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X-RAY DIFFRACTION IN LIQUIDS: A COMPARISON OF ISOMERS OF NORMAL HEPTANE AND OF CERTAIN CARBON CHAINS

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Abstract

With the $K\alpha$ doublet of molybdenum, diffraction ionization curves are reported on synthetic decane, 2–2–4 trimethyl pentane, 2 methyl hexylene 2 and the following eight isomers of normal heptane obtained from the Ethyl Gasoline Corporation: 2–2–3 trimethyl butane, 3–3, 2–3, 2–2 and 2–4 dimethyl pentane, 3 ethyl pentane, 3 methyl hexane, and 2 methyl hexane. The experiments are a continuation of those of Stewart and Morrow, Stewart, and Stewart and Skinner. The diffraction peak of synthetic decane occurs at precisely the same angle as of eight of the other normal paraffins containing from five to fifteen carbon atoms so that the diameter of the normal paraffin chain throughout this range, as computed by Bragg's diffraction law, is 4.64A. The experience with normal decane was a repetition of that with normal pentane previously reported by the author. The length of the chain is in agreement with the formula, $L=(1.24n+2.70)\times 10^{-8}$cm if n is the number of carbon atoms, and if the molecules may be regarded as longitudinally parallel and in square array in the plane normal to their lengths. The agreement is within less than one percent. With the exception of 2 methyl hexane wherein two diameters are found, and of 3 ethyl pentane which is a symmetrically branched structure, all the other heptane isomers, six in number, have diameters that are 1.04*A* larger than the normal paraffins. A consideration of this fact and of the alterations in density not in agreement with the formula just cited reach the conclusion that the molecular chains of the isomers are distorted either by bending or by another type of atom separation. A tentative conclusion is that the attachment of two CH_3 groups to the same atom may or may not increase the diameter by the same amount, this depending upon whether a third CH_3 branch is attached to an adjacent atom or to the next but one. The attachment of a CH_3 group on the next to end carbon atom seems, in the cases of 2 methyl hexane and 2 methyl hexylene 2, to produce two symmetrical branches of one CH_3 group each. Both this and the preceding conclusion are highly tentative but suggest the possibility of learning more of the nature of the chain by more extended experiments on isomers of normal paraffins. The foregoing experiments contribute not only to our knowledge of molecular structure but also to the evidence for the cybotactic state as one of importance in fundamental phenomena in liquids.

Introduction

In a series of articles by Stewart and Morrow[1], Stewart and Skinner[2], Morrow[3] and Stewart,[4] evidence has been brought forward to indicate

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[1] Stewart and Morrow, Phys. Rev. **30,** 232 (1927), and Proc. Nat. Acad. **13,** 222 (1927).

[2] Stewart and Skinner, Phys. Rev. **31,** 1 (1928).

[3] Morrow, Phys. Rev. **31,** 10 (1928).

[4] Stewart, Phys. Rev. **31,** 174 (1928), and Proc. Nat. Acad. **13,** p. 787 (1927).

that there is a molecular space arrangement in liquids, that this condition is important and in need of emphasis in the study of all fundamental liquid phenomena and that x-ray diffraction measurements in liquids are of value in the study of molecular structure. Incidentally such measurements have proved of distinct value in distinguishing between isomers of chain compounds. The reader is reminded of the view point of these contributions. The suggestion of a molecular space array in liquids is not new and is doubtless as old as crystalline theory itself. But the results of the experiments of this laboratory combined with general views concerning molecular forces, have brought the authors to the view that the ordered grouping of molecules is not crystalline, is unique in character and is worthy of a special name, "cybotaxis." The studies have not progressed to the point where the details of this cybotactic state may be stated. It is fairly evident, however, that the "straight" carbon chains with a carbon content of from one to fifteen atoms are arranged longitudinally parallel and with sufficient uniformity to give the effect of the existence at any instant of a large number of minute groups each of which is fairly regular. The orientation differs from point to point.[5] Indeed, the liquid state is a modified and exaggerated example of an "irregular crystal." Yet these somewhat regular minute groups, arranged irregularly among themselves, are not crystalline and differ fundamentally in that they are not in stable configuration. The view to be emphasized is that one should extrapolate, as it were, the conception of the arrangement of long molecules to short molecules. The cybotactic state continues to remain of importance with decreasing lengths of molecules even though the x-ray method of measurement becomes less effective. One should approach the liquid state from the conditions obtaining with long molecules in a liquid, and not from spherical molecules in the gaseous state. In the former case Bragg's diffraction law, $\lambda = 2d \sin (\theta/2)$ is used. In the latter the formula chosen is that originally derived by Ehrenfest[6] and by Debeye and Scherrer[7] and used by Keesom and Smedt,[8] Katz[9] and others,

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[5] Sogani has independently adopted this view, as is shown in a paper, Indian Journal of Physics, Vol. II. p. 97, (1927). Katz, Zeits. f. Physik **46**, p. 392 (1928), also mentions this with distinctness.

