To the organic chemist the relative positions of the atoms in the molecule, as also of the molecules in the crystal, are of fundamental importance; and it is with these relations that the X-rays deal in a manner which is new and unique. Moreover, the multiplicity of crystalline forms—and this is true of both organic and inorganic substances—each so precise and invariable, and so obviously related to the atomic and molecular forces, is a sign that if the forces were better understood it would be possible to account for the forms that are known, and possibly to build others that are unknown. But in order to acquire such a power we must learn the crystalline structure, so that the physical characteristics of the whole may in the end be referred to the characteristics of the individual atom. Progress has been made with the examination of the structure of some of the simpler inorganic crystals; but organic crystals have been neglected. Their molecular complexity has been somewhat of a deterrent. Yet, if a way could be found of making determinations of structure, in spite of the complexity, it seems likely that they would quickly be fruitful. The substitutions and additions which are so characteristic of organic chemistry take place in such an immense variety of combinations and grades that the slightest knowledge of the underlying mechanism might lead to useful comparisons and rules.

I have made a careful study of a few crystals, principally naphthalene and some of the naphthalene derivatives, in order to discover, if possible, some way of handling the complex molecules. The numerical results will be set out later, and may, I think, be taken as sufficiently accurate to make foundations for a theory.

I shall endeavour to show that the results can be explained, so far as can be seen at present, by supposing the benzene ring or naphthalene double ring to have definite form and size, preserved with little or perhaps no alteration from crystal to crystal, and that there are good *a priori* reasons for the supposition. If this principle be accepted the problem is simplified at once. Naphthalene itself is then to be regarded as a structure in which there is but one element, the naphthalene double ring, and no longer as an aggregate of 10 carbon atoms and eight hydrogen atoms of unknown mutual arrangement. A more complex molecule such as either of the naphthols is not to be regarded as an addition of one oxygen atom to these 18, an idea on which nothing can be built, but as a naphthalene double ring of the same size and form as before, except that one particular hydrogen has been replaced

by a hydroxyl group. It is then possible to think what changes in the disposition of the molecules might be caused by such a substitution and to compare conceivable solutions with observations on the dimensions of the new crystal. Such a method of procedure is obviously in good agreement with the ideas of organic chemistry.

It is convenient to distinguish the facts regarding crystalline structure which can be obtained by the goniometer and various other means, from the new facts which can be obtained by the use of X-rays. The former are recorded in crystallographic tables such as are given by von Groth in his "Chemische Krystallographie." Naphthalene may be taken as an example. In the fifth volume of von Groth's work, on p. 363, a description of naphthalene is given from which the following data are taken:—

MONOCLINIC PRISMATIC.

$$a : b : c = 1.3777 : 1 : 1.4364 ;$$

$$\beta = 122^\circ 49'$$

The monoclinic prismatic class has the highest symmetry of which the monoclinic system is capable, having a diagonal axis and a plane of symmetry perpendicular to it. The figures give the angular, but not the linear, dimensions of the unit cell of the structure (Fig. 1); the unit cell being the smallest volume, of which, by

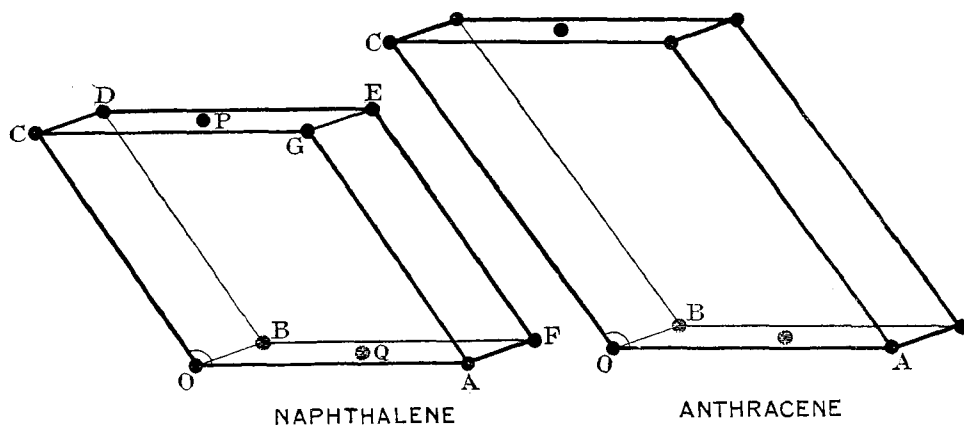


FIG. 1.—UNIT CELLS OF NAPHTHALENE AND ANTHRACENE DRAWN TO THE SAME SCALE.

	$OA = a$	$OB = b$	$OC = c$
Naphthalene ... ..	8.34	6.05	8.69
Anthracene ... ..	8.7	6.1	11.6
Naphthalene $\alpha = BOC = 90^\circ$ , $\beta = COA = 122^\circ 49'$ , $\gamma = AOB = 90^\circ$			
Anthracene $\alpha = BOC = 90^\circ$ , $\beta = COA = 124^\circ 24'$ , $\gamma = AOB = 90^\circ$			

continual repetition without any change in contents or disposition, the whole crystal can be formed. In any crystal it is possible to choose the unit cell in many ways, but they must all be capable of derivation from one another and must all have the same volume. The angular dimensions are to be considered as including the angular relations to one another of any pair of planes in the crystal, not merely of the planes bounding the cell.

It is also stated that the (001) face is the cleavage plane ; and that, in addition, the faces (110), (20 $\bar{1}$ ), (11 $\bar{1}$ ) are found as bounding planes of the crystal. The angles between various pairs of these faces are also given as observed. The specific gravity is stated to be 1.152. Other information is given by von Groth concerning the optical properties of the crystal ; also concerning the methods that have been adopted in growing the crystals from various solutions and the consequent effect on the development of different faces. These facts do not concern us for the moment, but they must be taken into account eventually.

The examination by X-ray analysis gives us the spacings between the planes and, therefore, the linear as well as the angular dimensions of the unit cell. The specific gravity being known, and the actual weight of the molecule, it is possible to find how many molecules are contained in each cell ; generally, two or four. In the case of naphthalene, it is found that, assuming the angular dimensions to be correctly given by the crystallographers, the linear dimensions are :—

$$a=8.34, b=6.05, c=8.69.$$

These figures are obtained in the following way :—

The actual length of the  $b$  axis being represented by  $b$ , the mass contained in the cell is

$$b^3 \times 1.3777 \times 1.4364 \times \sin 122^\circ 49' \times 1.152 \text{ A.U.}$$

(It is convenient in this work to extend the Angstrom system of units so that an A.U. of area is  $10^{-16}$  cm.<sup>2</sup>, of volume  $10^{-24}$  cm.<sup>3</sup>, and of mass  $10^{-24}$  gr.)

