PROGRESS IN THE CHEMISTRY OF FATS AND OTHER LIPIDS

Volume

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PREFACE

The articles in the present volume were originally intended for a new edition in English of the well-known HEFTER-SCHOENFELD "Chemie und Technologie der Fette und Fettprodukte", a project which, unfortunately, had to be abandoned in its early stages due to the untimely death of the Editor, Dr. H. SCHOENFELD. In order, however that his labours and those of numerous contributors should not have been in vain, it was decided to publish the completed and projected manuscripts in the form of an annual Progress Series, of which this is the first volume. This has naturally involved some change in the nature and scope of the original project, and in the present series the chemical, biochemical, physical and biophysical aspects of fats and other lipids will receive the main emphasis. The purely technological aspects of the subject will be dealt with in a forthcoming companion Progress Series.

It is intended that each section shall be an authoritative, critical and up-to-date survey of some special branch of this rapidly expanding subject, of value not only to the specialist but also to chemists, biochemists and medical scientists interested generally in lipid chemistry.

Owing to the unusual circumstances surrounding the origin of this series, the choice of topics in the first volume has necessarily been somewhat arbitrary, and the Editors ask the reader's indulgence on this score. In Volumes 2 and 3, which are in preparation, and in subsequent volumes a more considered balance will be possible.

The Editors would like to take this opportunity of expressing their gratitude to the contributors for their patience and understanding in the unavoidable delay consequent upon the change of plan, and for their co-operation in reviewing and bringing their manuscripts up to date.

The Editors and Publishers wish to dedicate this first volume to the memory of Dr. HENRY SCHOENFELD, whose death is deplored by all who knew him and his work.

August 1952.

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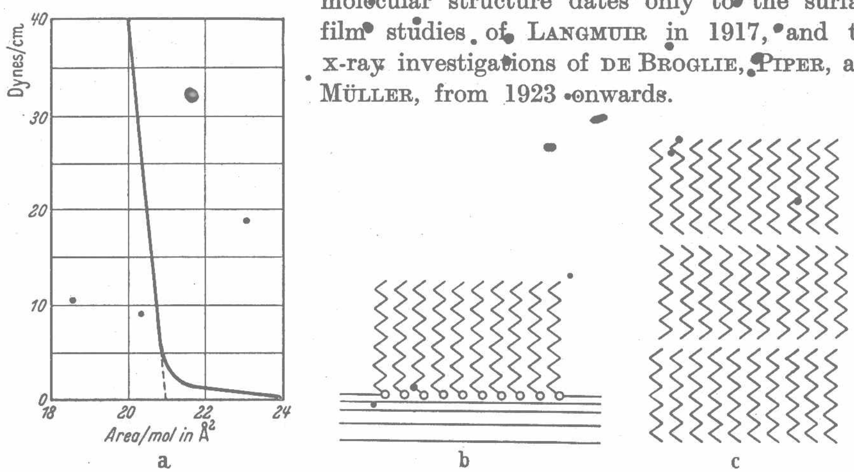
THE MOLECULAR STRUCTURE AND POLYMORPHISM OF FATTY ACIDS AND THEIR DERIVATIVES

T. Malkin

INTRODUCTION

ALTHOUGH OUR KNOWLEDGE of higher fatty acids goes back almost a century and a half to the classical work of CHEVREUIL, detailed knowledge of their molecular structure dates only to the surface film studies of LANGMUIR in 1917, and the x-ray investigations of DE BROGLIE, PIPER, and MÜLLER, from 1923 onwards.



a b c

Fig. 1.

LANGMUIR[1] showed that the higher fatty acids form solid and liquid films on water, which can be reduced in size to a certain limiting area, beyond which considerable pressures are required to effect further contraction (Fig. 1a). On the assumption that such films are monomolecular layers, LANGMUIR was able to show that, whilst the area occupied per molecule at this limiting area was practically constant at approximately 21 sq Å for all normal saturated acids, the thickness of the film was directly proportional to the carbon content of the acid. Consideration of his results in the light of the known diameter of the carbon atom led him to the view that these films consisted of a unimolecular layer of zig-zag hydrocarbon chains standing side by side, with their carboxylic acid heads in the surface of the water (Fig. 1b). This most fruitful idea could at once be extended to the crystalline state, which could be visualized as a pile of such solid films (Fig. 1c).

It is not unlikely that this conception led de Broglie[2], Piper[3], and Müller[4], independently, to examine soaps and fatty acids by means of x-rays, and to discover in them the widely separated reflecting planes which are related to the lengths of the molecules. These important results gave great impetus to the study of long chain compounds, and from this point our knowledge of the structure and polymorphism of fatty acids and their derivatives advanced rapidly.

X-RAY EXAMINATION

Both the single crystal and the powder method of x-ray investigation have been used for the study of fatty acids. The former is, by far, the more powerful and satisfactory, but unfortunately suitable single crystals are exceedingly difficult to obtain; moreover, the x-ray photographs require considerable skill, time, and patience to interpret. The powder method, on the other hand, involves a relatively simple technique and quickly gives valuable information concerning the main crystal spacings. It has consequently been much more widely used, and has proved to be of great value for purposes of identification, and also in the study of polymorphism.

