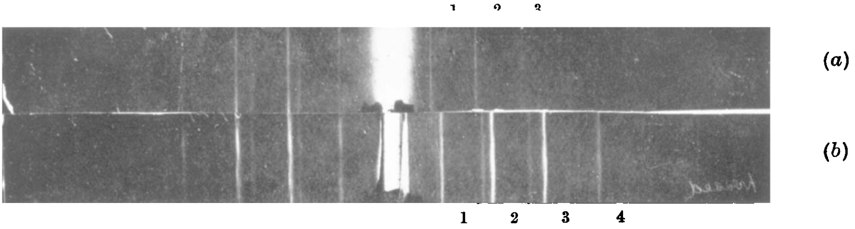
CCCLXXXIX.—*Alternation in Long-chain Compounds. New X-Ray Data for Long-chain Ethyl and Methyl Esters and Iodides, and a Preliminary Thermal Examination of the Esters.*

By THOMAS MALKIN.

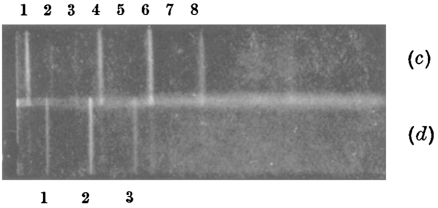
FRANCIS, PIPER, and MALKIN (*Proc. Roy. Soc.*, 1930, *A*, **128**, 224), who measured the large crystal spacings of a series of ethyl esters of the normal fatty acids, observed an unexpected increase in the spacings of certain equimolecular mixtures. The investigation has therefore been continued, and it is now found that ethyl esters exist in two crystalline forms, one of which is stable over a limited range of temperature near the m. p. The large spacings of the new form are longer than those of the normal form measured by the above authors, and this suggests the explanation of the increase noticed

PLATE I.

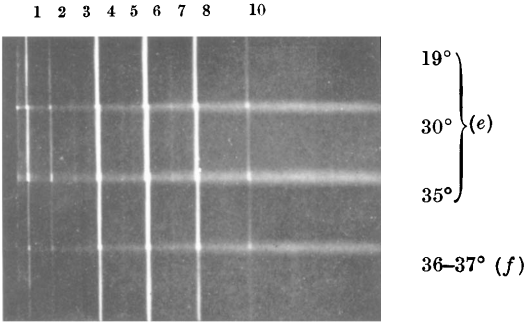
Ethyl stearate.



Methyl margarate.



Methyl stearate.



(*Index numbers refer to orders of reflexion.*)

[*To face p.* 2796.]

by them. In the case of mixtures, the change from the metastable form into the normal stable form is greatly retarded, so that a fused mixture solidifies and remains in the metastable condition over a considerable period.

The long spacings of a series of methyl esters have also been measured. In contrast to the ethyl esters, which crystallise in layers of single molecules, these crystallise in double molecules; moreover, evidence of a second crystalline form is found only in the case of methyl esters of acids containing an odd number of carbon atoms.

The bearing of these results on the phenomena of alternation will be discussed in a later section.

EXPERIMENTAL.

X-Ray Technique and Materials.—Throughout the work a Müller spectrograph and a Shearer X-ray tube were used (iron anticathode, $\lambda K\alpha Fe = 1{\cdot}932$). The specimens were mounted in two ways: (1) a thin layer of material crystallised from a solvent was pressed on to a glass strip (pressed layer), (2) a thin layer was melted on to the strip by means of a warm spatula, and allowed to solidify (melted layer).

The esters examined were prepared from the fatty acids used in the previous investigation, and the iodides were synthesised from these and purified by the author.

X-Ray Examination of the Esters.—*Ethyl esters.* Francis, Piper, and Malkin (*loc. cit.*) determined the large spacings (pressed layers) for a series of ethyl esters. Two missing members (C_{22} and C_{27}) have now been examined and the completed data for the series from C_{16} to C_{26} acids are given in Table I (*a*), and plotted in Fig. 1.

TABLE I.

Long spacings of ethyl esters of fatty acids (*in* Å.U.).

No. of C atoms in ester.	18.	19.	20.	21.	22.	23.	24.	25.	26.	27.	28.
(*a*) Pressed	23·0	24·6	25·5	26·8	28·0	29·2	30·1	31·4	32·1	33·9	34·6
(*b*) Melted		27·1	28·6	29·8	31·3	32·4					

The " pressed " spacing is also obtained from a melted layer, if this is allowed to cool to room temperature; but if the temperature is maintained a few degrees below the m. p., the longer spacing of another crystalline form appears.* This form is stable over a small range of temperature immediately below the m. p.