The mass of the hydrogen atom being 1.662 A.U., the mass of the molecule C<sub>10</sub>H<sub>8</sub> is  $128 \times 1.662 = 213$  A.U. Now, from the full results of the X-ray measurements which will be given presently, it is perfectly clear that there are two molecules in each unit cell. Hence, the value  $b$  is readily calculated, and the values of  $a$  and  $c$  also.

Besides these determinations of length, the X-ray method gives also the angle between any pair of planes, whether they form faces or not, provided that a measurable reflection can be found. Also, the relative intensities of the reflection by different faces, as well as the relative intensities of the spectra of different orders given by any one set of planes, yield information as to the distribution of the scattering centres and of the atoms which contain them.

There are two distinct methods of using the X-rays. In the one, which has been used from the beginning, a single crystal is employed. It need not usually weigh more than 2 or 3 milligrammes, and, in fact, it is more convenient that it should be small, since the pencil of reflected rays is then conveniently limited by the size of the crystal without the need for slits, which are still used, however, but as stops only. This method is at present the more precise of the two. Also it permits the measurement of the angles between reflected planes, a knowledge of which is often very useful for identifying the planes.

The second method, first used for crystal analysis independently by Debye, and by Hull, can be used when the crystal is in powder, and can, therefore, be employed when no single crystal can be obtained of sufficient size to measure by the first method. All the spectra of the different planes are thrown together on the same diagram or photograph, and must be disentangled. This is not so difficult as it might seem, because there are not more than one or two lines in each spectrum, and there is generally independent evidence as to the angular dimensions of the

crystal. The spectra of copper, and of some organic substances, shown in Figs. 2, 3, 4 and 5, were obtained in this way. The X-ray bulb employed was of the form

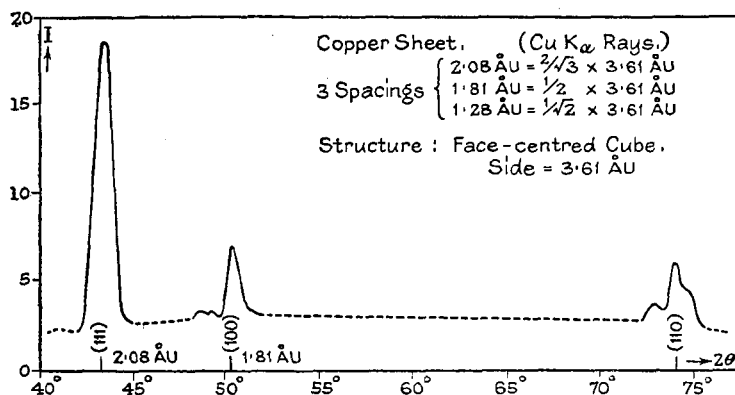


FIG. 2.—COPPER SPECTRUM, OBTAINED BY POWDER-IONISATION METHOD.

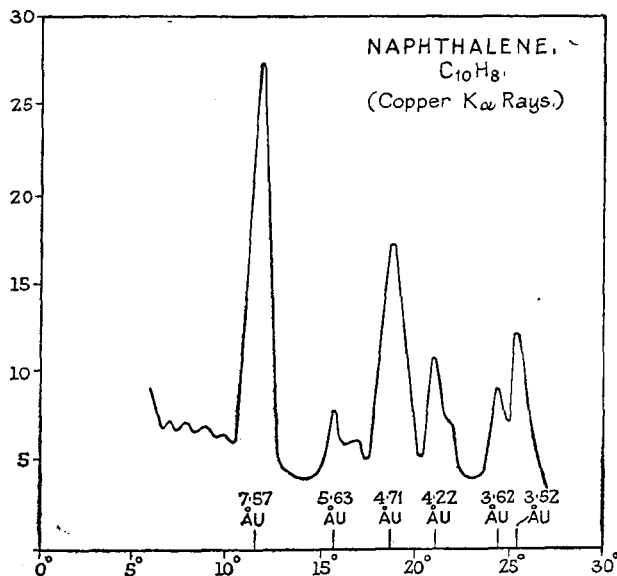


FIG. 3.—SPECTRUM OF NAPHTHALENE—POWDER METHOD. THE RESULTS AGREE WELL WITH THOSE OBTAINED BY THE SINGLE CRYSTAL METHOD, BUT ARE SLIGHTLY LARGER.

described by Müller.\* The way of using the powder in conjunction with an ionisation spectrometer has been described in the Proceedings of this Society.† Müller's

\* Phil. Mag., p. 419, September (1921).

† Proc. Phys. Soc., Vol. XXXIII., Part 4, p. 222, June (1921).

bulb is very well suited to this method. The spectrometer slit can be brought very close to the radiator; so that the slit becomes the source of a strong beam of rays which is sufficiently divergent to cover a large surface of the plate on which the

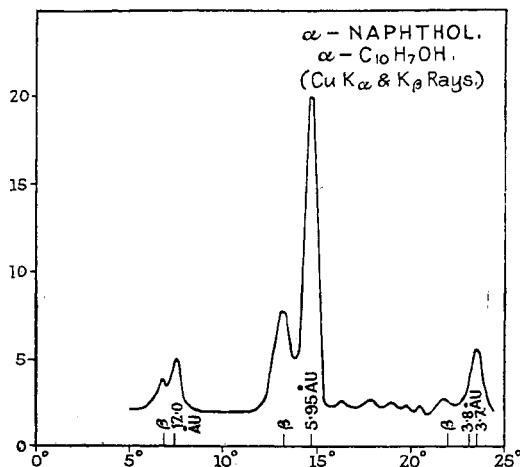


FIG. 4.—SPECTRUM OF  $\alpha$ -NAPHTHOL—POWDER METHOD.

