

AN X-RAY INVESTIGATION OF THE SERIES OF  
NORMAL SATURATED DICARBOXYLIC ACIDS AND  
RELATED COMPOUNDS.

by

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## Introduction.

In recent years several papers have appeared dealing with the investigation by means of X-rays of aliphatic organic compounds. These investigations have been productive of information which has been of extreme interest to the chemist as well as to the physicist and crystallographer.

In particular I would refer to the work of Müller, Shearer, and Saville<sup>1</sup>, who have examined the following series of compounds:-

Fatty acids	- $\text{CH}_3(\text{CH}_2)_n\text{COOH}$ .
Fatty acid esters	- $\text{CH}_3(\text{CH}_2)_n\text{COO}(\text{CH}_2)_m\text{CH}_3$ .
n-Hydrocarbons	- $\text{CH}_3(\text{CH}_2)_n\text{CH}_3$ .
Ketones	- $\text{CH}_3(\text{CH}_2)_n\text{CO}(\text{CH}_2)_m\text{CH}_3$ .

They have shown that the higher members of all these series exist in the crystal in the form of long chains, the unit cell being in the nature of a long prism, an arrangement suspected by chemists previous to the advent of the X-ray method of investigation. It would seem from their results that different series have different types/

<sup>1</sup> Müller J.C.S. 1923 vol. 123 p. 2043.

Shearer J.C.S. 1923 vol. 123 p. 3152.

Müller & Shearer J.C.S. 1923 vol. 123 p. 3156.

Saville & Shearer J.C.S. 1925 vol. 127 p. 591.

Müller & Saville J.C.S. 1925 vol. 127 p. 599.

types of chain structure. An attempt has been made by Müller and Shearer (*loc.cit.*) to deduce the various possible types of chain from a knowledge of the diameter of the carbon atom (1.5 Å.U.), and its tetrahedral arrangement in the diamond structure. Their theory seemed to be a close approximation to the truth when applied to the series of fatty acids and fatty esters, but the investigation of the hydrocarbon series has shown that it requires modification.

I have studied several more series of aliphatic compounds and it is my purpose in the succeeding pages to give the results of my work, together with any theoretical treatment which may arise from these results.

It is unnecessary for me to describe in detail the conclusions of these investigators whose papers I have mentioned, or to examine their experimental method in this introduction, as the information they have put before us now forms an important part of physical chemistry in the domain of molecular structure.

A large number of acids of the dicarboxylic acid series have been prepared in Edinburgh University as well as several diethyl and monoethyl esters of these acids.<sup>1</sup> In view of the interest attached to the above-mentioned/

<sup>1</sup>Fairweather Proc.Roy.Soc.Edin. 45 p.283 (1925)

" " " " " 46 p. 71 (1926)

-mentioned X-ray investigations, and also to the chemical and physical properties of the substances themselves, it was decided to examine them by means of X-rays. Before going to the results of my investigations it would be well to consider first our present knowledge of the physical properties of the dicarboxylic acids.

As is found in many homologous series, the series of normal saturated dicarboxylic acids affords an excellent example of alternation in properties between the odd and even members. This alternation is very much in evidence in the melting points of the acids. If we plot the melting points against the number of methylene groups in the chain we obtain two smooth curves, one for the odd and one for the even acids.<sup>1</sup> The odd acids lie upon an ascending curve, whilst the even acids lie upon a descending curve, the two curves becoming asymptotic, it would seem, as the higher members of the series are reached. The following table shows the melting points of the odd and even members/

<sup>1</sup>

Fairweather Phil.Mag.1926.1.p. 944.



members:-

Even Acids.

