CCCXLVI.—*An X-Ray Investigation of the Normal Saturated Dicarboxylic Acids and their Ethyl Esters.*

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A NUMBER of long-chain normal saturated dicarboxylic acids, $CO_2H{\cdot}[CH_2]_n{\cdot}CO_2H$, and their ethyl esters have been prepared in this laboratory (Fairweather, *Proc. Roy. Soc. Edin.*, 1925, **45**, 283; 1926, **46**, 71) and it has been confirmed (Fairweather, *Phil. Mag.*, 1926, **1**, 944) that the melting points of the normal dicarboxylic acids containing an even number of carbon atoms lie on a curve which is approximately the mirror image of the corresponding curve for the acids having an odd number of carbon atoms. On the other hand, the melting points of the diethyl esters of the acids, both odd and even, lie on one curve.

In view of these results, it was decided to investigate the dicarboxylic acids and their ethyl esters by the *X*-ray method. It was thought that information might thus be obtained regarding the

structure of these compounds, and differences discovered between the structures of the " even " and the " odd " acids.

Several of the lower members of the series of dicarboxylic acids have already been examined by means of *X*-rays by Trillat (*Compt. rend.*, 1925, **180**, 1329). He finds that the largest spacings of a number of the even acids of this series, when plotted against the number of carbon atoms in the molecule, lie on a line which is parallel to, but not coincident with, the corresponding graph for the odd acids.

Two monoethyl esters of these acids have also been examined.

EXPERIMENTAL.

The procedure adopted was that used by Shearer and his co-workers. Thin layers of the substances were pressed or melted on glass plates and formed into narrow strips about 2 mm. wide and 1 cm. long. The glass plate with its layer of material was oscillated through a small angle on each side of the zero-position for times varying from 30 minutes to 3 hours, on a Müller *X*-ray spectrometer, in the path of a beam of *X*-rays (copper K_α radiation) from a Shearer *X*-ray tube run at about 30,000—50,000 volts.

Photographs were easily obtained from the monoethyl esters, but less readily from the diethyl esters. The lower members of the acid series gave good spectra, but those with a large number of carbon atoms gave only on long exposure the lines corresponding to the spacing associated with the length of the chain. In particular, the acid $CO_2H{\cdot}[CH_2]_{32}{\cdot}CO_2H$, although it readily gave lines corresponding to the spacings 4·1 and 3·7 Å.U. characteristic of many long-chain substances (compare Müller, J., 1923, **123**, 2043; Shearer, *ibid.*, p. 3152), gave very faint reflexions from the set of planes associated with the length of the chain.

In the series of the dicarboxylic acids the following results (in Å.U.) were obtained :

Acid.	M. p.	d_1.	d_2.	d_3.	d_4.	d_5.
$C_9H_{16}O_4$	107°	9·56	4·67	3·87	3·28	—
$C_{12}H_{22}O_4$	129	13·25	4·17	3·77	2·98	4·63
$C_{13}H_{24}O_4$	113·5	13·3	4·70	3·93	3·21	—
$C_{14}H_{26}O_4$	126·5	15·4	4·13	3·71	2·97	—
$C_{16}H_{30}O_4$	125	17·4	4·14	3·67	—	4·60
$C_{18}H_{34}O_4$	124	19·55	4·12	3·69	2·95	4·63
$C_{22}H_{42}O_4$	123·8	23·6	4·13	3·75	—	—
$C_{26}H_{50}O_4$	123·5	27·8	4·16	3·74	2·97	4·62
$C_{34}H_{66}O_4$	123	35·9	4·11	3·67	2·98	4·51

The following are the results given by Trillat (*loc. cit.*) :

Acid.	M. p.	d_1.	Acid.	M. p.	d_1.
$C_4H_6O_4$	180 (185)°	4·5	$C_8H_{14}O_4$	140 (140)°	9·3
$C_6H_{10}O_4$	148 (153)	7·0	$C_9H_{16}O_4$	106 (107)	9·6
$C_7H_{12}O_4$	149 (103)	7·6	$C_{10}H_{18}O_4$	127 (133)	11·4

The figures in parentheses are the m. p.'s of the pure compounds as given by Fairweather.

An examination of these values shows that there is a considerable difference between the increment of d_1 in passing from an odd to an even acid (1·7—2·1 Å.U.) and that for the passage from an even to an odd acid (0·6—0·05 Å.U.).