[6] Ehrenfest, Proc. Amsterdam **17**, 1184 (1915).

[7] Debeye and Scherrer, Nachricthen Göttingen (1916). (See also P. Debeye Ann. d. Physik (4) **46**, p. 809 (1915).

[8] Keesom and Smedt, Proc. Amsterdam **25**, p. 118 (1922).

[9] Katz, Zeits. f. Physik **45**, 97 (1927).

[8] Stewart, Phys. Rev. **31**, 174 (1928).

[9] Dr. Calingaert describes the determination of the best values of densities as follows: In order to obtain the best values for d_4^{20} for the normal paraffin hydrocarbons from C^5 to C^{15}, the following method was used: the values given in International Critical Tables, and by R. E. Wilson and W. H. Bahlke in Industrial and Engineering Chemistry **16**, 115 (1924) were plotted on a scale of d_4^{20} versus "C", the number of carbon atoms in the molecule, reasonable correction being made where the values were not given at 20°. To these were added the value for n-butane given by L. I. Dana, Refrig. Eng. **12**, 387 (1926) and for n-pentane given by S. Young, and reported in Beilstein. A smooth curve was drawn through the points and the slope of that curve was also plotted against C. After smoothing out the slope curve, the corrections were reported to the density curve and the value read off the corrected curve. (The

wherein $\lambda = 2d \sin(\theta/2) \times 0.814$. This was originally derived for diatomic gas molecules, but gives consistent molecular volumes for short molecules if the assumption of closely packed spheres is made.

It is not the function of the current paper to give a resumé of the important work now being done in x-ray diffraction in liquids, but to continue the reports of the experimental results of this laboratory with the conclusions therefrom.

NORMAL PARAFFINS

In our earlier work[8] on normal paraffins, it was found that seven out of the nine normal paraffins had a diffraction peak at the same angle, namely 8.8°. The two expections were pentane and decane. When going to press, a sample of synthetic pentane, kindly prepared by the Eastman Kodak Company, was tested and found to have its diffraction peak at 8.8°. This new fact was added in a footnote. Since that time, through the courtesy of Dr. George Calingaert of the Ethyl Gasoline Corporation, a sample of synthetic decane was tested and found to have its diffraction peak at 8.8°. These alterations, shown in Fig. 1, are interesting for two reasons. They show the possibility of the x-ray diffraction as a method of distinguishing isomers from the normal paraffins and they prove that the normal paraffin chain has precisely the same "diameter" from pentane to pentadecane. This diameter is 4.64A if the diffraction peak is interpreted by Bragg's Law.

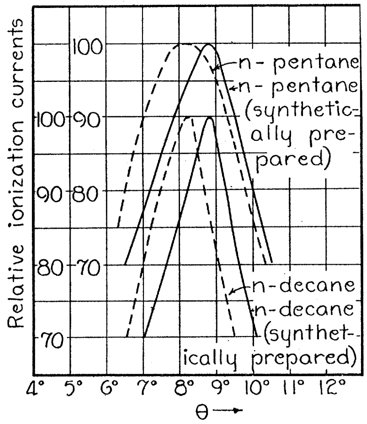

Fig. 1. Variation of diffraction-ionization curve with content of isomers.

Through the kindness of Dr. George Calingaert,[9] it is now possible to apply the best density values in computing the space occupied by the carbon atom in the chain. The density values for pentane, hexane, heptane, octane, nonane, decane, dodecane, tetradecane and pentadecane are 0.627, 0.660, 0.684, 0.702, 0.718, 0.731, 0.751, 0.766, 0.772. Since the paraffin chain is symmetrical, it is reasonable to assume that the molecules are arranged with lengths parallel and in a square array in a plane perpendicular thereto. The length of the chain can then be expressed by the formula,

$$L = \frac{(\text{Molecular weight}) \times (\text{Mass of } H \text{ atom})}{(4.64 \times 10^{-8})^2 \times \text{density}} \tag{1}$$

When these values are plotted, it is found that, with a variation of less than

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large discrepancies with some values given in I.C.T. are probably due to the fact that these values are not d_4^{20} as reported, but more likely d^{15} for pentane, and d^0 for decane and dodecane.)