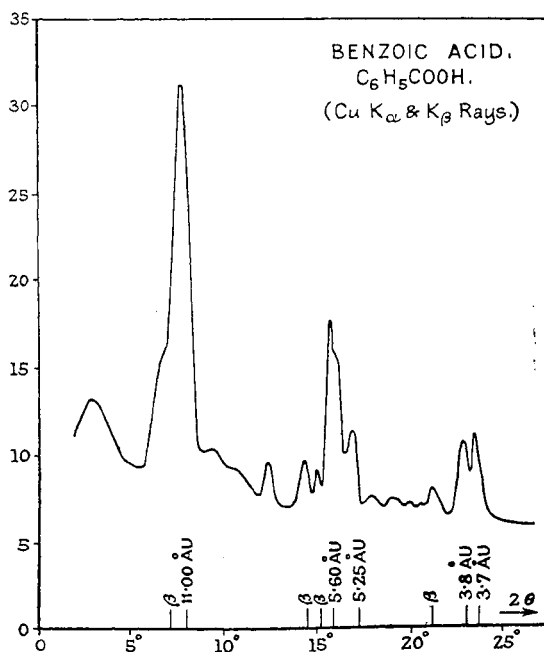


FIG. 5.—SPECTRUM OF BENZOIC ACID—POWDER METHOD.

powder is spread. By a known focussing action (X-rays and Crystal Structure, W. H. and W. L. Bragg, p. 31) the rays are converged upon the slit of the ionisation chamber. The anticathode used in these experiments was made of copper; the long wave lengths of the *K* series of copper give suitable angles of deflection even for the wide spacings that are found in organic crystals. The curve in Fig. 2 shows the spectrum of copper obtained by the use of copper-rays, and gives at once all the necessary information from which the structure of the copper crystal is derived. The piece of copper employed was of ordinary sheet, not prepared in any way. The spectra of the organic substances show how very diversified they are, and illustrate the power of a method of analysis which promises to be of great use, since every crystal has its own characteristic spectrum. The bulb was driven by a transformer

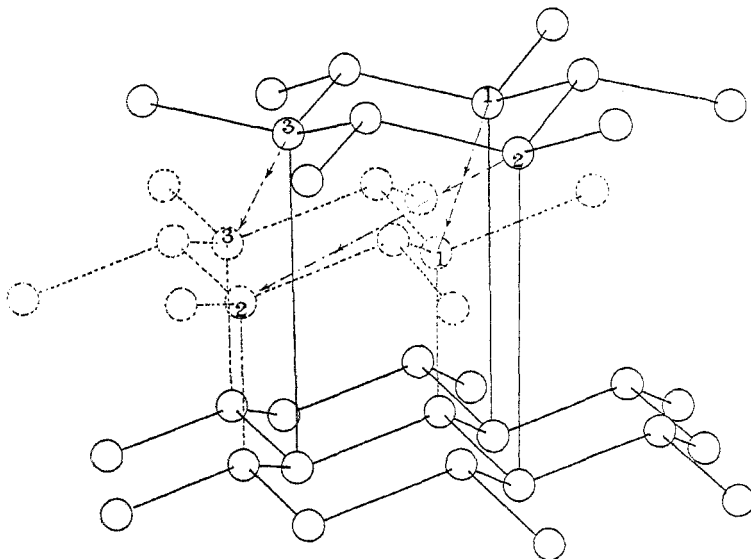


FIG. 6.—THE FINE LINES OF THE DIAGRAM SHOW THE STRUCTURE OF GRAPHITE. BY MOVING THE TOP LAYER TO THE POSITION SHOWN BY THE BROKEN LINES THE DIAMOND STRUCTURE IS OBTAINED.

capable of developing half a kilowatt; but not working to half of its full capacity. Each determination of a point on the curve took about 10 to 30 seconds.

We may now consider what reasons can be put forward for assuming the concrete existence of the benzene and naphthalene rings. If we examine the structure of the diamond we find that the atoms of carbon are tied together so that each is at the centre of gravity of four others. The distance from centre to centre is 1.54 A.U. As I have already pointed out\* the rigidity of the diamond and the open character of its structure, imply that great force is required to alter the orientation of any coupling with respect to the other three belonging to the same atom. Were it otherwise, all atoms would seek to be surrounded by as many neighbours as possible; the substance would be close packed, and its density would be more than double what it is. The structure of the diamond may also be looked on as consisting of a series of puckered

\* Proc. Phys. Soc., Vol: XXXIII., Part 5, August 15 (1921).

layers parallel to a given tetrahedral plane (see Fig. 6). A sharp blow may cleave the diamond, along one of these layers. If we take a model showing two layers as in graphite, lay hold of the upper layer, and move it to the new position shown in the figure, the structure is now that of diamond. I am following Hull's determination;\* Debye and Scherrer† would flatten out the puckers in the planes of graphite. The point is perhaps not important for our present purpose, but it is necessary, for descriptive purposes at least, to choose one form. According to Hull's measurements, the shortest distance between each pair of atoms lying in the same layer is shortened from 1.54 A.U.—the diamond spacing—to 1.50 A.U. The distance between two successive layers has been increased by 1.35 A.U. A carbon atom in one layer is now at equal distances from its three nearest neighbours in the next layer, the distance being 3.25 A.U.

The bonds between one layer and the next are now greatly weakened; the substance cleaves readily in thin flakes. One layer slides with great ease over the other, though the bonds between the atoms in any layer are at least as strong as before. When all the bonds were of the strong kind, the substance, as diamond, was the hardest thing known. When the one set of bonds has been weakened, the substance, as graphite, is used as a lubricant. Probably its efficiency as such depends both on the weakness of the one set of bonds and the strength of the other. Yet these new bonds are perfectly definite, and the distance between two layers and, therefore, the 3.25 distance between atomic centres is a perfectly constant and determinate quantity. It should be of great interest to compare the physical constants of graphite along and perpendicular to the axis, since in the two cases the two kinds of bonds are separately involved. Some of the comparisons would be difficult, but the thermal expansions can probably be compared by X-ray methods.

If the strong bonds between the atoms in a layer remain, and are even drawn a little tighter when the graphite form replaces that of diamond, it seems very reasonable to suppose that the single ring or multiple rings which are so clearly to be distinguished in the network may be separated out as such without loosening the bonds between their component atoms. In fact, these latter bonds might be expected to tighten even a little more. Let us assume that a single ring is a benzene ring, a double ring a naphthalene ring, and so on. Taking the spacings as given by Hull for graphite, the dimensions of the benzene and naphthalene frameworks are as shown in Fig. 7. The figure is constructed to show the arrangement of atoms in the naphthalene crystal, but it will also serve to illustrate the point under discussion. The carbon atoms *A* to *F* form a benzene ring, those from *A* to *J* the double ring of naphthalene.

The atom centres *A*, and *G*, are 0.71 A.U. above, and the centres *D* and *J* the same distance below the plane of the diagram which is supposed to contain all the remaining centres. It should be observed that circles are used to represent the atoms as a convenient method of designation, not as implying that the radius (1.50) may *always* be used in calculating the distance between the centre of any one atom, and the centre of any other atom.

We may now go on to consider individual crystals; and we take naphthalene first. It might have seemed more natural to attack the benzene crystal before the naphthalene; but the latter was chosen because it is a very well-shaped crystal, and is solid at ordinary temperature. Benzene can only be examined under special

\* Physical Review, X., p. 692, December (1917).