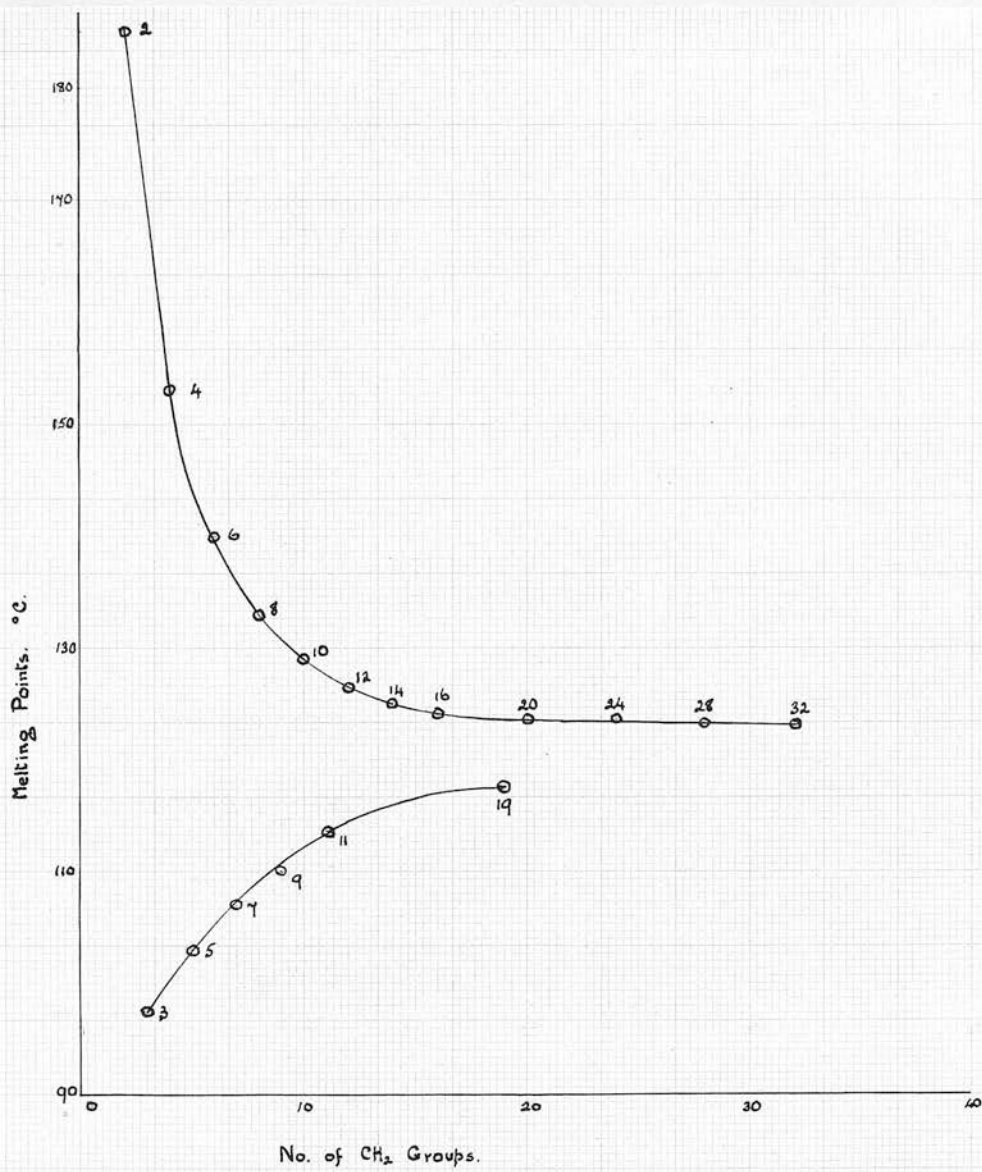
	n	M.P.°C		n	M.P.°C
HOOC(CH <sub>2</sub> ) <sub>2</sub> COOH	2	185	HOOC(CH <sub>2</sub> ) <sub>14</sub> COOH	14	125
HOOC(CH <sub>2</sub> ) <sub>4</sub> COOH	4	153	HOOC(CH <sub>2</sub> ) <sub>16</sub> COOH	16	124
HOOC(CH <sub>2</sub> ) <sub>6</sub> COOH	6	140	HOOC(CH <sub>2</sub> ) <sub>20</sub> COOH	20	123.75
HOOC(CH <sub>2</sub> ) <sub>8</sub> COOH	8	133	HOOC(CH <sub>2</sub> ) <sub>24</sub> COOH	24	1235
HOOC(CH <sub>2</sub> ) <sub>10</sub> COOH	10	129	HOOC(CH <sub>2</sub> ) <sub>28</sub> COOH	28	12325
HOOC(CH <sub>2</sub> ) <sub>12</sub> COOH	12	126.5	HOOC(CH <sub>2</sub> ) <sub>32</sub> COOH	32	123

