of your great countrymen, van Swieten and de Haën!" The end of the war found him tolerant and helpful toward starving enemy colleagues, and no proof of gratitude more touching than the laurel wreaths which Sudhoff, Wenckebach and Friedrich Müller laid upon his grave.

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SPECIAL ARTICLES

ON THE X-RAY DIFFRACTION EFFECTS FROM SOLID FATTY ACIDS

X-RAY diffraction effects have been obtained from solid films of numerous fatty acids and other long-chain carbon compounds.[1] These films have been made by allowing the molten substance to solidify on a glass or mica plate. The reflection photographs from such a preparation are not powder patterns, but they have as their conspicuous feature a series of several orders of an exceptionally large spacing.

It has sometimes been imagined that certain solids possess a regularity of molecular arrangement in only one or two dimensions. Such "smectic" substances[2] would thus be intermediate between crystals on the one extreme and amorphous solids on the other. The single reflections (and their higher orders) observed from various fatty acids and other long carbon-chain compounds have been cited[3] to show that they are such "smectic" substances. This conclusion has been doubted, however, by others.[4] From a different point of view, also, X-ray diffraction from the long carbon-chain solids is of interest. In the past the relatively short interplanar distances in such crystal gratings as calcite or gypsum have set a definite limit beyond which the X-ray spectrographs could not go in studying radiation. The much greater spacings (up to about 60A) found from these organic compounds, however, open up a correspondingly long wave-length range to direct investigation.

Several fatty acids have consequently been studied with the two fold purpose (1) of throwing light upon their possibly "smectic" nature and (2) of finding means of preparing them in the form best suited to their use as X-ray gratings. Most of the work happens, however, to have been carried out upon palmitic acid and, unless otherwise stated, these results refer to this particular long-chain compound.

It has recently been stated[5] that stearic acid is truly crystalline. The following experiments seem to show definitely that palmitic acid also is crystalline at ordinary temperatures. If a small amount of the pure acid is melted between two glass plates and cooled in such a way that solidification proceeds from a single point outwards, large areas of the resultant film prove on microscopic examination to have a common optical orientation. Fairly good interference figures are produced by these patches. An X-ray reflection photograph from such an acid film shows very strongly the characteristic several orders of large spacing, together with a few somewhat hazy lines from the more usual short spacings. If, on the other hand, crystallization is allowed to start at many points during the preparation of the solid film, the areas of optical homogeneity are greatly diminished in size. Such a film may be prepared by rapid cooling and is most readily obtained if the acid is not quite pure. In extreme cases the X-ray reflection photograph from such a film will show little or no evidence of the long spacing reflections. In their place appear several hazier lines of the sort typical of a powder photograph. This powder character is confirmed by the fact that the resulting photograph is substantially the same when the acid film is rotated as when it is held stationary in two arbitrarily placed positions. Similar photographs showing predominant powder reflections have also been made from impure erucic and, less easily, from fairly pure lauric acid.

Palmitic acid, in common with numerous other compounds of this class, can be obtained in flakes from various organic solvents. By cooling an acetone solution in a sealed tube, we have obtained single, very thin plates a centimeter across. These plates give good interference figures. Such flakes from acetone and from α-monochloronaphthalene are diamond-shaped with the interior acute angle 56°. They are biaxial with $+2V$ small, and with the optic axial plane apparently normal to the plane of the flakes and bisecting the acute angle. The acute bisectrix is inclined about 40° to the plane of the flakes. The refractive indices are: $\alpha = 1.495$, $\beta = 1.507$, $\gamma = 1.58$. Reflection spectrum photographs from one of these plates show the several orders of the large spacing with extraordinary intensity. Apparently on account

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[1] M. de Broglie and E. Friedel, Compt. rend. *176*, 738 (1923); A. Müller, *Trans. Chem. Soc.* (London) *123*, 2043 (1923); G. Shearer, *ibid.*, *123*, 3152 (1923); A. Müller and G. Shearer, *ibid.*, *123*, 3156 (1923); S. H. Piper and E. N. Grindley, *Proc. Phys. Soc. 35*, 269 (1923); R. E. Gibbs, *J. Chem. Soc.* (London) *125*, 2622 (1924).

[2] G. Friedel, *Ann. de Phys. 23*, 273 (1922).