The change is well shown in the case of ethyl stearate [Plate I, (*a*) and (*b*)]. A thin layer of ester was melted on a glass strip, mounted

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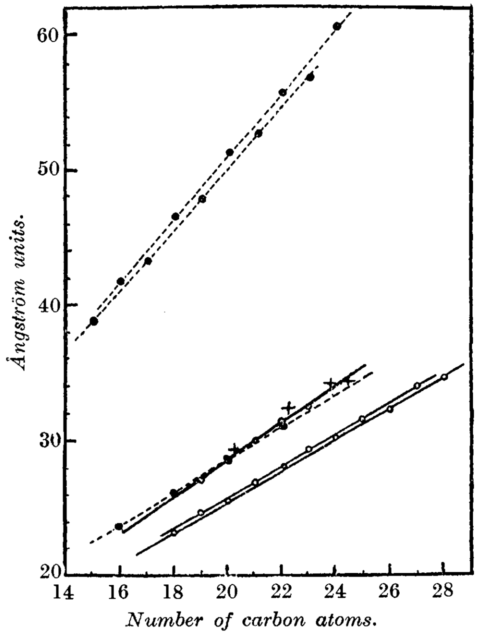
* Smith (this vol., p. 803) has described two forms of ethyl palmitate and ethyl stearate.

on the spectrograph, and quickly enclosed by a small electrically heated oven so as to maintain the temperature a few degrees below the m. p. The *X*-ray beam was first reflected for 3 hours to the right and then for the same time to the left. In the photograph, the more closely spaced lines on the right of (*a*) correspond to a wider crystal spacing than the normal spacing on the left, and thus, during the exposure, the unstable form had slowly changed to the stable. For comparison, a photograph of pressed ethyl stearate (*b*) is shown immediately below (*a*). (The faint lines on this photograph are due to β radiation, and are not to be confused with those of the new form, with which, by chance, they almost coincide.) The new spacings, which have been measured for the esters of margaric to heneicosanic acids, are given in Table I (*b*) and plotted in Fig. 1. The values obtained by Francis, Piper, and Malkin for mixed esters are also plotted in the figure, and are seen to fall reasonably close to the curve representing the metastable form.

FIG. 1.

X-*Ray data for ethyl and methyl esters of normal fatty acids.*



○ *Ethyl esters.* ● *Methyl esters.*
+ *Values obtained for mixed esters by Francis, Piper, and Malkin.*

Differences in the crystal spacings, such as those found in the two forms of ethyl esters, are regarded as being due to a change in the tilt of the chain with respect to the planes formed by the terminal groups. If, therefore, the diameter of the carbon atom is taken as 1·54 Å.U. (diamond), and a zig-zag chain of carbon atoms inclined tetrahedrally to each other is assumed, the above X-ray data for ethyl esters agree with a chain inclined at an angle of 67½° in the normal form, and a vertical chain in the metastable form.*

Methyl esters. Spacings for pressed and melted layers are given in Table II and plotted in Fig. 1.

TABLE II.

Long spacings of methyl esters of fatty acids (in Å.U.).

No. of C atoms in ester.	15.	16.	17.	18.	19.	20.	21.	22.	23.	24.
(*a*) Pressed	38·8	41·8	43·2	46·5	47·8	51·2	52·6	55·6	56·7	60·4
(*b*) Melted	38·8	23·6	43·3	26·0	47·8	28·4	—	30·9	—	—

Identical values are given for pressed and melted layers if the latter are allowed to cool sufficiently; but in the case of esters of odd acids, another crystalline form is found to exist over a moderate range of temperature near the m. p. The spacings for this form are given in Table II (*b*). The values for pressed layers correspond to planes separated by double molecules with chains tilted at angles of 63° and 67½° for esters of even and of odd acids, respectively. The values for the metastable form correspond to layers of single molecules with chains tilted at an angle of 75°.

The differences between methyl esters of odd and of even acids are illustrated in Plate I: (*c*) and (*d*) are photographs of pressed and melted layers of methyl margarate; (*e*) and (*f*) of pressed and melted layers of methyl stearate taken at different temperatures. Photographs (*c*) and (*d*) show a distinct change in type, both the intensity distribution and the spacings of the lines being different. In (*e*) and (*f*), there is no difference between pressed and melted layers, except that, in the high-temperature pressed layer (35°) and in the melted layer, the strong first order has become much weaker. This weakening of the first order probably explains why Shearer (J., 1923, **123**, 3153) reported methyl palmitate and stearate as single molecules. Shearer presumably used melted layers, in which case the first order is frequently missing, unless long exposures are given, and thus orders 4, 6, 8, would be regarded as 2, 3, 4, and the spacing consequently halved.