Although in this field the powder method preceded single crystal studies, it will be more instructive to deal first with the results of the single crystal method.

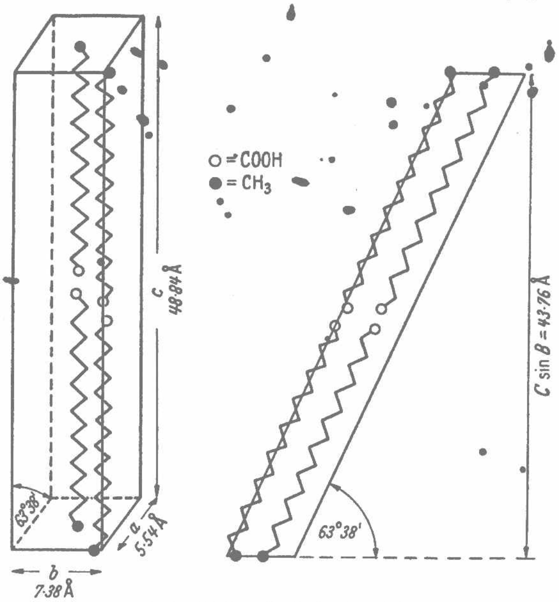


Fig. 2. Unit cell of stearic acid.

The unit cell of stearic acid

Müller[5] has shown that the unit cell is a long monoclinic prism of dimensions: $a = 5{\cdot}546$; $b = 7{\cdot}381$; $c = 48{\cdot}84$; $\beta = 63°38'$ (the angle between a and c). $c \sin\beta = 43{\cdot}76$ Å. Four molecules of stearic acid per cell (Fig. 2).

Two stearic acid molecules, associated at the carboxyl groups, lie along each of the four edges of the prism, surrounding a fifth pair in the centre. Two of these pairs, *i.e.* four stearic acid molecules, belong to the unit cell, the remaining three pairs being associated with adjoining cells. Müller showed that the carbon atoms of the hydrocarbon chains are joined to each other at the tetrahedral angle* in the form of a plane zig-zag (Fig. 3a).

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* Later work indicates that the angle is slightly greater than the tetrahedral, namely approximately 116° (*cf.* Piper[6], Malkin[7], Morrison and Robertson[8]).

The plane of the zig-zag is inclined to the axes *a* and *b*, and if the carbon chain be regarded as a long rod of elliptical cross section (Fig. 3d), a section of the cell, perpendicular to the *c* axis, may be represented by Fig. 3b.

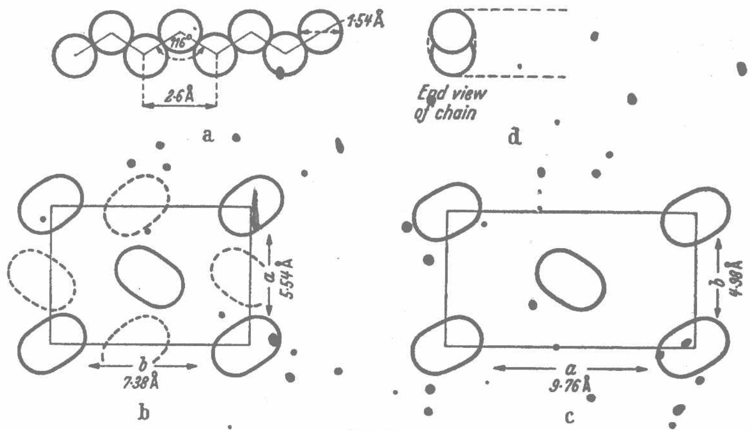

Fig. 3.

The discontinuous lines indicate the positions of the chains in the cell immediately above; these are slightly staggered, thus allowing the terminal methyl groups of both cells to be better accommodated. The structure is quite open for the volume of the carbon and oxygen atoms in each cell is only $272 \cdot 10^{-24}$ cm^3, compared with the cell volume $1792 \cdot 10^{-24}$ cm^3 so that there is ample room for the remaining hydrogen atoms. Indeed, the presence of much larger atoms does not appear to increase the cross section of the cell unduly, *cf* bromstearic acid (Table 1, last column).

Table 1

Acid	*a*	*b*	*c*	*β*	*c* sin *β*	*a b* sin *β*
Lauric[9]	9·76	4·98	36·9	48°6′	27·6	36·5
Palmitic[10]	9·41	5·0	45·9	50°50′	35·6	36·2
Stearic[5]	5·55	7·38	48·84	63°38′	43·76	36·6
Stearolic[5]	9·55	4·69	49·18	53°4′	39·28	35·8
Behenolic[5]	9·55	4·69	59·1	53°30′	47·51	36·0
α-Bromstearic[5]	11·04	4·9	52·88	43°15′	36·23	37·1
Hexadecane-dicarboxylic[11]	9·76	4·92	25·1	48°50′	18·9	36·2
Octadecane[5]	5·0	7·56	25·6	90°	25·6	37·8

Table 1 gives the unit cell data for monobasic acids so far investigated, together with that for a dibasic acid and a hydrocarbon, for comparison. All the crystals are built on the same plan and all the acids are monoclinic prismatic. The hydrocarbon differs only in being orthorhombic, *i.e.* the *c* axis is vertical to the base. The constancy of the cross-sectional area, *ab* sin *β*, is striking, and suggests a common mode of packing for the methylene groups of the chains. This is in agreement with the extensive thermal investigations of GARNER and co-workers (*cf.* KING and GARNER[12], for summary), who found practically a constant heat of crystallisation per methylene group for a wide variety of non-rotating forms of long chain compounds. The chains are more compact in the crystalline state than in surface films, the respective cross-sections being 18·2 and 20–21 . 10^{-16} cm^2.

