

AN X-RAY STUDY OF THE STRUCTURE OF SOME
ORGANIC MOLECULES.

By

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INTRODUCTION.

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INTRODUCTION

The work described in Parts I and II was carried out between 1926 and 1929, and has been published in two papers (Roy.Soc.Proc.A, vol.118,p.709, 1928; vol.125,p.542, 1929.) The object is to deduce from the X-ray evidence, in a qualitative manner, the form and disposition of certain aromatic molecules as they are built up in the crystal. This early work is essentially a preliminary to the more penetrating analysis set out in Part III, which describes the exact details of the anthracene structure based upon quantitative intensity measurements, and gives the atomic positions, the electron distribution, etc.

There is a vast field for the application of the X-ray method in organic chemistry. Although many interesting results have been obtained, no other organic compound has been worked out in the same detail as the anthracene structure which is described in Part III. An unusual interest, therefore, attaches to the results of this investigation, which are summarized by the contoured diagrams

on pp. 70 - 73. These diagrams may very fairly be described as X-ray 'pictures' of the anthracene molecule, taken from various view points. The most cursory examination is sufficient to show that the structural formulae of organic chemistry are fully confirmed by these results.

The analysis of other and more complicated organic structures will probably follow, and the results will be of great interest. There are, however, two chief difficulties which confront us in the analysis of organic structures, and which explain the delay in obtaining accurate results.

1). Experimental difficulties. Good crystals of organic compounds are often difficult to obtain, and are nearly always small and soft. Hence the methods ~~used~~ employed in making absolute intensity measurements in the case of inorganic crystals are not in general applicable. Very often only the photographic method can be used.

2). Difficulties in interpreting the results. These are the more formidable. In complex inorganic structures there are usually a few heavy atoms of relatively high reflecting power, and several much lighter atoms of low reflecting power. This difference in reflecting power

for X-rays can be taken advantage of in working out the results, and helps to eliminate many arrangements of the atoms as obviously impossible. But with organic compounds the atoms usually present, carbon, oxygen, nitrogen and hydrogen, are all, with the exception of the last, so nearly of the same reflecting power for X-rays that it becomes an excessively difficult task to distinguish them. Moreover, the number of atoms present in the molecule is usually very great, twenty or more being common. In addition to these difficulties, the atomic f-curves, which take account of the structure of the atom, are not at all well known for the light elements.

It might seem then that the detailed analysis by X-rays of complicated organic structures is an impossible task. Indeed with our present methods it would be so, were it not for the knowledge of these structures already won by the organic chemist. The theory of the tetrahedral arrangement of valency bonds in the carbon atom originated by van't Hoff, and the six membered ring structure for benzene due to Kekulé, form the starting points of the elaborate structural formulae of modern organic chemistry, which express the relative positions in space of the atoms composing the molecule. If we take these formulae as a guide, then with a knowledge of atomic distances obtained from the X-ray analysis of diamond, graphite and other simple structures,

it is possible to build up a reasonable model of the organic molecule. The position and exact form of the molecule in the crystal may then be described by means of a few general parameters based on the model, and the analysis can proceed. Otherwise we are confronted with the hopeless complexity of having three independent parameters for each atom.

In the papers presented here this method, originated by Sir William Bragg, is followed. It is shown ^(Parts I & II) that such models for naphthalene, anthracene and their derivatives are valid, and the relative position and orientation of the molecules in the crystal are investigated. The way is thus cleared for the more detailed analysis with exact intensity measurements, which is described in Part III

It is apparent then, that with our existing technique the analysis of the more complicated organic structures such as those dealt with in the present papers can only proceed by basing a model on the chemical structural formula, and subsequently with the aid of quantitative measurements of intensity, determining the exact positions of the atoms. The chemist may well ask, "What does the picture revealed by X-ray analysis add to the knowledge already expressed in the structural formula?" The structural formula of organic chemistry is one of the most

precise and perfect summaries of facts in the whole of science. It expresses the knowledge by means of which the chemist can not only predict the behaviour of the compound, but is able to build it up from the elements. And for the most practical purposes of chemistry it is really of little immediate importance what degree of reality is to be attached to the diagram.

Let us contrast the methods of deducing a structural formula in organic chemistry with the methods of X-ray analysis. No two processes could well be more different. In the former case the work proceeds in a very indirect manner, being based on long chains of arguments depending on reactions which lead from some simple compound to others more and more complex. X-ray analysis, on the other hand, is more akin than anything else to actually viewing the molecular structure through some super microscope in the light of x-rays. In fact it has been shown by W.H. and W.L. Bragg that the process of interpreting the X-ray beams diffracted by a crystal is mathematically analogous to the formation of the image in the optical case, on Abbe's theory of microscopic vision. It is true that there are some serious limitations to our means of interpreting the X-ray beams, and the work is not by any means straight forward, but if the analysis can be successfully performed we actually do obtain a 'picture' of the structure in a very real sense of the word. Only it is a picture formed

by radiation of wavelength some ten thousand times shorter than ordinary light employed in microscopes, and we can see a correspondingly greater amount of detail, a detail which actually takes us down to atomic dimensions.

Few more fascinating lines of research can be imagined than that of turning the new found powers of the X-ray microscope on those molecular structures which have been the subject of such patient research and inquiry for over a century.

Thus when we make the X-ray analysis of some organic structure already familiar to the chemist, we can say, as Sir William Bragg puts it, that we are 'seeing' for the first time what has been previously inferred. The picture we get will give us the positions of the atoms in the molecules, with their electron distributions and their relative arrangements, all in accurate measure. The extension of knowledge and the scope given for further inquiry are tremendous. It seems certain that the structural formulae of organic chemistry will be endowed with a new degree of reality, the consequences of which cannot at present be estimated.

A final point must be emphasised. The facts of chemistry probably represent the greatest compilation of knowledge of any of the exact sciences, yet the field is peculiarly limited, for chemistry deals almost exclusively with the

reactions between liquids and gases over a comparatively narrow range of temperature. The solid state of matter has until recently lain beyond the scope of its investigations. The importance of the solid state need hardly be emphasised; its place in the world in general is obvious. Moreover, a large number of complicated molecular structures, particularly relating to living organisms, cannot be transformed to the liquid or gaseous states without more or less complete disintegration. And it is precisely the solid state of matter with which the X-ray method essentially deals. Thus in addition to providing an entirely new type of information, X-ray analysis extends the field of knowledge to the solid state.

AN X-RAY INVESTIGATION OF THE STRUCTURE OF NAPHTHALENE,
ANTHRACENE, AND SOME DERIVATIVES.

PART I. NAPHTHALENE AND ANTHRACENE.

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AN X-RAY INVESTIGATION OF THE STRUCTURE OF NAPHTHALENE,
ANTHRACENE, AND SOME DERIVATIVES.

PART I. NAPHTHALENE AND ANTHRACENE.

1. Experimental Methods and Results.

The present paper describes a photographic examination of naphthalene and anthracene by the rotating crystal method. The crystal structures of these compounds have already been investigated by Sir William Bragg,* who has determined the following constants for the unit cells, etc., the axial lengths being given in Angstrom Units:-

	<i>a.</i>	<i>b.</i>	<i>c.</i>	$\beta.$	Space group.	Molecules per unit cell.	Density.
Naphthalene	8.34	5.98	8.68	122 44	C_{2h}^5	2	1.152
Anthracene	8.58	6.02	11.18	125 0	C_{2h}^5	2	1.250

Bragg has pointed out the similarity of these structures, and has shown that the increase in length of the *c* axis when we pass from naphthalene to anthracene (2.5 A.U.) is just what is required to accommodate the atoms forming an extra ring, if it be of the dimensions found in the diamond or graphite structures. This immediately gives a clue to the structure of these crystals in showing that the long

* Proc. Phys. Soc., vol. 34, p. 33 (1921); vol. 35, p. 167 (1923); and "X-Rays and Crystal Structure," p. 229 (1925).

axes of the molecules probably lie more or less along the g direction. The present investigation was undertaken in order to obtain more conclusive evidence on this point.

Rotation and oscillation photographs were taken with $Cu K\alpha$ and $K\beta$ radiation, and a small circular camera (radius = 2.87 cms.) was employed to hold the film. When necessary in the oscillation photographs, the $K\beta$ radiation was removed by means of a nickel filter. Most of the results were obtained from the analysis, by Bernal's method of interpretation*, of several series of overlapping oscillation photographs taken about the b axis of the crystal. The results are arranged in Tables A, B and C, which are based on the reciprocal lattice of the crystal. A full description of the tables and the means of making the intensity estimates is given on pages 34-36.

2. Space Group and Relative Position of Molecules.

A survey of the tables shows that in the case of both naphthalene and anthracene the ($h0l$) planes are halved when h is odd, the (010) is halved, and there are no other halvings. The only space group in the monoclinic system which accounts for these facts is C_{2h}^5 in the prismatic class.† But this space group requires four asymmetric molecules to complete the necessary symmetry, and only two

* 'Roy. Soc. Proc.' A, vol. 113, p. 117, (1926).

† Cf. Aslberg and Yardley ('Phil. Trans. Roy. Soc.' A, vol. 224, p. 221 (1924)).

TABLE A. NAPHTHALENE AND ANTHRACENE. PLANES {101}.

hk2 Nap. Anth.	hk1 Nap. Anth.	hk2 Nap. Anth.	hk1 Nap. Anth.	hk2 Nap. Anth.	hk1 Nap. Anth.	hk2 Nap. Anth.
009 v.w. v.w.						
008 v.w. v.w.-						
007 w. Ag.	207 w. Ag.					
006 w. v.d.	206 w. Ag.					
005 Ag. w.m.	205 Ag. w.					
004 m.s. m.	204 w.m. m.			404 Ag. w.		
003 S. w.m.	203 m.s. v.w.			403 v.w. v.d.		
002 S. m.s.	202 w.m. v.w.			402 w.m. Ag.		
001 v.s. v.s.	201 w.m. v.w.			401 v.w. Ag.		
	200 v.s. v.s.			400 w. v.w.		
	207 v.s. v.s.			407 v.w. v.w.		601 Ag. Ag.
	202 S. S.			402 w.m. w.		600 w. w.
	203 Ag. m.			403 Ag. v.w.		607 w.m. w.m.
	204 m. v.d.			404 m. Ag.		602 w. Ag.
	203 w.t v.w.			403 w. w.m.		603 w. v.w.
	206 Ag. v.w.			406 Ag. v.w.		604 m. v.w.
	207 w.t v.w.-			407 m.s. v.w.		605 w. w.m.
	208 v.w. Ag.			408 w.m. Ag.		606 Ag. v.d.
	209 Ag. w.			409 v.w. m.		607 m. Ag.
	206 w. Ag.			406 v.w. w.		608 m. Ag.
				407 v.w. w.		609 Ag. w.m.
				408 v.w. w.		606 w. w.

{010} SERIES:- 010 Abs. Nap. Anth. 020 m.s. m.s. Nap. Anth. 030 Abs. Ag. (FROM g AND c AXIS PHOTOGRAPHS.)

TABLE B. NAPHTHALENE AND ANTHRACENE. PLANES {hkl}.

hkl Nap. Anth.	hkl Nap. Anth.	hkl Nap. Anth.	hkl Nap. Anth.	hkl Nap. Anth.	hkl Nap. Anth.	hkl Nap. Anth.	hkl Nap. Anth.
019 Ak. w.							
018 Ak. w.							
017 w. Ak.	217 Ak. Ak.						
016 w. Ak.	216 Ak. Ak. 316 v.v. Ak.						
015 v.v. w.m.	215 Ak. Ak. 315 w. Ak.						
014 m. w.m.	214 v.v. Ak. 314 Ak. v.v.			414 w. w.			
013 w.m. v.v.	213 w. Ak. 313 Ak. v.v.			413 w.m. v.v.-			
012 w.m. v.v.	212 w. v.v. 312 w. v.v.			412 w. Ak.		513 w. Ak.	
011 m.s. m.	211 v.v. Ak. 311 w.m. w.			411 Ak. Ak.		512 v.v. Ak.	
	210 v.s. v.s. 310 v.m. w.t			410 m.s. m.s.		511 Ak. Ak.	611 Ak. Ak.
	217 v.s. v.s. 317 s. m.s.			417 s. s.		510 w. v.v.	610 v.v. v.v.
	212 v.v. m.- 312 Ak. v.v.			412 w. Ak.		517 w. v.v.	617 w.t w.
	213 m. Ak. 313 m. v.v.			413 m. v.v.		512 w. v.v.	612 w. Ak.
	214 m. v.t 314 m. m.s.			414 m. v.v.		513 Ak. Ak.	613 w. v.v.
	215 w.m. w.m. 315 m.s. m.			415 w.m. m.-		514 m. v.v.-	614 w. Ak.
	216 w. Ak. 316 v.v. Ak.			416 w. v.v. w.m.		515 v.v. m.	615 Ak. Ak.
	217 m. v.v. 317 Ak. Ak.			417 w. Ak.		516 v.v. Ak.	616 Ak. w.-
	218 v.v. w. 318 Ak. v.v.			418 w. Ak.		517 w.m. Ak.	617 v.v. Ak.
	219 Ak. w.m. 319 Ak. w.m.			419 Ak. w.t		518 w.m. Ak.	618 Ak. Ak.
	210 v.v. Ak. 310 w. Ak.			410 Ak. Ak.		519 v.v. w.m.	619 Ak. v.v.
	211 v.v. v.v. 311 w. Ak.			411 Ak. Ak.		510 Ak. Ak.	610 Ak. v.v.

TABLE C. NAPHTHALENE AND ANTHRACENE. PLANES {hkl}.

hkl Nap. Anth.	hkl Nap. Anth.	hkl Nap. Anth.	hkl Nap. Anth.	hkl Nap. Anth.	hkl Nap. Anth.	hkl Nap. Anth.	hkl Nap. Anth.
028 v.u. w.	128 Ah. Ah.						
027 v.u. Ah.	127 v.u. Ah.	227 Ah. w.m.					
026 w.m. Ah.	126 w. Ah.	226 w. w.	326 Ah. Ah.				
025 Ah. Ah.	125 w. v.u.	225 Ah. Ah.	325 Ah. Ah.				
024 w.m. m.	124 w. w.	224 w.m. v.u.	324 w. w.	424 Ah. w.			
023 m.s. w.	123 w. Ah.	223 v.u. Ah.	323 Ah. Ah.	423 w. Ah.	523 w.m. v.u.		
022 m. w.m.	122 v.u. Ah.	222 w. w.	322 Ah. Ah.	422 v.u. v.u.	522 w. Ah.		
021 u.s. s.	121 m.s. w.m.	221 m. w.m.	321 Ah. Ah.	421 v.u. v.u.	521 w. Ah.		621 Ah. Ah.
	120 s. s.	220 m. m.	320 m.s. m.s.	420 v.u. Ah.	520 Ah. w.		620 Ah. Ah.
	127 m. w.m.	227 w.m. w.	327 s. m.s.	427 m.s. m.s.	527 m. m.		627 u. w.m.
	122 s. w.t	222 w. Ah.	322 w. w.	422 m. w.	522 w.m. v.		622 w.m. w.
	123 m. w.m.	223 s. Ah.	323 m. w.	423 v.u. v.u.	523 v.u. Ah.		623 w. v.u.
	124 Ah. m.	224 m.s. m.s.	324 w. w.m.	424 m. v.u.	524 v.u. Ah.		624 v.u. v.u.
	125 Ah. Ah.	225 Ah. m.	325 w.m. w.	425 w.m. m.t	525 w.m. v.u.		625 v.u. Ah.
	126 w.m. Ah.	226 w. Ah.	326 v.u. w.m.	426 v.u. v.u.	526 v.u. w.		626 Ah. v.u.
	127 w.m. Ah.	227 w. Ah.	327 w.m. Ah.	427 w.m. Ah.	527 Ah. Ah.		627 v.u. Ah.
	128 Ah. w.	228 v.u. v.u.	328 w. Ah.	428 w. Ah.	528 v.u. Ah.		628 u.u. Ah.
	129 Ah. w.	229 Ah. Ah.	329 Ah. w.	429 v.u. Ah.	529 Ah. Ah.		629 v.u. v.u.
				430 v.u. v.u.	530 Ah.		630 v.u. v.u.

molecules are present in the unit cells of naphthalene and anthracene. Hence if all the halvings found are ~~from~~ true halvings we must ascribe a centre of symmetry to the molecules of naphthalene and anthracene in the crystalline state, which is the only possible molecular symmetry in this space group.

