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X-RAY DIFFRACTION IN LIQUIDS: SATURATED NORMAL FATTY ACIDS, ISOMERS OF PRIMARY NORMAL ALCOHOLS, AND NORMAL PARAFFINS

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The following results have been obtained in continuation of the investigation of Stewart and Morrow¹ on X-ray diffraction in liquids. The apparatus and method were the same as before. The conclusions will be presented with brevity anticipating publication in full in the near future.

I. Normal Fatty Acids.—The results for the fatty acids were obtained by Dr. Roger M. Morrow, using liquid samples at room temperature, including the eleven from formic (CH_2O_2) to undecylic ($\text{C}_{11}\text{H}_{22}\text{O}_2$) acids. The results are similar to those with the primary *n*-alcohols in two respects. (1) By the application of Bragg's law, two spacings are found, one of which is the lateral separation of the molecules lying in parallel collinear chains, and the other the separation of the planes passing transversely through the chains and containing the diffraction centers of the molecules. The lateral spacing is 4.55 A.U. for the samples having more than five carbon atoms to the molecule. This is in agreement with the work of Adam and others² on monomolecular films. (2) The longitudinal spacing varies linearly with the carbon content, the increase being 2.00 A.U. for two carbon atoms, one for each of two molecules.

As judged by density considerations, the chains are not normal to the transverse planes and in each spacing of the second kind there are two molecules in series, with associated COOH groups. A comparison of spacings in the liquid and crystalline states shows that the arrangement of molecules in liquids, or cybotaxis, is not that found in the crystalline state.

II. Isomers of Primary n-Alcohols.—Nine isomers were investigated and compared with the corresponding primary normal alcohols, one of *n*-butyl, five of *n*-amyl, one of *n*-hexyl and two of *n*-heptyl alcohol. The study was made by Professor E. W. Skinner of Olivet College and the present author. The differences found in the diffraction intensity curves

of an alcohol and its isomer are distinct and several conclusions, quantitative and qualitative, can be drawn. The attachment of CH_3 as a side branch alters the "diameter" by 0.6 A.U., and of OH by 0.4 A.U. The attachment of CH_3 and OH to the same atom in the chain increases the diameter by only 0.65 A.U. The measured "diameter" of the molecule is a mean value, but in the case of di-*n*-propyl carbinol there is a better resolution and the side attachment of OH increases the diameter in one direction by 0.45 A.U. and in the other not at all.

The existence is shown of associated polar groups giving two molecules in a continuous chain for each longitudinal spacing. When the OH group is not attached to the last or next to the last atom in the chain, this association disappears and there is but one molecule for each longitudinal spacing. This is in agreement with the experiments of others on similar chains in the solid state.

In one case, triethyl carbinol, the first, third and fifth orders of the side spacing are apparently present.

III. N-Paraffins.—Pentane, hexane, heptane, octane, nonane, decane, dodecane, tetradecane and pentadecane were studied by the author. There are five experimental points of interest.

1. In the ionization diffraction curve there is one peak only, instead of two as with the alcohols and fatty acids. The absence of the second peak, which would indicate 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.

2. The single peak is located at the same angle with each *n*-paraffin, excepting pentane and decane. These two are believed to be isomers and efforts will be made to secure and investigate the normal compounds. The lateral separation of molecules is approximately 4.6 A.U. and is essentially the same as in the liquids previously studied and referred to in this paper.

3. In six of the nine cases the diffraction intensity does not increase as one approaches 0° . The significance is not clear, though one is reminded of total reflection.

4. If one assumes the C atom to occupy a length in the chain of 1.3 A.U., as found by other observers of X-ray diffraction in solids, and the length of H, 1.0 A.U., 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% or a mean of 2%.

5. Two additional but faint peaks in the diffraction intensity curves are found with pentadecane and tetradecane. The corresponding spacings are 2.1 A.U., and 1.23 A.U. The nearness of these to the repetitive values of 2.0 A.U. and 1.26 A.U., which are found in a diamond, is suggested.

All of the foregoing indicates the importance of the X-ray diffraction study of liquids and adds strong evidence in favor of the interpretation on the basis of a molecular space array. The existence of this array or cybotaxis is of fundamental interest in an understanding of physical phenomena in liquids.

¹ Stewart and Morrow, *Physic. Rev.*, **30**, 9, 232 (1927).

² Adam, *Proc. Roy. Soc.*, **A101**, p. 452 (1922).

THE STRUCTURE AND DIMENSIONS OF THE BENZENE RING

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In a previous paper² the spherical atoms proposed by W. L. Bragg and W. P. Davey have been specialized and the cubic atom proposed by Lewis and developed by Langmuir extended to simple polyhedrons inscribable in spheres. It was shown in detail how these simple models could be built up into the various types of observed cubic and hexagonal lattices and how the lattice constants were geometrically related to the atomic radii. In the case of diamond and of graphite, it was found that these lattices could be built up of cubes having one corner (electron) shared in common and that the radius (half the body diagonal) was equal to 0.77 Å in diamond and 0.75 Å in graphite, giving a mean value for the radius of the carbon atom of 0.76 Å over the extremely wide range of physical conditions between diamond and graphite.

This paper is an account of the application of these ideas to the well-known problem of the structure of the benzene ring. A model of the benzene ring built up of cubes having corners shared in common, will first be presented by giving the coördinates of the cube centers (carbon nuclei) and the cube corners (possible electron positions) in terms of a parameter R (radius of the carbon atom) as is customary in point group theory. This will be followed by a note on the construction of a model of the benzene ring at a scale of two inches to the Ångstrom which represents a magnification of approximately 500 million diameters. After this there will be a brief discussion of the properties and possibilities of this model.

Coördinates of the Benzene Ring in Terms of R , the Radius of the Carbon Atom.—Cube Centers, Carbon Nuclei.

$$\pm 1.138, \quad 0.000, \quad \pm 0.804$$