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## A Study of Long Chain Organic Compounds by Electron Diffraction

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A layer of lard deposited upon a metal surface gives an electron diffraction pattern consisting of segments of diffuse inclined bands. These arise from line gratings made up of long hydrocarbon chains. The mean inclination of the axes of these chains to the surface normal is calculated to be  $27^\circ$ , and the separation of carbon atoms 2.50Å. The saturated glyceride, tri-stearin, yields a diffraction pattern of diffuse bands parallel to the surface, unlike the diffraction pattern from lard, although the latter is predominantly a mixture of glycerides. We believe that the inclination of the long hydrocarbon chains in lard is due to lack of saturation, although this hypothesis has not been tested. Diffraction patterns from stearic acid deposited upon a

metal surface also contain inclined bands. These are relatively well defined, and have inclinations which differ from one sample to another. This variation is attributed to the existence of large crystals the  $c$  axes of which are differently inclined to the plane of incidence. We calculate that this axis is always inclined  $33^\circ$  to the surface normal. A similar investigation of methyl stearate yields the angle  $25^\circ$ . For both stearic acid and methyl stearate the separation between diffraction bands corresponds to the atomic spacing 2.50Å. This is in good agreement with the known distance between alternate carbon atoms in a zigzag hydrocarbon chain.

SEVERAL experimenters have examined long chain organic compounds by electron diffraction.<sup>1</sup> The first to report an investigation of this kind were Thomson and Murison who studied long chain greases of the paraffin type deposited on metal surfaces. They, as well as later workers, obtained diffraction patterns consisting of several diffuse parallel and equally spaced bands on which appear a few fuzzy spots. These patterns are attributed to extremely imperfect crystals containing long hydrocarbon chains standing approximately normal to the supporting surface.

In general the materials studied in this manner have been mixtures of saturated single chain compounds containing carbon and hydrogen only. Although crystallographic data on such compounds are not extensive, they indicate that these often, if not always, crystallize in the orthorhombic system with the axis of the long chain parallel with one of the crystallographic axes. The observations by electron diffraction have been consistent with this type of structure, and from these observations it is deduced that paraffin type hydrocarbon compounds orient themselves upon a metal surface with the two short crystal axes lying in the plane of the surface.

### LARD

We decided to study an entirely different type of greasy compound. For this we chose commercial lard as a typical grease mixture of animal origin. Samples of lard were prepared on blocks of polycrystalline nickel which had been carefully polished and freshly cleaned. Diffraction patterns were obtained from these by scattering high speed electrons at very small glancing angles. Essentially similar patterns were found when lard was deposited by evaporation from benzene solution, when it was simply rubbed upon the metal surface, and when it was fused and allowed to flow freely. In still another experiment lard was deposited upon the naturally formed face of

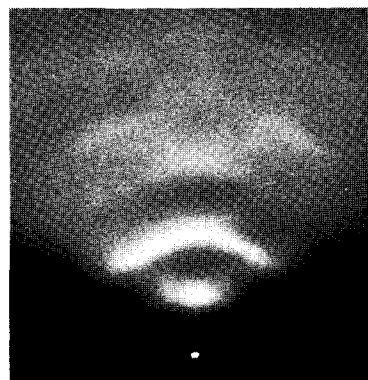
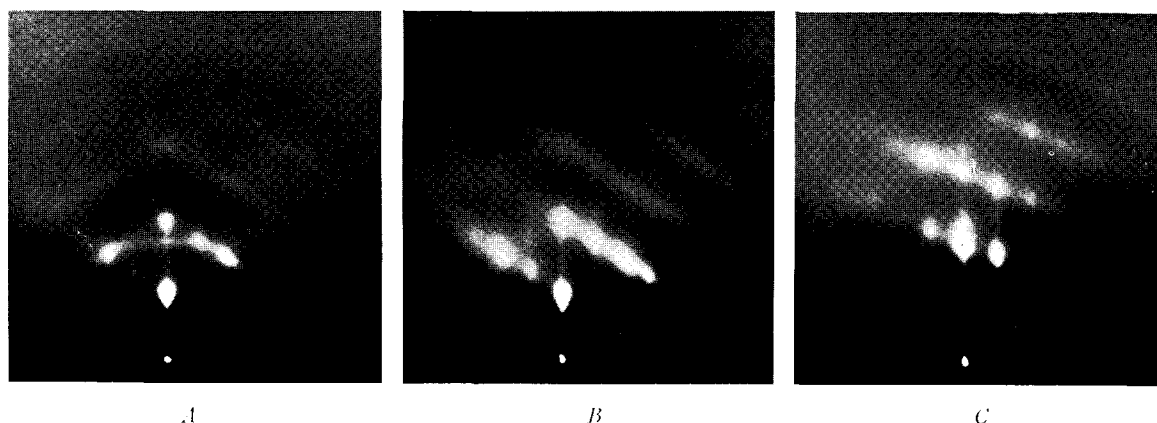


