METRICAL REPRESENTATION OF SOME ORGANIC STRUCTURES BY QUANTITATIVE X-RAY ANALYSIS[1]

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I. INTRODUCTION

The central problem of x-ray structural analysis is to determine the position in space of the atoms in the unit cell of the crystal. For most organic crystals this unit contains only a few chemical molecules, so it will be seen that the problem in its final aspect becomes similar to one of the major problems of chemistry, viz., the determination of the space arrangement of the atoms in the molecule. The difference, however, is significant. The chemical problem in general requires a knowledge of the *relative* arrangement and position of the atoms and bonds, but the complete solution of the x-ray problem demands in addition a quantitative knowledge of the electron distribution and of the interatomic distances involved, not only for one molecule but for that small group of molecules which together make up the crystal unit.

The x-ray problem is in fact so complicated for most organic compounds that it is usually quite impossible to solve it by starting from the x-ray data alone. It would involve the simultaneous evaluation of a number of parameters which might vary from a few dozen to a few hundred, while the absence of any atom of predominant scattering power is often an added complication. But there is no need to attempt this almost impossible task. It is much better to join forces with the chemist and make use of the extensive body of knowledge which already exists in the structural formulas of organic chemistry. If the structural formula is accepted as a basis, it then remains to make this framework metrical and find its orientation in the crystal. The chemist is perhaps not much concerned with the orientation of the molecule in the crystal, but unfortunately this aspect cannot be disentangled from the process of working out the quantitative details of the formula itself, a matter which is of the greatest interest to the chemist and physicist alike.

[1] Based on a paper read to the Chemical Society (London) at Manchester, England, on November 9, 1934.

In the actual process of analysis, then, it is usually convenient to start with a rough model embodying the knowledge we already possess regarding the molecule. By a "model" in this sense we need imply nothing more concrete than a concise mathematical expression of the relative positions of the scattering centers and probable order of the interatomic distances involved. We then proceed to find, by a process of trial and error, how this model, or a combination of such models, if the crystal unit contains more than one molecule, must be oriented with respect to the crystal axes in order to explain the intensities of the principal x-ray spectra. Such preliminary work is often facilitated by a knowledge of the optical and magnetic properties of the crystal. When an approximate solution has been obtained in this way there is usually no doubt as to its validity, because although the number of parameters involved is large, the number of equations determining these parameters is always much greater.

The structure reached in this manner is of great interest because it represents a confirmation of the structural formula by a method which is utterly different from the methods of organic chemistry. We may find, as in the case of anthracene, that the structure can be explained by means of three interlocked hexagonal rings of atoms of radius 1.3 to 1.6 A.U. These rings may be flat or they may be slightly buckled, and we can find approximately their orientation in the crystal. But the most interesting part of the work begins when we try to push the results further than this. If we can deduce the structure exactly, then different types of linkage between the atoms, single and double bonds, will probably reveal themselves by involving slightly different interatomic distances, and we shall be able to gain precise information about such important matters as valency angles, and so on. In brief we shall be able to place the structural formulas of organic chemistry on an exact metrical basis.

Now in practice it is not usually possible to obtain such detailed information by an extension of the method of trial and error which we have used to obtain the broad outline of the structure. In the case of anthracene just mentioned, a buckling of the carbon rings appears to improve the calculated results for many of the reflections. But again, the conception of a larger central ring, combined with a small change in the orientation, would seem to improve the agreements for other reflections. It is in fact quite impossible to study systematically all the small changes which might be wrought on our working model.

Fortunately, however, when the work reaches this stage the problem can be approached in another way, by the method of Fourier analysis.[2]

[2] The method of the Fourier series as applied to crystal analysis was suggested by W. H. Bragg (Phil. Trans. **215A**, 253 (1915)), and further developed by Duane (Proc.

Each x-ray reflection given by the crystal can be thought of inversely as representing a certain average sinusoidal distribution of scattering matter, or electron density, running through the crystal, whose amplitude can be related to the measured intensity of the reflection. By combining the distributions obtained from all the reflections we can measure, it is possible to build up a more or less complete picture of the structure. Expressed mathematically, the intensity of each reflection enables us to calculate the coefficient of the corresponding term in a triple Fourier series which expresses the average electron density at every point in the crystal.

There are, unfortunately, many difficulties in the method, the most fundamental being our ignorance of, or rather the impossibility of measuring, the phase constant which belongs to each term in the series. Only the magnitude of the reflection can be measured. But this is just when the chemist comes to the rescue. The approximate solution which we have already determined by making the fullest use of our existing knowledge of the molecule is sufficiently accurate to determine the phase constants for most of the reflections which in practice it is possible to measure. It is then possible to apply the Fourier analysis, and its application leads to a considerable refinement of the results already obtained. For example, the different possibilities which we mentioned in the case of the anthracene structure are all found to lead to the same values for the phase constants (which can only be 0 or π for centrosymmetrical structures[3]). Therefore,

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Nat. Acad.Washington **11**, 489 (1925)), Havighurst (Proc. Nat. Acad. Washington **11**, 502 (1925)), Compton ("X-Rays and Electrons," p. 151 (1926)), and W. L. Bragg (Proc. Roy. Soc. **123A**, 537 (1929); *The Crystalline State*, Vol. I, p. 221 (1933)). Reference should be made to these works for full mathematical details of the method.