† Phys. Zeit., 13, p. 297 (1917).



temperature conditions and then only, with convenience, as a mass of small crystals. The study of benzene and some of its derivatives has been begun, but the greater attention has been given to the naphthalene crystals, and I will describe now the results that have been obtained in their case.

In the second column of Table I. are given the angles between certain pairs of planes as calculated from the data already given, viz. :—

$$a=8.34, b=6.05, c=8.69, \beta=122^{\circ}49',$$

and in the third the corresponding values as observed.

TABLE I.

Angles between.	Calculated.	Found.
100 : 001	57°11'	57°16'
110 : 11 $\bar{1}$	36°32'	36°34'
20 $\bar{1}$ : 001	85°45'	85°48'
021 : 001	67°47'	67°35'
20 $\bar{1}$ : 10 $\bar{1}$	30°21'	30°23'
210 : 21 $\bar{1}$	24°12'	24°24'

These figures are quoted in order to show that the X-ray method gives angular measurements with sufficient accuracy. Indeed the agreement between the values in the two columns is as good as is usually reported by different observers who have used the goniometer (*see* the descriptions recorded by von Groth); and the X-ray method could really be relied on to a minute of arc if the necessary care and time were justified. In this case no special pains were taken.

In the next table are set out the results of the linear measurements. They are compared with calculations based on the assignment of *one* molecule to each cell, which is equivalent to supposing each corner of the cell to represent a molecule. The object of making this provisional assumption is to show how the position of the second molecule can be found by comparing the observed with the calculated results.

TABLE II.

Plane.	Calculated spacing.	Observed spacing.	Nature of reflection.
100 .....	7.00	3.46	Strong: indication of spacing 6.92
010 .....	6.05	2.95	Very weak.
001 (Cleavage)	7.30	7.30	Very strong: also higher orders.
110 (Natural)	4.59	4.55	Strong.
11 $\bar{1}$ (Natural)	4.70	4.63	Moderate.
20 $\bar{1}$ (Natural)	4.17	4.12	Strong.
021 .....	2.79	2.76	Very weak.
10 $\bar{1}$ .....	7.51	3.71	Very weak.
210 .....	3.04	2.99	Strong.
21 $\bar{1}$ .....	3.44	3.39	Strong.

No reflection obtained from following planes :—

$$011, 012, 10\bar{2}, 101, 111, 22\bar{1}, 112, 11\bar{2}, 221, 21\bar{2}, 211, 212.$$

The table shows that the 100 and 010 spacings are only half what they should be if there were molecules at cell corners only. (N.B.—Only one-eighth of a corner molecule is within the cell, and the whole eight count for one whole molecule within

the cell.) But the 001 spacing is right. We conclude that there is a molecule at each of the points  $P$  and  $Q$  (see Fig. 1), each contributing half a molecule to the cell: and that these are in all respects similar to the corner molecules. Molecules placed at  $P$  and  $Q$  interleave the planes 100, 010, and also  $10\bar{1}$  by other planes of equal density which halve the corresponding spacings. The planes 110,  $20\bar{1}$ ,  $02\bar{1}$ , are unaffected because they already contain  $P$  and  $Q$ .

It should be mentioned, however, that the 100 plane seemed to give a small spectrum at half the angle which gave the principal reflection; this would indicate that the second molecule was not quite similar, in orientation or some other particular, to the first, or was not exactly at  $P$  and  $Q$ . This is also suggested by the fact that  $210$  and  $2\bar{1}\bar{1}$  give the calculated spacings, whereas half values might be expected.

Although so much information is given in these tables, some of which we have used and some of which we cannot fully use for lack of knowledge, yet it would be hopeless to try to arrange the eighteen atoms of naphthalene on the basis of what has been learnt, without some helpful hypothesis. But we now take the naphthalene double ring as described. Its dimensions are such that it seems quite possible to fit two of them into the cell, if we had some indication as to their orientation thereto.

As to this we get a strong hint from a comparison of naphthalene with anthracene ( $C_{14}H_{10}$ ), whose construction shows three rings in a line, as against the two of naphthalene. The crystallographic data of the latter are:—

$$a : b : c = 1.4220 : 1 : 1.8781, \quad \beta = 124^{\circ} 24'.$$

$$\text{Specific gravity} = 1.15.$$

The crystals themselves are very small flakes, and it was not possible to find one which could be conveniently treated by the single crystal method. However, by pressing a number of them together against a flat disc, so that all the 001 planes were parallel thereto, however oriented they might be otherwise, it was easy to get a sufficiently accurate determination of the 001 spacing, and therefore the linear dimensions of the unit cell. It appeared that there were two molecules to the cell, as for naphthalene. The dimensions were:—

$$a = 8.7, \quad b = 6.1, \quad c = 11.6.$$

If these dimensions are compared with those of naphthalene (see Fig. 1), it will be seen that while  $a$ ,  $b$ , and  $\beta$  remain nearly the same, the  $c$  axis has lengthened considerably, the difference amounting to 2.9 A.U. nearly. Now the extra ring, if of the benzene dimensions, should be responsible for an addition of 2.5 A.U. nearly to the molecule.

It is reasonable to conclude that the molecules in both crystals lie end to end along the  $c$  axis, and that the structures are similar.

The over-all lengths of the two molecules, without allowance for the hydrogen atoms at their ends, that is to say, in the  $\beta$ -positions, are 6.41 and 8.86 respectively. There is, therefore, a vacant space between the ends of two molecules of rather more than 2 A.U., into which two hydrogen atoms have to be fitted. This agrees very well with what might be expected; only it must be remembered that we have no definite indication from studies of crystal structure as to the actual distance between the centres of a carbon and a hydrogen when united by a valency bond, nor between two hydrogen atoms not so united.

We have still to decide in what plane, passing through the  $c$  axis, the molecule is to be placed, and we have less clear indications with respect to this point than those that have guided us hitherto. On making up a model, however, it is seen that it is much more likely that the plane of the molecule lies nearer to the  $ac$  plane than the  $bc$  plane. The molecules lock together much better if that is so. Moreover, if the molecules lie in the  $bc$  plane, they would be close neighbours in that plane, and at the same time there would be wide gaps between consecutive planes. The plane 100 should, therefore, be prominent, most probably a natural face, perhaps even a cleavage plane: whereas it is neither of these things. But if the molecules lie in the 010 plane the form of the crystal seems much easier to understand, as we shall see later. The  $\beta$ -hydrogens of each molecule lie up against the corresponding hydrogens of the next and the 001 plane passes through them all. It would appear to be the weakest junction in the crystal, and therefore the 001 plane is the cleavage plane.

