CCCVI.—*An X-Ray Study of Some Structural Modifications of Long-chain Compounds.*

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THERE is now considerable evidence showing that in several homologous series of long-chain compounds a linear relation exists between the length of the chain of carbon atoms and an important crystal-spacing which is comparable with the length of the molecule. It is tempting to employ measurements of these long spacings as a means of identification of such compounds: in fact, several successful analyses have been made (Robinson, *Nature*, 1925, **116**, 45; Trillat, *Compt. rend.*, 1925, **180**, 1330; Piper, Brown, and Dyment, J., 1925, **127**, 2194). We have found, however, that there are modifications and distortions in many substances which may cause the *X*-ray measurements to be very misleading, and a systematic study is now described of the following three effects:

(1) Alternative forms of the same substance.

(2) Distortions caused by mounting the specimen for *X*-ray examination.

(3) The influence of impurities on crystal-spacing.

(1) *Alternative Forms of Fatty Acids.*

With one exception all the fatty acids we have examined give *X*-ray photographs which show that they can exist in at least two forms, each having its own long spacing. It has already been found by Müller (J., 1925, **127**, 602) that the normal paraffin hydrocarbons, when kept at suitable temperatures, show two alternative long spacings. The spacings we have found for the fatty acids, however, are independent of the temperature, the value obtained depending only on the treatment followed in mounting the specimen, and on the manner of preparation of the acid.

It is not easy to obtain large single crystals of these acids for study by the usual methods, but, as Müller has shown (J., 1923, **123**, 2043), if a thin layer of the substance is melted on a glass strip, the planes it is wished to measure lie parallel to the surface of the glass. This author finds that the same effect is obtained by pressing

TABLE I.

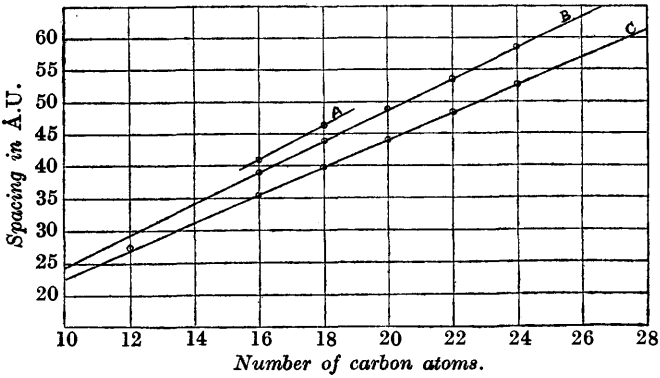
Acid.	Formula.	M. p.	Spacings (Å.U.).		Method of preparation.
			Pressed.	Melted.	
Lauric.	$C_{12}H_{24}O_2$	44·5°	27·4	—	Kahlbaum's (*K*) purified by crystallisation from dilute ethyl alcohol.
Palmitic (*K*).	$C_{16}H_{32}O_2$	64	41·0 *w* 35·6 *s*	35·65	Kahlbaum's (*K*). Ethyl ester fractionated and hydrolysed; acid finally crystallised from acetone and from benzene.
Palmitic (*K*).			39·08		Single crystal of preceding specimen.
Palmitic (*O*).		63·5	35·7	35·7	Potash fusion of potassium oleate.
Stearic (*K*).	$C_{18}H_{36}O_2$	71	46·6 *s* 39·9 *w*	39·9	Purified as in the case of palmitic acid (*K*).
Stearic (*K*).			43·98		Single crystal of preceding specimen.
Stearic (*O*).		71	44·0	40	Ethyl oleate fractionated, and reduced with H_2 in presence of colloidal Pd.
Eicosanic.	$C_{20}H_{40}O_2$	75	49·0 *s* 44·3 *w*	44·2	From Dr. Steuwer. Potash fusion of erucic acid (Ehrenstein and Steuwer, *J. pr. Chem.*, 1922—23, **105**, 199).
Eicosanic.		75	44·1	44·1	From Prof. Morgan. Same method as above (*J.S.C.I.*, 1924, **43**, 347T).
Behenic.	$C_{22}H_{44}O_2$	81	53·7 *s* 48·5 *s*	48·6	By reduction of erucic acid.
Tetracosanic.	$C_{24}H_{48}O_2$	83·5	58·5	52·8	From Dr. Brigl. Synthesised from behenic acid (*Z. physiol. Chem.*, 1922, **119**, 280).
Lignoceric.	$C_{24}H_{48}O_2$	83·4	58·4 *s* 52·9 *w*	52·7	From Dr. Brigl (*loc. cit.*). From beechwood tar.