The series which represents the electron density, ρ, as projected along any direction in the crystal, for example, along the a-axis of a centrosymmetrical monoclinic crystal, is

$$\rho(y, z) = \frac{1}{bc \sin \beta} \sum_{-\infty}^{+\infty} \sum_{-\infty}^{+\infty} F(0kl) \cos 2\pi(ky/b + lz/c)$$

$F(0kl)$ is the "structure factor" of the reflection $(0kl)$, that is, the ratio of the wave amplitude scattered by the whole contents of the unit cell to that which would be scattered by a single electron under the same conditions. It is a quantity whose magnitude can be calculated from the measured intensity of the x-ray reflection; the experimental side of x-ray crystal analysis thus consists largely in making accurate determinations of F. But the sign of F, whether positive or negative, represents the "phase constant" of the reflection, and can only be determined by preliminary trial and error analysis.

[3] If the structure as a whole has a center of symmetry, then this symmetry must apply to each component sinusoidal distribution of density which goes to build up the structure in the Fourier synthesis. Thus either the trough or the peak of each such distribution must coincide with the center of symmetry. Any intermediate position would destroy this symmetry.

the final result obtained by the application of this method is independent of the precise nature of the initial assumptions. We are justified in saying that the method of Fourier analysis renders possible a direct approach to the finer details of the structure.

This statement, however, must be immediately qualified by adding "but not too fine detail." We employ a series to represent the structure, and this series is, of course, never quite complete. It is artificially terminated at some point by the experimental conditions (limitation of wave length, etc.). If some terms of appreciable magnitude are excluded from our series, the resulting picture of the structure will be deficient, and may also include some false detail. This question has been carefully examined by Bragg and West (6). Most organic compounds, however, have a low melting point, and consequently the atoms in the crystal have a considerable thermal movement. This movement has the effect of smearing out the picture to some extent, with the result that the series are usually found to be naturally convergent within the region covered by the experiment.

Bearing in mind these shortcomings of the method we may now go on and consider some of the results which have been obtained by the application of this intensive method of analysis to certain well-known organic compounds. The choice of compounds may seem rather odd and perhaps uninteresting to the organic chemist, but in selecting the compound for detailed analysis we must be guided by many considerations. Reasonably good *single* crystals are, of course, usually essential, though they may be quite small. This at once excludes, or renders very difficult, the examination of many interesting compounds, particularly simple structures containing only a few atoms, which are nearly always liquids or gases at the ordinary temperature. Again, even when provided with good crystals, preliminary examination often shows the structure to be unexpectedly complicated, in that many molecules are built together into the crystal unit (which must be dealt with as a whole). The complication in this case is perhaps more apparent than real, but it does greatly increase the experimental and also the numerical work involved, so for the time being the consideration of such structures has been deferred.

In the examples which follow the crystals are all monoclinic, the space group being $P2_1/a$ (C_{2h}^5) in each case, and the two molecules in the unit cell each possess a center of symmetry. They are chosen to illustrate the type of result now being attained, but of course many other compounds, which cannot be discussed in detail in this article, have been extensively analyzed by the x-ray method. With relatively simple organic compounds, extremely accurate results have been obtained by Wyckoff (25, 26, 27) in his analysis of urea and thiourea. More recently, Wyckoff and Corey (27) have extended their measurements to hexa-

methylenetetramine, whose cubic symmetry is an uncommon feature of organic compounds. The early analysis of this compound by Dickinson and Raymond (9) was one of the first precise determinations of organic crystal structure. Among the more complicated structures, the work of Muller (17) on the long chain hydrocarbons is well known, and special reference should be made to the analysis of hexamethylbenzene and hexachlorobenzene by Lonsdale (14, 15), diphenyl and triphenyl by Dhar (7) and Pickett (19), chrysene by Iball (12), and to the recent work on cyanuric triazide by Knaggs (13). Convenient summaries of the work on a great many other organic compounds which have been studied, but usually without quantitative intensity measurements, will be found in the *Strukturbericht* of Ewald and Hermann (1931) and in a previous article by Hendricks.[4]

II. ANTHRACENE AND NAPHTHALENE

Figure 1 shows the final results of the Fourier analysis of anthracene (20) when the structure is projected along the direction of the *b*-axis. In this and all the other examples given below a two-dimensional Fourier series has been employed, following the method first used by W. L. Bragg (5), which gives a projection of the whole structure along a certain direction in the crystal. The structure in three dimensions can usually be built up by putting together the results of three or more projections of this kind. In the present examples only the projection which gives the most complete view of the individual molecule will be used, but it will be understood that the details of the structure have been worked out with the aid of the other projections.

Now, as we have seen, this contoured map of the electron distribution in anthracene is built up entirely from the experimental measurements of intensity, only the signs of the terms being taken from the trial structure; moreover, these signs are independent of the precise nature of the initial assumptions. The first thing to note is that the atoms are round where they are clearly resolved. Of course, the plane of the molecule is actually inclined at a high angle of over 60° to the plane on which the projection is drawn, so that certain pairs of atoms overlap in the picture and form unresolved ovals. The exact position of these atoms can usually be obtained from the other projections. Now atoms with spherical symmetry were assumed in the trial structure, but they were placed at points differing somewhat in position from those now found. The fact that the atoms, although shifted, remain round, is a confirmation of the whole analysis. If any considerable errors were involved, experimental or theoretical, there would be no particular reason for the atom remaining round.