It often happens that the determination of a space group depends upon the determination of the crystal class, regarding which only superficial evidence may be available. Thus it is sometimes possible to avoid the assumption of molecular symmetry by relegating the crystal to a lower symmetry class which does not require it. In the present example, however, if the (010) halving is real, there is no space group available in any of the lower symmetry classes that will account for the halvings found. It therefore becomes necessary to assume a centre of symmetry in these molecules.

These centres of symmetry have a fixed position amongst the elements of symmetry comprising the space group C_{2h}^s . If we choose one centre as origin, then the position of the other centre is $(\frac{1}{2}a, \frac{1}{2}b, 0)$. This may be seen in the following way. First of all suppose there are four asymmetric molecules in the unit cell, and let (x, y, z) be the coordinates of any point (atom) on one of the molecules referred to the a, b , and c crystal axes as axes and any lattice point as origin. Then the coordinates of the

equivalent points on the four molecules are as follow,
 (expressed as fractions of the axial lengths)

$$\begin{array}{llll}
 x, & y, & z; & A \\
 x + \frac{1}{2}, & -y + \beta, & z; & \text{reflected molecule B} \\
 -x + \alpha, & y + \frac{1}{2}, & -z + \gamma; & \text{rotated molecule C} \\
 -x + \frac{1}{2} + \alpha, & -y + \frac{1}{2} + \beta, & -z + \gamma; & \text{reflected rotated molecule D}
 \end{array} \left. \vphantom{\begin{array}{l} A \\ B \\ C \\ D \end{array}} \right\}, (1)$$

where α , β and γ are parameters which have to be determined. It is not in general possible to represent the positions of a molecule and its mirror image by means of two points unless the molecule itself has certain symmetry properties, e.g. a centre of symmetry. But suppose the molecules have certain approximate symmetry properties, and that we can thus represent their positions approximately by means of points, then with such a representative point as origin the positions of the four molecules in the unit cell are denoted by the following coordinates:-

$$\begin{array}{llll}
 0, & 0, & 0 & \dots\dots A \\
 \frac{1}{2}, & \beta, & 0 & \dots\dots B \\
 \alpha, & \frac{1}{2}, & \gamma & \dots\dots C \\
 \frac{1}{2} + \alpha, & \frac{1}{2} + \beta, & \gamma & \dots\dots D
 \end{array} \left. \vphantom{\begin{array}{l} A \\ B \\ C \\ D \end{array}} \right\}. (2)$$

It can readily be seen that when and only when $\alpha = \frac{1}{2}$,
 $\beta = \frac{1}{2}$, $\gamma = 0$, the number of molecules is reduced to two, A coinciding with D, and B with C, at the points $(0,0,0)$ and $(\frac{1}{2}, \frac{1}{2}, 0)$. Introducing these values for α , β and γ the general coordinates (1) now become

$$\begin{array}{rcl}
 x, & y, & z \dots\dots\dots A \\
 \text{Centre of symmetry} & & \\
 -x, & -y, & -z \dots\dots\dots D \\
 & & \\
 x + \frac{1}{2}, & \frac{1}{2} - y & z \dots\dots\dots B \\
 \text{Centre of symmetry} & & \\
 \frac{1}{2} - x, & y + \frac{1}{2}, & -z \dots\dots\dots C
 \end{array} \quad (3)$$

A and D lying on one molecule with a centre of symmetry at (0,0,0) and B and C on the second molecule with a centre of symmetry at (1/2,1/2,0). The molecule BC can be derived from AD either by a reflection in the ac plane or by a rotation of amount π about the b axis, accompanied by a shift of 1/2a, 1/2b. We have thus determined α, β and γ by making use of the fact that there are only two molecules in the unit cell.

By means of the coordinates (3) these results may be put in analytical form. The geometrical structure factor for any plane {hkl} , which gives the ratio of the amplitude actually reflected by the plane to the amplitude which would be reflected if all the atoms lay in the plane (all in phase) may be written

$$S = \left| \sum_{r=1}^m \sum_{p=1}^n A_{pr} e^{2\pi i(x_p h/a + y_p k/b + z_p l/c)} \right|, \quad (4)$$

where A_{pr} is the reflecting power and (x_{pr}, y_{pr}, z_{pr}) the coordinates of the p-th atom in the r-th molecule in a unit

cell built up of m molecules that each contain n atoms. For this purpose it is convenient to restrict the term "molecule" to mean the asymmetric crystal unit, which in the present example consists of one half of the chemical molecule. The general coordinates of equivalent points on these crystal units referred to a centre of symmetry as origin are given in (3). We can now carry the summation of the structure factor over the molecules, using these general coordinates. On simplifying the result we obtain the following two expressions, which are quite general and apply to any crystal of space group C_{2h}^s , when the coordinates are referred to a centre of symmetry as origin.

$$S = \sum_{p=1}^{p=n} 4A_p \cos 2\pi(x_p h/a + z_p l/c) \cdot \cos 2\pi y_p k/b \quad (5)$$

when $(h + k)$ is even

and

$$S = \sum_{p=1}^{p=n} 4A_p \sin 2\pi(x_p h/a + z_p l/c) \cdot \sin 2\pi y_p k/b \quad (6)$$

when $(h + k)$ is odd.

The remaining summation has to be taken over that group of n atoms which make up the crystal unit.

It is easily seen that the space group halvings are accounted for in these expressions. When h is odd and $k = 0$ ($\{h0l\}$ halving), expression (6) applies, and is equal to zero. Similarly when k is odd and h and l are both zero ($\{010\}$ halving) expression (6) again applies, and is again zero.

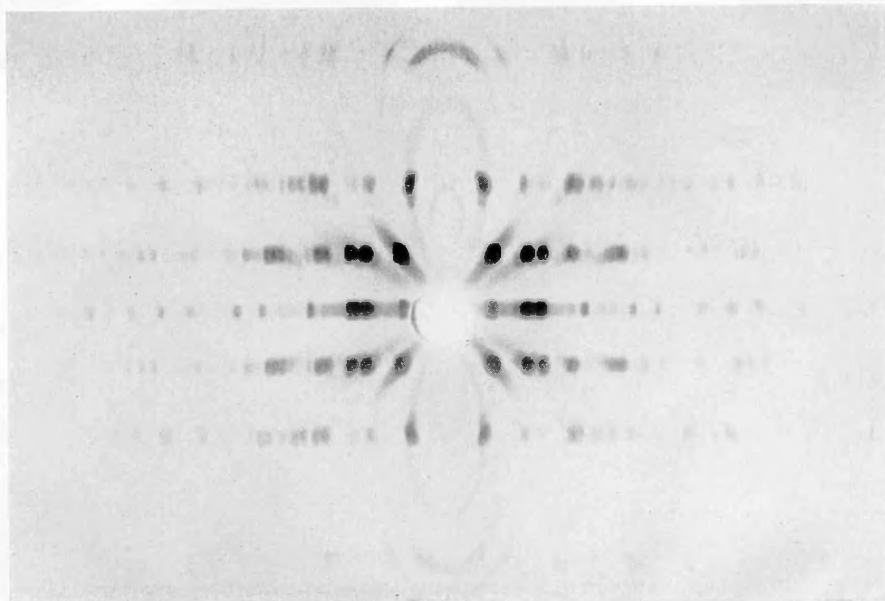
3. Orientation of the Molecules.

Some typical rotation photographs are reproduced in Plates 7 and 8. The naphthalene photographs are more difficult to take owing to the rate at which a small crystal volatilizes, and so in general a larger crystal and somewhat less accurate setting had to be employed than for anthracene, but this drawback did not lead to any ambiguity in the interpretation of the results. The striking similarity between corresponding photographs of naphthalene and anthracene is at once apparent, and points to similarity of underlying structure. The distance between the layer lines in the b axis rotation photographs of the two crystals (plate 7) is almost identical, showing that the length of the b axis is practically the same in naphthalene and anthracene. The c axis, however, (plate 8) is considerably longer in anthracene than in naphthalene, the fourth layer line in naphthalene lying a little beyond the fifth layer line in anthracene, showing that the c axis in anthracene is rather more than $5/4$ times as long as the c axis in naphthalene.

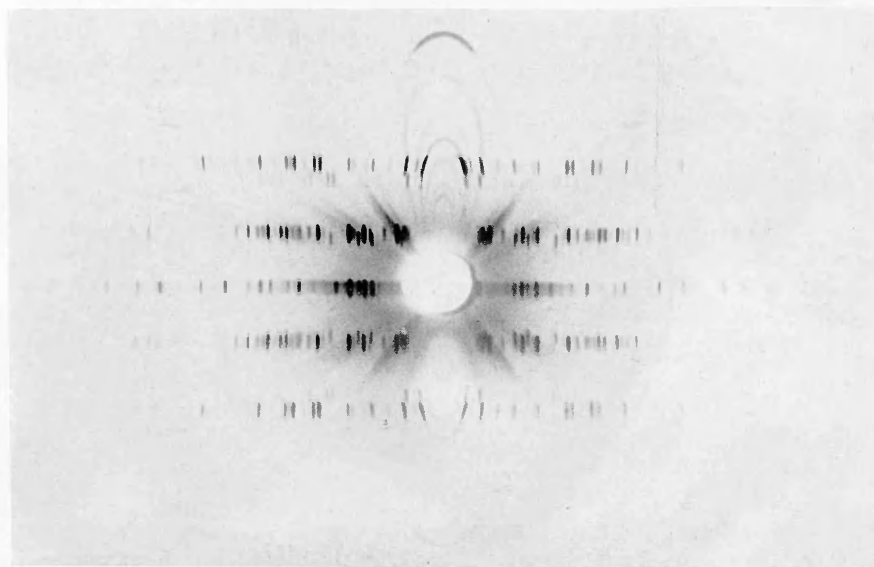
The position of the X-ray reflections on the film gives information about the geometry of the space lattice, i.e., about the relative positions of the units which build up the crystal. The intensity of the reflections, however, gives information of a more fundamental type, concerning the structure of these units themselves. Now a study of the c axis photographs of naphthalene and anthracene

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Roy. Soc. Proc., A, vol. 125, Pl. 7.



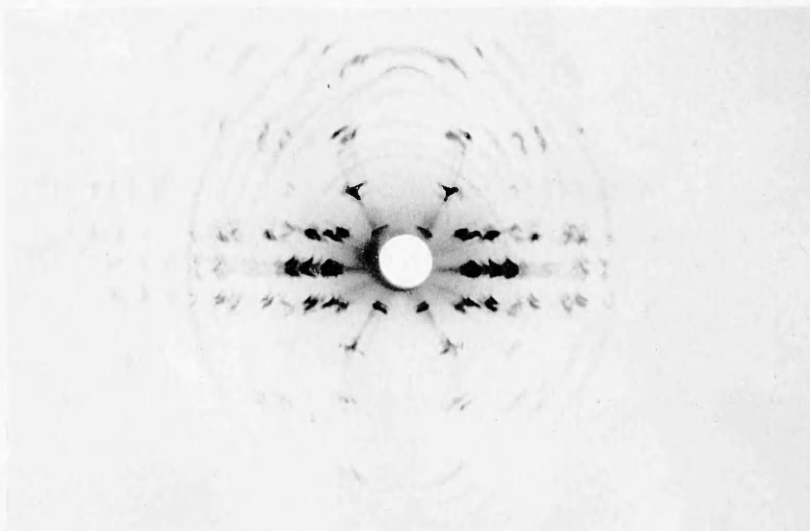
Naphthalene—Rotation about *b* axis.



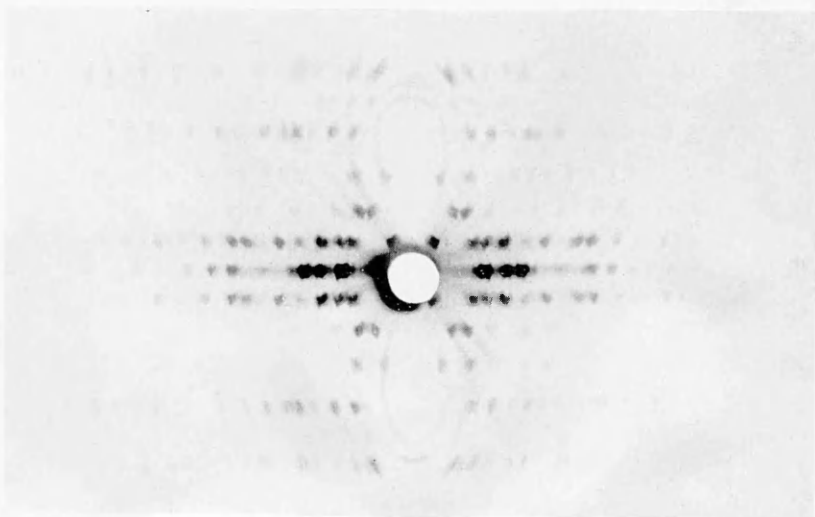
Anthracene—Rotation about *b* axis.

Robertson.

Roy. Soc. Proc., A, vol. 125, Pl. 8.



Naphthalene—Rotation about *c* axis.



Anthracene—Rotation about *c* axis.

(plate 8) reveals a very important fact.* On the equatorial layer lines in the two photographs the position and intensity of the reflections are practically the same. This means that when the structures are viewed along the c axis, not only the geometry of the lattice, but also the fundamental structure and position of the crystal units or molecules must be very similar in the two cases. That is to say, they must be similar in their projection along the c direction of the crystals. In view of the chemical structure this can only mean that the long axes of the molecules must lie more or less along the c axes of the crystals, as in fig.a:-

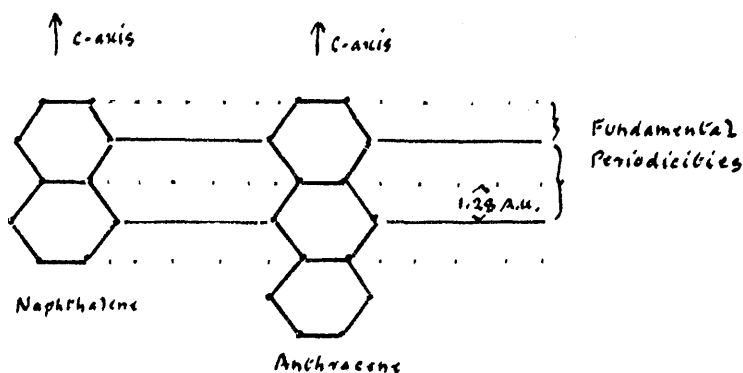


Fig. a.

