MOLECULAR STRUCTURE AS INTERPRETED BY X-RAY DIFFRACTION MEASUREMENTS IN LIQUIDS

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The x-ray diffraction halos obtained in liquids have been known since 1916, but only during the past few years has any endeavor been made to use x-ray diffraction as a means of studying molecular structure.

It is not the purpose of this paper to give a historical account of even the recent experiments. Because of the limited space it is deemed advisable to present only the results obtained in the laboratory of the author, for by this policy a simpler and more connected account is possible, yet without giving an incorrect impression as to the present state of the subject. For the history and development of the diffraction of x-rays in liquids, Drucker's paper (1) should be consulted. In the author's first contribution (2) he adopted the theory that the molecules of the liquid are not in independent motion, and that, on the contrary, each molecule has a marked effect upon the orientation of its neighbors, particularly if the molecules are not symmetrical. There results a molecular arrangement called *cybotaxis,* which here and there throughout the liquid, proves to be sufficiently orderly to cause x-ray diffraction effects. Indeed, the liquid acts as if composed of very imperfect and small crystals of the substance. According to this view, Bragg's diffraction law, $\lambda = 2d \sin \theta/2$ should apply for the determination of the separation of the sets of the most sharply marked planes containing diffraction centers.[1] There are several reasons for believing that such an approximation to space arrangement must exist in liquids. Perhaps the simplest way of appreciating the viewpoint is to recognize that the differ-

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[1] λ is the wave length of the x-rays, d the separation of planes, and θ the angle of the deviation of the ray by diffraction.

ence between a liquid and a solid is not caused by discontinuities in the laws of force applicable at molecular ranges, but by a difference in the stability of configuration. The actual force between molecules in the two cases cannot be greatly different as is witnessed by the relatively small differences in the latent heats of evaporation. But doubtless the most effective reason for the belief in the molecular space arrangement in liquids, or the cybotactic condition, is contained in the nature of the results obtained by the use of the application of Bragg's law to measurements in liquids. The discussion of the paper, however, will assume the correctness of the method.

It is to be understood that the present discussion will not include any consideration of "liquid crystals." In these the molecules are very long. It has been found that there is a space arrangement of the molecules, the long chains being parallel and hence lying in parallel planes. The "liquid crystalline" condition may be regarded as an extreme case of the phenomena discussed in this paper.

Practically all the observations of other workers have been made with the method of photography, using halos and drawing conclusions from the density of the silver of the film. In the series of experiments of the author, the Mo Kα radiation, filtered by zirconium oxide, a slit spectrometer and an ionizing chamber are utilized. The x-rays, in passing through the liquid, are in part diffracted and the ionization chamber determines the relative intensities of the x-rays at different angles of diffraction. The monochromaticity of the radiation is very important in an attempt to attain high accuracy in the location of the diffraction peaks on the curves showing the variation of relative intensity with the angle of diffraction. For this reason it is advisable to make comparisons among observations taken with the same equipment. This is an additional reason why the results reported upon in this paper are limited to the observations in the laboratory of the author. A detailed explanation of the conclusions here presented can be found in the published articles of the author and his co-workers (3). All observations were made at room temperature excepting in a few cases where a hot air blast was used to bring the compound just above the melting point.

DIAMETERS OF STRAIGHT CHAIN MOLECULES

Measurements have been made upon primary *n*-alcohols, *n*-paraffins, and *n*-monobasic fatty acids. Figure 1 shows the nature of the experimental results for the primary *n*-alcohols. The number of carbon atoms in the molecule is indicated by the