It will be noted that the crystal data for stearic acid differ from those of lauric and palmitic in that the *a* and *b* axes are in the reverse order of magnitude. These two structures represent the two most important modifications of even-membered fatty acids, namely the stable C form (lauric, palmitic) and the less stable B form (stearic) (see Fig. 3b and c).

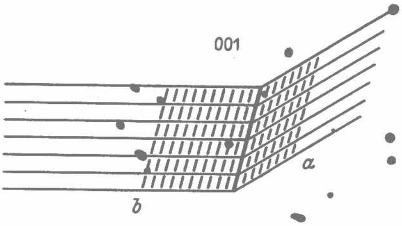

Fig. 4.

The main forces holding the molecules together are the lateral forces between the methylene groups of the chains, for GARNER, MADDEN and RUSHBROOKE[13] have shown that the heat of crystallisation of the terminal groups is negative. Consequently, the main crystal growth is along the *a* and *b* axes, and the general habit is to form exceedingly thin flakes with well-developed 001 faces (Fig. 4).

This explains the difficulty, referred to earlier, in obtaining suitable single crystals for x-ray work. Fortunately, this structure is not without its own special advantage, for the regular layers of molecules between the flake surfaces lend themselves well to the determination of *d*, the distance between the 001 planes, by x-ray powder methods.

As would be expected from the above results of GARNER *et al.*, the 001 planes which consist of terminal methyl groups are the best cleavage planes of the crystal.

X-ray powder photographs

Powder photographs usually exhibit a somewhat complex system of lines due to reflections from all the main planes of the crystals. They are of considerable value for purposes of identification, and for indicating changes in structure, but except for crystals of high symmetry, their interpretation in terms of the unit cell is a matter of some difficulty.

Long spacings

In the case of long chain compounds, however, there is a simplification due to the fact that the molecules are so long, compared with their width; consequently, the 001 planes, across which they lie, are much more widely separated than all others, and give rise to reflections which are readily identified. Moreover, since long chain compounds crystallise in flakes, with the 001 planes parallel to the flake surface, a specimen pressed lightly on to a flat surface, is ideally oriented for reflections from these planes, and usually gives rise to them exclusively. The distance between these planes is termed the "long spacing" (d); it is related to the c axis of the unit cell by the equation $d = c \sin \beta$, where β is the monoclinic angle (*cf.* Fig. 2). This angle is also the inclination of the long chains to the 001 planes. It was shown by Piper and Grindley[3] for soaps, by Müller[4] for fatty acids, and by Müller and Saville[14] for hydrocarbons that the long spacings, plotted against the number of carbon atoms in the compound, fall on a straight line, and this is true for all homologous series, provided that spacings of comparable crystalline forms are plotted. Thus, spacings of odd and even members of a series, or of different polymorphic forms, may fall on different straight lines (see Fig. 5a). From the slopes of these lines, which give the increments in the long spacing per carbon atom, it is easy to determine the inclination of the chains to the 001 planes. An increment of 1·3 Å (the maximum found experimentally) (see also Fig. 3a) indicates that the molecules lie vertically across the planes, whilst the ratio of any smaller increment, i, to this maximum value, gives the sine of the angle of tilt, *i.e.* $i/1{\cdot}3 = \sin \beta$. The intercept of these lines at $C = 0$ is a measure of the contribution of the end groups to the long spacing. As a simple illustration, the hydrocarbon, octadecane, may be considered. This can be regarded as 18 methylene groups and two terminal hydrogen atoms,

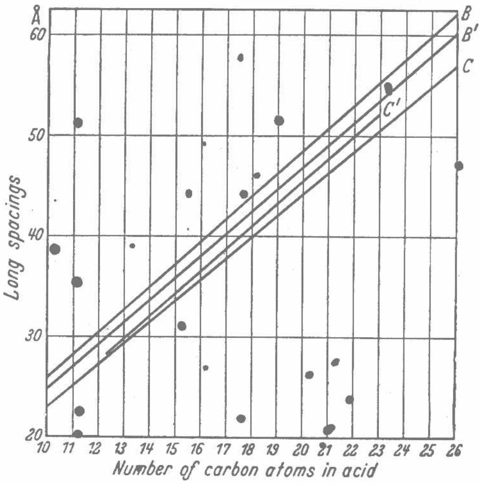

Fig. 5a. Long spacings of fatty acids. *B C* (even), *B' C'* (odd).