FIG. 1. Electron diffraction pattern from a layer of lard upon a block of polished nickel. ( $\lambda=0.051\text{\AA}$ .)

<sup>1</sup> The earliest papers are: Thomson and Murison, *Nature* **131**, 237 (1933); Nelson, *Phys. Rev.* **44**, 717 (1933); Murison, *Phil. Mag.* **17**, 201 (1934).

FIG. 2. Diffraction patterns from stearic acid. ( $\lambda=0.051\text{\AA}$ .)

a single crystal of carborundum, and in this case also the pattern was like those found earlier.

A typical diffraction pattern obtained from lard is shown in Fig. 1. The diffuse smears of this figure are portions of two sets of parallel bands, the members of each set being equally spaced and inclined at angles of about  $27^\circ$  to the plane of the specimen surface. Except for this inclination the features of Fig. 1 are rather like those observed for paraffin, and we interpret them in an analogous manner. The two sets of bands correspond to hydrocarbon chains which are inclined to the surface normal by angles within a range about  $27^\circ$  but are otherwise unrelated.

To see how this comes about we consider first the diffraction effect of a single chain of carbon atoms. We designate by  $d$  the separation of atoms measured along the direction of the chain, by  $\alpha$  the angular inclination of the chain to the surface normal, and by  $\varphi$  the azimuth of the chain measured from the plane of incidence. This chain of carbon atoms would give rise to diffraction cones intersecting the photographic plate in lines approximately straight, parallel and equally spaced.<sup>2</sup> These lines are described by the equation

$$y = n \frac{L\lambda}{d \cos \alpha} + x \tan \alpha \sin \varphi \quad (1)$$

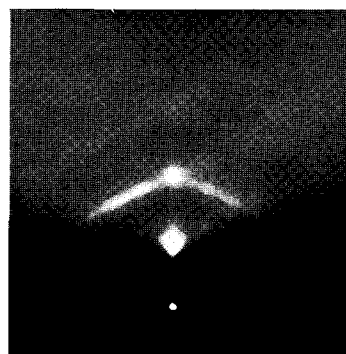
where  $x$  and  $y$  are coordinates in a Cartesian system with its origin at the intersection of the primary beam with the photographic plate and its  $x$  axis parallel to the supporting surface. ( $\lambda$  is

<sup>2</sup> Except for the very special case of  $\alpha$  near  $\pi/2$  and  $\varphi$  near zero.

the electron wave-length,  $L$  the distance from specimen to photographic plate and  $n$  any whole number.)

The common slope of the lines is  $dy/dx = \tan \alpha \sin \varphi$ , and their intersections with the  $y$  axis are  $nL\lambda/d \cos \alpha$ . We note that if  $\varphi$  is varied while  $\alpha$  remains fixed the lines are turned about these fixed intersections. The slopes can be varied from  $-\tan \alpha$  to  $+\tan \alpha$ ; the angles which the lines make with the  $x$  axis are varied from  $-\alpha$  to  $+\alpha$ . As the azimuth plane of the molecule is rotated the diffraction lines sweep out symmetrical pairs of sectors of angular width  $2\alpha$ . If all the molecules in the diffracting material have the same value of  $\alpha$  but are randomly disposed in azimuth these sectors will appear on the pattern. They will not be uniformly intense across their widths, but most intense at the edges and least intense at the centers.

The diffuse bands of Fig. 1 are the edges of these predicted sectors. Nevertheless only short

FIG. 3. Diffraction pattern from methyl stearate. ( $\lambda=0.051\text{\AA}$ .)

sections of the bands appear, and their behavior at the  $y$  axis is not that to be expected from the analysis just given. We must assume that  $\alpha$  also is somewhat variable from one chain to another. From Eq. (1) one finds that, for  $\varphi = \pi/2$  which is the most important case, as  $\alpha$  varies a line will remain at a fixed distance from the origin and its inclination will remain equal to  $\alpha$ .