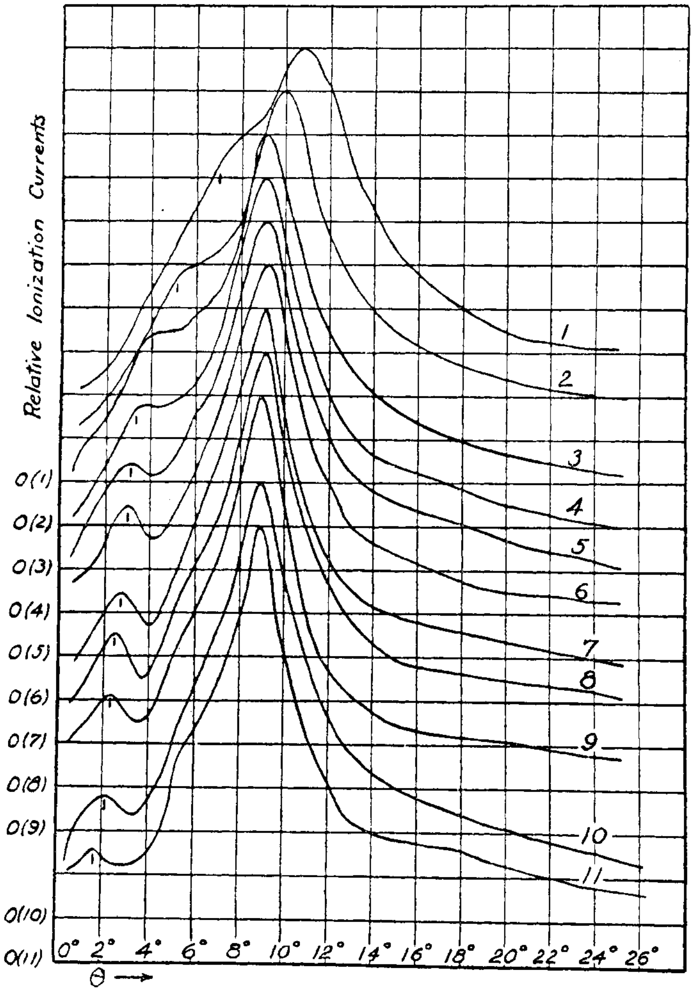


Fig. 1. The X-ray Diffraction Curves for Primary *n*-Alcohols Containing One to Eleven Carbon Atoms

number of the curve, all the alcohols between methyl and lauryl alcohol being included. The curves are shifted vertically so that they may be compared on one diagram. The readings of ionization current at the peak of the curves have been made alike, so that the values are only relative for any one curve and not between curves. The interpretation is that the more prominent peaks are caused by the most marked arrangement of the molecules. With elongated molecules, such as in the alcohols, the molecular forces are certainly unsymmetrical and one may expect a molecular arrangement corresponding to this lack of symmetry. In other words, the most marked arrangement would seem to be caused by the "shape" of the molecules; and this would be a parallel arrangement of molecules. The most prominent peak would then correspond to the separation of the parallel planes in which the molecules lie and the separation of these parallel planes would be regarded as the diameter of the molecules. It is noticed that the more prominent peak of each curve of figure 1 is not at the same angle of diffraction. Using Bragg's law the various separations of planes or of molecular diameters are computed and the results for the various *n*-alcohols are shown in figure 2. (The second peak in the *n*-alcohol curves will be mentioned at a later point). In a manner similar to those with the alcohols, measurements were made on fatty acids and upon paraffins and these results are indicated in figure 2. Several interesting points are observed. (1) The diameter of the paraffin chain is independent of its length. This is but one of the numerous verifications of the correctness of the acceptance of the measurements as the diameter of the atom. (2) The *n*-alcohols and the fatty acids have diameters which are practically independent of length of chain, if the chain contains at least four or five carbon atoms. (3) The variation of the diameter with a less number of carbon atoms is what we would expect from the view that the carbon atoms do not form a straight but a staggered chain. (4) Since the diameter of a carbon atom may be regarded as approximately 1.5 Å. u., the magnitude of the diameters also leads to the conclusion that the carbon atoms are not in a straight but a zig-zag line, somewhat similar to the lines that can be drawn connecting carbon atoms in the diamond. Any detailed discussion of their precise arrangement in these chains would exceed our experimental evidence and is omitted from this article. (5) According to figure 2, with the