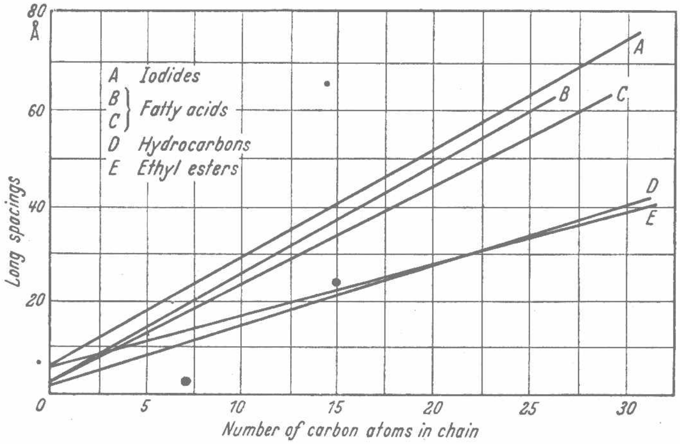

Fig. 5 b.

and since the tilt of the chain (β) is known to be 90°, the contribution of the methylene groups to the long spacing is $18 \times 1{\cdot}3$ Å $= 23{\cdot}4$ Å. Müller[5] gives 25·6 Å for the long spacing, so that the terminal hydrogen atoms contribute 2·2 Å, a distance which is practically identical with the intercept of the hydrocarbon line at $C = 0$. (*cf.* also Saville and Shearer[15] for ketones.) (See Fig. 5b for variations in intercept.)

The linear relationship between long spacings and carbon content is clearly of importance for purposes of identification, particularly for higher members of homologous series, where m.p. differences become small. The work of Piper *et al.*[16] (hydrocarbons), Francis *et al.*[17] (fatty acids) and Piper and Chibnall *et al.*[18] (fatty acids, alcohols, and ketones) well illustrates this application of the x-ray method.

Shearer *intensity variations*[15, 19]

A consideration of the long spacings data of various homologous series shows that there are two main types of compounds, namely, those in which the

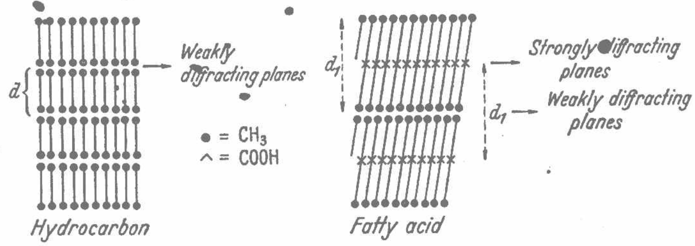

Fig. 7.

001 planes are separated by single molecules (hydrocarbons, ethyl esters, ketones except methyl ketones) and those in which the planes are separated by double molecules (fatty acids and their salts and methyl esters, alcohols, methyl ketones and halides). Molecules containing a highly polar terminal group, particularly one capable of hydrogen bonding, would be expected to belong to the second group.

Apart from the magnitude of the spacing, the two types can usually be distinguished by a difference in the intensities of the lines on the x-ray photograph. In the first group, there is normally a gradual diminution of intensity, passing from the 1st to the *n*th order, whilst in the second group there is a marked weakening of the even orders (see Fig. 6). Shearer has investigated mathematically the distribution of intensities of x-ray spectra of long chain compounds, and has shown how the intensities are related to variations in the density of scattering matter along the chains. His main conclusions will be understood from the following simple treatment.

The main scattering of x-rays in long chain compounds is due to the electrons of the methylene groups, but at the terminal methyl groups, where hydrogen concentration is high, electron density is low, and therefore the methyl plane is one of lower scattering power than the main body of the crystal. On the other hand, the presence of oxygen or other heavy atoms (acids, alcohols, iodides) gives rise to planes of higher scattering power than the main body. With double molecules, such as acids and alcohols, the two types of planes are the same distance apart and midway between each other, (Fig. 7). Reflections will therefore be given from them for the same angle of incidence, but odd order reflections will be in exactly opposite phase whilst even order reflections will be in phase. Since, however, the diffraction effects are in opposite sense, that is, due to a deficit or to an excess of electrons, they neutralise each other when in phase. Thus, if the deficit were exactly equal to the excess, the even orders would disappear. Shearer showed that, in general, a dense groups situated $1/n$th way down the chain, would cause the nth order to weaken or disappear. Fig. 8 gives examples of the Shearer effect and a further beautiful illustration due to Professor Piper is given in Fig. 9. This effect has obvious applications to the solution of structural problems (*cf.* Robinson[20], Piper and Chibnall[18], Velick[21].

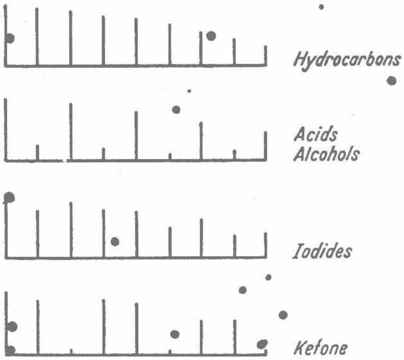

Fig. 8. *Hydrocarbon.* Weak methyl planes only. Steady diminution in intensity. *Acids, alcohols.* Weak and strong scattering planes. Electron excess > deficit. Weak even orders. *Iodides.* Electron density round iodine so greatly exceeds deficit at methyl planes that weakening of even orders is slight. *Ketone.* Keto group $\frac{1}{3}$ way down the chain. 3rd order disappears.

