FEBRUARY, 1928 *PHYSICAL REVIEW* *VOLUME 31*

X-RAY DIFFRACTION IN LIQUID NORMAL PARAFFINS

BY G. W. STEWART

ABSTRACT

X-ray diffraction as a function of angle in liquid pentane, hexane, heptane, octane, nonane, decane, dodecane, tetradecane and pentadecane.—In the ionization diffraction-angle curve, there was one diffraction peak only, instead of two as found by Stewart, Morrow and Skinner with the primary alcohols and normal fatty acids. The absence in the *n*-paraffins of the second peak, which, in the alcohols and fatty acids, indicated a longitudinal spacing, is explained qualitatively by a consideration of the longitudinal molecular forces. These could not produce as uniform a longitudinal arrangement as occurs in the other compounds. The single peak was located at the same angle with each *n*-paraffin, excepting, at first, pentane and decane. Subsequent purification of the pentane produced no alteration in the peak position but when the sample was finally made synthetically, the peak came into coincidence with that of the other seven. The decane is believed to contain isomers. The lateral separation of molecules is approximately 4.6A and is essentially the same as in the liquids previously studied and referred to in this paper. In six of nine cases, the diffraction intensity does not decrease as one approaches 0°. The significance is not clear though one is reminded of total reflection and also of refraction. If one assumes the C atom to occupy a length in the chain of 1.3A, as found by other observers of x-ray diffraction in solids, and the length of H, 1.0A, and if one assumes the volume occupied by a molecule to be the square of the lateral spacing times the molecular length, then the computed values of densities of the seven normal paraffins are correct to within less than 4 percent or a mean of 2 percent. Two additional but faint peaks in the diffraction intensity curves are found with pentadecane and tetradecane. The corresponding spacings are 2.1A and 1.23A. The nearness of these to the repetitive values of 2.0A and 1.26A which are found in a diamond, is suggestive.

THIS is a continuation of the studies of Stewart and Morrow,[1] Stewart and Skinner,[2] and R. W. Morrow[3] wherein the molecular space arrangement has been shown to be significant in liquid primary normal alcohols, a few of their isomers and liquid fatty normal acids. As will be shown, the present results upon liquid *n*-paraffins are in harmony with the view that the molocules are oriented, and that the separation of the molocules in a direction perpendicular to their lengths is the same as in primary normal alcohols and in fatty acids.

Pentane, hexane, octane and decane were obtained from the Research Laboratory of the Eastman Kodak Company. Heptane, nonane, dodecane, tetradecane and pentadecane were made especially for us by the Northwestern Public Health Institute, through the kindness of Professor F. C. Whitmore.

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[1] Stewart and Morrow, Phys. Rev. **30**, 232 (1927).

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

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

Apparatus, method and results. The apparatus and method are essentially the same as that previously described. In Fig. 1, are shown the diffraction curves of normal pentane, hexane, heptane, octane, nonane, decane, dodecane, tetradecane and pectadecane.