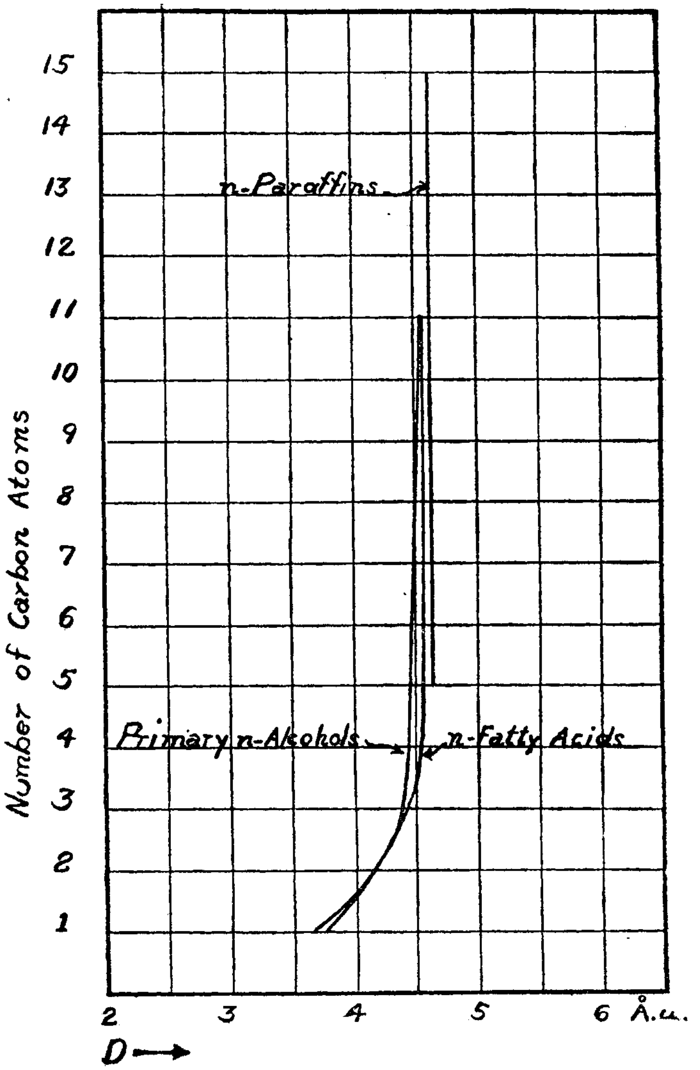


FIG. 2. THE DIAMETER OF THE MOLECULE AS DEPENDENT UPON CARBON CONTENT IN PRIMARY n-ALCOHOLS, n-MONOBASIC FATTY ACIDS AND n-PARAFFINS

highest content of carbon atoms, the diameters of the *n*-monobasic fatty acids and the *n*-alcohols, 4.55 Å.u., are the same to within the error of measurement. But the *n*-paraffins have a greater diameter, 4.64 Å.u. This may be ascribed, not to the differences at the ends of the chains, but rather to the difference in the rigidity of the chains. This conclusion receives further verification at a later point in the report.

In the case of the *n*-paraffins, the curves for which are not shown, there is only one important diffraction peak. Here probably the arrangement of molecules disclosed is limited to but one set of planes containing the lengths of the chains. Thus the arrangement is not very complete. The molecules lie parallel, but their positions in the direction of the length are somewhat indifferent. But the *n*-paraffins furnish a splendid opportunity for determining the length along the molecule of the space occupied by the carbon atom. It is found that, if one takes the best values of densities and computes from them the lengths of the molecules, and assumes the area occupied by the molecule is the square of the diameter, 4.64 Å.u., the following formula gives the correct value of the computed length:

$$L = 1.24\ n + 2.70\ (\text{Å.u.}) \qquad (1)$$

Here n is the number of carbon atoms and 2.70 Å.u. is allowed for the two hydrogen atoms at the ends of the molecules. The value 2.70 may be in considerable error, but the 1.24 is probably within 1 per cent of the actual value.

DOUBLE MOLECULES PRODUCED BY THE POLAR GROUPS, OH AND COOH, IN STRAIGHT CHAINS

The second and smaller peak in the *n*-alcohol diffraction curves in figure 1 shows an additional set of planes and these planes are separated by distances that are much greater than the length of one molecule and much less than the length of two molecules, if these lengths are estimated from equation (1). Moreover, these distances of separation of the planes increase linearly with the number of carbon atoms, as is shown in figure 3 where the results for both the monobasic fatty acids and *n*-alcohols are given. This verifies the conclusion in the preceding paragraph with regard to the diameter of the molecule, for, according to that interpretation, the diameter does not vary linearly with the number of carbon atoms, whereas the length does. A careful consideration of