The apparatus used for the fractionation of the above esters is described by Armstrong, Allan, and Moore (*J.S.C.I.*, 1925, **44**, 65T), and consists of a distillation flask provided with a two-bulbed neck packed with glass beads. The following data were obtained: Ethyl palmitate, b. p. 157°/2 mm., 154°/1·5 mm.; ethyl stearate, b. p. 182°/2 mm.; ethyl oleate, b. p. 172°/2 mm., n^{15° 1·4536; ethyl erucate, b. p. 218°/3 mm., 247°/12·5 mm.

flakes of compounds that crystallise in plates on the glass strip, and Trillat (*loc. cit.*) has obtained brilliant photographs from films formed by evaporating a few drops of an alcoholic solution on a plate. We have used all three types of layer.

Generally speaking, a pure crystalline acid, when pressed on a plate with only sufficient force to cause the flakes to adhere with the minimum breakage, gives a photograph showing two sets of lines (Plate I). One set is due to the spacing discovered by Müller (*loc. cit.*, 1923), and we have called this the " C " spacing. The other lines, " B," arise from more widely separated planes. When the acid is *melted* on the mount the " C " lines alone appear, and in some cases the pressed flakes have given only " C " or only " B " lines. In Table I, spacings that are bracketed have been photographed simultaneously, and the relative strengths of the lines given by each are indicated by the letters *w*, weak, or *s*, strong. We have obtained specimens from the greatest possible variety of sources, used as many methods of preparation as possible, and sought a very high degree of purity. Our grateful thanks are due to the various donors of material whose names appear in col. 6 of Table I. The m. p.'s were obtained with a standard Anschütz thermometer.

FIG. 1.



In Fig. 1, the spacings from Table I are plotted against the number of carbon atoms in the molecule, and it will be seen that, with two exceptions, they lie on the two non-parallel straight lines B and C. Of these lines, C is that given by Müller, who showed that it could be accounted for by assuming that the spacings were due to planes separated by the lengths of two molecules placed end to end, and that the carbon atoms occupied a mean length of 1 Å.U. in the chain. On the same grounds, the type of chain that will give a " B " spacing requires an effective chain length of 1·21 Å.U. per carbon atom,

PLATE I.

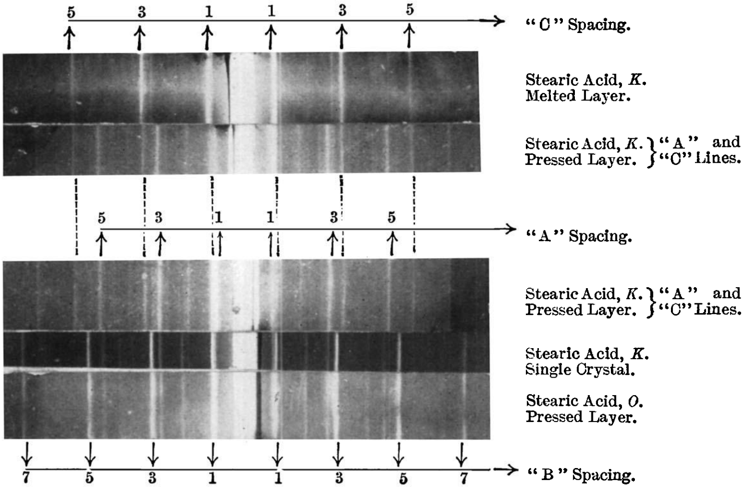
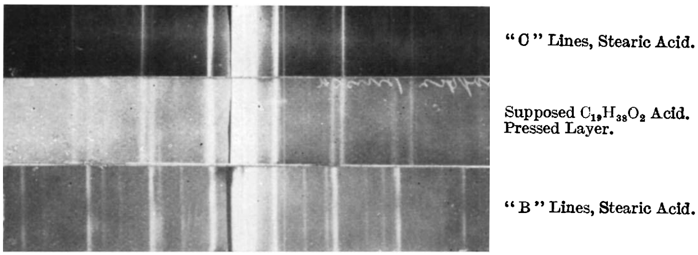


PLATE II.