1 percent, these lengths correspond to the following formula, expressed in Ångstroms or 10^{-8} cm,

$$L = 1.24n + 2.70 \qquad (2)$$

wherein n is the number of carbons in the chain and 2.70×10^{-8} is the length occupied by the two H atoms at the terminals of the chain. As stated in the earlier article,[8] Müller and Saville[10] found a length of 1.3A* for each additional CH_2 in solid hydrocarbons and Piper, Brown and Dyment[11] found a length of 1.22A. If instead of a square array the densest packing were assumed, the volume occupied would be $L' \times 4.63 \times 4.63 \sin 60° \times 10^{-16}$ and L' would be 15 percent greater than L. But in view of the measurements on solid hydrocarbons the assumption of a square array seems justified.

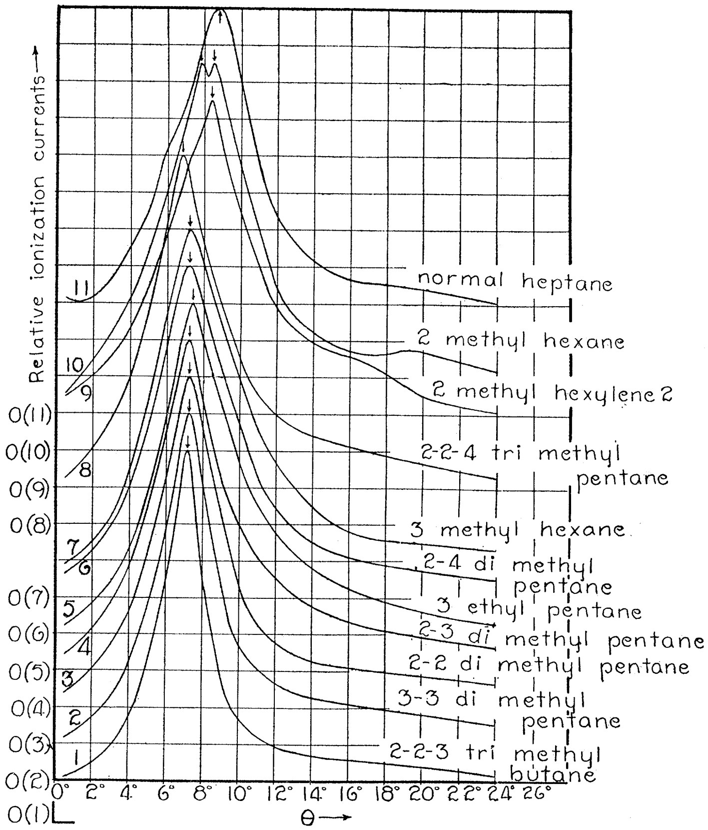

Fig. 2. Ionization-diffraction curves for n-heptane, eight isomers, an octane and 2 methyl hexylene 2.

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[10] Müller and Saville, Jl. Chem. Soc. **27**, 509 (1925).

* A is used for Ångstroms or 10^{-8} cm.

[11] Piper, Brown and Dyment, Chem. Soc. Jl. **127**, 2194 (1925).

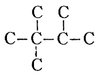
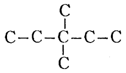
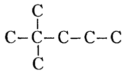
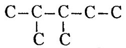
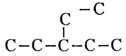
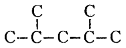
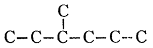
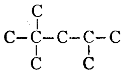
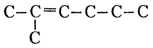
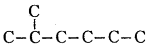
METHOD AND EXPERIMENTAL RESULTS

There has been no material alteration of the method or equipment as described in the previous papers from this laboratory to which reference has been made. In Fig. 2 are shown the ionization diffraction angle curves for the following: 2-2-3 trimethyl butane, 3-3 dimethyl pentane, 2-2 dimethyl pentane, 2-3 dimethyl pentane, 3 ethyl pentane, 2-4 dimethyl pentane, 3 methyl hexane, 2-2-4 trimethyl pentane, 2 methyl hexylene 2, 2 methyl hexane, and normal heptane. Nine of these are heptanes and one an octane, and the 2 methyl hexylene 2 is added for the purpose of a desired comparison.