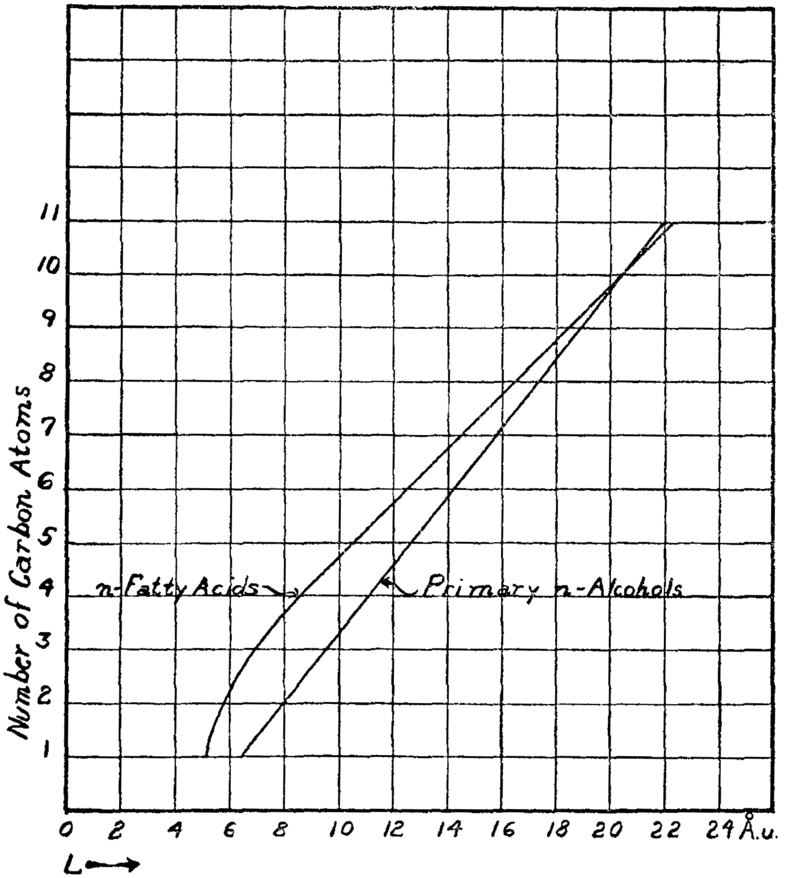


FIG. 3. SEPARATION OF PLANES (CAUSED BY LENGTH OF DOUBLE MOLECULES) AS DEPENDENT UPON NUMBER OF CARBON ATOMS

the values of the long separation of planes shows that these planes are produced by the arrangement (1) of the molecules as double molecules, two OH groups being together and the two molecules forming one straight chain, and (2) of two such double molecules lying side by side with the two pairs of OH groups not directly adjacent, but slipped by one another so that the set of planes containing them is not normal to the length of the chain. The significant point is that the second peaks in the cases of the two series of straight chain compounds referred to, indicate double molecules with the OH (or COOH) groups together and both molecules pointing in the same line away from the pair of OH (or COOH) groups. The pairing is by a head to head and not a head to tail arrangement.

DOUBLE MOLECULES CONDITIONED ON THE POSITION OF POLAR GROUP OH IN CHAIN MOLECULES

Table 1 is a table of isomers of certain *n*-alcohols, together with the *n*-alcohols. An examination of this table will show that there are these paired or double molecules in every case where the group OH is attached to the end carbon atom or the one next to the end, but that if the OH is in a branch elsewhere, the straight chain pairing ceases. Then the length, as determined by the separation of planes, agrees closely with the estimate of the length of a single molecule made from equation (1), and the OH groups in parallel molecules lie in planes perpendicular to the molecular lengths.

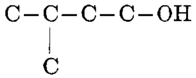
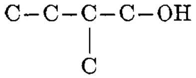
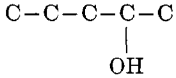
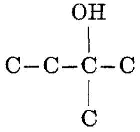
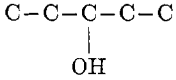
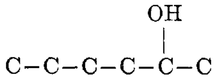
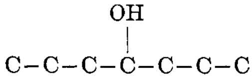
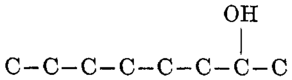
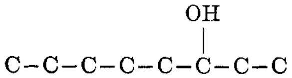
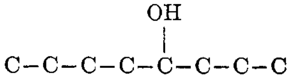
Precisely the same experience is found with the isomers of *n*-octyl alcohols prepared by Professor E. Emmet Reid of Johns Hopkins. 1- and 2-Octanol give the double molecules and 3- and 4-octanol, single molecules, as shown in table 1. So far as tested by the author, the methylheptanols with the OH group in the 1 or 2 position show double molecules, whereas those with the OH group in the 3 or 4 position show single molecules. It would seem that a generalization is practically justified, namely, that the double molecules in the straight chains depend upon the attachment of the OH group to the carbon atom at the end or next to the end of the chain.

EFFECT OF BRANCHES UPON DIAMETER OF CHAIN MOLECULES

Table 2 shows the effects of an OH or a CH_3 or of the combination when placed in a branch of the straight chain molecule. It is noted that the change in diameter is not the same in all cases