Were the molecules placed in any other direction, the projection along the c axis would be different in the two cases.

The other layer lines contain the reflections from the general plane (hkl) and give information regarding the structure as viewed from all points. Thus in the naphthalene

* The significance of these photographs was first pointed out by Sir William Bragg [*Z. f. Krist.*, vol. 66, p. 22 (1927) ; *Nature*, vol. 121, p. 327 (1928)] .

photograph the reflections fade away in the second but are enhanced again on the third and fourth layer lines. In anthracene, the fourth and fifth layer lines are enhanced. It should be noted that these enhancements, though affecting different layer lines in the two photographs, occur at about the same actual positions on the films. This indicates that although the c axes in the two crystals are of different lengths, yet a fundamental periodicity of about the same absolute amount occurs along the c direction of the two structures. A glance at the chemical structure will show that this may be expected.

In order to investigate this periodicity more fully we require to examine many more reflections than are recorded on these c axis rotation photographs, which only show four layer lines above the equator in naphthalene ($l = 4$) and five in anthracene ($l = 5$). The detailed analysis of the b oscillation photographs given in tables A-C are most suitable for our purpose, as they contain an account of the reflections from planes whose l index goes up to the value 10.

We can proceed by making a statistical investigation of all the reflections* recorded in these tables. A number is assigned to each reflection[#] (v.s.=7, s.=6.....v.w.=1)

* Bragg has made a similar investigation of the reflections from anthracene, with less complete data than is now available. (Z.f.Krist., vol. 66, p. 22 [1927]).

Cf. h. 36

and for all planes with a given \underline{l} index these numbers are added together and plotted on a curve. If there is enhancement for a given value of \underline{l} it will be shown by a peak on the curve, and a measure of the periodicity causing it will be obtained by dividing the axial length by the value of the index \underline{l} at which the peak occurs.

The curves obtained from naphthalene and anthracene are shown in fig. b, where the horizontal scale is l/c . This scale measures the reciprocal of the periodicity, if any,

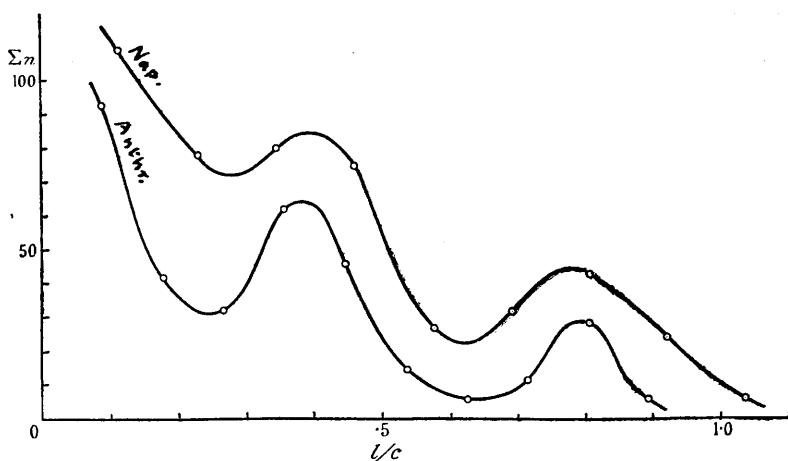


FIG. 1.

occurring along the \underline{c} axis of the crystal, and the same periodicity in the two crystals will be indicated by maxima on the curves appearing at the same point on the horizontal scale. The similarity of the curves is at once apparent, and we see that in both naphthalene and anthracene there are

distinct maxima at 0.38 and 0.78 on the reciprocal scale, giving periodicities of 2.63 A.U. and 1.28 A.U. for both crystals along the direction of the c axis. The fact that the curve for naphthalene lies wholly above the curve for anthracene is due only to the experimental defect of using a larger crystal of naphthalene which in general gave stronger reflections than were obtained from anthracene.

Thus in both naphthalene and anthracene we have distinct evidence of a fundamental periodicity along the c axis of amount 1.28 A.U., and a secondary periodicity of approximately twice that amount, viz., 2.63 A.U. These periodicities afford striking evidence of a chain like structure along the c axis, very similar to that observed in the long chain hydrocarbons investigated by Muller.* The effect in naphthalene and anthracene is made clear from fig.a, where we see that the molecule can be regarded as composed of two zig-zag chains side by side. If the distance between the carbon atoms in the hexagons is 1.42 A.U. as in graphite, then the periodicity is $\sqrt{3}/2 \times 1.42 = 1.23$ A.U., which is very near the observed value (1.28 A.U.).

As regards the lateral distribution of the molecules in the ab plane, we have seen that the similarity of the equatorial layer lines in the c photographs of naphthalene and anthracene show that their projections on this plane (projections along the c axis) must be very similar in the two cases. From a consideration of the relative ~~in~~

* 'Roy. Soc. Proc.' A, vol. 120, p. 437 (1928) etc.

intensities of certain reflections it can be shown that no simple structure with the "plane" of the molecule parallel to either the a or the b axes is possible, but that the molecules must occupy some intermediate position. More precise information on this point, however, must await the exact measurement of the intensities of the reflections.

4. Summary.

The crystal structures of naphthalene and anthracene have been examined by the rotating crystal photographic method, and the results are classified in tables A-C. In each case the space group is C_{2h}^5 , and there are two molecules in the unit cell. The molecules possess a centre of symmetry, and the relative positions of these centres are $(0,0,0)$ and $(\frac{1}{2}a, \frac{1}{2}b, 0)$. The geometrical structure factor for this case is given.

It is shown that the long axes of the molecules must lie approximately along the c axes of the crystals. Two distinct periodicities in this direction are determined from a statistical investigation of the intensities, of amounts 1.28 and 2.63 A.U., which correspond to the zig-zag chain structure of the ~~of the~~ molecules as placed along the c axes.

PART II.

NAPHTHALENE TETRACHLORIDE AND DICHLOR-
NAPHTHALENE TETRACHLORIDE.

.....

PART II. NAPHTHALENE TETRACHLORIDE AND DICHLOR-
NAPHTHALENE TETRACHLORIDE.

The crystal structure of naphthalene tetrachloride has been investigated by Sir William Bragg,* who finds it to consist of a monoclinic body centred lattice containing four molecules of $C_{10}H_8Cl_4$ per unit cell. The orientation and the structure of the molecules suggested (loc.cit.) is in harmony with the dimensions of the unit cell, and explains the chief features of the intensities of the most prominent spectra. In the present paper this structure is further examined by the rotating crystal method and, by means of a comparison with 1.2.3.4.5.8.-hexachlornaphthalene-1.2.3.4.-tetrahydride (referred to hereafter as dichlor-naphthalene tetrachloride), an attempt is made to locate the halogen atoms. Several naphthalene derivatives were investigated, and the dichlor-tetrachloride was finally selected for a detailed examination because the crystal structure is very closely similar to that of naphthalene tetrachloride, and hence a direct comparison of intensities, etc., becomes possible.

The dimensions of the unit cells of these chlorides compared with naphthalene are given below:-

*'X-Rays and Crystal Structure', p. 253 (1923); 'Z. für Krist.', vol. 66, p. 22 (1927).

Compound.	a.	b.	c.	β .	Space group.	Mols. per unit cell.	Density
Naphthalene	8.34	6.0	8.7	122° 49'	C_{2h}^5	2	1.152
Naphthalene tetrachloride	7.9	10.3	14.2	112° 40'	C_s^4 or C_{2h}^6	4	1.67
Dichloronaphthalene tetrachloride	7.8	12.3	13.9	116° 14'	C_s^4 or C_{2h}^6	4	1.87

These data agree reasonably well with the axial ratios recorded in Groth,* except that in the case of naphthalene tetrachloride the length of the c axis is now found to be doubled, and in the case of the dichlor-tetrachloride we have interchanged the a and c of Groth.

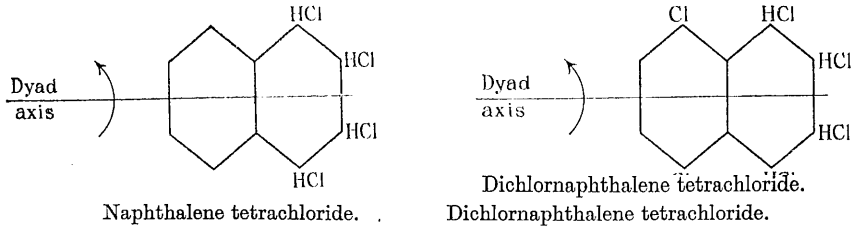
The X-ray results (see below) show that in the case of these two chlorides the general plane $\{hkl\}$ is halved when $h+k+l$ is odd, and that all the $\{h0l\}$ planes are halved. The lattice is therefore body-centred (Γ') and the space group must be either C_{2h}^6 (monoclinic prismatic) or C_s^4 (monoclinic domatic).† It is not possible to distinguish between these two cases by any known X-ray method.

There is, however, certain other evidence which is strongly in favour of the latter space group, and which therefore leads us to infer, as Bragg has pointed out (loc.cit.), a hitherto ~~unsuspected~~ unsuspected polarity in the crystal. First let us consider the requirements of the monoclinic prismatic group C_{2h}^6 . The elements of symmetry are a glide plane and a dyad rotation axis, and eight asymmetric molecules are required to form the unit cell. As only

* 'Chem. Kristallographic', vol. 5, pp. 348, 349

† 'Phil. Trans.' A, vol. 224, p. 229, (1924).

four molecules are actually present in these crystals, each molecule must possess either a centre or a dyad axis of symmetry along the b axis of the crystal. It is certain that if the crystal molecule bears any resemblance to the structural formula advanced from chemical considerations, then a centre of symmetry is impossible, and a dyad axis could only lie along the long axis of the molecule as indicated below.



In other words we must place this axis of the molecule along the b axis of the crystal. ■ We cannot disprove this possibility directly, but we shall see that all the evidence points to the axis of the molecule being nearly coincident with the C axis of the crystal, as in the case of naphthalene and anthracene. It is in view of this evidence that we are led to reject the monoclinic prismatic space group and adopt the lower symmetry of the domatic class. The space group C_2^4 , containing only a glide plane of symmetry, requires only four asymmetric molecules per unit cell. No molecular symmetry is possible.

It will be adopted in the following discussion as the most

reasonable working hypothesis.

In this space group we now require to determine as far as possible the relative position of the original and the reflected molecule. Bragg has made use of the fact* that if this approximates to certain values, then certain sets of planes tend to give weak reflections, and hence from a study of these the approximate position of the reflected molecule may be determined, provided that the molecules (the standard molecule and the reflected molecule) present approximately the same appearance when viewed from all points.

In his investigation of the tervalent metallic acetyl-acetones W.T.Astbury† has discussed this method of locating the position of molecules, and has pointed out that, for example, when the odd hyperbolae are almost completely obliterated in a rotation photograph, then the molecule ~~wh~~ which subdivides the primitive translation parallel to the rotation axis must possess ' ' approximately that element of symmetry which is involved in deriving it from the molecules at the ends of the primitive translation."

This method of locating molecules therefore appears to have a wide application, and if applied carefully it may in certain cases give information regarding the position of important groups of atoms, leading to the correct

* *Loc.cit.* † (*Ray. Soc. Proc.*), A, vol. 112, p. 457 (1926)

orientation of the molecule. The effects, however, may be small, and we may not be able to distinguish them by simple inspection of a rotation photograph; because the operation of the space group halvings will in general cause the absence of many strong reflections from certain layer lines, and this effect may be mistaken for a weakening of the reflections from the general plane.

We can proceed by making a classification of all the reflections in such a way that the different effects can be clearly distinguished. By means of Bernal's method of interpretation,* which has been followed in all the work described here, indices can be assigned with certainty to all the reflections. In arranging the results so as to obtain the information required, several points must be noted.

(1) We must interpret all the reflections occurring in rotations about any axis within a certain range. In the present example, all reflections up to $\xi = 1.50$ have been interpreted on five layer lines in photographs taken about the b axis. With the $K\alpha$ rays from a copper anticathode this gives about three hundred planes in each crystal, which is enough to give good averages of the intensities for certain sets. In more complicated crystals with larger unit cells a smaller ξ value would doubtless give sufficient planes for classification. But it is important to classify all planes up to a selected ξ value.

* 'Roy. Soc. Proc.', A, vol. 113, h, 117, (1926).

(2) Before recording a plane absent we must make sure that it has been in a reflecting position. In other words the instrumental limits must be clearly indicated in the classification.

(3) Planes absent owing to the operation of space group halvings must be distinguished from those whose absence is due to other causes, and allowances made in comparing the intensities of certain sets.

These points can be most clearly set forth by arranging the results in the form of a series of tables based on the reciprocal lattice of the crystal. Each table contains an account of the reflections observed along one layer line in the crystals. The limits of the region interpreted ($\xi = 1.50$ for naphthalene tetrachloride) and the instrumental limits are indicated by a full line across the column —————. Planes which have been in a reflecting position and found to be absent are marked Abs. Reflections which are absent on account of space group halvings are simply omitted. The regularity of the resulting pattern on the tables at once indicates the type of lattice. The body centred lattice in these crystals is the cause of the staggered effect, analogous to the appearance of an oscillation photograph taken about the b axis.

The intensities of reflection have in most cases been estimated by eye from overlapping oscillation photographs.

No great accuracy is claimed for the results, but by comparing the $K\alpha$ (copper) reflections with the $K\beta$ reflections, an approximate idea of the intensities is obtained. The following table indicates the standard adopted:-

	Intensity, I.	n .
v.s. = very strong	100	7
s. = strong	42	6
m.s. = medium strong = β of v.s.	18	5
m. = medium = β of s.	7	4
w.m. = weak medium = β of m.s.	3	3
w. = weak = β of m.	1.3	2
v.w. = very weak = β of w.m.	0.5	1

The ratio of the intensity of the $K\alpha$ line to the $K\beta$ line of copper is about 5.7 to 1 on the photographic plate i.e., after passing through the aluminium window of the X-ray tube (1/1000 in.),* so that, putting v.s.= 100, we find the approximate values of the other standards as given above. If, however, the crystal absorbs the X-ray beam considerably, as is the case with these chlorides, it is likely that the observed ratio of α to β will be still further reduced by differential absorption. The number n , which simply indicates the order of intensity, has been used in comparing the intensities of sets of planes. The number n is not proportional to the intensity I but is a linear function of the logarithm of the intensity. Taking the ratio of the intensity of the α to the β

* 'Roy. Soc. Proc.', A, vol. 115, p. 645 (1927)

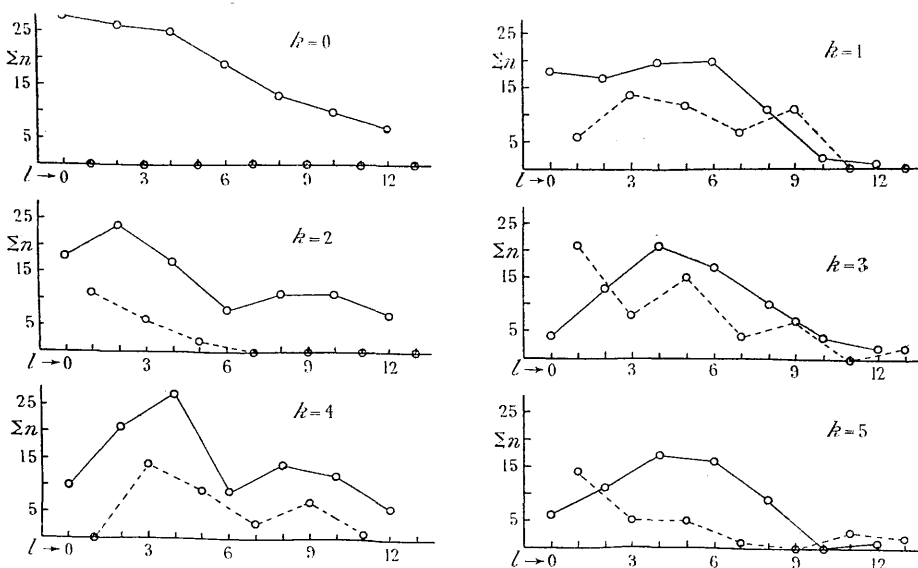
reflection as 5.7 to 1 and using common logarithms,

$$n = A \log I + B$$

where $A = 2.64$ and $B = 1.71$.