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and is probably a co-planar zig-zag of atoms with the lines joining successive centres inclined at an angle of 109° 28′ (Müller and Shearer, J., 1923, **123**, 3159).

The " B " spacing is the true (single) crystal-spacing; it appears to be due to the type of chain assumed by the molecule when the pure acid crystallises slowly. The " C " spacing is always found when the crystallisation has taken place rapidly or under constraint, as in the case of acids melted on glass or of the rapidly-evaporated films studied by Trillat. We find also that the presence of an impurity causes the acid to assume the " C " form (see section 3). The difference between the two forms does not appear to be inherent in the molecule, but is rather due to external causes that have affected the crystallisation.

In addition to these " B " and " C " spacings, both stearic and palmitic acids obtained from purified Kahlbaum acids and carefully pressed on a glass plate have given lines due to a still larger " A " spacing. The lines are most marked in the case of stearic acid, and are shown in Plate I in company with the fainter " C " lines that were photographed simultaneously. Below this photograph are shown the lines due to the " B " spacing obtained from a large single crystal of the same specimen of acid, and from another specimen that was prepared from oleic acid. The last two show only the " B " lines, although the acids have identical m. p.'s. We at first attributed the " A " spacing to the single crystal, and thought that perhaps the " B " spacing occurred when the acid had been prepared from a substance containing doubly-linked carbon atoms, but we eventually obtained large single crystals from both the Kahlbaum stearic and palmitic acids and found that they had the " B " spacing. The " A " lines on the stearic acid photograph (Plate I) cannot well be attributed to impurity—they are too strong and too permanent. To test the permanence of this form the acids were again esterified, and the esters redistilled and reconverted to the acids. There was no change in the m. p.'s, and when the flakes were pressed on glass the photograph again showed the " A " lines in company with the " C," but, if anything, more strongly. When the acids were melted on the mount, the " C " lines only appeared as before. In the case of palmitic acid the " A " lines are weak, but very persistent. The difference between the " A " spacings for palmitic and stearic acids is 5·6 Å.U., which means that, if this is a third type of chain, each carbon atom in it occupies an effective length of 1·4 Å.U. This is approximately the size of a carbon atom in the chain typical of a normal hydrocarbon, *i.e.*, 1·3 Å.U. It is noticeable that, though both " A " and " C " or " B " and " C " spacings occur simultaneously, we have not obtained " A " and " B " on the same plate.

It seems therefore that the chains giving rise to the " A " and " B " spacings are different in the molecule itself, and are not due to conditions affecting the crystallisation. It will also be noticed that the spacing 46·5 Å.U. falls on the B graph at 19 carbon atoms, and on the C line at 21 carbon atoms. This is fortuitous; it does not indicate the presence of either a $C_{19}H_{38}O_2$ or a $C_{21}H_{42}O_2$ acid, since the spacings of odd- and even-numbered acids do not correspond.

Two specimens of stearic acid (*O*, Table I) were prepared by the reduction of ethyl oleate. In one case the ester was fractionated and in the other the acid was purified by crystallisation alone, but in both cases the photographs showed only " B " lines for crystal flakes and only " C " lines when the acid was melted.

Stearic acid has the same m. p. in the three forms that give rise to the " A," " B," and " C " spacings, and in each form the crystalline planes are separated by the length of two molecules. It is probable, therefore, that the linkages of the carboxyl groups are very similar in the three forms. The linear relation between the " B " spacings and the number of carbon atoms probably breaks down sooner than that between " C " spacings and the carbon content, since the slope of the graph is such as to give a negative intercept on the axis of spacings. The evidence definitely suggests that the higher members of the fatty-acid series exist in two forms, " B " and " C," each having its characteristic chain, and that palmitic and stearic acids have yet a third form. It is hoped to obtain more information on the " A " spacings from a series of acids synthesised from the Kahlbaum (*K*) stearic acid.