TABLE 1

Double molecules as dependent upon the position of the OH group

NAME	SECOND PLANAR DISTANCE	STRUCTURE
	Å.u.	
n-Amyl alcohol................	12.6	C–C–C–C–C–OH
Isoamyl alcohol...............	12.2	 $\mathrm{C-\underset{\underset{C}{\vert}}{C}-C-C-OH}$
sec-Butylcarbinol..............	11.3	 $\mathrm{C-C-\underset{\underset{C}{\vert}}{C}-C-OH}$
sec-Amyl alcohol..............	11.3	 $\mathrm{C-C-C-\underset{\underset{OH}{\vert}}{C}-C}$
tert-Amyl alcohol..............	8.5	 $\mathrm{C-C-\overset{\overset{OH}{\vert}}{\underset{\underset{C}{\vert}}{C}}-C}$
Diethylcarbinol...............	8.9	 $\mathrm{C-C-\underset{\underset{OH}{\vert}}{C}-C-C}$
n-Hexyl alcohol...............	14.2	C–C–C–C–C–C–OH
Methyl-*n*-butylcarbinol........	14.9	 $\mathrm{C-C-C-C-\overset{\overset{OH}{\vert}}{C}-C}$
n-Heptyl alcohol..............	15.7	C–C–C–C–C–C–C–OH
Di-*n*-propylcarbinol...........	10.5	 $\mathrm{C-C-C-\overset{\overset{OH}{\vert}}{C}-C-C-C}$
1-Octanol.....................	16.8	C–C–C–C–C–C–C–C–OH
2-Octanol.....................	14.6	 $\mathrm{C-C-C-C-C-C-\overset{\overset{OH}{\vert}}{C}-C}$
3-Octanol.....................	11.3	 $\mathrm{C-C-C-C-C-\overset{\overset{OH}{\vert}}{C}-C-C}$
4-Octanol.....................	11.7	 $\mathrm{C-C-C-C-\overset{\overset{OH}{\vert}}{C}-C-C-C}$

for a similar branch. CH_3 in a branch increases the diameter in amyl alcohol 0.6 Å.u., in octyl alcohol 0.5 Å.u., but in heptane from 0.6 to over 1.0 Å.u. OH in a branch increases the diameter 0.4 Å.u. in amyl, 0.35 Å.u. in hexyl, 0.45 Å.u. in heptyl and scarcely a noticeable amount in octyl alcohol. The combination

TABLE 2

Increase in diameter (Å.u.) caused by branches

INCREASE			ALCOHOLS		INCREASE			
2C on different atoms	2C on same atom + 1C on another	2C on same atom	Name	Number of isomers	OH + CH_3 on same atom	CH_3	OH	OH + CH_3 on different atoms
		0.55	Butyl	1				
			Amyl	5		0.5 0.7	0.4 0.45	0.65
			Hexyl	1			0.35	
			Heptyl	2	0.65		0.45	
			Octyl	3			0.0 0.0 0.0	
			Octyl	3	0.30 0.22 0.38			
			Octyl	4		0.25 0.26 0.56 0.23		
			Octyl	9				0.26 0.32 0.26 0.43 0.56 0.41 0.53 0.16 0.28
			n-PARAFFINS					
1.04		1.04	Heptane	8		0.61		
1.04	1.05	1.04				1.04		
		1.04						
	1.37		Octane	1				

of both CH_3 and OH in branches, whether with same carbon atom or not, does not seem to give a greater increase than CH_3 alone. Other items can be found by reference to table 2. The variations may not be attributed rightly to the compounds, because the possible errors due to impurity are not fully eliminated. But the distinctly larger effect of the branches on the molecular diameter in the case of paraffins is sufficiently marked to reach the conclusion, already suggested above, that the paraffin chains do not retain their rigidity of shape. On the other hand, the alcohol molecules seem to retain their "straight" characteristic. The experience with the isomers gives increased confidence in the correctness of the method of x-ray examination.

BENZENE AND CYCLOHEXANE RINGS

The writer has examined the following derivatives of benzene and cyclohexane: benzene, toluene, *o*-, *m*- and *p*-xylene, mesitylene, ethylbenzene and isopropylbenzene; cyclohexane, methylcyclohexane, *o*-, *m*- and *p*-dimethylcyclohexane; phenol, aniline, cyclohexanol and cyclohexanone; 2-hydroxy-1, 3-dimethylbenzene and three isomers, *o*-, *m*- and *p*-toluidine, and *o*-, *m*- and *p*-cresyl methyl ether. It seems that the examination of the benzene and cyclohexane derivatives gives certain results that are obtained more directly than in the examination of crystals. For example, one is able to secure the thickness of the rings very directly because the most prominent diffraction peaks in these substances, which are caused by molecular shape, correspond to the thicknesses of these rings. That the rings are flat is attested not only by the marked asymmetry which gives these strong diffraction intensities, but also by the small alteration in the so-called thickness with substitutions. As an illustration, in table 3 are given the changes that occur in the thickness of the rings with simple substitutions. It is noted that the substitution of OH and NH_2 produces alterations which are too small to measure. Also, CH_3, C_2H_5, and $CH(CH_3)_2$ produce increases in thickness that are only small fractions of the diameter of the space they would occupy. The thicknesses of benzene and of cyclohexane are 4.70 and 5.10 Å.u., respectively.