[4] See Chemical Reviews 7, 431 (1930).

The next thing we note about the structure is its regularity. The rows of atoms along the molecule, B, D, F, lie very accurately on parallel straight lines. Across the molecule, too, the lines joining pairs of atoms, DD', BF', are parallel. When the complete structure is worked out with the aid of the other projections it is found that the carbon rings are regular plane hexagons, the carbon to carbon distance being everywhere 1.41 A.U. This result is in harmony with our ideas of the chemical structure.

The chemist is, however, aware of another feature in the properties of anthracene. The 9, 10- or meso-positions on the middle ring are mark-

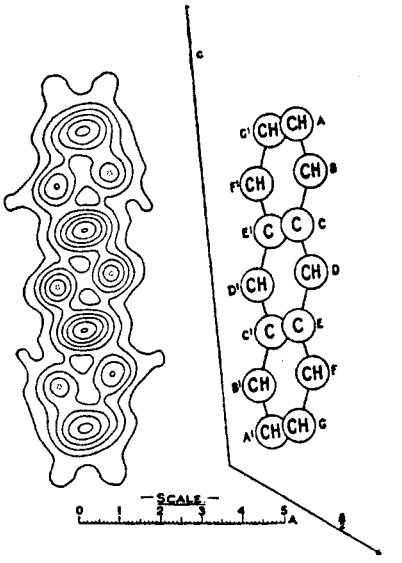

FIG. 1. Fourier projection map of the anthracene molecule, along the b crystal axis. Each contour line represents a density increment of 1.27 electrons per square Ångström unit. The dotted centers at D and B mark densities of just over seven and just under six electrons, respectively. The plane of the molecule makes an angle of about 62.4° with the plane of the projection.

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edly different in reactivity from the ordinary benz-positions of the end rings. Although carrying only one hydrogen atom, the meso-positions behave more like aliphatic than aromatic centers. Does the x-ray picture reveal any difference at these centers? As regards dimension there is no distortion of the structure at these points. The interatomic distances are the same as in the other rings. But there is a marked difference in the peak values of the electron density. On the meso-position it is about 7 electrons per square A.U., whereas on the benz-position it is only 5.5 to

6 electrons. The value seems to fall away as we pass outwards from the center of the molecule.

The meaning of this result is somewhat difficult to interpret. We must, of course, be cautious in accepting too fine detail in the picture. If the experimental measurements were made more accurate, and if still weaker reflections were included in the series, would the result persist? Probably it would, because it seems large enough to be real. But the density recorded on the atoms must depend in its absolute value very greatly on the temperature. Near the melting point all the values will be lower, owing to increase in the thermal movement, while at a lower temperature the peaks will be sharpened.

Further work has shown that a small falling-off in density at the end atoms seems to be a rather general effect in structures of this type, which are characterized by a very strong cleavage plane crossing the ends of the molecules. This cleavage plane corresponds to a large region of low or zero density in the projection. (Compare figure 3.) Now if we imagine an isolated carbon atom the F values applicable to organic compounds show that the electron density, instead of falling off abruptly to zero at the outside of the atom, tails away slowly, leaving a fringe around the atom,—an effect due partly to the temperature factor and partly to the outermost loosely bound electrons, which make little or no contribution to the x-ray reflection, and consequently appear in the Fourier synthesis as a more or less uniform background of density. Thus all the atoms inside the molecule are overlapped by their neighbors to a small extent, but those that border the large gap of the cleavage plane are overlapped like this on one side only. This is probably the explanation of the more general small falling-off in the peak values of the density of the outside or end atoms that is observed in the case of many compounds. But in anthracene the difference at the meso-atoms seems somewhat greater than can be explained in this way.

The molecules of naphthalene in the crystalline state display a very similar orientation to those of anthracene. Indeed, it was the striking similarity between the two crystals which attracted the attention of Sir William Bragg (3) in one of the earliest applications of the x-ray method to organic crystals. Figure 2 shows the Fourier projection map of naphthalene (21) which corresponds to the anthracene projection of figure 1. The dimensions of the rings are found to be the same as in anthracene, i.e., regular plane hexagons, with the carbon centres 1.41 A.U. apart. This repetition of the strictly planar structure, with the 1.41 A.U. interatomic distance, which emerges from an *entirely different set of experimental measurements*, is of great significance. It has long been known that in graphite (2) the atoms are arranged in sheets of condensed planar

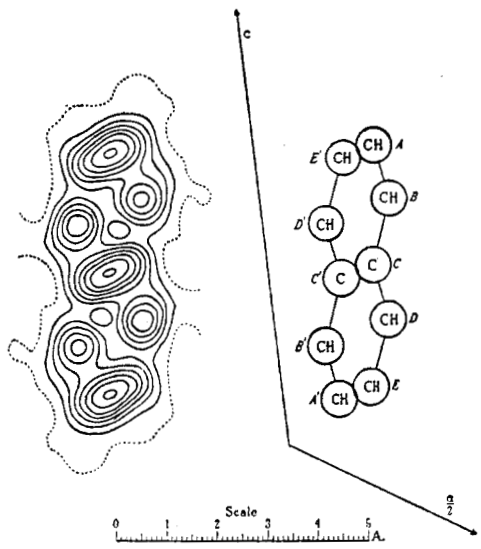

FIG. 2. Naphthalene projected along the b crystal axis. In this and all the subsequent maps each contour line represents a density increment of one electron per square Ångström unit, and the one electron line is dotted. The plane of the naphthalene molecule is here inclined to the plane of the projection at an angle of about 64.5°.