Odd Acids.

	n	M.P.°C		n	M.P.°C
HOOC(CH <sub>2</sub> ) <sub>1</sub> COOH	1	(132)	HOOC(CH <sub>2</sub> ) <sub>9</sub> COOH	9	110
HOOC(CH <sub>2</sub> ) <sub>3</sub> COOH	3	97.5	HOOC(CH <sub>2</sub> ) <sub>11</sub> COOH	11	113.5
HOOC(CH <sub>2</sub> ) <sub>5</sub> COOH	5	103	HOOC(CH <sub>2</sub> ) <sub>13</sub> COOH	13	117.5
HOOC(CH <sub>2</sub> ) <sub>7</sub> COOH	7	107			

(n represents the number of methylene groups.)

Representing these values graphically we obtain the following very interesting curves:-



Another physical property which shows the alternation between the odd and even members is the solubility in water.<sup>1</sup>

100 ccs. of the aqueous solution at 20°C contain:-

<u>Even Acids.</u>			<u>Odd Acids.</u>		
	n	grams.		n	grams.
Oxalic	0	8.6	Malonic	1	73.5
Succinic	2	5.8	Glutaric	3	63.9
Adipic	4	1.4	Pimelic	5	5.0
Suberic	6	0.16	Azelaic	7	0.24
Sebacic	8	0.10			

In addition to these, it is a well-known fact that the even members are produced by the direct oxidation of suitable substances, whereas the yield of the odd members is very small, the substance as a rule being oxidised to the next lower even member.

These points will suffice to indicate the alternation in this series. It is of interest to note that in both the melting points and the solubilities, the alternation becomes less obvious as we go up the series.

In general, it has been observed that the most pronounced cases of alternation in homologous series occur/

<sup>1</sup>Challenor & Thorpe J.C.S. 1923 vol.123p.2482.

occur where there is a terminal polar group such as carboxyl in the molecule. Also, the alternation is most marked in the properties of the substances in the crystalline state, such as melting points, heats of crystallisation, solubilities, and molecular volumes.<sup>1</sup> Hence it is most probable that the explanation of such alternation is to be found in the crystal structure of the substances.

<sup>1</sup> Garner & Ryder J.C.S. 1925 vol. 127. p.720.

Garner & Randall J.C.S. 1924 vol. 125. p. 881.

Apparatus.

As the apparatus is well known, I need only give a short description of the essential parts.

X-ray tube. The tube used was of the Shearer pattern and was fitted with a copper anticathode. The copper anticathode was employed throughout the investigations. The anode and anticathode were water-cooled, the same stream of water being used for both. The aluminium cathode was cooled by a small thermo-syphon and heating was further retarded by a cylindrical brass vessel containing water.

The tube was evacuated by the following system of pumps. The first stage was obtained with a double-acting oil pump. This was connected through a 'Winchester' bottle acting as a reservoir to two mercury pumps of simple design placed in series, and thence to the X-ray tube. The mercury pumps constitute the second stage. Connection was also made direct from the reservoir to the X-ray tube. In this lead was placed a length of glass capillary tubing of very fine bore with two screw clips, one at either end. By this means the vacuum could be regulated by a very fine adjustment. As the air is removed from the tube by the pumps more air is introduced through this leak, and the tube/



tube works steadily when the amount of air removed in unit time equals the amount introduced, i.e. after the desired state of vacuum has been reached.

All air and water connections were made with composition tubing, the minimum amount of rubber tubing being used. In the neighbourhood of the mercury pumps glass tubing was employed. All joints were made vacuum-tight by means of a paste of ordinary red sealing-wax and methyl alcohol.