It must be observed that in the junctions between molecule and molecule there are forces far weaker than the valency forces, which latter unite the atoms of the

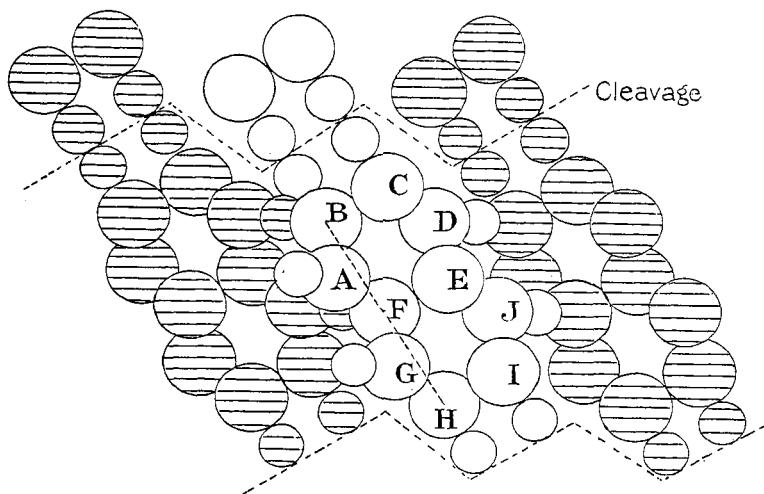


FIG. 7.—SHOWING MUTUAL RELATIONS OF THREE NAPHTHALENE MOLECULES AND PARTS OF OTHERS.

The unshaded circles between the two cleavage planes represent a molecule as at  $Q$  (Fig. 1). The shaded represent molecules  $B$  and  $F$  in the same figure. The small circles represent hydrogen atoms, but their size is uncertain.

Diameter of carbon atom = 1.50.  $BH = 4.92$ . Projection of  $AD$  on the plane of the diagram = 2.50.

same molecule. It is the former which bind the molecules into the crystal, nevertheless.

When the model is put together in the way now indicated it is found that all the  $\alpha$ -hydrogens, those that are attached to the sides of the molecule, lie up against carbon atoms of the next molecule, and that there is an appropriate space waiting for each, of magnitude about 1 A.U., the actual value depending on the orientation

of the molecule. The forces exerted at these junctions, though far weaker than valency forces, are stronger than the forces between two  $\beta$ -hydrogens; and therefore if the crystal is ruptured it is the latter which give way first. The forces exerted by the  $\alpha$ -hydrogens do so across the 110 and  $\bar{1}\bar{1}0$  planes, and it is not surprising to find that the latter make natural faces of the crystal and give a strong reflection. The structure now found is a very empty one: it is like lace-work in space. That must be expected, since the specific gravity is so low. The structure is shown in Figs. 7 and 7A.

We may now attempt to find the structure of a naphthalene molecule in which some complexity has been introduced by a substitution. We take acenaphthene. Dr. J. B. Cohen was kind enough to give me some good crystals weighing each a few milligrams.

In this case the molecule has been made lop-sided by the substitution of a group of two carbon and four hydrogen atoms for the two hydrogens on one side. It is a

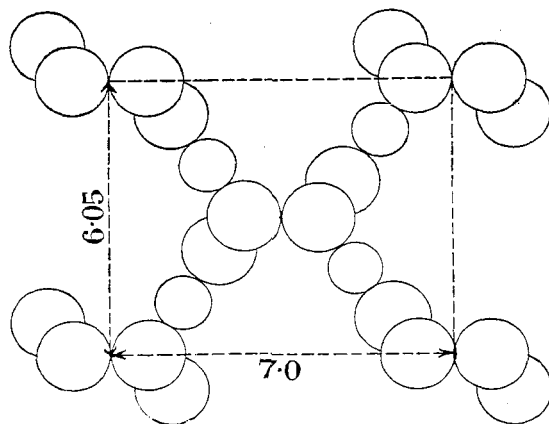


FIG. 7A.—SECTION OF NAPHTHALENE CELL PERPENDICULAR TO THE AXIS OF  $c$ , SHOWING  $\alpha$ -HYDROGENS CONNECTING THE MOLECULES SIDE TO SIDE.

striking fact that the crystal has now gained in symmetry; the unit cell is rectangular. The crystallographic data are:—

Orthorhombic (with the fullest symmetry of that class)—

$$a : b : c = 0.5903 : 1 : 0.5161.$$

It appears that there are four molecules to the cell, and that

$$a = 8.32, \quad b = 14.15, \quad c = 7.26 \quad (\text{see Fig. 8.})$$

The doubling of the number of molecules, as compared with naphthalene, suggests that symmetry has been obtained by an arrangement in which two of the unsymmetric molecules are the images of the other two across one of the principal planes,  $ab$ ,  $ac$ , or  $bc$ .

As the symmetry is so high, it is natural to test first the hypothesis that there is a molecule at each corner of the unit cell, and one in the middle of each face, which

arrangement will account for four molecules. The calculated spacings in the following table are in accordance with this supposition.

TABLE III.

Plane.	Calculated spacing.	Observed spacing.	Remarks.
100 (Natural) .....	4.16	4.16	Moderate strength
010 (Cleavage) .....	7.07	7.1*	—
001.....	3.63	3.63	Moderate strength
110 (Natural) .....	3.57	7.18	Moderate strength
101.....	2.74	2.74†	Very weak
011.....	3.23	3.19	Very weak
111 (Natural) .....	5.10	5.1	Weak

There is complete agreement, except for the 110 plane. Assuming that there will be an explanation of this as we proceed further, we now look where a molecule

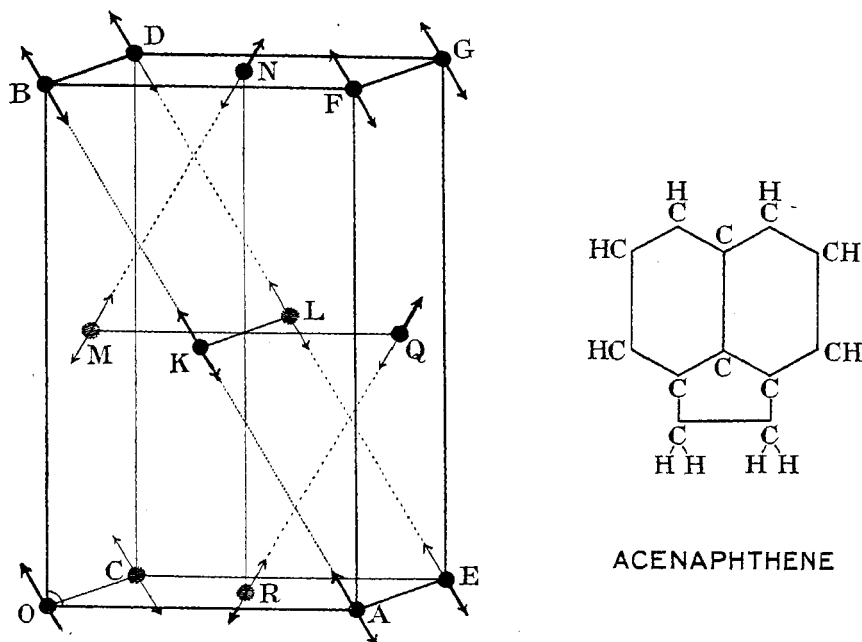


FIG. 8.—UNIT CELL OF ACENAPHTHENE, CONTAINING FOUR MOLECULES.  
 $OA=8.32$ ,  $OB=14.15$ ,  $OC=7.26$ .