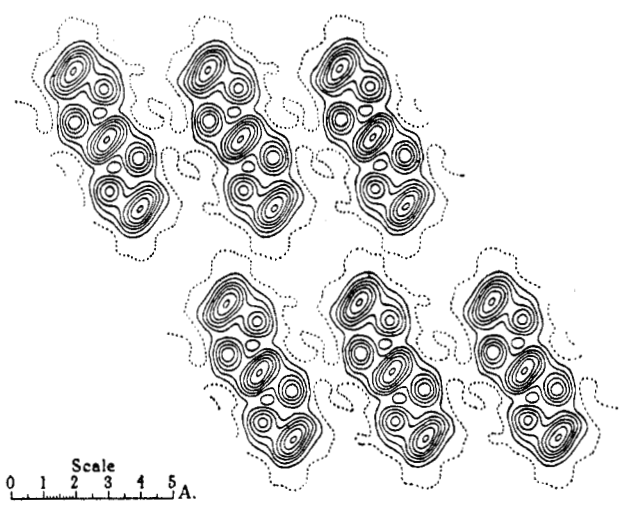

FIG. 3. A smaller scale projection of the naphthalene structure along the b crystal axis, showing how six molecules are built together in the crystal.

hexagons, the centers being 1.42 A.U. apart, and the distance between the layers being 3.41 A.U. In hexamethylbenzene also (14), where all the atoms reside on the basal plane of the crystal, similar relations hold. We now see that in complicated aromatic structures, where the molecules are inclined at various angles to all the crystal axes and planes, the molecule itself does not suffer any distortion, but remains a small *rigid* framework, held by the surrounding forces in some definite orientation.

In the naphthalene projection (figure 2) the peak values of the density are now all much more nearly equal than in anthracene, although there is a small falling-off at the end atoms when the structure is projected along the *a* crystal axes. Figure 3 shows the projection on a smaller scale, and illustrates how a group of six molecules is built together in the crystal. The strong (001) cleavage plane passes across the ends of the molecules, through a region of very low electron density. It should be noted that in this diagram (and in figure 5) the central molecule in each row is the same as the others. This is only true, however, of this particular direction of projection, viz. along the *b*-axis. The central molecule is actually half a translation along the *b*-axis, out of the plane of the paper, and it is also inclined to the plane of the paper in the opposite sense to that of the end molecules. In other words, it is derived from the end molecule by a reflection in the plane of the paper, or by a rotation of 180° about the *b*-axis. The side atoms of the molecules are thus not actually as close as they appear in this projection.

III. DURENE AND BENZOQUINONE

As we have now determined the form of the molecule in these fused ring aromatic compounds, let us pass on to the consideration of some substituted benzene derivatives, when the variety of the chemical reactions is larger and many interesting problems present themselves. Symmetrical tetramethylbenzene (durene) is suitable for a detailed analysis (22), and the Fourier projection along the *b*-axis is shown in figure 4. In this case all the atoms in the molecule are separately resolved. The measurements which have been made show again that the benzene ring is a regular plane hexagon structure of dimensions similar to those obtained for naphthalene and anthracene, although the inclination of the molecule to the plane of the drawing causes a large apparent distortion. Figure 5 shows on a smaller scale how a group of molecules is arranged in the crystal.

The chief interest in this structure perhaps lies in the situation of the methyl groups. If the substitution were entirely symmetrical, the three valencies of the carbon atom would make angles of 120° with each other. Careful measurement shows, however, that this is not exactly the case. There is a small, but apparently definite displacement of the methyl

groups away from each other towards the unsubstituted positions of the ring. Figure 6 shows the actual dimensions of the molecule worked out from this and other projections. The displacement of the methyl groups

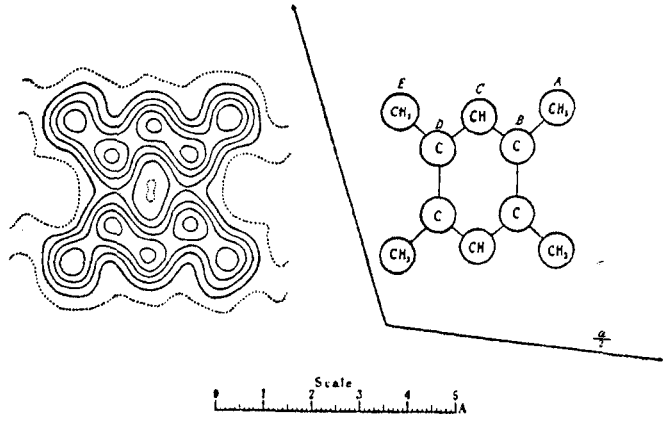

FIG. 4. Durene (*sym*-tetramethylbenzene) projected along the *b* crystal axis. The plane of the molecule is inclined at an angle of about 48.6° to the plane of the projection, causing a large apparent distortion in the shape of the hexagonal benzene ring. The methyl groups suffer a small but apparently true displacement away from each other towards the unsubstituted position.