Short spacings ("side spacings")

Müller[4], in his first paper on fatty acids, observed on his photographs, in addition to the sharp lines of the long spacings, two diffuse lines further out from the centre. Unlike the long spacings, these did not vary with the carbon content of the acids, but were approximately constant at 4·1 and 3·7 Å. Shearer[22] observed the same spacings for a series of esters, and in a later paper on hydrocarbons Müller and Saville[14] found similar spacings of 4·2 and 3·8 Å, which they termed "side spacings". Although this expression is in fairly common use, it will be more consistent, in view of the term "long spacing", to refer to them as short spacings.

Except in the case of glyceride studies (see Vol. II), short spacings have not been so fully investigated as long spacings. They are reflections from planes associated with the shorter a and b axes of the unit cell, and the spacings usually reported are the strongest of a complex group. Where the stronger reflections have been identified they are known to be from the planes:— 110 (B and C forms of acids; hydrocarbons), 200 (C form of acids; hydrocarbons), 020 (B form of acids).

As mentioned earlier, pressed layers usually give rise to long spacings only, but side spacings are also obtained if the specimen is oriented more at random, as for example, if a melted layer, a rod, or a packed capillary of the specimen is used. A rod has, in fact, a preferred orientation for short spacing reflection, and long spacings may be absent.

One of the main uses of the study of short spacings is in the detection of polymorphic changes, for all the members of any particular homologous series, if in a comparable crystalline form, give rise to the same characteristic set of short spacings (see Fig. 6). It is true that polymorphism has frequently been detected by changes in the long spacing, but numerous cases of polymorphism are known where the long spacing does not alter, for example, odd-membered hydrocarbons and alcohols, and 1-monoglycerides.

Probably the most important advance arising from short spacing studies was the recognition of vertical rotating, or α-forms of hydrocarbons, alcohol and esters. Müller[23] observed that hydrocarbons changed, a few degrees below their m.p.s., into a form which gave a single strong short spacing of ≏4·12 Å, instead of the two normally observed. This involves an increase in symmetry to hexagonal, a change difficult to visualise with rigid, zig-zag chains, and Müller was forced to the conclusion that the chains rotated as a whole, and behaved as long, cylindrical rods. A similar view had earlier been advanced by Hendricks[24] to explain anomalies in the structure of amylamine hydrochloride, which exhibits tetragonal symmetry. The change is illustrated in Fig. 10. Vertical rotating forms giving a single short spacing of ≏4·12 have subsequently been found by Bernal[25] for alcohols and by Malkin for esters[26] and 1-monoglycerides[27].

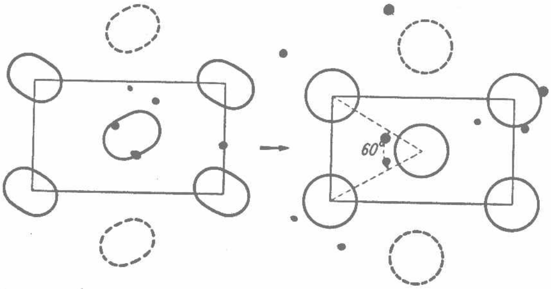

Fig. 10. Change from non-rotating to rotating forms. Rectangles represent cross-sections through the unit cells, perpendicular to the long axes of the chains.

Since the forces round a rotating molecule are radially symmetrical, there is no tendency to tilt, and such molecules lie vertically across the 001 planes. Consequently, when a tilted non-rotating form assumes rotation, it assumes at the same time the vertical form, and there is an increase in the long spacing. This increase, by itself, does not, however, indicate a change to a rotating form, for vertical non-rotating forms are known (odd hydrocarbons and odd alcohols) which have the same long spacing whether rotating or not. A rotating, or α-form, can therefore be recognised only by the presence of a single strong side spacing of ≏4·12 Å, and by the fact that it is uniaxial (*cf.* Malkin[28]).

Determination of crystal spacings

The method is illustrated by Fig. 11. A narrow beam of x-rays falls at grazing incidence on the specimen S, which is slowly rocked by a cam mechanism through an angle of about 15°. Reflections, which are recorded on film or plate F, occur at angles of incidence θ_1, θ_2, θ_3 etc., determined by the Bragg equation, $n\lambda = 2d\sin\theta$, where λ is the wavelength of the x-rays, $n = 1, 2, 3$ etc. the order of reflection, and d is the crystal spacing. After an exposure of from 15–20 minutes (for an x-ray tube running at 12–15 mÅ), the specimen is turned through 180° and a similar exposure is made on the other side of the film. Fig. 12 shows a **Müller** spectrograph, which has been in use for many years and is still probably the best type for general long chain work.

In practice, x-rays from a Cu target, $\lambda K_{\alpha_1+\alpha_2} = 1{\cdot}54$ Å are most frequently used, the β-radiation being filtered out by covering the x-ray window with nickel foil of ⌓0·02 mm thickness. x-rays from Ni, Co, and Fe targets with Co, Fe, and Mn filters respectively, have suitable wavelengths for long chain work, and may also be used. The slit is ⌓0·25 mm wide by 1 cm deep, and the front of the slit system should preferably be the same distance from the specimen as the latter is from the film. The distance from specimen to film must be known accurately and it is usually determined by a calibration with calcite = 3·029 Å, rock salt = 2·814 Å, or mica = 9·845 (1st order). For simplicity in calculation, this distance should be an integer, 5–10 cm being a convenient range.