We believe that the observed diffraction pattern arises from hydrocarbon chains distributed randomly in azimuth and inclined at somewhat differing angles to the surface normal. Because of the complex nature of lard and the extreme fuzziness of the features of Fig. 1 it seems unprofitable to attempt to carry the analysis further. We can, however, conclude that most of the hydrocarbon chains in lard are inclined to the surface normal by angles in the neighborhood of  $27^\circ$ . The separation of carbon atoms,  $d$ , can also be calculated. From Eq. (1) the distance between adjacent bands is given by

$$D = \frac{nL\lambda}{d(1 - \cos^2 \varphi \sin^2 \alpha)^{\frac{1}{2}}} \quad (2)$$

As the diffuse bands represent the edges of the sectors we have  $\varphi = \pi/2$ , and Eq. (2) allows us to calculate  $d = 2.50\text{\AA}$ .

We have investigated some of the compounds which might be in lard. As it is known to be a mixture of glycerides of long chain organic acids plus small amounts of free acids we chose to study stearic acid and tri-stearin, a glyceride of stearic acid. These compounds are not exactly typical of the constituents of lard because the chains of both are completely saturated whereas the natural product is known to contain a considerable proportion of unsaturated chains.

We have found that tri-stearin produces a diffraction pattern of straight lines lying parallel to the supporting surface, entirely unlike the pattern obtained from lard. Separations of these lines correspond again to the spacing  $2.50\text{\AA}$ . Lines of even order are strong and lines of odd order weak. From this pattern we predict that the structure of tri-stearin will probably be found to be orthorhombic.

Examples of diffraction patterns from stearic acid are shown in Fig. 2. Although these exhibit inclined lines and resemble the pattern from lard in a rather striking fashion, it is known that lard

contains little free acid. We were then led to test a mixture made up of tri-stearin and a small percentage of free stearic acid. This mixture gave the diffraction pattern of tri-stearin, without any observable modification due to the acid. It is interesting to note that the mixture is very different from lard mechanically. We now believe that the inclination of the long hydrocarbon chains in lard is due to lack of saturation of these chains in the acid radicals in the glycerides. This hypothesis has not been tested as we have been unable to obtain glycerides of unsaturated long chain acids which are solid at room temperature.

#### STEARIC ACID

The diffraction patterns of Fig. 2 were produced by stearic acid deposited upon polished nickel by evaporation from benzene solution. Although these patterns exhibit fairly well defined spots characteristic of single crystals, they also show the inclined bands which are attributed to the separate molecules. We conclude that the crystals are extremely imperfect, so imperfect that diffraction patterns from the independent line gratings of separate molecules are still evident.

Microscopic examination shows that layers of stearic acid have a strong tendency to form large crystals. Differences in disposition and size of these crystals undoubtedly account for the differences between the patterns of bands in Fig. 2.

The first of these, Fig. 2A, resembles the lard pattern. The equal intensities and inclinations of the two sets of bands in this figure indicate that the stearic acid crystals are more or less randomly disposed in azimuth. The actual inclinations and spacings of the observed bands will then correspond to long hydrocarbon chains lying in the two azimuths normal to the primary beam. That this assumption is true is borne out by the fact that most stearic acid diffraction patterns exhibit bands having approximately the same inclination as those of Fig. 2A. This inclination occurs most frequently although substantially smaller inclinations are sometimes found, and even bands parallel to the surface are observed in rare cases.

The single set of bands of Fig. 2B has the same inclination as the two sets of Fig. 2A. This single set of bands corresponds to hydrocarbon chains

lying in *one* azimuth normal to the primary beam direction, or at least in azimuths within about  $25^\circ$  (estimated by means of Eq. (1)) of this normal position. The lack of sharpness of the features of Fig. 2B suggests that the pattern does, in fact, arise from many crystals the hydrocarbon chains of which are located in different azimuths. The bands of Figs. 2A and 2B yield the values  $d=2.50\text{\AA}$  and  $\alpha=33^\circ$ .