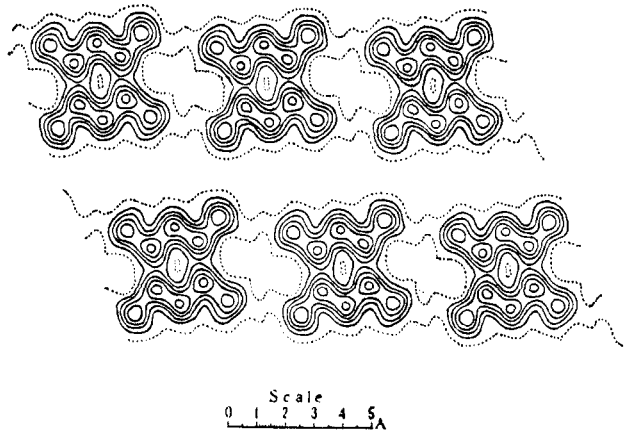

FIG. 5. A small scale map of the durene structure. Note the large gap of low density along the cleavage plane.

is seen to be only 3°, but there is no doubt that this figure would increase if more bulky groups were substituted. By extending the work to other examples we may hope to approach the problems of stereochemistry in a quantitative manner.

The main result of the work we have illustrated so far has been to show that the benzene ring, whether in condensed ring systems or in a simple substituted benzene derivative, is an apparently rigid structure in the form of a regular plane hexagon. The carbon to carbon distance, equal to the "radius" of the ring, has the very constant value of 1.41 A.U. The radius of the ordinary tetrahedral carbon atom as in diamond is 1.54 A.U., so that we have here a new kind of tervalent atom of smaller size, with three coplanar valencies making angles of 120° with each other. We have no evidence of the alternating double and single bonds of the Kekulé formula, but of course we should not expect to be able to find these, because the essential feature of the Kekulé formula is that the double and single bonds are supposed to be continually changing position, or to be otherwise in equilibrium, in a manner which makes all six corners of the ring equivalent. Our results are in accord with the modern conception of a ring in which the links are of intermediate character between the double and single

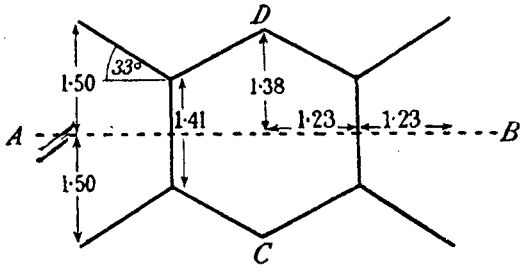

FIG. 6. Dimensions of the durene molecule obtained from the complete structure determination.

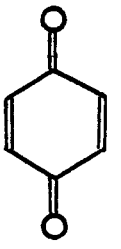

FIG. 7. Benzoquinone

bond. Now if we examine a compound in which the "double bonds" of the ring have been stabilized, for example, by the introduction of divalent groups, then it might be possible to detect some distortion in the dimensions of the ring caused by contraction at the double bonds and alteration of the valency angles.

This has actually been carried out in the case of benzoquinone (24). The compound carries two oxygen atoms in the *p*-positions, so that there is now only one way in which the ring bonds can be arranged (disregarding the "peroxide" formula, which seems rather improbable and is, in fact, definitely ruled out by the following work). The chemistry of the compound supports this formulation, as bromine, etc., can be taken up at the double bonds (cf. figure 7).

The x-ray analysis of this compound shows that the molecular planes are nearly parallel, but unfortunately the molecules are found to interleave one another in a manner which makes it difficult to obtain a clear two-

dimensional Fourier projection. In the trial structure a regular benzene ring was assumed, so it is of interest to see if any deviation from this regularity is brought to light by means of the Fourier analysis. The best projection that can be obtained is shown in figure 8, where the molecules are viewed at a fairly high angle. It will be seen that the two oxygen atoms and two of the carbon atoms are clearly resolved, but the precise position of the other carbon atoms is obscure. The other projections yield even less definite information.

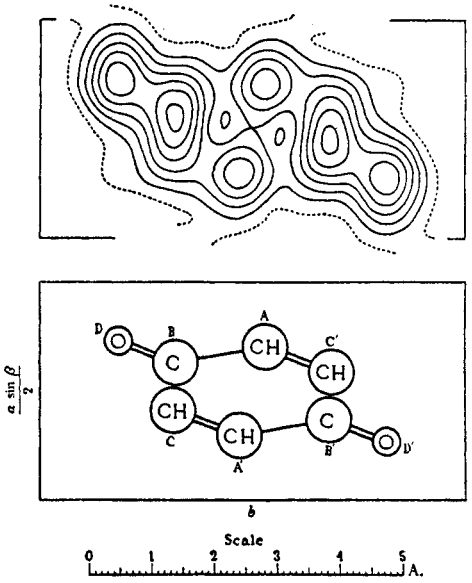

FIG. 8. Benzoquinone projected along the c crystal axis. The high inclination of the plane of the molecule to the plane of the projection (about 59.5°) makes the resolution of certain atoms difficult.