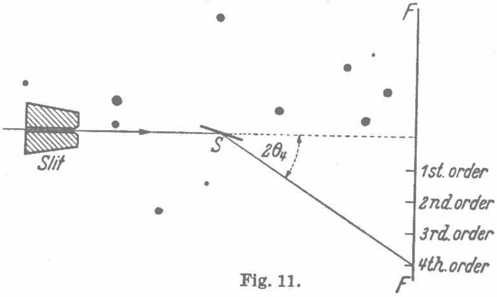

Fig. 11.

The specimen is mounted by pressing as thin and as even a layer as possible on to the centre of the plate glass mount, to give a surface of about 1 cm by 5 mm (where necessary, a smaller area can be used), or a melted layer is allowed to solidify by lightly running a slightly heated spatula over a pressed layer. The former usually gives long spacings only, whilst the latter gives both long and short. When short spacings are required, rods or capillaries of the specimen are used; the former may be extruded from a metal die, or in certain favourable cases the molten specimen can be drawn into a glass capillary, and ejected after solidification. Where specimens do not extrude well, they may be packed into capillaries of lithium borate glass, cellophane, or goldbeaters' skin. The specimens should be rotated during exposure. Capillaries give rise to both long and short spacings, but rods give rise mainly to short, although long may be present. Rods and capillaries are normally used with circular cameras; they should not greatly exceed 0·5 mm in diameter, or a correction similar to the one given in the following paragraph will be necessary. Rods and capillaries give good photographs in ten minutes, compared with thirty to sixty minutes for a layer, and the rod technique is therefore admirable for exploratory work on polymorphism.

In calculating the spacing, half the distance between corresponding lines on either side of the centre, divided by the fixed distance from specimen to film, gives tan 2θ, from which θ, $\sin\theta$, and hence d, the spacing, are readily obtained. Owing to the variation in the thickness of the specimen layer, the distance from specimen to film is indeterminate to a fraction of a millimetre, and although this can be adjusted by trial on the spectrograph, a correction which diminishes with increasing order of reflection can be usefully applied. The correction involves a trigonometric relation, but for the small angles concerned, a linear correction is sufficiently accurate. The method is illustrated from an actual experiment (stearic anhydride).

Table 2

Order of reflection	$\sin\theta$	$\frac{\sin\theta}{n}$	*Correction**	*Corrected* $\frac{\sin\theta}{n}$
1	0·01995	0·01995	—0·0006/1	0·01935
3	0·05865	0·01955	—0·0006/3	0·01935
5	0·09745	0·01949	—0·0006/5	0·01937
7	0·13615	0·01945	—0·0006/7	0·01936

* The correction may be positive or negative for layers. From $n = 2d \sin\theta$, $d = \frac{n}{\sin\theta} \cdot \frac{1{\cdot}54}{2} = \frac{0{\cdot}77}{0{\cdot}01936} = 39{\cdot}8$ Å, that is, the spacing is given by dividing 0·77 by $\frac{\sin\theta}{n}$.

POLYMORPHISM

Fatty acids—Piper *et al.*[29], from a study of long spacings, first showed that even-membered fatty acids are polymorphic, existing in two and sometimes three modifications, each giving a different long spacing. The forms were termed *A*, *B*, and *C*, the spacings decreasing in magnitude in that order. A little later, de Boer[30] obtained similar results for odd fatty acids, thus confirming earlier observations of Garner and Randall[31], who found during their thermal investigations that nonoic and undecoic acids exist in two enantiotropic modifications. These results have been extended by several workers[17, 32, 33, 34, 35] and are summarised as follows.

Even acids—With the exception of capric acid, which has been found only in the *C* form, all higher acids exist in two main forms, *B* and *C*; the former is obtained only from solvents, preferably of the non-polar type (benzene, toluene), whilst the latter is usually obtained from polar solvents (acetic acid, alcohol), and is always formed when the fused acids solidify. Myristic, palmitic and stearic acids may also crystallise in the *A* form, but whilst myristic is usually obtained in this form alone from non-polar solvents, palmitic and stearic separate as a mixture of *A* and *C* forms, under conditions which it has not been found possible to specify. The *A* form has not been reported for acids higher than stearic.

When *A* and *B* forms are heated to 10 or 15° C below their m.p., they are transformed irreversibly, and without appreciable heat of transition, into the *C* form, which thus appears to be the stable modification. All forms, therefore, melt at the same temperature, that is, the m.p. of the *C* form.

Odd acids—The polymorphism odd of acids is more complex than that of the even, and the literature is somewhat confusing, owing to a lack of uniform nomenclature. **Garner** and **Randall**[31], who first showed that odd acids are dimorphous, used the term α for the form which first separates from the melt, and β for the form into which the α-form changes on cooling. **de Boer**[30] later found that the α-forms change on cooling into one or other of two forms, which he termed β_{i} and β_{ii}, and finally **Piper**[32] reported four forms, which he termed A', B', C', and D', in harmony with his even acid nomenclature. In view of the use of the term α-form to denote vertical rotating forms, none of which have been found in the acid series, it is preferable to use **Piper**'s terminology, in which case the above α, β_{i} and β_{ii} forms become C', A', and B' respectively.