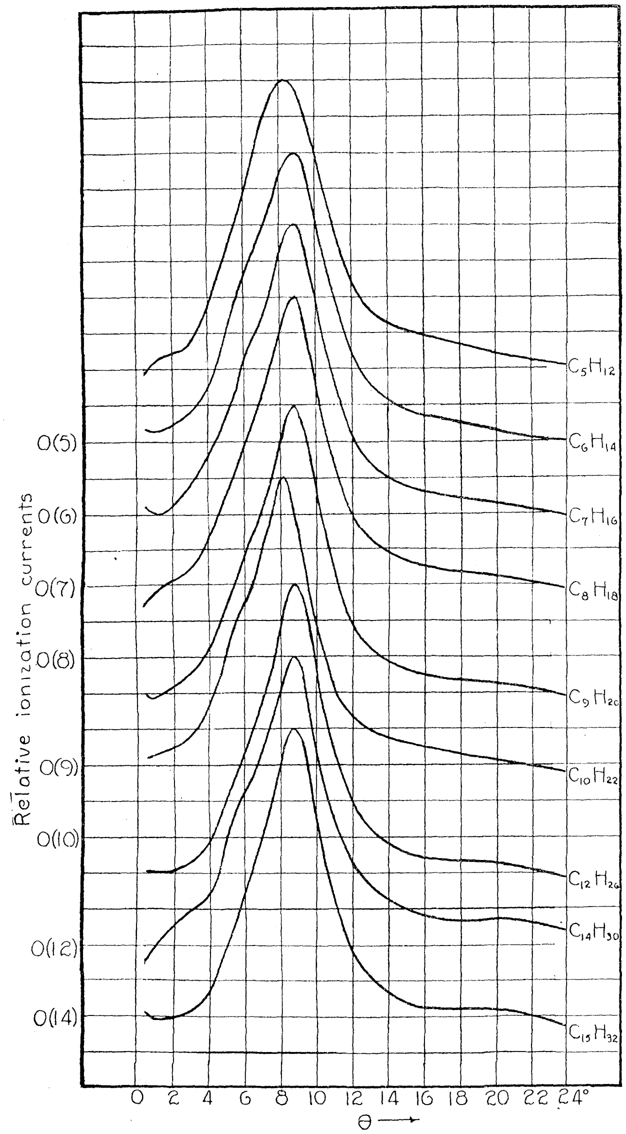

Fig. 1

Discussion of results. The chief feature of the curves in Fig. 1, as compared with those obtained for the primary normal alcohols and the normal fatty acids, is the existence of but one peak. The positions of the two peaks in these other compounds were interpreted as caused by the spacing between the molecules lying in a parallel collinear arrangement, and by the length of the molecule, or, rather, by the length of two molecules in series having attached polar groups. The latter peak indicated the much lesser intensity of diffraction. It is not surprising that in the case of the normal paraffins, with the electron content more uniformly distributed, this peak of feeble intensity was not found. The reason that the intensity with the primary *n*-alcohols and normal fatty acids is small, may be found in the difference in the uniformity of the arrangement longitudinally and transversely and in the concentration of electrons. The molecular binding forces that determine the side by side array may be greater, or they may be more effective in producing uniform parallel spacing because of the length of the chain over which the forces act. The side spacing would be in evidence, even though the ends (or centers) of the adjacent molecules did not lie approximately in a plane. On the other hand, the longitudinal spacing might be regular in any one of the successive parallel chains, but yet without the termini of the molecules lying in transverse approximate planes. In short, there may easily be longitudinal slippage with the diffraction intensity determined by the degree of the definiteness of these transverse planes. Obviously, the primary *n*-alcohols and *n*-fatty acids, with the OH and COOH groups, would, on account of the mass concentration, have greater longitudinal uniformity of arrangement among the parallel chains. Thus, the absence of the second peak with *n*-paraffins rather emphasizes the correctness of the former interpretation of the two peaks. It accentuates the interpretation that we are dealing with a space arrangement giving x-ray diffraction effects that should be interpreted as caused by something more than merely averaged distances between molecules.

The point of greatest quantitative interest is the fact that the single peak has a maximum at little more than 8.8° (averaging 8.83°), in all excepting two cases. In accord with Bragg's Law using a wave-length of 0.712A, 8.83° indicates a spacing of 4.63A. This is, within error of observation, the same as with the similar chains in the primary *n*-alcohols and the normal fatty acids. As previously interpreted, this represents the separation of the molecules in a direction normal to their lengths. With the paraffins the separation remains constant although the molecular length is doubled. This justifies the previous interpretations and shows that a wholly random orientation of molecules does not occur.

It is noticed that the maxima with pentane and decane are at a distinctly less angle. The research laboratory of the Eastman Kodak Company kindly further purified the pentane but the position of the peak persisted with the new sample. The interpretation at present is that the presence of isomers of heptane and decane cause these displaced angles. This explanation is reasonable in the light of the experiments on the primary *n*-alcohol isomers. This point should be settled by additional investigation with purer liquids.[4]

The third point is the evidence in six of the nine curves that the radiation is not approaching zero at 0° for there is noticeably increased scattering as the angle of diffraction becomes less than 1°. While the observations have not been carried to the extent that the quantitative differences between the *n*-paraffins at this small angle are certain, nevertheless there is no doubt but that there is a definite difference at small angles between the *n*-paraffins and the *n*-alcohols. This same effect has been found by Sogani[5] with liquid pentane, hexane heptane and octane but not with cyclo-hexane. He does not comment upon this fact although it is shown clearly in his photographs. One is inclined to think at once of the explanation as similar to that of total reflection at almost glancing angles or of refraction. But it is not clear why this phenomenon appears only in some and not in all of the paraffins.

Müller and Saville[6] studied the solid *n*-hydrocarbons having 17, 18, 19, 20, 21, 22, 24, 27, 31 and 35 carbons. They reached the conclusion that these solids were crystalline and of two stable forms, and that the increase of length of the chain molecule per additional CH_2 is 1.3A. Piper, Brown and Dyment[7] in an investigation of solid hydrocarbons in paraffin wax, with carbon content believed to be from 22 to 34 atoms, found the long spacings such that there is an increase of 1.22A for each CH_2 added to the chain. If we take the approximate value of 1.3A, assume the diameter of the H atom to be 1.0A and compute the densities as if the chains were parallel, normal to the long spacing planes, and in cross section occupying corners of squares, density values very near to the correct ones were obtained. The density is computed to be,

$$\rho = \frac{(\text{Molecular weight} \times \text{mass of } H)}{(4.63)^2 \times \text{length of chain}}$$

The values found for all excepting pentane[8] and decane are 0.683, 0.694, 0.713, 0.722, 0.747, 0.761, and 0.765. The corresponding values given by the International Critical Tables are 0.66, 0.707, 0.718, 0.768, 0.765 and 0.772.