Closer inspection of this diagram, however, at once reveals a departure from regularity in the form of the ring. In a regular plane hexagon opposite sides are parallel to each other and to the line through the center joining the other two corners (cf. figure 9), and these lines will remain parallel in any projection of the structure. Now although the precise position of the overlapping side pairs of carbon atoms is obscure, it can be seen that the line on which they lie is definitely not parallel to the line through the center of the ring joining the other two carbon atoms. The effect, however, is not very reliable, because of the influence of the adjoining atoms whose overlap will tend to pull the line round in any case.

In order to get a fair comparison the central ring in anthracene, which happens to display a closely similar orientation in the crystal, has been isolated, and is shown in the upper part of figure 10. Now we know from other projections that the anthracene ring is very exactly a regular plane hexagon. And although the influence of adjoining atoms is here very similar to what it is in benzoquinone, it can be seen that the ovals now remain reasonably parallel in general direction to the line through the center. The lower part of the figure shows the benzoquinone projection, and the convergence of the lines is pronounced.

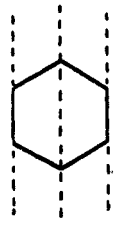

FIG. 9. Regular hexagon

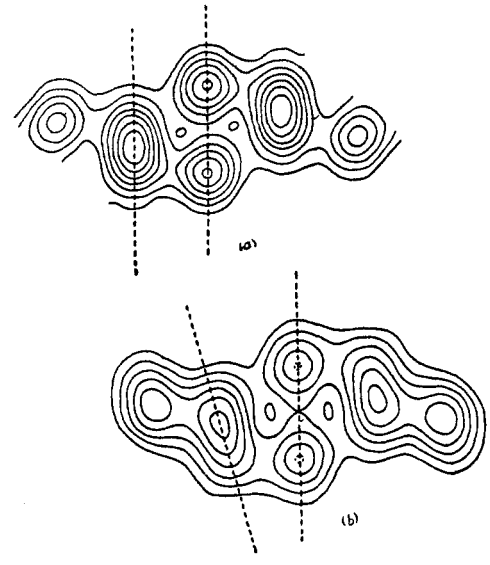

FIG. 10. The central ring of anthracene (*a*) compared with the carbon ring in benzoquinone (*b*).

Apart from the distortion of the ring, the carbon to oxygen distance is of interest in the compound. This cannot be measured very directly because the carbon atom to which the oxygen is directly attached remains obscured in all the projections. We can, however, measure quite accurately the distance between the oxygen and the carbon one place removed round the ring, and also the distance between the two oxygen atoms. From these measurements we can work out the direct carbon to oxygen distance. If a regular benzene ring is assumed the distance obtained is 1.31 A.U., but if allowance is made for the distorted ring, the carbon to oxygen distance is only 1.14 A.U.

The band spectrum analysis of carbon dioxide (1) gives the carbon

oxygen distance as 1.15 A.U. (The results from attempts at the crystal analysis of solid carbon dioxide are rather variable.) In urea (11, 25, 27) the crystal results are consistent with a somewhat higher value for the carbon to oxygen distance of 1.25 A.U. The ketonic oxygen in benzoquinone is thus seen to be rather similar to the oxygen in carbon dioxide if the distorted ring is correct.

The molecular model which gives the best explanation of all the Fourier projections of the benzoquinone structure is illustrated in figure 11. (It will be noticed that the convergence of the dotted lines is not so pronounced now as it was when the molecule was viewed at a high angle in figures 8 and 10.) Carbon atoms connected by a double bond are 1.32 A.U. apart, and those connected by a single bond are at the greater distance of 1.50 A.U., while the angle between the single bonds has the tetrahedral value of 109½°, and between the double and the single bonds 125°. Owing to the peculiarities of this structure the results are not so clear cut

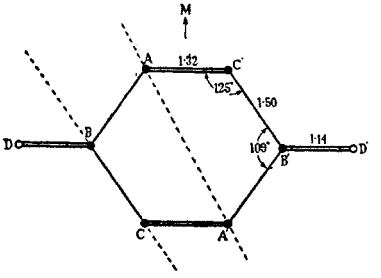

FIG. 11. Dimensions of the benzoquinone molecule

and definite as they were, for example, in durene and anthracene. An alteration of a few degrees or a few hundredths of an A.U. in these figures would not have much effect on the projections. But the general conclusion is that the x-ray evidence is rather definitely in favor of the distorted ring, as opposed to the regular benzene ring.

IV. DIBENZYL

The x-ray analysis of one further compound will be considered, because it introduces a type of problem which we have not come across in the previous examples, viz., that arising from the possibility of free rotation of groups about a single bond. In durene the $-CH_3$ groups are attached to the benzene nucleus by a single bond, but as the hydrogen atoms have an almost inappreciable effect on the x-ray scattering, we cannot make any very reliable observations of their position. But in dibenzyl (23) we have two benzene rings connected by two $-CH_2$ groups, and free rotation

should be possible about the bonds between the rings and the —CH_2 groups, and between the —CH_2 groups themselves, so that the molecule as a whole has several degrees of freedom. The symmetry of the structure tells us at once that in the crystal the benzene rings are parallel and oriented in the same way, because the molecule contains a center of symmetry. There remains the problem of finding the orientation of the molecule in the crystal, and also its exact shape, i.e., whether the benzene rings are coplanar, or whether though parallel they lie in different planes. Two possibilities are illustrated in figures 12 and 13.