Tables I-V show the reflections observed in photographs taken about the \underline{b} axis of the two crystals investigated. Other important planes like the (010) series, which require to be measured in photographs about other axes, are given later.

Figs. 1-6 show the distribution of intensities in naphthalene tetrachloride plotted as Σn against the \underline{l} index (horizontal columns in the tables). The corresponding diagrams for the dichlor-tetrachloride (not shown) are very similar, though somewhat more confused.



FIGS. 1-6.—Naphthalene Tetrachloride.

TABLE II.—Planes {*h* 1 *l*}.
A = Indices {*h* *k* *l*}.
B = Intensity of reflection in naphthalene tetrachloride.
C = Intensity of reflection in dichloronaphthalene tetrachloride.

<i>l</i>	<i>A</i>	<i>B</i>	<i>C</i>	<i>A</i>	<i>B</i>	<i>C</i>	<i>A</i>	<i>B</i>	<i>C</i>	<i>A</i>	<i>B</i>	<i>C</i>	<i>A</i>	<i>B</i>	<i>C</i>	<i>A</i>	<i>B</i>	<i>C</i>	
12	0111	Abs.	w.m.																
11	019	m.	w.	110	Abs.	m.													
10	017	w.	m.s.	219	w.	w.m.													
9	015	w.m.	Abs.	217	v.w.	v.w.	318	Abs.	Abs.										
8	013	m.	m.s.	215	v.w.	v.w.	316	w.m.	w.	417	Abs.	v.w.	516	v.w.	Abs.				
7	011	w.	w.?	213	v.w.	v.w.	314	w.m.	Abs.	415	v.w.	Abs.	514	v.w.	Abs.				
6				211	v.w.	m.	312	m.	w.m.	413	Abs.	Abs.	512	v.w.	v.w.				
5				211	Abs.	v.s.	310	v.w.	m.s.	411	v.w.	Abs.	510	w.	v.w.				
4				213	m.	Abs.	312	v.w.	Abs.	413	w.m.	w.m.	512	Abs.	Abs.	613	Abs.	Abs.	
3				215	w.m.	m.	314	w.	m.	415	w.m.	w.m.	514	w.m.	w.m.	615	w.	Abs.	
2				217	w.	w.	315	m.	m.	417	v.w.	m.	515	v.w.	Abs.	617	v.w.	Abs.	
1				219	w.m.	m.	315	w.	w.	419	v.w.	Abs.	518	w.	w.m.	619	v.w.	v.w.	
0				211	Abs.	v.w.	3110	Abs.	Abs.	411	Abs.	w.m.	5110	w.	Abs.	611	v.w.	v.w.	
1				213	Abs.	w.	3112	v.w.	Abs.	413	Abs.	Abs.	5112	Abs.	v.w.	6111	Abs.	Abs.	
2				215	Abs.	v.w.	3113	Abs.	w.	4113	Abs.	Abs.	5113	Abs.	v.w.	6111	Abs.	Abs.	

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TABLE IV.—Planes {h k l}.
 A = Indices {h k l}.
 B = Intensity of reflection in naphthalene tetrachloride.
 C = Intensity of reflection in dichloronaphthalene tetrachloride.

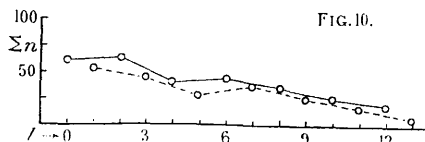
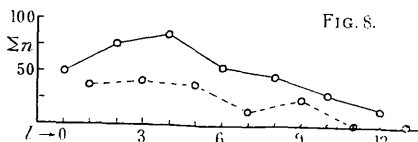
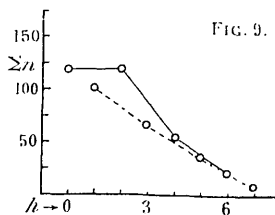
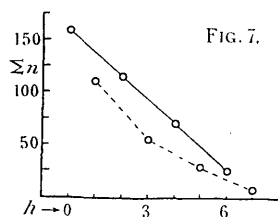
l	A	B	C	A	B	C	A	B	C	A	B	C	A	B	C	A	B	C
12	0311	Abs.	v.w.															
11	039	w.	m.	1310	v.w.	v.w.												
10	037	Abs.	Abs.	138	w.m.	w.m.	239	v.w.	v.w.									
9	035	m.	m.s.	136	m.	v.w.	237	Abs.	m.	338	Abs.	w.	437	v.w.	Abs.			
8	033	m.	m.	134	m.s.	v.w.	235	m.s.	Abs.	336	w.	v.w.	435	w.	Abs.	536	v.w.	Abs.
7	031	s.	v.s.	132	m.s.	w.	233	v.w.	w.m.	334	w.m.	w.	433	Abs.	Abs.	534	v.w.	Abs.
6				130	Abs.	w.	231	m.	w.m.	332	w.	v.w.	431	w.	v.w.	532	w.	v.w.
5				132	w.m.	s.	231	m.	v.w.	330	v.w.	Abs.	431	w.m.	w.m.	530	v.w.	Abs.
4				134	s.	m.s.	233	w.	s.	332	v.w.	v.w.	433	v.w.	Abs.	532	Abs.	w.
3				136	m.	m.	235	m.	Abs.	334	m.	w.	435	Abs.	w.m.	534	v.w.	v.w.
2				138	w.m.	w.m.	237	v.w.	m.s.	335	m.	w.m.	437	v.w.	Abs.	535	v.w.	v.w.
1				1310	v.w.	v.w.	239	w.	Abs.	336	w.	v.w.	439	w.	w.	538	v.w.	Abs.
0				1312	w.	v.w.	2313	v.w.	Abs.	3312	Abs.	v.w.	4313	v.w.	w.	5312	Abs.	v.w.
1				132	w.m.	s.	233	w.	s.	333	v.w.	v.w.	435	Abs.	w.	533	Abs.	w.
2				134	s.	m.s.	235	m.	Abs.	335	m.	w.m.	437	v.w.	Abs.	535	v.w.	v.w.
3				136	m.	m.	237	v.w.	m.s.	336	w.	w.	439	w.	w.	536	v.w.	v.w.
4				138	w.m.	w.m.	239	w.	Abs.	338	Abs.	w.	439	w.	w.	538	v.w.	Abs.
5				1310	v.w.	v.w.	2311	Abs.	w.m.	3310	Abs.	w.	4311	Abs.	Abs.	5310	w.	Abs.
6				1312	w.	v.w.	2313	v.w.	Abs.	3312	Abs.	v.w.	4313	v.w.	w.	5312	Abs.	v.w.
7																		
8																		
9																		
10																		
11																		
12																		
13																		

0 1 2 3 4 5 6 7 h

The general weakness of the reflections from planes with the l index odd is at once obvious. There is, however, another effect. We see that the diagrams for $k = 1, 3$ and 5 are much more confused, especially at the ends, than the $k = 0, 2$ and 4 diagrams. The explanation of this is to be found in another tendency for weak planes when h is odd. Bearing in mind the general halving when $h+k+l$ is odd, we have

h odd	$k = 0$	l odd	Spacegroup halvings.
h even	$k = 1$	l odd	Opposing effects.
h odd	$k = 2$	l odd	Double weakening effects.
h even	$k = 3$	l odd	Opposing effects.
h odd	$k = 4$	l odd	Double weakening effects.
h even	$k = 5$	l odd	Opposing effects.

We may summarise these effects by adding up the intensity numbers for all the planes. Fig. 7 shows these numbers plotted against the h index (vertical columns in the tables)



Figs. 7, 8.—Naphthalene Tetrachloride.
 Σn summed from $k = 1$ to $k = 4$ only.

Figs. 9, 10.—Dichloronaphthalene Tetrachloride.
 Σn summed from $k = 1$ to $k = 4$ only.

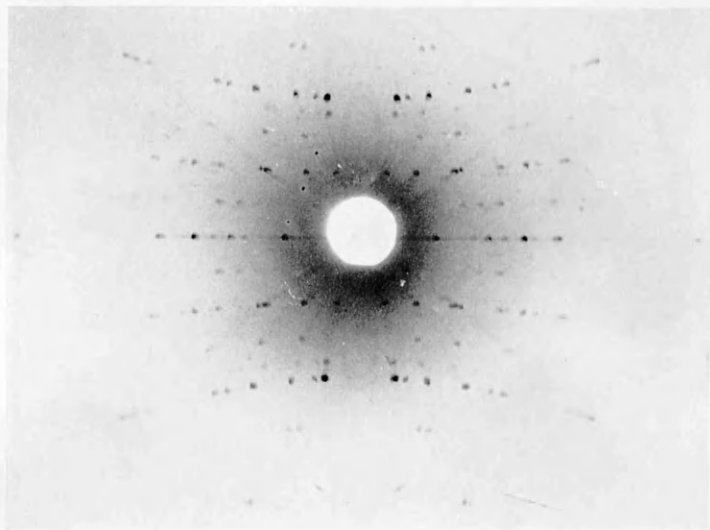
The intensity numbers are summed from $k = 1$ to $k = 4$ only in order to eliminate the effect due to the general halving of the $\{h0l\}$ planes when h is odd. $k = 5$ is not included because we must have an equal number of k odd planes and k even planes in order to eliminate the alternating effect due to the tendency for weak planes when l is odd. The tendency for weak planes when h is odd is now obvious. Fig. 8 summarises in the same way the tendency for weak planes when l is odd.

Figs. 9 and 10 are prepared in exactly the same way from the data for dichloronaphthalene tetrachloride, and show that the same effects to a less extent are operating. We may note that in this case the tendency for weak planes when h is odd is at least as strong as the tendency when l is odd. Reference to this fact will be made later.

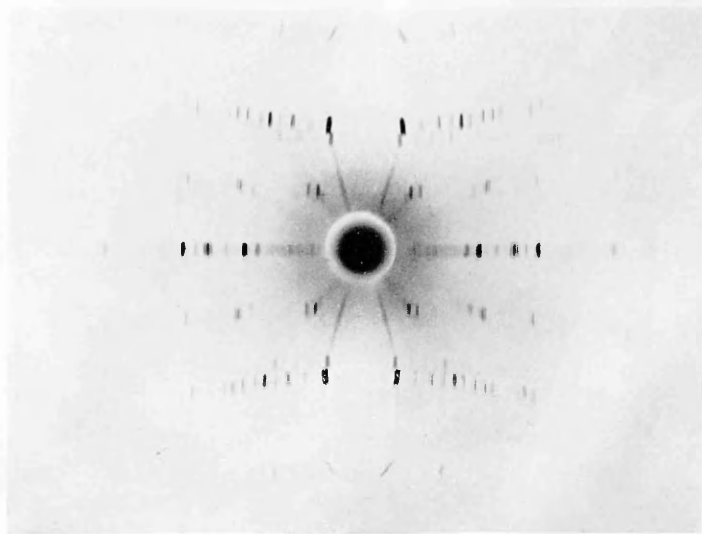
The weakening effects which are most pronounced, viz. when l is odd in naphthalene tetrachloride, and when h is odd in dichloronaphthalene tetrachloride are readily seen on the rotation photographs about the c and the a axes respectively in these crystals (Plate 17). In naphthalene tetrachloride the intermediate hyperbolae, which contain all the reflections when l is odd, are very faint. The great strength of the fourth hyperbola is interesting (cf. fig. 8). This photograph was taken with a very minute crystal, measuring about half a cubic mm. With larger crystals the absorption is very great, and

Robertson.

Roy. Soc. Proc., A, vol. 118, Pl. 17.



Naphthalene Tetrachloride. (Rotation about *c* axis.)



Dichloronaphthalene Tetrachloride. (Rotation about *a* axis.)

the intensity of the resulting broken reflections is hard to estimate. In dichloronaphthalene tetrachloride the intermediate hyperbolae contain all the h odd reflections which are seen to be relatively weak. The crystal in this case was a small needle whose axis was the a axis. This form is typical of dichloronaphthalene tetrachloride. One advantage of the diagrams over the photographs is shown in the much larger range recorded. For instance, in fig.8 we can compare the intensities of planes up to $l = 13$, whereas in the photograph about the c axis only about five hyperbolae ($l = 5$) are visible. The planes with higher indices are recorded in oscillation photographs about the b axis (using a circular camera).

In seeking an explanation of the above facts we must consider the position of the reflected molecule in the unit cell. If A represents a standard molecule, then an exactly similar molecule A' is situated at the centre of the cell. The reflected molecule B is derived from A by a reflection in the ac plane plus a translation of $\frac{1}{2}c$ along the c axis and may lie anywhere along B_1B_2 (fig.11(a),).

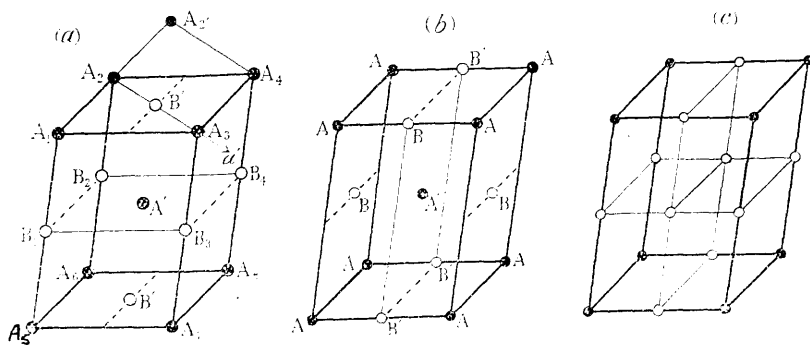


FIG. 11.