If computations are made from the densities of benzene and cyclohexane and if it is assumed that, in each case, the molecules are grouped as flat disks would be piled, then the dimensions of benzene and cyclohexane rings as determined by these experiments are as shown in figure 4. The literature on crystal measurement shows that the thickness of the benzene ring is only 3 Å.u. But this value is obtained not directly from the x-ray measurements in crystals but from the arrangement in carbon atoms in the diamond and in graphite. In short, the x-ray measurements in crystals determine the dimensions of the unit cell but do not measure the thickness as directly as has been done in these liquid experiments. In view of the evidence justifying the correctness of our method, one may be confident that the thicknesses of these rings in liquids are as shown in figure 4. Here are shown also the dimensions of hexagons having areas equivalent to those computed for benzene and cyclohexane. Also the diameters of the alcohols, acids and paraffins. The comparison shows a striking equality of the latter to the diameter of the benzene ring. This would lend weight to the view of the staggered arrangement of the carbon atoms in the benzene ring, for the evidence in figure 2 and in the value 1.24 Å.u. in equation (1) is that the carbon atoms are staggered. It may also be added here that all of the tests made on the derivatives of benzene and cyclohexane indicate that the

TABLE 3

Increase in diameter produced by substitution. Benzene alone, 4.70 Å.u. Cyclohexane, 5.10 Å.u.

NAME	STRUCTURE	INCREASE IN DIAMETER IN Å.U.
Phenol	C_6H_5OH	0.07
Aniline	$C_6H_5NH_2$	0.05
Cyclohexanol	$C_6H_{11}OH$	−0.06
Cyclohexanone	$C_6H_{10}O$	−0.06
Toluene	$C_6H_5CH_3$	0.36
Methylcyclohexane	$C_6H_{11}CH_3$	0.25
Ethylbenzene	$C_6H_5C_2H_5$	0.29
Isopropylbenzene	$C_6H_5CH(CH_3)_2$	0.65

corresponding "rings" are in each case fixed units in the structure of the molecule.

The benzene and cyclohexane rings show also the existence of polar molecules. With cyclohexanol, there is a second set of planes accounted for by the double molecules produced by the juxtaposition of the OH groups of two of the molecules of two disks lying in a plane. Phenol shows the same characteristic. All four of the hydroxydimethylbenzenes show these double molecules, two of them, however, very faintly. In all these cases, however, the second set of planes is fairly normal to the set of planes parallel to the disks. This is known from the fact that

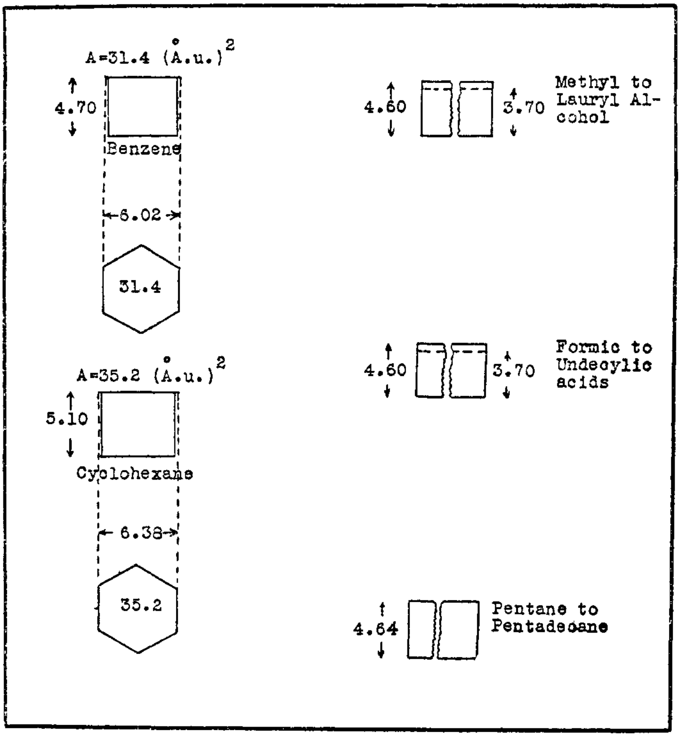


FIG. 4. COMPARISON OF THICKNESS OF BENZENE AND CYCLOHEXANE WITH DIAMETERS OF STRAIGHT CHAINS

the distance measured between planes is, according to computations, equal to twice the length of a molecule.