The sharp features of Fig. 2C suggest that this pattern is produced by a single imperfect crystal. That this is true is evidenced further by the fact that the inclination of the lines of Fig. 2C is only  $24^\circ$ . From the relation  $dy/dx = \tan \alpha \sin \varphi$  we can calculate the azimuth,  $\varphi$ , which corresponds to the slope  $dy/dx = \tan 24^\circ$  assuming, of course, the value  $\alpha=33^\circ$  obtained from Figs. 2A and 2B. This calculation yields  $\varphi=45^\circ$  (or  $135^\circ$ ) as the azimuth of the hydrocarbon chains producing the pattern of Fig. 2C. If this value of  $\varphi$  is substituted into Eq. (2) together with  $\alpha=33^\circ$  and  $d=2.50\text{\AA}$  we obtain  $D=8.6\text{ mm}$  as the spacing of the lines of Fig. 2C. Direct measurement gives  $8.5\text{ mm}$ . (The separations in Figs. 2A and 2B, from which the value  $2.50\text{\AA}$  was calculated, are  $8.0\text{ mm}$ .)

It is interesting to compare the angle  $\alpha=33^\circ$  and the spacing  $d=2.50\text{\AA}$ , obtained from these experiments, with the results of measurements upon single crystals of stearic acid. Müller<sup>3</sup> gives  $2.51\text{\AA}$  as the distance between alternate carbon atoms in the zigzag chain of the acid and, for the  $\beta$  modification, he has found the angle between the  $c$  axis and the normal to the basal plane to be  $26^\circ 22'$ . For the  $\alpha$  modification<sup>4</sup> this angle is reported to be  $39^\circ 10'$ . New and, as yet, unpublished electron diffraction measurements<sup>5</sup> by us upon single crystals of stearic acid formed by evaporation from benzene solution have shown that these crystals orient themselves upon any surface with the two shorter axes in the plane of the surface. These measurements show, furthermore, that the shorter axes are at right angles and have the lengths reported by Thibaud and Dupré la Tour. (We have not yet succeeded in determining a possible length and inclination for the  $c$  axis.) From these unpublished experiments we feel justified in believing that the very imper-

fect stearic acid crystals, with which we are concerned here, have the form of the  $\alpha$  modification. We are unable to reconcile our angle  $33^\circ$  with the reported angle  $39^\circ 10'$ . It is, of course, possible that Thibaud and Dupré la Tour chose a unit cell in which the  $c$  axis is not parallel to the long hydrocarbon chain. No other choice would, however, have given an angle in agreement with ours without making the  $c$  axis too short to contain two molecules end-to-end, which is apparently the way they must be arranged.

We have given reasons above for believing that the pattern of Fig. 2C is formed by a single crystal, and we have calculated its orientation. We ought then to be able to account for the rather well defined spot pattern of this figure. In this we have not succeeded. Even if our data could be reconciled with those of Thibaud and Dupré la Tour, there would not be sufficient information at hand regarding relative intensities of different reflections from a crystal of the  $\alpha$  modification. We are now engaged in studies of single crystals of this sort by the transmission method,<sup>6</sup> and hope soon to be able to clear up the present uncertainties.

It has seemed important to us to test whether or not the inclination of the hydrocarbon chains is the same in various stearic esters as in stearic acid itself. Microscopical examination of layers of methyl stearate deposited by evaporation from benzene solution has not disclosed any observable crystals. We conclude that they must be extremely small. This conclusion is in accord with the fact that diffraction patterns from different samples of methyl stearate are similar and indicate hydrocarbon chains randomly distributed in azimuth. Such a pattern is shown in Fig. 3. This yields  $d=2.50\text{\AA}$  and  $\alpha=25^\circ$ .

The inclinations of the hydrocarbon chains of stearic acid ( $33^\circ$ ) and of methyl stearate ( $25^\circ$ ) differ by an amount which we believe greater than experimental error. This difference suggests that if we were to study higher single chain stearic esters we should find hydrocarbon chains standing more nearly normal to the supporting surface. We propose to carry out such investigations.

We are indebted to Dr. C. J. Davisson for many helpful suggestions and criticisms.

<sup>3</sup> Proc. Roy. Soc. **A114**, 542-561 (1927).

<sup>4</sup> Thibaud and Dupré la Tour, J. Chim. Phys. **29**, 153-167 (1932).

<sup>5</sup> See, however, Storks, Phys. Rev. **50**, 396 (1936).

<sup>6</sup> See Fig. 4 in a note by K. H. Storks and L. H. Germer, Phys. Rev. **50**, 676 (1936).