of length about 8.69 (as in naphthalene) may be placed in position, and observe that  $KB=KF=\sqrt{(4.16^2+7.07^2)}=8.23$ , and these two are images of each other in the 100 plane. This is not quite long enough. Let us, however, suppose provisionally that the molecules at the corners of the cell and at  $K$  and  $L$  lie parallel to  $AB$ , and with their planes coincident with (001). Let those at  $MNR$ , which between them contribute to the cell the other two molecules that belong to it, lie in the parallel

\* Not observed directly, but inferred from other observations.

† There is an indication that alternate planes differ somewhat.

plane, but slope the other way, parallel to  $MN$  or  $QR$ . If this is so, we see why the 110 plane  $ABDE$  in the figure seems to have a double spacing; it is because the two sets of molecules—viz., such as  $A, B, D, E$  of the one set, and  $M, N, Q, R$  of the other, are very differently disposed towards this plane. One set lies parallel to it, the other not. Consequently the spacing is twice what it would have been had the molecules been all alike with respect to this plane, and is equal to the perpendicular from  $F$  or  $G$  upon the plane  $ABDE$ . This is true of the 110 plane alone, out of those set out in the table above.

Once more the cleavage plane (*e.g.*,  $BDGF$ ) passes through the junctions of  $\beta$ -hydrogens. On constructing a model it is found that the projecting addition on the side of a molecule seems to engage with a neighbouring molecule on that side of the latter on which its own addition does not lie. The crystal is thus laced together;

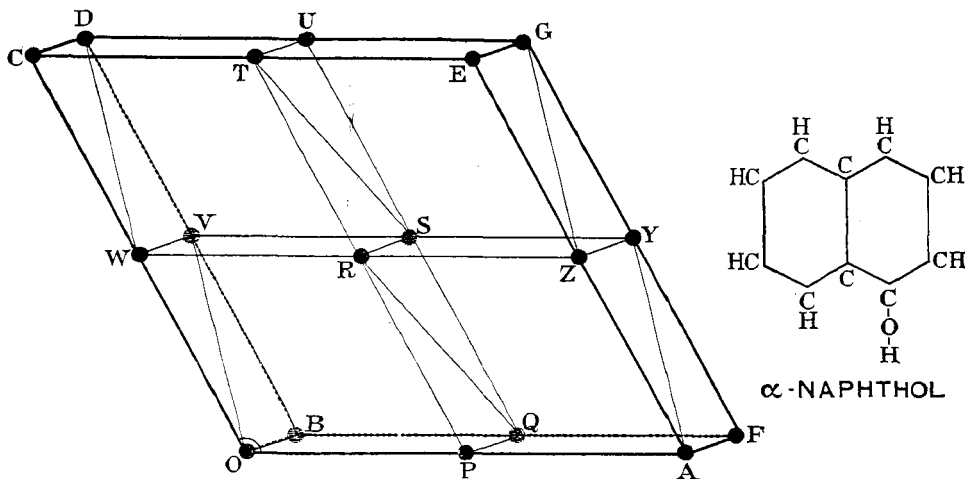


FIG. 9.—UNIT CELL OF  $\alpha$ -NAPHTHOL, CONTAINING FOUR MOLECULES.  
 $OA = 13.1$ ,  $OB = 4.9$ ,  $OC = 13.4$ ,  $\beta = 117^\circ 10'$ .

and in lines which for alternate layers parallel to the cleavage plane (010) are parallel to  $OE$  and  $AC$  respectively.

The two points left doubtful are the small difference between the length of the molecule in this crystal and in naphthalene, and the fact noted with respect to the plane 101 (*see* the table).

We now take  $\alpha$ -naphthol. Here one of the hydrogens at the side of the molecule has been replaced by  $OH$ . It was difficult to obtain without special preparation a crystal large enough for the single crystal method; but on sorting over a considerable amount of material a few flakes were found, each two or three millimetres across and a fraction of a millimetre thick. With one of these some very good observations were made, as recorded in the table below. The crystallographic data are:—

Monoclinic prismatic.

$$a : b : c = 2.7483 : 1 : 2.7715, \beta = 117^\circ 10'.$$

$$\text{Specific gravity} = 1.224.$$

It is natural to suppose that the similarity of these figures to naphthalene, when the

$a$  and  $c$  have been halved, means that the naphthalene cell has been increased four times in order to allow all the four  $a$  positions to be represented in due order. But it turns out that the crystal is of a totally different structure. There are four molecules in the cell (*see* below), as defined in accordance with the above data. If the naphthalene cell had been repeated four times, there would have been eight molecules in the larger cell.

The linear dimensions are :—

$$a=13.1, \quad b=4.9, \quad c=13.4 \text{ (see Fig. 9)}$$

and it is clear that the molecules are placed as in the figure, one at each point indicated by a letter. This is, perhaps, seen most readily if the calculated figures of the following table are reckoned as if there were one molecule at each corner of the large cell only—*viz.*, *OAFBCEGD*. We then have the following comparison :—

TABLE IV.

Plane.	Calculated spacing.	Observed spacing.	Remarks.
Cleavage 001 .....	11.92	12.00 *	Strong
002 .....	5.96	5.95*	Very strong
210 .....	3.75	3.76	Weak
21 $\bar{2}$ .....	3.69	3.68	Rather weak
100 .....	11.82	...	...
200 .....	5.91	5.84	...
10 $\bar{1}$ .....	11.38	...	...
20 $\bar{2}$ .....	5.69	5.62	†

Also angles between 210, 21 $\bar{2}$     36° 24' (calc.)    36° 16' (obs.)  
and between            10 $\bar{1}$ , 100    57° 48'    ,,    58° 5'    ,,

In the cases where a bracket occurs in this table, it is meant that a reflection shows the existence of a certain spacing between planes, while a very strong reflection at twice this glancing angle shows that this spacing is halved by other planes differing considerably from the first. See, for example, Fig. 4, where a small peak shows the 001 spacing 12.00, and a much larger peak at twice the angle corresponds to half the spacing. This agrees with a supposition that there are molecules at every point indicated by a letter, but those at *VSYZRW* are very different in some way from the others.