We have to determine a parameter which as far as possible expresses its position along this line.* The molecule B' is derived from A' in the same way as B is derived from A . Suppose that the reflected molecule bears some resemblance to the original molecule from all points of view and that we can therefore place it at a more or less definite position with respect to the original molecule. Consider first the arrangement shown in fig.11(a), where the reflected molecule B , subdivides the primitive translation A, A_s . The length of the c axis is approximately halved and we shall get weak planes when the corresponding index l is odd, because all such planes are interleaved with reflected molecules. If the reflected molecule were exactly like the standard molecule, and were situated exactly at $B, , \dagger$

* If A is a point representing the position of a standard molecule, we cannot in general define the position of the reflected molecule by another point such as B . Let the coordinates of A be x, y, z , with the a, b , and c directions as axes. Then the coordinates of the equivalent point on the reflected molecule are $x, -y + \rho, z + \frac{1}{2}c$, where ρ has to be determined. If, however, we can infer an approximate plane of symmetry in the molecule, as is probable in this case, then any point situated on this plane can be thought of as representing approximately the position of the molecule in question.

† It is convenient in this work to refer the indices to the body centred cell containing four molecules. The real "unit" cell, of course, is only half this size and contains two molecules.

then $B, B_2, B_3, B_4, A_5, A_6, A_7, A_8$ would become the unit cell,[†] and the \underline{l} odd planes would entirely disappear. We see that, generally, given the necessary similarity between the standard molecule and the one derived from it by a symmetry operation (cf. p. 33 and Astbury, loc.cit.), then those planes will tend to be weak which have the index corresponding to the direction which is subdivided by the symmetry molecule as an odd number. The extension to more than one subdividing molecule is obvious.

For example, in fig. 11(a) the second reflected molecule B' subdivides the primitive translation $A_2 A_3$. Change the unit cell so that this direction \underline{a}' is the new \underline{a} direction. Then the indices $h'k'l'$ referred to the new cell are given by $h' = h + k$, $k' = k$, $l' = l$, and we get weak planes when \underline{h}' is odd, i.e., when $h+k$ is odd, and therefore when \underline{l} is odd, because $h+k+l$ is even. Hence the effect of both reflected molecules is to give weak planes when \underline{l} is odd and there is no other effect.

It can be seen in the same way that in the structure shown in fig. 11(b) the effect of both reflected molecules is to produce weak planes when h is odd.

But the results show that in the case of naphthalene tetrachloride and dichloronaphthalene tetrachloride both these effects are present, the \underline{l} odd effect being predominant in the former crystal and the \underline{h} odd effect in the latter.

If the reflected molecule were in some intermediate position between that shown in fig.11(a) and fig.11(b), there would be no tendency to either effect. A structure such as that shown in fig.11(c), where the lattice is no longer body centred, would give rise to both effects, the unit cell being effectively quartered, but such a structure is impossible within the space group we are considering (C_3^4). Under these circumstances we can only conclude that the molecule functions as if it were effectively in both the positions required by figs. 11(a) and 11(b). A simple explanation of this anomaly presents itself when we consider the probable structure of the molecule as built into the crystal. The chemical structure indicates that the four chlorine atoms are attached to one carbon ring, and the approximate plane of symmetry which is required in the molecule to account for the tendency to give weak sets of planes indicates that the chlorine atoms must be approximately symmetrically placed on either side of the ring. If now we place the molecule along the c axis of the crystal, the appearance when viewed along that axis can be roughly indicated by fig.12, where the ovals are taken to represent ~~the~~ an end on view of the region occupied by the carbon rings, and the crosses indicate the approximate location of the halogen atoms on either side of the molecule. We do ^{not} require at present to discuss

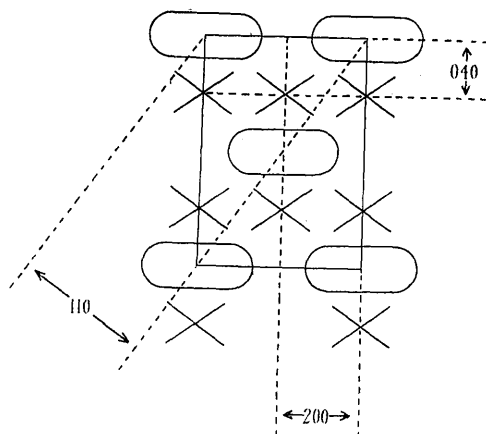


FIG. 12.—Projection of Unit Cell on ab plane (001).

the exact position of these atoms. We now see that whereas the molecule as a whole, and the carbon rings considered by themselves, conform to the structure of fig.11(a), yet the groups of halogen atoms, considered by themselves, conform to the other type of structure shown in fig.11(c). We may therefore conclude that the tendency for weak planes when \underline{h} is odd is due to the effect of these groups of atoms, which virtually lie on a different type of lattice. Confirmation is obtained from dichloronaphthalene tetrachloride. We now have six chlorine atoms instead of four, and the latter effect predominates. In the case of this crystal, however, the increase in the length of the \underline{b} axis (12.3 instead of 10.3) must affect the structure shown in fig.12, probably in disturbing the alignment of the halogen atoms. It is not surprising,

therefore, that we get more confusing relations in the diagrams (figs.9,10).

Having found ~~the~~^a probable orientation and arrangement of the molecules in these crystals, we can now proceed to a qualitative examination and comparison of the intensities of the most important reflections, as a preliminary to the development of an exact structure factor. Take first the case of the {010} planes. The observed results are as follow, measured on rotations and oscillations about the a and c axes:-

	Naphthalene tetrachloride.	Dichlornaphthalene tetrachloride.
020	trace	w.m.
040	v.s.	m.
060	trace	v.w.
080	m +	w.m. +
0, 10, 0	Abs.	w.m. +
0, 12, 0	w.	Abs.

The almost exact quartering in the case of naphthalene tetrachloride is explained by fig.12. Summing atomic numbers, $C_{10}H_8 = 68$ and $Cl_4 = 68$, so that the chlorine atoms should be equal in reflecting power to the carbon ~~atoms~~ rings. The distance from the centres of the chlorine atoms to the centres of the carbon atoms must be almost exactly $\frac{1}{4}b = 2.58$. We may note here that, in order to explain the very perfect quartering observed in the higher orders, calculation shows that we require to assume almost flat carbon rings in the naphthalene tetrachloride molecules.

If the rings were like those in the diamond structure, built in strictly tetrahedral manner, then the tenth order should be stronger than the twelfth, whereas we find a distinct twelfth order and no trace of the tenth. In the case of dichloronaphthalene tetrachloride we have $C_{10}H_6 = 66$ and $Cl_6 = 102$, so that we should now expect the 020,060,..... to appear, which is in agreement with the facts. These orders, however, are somewhat stronger than we should expect by simply increasing the weight of the halogens. The increase in the length of the b axis indicates, as we have seen, that some displacement across the plane has most likely occurred as well. Although this must have a very marked effect on the intensities of all the higher orders, we can neglect it in the general discussion of the simple planes given below.

Consider next the following planes:-

	Naphthalene tetrachloride.	Dichloronaphthalene tetrachloride.
200	s.	m.s.
400	v.s.	s.
600	v.w.	Abs.
110	m.s.	s.
220	v.s.	v.s.
330	v.w.	Abs.
440	m.s.	w.

Reference to fig.12 will show that in these sets of planes we should not expect much change in the relative

intensities of the reflections between the two compounds provided that the two additional substituted chlorine atoms in dichloronaphthalene tetrachloride are situated somewhere beneath the other halogens. Such a substitution would increase the weight of some of the scattering centres without materially affecting their distribution across the plane. This inference is again in accordance with the results.

Let us now make a projection on the bc plane (parallel to the a axis) of the structure thus far obtained. The appearance is shown in fig.13, where the crosses as before indicate the region occupied by the halogen atoms, and the

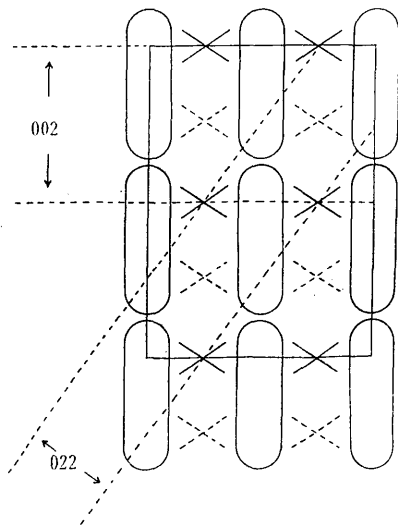


FIG. 13.—Projection of Unit Cell on *bc* plane (100).

oblongs a side view of the carbon rings. The dotted crosses represent the region of the substituted chlorine atoms,

situated beneath the others. We now see that these substituted atoms will greatly alter the distribution of the scattering centres across the (011) and the (002) planes, and hence we should expect pronounced changes in the relative intensities of the orders of these planes when the two compounds are compared, and the following observed results show that this is the case:-

	Naphthalene tetrachloride.	Dichloronaphthalene tetrachloride.
011	w.	w.
022	v.s.	v.w.
033	m.	m.
044	s.	Abs.
002	s.	v.w.
004	m.s.	s.
006	w.m.	w.
008	w.	w.

We can see at once from fig.13 why the strong (002) of naphthalene tetrachloride nearly disappears in dichloronaphthalene tetrachloride, and is replaced by a strong (004).

Other confirmations of this view of these structures are obtained from a study of some (h0l) planes. As all these planes are halved by space group considerations, we now only require to take account of the f configuration of one molecule. Fig.14 shows the projection of one quarter of the unit cell on the ac plane. The molecule now lies in the plane of the paper. If we adopt the flat ring of graphite, the distance from centre to centre

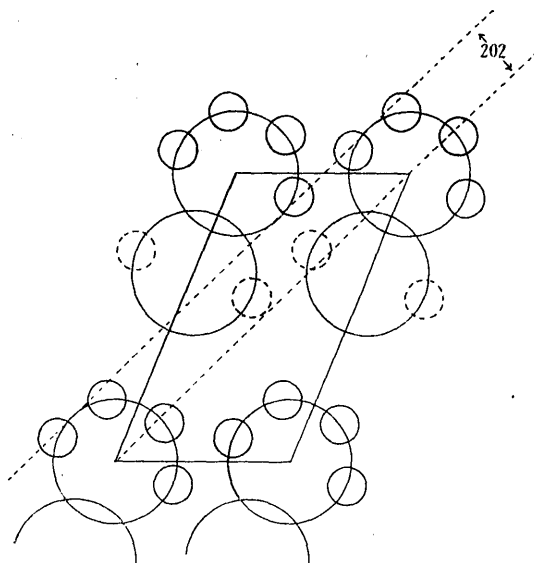


Fig. 14.—Projection of Quarter of a Unit Cell on ac plane (010).

of the carbon atoms = 1.41 A.U., and this is the radius of the atom centres which lie on the large circles in the diagram.* If we adopt the tetrahedral ring, as in the diamond, and place it as required to account for the position of the chlorine atoms, i.e., with a minimum extension along the b axis, then it will project into exactly the same diagram on this plane, where r the radius of the atom centres, and the distance from centre to centre in the projection, is given by

$$r = 2/3\sqrt{2}D = 1.41 \text{ A.U.}$$

when D the diameter of the carbon atom is now taken as 1.50 A.U.

* (cf. Bragg 'X-Rays and Crystal Structure' p. 237 (1913))

It is therefore obvious that the (h0l) planes contain no information as to whether the graphite or diamond structure is present in this case.

The positions of the centres of the chlorine atoms to be expected from chemical considerations are indicated by small circles, the two substituted atoms being shown by a broken line. The carbon atoms are not shown.

Consider the following (h0l) planes:-

	Naphthalene tetrachloride.	Dichloronaphthalene tetrachloride.
202	v.s.	Abs.
404	v.w.	v.w.
20 $\bar{2}$	v.s.	Abs.
40 $\bar{4}$	w.m.	m.

The diagram shows the effect of the chlorine atoms in making the (202) strong in naphthalene tetrachloride and absent in dichloronaphthalene tetrachloride.

Based upon the dimensions and orientation discussed above, an exact structure ^{factor} can be developed which explains most of the prominent features in the intensities of the (h0l) planes. Its discussion, however, is postponed for the present, owing to ~~some~~ uncertainties which enter into the exact treatment of so complicated a molecule.

SUMMARY.

The structures of naphthalene tetrachloride and 1.2.3.4.5.8.-hexachloronaphthalene-1.2.3.4-tetrahydride have been examined by the rotating crystal method, and are found to be closely similar. The lattices are body centred, and the most probable space group is C_s^4 , with four asymmetric molecules per unit cell. This involves a polar crystal.

The parameter of the reflected molecule is determined by a statistical investigation of the intensities of the general plane, based upon Bernal's method of interpretation. This also leads to an approximate location of the halogen atoms, which are found to lie on what is virtually a different type of lattice.

A comparison of the intensities of the simple axial planes, and some others, in the two crystals shows that the two additional substituted chlorine atoms in dichloronaphthalene tetrachloride must lie somewhere beneath the added chlorine atoms when we view the structure along the c axis. In view of the chemical structure this can only mean that the long axis of the molecule is approximately coincident with the c axis of the crystal, with the chlorine atoms on either side of the molecule interleaving the carbon rings. The intensity distribution in the higher orders of certain planes requires an almost flat carbon ring as in the graphite structure.

PART III.

A QUANTITATIVE X-RAY INVESTIGATION OF THE
CRYSTALLINE STRUCTURE OF ANTHRACENE.

Part III.

A Quantitative X-Ray Investigation of the Crystalline Structure of Anthracene.

In Part I it was shown that the long axis of the anthracene molecule must lie more or less along the a axis of the crystal, but less definite indication was obtained regarding the lateral disposition of the molecules. Subsequent work by Bragg and independently by Banerjee ¹⁾, based on the measurement of a few X-ray intensities, and also upon optical and magnetic measurements, has indicated that the 'plane' of the anthracene molecule probably makes an angle of about 25° with the bc crystallographic plane.

At the commencement of the present work, then, it could be taken that the structure of anthracene was approximately known. It was very important, however, to confirm these results by more accurate and more extensive intensity measurements, and also to attempt to work out the finer ~~data~~ details of the structure. For example, it was not known if the carbon rings were quite flat, like the graphite structure, or slightly puckered, perhaps intermediate between the diamond and graphite type. The evidence seemed to point to the latter possibility. The carbon to carbon distance was not accurately known. The only estimate obtained was 1.48 A.U., which is again intermediate between the diamond

¹⁾ 'Nature', vol. 125, p. 456 (1930)

(1.54) and the graphite (1.42) distance.

As the anthracene structure involves 21 parameters without considering the hydrogen atoms, its complete determination is a very complicated task. With the results already obtained it was obviously a case for the application of Fourier analysis, and this method has been extensively used in the present investigation. Briefly, the procedure has been as follows. First of all the parameters were determined as far as possible by trial and error, and then a preliminary Fourier analysis was carried out for two zones of reflections (about the b and c crystallographic axes). From the results of this analysis the values of the coordinates of the atoms were refined, and it was now found that a much better agreement was obtained between the observed and the calculated values of the reflections. This was chiefly due to the presence of a hitherto unsuspected tilt in the axis of the molecule away from the ac plane. With the revised values of the coordinates it was now possible to make sure of the phase constants of some of the weaker reflections which had previously been doubtful. The intensity measurements were now checked and made as accurate as possible and a final double Fourier analysis carried out for the zones about the three crystallographic axes. The results of this final analysis are set out and discussed in this paper.