From the fact that methyl esters crystallise in double molecules,

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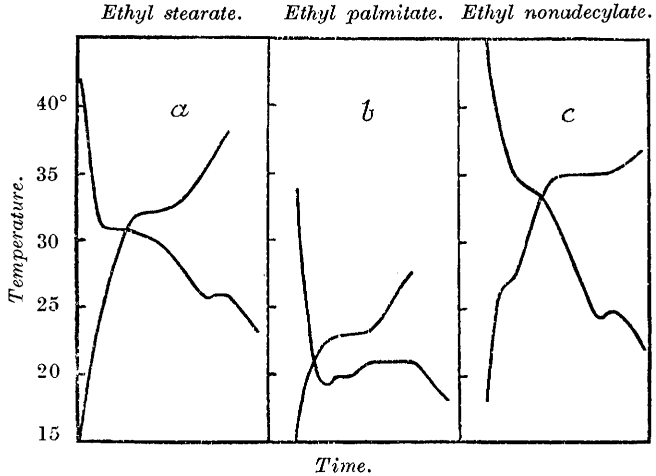
* Actually, the data for the metastable form require the carbon atoms to be joined at an angle slightly greater than the tetrahedral, namely, 118°. Ingold (J., 1921, **119**, 305) deduced theoretically an angle of 115° between methylene groups, and Piper (J., 1929, 237) found 111° 46′ in the case of acid salts of fatty acids.

it appears that the methyl group has some power of co-ordination similar to that of the hydrogen in carboxylic acids. This power, although much weaker in the esters, is, however, sufficient to account satisfactorily for the unexpected fact that methyl esters melt at a slightly higher temperature than the corresponding ethyl esters.

Thermal Examination of the Esters.—Cooling curves of ethyl esters, from ethyl margarate upwards, show two distinct arrests. In all cases the liquid changes to a transparent solid, which on further cooling becomes white and opaque, the visible changes corresponding with the arrests in the curve and also with the changes in crystal spacings. The stability of the transparent form of esters of odd acids is greater than that of esters of even acids, and the change in the case of the former is reversible. This is shown either by the X-ray method or by heating curves. In the case of even esters, it is not yet possible to decide whether the change is reversible or not : neither method gives evidence of reversibility.

FIG. 2.



Typical cooling and heating curves are shown in Fig. 2 (a) and (c). In the case of ethyl palmitate, Fig. 2 (b), the two arrests are superimposed, and therefore this ester could not be maintained in the metastable form long enough for an X-ray exposure.

Table III gives the setting point and temperature of transition for a number of ethyl esters. The former lie on a smooth curve.

Cooling curves for methyl esters of odd acids show two arrests and are of the same type as that given in Fig. 2 for ethyl stearate. The change from metastable to normal form appears to be irreversible.

Curves for methyl esters of even acids are of the normal type with a single arrest at the setting point.

Alternation in Long-chain Compounds.—Baeyer (*Ber.*, 1877, **10**, 1286) first noted the alternation in the m. p.'s of mono- and di-basic long-chain acids, and later Biach (*Z. physikal. Chem.*, 1905, **50**, 43) adduced evidence to show that alternation is a general property exhibited by other physical constants such as boiling point, solubility, molecular heat, refraction, and rotation, a view supported by Pauly (*Z. anorg. Chem.*, 1922, **119**, 271) and Nekrassow (*Z. physikal. Chem.*, 1927, **128**, 208). On the other hand, Garner and Ryder (J., 1925, **127**, 720) showed that there is no alternation in the molecular volumes of liquid fatty acids, and Verkade, Coops, and Hartman (*Rec. trav. chim.*, 1926, **45**, 373, 585) found no alternation in constants referring to the liquid state, in the case of di- and mono-basic acids and methyl esters of the former. A critical survey of the available data supports the view of the last authors, *viz.*, that alternation occurs only in constants referring to the solid state.

TABLE III.