The result of the x-ray analysis shows that the benzene rings do lie in different planes, and that these are in fact almost perpendicular to the plane containing the zigzag of the connecting —CH_2 groups, as shown in figure 13. The projection of the structure along the *b*-axis, obtained by Fourier analysis, is shown in figure 14. We see that the benzene rings are apparently quite regular. The connecting —CH_2 groups are separately resolved, so that their position can be estimated with some accuracy.

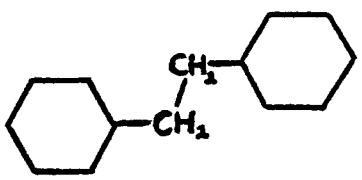

FIG. 12. Dibenzyl, planar molecule

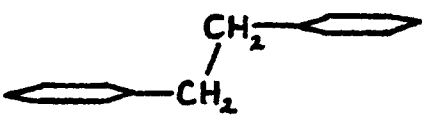

FIG. 13. Dibenzyl, three-dimensional molecule

In a complicated structure like this, however, it is very necessary to study the other projections as well, in order to build up a complete three-dimensional picture of the molecules.

The final results show that the benzene rings are of the usual regular hexagon type, that the connecting —CH_2 groups are situated at 1.47 A.U. from the aromatic carbon, and that the distance between the CH_2 groups is 1.58 A.U. (This latter figure is a little uncertain. The overlapping effect of the hydrogen atoms may account for the deviation from the diamond value of 1.54 A.U.) The angle of the —CH_2—CH_2— zigzag works out at 111°, which is as near to the tetrahedral value as we can expect, considering the experimental uncertainties. The planes of the rings do not appear to be strictly perpendicular to the plane of the —CH_2—CH_2— zigzag, being apparently turned round by about 16°. The nature of the projection makes it difficult to be quite sure of this distortion from regularity. Although the figure seems large enough to be significant, it only means that the planes of the rings are some 4 per cent closer together than they would be in a perfectly regular model.

It is most likely that in the liquid or gaseous states free rotation can take place about the single bonds in this compound, and that in the crystal the molecule assumes this particular form because it is best adapted to the van de Waals forces. The chemical evidence of free rotation lies in the fact that there is only one compound known, and not two distinct compounds as in stilbene, where a double bond unites the groups. In dibenzyl, if the molecule had only one stable configuration, it would seem to account for the known facts just as well as the conception of all possible configurations being equally favored. This question might have bearings

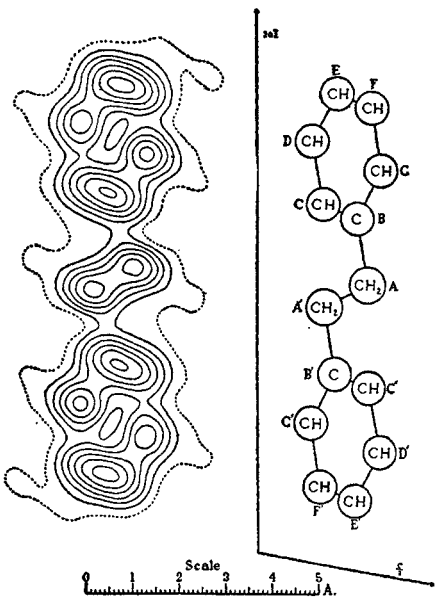

FIG. 14. Dibenzyl projected along the *b* crystal axis. The benzene rings lie in parallel planes, about 1.42 A. U. apart, and inclined to the plane of the drawing at about 58.8°.

of chemical interest, and could probably be tested by x-ray or electron diffraction experiments on the vapor of the compound.

It is of interest to note that in discovering the arrangement of the atoms in the dibenzyl molecule we have had to go considerably beyond the information contained in the chemical formula, which, of course, says nothing about the *absolute* position of the rings with respect to the $-CH_2$ groups. We are thus led to consider the possibility of quantitative analysis of organic compounds whose structure has not been fully determined by chemical methods. If very little is known about the structure chemically,

then it would still appear rather hopeless to attempt the problem by means of x-ray analysis. But if the main outlines of the structure have been determined by chemical means, then it does not seem impossible that the remaining detail might be fixed by x-ray analysis. The difficulty in practice is that the organic problems which it would be most interesting to attempt to solve in this manner usually involve molecules containing a very large number of atoms, compared to the number in those simple structures we have been considering. This complication enormously increases the labor of the analysis. But by improvement in technique, and by studying the social habits of the molecules in the simpler crystals which have so far yielded to analysis, we may in time gain enough experience to make a reasonable attempt in this direction.

V. CONCLUSION. SUMMARY OF INTERATOMIC DISTANCES

In the preceding pages we have dealt with those organic structures which have, up to the present time, been most intensively analyzed by the x-ray method. The results obtained illustrate the great power and beauty of this method of investigating problems of molecular structure in the solid state. Perhaps the most striking feature of the results is the amazing verification which they afford of the stereochemical conceptions of organic chemistry. Of course it may be argued that these fundamental formulas did not stand in any need of verification—they were firmly established by chemical methods long before the diffraction of x-rays was discovered, indeed before the discovery of x-rays at all. But the experimental methods employed in building up the molecular maps which illustrate this paper are so remote from the reactions and syntheses which establish the chemical structural formulas, that the verification afforded is of considerable philosophical interest. The structural formulas are now endowed with a new degree of reality—not necessarily more profound, but certainly quite a different reality.