Measurement of Intensities.

Like most organic compounds, anthracene forms crystals which are usually small and friable, unsuitable for cutting or grinding into sections. The best method for measuring the integrated reflections from such crystals therefore appears to be that of completely immersing a small single crystal in the X-ray beam. As this method, although tested ¹⁾, has not been much used in quantitative work, Mr. B. W. Robinson in this laboratory has conducted a parallel investigation into the validity of the whole method, with special reference to anthracene, and has also determined the absolute values of some of the anthracene reflections. For the purposes of this paper, then, the writer has only required to measure the relative values of the integrated reflections from anthracene. These measurements were then calibrated with Robinson's absolute values, using one of his measured crystals for the purpose.

Two methods of measuring the intensities have been used, the ionisation spectrometer and the integrating photometer devised by Robinson. The photographic method seems to be the most suitable for obtaining a complete survey of a large number of reflections, such as those required for making the two-dimensional Fourier analyses. There is less chance of missing certain reflections, which may be comparatively weak, yet valuable for

1) W. H. Bragg, 'Phys. Soc. Proc.', vol. 33 p. 304 (1921).

completing the detail in the analyses. But in general the more important reflections have been measured both by the ionisation and photographic methods, and the following list is typical of the agreement obtained by the two methods. The figures give the integrated intensity in arbitrary units.

hkl.	Ionisation spectrometer.	Robinson's photometer.
200	1000	982
20 $\bar{1}$	652	645
20 $\bar{2}$	253	258
001	711	667
002	192	194
003	52	59
004	81	72
005	32	31

The effect of extinction on the strong reflections is discussed by Robinson, but it may be mentioned here that we believe that by using sufficiently small crystals, weighing about one tenth of a milligram, the effect is largely eliminated. In making the relative measurements the smallest possible crystals were used in estimating the strong reflections, although slightly larger ones were occasionally used in measuring the weaker reflections, which do not appear to be affected by extinction.

Most of the measurements were made with copper radiation ($\lambda = 1.54$). With this wavelength the absorption of the beam

in the crystal is quite considerable, but again, with very small crystals, the effect is small. It did not seem practicable to apply a separate correction to each of the relative measurements to allow for the shape of the crystal, and the largest errors will probably be due to the varying thickness of ~~the~~ crystal presented to the beam at each reflection. Several crystals of different shapes were usually measured, with good agreement except in extreme cases. In general, crystals with a nearly square section perpendicular to the rotation axis were sought ~~for~~, those in the form of thin flakes being avoided.

~~The following~~ Table gives the value of the structure factor for each reflection in absolute units, and it is compared with a value calculated from the coordinates found for the atoms (which are given on p. 60) and from an F-curve for carbon based on the measured reflections from graphite ¹⁾. The value of the structure factor is obtained from the measured reflection by the usual formulae for the "imperfect" crystal.

¹⁾ Bernal, 'Proc. Roy. Soc., A, vol. 106, p. 749 (1924); Rundle, vol. 113, p. 499 (1927).

Table I.—Measured and Calculated Values of the Structure Factor.

<i>hkl.</i>	$\sin \theta$ Cu K α .	F calc.	F measured.	<i>hkl.</i>	$\sin \theta$ Cu K α .	F calc.	F measured.
200	0.219	+60.5	59	20 $\bar{0}$	0.658	+10.5	8.5
400	0.438	-6.5	3	404	0.691	-6	6
600	0.657	-8.5	7	403	0.621	-7	7
020	0.256	-19.5	24.5	402	0.553	+5	< 4
040	0.511	-2	< 3	401	0.494	-0.5	< 3
001	0.084	+34	30	40 $\bar{1}$	0.395	+3	< 3
002	0.168	-20.5	22	40 $\bar{2}$	0.368	-4.5	6.5
003	0.252	+12	14.5	40 $\bar{3}$	0.359	+4	6
004	0.336	-20	22	40 $\bar{4}$	0.368	-0.5	< 3
005	0.420	-12	16	40 $\bar{5}$	0.395	-13.5	11.5
006	0.504	+5	< 4	40 $\bar{6}$	0.437	+6.5	< 4
007	0.588	-1	< 4	40 $\bar{7}$	0.620	+28.5	22
008	0.672	-4.5	< 4	40 $\bar{10}$	0.690	+10.5	9
009	0.756	-7	3	CO1	0.613	-15	12
				CO2	0.576	-3	< 4
011	0.152	-9	9	CO $\bar{3}$	0.550	+5	< 4
012	0.209	-3.5	3.5	CO4	0.538	-3.5	< 4
013	0.280	+2	4.5	CO5	0.538	-19.5	18.5
014	0.358	+8.5	12.5	CO6	0.550	-5.5	6
015	0.435	+13.5	14	CO $\bar{9}$	0.658	+18	15.5
016	0.518	+0.5	< 4	CO $\bar{10}$	0.709	+17.5	15
017	0.600	-5	< 5	804	0.735	-1	< 4
018	0.683	+9	6	805	0.720	-8.5	8.5
019	0.767	+8.5	5.5	80 $\bar{6}$	0.715	-8.5	7
021	0.270	-17	17	80 $\bar{7}$	0.720	+2	< 4
022	0.305	+5.5	8.5				
023	0.359	-0.5	5.5	110	0.167	+57	50.5
024	0.421	-13	15.5	210	0.253	+44.5	48.5
025	0.491	+3	< 4	310	0.352	+7	11.5
026	0.565	-2	< 5	410	0.457	+21	24.5
027	0.640	-0.5	< 5	510	0.563	-6.5	4.5
028	0.719	+11.5	8	120	0.277	+21	19
031	0.393	+17	19	220	0.335	-10.5	13
032	0.418	0	< 3	320	0.416	+24	25.5
033	0.458	-5.5	7.5	420	0.506	-1.5	< 3
034	0.509	-13.5	14.5	520	0.604	+5.5	8
035	0.567	-16	14.5	130	0.397	-20	19.5
036	0.631	-3	< 5	230	0.440	+2	< 3
041	0.520	-3	< 4	330	0.504	-6	7
042	0.540	+0.5	< 4	430	0.581	+2	< 4
043	0.571	-1.5	< 5	140	0.521	-1.5	< 3
044	0.612	-0.5	< 5	240	0.556	-2.5	< 4
045	0.661	+12.5	11.5				
051	0.646	+1	< 5	114	0.430	-15	14
052	0.662	-1.5	< 5	113	0.353	+5	6
053	0.688	+9.5	7	112	0.278	0	< 3
054	0.723	+5.5	< 6	111	0.214	-8.5	9.5
				11 $\bar{1}$	0.158	+26	23.5
205	0.577	-8.5	8	11 $\bar{2}$	0.187	-12.5	12
204	0.495	-23.5	22.5	11 $\bar{3}$	0.244	+11.5	12.5
203	0.418	-4	4.5	114	0.310	-17	17.5
202	0.345	+4	4.5	115	0.388	-14	16.5
201	0.278	-5	5	222	0.427	+5.5	6
20 $\bar{1}$	0.184	+46	43	221	0.375	-13	13
20 $\bar{2}$	0.184	-25.5	27	221	0.314	+6.5	5
20 $\bar{3}$	0.220	+10.5	14.5	222	0.314	+2.5	< 3
204	0.275	+0.5	3	22 $\bar{3}$	0.336	+1.5	< 3
205	0.342	-7	5	224	0.372	-21.5	23.5
206	0.418	+8	5	225	0.427	-19.5	19.5
207	0.498	-6.5	< 4				
208	0.576	+3.5	< 4				

Fourier Analysis of Experimental Results.

From the preceding tables it will be seen that there is a fairly good average agreement between the measured and calculated values of F . The atomic f -curve derived from graphite, upon which the calculated values are based, cannot be expected to fit the anthracene results exactly. No allowance has been made for the hydrogen atoms; and it will be seen from the following analysis that slightly differing curves ought to be applied to the different atoms in the molecule. But the agreements obtained seem to be sufficient to determine the phase constant of each member beyond any reasonable doubt; that is, in this case, whether the sign of the structure factor is positive or negative. With this information it is then possible to proceed with the Fourier analysis, which has the great advantage of presenting the structure directly from the experimental measurements, only the sign of the terms being taken from the calculated results.

The method of the double Fourier series was first developed by W.L.Bragg* and the theory is described in his paper. The arrangement of the results adopted here is also similar to that employed by him. By this method the distribution of scattering matter in the unit cell as projected along any zone axis can be calculated. The density of scattering matter per unit area, $\rho(y,z)$, for the projection along the a axis is

$$\rho(y,z) = \frac{1}{A} \sum_{-\infty}^{+\infty} \sum_{-\infty}^{+\infty} F(hkl) \cos 2\pi(hy/a + lz/c)$$

* 'Roy. Soc. Proc.' A, vol. 123, h. 537 (1929)

A being the area of the plane upon which the projection is made. Corresponding formulae apply for the projections along the other zone axes, the coefficients in the Fourier series being the structure factors for the planes in the zone. For convenient reference these coefficients with their signs are collected below in Tables II, III, and IV for the projections along the three crystallographic axes.

It will be seen that the values of the coefficients which terminate the series are mostly fairly small compared with the initial values. In a comparatively soft organic compound like anthracene (melting point, $217^{\circ}\text{C}.$) the temperature factor is probably fairly large. This has the advantage of making the series fairly rapidly convergent without the necessity of applying an artificial temperature factor as has been suggested for certain inorganic compounds.*

Tables V, VI and VII give the summations for the projections along the three crystallographic axes, the figures corresponding to the series

$$S(y,z) = \sum \sum F(0kl) \cos 2\pi (ky/b + lz/c)$$

$$S(x,z) = \sum \sum F(h0l) \cos 2\pi (hx/a + lz/c)$$

$$S(x,y) = \sum \sum F(hk0) \cos 2\pi (hx/a + ky/b)$$

In the tables the figures have been divided by 10, so that the actual electron density per unit area is obtained from these

* W.L. Bragg and J. West, 'Phil. Mag.', vol. 10, p. 839 (1930).

figures by multiplying by 10 and dividing by the area of the plane upon which the projection is made.

The distribution of scattering matter in these projections is shown in figs. 1A to 4A. In each case the projection has been made on a plane perpendicular to the axis. The contour lines are drawn through points of equal density at intervals of 100 in the values of S . Alongside each diagram is a drawing on the same scale showing the positions of the atoms and how they are linked together to form the anthracene molecules. (Figs. 1B to 4B).

The projection along the a axis (fig. 1) shows one complete unit cell and a small part of ~~another~~ the next cell, which is added to show the extent of the gap between the ends of the molecules. In this projection the different molecules do not separate, because the centre one, which lies half a translation along the a axis in front of the others, overlaps them on either side. Some of the individual atoms, however, are quite clearly separated.

The projection along the b axis is the most striking, in that the individual molecules as well as many of the atoms are clearly separated. Fig. 2 shows a single molecule on a large scale, occupying one half of the unit cell. Fig. 3 shows on a smaller scale the mutual relations of six molecules. The centre ones, which are dotted, are identical with the others in this projection, but are actually removed half a translation along the b axis (perpendicular to the paper).

In the projection along the c axis (fig. 4) the molecules, seen end on, are very clearly separated, but not the individual atoms.

The diagram shows the mutual relation of five molecules, the dotted line being the boundary of the unit cell.

Crystal Data.

Anthracene. Melting point 217°C . Monoclinic prismatic.

$a = 8.58$, $b = 6.02$, $c = 11.18$ A.U. $\beta = 125^{\circ}$. Space group C_{2h}^5
($P2_1/a$). 2 molecules of $C_{14}H_{10}$ per unit cell. Total number
of electrons per unit cell, = $F(0,0) = 188$.

Table II. Values and Signs of $F(0kl)$.

When k is even, $F(0kl) = F(0k\bar{l})$

When k is odd, $F(0kl) = -F(0k\bar{l})$.

	k					
	0	1	2	3	4	5
9	-3	+5.5				
8	-	+6	+8			
7	-	-	-			
6	-	-	-	-		
5	-16	+14	-	-14.5	+11.5	
4	-22	+12.5	-15.5	-14.5	-	-
3	+14.5	+4.5	-5.5	-7.5	-	+7
2	-22	-3.5	+8.5	-	-	-
1	+30	-9	-17	+19	-	-
0	+188	-	-24.5	-	-	-
1	+30	+9	-17	-19	-	-
2	-22	+3.5	+8.5	-	-	-
3	+14.5	-4.5	-5.5	+7.5	-	-7
4	-22	-12.5	-15.5	+14.5	-	-
5	-16	-14	-	+14.5	+11.5	
6	-	-	-	-		
7	-	-	-			
8	-	-6	+8			
9	-3	-5.5				

Table III. Values and Signs of $F(h0l)$. h is always even.

		h				
		0	2	4	6	8
1	9	-3				
	8	-				
	7	-				
	6	-				
	5	-16	-8			
	4	-22	-22.5	-6		
	3	+14.5	-4.5	-7		
	2	-22	+4.5	-	-	
	1	+30	-5	-	-	
	0	+188	+59	-3	-7	
	1	+30	+43	-	-12	
2	-22	-27	-6.5	-		
3	+14.5	+14.5	+6	-	-	
4	-22	+3	-	-	-	
5	-16	-5	-11.5	-18.5	-8.5	
6	-	+5	-	-6	-7	
7	-	-	-	-	-	
8	-	-	-	-	-	
9	-3	+8.5	+22	+15.5		
10	-	-	+9	+15		

Table IV. Values and Signs of $F(hk0)$.When $(h+k)$ is even, $F(hk0) = F(\bar{h}k0)$ When $(h+k)$ is odd, $F(hk0) = -F(\bar{h}k0)$.

		k			
		0	1	2	3
h	6	-7	-	-	.
	5	-	-4.5	+8	
	4	-3	+24.5	-	
	3	-	+11.5	+25.5	-7
	2	+59	+48.5	-13	-
	1	-	+50.5	+19.	-19.5
	0	+188	-	-24.5	-
	1	-	+50.5	-19	-19.5
	2	+59	-48.5	-13	-
	3	-	+11.5	-25.5	-7
	4	-3	-24.5	-	
5	-	-4.5	-8		
6	-7	-	-		

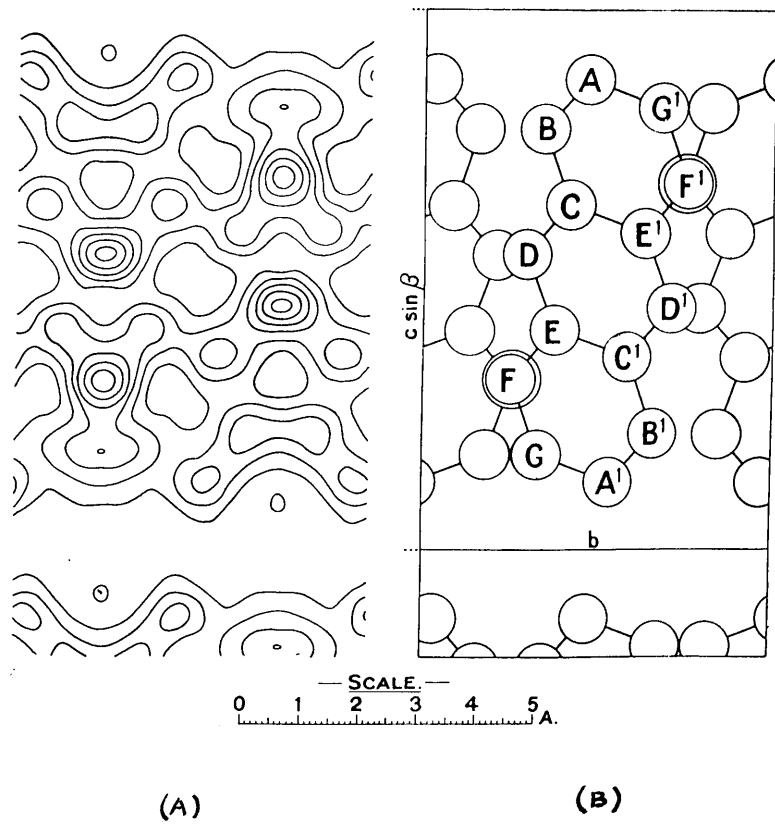


Fig. 1. Projection along a axis.