	Setting point.	Transition point.	Capillary m. p.*
Ethyl palmitate	19·8°	21·0°	25°
,, margarate	25·0	9·5	28
,, stearate	30·75	25·5—26·0	34
,, nonadecylate	35·5	24·3—24·7	37·5
,, eicosanate	40·5	32—35	41·0
,, behenate	47·1	34·5	48·0

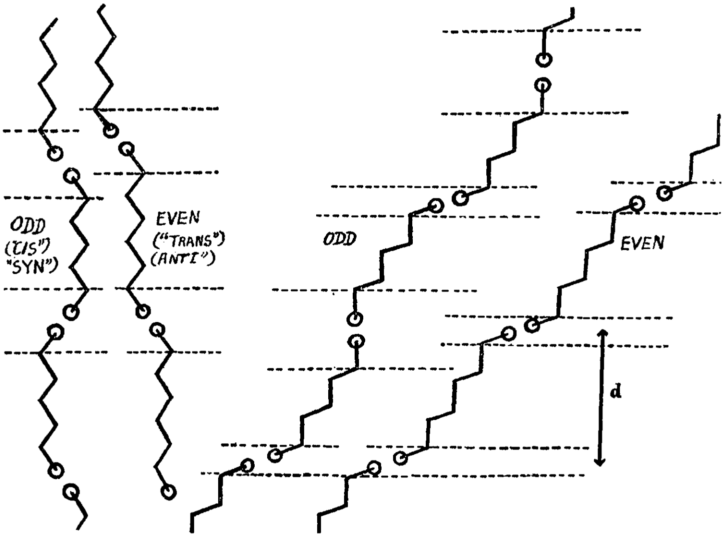
* Capillary melting points of long-chain compounds are usually slightly higher than setting points.

Differences between compounds of odd- and even-carbon content have been attributed to various causes; for instance, Biach (*loc. cit.*) considered that the carbon atoms in the chain are linked alternately by strong and weak bonds, and Cuy (*Z. anorg. Chem.*, 1921, **115**, 273) and Pauly (*loc. cit.*) assumed that the carbon atoms are alternately positive and negative. Either of these effects would obviously produce a difference between odd and even members. 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 the *syn*-position (see Fig. 3). This view has been elaborated by Nekrassow (*loc. cit.*) and by Müller (*Proc. Roy. Soc.*, 1929, *A*, **124**, 318).

The difficulty with regard to these theories is that they imply alternation in all long-chain compounds, whereas, actually, the normal paraffins, methyl ketones, primary alcohols, and ethyl esters do not show this phenomenon. One would expect, therefore, some important crystallographic difference between the above series and alternating series, and this is found to be the case. If one considers the form stable at the melting point, *all the above non-alternating series possess vertical chains, whereas alternating series possess tilted chains.**

A vertical chain requires an increase in length of chain per carbon atom of approximately 1·3 Å.U.; the increase found for ethyl esters is 1·32, for paraffins 1·3 and 1·25 (Müller, J., 1925, **127**, 602; *Proc. Roy. Soc.*, 1930, *A*, **127**, 422), for ketones 1·3 (Saville and Shearer, J., 1925, **127**, 595), and for alcohols 1·29 (Malkin, *J. Amer. Chem. Soc.*, 1930, **52**, 3739). In alternating series, the chains are tilted, as shown in the case of fatty acids (Piper, *Trans. Faraday Soc.*, 1929, **25**, 348), dibasic acids (Normand, Ross, and Henderson, J., 1926, 2632; Caspari, J., 1928, 3236), iodides (this paper), and nitriles (unpublished).

FIG. 3.



Vertical chains. *Tilted chains.*

Terminal groups are represented by circles, and terminal planes by discontinuous lines. d = Long crystal spacing (2d in the case of double molecules).

It appears, therefore, that *alternation is caused by some effect resulting from a tilted chain* (see Malkin, *Nature*, 1931, **127**, 126), and the nature of this effect is illustrated by Fig. 3.

In the case of vertical chains, there is no fundamental difference in the terminal planes between odd and even chains, and the density

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* Prior to the discovery of the second crystalline form, ethyl esters appeared to be an exception to this.

of packing is the same in these planes. In the case of tilted chains, however, there is an obvious difference between even and odd. The even are separated by similar closely packed planes, whereas the odd are separated by alternate loosely and closely packed planes. The crystalline structure of odd members would therefore be expected to be less stable, which is in agreement with their lower m. p.'s.

The above views are in harmony with the work of Garner and Randall (J., 1924, **125**, 881), Garner, Madden, and Rushbrooke (J., 1926, 2491), and Garner and King (J., 1929, 1849), who have shown that carbon chains in odd and even acids have the same structure, and have pointed out that alternation is due to some difference in the arrangement of the terminal groups. Piper (*loc. cit.*) came to the same conclusions from his *X*-ray investigations.