Since the X-ray tube has considerable rectifying properties it can be excited from a transformer without recourse to any other rectifier. The primary of the transformer was connected to the 230 volt (A.C.) circuit through a variable resistance, the current through the primary being about 5 amperes when the tube was 'soft'. When the tube was generating X-rays in a steady manner the current diminished spontaneously to 2-3 amperes. The transformer was designed to step up the voltage from 230 to 64,000 volts, the actual voltage employed depending on the state of the vacuum. The anticathode end of the tube was earthed, the corresponding terminal of the transformer secondary circuit being connected to a different earth. The other secondary terminal of the transformer was connected to the/

the cathode end of the tube by a wire free from bends. The minimum potential required to excite the characteristic copper radiation is approximately 9,000 volts, but the tube was run at about 40,000 volts and 5 M.A.

The tube was dismantled regularly for cleaning. The glass part became periodically coated internally with a thin metallic film which was removed with nitric acid. In addition the aluminium cathode became pitted, so that it had to be refaced at regular intervals.

As a rule the tube worked perfectly, any variations from its smooth running being usually due, either to fluctuation in the gas pressure, which affected the rate of pumping, or to over-heating of the cathode.

Spectrograph. A Müller X-ray spectrograph was used. Since it is one of Hilger's standard instruments, a description need not be given here. The width of slit employed throughout my investigations was 0.19 mm. The distance from the outer face of the slit to the axis of rotation of the crystal table was made equal to the distance from the axis of rotation to the centre of the photographic plate, in order to obtain a well-defined photograph. These distances were measured as accurately as possible with a steel rule and the result verified by an examination of a rock salt crystal with the apparatus as explained later.

Experimental Method.

The substances to be investigated were in the powder form. A small quantity of the powder was pressed on a small glass plate. This was mounted on the crystal table with plasticene, and the crystal table rotated through a small angle while being subjected to the action of the X-rays. The reflected radiation was received on a photographic plate placed directly behind. After the usual manner reflections were obtained on both sides of the primary beam. The relative positions of slit and crystal table were so adjusted that there was no overlapping of the primary beam for the two zero positions of the crystal table. The exposure required to obtain a well-defined system of lines varies with the substance under examination. The higher members of all series require a longer exposure than the lower members.

The plates were measured by means of a steel rule, distances being estimated to 0.01 cm. To facilitate the measurement, the plates were placed on a sheet of milk glass with an electric lamp beneath. This arrangement serves to emphasise the blackness of the lines with respect to the unaffected parts of the plate.

Calculation of Results.

For the calculation of results we have to make use of two expressions -

$$2l = 2t \tan 2\theta, \quad (1)$$

and

$$n\lambda = 2d \sin \theta \quad (2)$$

The significance of the terms is as follows:-

$\lambda$  = wave-length of X-radiation

$d$  = crystal spacing

$n$  = order of spectrum

$\theta$  = deviation, i.e. angle between directions of primary and reflected beams.

$2l$  = distance between images corresponding to both orientations of the crystal.

$t$  = distance of plate from axis of rotation of crystal.

The first expression is a relation connecting deviation and linear displacement, and the second a relation connecting order of reflection and wave-length with deviation and crystal spacing. The derivation of the first expression is obvious, and the second is the well-known condition for reflection of ordinary light from piles of parallel plates, and was first applied to X-ray problems by W. L. Bragg.

Using a rock salt crystal we can calculate  $t$  as mentioned above (p.10) since we know accurately the spacing/

spacing of its (100) planes.

$$2d \text{ for rock salt} = 5.628 \text{ \AA.U.}$$

$$\lambda = 1.541 \text{ \AA.U. (Copper K}_{\alpha}\text{ radiation).}$$

A knowledge of these two quantities gives us the value of  $\theta$  by means of (2), and if we measure  $2l$  and introduce this value of  $\theta$  into (1) we obtain  $t$ .

$$\text{By direct measurement } t = 7.03 \text{ cms.}$$

$$\text{By above method } t = 7.025 \text{ cms.}$$

This value of  $t$  is employed in all the calculations of spacings made in this work.

Note:- This method of verification of  $t$  only holds, of course, when the apparatus is correctly adjusted.



Experimental.