DISCUSSION OF DERIVED RESULTS

In Table I are given the results obtained from the curves in Fig. 2, using Bragg's Law $\lambda = 2d \sin(\theta/2)$ and the wave-length of the approximately monochromatic beam 0.712A.

TABLE I. *Structure and diameters of molecules.*

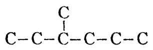
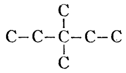
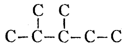
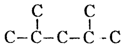
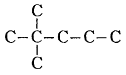
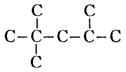
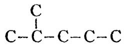
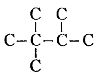
Name	Structure	Diameter in 10^{-8} cm	Increase in diam. in 10^{-8} cm	Width of Peak
(1) 2–2–3 Trimethyl butane	 $C-\underset{C}{\overset{C}{C}}-\overset{C}{C}-C$	5.69	1.05 ± .05	1.7°
(2) 3–3 Dimethyl pentane	 $C-C-\underset{C}{\overset{C}{C}}-C-C$	5.68	1.04 ± .05	2.4°
(3) 2–2 Dimethyl pentane	 $C-\underset{C}{\overset{C}{C}}-C-C-C$	5.68	1.04 ± .05	2.8°
(4) 2–3 Dimethyl pentane	 $C-\underset{C}{C}-\underset{C}{C}-C-C$	5.68	1.04 ± .05	2.8°
(5) 3 Ethyl pentane	 $C-C-\overset{C-C}{C}-C-C$	5.51	0.87 ± .05	3.2°
(6) 2–4 Dimethyl pentane	 $C-\overset{C}{C}-C-\overset{C}{C}-C$	5.68	1.04 ± .05	3.6°
(7) 3 Methyl Hexane	 $C-C-\overset{C}{C}-C-C-C$	5.68	1.04 ± .05	3.5°
(8) 2–2–4 Trimethyl pentane	 $C-\underset{C}{\overset{C}{C}}-C-\underset{C}{C}-C$	6.00	1.37 ± .05	2.8°
(9) 2 Methyl Hexylene 2	 $C-\underset{C}{C}=C-C-C-C$	4.85	0.21 ± .05	3.6°
(10) 2 Methyl hexane	 $C-\overset{C}{C}-C-C-C-C$	$\begin{cases}5.25\\4.84\end{cases}$	$\begin{cases}0.61 \pm .05\\0.20\end{cases}$	4.3°
(11) Normal heptane	C–C–C–C–C–C–C	4.64	0.00 ± .05	3.6°

(1) *General remarks.* Of the heptanes, there is one unusual case, 2 methyl hexane, wherein two diameters are found. With this exception, there are only two alterations in diameter for seven isomers. Six of them have an increase in diameter of 1.04A and one of 0.87A. A comparison of the struc-

tural differences in the molecules can hardly be said to account for this similarity. For example, one CH_3 and two CH_3 branches attached to the same atom or to different atoms seem to have the same effect upon the diameter. If a comparison is made with the alcohol isomers, it is found that 1.04A is roughly twice the increase in diameter of an alcohol chain when CH_3 or OH is attached as a branch. Also, the consistency in the results of the alcohol isomers seems to be not so much in existence here. The difference in the results for the paraffin and alcohol isomers is probably caused by a difference in the distortion of the two chains. The case of 2 methyl hexane will be discussed at a later point.

(2) *Distortion of chains.* As noted in a previous paragraph, the assumption of a square array of the normal paraffin molecules gives entirely consistent values for the length in the chain of the carbon atoms and of the terminal hydrogen atoms. Much confidence can be placed in these values because they agree for the nine normal paraffins to within a variation of less than 1 percent. The "straight" portion of the chains with the isomers should have the same values for the carbon and hydrogen atom lengths or the chain may be said to be distorted. If the square array is now assumed, it is possible to compare the lengths of the isomer chains, obtained by the measurements of diameters and the use of an equation of the form of (1), with the lengths computed by Eq. (2). They will be denoted by L_1 and L_2 respectively. The results are given in Table II. There is also included an octane, 2-2-4 trimethyl pentane.