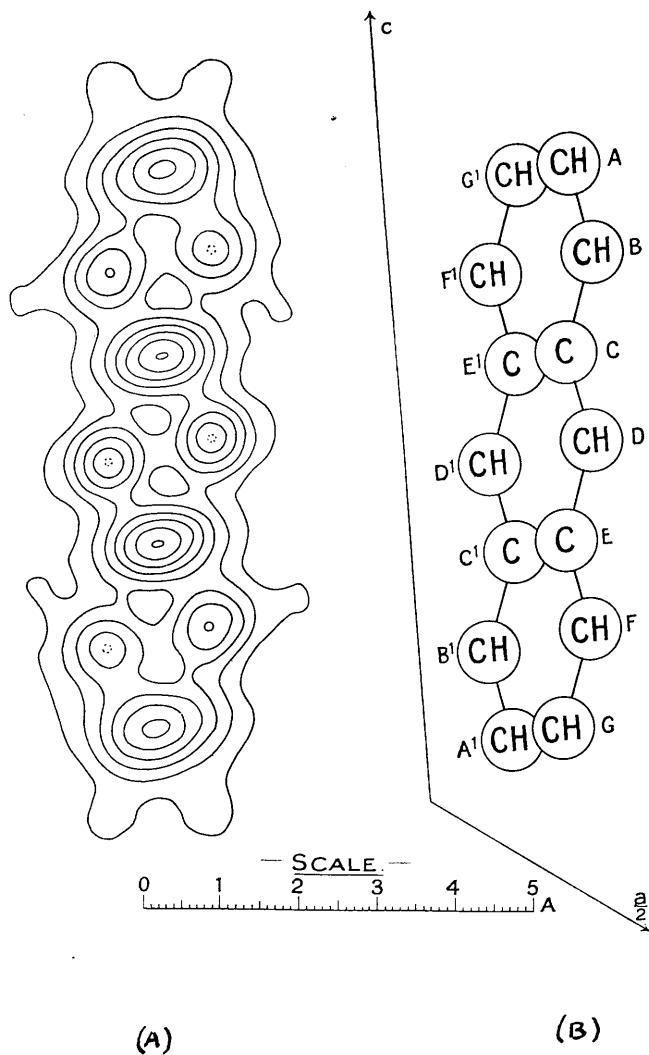


Fig. 2. Projection along b axis. The dotted centres corresponding to atoms D and B mark densities of 560 and 440 respectively.

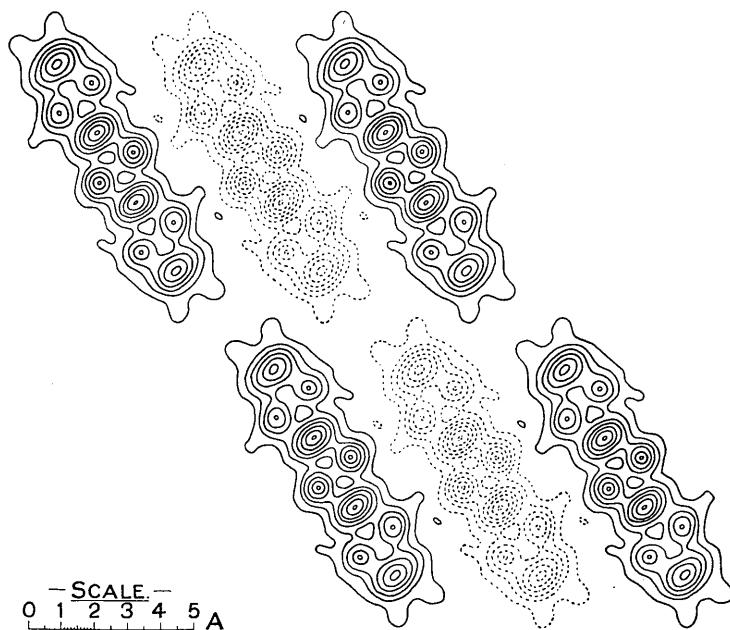


Fig. 3. Projection along b axis, showing mutual relations of six molecules.

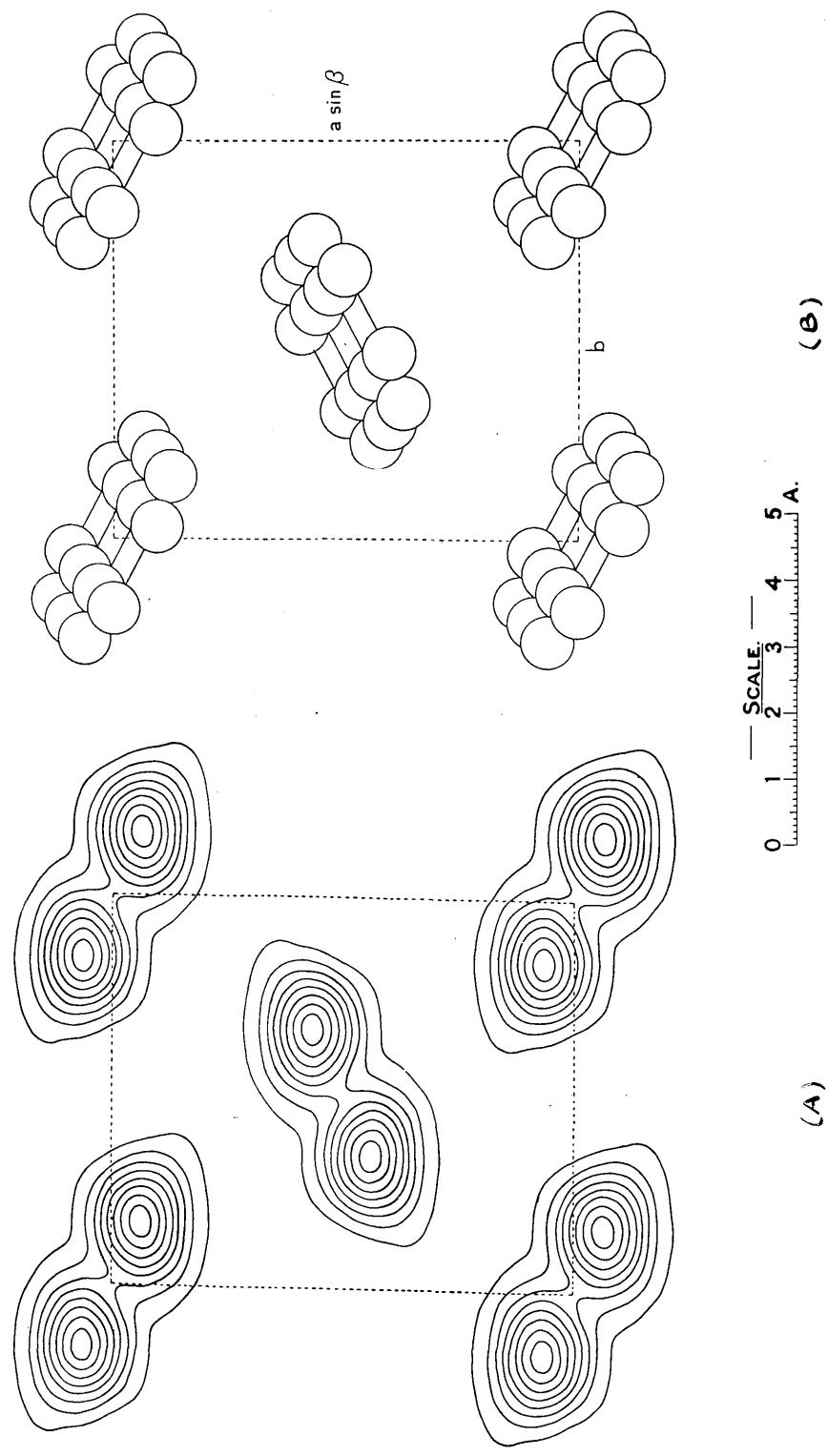


Fig. 4. Projection along z axis, showing five molecules.

Table V. Projection along the a axis.

$S(y,z) \times 10^{-1}$.

4	0	5	9	10	9	6	4	6	9	10	9	5	0	4
5	5	5	7	8	9	7	5	4	5	7	9	5	1	3
9	7	3	4	8	12	14	12	8	5	5	6	8	7	6
8	7	5	9	18	26	30	26	19	12	8	10	12	14	16
7	8	11	18	27	33	33	29	23	16	14	16	20	23	25
15	18	24	28	29	27	22	18	17	17	21	27	31	35	36
28	32	35	35	28	19	12	10	11	16	22	27	31	34	36
31	33	36	34	26	17	10	8	9	12	15	18	22	28	32
17	19	21	20	17	12	8	7	6	5	5	11	22	35	43
5	7	11	14	15	15	14	9	4	2	4	14	31	50	63
3	7	14	22	28	29	26	18	10	6	9	19	34	49	58
9	14	21	29	35	37	33	24	19	18	22	28	34	37	38
27	27	27	27	27	26	23	20	20	26	33	37	36	29	24
54	47	36	25	17	13	10	10	15	22	29	32	28	21	15
58	49	34	21	11	6	5	6	8	11	13	16	17	14	12
33	28	20	13	7	6	6	6	6	6	7	13	20	28	33

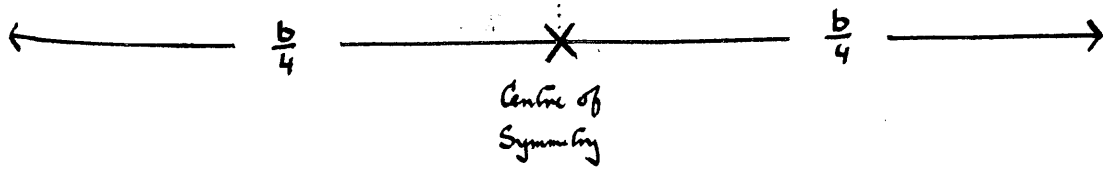


Table VI.—Projection along the *b* axis.

$S(x, z) \times 10^{-1}$.

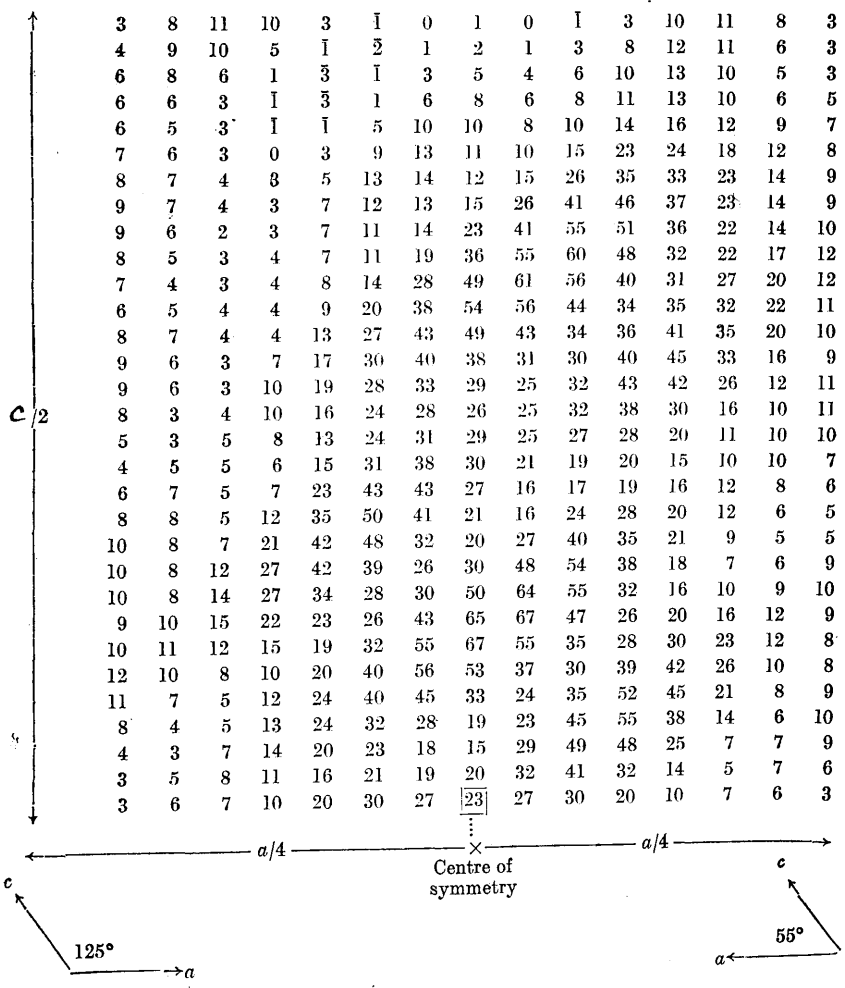


Table VII. Projection along the c -axis.

$$S(x, y) \times 10^{-1}$$

6	5	4	4	5	11	20	33	44	53	56	54	47	39	33
6	5	3	3	8	16	30	45	61	72	77	74	66	53	42
7	6	4	5	11	22	35	52	68	80	85	83	74	60	46
7	5	6	6	13	22	35	48	60	70	75	73	65	54	41
5	6	6	9	12	19	27	36	43	49	51	50	45	37	29
6	6	7	8	10	13	17	20	24	26	27	26	24	21	17
6	7	7	8	8	9	10	11	12	13	12	12	11	11	10
8	8	8	7	8	7	7	7	8	8	8	8	8	8	9
8	8	7	7	7	7	7	7	8	8	8	8	8	8	8
9	8	7	6	6	6	7	7	7	7	8	7	8	7	8
12	10	8	6	6	5	5	6	5	5	5	6	6	6	5
21	15	10	7	6	5	5	5	5	4	4	5	5	5	6
28	19	12	10	9	8	7	7	6	5	4	5	6	7	7
32	23	18	15	16	16	16	13	11	8	6	6	7	7	8
32	27	27	28	31	33	31	27	20	13	8	6	5	6	7
31	33	40	47	54	56	53	44	33	20	11	5	4	4	5

 $\frac{b}{2}$

The Structure Deduced from the Fourier Analysis.