As was found in the researches of Müller, Shearer, Saville, etc., on several series of long-chain compounds, there is one plane in the crystal which has a much larger spacing than any of the others, and the magnitude of this spacing is very simply related to the number of carbon atoms in the molecule. As we move up any of these series, step by step, by the continued addition of a  $\text{CH}_2$  group, this spacing increases correspondingly. It is obvious that the molecules in the crystal must be oriented lengthwise between these planes, as no other orientation would give rise to the above result. The direction of length of the molecular chain is not necessarily perpendicular to this plane, but for any one series the angle which this direction of length makes with the normal to the plane remains approximately constant.

Several of the lower members of the series of dicarboxylic acids have already been examined by means of X-rays by Trillat.<sup>1</sup> He found that the principal 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./

<sup>1</sup> Compt. rend. 1925, 180, p.1,329.

acids.

His results are as follows:-

Acid	M.P.°C	d, (ÅU)
$\text{HOOC}(\text{CH}_2)_1\text{COOH}$	180(185)	4.5
$\text{HOOC}(\text{CH}_2)_2\text{COOH}$	148(153)	7.0
$\text{HOOC}(\text{CH}_2)_3\text{COOH}$	149(103)	7.6
$\text{HOOC}(\text{CH}_2)_4\text{COOH}$	140(140)	9.3
$\text{HOOC}(\text{CH}_2)_5\text{COOH}$	106(107)	9.6
$\text{HOOC}(\text{CH}_2)_6\text{COOH}$	127(133)	11.4

The figures in parentheses are the melting points of the pure compounds as given by Fairweather (loc.cit.)

I found that 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  $\text{HOOC}(\text{CH}_2)_{32}\text{COOH}$ , although it readily gave lines corresponding to the spacings 4.1 and 3.7 ÅU., characteristic of many long-chain substances (cf. Müller, Shearer etc. loc.cit.), gave very faint reflections from the set of planes associated with the length of the chain.

Following/

Following are the results obtained:-.