The thickness of the molecule of a benzene or a cyclohexane derivative depends not only upon the substitutions but upon their location as well. Several *ortho*, *meta* and *para* derivatives were investigated and the increases in thickness over the thicknesses of the unsubstituted rings were obtained. These derivatives, with the corresponding increases in thickness stated respectively in parentheses after each one, are as follows: *o*-, *m*- and *p*-dimethylcyclohexane (0.52, 0.54, 0.39 Å.u.), *o*-, *m*- and *p*-xylene (0.81, 0.65, 0.47 Å.u.), *o*-, *m*- and *p*-toluidine (0.42, 0.37, 0.26 Å.u.), and *o*-, *m*- and *p*-cresyl methyl ether (0.80, 0.51, 0.16 Å.u.). Bearing in mind that differences more than 0.05 Å.u. are probably real, it is certain that in these four derivatives the *para* position gives the least thickness of ring. This is of course significant, but it may be too early to generalize from these four only. For example, similar observations, for the most part on other derivatives, have been made by Sogani (4), Krishnamurti (5), and Herzog and Janke (6) with the di-*n*-propylcarbinol and 2-methylhexane. In the former, the diameters clearly measure 4.85 Å.u. and 4.5 Å.u. The second value is precisely the diameter of the corresponding *n*-alcohol. This means that the di-*n*-propylcarbinol is to be regarded as a straight chain with the OH as a branch. This is further verified by the fact that the measured distance of separation of a third set of planes, 10.5 Å.u., is the length of the single molecule as computed by equation (1). The separation of planes by the length of one molecule is in accord with the previous statement that double molecules are not formed by OH unless the attachment is to the carbon atom at the end or next to the end. The other example is 2-methylhexane. This compound, which was prepared very carefully by the Ethyl Gasoline Corporation and has subsequently been tested for purity, gives two diameters, one 5.25 Å.u. and the other 4.84 Å.u. The former is .61 Å.u. greater than the diameter of *n*-heptane and the latter .20 Å.u. greater. The increase in two diameters agrees with the previous conclusion that the paraffin molecule is easily distorted. It is a significant fact that the groups of the molecules in any one case may be so regular in structure as to enable two diameters to be measured, and, as with di-*n*--propylcarbinol, the molecular length in addition.

PURITY OF COMPOUNDS

It is obvious that x-rays can not be used to determine the nature of an impurity in a liquid, but x-rays sometimes give helpful and convincing evidence. Our first experience was with an impurity in decyl alcohol. Our observations showed that the sample contained heavy molecules. We suspected bromine. The Eastman Kodak Company kindly redistilled the decyl alcohol. Then it gave results which were in accord with those of the other *n*-alcohols. Our second experience was with *n*-pentane. This gave a diffraction peak at 8.1°, which was not the same as for the other *n*-paraffins. But upon request, the Eastman Kodak Company prepared a sample of synthetic *n*-pentane, and the peak was found at 8.8°, or exactly the position of the diffraction peaks in the other *n*-paraffins, with the exception of *n*-decane. Through the kindness of Dr. George Calingaert, we were able to secure *n*-decane synthetically prepared. Again a similar shift in the diffraction peak took place and *n*-decane gave the same diffraction peak as the other *n*-paraffins. The fourth experience was with mesitylene. It possessed a second peak, to which reference has already been made, and it was thought that this might be caused by an impurity. The Eastman Kodak Company kindly redistilled the sample, with the result that the second peak increased in relative intensity. This shows that the slight impurity actually interfered with the arrangement of the molecules producing a second set of planes.

NATURE OF A SOLUTION

The above remarks on purity are made merely to indicate the unexpected usefulness of the x-ray diffraction study of molecular structure. It is not the purpose of this paper to go beyond a discussion of molecular structure but attention might well be called also to the importance of these x-ray studies as indicating the nature of a solution. If, as it is here claimed, the liquid forms temporary groups of molecules, then one might expect that in a solution we would have the solute participating in the molecular structure space arrangement of the solvent, as is really the case in solid solutions. So far as the experiments in our laboratory and abroad have shown, this picture indeed proves actually to occur and we have a simple conception of a solution. This view is that the solute participates in the molecular space array of the solvent. It must not be supposed, however, that this simple picture is an adequate one. The findings of x-rays from diffraction in solutions are not yet sufficiently extensive to give the varied details.

When one examines with care the evidence which is only briefly sketched in the foregoing, he can scarcely avoid being impressed with the simplicity and directness of the interpretation of the results in terms of the cybotactic condition. Moreover, he realizes that the molecular forces involved are comparable to those found in the crystalline form of the same material, and that thus both the x-ray evidence and general considerations give great confidence in the essential correctness of the theory of the cybotactic condition. As to just how temporary any given small orderly group may be, there is as yet no evidence. Doubtless the orderliness of the arrangement changes from time to time at any point. That the semi-orderly groups occupy a large part of the volume, is shown by the comparison of the intensity of diffraction with the liquid and the solid. In several cases examined, the intensity of diffraction from the liquid at a peak is approximately as large as that from the solid (the same liquid frozen) at its corresponding peak. We are dealing, therefore, not with the unusual but with the usual when we describe the liquid as containing orderly groups. With this conception, our picture of several liquid phenomena will be altered. For example, the vibrations of the molecules are not independent and the kinetic and potential energies are cared for by acoustic waves, much as in a crystal. In fact, preliminary observations show a variation with temperature much like that with crystals. The theories of liquid phenonema should now be examined with cybotaxis as a hypothesis.