It is clear, moreover, from Fig. 3, that owing to the occurrence of alternate wide planes, the long spacings of odd alternating compounds should be slightly longer than those of the even, whereas in the case of non-alternating compounds the spacings of odd and even should increase linearly. This is found to be the case. *X*-Ray data for any alternating series, when plotted, fall on two almost parallel straight lines separated by about 0·5—1 Å.U. according to whether single or double molecules are measured, the upper line representing the odd members.

The iodides are interesting in this connexion, since, exceptionally, those with an *odd* carbon content melt at the higher temperature. A series has therefore been prepared and examined by means of *X*-rays (see Table IV and Fig. 4). The intensity distribution indicates an arrangement of double molecules. It will be seen that this reversal of the normal behaviour with regard to m. p. is accompanied by a similar reversal in the spacings, and the line representing the *even* iodides is now the upper one. This is probably due to the large iodine atom having the same effect as an additional carbon atom, and thus giving an even chain the properties of an odd. A similar effect would be anticipated in the case of chlorides and bromides, and since there are no data in the literature, these compounds are being prepared for investigation.

TABLE IV.

Long spacings for higher alkyl iodides (*in* Å.U.).

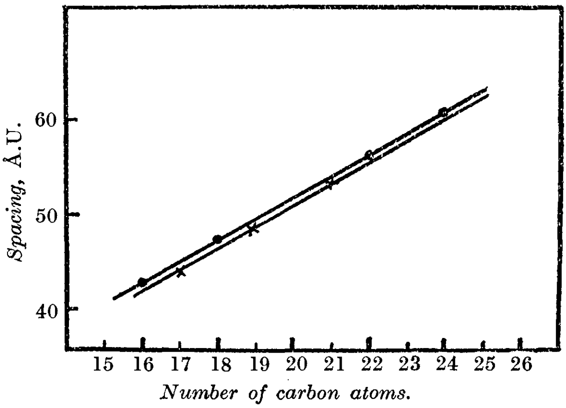
Carbon content.	16.	17.	18.	19.	21.	22.	24.
Long spacing (pressed layers).........	42·6	44·0	47·2	48·5	53·5	56·2	60·8

Other experimental facts support the view that alternation is a consequence of a tilted chain. Thus, the molecular volumes of solid odd fatty acids are greater than those of even (Garner and Ryder, J., 1925, **127**, 721), and further, the chains of odd alternating series are slightly less tilted than those of the even (see Caspari, *loc. cit.*; and compare the methyl esters, this paper). It is clear from Fig. 3 that alternate wide planes in the case of odd chains would cause both these effects.

The difference in tilt between odd and even chains possibly explains the small differences in the increment of heat of crystallisation per methylene group found in the case of odd and even acids by Garner and King (*loc. cit.*). The data available indicate that a vertical chain is more loosely packed than a tilted one; for instance, the density of nonacontane (vertical) is 0·95 (Müller, *Proc. Roy. Soc.*, 1928, *A*, **120**, 440), whilst that of stearic acid (tilted) is 1·04 (*idem, ibid.*, 1927, *A*, **114**, 547), and consequently the forces holding the chains together would be expected to be smaller in the case of the vertical chains. In agreement with this, Garner and King (*loc. cit.*) have shown that the increment in heat of crystallisation per methylene group for even acids (tilted) is 1·03 Cals., for odd acids (slightly less tilted) 0·965 Cal., and for hydrocarbons (vertical) 0·608 Cal. (Garner, van Bibber, and King, this vol., p. 1533).

FIG. 4.

X-*Ray data for normal long-chain iodides.*



Summary.

Ethyl and methyl esters of the higher fatty acids have been examined by means of *X*-rays, and the long crystal spacings determined. Two crystalline forms of the ethyl esters are shown to exist; one form is stable over a small range of temperature immediately below the m. p., but changes on cooling to the form obtained when the esters are crystallised from solvents. In the case of methyl esters, it is shown that only esters of odd fatty acids exist in two

crystalline forms, one form again being stable over a small range of temperature immediately below the m. p.

Methyl esters crystallise in layers of double molecules, and ethyl esters in layers of single molecules, and it is suggested that this is the cause of the slightly higher m. p.'s of the former.

The theory of alternation is discussed, and the view advanced that the essential feature of an alternating series is that the zig-zag carbon chain is tilted with respect to the terminal planes.

My best thanks are due to Dr. S. H. Piper for his friendly interest in the work and for much advice on *X*-ray technique.

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