TABLE II. *Variation of L from computed value.*

Name	Structure	L_2	L_1	L_2-L_1	(L_2-L_1) $/L_2$
3 Methyl hexane	 $C-C-\overset{C}{C}-C-C-C$	10.14	7.46	2.68	25.4
3-3 Dimethyl pentane	 $C-C-\overset{C}{\underset{C}{C}}-C-C$	8.90	7.38	1.52	17.1
2-3 Dimethyl pentane	 $C-\overset{C}{C}-\overset{C}{C}-C-C$	8.90	7.38	1.52	17.1
2-4 Dimethyl pentane	 $C-\overset{C}{C}-C-\overset{C}{C}-C$	8.90	7.61	1.29	14.5
2-2 Dimethyl pentane	 $C-\overset{C}{\underset{C}{C}}-C-C-C$	8.90	7.61	1.29	14.5
2-2-4 Trimethyl pentane	 $C-\overset{C}{\underset{C}{C}}-C-\overset{C}{C}-C$	8.90	7.54	1.36	15.3
2 Methyl hexane	 $C-\overset{C}{C}-C-C-C$	10.14 10.14 9.61	10.47 8.87 9.63	+.33 1.27 0.00	−3.1 12.5 0.0
2-2-3 Trimethyl butane	 $C-\overset{C}{\underset{C}{C}}-\overset{C}{C}-C$	7.66	7.45	.21	2.7

The last column shows that the lengths are from 25 to 2.7 percent (2 methyl hexane excepted) less than they should be if undistorted. Hence the conclusion favors definite distortion. But a further examination shows that there are two corroborating points. First, the greatest distortion is that of 3 methyl hexane, and the structure of the molecule, with a CH_3 branch on one side and near the center, is favorable to distortion. Second, the one having the least distortion, 2-2-3 trimethyl butane, is the shortest molecule of the group, is one of the best balanced against distortion, and Fig. 2 shows that it gives distinctly the sharpest peak of any of the compounds there shown. In fact, it has one of the sharpest liquid peaks yet found in this laboratory. That it may be well balanced against distortion is recognized if one makes the reasonable assumption that the carbon atoms are not in a straight chain and the three branches are not in the same plane.

Table II is arranged approximately in the order of the magnitude of distortion so that any connection between this and the character of the molecular structure may be readily seen. Or, expressed in another way, one might hope the results to indicate the detailed character of the chain. For example, do the results indicate that the normal chain is a spiral with the lines joining centers of the carbon atoms having an angle of 109°28′, and with the spiral completed by a fourth atom? The results do not give an answer. One reason is that the distortion may be too great to betray the detail of the normal chain. Another is that we may be pushing the results further than the purity of the compounds warrant. At any rate, while there is no definite answer reached as to detailed structure, the results are not inconsistent with the assumption of distortion.

The results give evidence either for distortion with all the isomers or for a closer packing. But the differences from 25.4 to 2.7 percent can scarcely be accounted for by differences in packing, and distortion is proved in either event. This distortion would probably consist not only of bending but of alterations in the separation of the carbon atoms. The distortion also accounts for the similarity in change in diameter and the difference shown by comparison with alcohol isomers, both of which were mentioned under (1) above.

(3) *3 Ethyl pentane.* This molecule is a symmetrically branched chain. It can scarcely be classed with the other heptanes in the preceding discussion on distortion.

Table I shows that its increase in diameter is only 0.87A. This may be accounted for by a symmetrically branched chain with the three branches in the same plane and forming angles of 60° with each other. But one might expect that two diameters would be shown instead of one. Doubtless the lack of uniformity in the groups is the explanation.

Assuming the same structure, and making a reasonable allowance for the central carbon atom, the value of L_2 becomes 8.30A. L_1 as computed by Eq. (1) is 7.84A. The distortion as measured by $(L_2-L_1)/L_2$ is only 5.5 percent.

(4) *2 methyl hexane, and 2 methyl hexylene 2.* The 2 methyl hexane gives two diameters. This is the second case in the work of this laboratory when the resolving power of the liquid groups was sufficient to give two diffraction peaks for an isomer. The other case is that of di-n-propyl carbinol. Using one of these peaks, $(L_2-L_1)/L_2$ gives -3.1 percent and with the other it is $+12.5$ percent. If, instead of this procedure, the product of the two diameters be used in measuring L_1 its value would be 9.63A. If it is assumed that five of the carbon atoms are in a "straight" chain, that the length of the fifth molecule along the chain belongs half to the straight portion and half to one of the branches, and if the angle between the branches is 60°, then the length L_2, computed by Eq. (2), is 9.61A. L_2 and L_1 are essentially equal. This seems to give evidence that the only distortion in the chain is the branching of the CH_3 groups from the last carbon atom.