The C' form is always the first to separate from the molten acid, and this changes, some 10–20 degrees below the solidifying point, into one or more of the other forms. The transition is irreversible from C_{13} upwards, and reversible from C_{11} downwards. C_{17} and higher acids always change from the C' to the B' form, which is also the form obtained from solvents, and acids higher than C_{17} have been observed only in these two forms.

The C' forms of C_{13} and C_{15} acids change to A' or B' forms, or to a mixture of these, on cooling, and the same forms are obtained from solvents; but if a single form only is obtained, it is the A' form for C_{13} and the B' form for C_{15} acid.

Undecoic acid, which melts only a little above room temperature, is usually found to be in the C' form, but on cooling it changes reversibly into the A' form. It has not been observed in the B' form.

Pure D' forms have not been isolated, and conditions for their formation have not been determined. They are always associated with A' or B' forms, and appear to be present in minor amounts.

Ethyl esters—The dimorphism of ethyl esters was reported independently by **Malkin**[36, 37], **Smith**[38], and **Phillips** and **Mumford**[39], who showed that, from the palmitate upwards, they solidify from the molten state in a transparent form, α, which changes to an opaque form, β, on cooling. The two forms were shown by x-ray investigation to possess vertical rotating (α), and tilted (β) chains, and therefore the terms α and β, which were originally given without any structural connotation, may conveniently be retained, since α and β are now generally accepted as meaning vertical rotating (α), and non-rotating (either vertical or tilted) (β).

King and **Garner**[40] found that the heat of crystallisation per methylene group for the α and β forms is 0·708 and 1·04 cal respectively, so that the heat of transition is considerable. Consequently, heating and cooling curves are very suitable for the study of these changes (see Fig. 13).

The dimorphism of this group can best be understood from a consideration of the m.p. curves in Fig. 14. M.p.s of β-forms lie on two smooth curves, the upper representing esters of even acids, whilst m.p.s of α-forms lie on a single curve which cuts the other two. Since the higher melting forms must be the more stable, the dimorphism is monotropic for esters to the left of the α-curve and enantiotropic for those to the right. In the cases of ethyl pentadecoate and eicosoate, which lie on the intersections of the curves, the α- and β-forms melt so near to each other, that it is difficult to decide whether the changes are monotropic or enantiotropic. Ethyl myristate and lower members of the series differ from the higher, in separating from the melt in the opaque β-forms, and pure α-forms have not been shown to exist; but by stabilising the α-forms by means of homologous impurity, **Phillips** and **Mumford**[41] were able to obtain extrapolated values for their m.p.s. These authors also reported a third form of esters, which they termed γ, but there is no x-ray evidence to support the existence of this form.

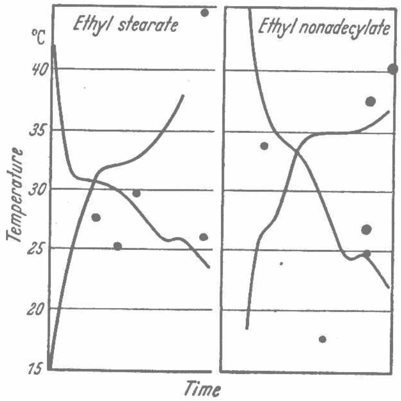

Fig. 13.

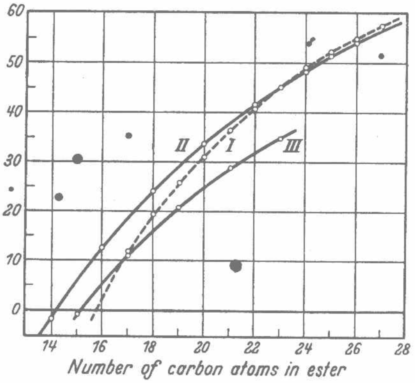

Fig. 14. M.p. curves of ethyl esters.

Methyl esters—The stable forms of methyl esters crystallise in double molecules, which lie tilted across the 001 planes, and it appears, therefore, that the methyl group possesses some power of co-ordination similar to that of the hydrogen atoms of the carboxyl group. From the low m.p. of methyl esters, this association is clearly much weaker than with acids; but it would account for the fact that methyl esters melt slightly higher than the corresponding ethyl esters. It is interesting to note that methyl ketones also crystallise in double molecules, whereas ethyl and higher ketones crystallise in single molecules.

Apart from changes very close to the m.p., which have not been studied by x-rays (see **Francis** and **Piper**), esters of even acids do not exhibit polymorphism. Esters of odd acids, however, exhibit monotropic dimorphism, and separate from the melt in a form which consists of layers of single molecules, tilted at an angle of 75°. There is, however, some doubt concerning the true nature of this form, since **Garner** and **King**[42] find its specific heat to be unusually high, *viz.* 0·62 cal/g, which is more in harmony with a vertical rotating form.

Heating and cooling curves for the odd acid esters are similar to that shown in Fig. 13 for ethyl stearate.