(2) *Distortions due to Mounting.*

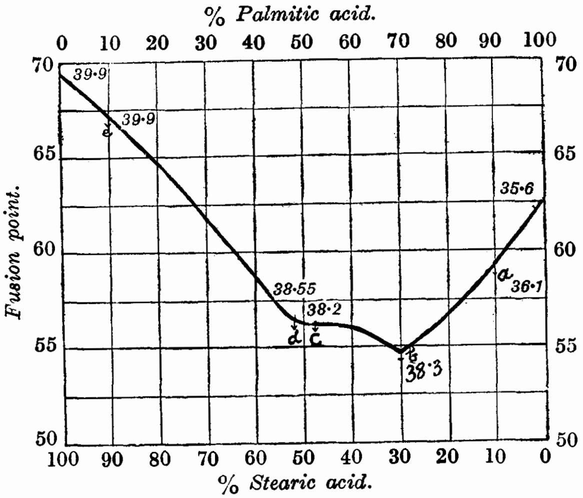
Data published by different observers for spacings of the same substance appear to differ by amounts greater than the probable experimental error. In Table II are a number of measurements of the spacings of five pure long chain compounds mounted in the three ways mentioned in section (1), and it will be seen that some of the differences mentioned may be due to varying technique. The spacings are in most cases calculated from five measured orders, and the different orders on the same plate agree to about 0·2%. Pressed crystals, which give more orders and denser lines, usually show the best agreement.

Pressed and melted hydrocarbons show the greatest variation with treatment. It is possible that the different spacings are due to modifications comparable with the " A," " B," and " C " type of the fatty acids, but on the whole the evidence indicates a distortion of the lattice increasing in amount with the degree of intimacy of contact with the mounting, since the spacings of the melted form

TABLE II.

Substance.	M. p.	Solvent.	Spacings in Å.U.		
			Melted.	Pressed.	Evap.
Triacontane.	66°	Benzene.	40·7	40·3	—
		Ether.	40·8	40·4	—
Tetracosane (from paraffin wax).	51·9	Benzene.	33·4	32·7	33·15
		Ether.	33·4	32·86	—
		Acetone.	33·45	32·86	—
Ethyl palmitate.	25	Petrol. Ether.	23·2	22·95	23·2
Palmitic acid.	64	Acetone.	35·6	35·65	—
		Ether.	35·54	35·7	—
Thallium palmitate.	115	Alcohol.	38·8	38·7	—

FIG. 2.



Mixed melting points; palmitic–stearic acids (de Visser).
(The figures on the curve are the "C" spacings in Å.U. shown in Table III.)

differ more from those of the pressed than from those of the evaporated forms. All the first three substances have one molecule between the planes; the acid and the soap have two, and it appears that the former class is the more easily distorted. As would be expected the solvent has no influence on the crystal spacing, and the nature of the mount, so far as we have examined it, has no important influence on the amount of distortion.

These variations must be not confused with the alternative spacings described by Müller for the normal hydrocarbons.

We are indebted to Mr. Dennis Brown for taking several of the photographs involved in Table II.

(3) *The Influence of Impurities.*

The system studied is a mixture of the carefully purified palmitic and stearic acids (Table I). De Visser has made a study of the mixed m. p.'s of these acids (*Rec. trav. chim.*, 1898, **17**, 182); they were therefore selected in preference to more widely-separated acids; a few mixtures of such acids have also been photographed.

Fig. 2 is a reproduction of de Visser's fusion-point curve, and on it are marked the mixtures, *a*, *b*, *c*, *d*, and *e*, that were photographed. A melted layer was used in each case, and mixture *c*, which de Visser states to be a constant-crystallising mixture, was also examined in the form of crystal flakes and when evaporated. The results are shown in Table III.

TABLE III.

"C" Spacings of Mixtures of Palmitic and Stearic Acids.

			Spacings in Å.U.			
	Composition.	M. p.	Melted.	Pressed.	Evap.	Notes.
	Stearic acid.	71°	39·9	39·9		
e.	90% Stearic. 10% Palmitic.	68·8	39·9			
d.	52·6% Stearic. 47·4% Palmitic.	57·6	38·55	39·6*		Equimolar.
c.	47·5% Stearic. 52·5% Palmitic.	57·3	38·2	39·6*	39·6	Constant-crystallising (?).
b.	30% Stearic 70% Palmitic.	55·4	38·3			Eutectic.
a.	10% Stearic. 90% Palmitic.	61·8	36·1			
	Palmitic acid.	64	35·65	35·6		

* The composition of these mixtures altered on crystallisation; the proportion of stearic acid increased in *d* to 65% and in *c* to 55%.