(5) *Effect of point of attachment of branches.* The increase in diameter with the two CH_3 groups attached either to adjacent or non-adjacent carbon atoms seems to alter the diameter by the same amount, 1.04A. This is shown by the 3-3, 2-2, 2-3 and 2-4 dimethyl pentanes.

The attachment of the two CH_3 groups to the same atom may or may not increase the diameter by the same amount, 1.04, this depending upon whether a third CH_3 branch is attached to an adjacent atom (2-2-3 trimethyl butane) or a non-adjacent one (2-2-4 trimethyl pentane). Inasmuch as only one comparison is made, the conclusion is highly tentative.

The attachment of a CH_3 group on the next to the end C atom may alter the end of the chain causing a symmetrical arrangement of the two CH_3 groups and increasing the diameter of the molecule by a relatively small amount. This is illustrated by 2 methyl hexylene 2 and 2 methyl hexane. They both have an increase of diameter of about 0.2A as compared with an increase in the alcohol chains of 0.5A for a CH_3 branch.

These experiments suggest the possibility of reaching fairly definite conclusions as to the detailed nature of the paraffin chains. This would require experiments on a large number of isomers of the normal paraffins.

(6) *Comparison of the chains of the normal primary alcohols, saturated fatty acids and paraffins.* In connection with the foregoing discussion on the distortion of the straight chain in the case of an isomer, it is appropriate to refer to the data for the dependence of diameter upon the carbon content in the cases of the three normal series thus far tested in this laboratory. These data are found in the articles by Stewart and Morrow, Morrow and Stewart to which reference has already been made. The variation in diameter with primary normal alcohols varies linearly from eleven carbon atoms to three, the total variation being from 4.5A to 4.3A. From three carbon atoms to one, a rapidly increasing change sets in. The chains of the saturated normal fatty acids are, on the contrary, quite constant in diameter from eleven carbon atoms to four, and from four to one carbon atom its rapid decrease agrees, as nearly as can be determined, with the case of the alcohols. The normal paraffins have a diameter of 4.64A which is constant from fifteen to five carbon atoms content. The three do not appear to have like diameters

at any length except with less than four carbon atoms. Moreover the alcohols vary linearly while the paraffins and acids remain constant. This strengthens the view that the detailed nature of the chain, both as to diameter and longitudinal separation of carbons, depends upon the terminal groups.

There is also evidence that the isomers of primary normal alcohols do not have the amount of distortion found in the paraffin isomers. This can be shown by the comparisons of the measured lengths with those computed by a formula similar to Eq. (2). If it is assumed that the longitudinal separation of carbon atoms in the primary normal alcohols is the same as in normal paraffins, i.e., 1.24Å, then a consideration of the primary normal alcohol data shows that the atom of oxygen occupies the same longitudinal length as the carbon atom. Then Eq. (2) may be used provided n refers to O as well as to C. Computations with Eq. (2) may then be made of the lengths of the molecule of the alcohol isomers and compared with the projections of the lengths taken normal to the planes. When this is done, and double molecules are assumed, the angle of projection does not vary more than a few degrees, i.e., from 40° to 45°, with the exception of diethyl carbinol, di-n-propyl carbinol and tertiary amyl. With the first and second the angle becomes approximately zero, if single molecules are assumed. They are the only ones in which OH is a branch attached not to a carbon adjacent to the terminal atom. If this be the correct interpretation then the alcohol chain seems more fixed than the paraffin chains, even with the OH group in a branch, both because of the lack of a wide divergence in angle and because of the agreement of computations and measurements in the two cases cited. Tertiary amyl gives a considerable divergence of angle, approximately 10° less than that cited above.

General Conclusions

Stated in a broad way the conclusions are that the paraffin carbon chains are distorted by branch groups, that the normal paraffin chains have the same diameter irrespective of length if containing more than five atoms, that the x-ray diffraction method in liquids seems to promise a considerable amount of knowledge concerning the structure of carbon chains, and that as evidence accumulates it increasingly favors the interpretation of the author as to the cybotactic state in liquids and the recognition of its importance in all fundamental liquid phenomena.

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