The reflection of 100 in the powder photograph would be indistinguishable from 001, and perhaps also the 10 $\bar{1}$ . The powder method does not give very clear indications, therefore, of the existence of the spacings 11.82 and 11.38, because all that is observed may be due to the 11.92, which must be strong, as 001 is the cleavage plane. The single crystal method gave the proper reflection of the 200 and 20 $\bar{2}$  planes, as shown in the table; but the reflections belonging to the double spacings 100 and 10 $\bar{1}$  were not looked for, and probably would have been very hard to find with so small a crystal. However, the combined data are amply sufficient for the conclusion that the four cells in the figure really imply four different orientations of the molecule, and that if we place molecules exactly at the corners of the large fourfold cell the other molecules are very nearly at all the other corners.

\* Powder method only.

† The symbol 002 is used to denote the second order reflection of 001. When it is abnormally strong, it follows that the 001 planes are interleaved.

We have this further indication that, though the half of the  $c$  axis,  $OW=6.7$ , is too short to take in the naphthalene molecule, yet the distance  $OV$  is equal to  $8.3$ , exactly the distance into which the molecule seemed to fit in acenaphthene. Once again, then, it would seem that these lopsided molecules lie criss-cross, as represented by the lines parallel to  $OV$  in the figure; but they now lie edgeways on top of one another, not flatways, as in the other crystal. It is the " $a$ " axis that now runs along the line of crossings, not the " $c$ " axis. The cleavage plane again passes through the  $\beta$ -junctions.

When a model is made, it is found that the hydroxyl groups fit into their places very naturally, and that if they link together the tops of the molecules in any one layer parallel to the 001 plane, they link in the same way the bottom ends in the next layer. This brings pairs of hydroxyl groups rather close together, as one might expect; and it looks as if the attraction existed specially between the two oxygens. The attraction is exerted across every alternate 001 plane. The other 001 planes are the cleavage planes. All the other linkings appear to be done by  $\alpha$ -hydrogens.

The crystallographic data of  $\beta$ -naphthol are:—

$$a : b : c = 1.3662 : 1 : 2.0300 ; \beta = 119^{\circ}48'$$

$$\text{Specific gravity} = 1.217.$$

This has been examined by the powder method only, as a single crystal was not readily obtainable. There is a very strong reflection for the spacing  $7.90$ . This is sufficient to fix the linear dimensions of the cell. If we put

$$a = 5.85, b = 4.28, c = 8.7 \quad (\text{see Fig. 10})$$

the weight of material in the cell is equal to that of one molecule, and the 001 spacing is  $7.76$  in close agreement with what is found.

Comparing these figures with those for the smaller cell of  $\alpha$ -naphthol such as  $OBQPWVSR$  (Fig. 9) which are  $6.55$ ,  $4.9$  and  $6.7$  respectively, it is clear that the removal of the  $OH$  group from the side to the end of the molecule has caused the cell to shrink sideways in both  $a$  and  $b$  directions and to grow along the  $c$  axis; this confirms the hypothesis that the molecules in these crystals lie mainly along the  $c$  axis. The cleavage plane still cuts across the  $\beta$ -junctions.

The question naturally arises as to whether this is really the unit cell. Ought it not to be multiplied by four, as for  $\alpha$ -naphthol, because there are four  $\beta$ -positions, as well as four  $\alpha$ -positions? The evidence in favour of the extension seems very strong. In the first place, it would be the only case, if the present crystallographic data were correct, in which a cell contained one molecule only. Moreover, if all the molecules were oriented alike, their dissymmetry would lower the symmetry of the crystal. The symmetry which is assigned to it can only be obtained by making the unit cell large enough to contain four molecules so that all the  $\beta$ -positions may be represented. Also the hydroxyl groups will surely tend to draw together and cause pairs of molecules to point opposite ways. For these reasons alone it seems likely that the structure is really the same as that of  $\alpha$ -naphthol. The length  $OV$  which was  $8.3$  for  $\alpha$  naphthol becomes  $9.7$ , a growth of  $1.4$  which seems consistent with the value of the diameter of the oxygen atom, viz.,  $1.30$ .\*

No other naphthalene derivatives have yet been examined by the X-ray methods, but there are, of course, large numbers that may be expected to give useful results.

\* W. L. Bragg, Phil. Mag., p. 169, Aug., (1920).



It is worth remarking that the unit cell of  $\alpha$ -naphthylamine has almost exactly the same dimensions as that of acenaphthene, if it be supposed to contain four molecules. Both are rectangular; the acenaphthene dimensions are :—

$$a=8.32, b=14.15, c=7.26,$$

those of  $\alpha$ -naphthylamine are :—

$$a=8.62, b=14.08, c=7.04,$$

provided that the  $a$  and  $b$  axes of the crystallographers are interchanged in the latter crystal. Their habits also correspond closely, and although the latter crystal has no clear cleavage plane it has a very prominent (010) face which may represent the 010 cleavage of the former. Assuming that the arrangement is therefore the same in the two crystals, the length of the molecule in the new case is  $\sqrt{(4.31^2 + 7.04^2)} = 8.25$ ; as against 8.23 for acenaphthene and 8.31 for  $\alpha$ -naphthol. In all these three cases the lopsided lines of molecules are laid criss-cross upon one another,