Morgan and Bowen (*J. Soc. Chem. Ind.*, 1924, **43**, 348 T) state that certain binary higher saturated fatty-acid mixtures show evidence of the formation of compounds of one molecule of each acid. It was of interest, therefore, to examine such an equimolecular mixture, since if the double molecule consists of one stearic and one palmitic chain with the carboxyl groups in contact, the *X*-ray spacing should be the mean of the spacings of the two pure acids. The value obtained is too high for this interpretation.

In the case of the *c* mixture the spacings obtained from the three different types of mounting varied so considerably that we were led to examine it more closely. We are convinced that this is not a constant-crystallising mixture, and that such a mixture does not exist, since when alcohol, benzene, or acetone is used as a solvent, the mixture in each case becomes richer in stearic acid on crystallisation.

Whilst the spacing obtained from any given melted mixture appears to depend slightly on the conditions under which the layer is formed (rate of cooling, etc.), it may be stated that the photograph, will, as a rule, show a distorted spacing of the longer chain, except for high proportions of the lower acid when it approaches the shorter chain. We have not obtained any plates showing the lines of both stearic and palmitic acids, but with more widely separated acids, such as lauric and behenic or lauric and palmitic acids, a photograph from a melted layer shows the spacings due to the chains of each acid with apparently very little distortion. The plates are usually faint and show only first- and third-order lines.

When either *c* or *d* mixture was crystallised from alcohol by complete evaporation of the solvent, the crystals obtained were small but looked satisfactory. The m. p.'s were 58·5° and 61·5° respectively. If these crystals were pressed on a glass plate the photograph still showed only one set of lines, the " C " lines of stearic acid almost undistorted. It is very remarkable that such impure mixtures should give a photograph indistinguishable from that of a pure acid except for the small number of orders. It is easier to explain the distorted spacing of the melted-mixture plates, where the particular acid in excess of the eutectic proportion will separate first as the mixture cools, and cannot be expected to crystallise normally in the presence of a quantity of impure molten acid. The 90% palmitic acid mixture differs more from pure palmitic acid than does the 90% stearic acid from pure stearic acid, as would be expected, since the former is much closer to the eutectic proportions.

The difficulty of interpreting an *X*-ray photograph is well illustrated by the following example. The acid in question was obtained from the oxidation products of paraffin wax *; it had m. p. 58° and an acid value corresponding to $C_{19}H_{38}O_2$, and it crystallised in beautiful flakes. The *X*-ray photograph obtained from a layer of these flakes pressed on a glass plate is reproduced in Plate II, together with a plate of the " C " stearic acid lines above, and the " B " stearic lines below. The spacings calculated are 43·8 and 39·9 Å.U., practically the " B " and " C " spacings of stearic acid. When the acid was melted, only the spacing of 39·9 appeared. Except for the fact that the value of 43·8 differs rather more from the " B " spacing of stearic acid than we should expect, this is what a pure specimen of stearic acid may give. The m. p. and the acid value make it obvious

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* A complete account of other acids from the same source will be communicated later.

that this cannot be the correct explanation. It is, however, possible that the value of 43·8 is a distorted version of the "C" spacing of eicosanic acid, and the presence of this acid as an impurity would explain both the acid value and the m. p. This is very likely the correct explanation, although it is difficult to reconcile it with the results obtained from mixed stearic and palmitic acids, in which both crystalline and melted mixtures showed only the longer chain, but here we have the case of both spacings for the mixed crystals and the *shorter* chain for the melted layer. The data published for the odd-numbered acids are not very satisfactory, and it is possible that more detailed information from pure synthetic odd-numbered acids will throw some light on this anomalous behaviour. It is also possible that the behaviour of mixed stearic and palmitic acids is not typical. It is, however, clear that the evidence from *X*-ray photographs must be used with great caution; it is, for example, easy to confuse the "C" spacing of eicosanic acid with the "B" spacing of stearic acid, unless the conditions of the experiment are studied.

Summary.

X-ray measurements show that the higher fatty acids have at least two forms of chain, of which the longer is that appearing in the true single crystal. The longer chain is always converted to the shorter when the acid is fused, but there is no difference in the m. p.'s of the two forms. Stearic and palmitic acids appear to have three possible chains.

Measurements of the long crystal spacings must be employed as a means of identification with great care, since not only may the crystals exist in two or more forms, but in many cases they are easily distorted by treatment in mounting and by the presence of impurity, especially if the impurity is similar in nature and has nearly the same number of carbon atoms in the molecule.

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