The studies thus far have emphasized, by agreement with chemical beliefs, confidence in the existence of the cybotactic condition in liquids. The foregoing evidence leads to the hope that examination of liquids by means of x-rays may lead to many contributions to molecular structure as well as to liquid structure.

GENERAL CONCLUSIONS

The general conclusions that may be drawn from a study of the details of the experiments briefly reviewed above, are as follows:

1. The diameters of the straight chain molecules—*n*-alcohols, *n*-monobasic fatty acids and *n*-paraffins—are relatively as follows: 4.55, 4.55 and 4.64 Å.u., respectively.

2. The distance occupied by a carbon atom in the *n*-paraffin molecule is 1.24 Å.u., and the assumption that the same value occurs in the other two straight chain molecules leads to consistent results. The formula for the length of the *n*-paraffin molecules is

$$L = 1.24\ n + 2.70\ \text{Å.u.}$$

where n is the number of carbon atoms and 2.70 Å.u. is the allowance for the two terminal hydrogens.

3. The terminal polar OH and COOH produce a doubling of the molecules with the polar groups adjacent to one another and the molecules forming a straight chain twice the length of one molecule. The polar group OH will cause this doubling if attached to the end carbon atom or the atom next to the end, but if in a branch elsewhere, this kind of doubling of the molecule ceases. Inasmuch as the molecules are lying side by side, the attachment of the polar group at the side instead of causing any form of doubling that can be detected by the x-rays aids and possibly increases the regularity of the arrangement of molecules in the cybotactic groups. There is no reason herein for saying that the effect of the polar group OH is less in one case than in the other. The effect is merely different.

4. The effect of branches upon the diameter of the chain molecules indicates that the *n*-alcohol chains are fairly rigid in comparison with the *n*-paraffin chains. The latter seem to bend with the attachment of a simple branch.

5. The benzene and cyclohexane molecules have a distinct flatness. The thicknesses are 4.7 and 5.1 Å.u., respectively. The areas of these molecules in a plane perpendicular to the thicknesses are, respectively 31.4 and 35.2 (Å.u.)^2 A polar group OH as a substituent may cause a doubling of molecules in the plane of the disks.

6. The *para* position of two substituents in benzene and cyclohexane gives the least thickness of the molecules.

7. The conception of benzene and cyclohexane molecules as having somewhat the same structure as the straight chain but forming a kind of ring, is in accordance with the x-ray measurements.

8. X-ray measurements are of some value in distinguishing between a compound and its isomer. They are also capable of detecting the presence of small quantities of heavy atoms.

9. A consideration of all these measurements leads to an increased conviction of the correctness of the view that molecules in liquids in general are in a cybotactic condition. That is, they arrange themselves into semi-orderly temporary groups. This fact is important in a consideration of the nature of a solution and many liquid phenomena.

10. There are numerous details concerning specific molecules that are shown by the experiments, but which cannot be enumerated in an abstract. For example, di-*n*-propylcarbinol is found to be a "straight" chain with the OH as a branch.

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REFERENCES

(1) DRUCKER: Physik. Z. **29**, 273 (1928).
(2) STEWART AND MORROW: Phys. Rev. **29**, 919 (1927); **30**, 232 (1927).
(3) STEWART AND MORROW: Primary Normal Alcohols. Phys. Rev. **30**, 232 (1927). STEWART AND SKINNER: Comparison of Certain Primary Normal Alcohols and Their Isomers. Phys. Rev. **31**, 1 (1928). MORROW: Normal Monobasic Fatty Acids. Phys. Rev. **31**, 10 (1928). STEWART: Liquid Normal Paraffins. Phys. Rev. **31**, 2 (1928). STEWART: Comparison of Isomers of Normal Heptane and Certain

Chains. Phys. Rev. **32**, 153 (1928). Stewart: Theory of X-ray Diffraction in Liquids. Phys. Rev. **32**, 558 (1928). Stewart: Benzene and Cyclohexane and Certain of Their Derivatives. Phys. Rev. **33**, 889 (1929). Stewart: Comparison of Certain Isomers of Primary Normal Octyl Alcohol. Not yet completed for publication.

(4) Sogani: Indian J. Phys. **2**, Pt. I, 97 (1927).

(5) Krishnamurti: Indian J. Phys. **2**, Pt. III, 355 (1928).

(6) Herzog and Janke: Z. Physik. **45**, 194 (1927).