Table 3—Long spacings of fatty acids and their derivatives

No. of C atoms in acid	m.p. °C	Acids							Methyl esters		Ethyl esters		Anhydrides[54]	K salts	Acid K salts	Thallous salts[55]
		Even			Odd											
		A	B	C	A′	B′	C′	D′	Double	Single	α	β				
10	31·6			23·0									23·3			26·0
11	29·3				30·1								22·2	27·5		28·0
12	44·2		30·6	27·3									27·9	30·2	35·2	30·3
13	41·5				35·0	31·3	29·8	25·8					25·6	31·9		32·3
14	54·4	36·6	35·0	31·6					38·8				31·9	34·0	40·5	34·0
15	52·3				40·0	35·8	34·2	29·9	41·8	23·6			29·8	35·8	42·9	36·0
16	62·9	41·0	39·1	35·6					43·5			23·0	35·8	37·9	45·3	38·1
17	61·3				44·4	40·3	38·6	33·9	46·3	26·0	27·1	24·8	33·5	39·8	48·1	40·1
18	69·6	46·6	43·8	39·8					48·0		28·6	25·8	39·8	42·0	50·5	42·2
19	68·7					44·5	43·2		50·8	28·4	29·8	27·0		43·8	53·0	
20	75·4		48·5	44·2					52·3		31·3	27·9		46·5	55·7	
21	74·3					49·3	47·8		55·3	30·9	32·4	29·4		47·9	58·4	
22	80·0		53·0	48·3					57·0			29·9		50·7	60·8	
23	79·1					53·4			60·0			31·5		51·8	63·3	
24	84·2		57·8	52·6					61·7			32·2		54·5	65·9	
25	83·5					57·7			64·6			33·6				
26	87·7		62·2	56·3					66·2			34·5				
27	87·5					62·0						35·7				
28	90·9		67·2	61·1					70·8			36·7				
29	90.3					66·4			73·8			38·1				
30	93·6		71·4	65·2					75·3			38·8				
31	93·0					70·4										
32	96·0		76·3	69·3					80·0			41·1				
34	98·2		80·5	73·3					84·2			43·5				
35	98·3					78·8										
36	99·9		85·3	78·1					89·3			46·3				
38	101·6		90·0	82·1					93·0			48·1				
46	106·9		108·2	99·1								57·5				

Table 4—Short spacings and tilts of fatty acids and their derivatives

	Short spacings	Tilts*
Even Acids *A*	3·63s 3·79s 4·51s 4·65s	73° 45′
B	3·69s 3·95w 4·09m 4·23m 4·43w	62° 38′
C	3·70m 4·14s 4·42w	52° 56′
Odd acids *A′*	3·69s 3·95vw 4·59s	69 41′
B′	3·62m 3·86m 3·97w 4·14vs	57° 21′
C′	4·05s 4·27m 4·41m 4·6w	59° 12′
Ethyl stearate	3·69s 4·08s 4·28w 4·46vw	62° 45′
Ethyl nonadecylate	3·68s 4·12s 4·28vw 4·44w.	62° 45′
Methyl stearate	3·69s 4·05s 4·28w 4·46vw	61° 40′
Methyl nonadecylate (double molecules)	3·68s 4·09s 4·30w 4·45w	61° 40′
Anhydrides. Even	3·68s 3·94m 4·12s	49° 54′
Odd	3·50m 3·75w 3·97m 4·48s 4·63s	46° 3′

* Tilts calculated on the assumption that the angle between carbon atoms is 116°.
s = strong, vs = very strong, m = moderate, w = weak.

ALTERNATION IN LONG CHAIN COMPOUNDS

Baeyer[43] first noted the alternation in the m.p.s of mono- and di-basic long chain acids, and later **Biach**[44] adduced evidence to show that alternation is a general property of long chain compounds, exhibited by other physical constants such as boiling point, solubility, molecular heat, refraction and rotation, a view in which he was supported by **Pauly**[45] and **Nekrassow**[46]. On the other hand, **Garner** and **Ryder**[47], and **Verkade**, **Coops** and **Hartman**[48] found no alternation in constants referring to the liquid state, and all subsequent work supports the view of the last authors, that alternation occurs only in constants referring to the solid state.

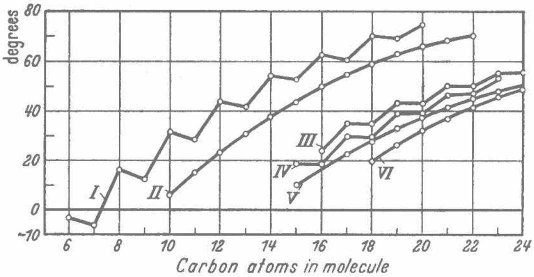

Fig. 15. Alternating and non-alternating series. *I* Fatty acids; *II* Alcohols; *III* Iodides; *IV* Methylesters of fatty acids; *V* Paraffins; *VI* Ethylesters of fatty acids (α form).

This striking property has naturally given rise to a number of theories; for instance, **Biach** considered that the carbon atoms are linked by alternate strong and weak bonds, whilst **Cuy** and **Pauly** suggested that the carbon atoms are alternately positive and negative. **Pauly** also suggested that the chain is in the form of a tetrahedral zig-zag, and that, consequently, the terminal groups in even and odd chains are respectively in the "anti" and "syn" positions, a view supported by **Nekrassow** and **Müller**[49].

These theories, however, imply that alternation occurs in all long chain compounds, whereas it is well known that normal paraffins, methyl ketones,