In the above series, the average value of d_1 for the addition of two CH_2 groups is 2·1 Å.U. The measurements are in agreement with Müller and Shearer's conclusions as to the nature of the carbon chain in the fatty acid series (J., 1923, **123**, 3156), and the figures indicate that only one molecule lies between each pair of reflexion planes.

Regarding the difference in increment in d_1 in passing from an even to an odd acid and *vice versa*, Müller and Shearer (*ibid.*, p. 3161) suggested a type of carbon chain which, if placed with its direction of length normal to the long-spacing plane, would give rise to a difference between odd and even members of a series, the increments being of the same order as those given above. There is no *a priori* reason to assume that the molecules are arranged parallel to the normal to the reflecting plane; they may be inclined at any angle to it and the differences in the rates of increase in d_1 per CH_2 group observed from one series to another may be ascribed to a variation of this angle. This view receives direct experimental support from the measurements of single crystals of stearic acid by Müller (*Nature*, 1925, **116**, 45). He has shown that the crystal is monoclinic with a β angle of 120°, so that the c axis is inclined at 30° to the normal to the long-spacing plane (001). It is probable that the direction of length of the molecule coincides approximately with the c axis, so that it would make an angle of 30° with the normal to the plane.

With a zig-zag chain lying parallel to the normal, the addition of each CH_2 group would always result in the same increase of spacing; if the chain were tilted away from the normal, the even members would lie on one line and the odd members on an adjacent parallel line, and the increment in passing from an even to an odd acid would differ from that in passing from an odd to the next even acid—results which are in agreement with those actually found in both the fatty and the dicarboxylic acids.

As the series is ascended, the difference in d_1 between an even member and the next odd member diminishes, and thus the higher members of the series show little difference between an odd member and the even member immediately preceding it. This can be connected with the fact that the two melting-point curves of the odd and the even acids become asymptotic as the higher members of the series are reached.

The spacings d_2, d_3, d_4, and d_5 are much shorter than those associated with the length of the molecule. The spacings d_2 and d_3, which are about 4·1 and 3·7 Å.U., respectively, agree closely with those found by Müller and Shearer for the fatty acids and their esters, and are characteristic of many long-chain compounds. The two odd acids examined, *viz.*, the C_9 and the C_{13} acids, exhibit quite different values for the d_2, d_3, and d_4 spacings. The value given under d_2 agrees fairly well with the value for d_5 found for some of the even acids, and it may be that the line corresponding to the d_2 spacing is missing for the odd acids. If the spacings d_2, d_3, and d_4 are connected with the cross-section of the molecule, as is suggested elsewhere, it is clear that the structure of the odd acids differs materially from that of the even acids.

The lines corresponding to the spacings d_2 and d_3 appeared very readily in all cases, but in some cases those of the d_4 and d_5 spacings were not very distinct. In the lower members of the series the lines were well defined, but in the higher members the lines were more diffuse and so the degree of accuracy in measurement was diminished.

The crystal structure of succinic acid has been completely worked out by Yardley (*Proc. Roy. Soc.*, 1924, **105**, 451); the spacing found by her for the (010) plane, *viz.*, 4·46, is numerically equal to the value of d_1 found by Trillat for succinic acid. The spacings for the (011) and (101) planes, *viz.*, 4·71 and 3·69, respectively, are also approximately equal to the values for d_5 and d_3, respectively, found for the dibasic acid series.

In the series of the esters of the dicarboxylic acids the following results were obtained :

	M. p.	d_1.	d_2.	d_3.	d_4.	d_5.
$(CH_2)_{11}(CO_2Et)_2$	20°	22·7	—	—	—	4·63
$(CH_2)_{12}(CO_2Et)_2$	27	23·7	4·09	3·64	—	—
$(CH_2)_{16}(CO_2Et)_2$	43	28·5	4·08	3·56	—	—
$(CH_2)_{20}(CO_2Et)_2$	56	33·6	4·14	3·70	—	4·63
$(CH_2)_{28}(CO_2Et)_2$	74	43·7	4·10	3·69	—	4·53
$(CH_2)_{32}(CO_2Et)_2$	80	49·0	4·17	3·71	—	4·63

As mentioned above, the melting points of all these esters lie on one curve. The value given for d_1 for the first ester in the list is doubtful. Since the melting point was low (20°), the photograph was not a good one, and lines corresponding to spacings of 22·7 and 23·9 were obtained. It is our intention to investigate this ester again under more suitable conditions of temperature.