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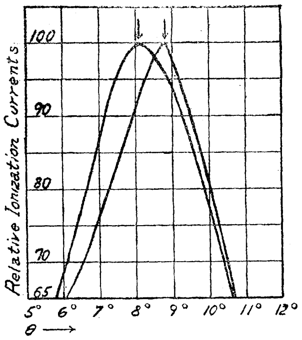
[4] Since submitting the manuscript for this article, the research laboratory of the Eastman Kodak Company has supplied the writer with a sample of synthetic *n*-pentane. It was made from propyl and ethyl iodides. This third sample when compared with the second shows, as illustrated in the accompanying drawing, that the peak now appears at 8.8°, instead of 8.1°, and that it has become much narrower. This relatively large change in θ is both interesting and suggestive. The peak for *n*-pentane, made synthetically, now coincides with the other seven, leaving additional tests upon *n*-decane for the future.



[5] Sogani, Indian Jour. of Phys. **1**, 237 (1927).

[6] Müller and Saville, Jl. Chem. Soc. **27**, 599 (1925).

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

[8] The computed density of the *n*-pentane mentioned in footnote 4 is found to be 0.66, within 4 percent.

The maximum difference between the computed and the correct values is less than 4 percent and the mean difference is less than 2 percent. The agreement may be regarded as an interesting consistency between the arrangement in a liquid and that found in the solid.

Diffraction curves were taken from 0° to 50° with pentadecane and tetradecane. An unmistakable maximum occurred at 19.4° and 19.0° respectively. The peak was only about 10 percent of the total height of the curve. With lauryl alcohol[1] there was a small peak at 19°. Apparently in none of these curves can the additional peak be merely one of a higher order. In the cases of pentadecane and tetradecane there is also a second additional peak at about 33.5°. The two spacings corresponding to 19.4° and 33.5° are 2.1 and 1.23A respectively. As pointed out by Müller and Shearer[9] linkages of carbon atoms can be found in the diamond, with distances of separation projected on a median line of both 1.26A for single and 2.0A for certain pairs of atoms. The inference from the earlier part of this paper is that the 1.23A spacing arises in the distance of separation of the carbon atoms along the chain. Perhaps the 2.1A spacing has a significance suggested by the crystal. However, these interpretations are merely tentative. With triethyl carbinol[2] there was found a corresponding peak at approximately 20° and this was interpreted as the third order peak.

There are several recent reports which have a definite bearing upon the material of the present paper. J. A. Prins[10] has recently investigated certain liquid surfaces and has obtained a band of 5.0A for liquid *n*-octane. This is somewhat larger than our value of 4.63A which is undoubtedly caused by the volume and not the surface. An investigation of the crystal structure of *n*-pentane, *n*-hexane, *n*-octane has recently appeared by McLennan and Plummer.[11] They show that at liquid air temperature these compounds show either the monoclinic or the orthorhombic modification. For the latter he finds that the spacing caused by the "diameter" of the molecules, or the length of CH_2, is a little more than 4.3A which is much less than our value of 4.6A. He is also led to believe that the carbon chain is straight, which is not in accord with the view that appears in the work of other investigators[12] of compounds in solid form having similar chains. Neither is it in harmony with the work of this laboratory in liquids. But in the monoclinic form McLennan and Plummer find a "medium strong" line at 4.61A. On the whole the crystal results would indicate that our liquid space array is more similar to the monoclinic than to the orthohombic modification. From our previous papers it is clear that the liquid space array or the cybotactic state is not like any crystal modification.

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[9] Müller and Shearer, Jl. Chem. Soc. **123,** 3156 (1925).

[10] Prins, Physika **6,** 315 (1926).

[11] J. C. McLennan and W. G. Plummer, Trans. Roy. Soc. of Canada **21,** 99 (1927).

[12] Trillat; Piper Brown and Dement; Müller and Saville; Shearer; Saville and Shearer; references to whose articles have been given in the other papers of Stewart and Morrow, R. W. Morrow, and Stewart and Skinner, loc. cit.

J. R. Katz[13] has recently published the results of x-ray diffraction measurements for a large number of liquids including some *n*-alcohols, and their isomers, monobasic acids and *n*-paraffins. His experimental results are in harmony with ours so far as the angle of maximum intensity of diffraction is concerned. But Katz did not find the second inner significant peak which is of prime importance. His report shows that Keesom's formula, wherein the distance is determined by Bragg's law and division by 0.814, does not give molecular mean distances with long molecules. The difficulties that confront Katz in the application of Keesom's formula seem to be removed by the view point of the series of papers from the laboratory of the author. A discussion of this matter can be undertaken to greater advantage in a separate paper.

I am especially indebted to Dr. F. C. Whitmore of Northwestern University for the preparation of the chemicals specified and to Mr. W. D. Crozier, research assistant, for his valuable aid in obtaining the data.

Physics Laboratory,
State University of Iowa.

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[13] J. R. Katz, Zeits. f. Physik **45**, 97 (1927).