[3] M. de Broglie and E. Friedel, *op. cit.;* E. Friedel, Compt. rend., *180*, 269 (1925).

[4] J. W. MacBain, *Nature*, *113*, 554 (1924); *114*, 49 (1924).

[5] R. E. Gibbs, *op. cit.*

of the large solubility and temperature coefficient of solubility of palmitic acid in acetone, it has not yet, however, been possible to find on the single crystals removed from their solutions the small prism and pyramid faces necessary for a more detailed crystallographic study.

The results stated above are in agreement with the recently published statement[6] that the fatty acids, or some of them at least, form monoclinic crystals. They also do not conflict with other experimental results recently obtained[7] from palmitic acid. Inasmuch as these latter results are stated to be qualitatively of the same character as those furnished by the typical "smectic" compounds and since palmitic acid prepared under similar conditions shows all the expected reactions of a crystal towards X-rays and light, it seems necessary to conclude that as yet there is no X-ray diffraction evidence for the existence of "smectic" or other substances intermediate in molecular arrangement between true crystals on the one hand and amorphous substances on the other.

The fact that intense large spacing reflections are obtained from films of acid solidified on glass plates is probably not, as many seem to have supposed it to be, indicative of a close similarity between such films and oil films on water. In the latter case existing molceular orientation is to be attributed to a sort of chemical reaction between the water and one end of the oil molecules. In the solid acid films the glass backing is to be considered as chemically inert. These films are sometimes oriented because under appropriate conditions relatively few crystal nuclei are formed during solidification and the comparatively large individuals that result have the strongly platy habit characteristic of these crystals. It is in accord with such a view that working the solid films[8] increases the intensity of the long spacing reflections by making the platy crystals more nearly parallel to one another and to the glass sheets on which they are mounted. Graphite with a similar crystal habit behaves in the same fashion. It is also in accord with this view that the presence of other acids as impurities in the sample under investigation weakens the intensities of the large spacing reflections by multiplying the number of crystal nuclei and thereby interfering with the growth of the large oriented crystal plates. Because they melt nearer to room temperature it should be easier under the same conditions of cooling to make large-crystal films of the simpler fatty acids than of the more complex ones. In these experiments it has been found easier to make good films of capric and lauric acids than of those with much longer carbon chains.

The regular increase in the number of carbon atoms in the chain of these fatty acids and other long-chain compounds has been used to estimate the diameter of the carbon atom in these compounds.[9] This would of course be legitimate only in case the carbon chains were perpendicular to the reflecting plane. Our microscopic examination—in particular the behavior of the interference figures on rotation of the sample—shows clearly that no axis of symmetry is normal to this plane. It is therefore necessary to conclude that the long carbon chains are inclined at an angle to the reflecting face and that the increase in spacing with number of carbon atoms is not a simple and direct measure of carbon-to-carbon distances. The value of this angle can not be told in advance of crystallographic measurement. Furthermore, though apparently it changes in regular fashion in passing from acid to acid, this angle is very probably not the same for any two acids.

SUMMARY

Powder reflections, as well as single face reflections of large spacing, have been obtained from palmitic and other fatty acids. Single specimens with all the optical properties of a crystal and giving the same large spacing X-ray reflections as solidified films on glass have been grown from solution of palmitic acid in acetone. This acid, at least, therefore appears to be truly crystalline under these conditions and not in a "smectic" or other sub-crystalline state. Since the X-ray data from this acid are strictly analogous to those from other typical "smectic" substances, it seems necessary further to conclude that no definite X-ray evidence yet exists for this "smectic" state.

The symmetry of palmitic acid is either monoclinic or triclinic and the long carbon chains are not normal to the face producing the large spacing reflections. Such spacings are therefore not direct measures of the lengths of these chains.

By growing single plates of the acid from solution more intense reflections from the long spacings have been obtained than from films made by solidifying the acid on glass or mica. Such single crystals may prove especially useful as gratings in long wave length X-ray spectrography.

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[6] W. H. Bragg, *Nature, 115,* 266 (1925).

[7] J. J. Trillat, Compt. rend., *180,* 280 (1925).

[8] W. H. Bragg, *op. cit.*

[9] A. Müller, *op. cit.*; G. Shearer, *op. cit.*