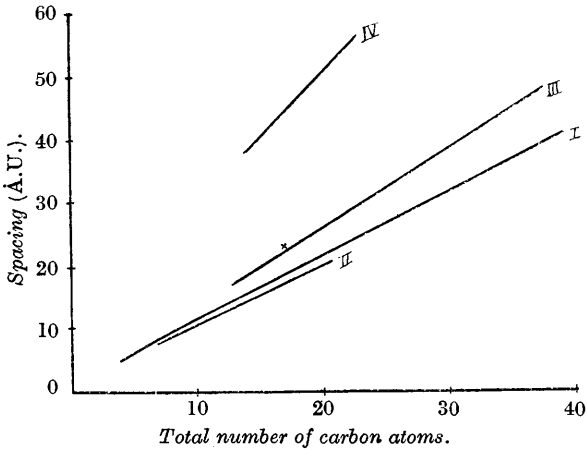
For the diethyl esters the increment in d_1 is 1·2—1·3 Å.U. per CH_2 group. These figures indicate that only one molecule lies between each set of reflexion planes. The increment in length for each carbon atom added to the chain is greater for the esters

than for the corresponding acids, and the structure is probably similar to that assigned by Müller and Shearer to the alcohols. The one odd ester examined fits into the same series as the even esters, and this is in agreement with the fact that the melting points all belong to one series. The spacings for d_2, d_3, and d_5 were the same as in the case of the acids.

The following results were obtained for the monoethyl esters of the dicarboxylic acids :

	M. p.	d_1.	d_2.	d_3.
$CO_2Et\cdot(CH_2)_{12}\cdot CO_2H$	55°	42·1	4·14	3·66
$CO_2Et\cdot(CH_2)_{16}\cdot CO_2H$	71	50·5	4·12	3·66

FIG. 1.



I *Dicarboxylic acids (even members).* II *Dicarboxylic acids (odd members).* III *Diethyl esters of the dicarboxylic acids (even members).* × *Diethyl ester of a dicarboxylic acid (odd member).* IV *Monoethyl esters of the dicarboxylic acids (even members).*

The odd-order reflexions from the d_1 planes were much stronger than the even-order reflexions. As was expected from the presence of a carboxyl group at one end of the molecule and an ethyl group at the other, the values obtained for d_1 are in agreement with the assumption that the reflexion planes associated with d_1 are separated by a distance approximating to twice the length of the molecule. The increment in d_1 per CH_2 group is 2·1 Å.U. or 1·05 Å.U. per molecule. This would indicate that the monoethyl esters have the same type of chain as the acids.

The figure shows the results plotted graphically along with those given by Trillat (*loc. cit.*). The actual rate of increase per CH_2 group in the dibasic acid series is very nearly the same as that found by Müller for the fatty acids, after allowing for the double layer in

the latter case, whilst the ethyl esters show a rate of increase similar to that of the corresponding esters of the fatty-acid series. It will also be noted that, for the dicarboxylic acids with a small number of carbon atoms in the chain, the graph departs from the straight line.

In view of the difficulty in obtaining good lines corresponding to the d_1 spacing in the case of the C_{34} acid, the following additional experiments were tried. Instead of pressing or melting the acid on a piece of glass, a large crystal of rock salt was used. When the acid was melted on, distinctly better photographs were obtained than when glass was used as the supporting medium. When the acid was merely pressed on, the results were no better than with glass. The polar character of the rock salt apparently caused more of the molecules to be oriented in the appropriate direction. When a fused silica plate was used in place of glass in the case of the C_{18} acid, the results were not quite so good as those obtained when glass was employed. An additional advantage in using rock salt is that its reference lines can be obtained on the same plate, thus facilitating the measurement of the plate.

Conclusions.

This investigation shows that the even and the odd members of the dicarboxylic acids belong to two distinct series. So far as the results go, the odd and the even members of the diethyl esters of these acids form one series. From the spacings observed, it is concluded that the monoethyl esters contain two molecules, whilst the other substances examined contain only one molecule between successive reflecting planes.

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