The greatest difference lies in the exact metrical representation of the structures which has now been achieved. The interatomic distances appear as constants which are definitely characteristic of certain types of binding between the atoms. These constants can be related to the heats of formation and other physical properties, and furnish data for theoretical investigation. The minimum intermolecular distances between certain groups belonging to adjoining molecules in the crystal are also characteristic constants which must prove of importance in the quantitative study of reactions.

Many other organic compounds besides those dealt with in the preceding pages have been investigated by the x-ray method, with varying degrees of success and completeness. These are included in a table of interatomic

TABLE 1

Atomic distances in organic compounds by x-ray analysis

COMPOUND	INTERATOMIC DISTANCE IN A.U.		MINIMUM INTERMOLECULAR DISTANCE IN A.U.		TYPE OF STRUCTURE AND ANALYSIS	REFERENCE
Diamond	C—C	1.541			Cubic	(4, 10)
Graphite	C—C	1.42	C ... C (between layers)	3.41	Hexagonal layer structure	(2)
Hexamethylbenzene	C—C aromatic C—CH_3 aromatic-aliphatic	1.42 1.48			Triclinic layer structure (trial analysis)	(14)
Cyanuric triazide	C—N in ring C=N in ring C—N outside ring N≡N terminal N=N	1.38 1.31 ~1.38 1.11 1.26	N ... N	3.12	Hexagonal layer structure (One Fourier projection)	(13)
Nonacosane	CH_2—CH_2 aliphatic	1.553*	CH_2 ... CH_2	3.6–3.9	Linear structure	(17)
Hydrocarbon series C_nH_{2n+2}	CH_2—CH_2 aliphatic	1.534*			Linear structures	(18)
Anthracene	C—C aromatic	1.41	CH ... CH	3.7	Three Fourier projections	(20)
Naphthalene	C—C aromatic	1.41	CH ... CH	3.6	Three Fourier projections	(21)
Durene	C—C aromatic C—CH_3 aromatic-aliphatic	1.41 1.47	CH_3 ... CH_3	3.9	Three Fourier projections	(22)
Dibenzyl	C—C aromatic CH_2—CH_2 aliphatic C—CH_2 aromatic-aliphatic	1.41 1.58 1.47	CH_2 ... CH CH ... CH	4.1 3.7	Three Fourier projections	(23)

Benzoquinone	C—C in ring C=C in ring C=O	~1.50 ~1.32 ~1.14	C ... CH C ... O O ... O	3.45 3.36 3.62	Three Fourier projections	(24)
Chrysene	C—C aromatic	1.41	CH ... CH	3.4	One Fourier projection	(12)
p-Diphenylbenzene	C—C aromatic C—C between rings	1.42 1.48	CH ... CH	3.9	One Fourier projection	(19)
Hexachlorobenzene	C—Cl	>1.79			One Fourier projection	(15)
Urea	C—NH_2 C=O	1.37 1.25	NH_2 ... O	3.2	One Fourier projection (tetragonal)	(11, 25, 27)
Thiourea	C—NH_2 C=S	1.35 1.64	NH_2 ... NH_2 NH_2 ... S	3.8 3.4	One Fourier projection	(26)
Hexamethylenetetramine	CH_2—N	1.42			One Fourier projection (cubic)	(9, 27)
β-Benzene hexabromide	CH—Br	1.94†	Br ... Br	3.74	Trial analysis (cubic)	(8)
β-Benzene hexachloride	CH—Cl	1.81†	Cl ... Cl	3.59	Trial analysis (cubic)	(8)
Diphenyl	C—C aromatic C—C between rings	1.42 1.48			Trial analysis	(7)
Oxalic acid dihydrate	C—C aliphatic C—O oxalate	1.59 1.25	O ... O oxalate O ... H_2O	3.21 2.60	Trial analysis	(28)

* Assuming tetrahedral angle.

† Assuming tetrahedral cyclohexane ring.

and intermolecular distances (table 1), which forms a convenient summary of this review. Generally it is only in the case of carbon itself and a few specially simple structures that the measurement of interatomic distance can be carried out in anything like a straightforward manner. In the vast majority of organic crystals the structures are very complex and of low symmetry. The number of variables is so great that estimates of interatomic distance made by trial and error analysis in these cases are often unreliable. But when accurate intensity measurements are made, and the results are refined by the application of intensive Fourier analysis, as in the examples dealt with in this paper, then the estimate of interatomic distance obtained really amounts to a direct measurement. This kind of exhaustive analysis is very difficult and laborious, but it is the only kind of real value in dealing with complex organic molecules. As some guidance to the weight to be attached to the data in the following table, the type of analysis is indicated. In a few structures the atoms all reside on some simple crystal plane (layer structures), or in rows along some axis (linear structures). In these cases a less exhaustive analysis can yield accurate results. But they are exceptions. In the vast majority of organic crystals the orientations of the molecules do not bear a simple relation to the crystal axes.

The table might be extended by the inclusion of many other compounds which have been analyzed by the method of trial and error only. But unless such structures have some simplifying feature, the estimates of interatomic distances are not likely to be very reliable, and so results of this kind have in general been omitted.

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