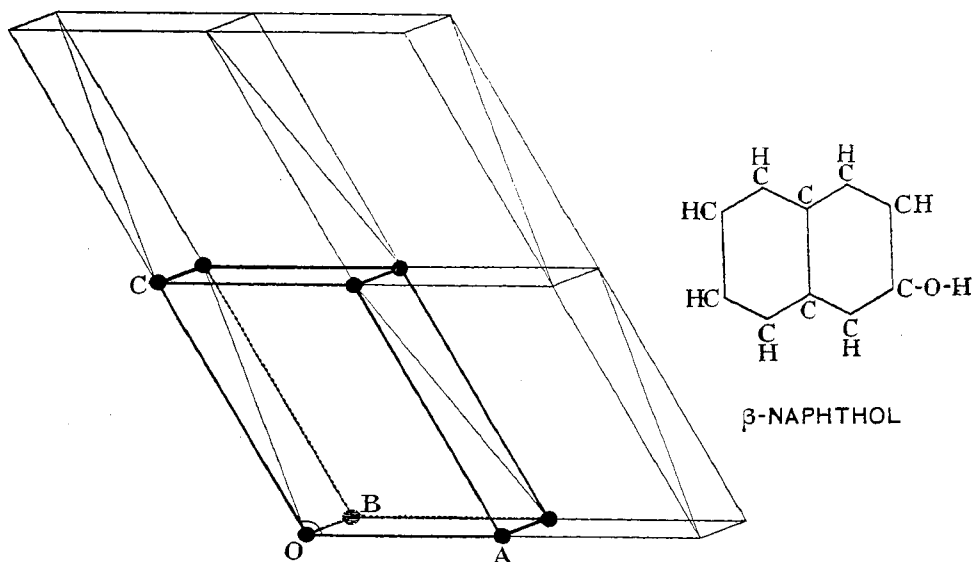


FIG. 10.—UNIT CELL OF  $\beta$ -NAPHTHOL, IN THICK LINE, CONTAINING ONE MOLECULE.  
 $OA=5.85, OB=4.28, OC=8.7, \beta=119^\circ 48'$ .

whereas in naphthalene the lines are parallel to each other. The somewhat greater length of the molecule in naphthalene, viz., 8.7, may be connected with the difference in arrangement.

I have made some measurements of benzene compounds, but the analysis of the results is incomplete; and until benzene itself is examined data are wanting that must be important. It is worth mentioning, however, that benzoic acid has a very wide spacing between the (001) planes. The dimensions of the unit cell containing four molecules, are :—

$$a=5.44, b=5.18, c=21.8, \beta=97^\circ 05'$$

Experiment by the powder method shows that there is a very strong 10.9 spacing

implying that the sheets of molecules lie at this distance apart parallel to the 001 plane. If the crystallographic data are correct these sheets differ alternately. Even a 10.9 spacing is very wide, and this suggests that extended *COOH* groups are required to bridge across the intervening space. Such a bridge may be made, of course, by a *CO* extension from one ring joining on to an *OH* extension from another ring. These bridges part very easily, it would appear; the crystal flakes at the least touch.

The work that I have now described may conveniently be divided into two parts. The first is experimental, and shows, I think, that a large mass of new and valuable information respecting the linear dimensions of organic crystals is to be gained by the methods of X-ray analysis. In the second, I have ventured to suggest and apply a certain principle, viz., that the benzene and naphthalene rings as well as other ring combinations have actual form and dimensions which are nearly, if not quite, the same when they are built into different compounds. Such a principle requires much more illustration before it can be finally established; for the present, however, it shows promise of providing an entry into a very wide field which otherwise seems difficult to break into.

Moreover, the idea fits in extremely well with the work of Langmuir on surface films, and with such results as those described by Adam,\* and with the ideas and experimental results of several other workers.† We see clearly that the forces that bind atoms together are of more than one kind. The very strong valency bonds, whether explained as due to electron sharing, or in any other way, are exemplified by all the linkings in diamond and by the linkings in the planes of the graphite flakes. But, besides these are other bonds of much weaker character, such as those extending between an atom in one graphite sheet and its three nearest neighbours in the next. Such bonds as these unite the molecules of the organic compound so as to form the crystal. They are of varying degrees of strength; the cleavage plane shows where they are weakest. They are definitely associated with special points on the molecule as we see from the facts of crystallisation. When a crystal forms in a liquid, or by sublimation, the molecule that attaches itself correctly, and with proper orientation to others already in position, is the one that stays there and resists the tendencies of other drifting and thermally-agitated molecules to remove it. It is fixed by the attachment of certain points on its own structure to certain points on the structure of the other molecules. The beautiful exactness of crystal structure is evidence of the precision with which this adjustment is made; and at the same time of the definite molecular form without which precision would be impossible.

The molecules of naphthalene arrange themselves side by side, the  $\alpha$ -hydrogens of each molecule seeking to attach themselves to the carbon atoms of its neighbours; valency bonds do not enter into this. Whether there is some special tendency to make an attachment with a carbon atom in the centre of the molecule as seems to be the case, or whether the general slant of the molecules is due to some other cause, is a matter for further inquiry. But it is the side-to-side combination that is preferred in comparison with the end-to-end; the former gives up more energy than the latter. Consequently the crystal grows out quickly into thin sheets. We may further imagine that sometimes, and more often in certain crystals than in others, as well as more often with respect to one plane in a given crystal than to other planes, the

\* Proc. Roy. Soc., XCIX., July (1921.)

† See a list given by Adam, loc. cit. p. 351.

geometry may permit a molecule to attach its active points to those of other molecules, already settled, in more than one way which does not carry on the regularity of previous attachments. The crystal starts a new growth, and twinning results.

The surface films studied by Langmuir and by Adam and others were not formed of aromatic compounds such as the few that have been investigated as crystals. But the strength of the side-to-side attachment of their molecules as compared with the end-on attachments seems to be exactly the same in effect and to lead to similar results. In a mass of oleic acid the long molecules are lying in all ways, and their heat motions do not give them a chance of attaching themselves at sufficient points at the same instant. But when the hydroxyl ends of some of them root themselves in the water, these molecules are held quiet for a moment and the others quickly slip into their places and link on side to side. So the film spreads out quickly over the water. It is a kind of catalytic action; the water does not itself draw the film flat, but helps the molecules of the film to arrange themselves. In a sense, the film has negative surface energy.

The arrangement of molecules in crystals or in surface films or interfaces between liquids and solids cannot be fully explained as due to forces which are merely functions of the distances between their centres. Confining ourselves to the cases where there is no obvious separation of electron charges, as there is none in the crystals described above, it is clear that we must think of the molecules as bodies of very definite form. These attachments to one another are made at definite points and the forces there exerted may have very short ranges. The molecules are locked into crystalline structure, when attachments are made at sufficient points, and the whole has the stability of an engineering structure. It may well be that in a liquid there are always some completed attachments, but insufficient in number to give rigidity to the whole. In a gas there are no attachments at all.

I have to thank Mr. Shearer for his assistance in examining crystals by the powder method, which method he has greatly improved; and Mr. J. Reid, for the labour and skill which he has devoted to making models.

Part of the apparatus employed was obtained through a grant from the Department of Scientific and Industrial Research.

I should also like to thank the General Electric Company of America for their great kindness in presenting me with Coolidge X-ray bulbs of special design.

Dr. C. CHREE, in moving a vote of thanks, said that the President's researches had opened up fascinating vistas of investigation, which should lead to momentous discoveries.

Sir R. ROBERTSON, expressing the hope that these accurate measurements and brilliant speculations would in time be applied to the compounds of nitrogen, seconded the vote of thanks, which was carried by acclamation.