Several encouraging features are immediately evident from the contour diagrams. The carbon atoms which are sufficiently removed from their neighbours to separate clearly show a fairly high degree of spherical symmetry. Without such symmetry, of course, the analysis of organic compounds by atomic f -curves, which is a necessary preliminary to any Fourier analysis, would ~~not~~ be ^{very difficult.} ~~directly possible~~. Again, in the projection along the b axis, the outlying atomic centres (B, D and F) are seen to lie quite accurately on a straight line, and this line is parallel to the line joining the peaks of the unresolved centres, AG', CE', etc. This regularity in the molecule is most striking, and is in harmony with our ideas of the chemical structure.

It will be noticed that in the projection along the b axis the outlying atoms, B, D and F, stand out clearly as isolated peaks, while in the a axis projection the inner atoms, A, C and E are quite clearly separated. Thus in one or other of the projections we get a clear picture of every atom in the molecule, with the exception of G, which is always somewhat obscured by its neighbours.

The molecule is inclined at varying angles to all the crystallographic axes; nevertheless, it is easy to apply a direct test of the form of the carbon rings. If these rings are regular plane hexagons, then the short cross lines,

AG', CE', EC', and GA' will be parallel to and one half as long as the long cross lines BF', DD', and FB' in every projection. The test is rendered a little difficult because of the unresolved centres, but when the most reasonable positions are assigned to these centres it is found to hold to quite a high degree of accuracy.

It is now easy to obtain the actual orientation of the molecule in space. As the crystal is monoclinic it is convenient to use an axis, c' , perpendicular to the a and b axes. The apparent angle which the long axis of the molecule makes with this c' (vertical) direction in the projection along the a axis is 8.0° , and in the projection along the b axis, 30.1° . From these figures a simple calculation gives the actual angles, α , ψ and γ which the long axis of the molecule makes with the a , b , and c' axes as

$$\alpha = 119.7^\circ \quad \cos \alpha = -.495$$

$$\psi = 96.9^\circ \quad \cos \psi = -.121$$

$$\gamma = 30.7^\circ \quad \cos \gamma = +.860$$

(The angle with the c crystallographic axis is 8.5°)

In the same way for the cross lines CE', DD', etc., the average apparent angle with the c' (vertical) direction measured on the a axis projection is 69.6° and on the b axis projection 46.9° . For the actual angles α' , ψ' and γ' with the a , b , and c' axes these figures give

$$\alpha' = 69.6^\circ \quad \cos \alpha' = +.349$$

$$\psi' = 28.6^\circ \quad \cos \psi' = +.878$$

$$\gamma' = 70.9^\circ \quad \cos \gamma' = +.327$$

The real angle between the long axis of the molecule and the cross lines DD' , etc. is ~~cos~~^{arc} $(\cos \alpha \cos \alpha' + \cos \psi \cos \psi' + \cos \gamma \cos \gamma')$ and with the above figures this works out at 89.9°.

This is a very satisfactory result, because it shows in a more precise way that the molecule is built from regular hexagon rings.

The radius of these hexagons, which is equal to the carbon to carbon distance, can readily be measured on the projections. In the projection along the b axis it is one half of the distance between the outlying atoms BF' , DD' , and FB' . This is quite accurately constant, and is equal to .67 A.U. in this projection. Combined with the direction cosines given above, this gives a value of 1.41 A.U. for the real radius.

In the projection along the a axis the average distance between the inner atoms, CE' , EC' , etc., is 1.32 A.U., which combined with the direction cosines again gives a value of 1.41 A.U. for this interatomic distance.

The periodicity along the molecule, that is, the distance between the lines joining the centres AG' , BF' , CE' , DD' , etc., measured along the axis of the molecule, is quite reasonably constant. In the a projection it averages 1.07 A.U., and in the b projection 1.20 A.U. Combined with the direction cosines these figures give 1.23 and 1.21 A.U. for the real periodicities.

The mean value, 1.22 A.U., is equal to $(1.41 \times \sqrt{3}/2)$ A.U., the value required by a regular hexagon structure.

All the above information is, of course, contained in a statement of the coordinates of the atoms. But it has been given in the preceding form because it is sometimes easier to measure the angle between certain lines in these diagrams than to locate the atomic centres accurately. The parameters as measured directly from the diagrams are now given in table VIII. The figures in bold type refer to atoms which separate clearly as more or less circular masses in one or other of the diagrams. The remaining atoms are too near their neighbours and appear as unresolved ovals, but the probable position of the centres can be estimated fairly well. It will be seen that only 14 of the 21 parameters can be directly measured from the diagrams. The z coordinates are estimated separately from the b and c axis projections, and the agreements obtained may be considered satisfactory, remembering that the two projections are based on different sets of experimental measurements.

Table VIII. Coordinates. Centre of Symmetry as Origin.

Atom. of fig. 3.	x A.U.	$\frac{2\pi x}{a}$	y A.U.	$\frac{2\pi y}{c}$	From a fig. z A.U.	From b fig. z A.U.	$\frac{2\pi z}{c}$ (mean)
A.	.81	33.8	.19	11.4	4.17	4.10	133.0
B.	<u>1.06</u>	<u>44.6</u>	.94	<u>56.5</u>	<u>3.14</u>	<u>3.11</u>	<u>100.5</u>
C.	.54	22.5	.49	<u>29.5</u>	<u>1.57</u>	1.55	<u>50.3</u>
D.	<u>.81</u>	<u>34.1</u>	1.24	74.4	.55	<u>.57</u>	<u>18.0</u>
E.	.28	11.9	<u>.78</u>	<u>46.8</u>	<u>-1.00</u>	<u>-.98</u>	<u>-31.9</u>
F.	<u>.56</u>	<u>23.5</u>	<u>1.53</u>	<u>91.4</u>	<u>-2.02</u>	<u>-1.98</u>	<u>-64.4</u>
G.	.02	0.6	1.06	63.6	<u>-3.60</u>	<u>-3.54</u>	<u>-115.0</u>

Intermolecular Distances.

The distances between atoms on neighbouring molecules are in marked contrast to the distance of 1.41 A.U. which has been found for the linked carbon atoms within the molecule.

The molecule in the centre of the (001) face is derived from the corner molecule by a reflection in the (010) plane, or by a rotation about the b axis, and a shift of $\frac{1}{2}a, \frac{1}{2}b$. Each molecule consists of two chains of seven carbon atoms, one chain being the inversion of the other. The coordinates of one such chain, forming an asymmetric unit, are given in table VIII. The whole unit cell can be built up from these coordinates (x, y, z) in the following way

$x,$	$y,$	z	. . . (1) Standard unit	} Standard molecule
$-x,$	$-y,$	$-z$. . . (2) Inversion of (1)	
$4.29 + x,$	$3.01 - y,$	z	. . . (3) Reflection of (1)	} Reflected molecule
$4.29 - x,$	$3.01 + y,$	$-z$. . . (4) Inversion of (3)	

It is then easy to calculate the distances between the centres of atoms in adjacent molecules. The distance between the standard and the reflected molecule varies from atom to atom owing to the inclination of the molecules, but the shortest distance found is about 3.77 A.U. Between the molecules at the ends of the b axis, the closest distance of approach is 3.80 A.U. Between those at the ends of the c axis the

gap is somewhat greater, reaching a minimum of 4.06 A.U. Owing to the molecules being inclined at about 30° to the vertical position, the distance between the ends of a standard molecule and a reflected molecule one translation along the c axis is ^{less} shorter, reaching a minimum of about 3.67 A.U. This is the closest distance of approach which has been found between the centres of atoms in adjacent molecules.

Comparison with Other Structures.

It is interesting to compare these distances with those determined in other structures involving the carbon atom. The carbon to carbon distance within the molecule of 1.41 A.U. compares with a corresponding distance of 1.42 A.U. in graphite ¹⁾ and hexamethylbenzene ²⁾. In the graphite structure there are two atoms on a vertical axis 3.41 A.U. apart (the distance between the layers) and six symmetrically distributed about it at 3.70 A.U. The (001) spacing in hexamethylbenzene is 3.70 A.U. For the long chain hydrocarbon $C_{24}H_{60}$ Muller ³⁾ found the distance of nearest approach between two centres on two neighbouring molecules placed end to end to be approximately 4.0 A.U., and for the same hydrocarbon the distance of nearest approach between two centres on two adjacent molecules placed sideways to lie between 3.6 and 3.9 A.U.

1) Bernal, loc.cit.

2) Lonsdale, loc.cit.

3) Muller, 'Roy.Soc.Proc'.A, vol.120, p.437(1928).

The Electron Distribution.

The Fourier projections which have been made reveal some particularly interesting features, which are most noticeable in the projection along the b axis (fig.3). On the central carbon atoms, D and D' , which are the "meso-" positions in anthracene, the electron density reaches a height of 560 in the value of S. These atoms are very circular and rise to moderately sharp peaks. The atoms in the "benz-" positions, however, are somewhat flatter and more spread out, the electron density rising to a value of 500 on F, and only about 460 on B. The height of the peak is thus seen to fall away as we move further out from the centre of the molecule. The same effect is noticeable in the case of the unresolved centres, CE' being 700 and AG' only a little over 600 units at the maximum. Further, the form of the first contour line shows quite pronounced bulges around the atoms in the end benzene rings, which are absent from the atoms of the central ring.

Considerable caution, however, is necessary in accepting finer detail of this kind in the structure. The Fourier series is necessarily incomplete, the measurements being limited by the wave-length and the experimental conditions. This limitation is very liable to introduce false detail to the picture, similar to diffraction effects in the case of an optical instrument.* In the present analysis the concluding

* Compare W.L. Bragg and J. West, *loc. cit.*

coefficients are generally fairly small, but it is quite possible that if still more terms could be added they would have the effect of smoothing out some of the detail.

At the same time, the fall in the peak values of the electron density as we pass out from the centre of the molecule, combined as it is with a slight broadening of the structure, are rather pronounced experimental facts which it seems somewhat difficult to explain in this way. Are they perhaps connected with the well known chemical difference between the "meso-" and the "benz-" positions in anthracene? In most anthracene reactions the meso-positions are first attacked, and substituents only enter the end benzene rings at a later stage. It would seem that these chemical facts must ultimately be explained by some difference in the electron configuration.

Again, the effect might be explained by thermal agitation if we imagine the molecule oscillating slightly about its centre. The more outlying atoms would then have the largest amplitudes, with the consequent effects of broadening the picture and lowering the peak values of the electron density. Against this view it may be considered that oscillations about any axis with such a high moment of inertia are improbable. It must be remembered, however, that the crystal molecule is far from being a free body in space. It is surrounded by other molecules, and in fact it appears to be somewhat more closely bound to its neighbours on either side than to those at either end of the

c axis. Between the ends of the molecules, in the (001) plane, the electron density falls to very low values. It is only in this region that occasional small patches of negative density occur. The (001) plane, moreover, is the cleavage plane, and by far the most important natural face on the crystal. Hence the bonds between the ends of the molecules must be very weak. Between the sides of the molecules, on the other hand, the (100) and the (010) planes never appear as faces on the crystal. The (110) face is developed, but never to anything like the extent of the (001) face. It may be possible, then, that the relatively looser binding between the ends of the molecules will permit an oscillation about their centres capable of explaining the observed facts. The point could perhaps be decided by an investigation of the structure at different temperatures, especially near the melting point.

The form of the scattering centres given by the Fourier analysis is conveniently studied by making a relief model of the projections. When this is done for the projection along the b axis, the difference between the meso- and the benz-carbon atoms is very noticeable. On calculating the electron distribution in the carbon atom from the measured reflections of graphite, it is found that the graphite carbon atom is similar to the atoms in the end rings of the anthracene structure, but that in the anthracene middle rings the atoms are more sharply defined.

It is difficult to make an accurate electron count because even the centres which stand out most clearly actually overlap to a considerable extent in all the projections. An estimate has been made, however, of the electron distribution along the molecule in the following way. The atoms appearing in the projection along the b axis (fig.3) were divided into groups of two by drawing parallel lines between the pairs AG' , BF' , CE' , DD' , etc., at a constant distance apart, equal to the mean distance between these groups. The procedure will be clear from fig.6. The number of electrons in each section was then obtained by adding the appropriate figures in Table VI. These figures in table VI can be taken as giving the mean value of $S \times 10^{-1}$ in small cells each $1/1800$ th. of the area of the unit cell. The actual number of electrons in a given area is thus obtained by adding up these figures and dividing by 180. Fig.5~~6~~ gives the result of this electron count. The figures in brackets are the number of electrons which we should expect to be associated with the centres from the chemical structural formula.

It is interesting to observe that the tertiary carbon atoms give the lowest count of 11.9; at the same time it can hardly be said that the effect of the hydrogen atoms is fully evident. The bulges seen on the first contour line at the ends of the molecule are not included in the estimation. They account for a residue of about 2 electrons.

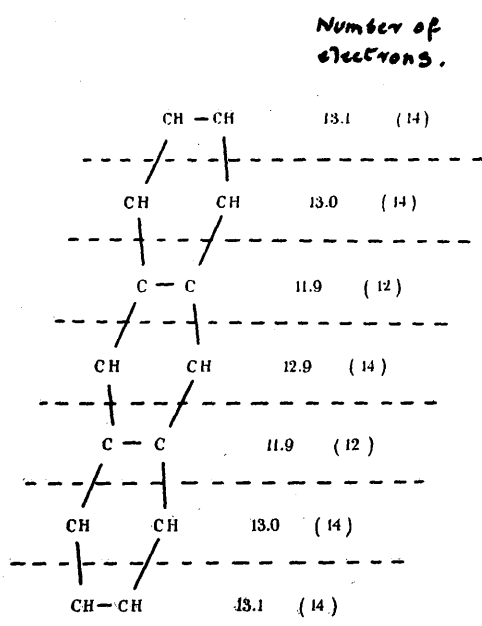


Fig. 5. *Electron count in Anthracene.*

Summary.

The anthracene structure, which was already partly known, has been investigated in detail. The intensity measurements have been made as accurate and as complete as possible, and a double Fourier analysis carried out for the zones about the three crystallographic axes. From the results of this analysis the details of the structure are deduced. The carbon atoms are found to lie quite accurately at the corners of three regular plane hexagons, the distance from centre to centre being 1.41 A.U. This molecule is, however, inclined at varying angles to all the crystallographic axes. These angles have been determined, and the structure is completely defined by a statement of the direction cosines of the long and the cross axes of the molecule which are given on p. 76, 77. The 21 parameters of the structure have been determined from the analysis and are given on p. 80. All the carbon atoms in the molecule except one are resolved as circular masses in one or other of the projections.

The closest distance of approach between atoms in adjacent molecules is about 3.67 A.U., in marked contrast to the distance of 1.41 A.U. between the atoms within the molecule.

The peak values of the electron density are highest for the carbon atoms in the meso-positions, and fall off a little in the end benzene rings. This effect is accompanied by a slight broadening of the structure, and may be connected with the chemical difference between the meso- and benz-positions, or

P
with thermal agitation. The electron count is in good agreement with the chemical structure, showing a minimum value at the tertiary carbon centres.

In conclusion, I wish to thank my wife for the help received in dealing with the large amount of numerical work involved in this analysis.

An investigation of this kind, which represents the X-ray method at its full power, is only possible after much gradual development of methods on the part of many people, and I am particularly indebted to Sir William Bragg, F.R.S., not only for his continual interest in the work, but for placing at my disposal many of his earlier, and often unpublished, results.

To the managers of the Royal Institution I am grateful for the facilities provided at the Davy Faraday Laboratory.