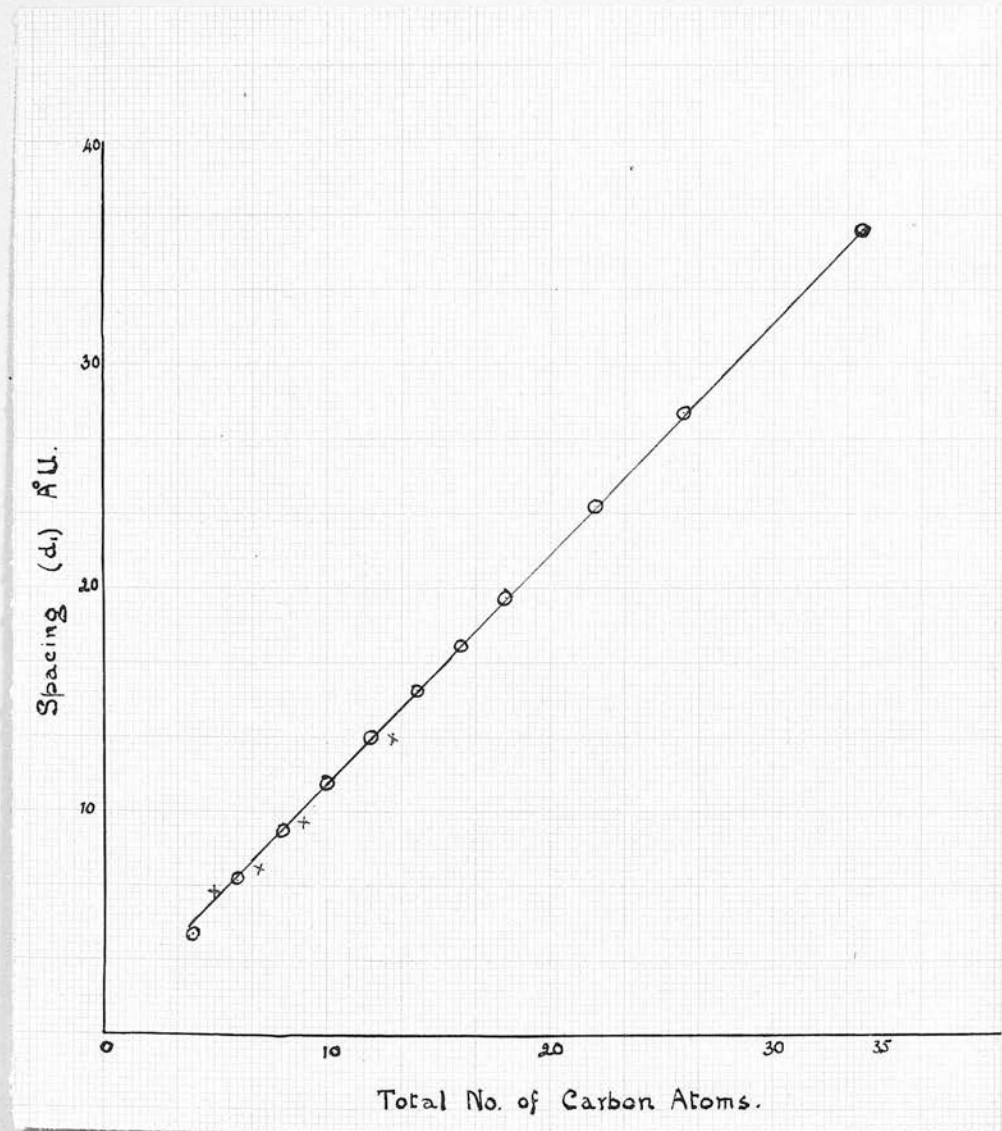
ACID	M.P.°C.	d <sub>1</sub>	d <sub>2</sub>	d <sub>3</sub>	d <sub>4</sub>	d <sub>5</sub>
HOOC(CH <sub>2</sub> ) <sub>1</sub> ·COOH	132	3.77?	4.18	3.85	3.00	4.79
HOOC(CH <sub>2</sub> ) <sub>2</sub> ·COOH	185	4.43?	-	3.74	-	-
HOOC(CH <sub>2</sub> ) <sub>3</sub> ·COOH	97.5	6.40	4.09	3.72	3.84 } 3.27 }	4.54
HOOC(CH <sub>2</sub> ) <sub>4</sub> ·COOH	153	6.90	4.15	3.83 } 3.70 }	3.32 } 2.88 }	4.60
HOOC(CH <sub>2</sub> ) <sub>5</sub> ·COOH	103	7.65	-	3.78	3.68	4.64
HOOC(CH <sub>2</sub> ) <sub>6</sub> ·COOH	140	9.05	4.18	3.65	2.98	4.66
HOOC(CH <sub>2</sub> ) <sub>7</sub> ·COOH	107	9.56	-	3.87	3.28	4.67
HOOC(CH <sub>2</sub> ) <sub>8</sub> ·COOH	133	11.19	4.15	3.75	2.99	4.63
HOOC(CH <sub>2</sub> ) <sub>9</sub> ·COOH	129	13.25	4.17	3.77	2.98	4.63
HOOC(CH <sub>2</sub> ) <sub>10</sub> ·COOH	113.5	13.80	-	3.93	3.21	4.70
HOOC(CH <sub>2</sub> ) <sub>12</sub> ·COOH	126.6	15.40	4.13	3.71	2.97	-
HOOC(CH <sub>2</sub> ) <sub>14</sub> ·COOH	125	17.40	4.14	3.67	-	4.60
HOOC(CH <sub>2</sub> ) <sub>16</sub> ·COOH	124	19.55	4.12	3.69	2.95	4.63
HOOC(CH <sub>2</sub> ) <sub>20</sub> ·COOH	123.8	23.60	4.13	3.75	-	-
HOOC(CH <sub>2</sub> ) <sub>28</sub> ·COOH	123.5	27.80	4.16	3.74	2.97	4.62
HOOC(CH <sub>2</sub> ) <sub>32</sub> ·COOH	123	35.90	4.11	3.67	2.98	4.51

Discussion.

The  $d_1$  spacing is the spacing we associate with the length of the molecule. The columns  $d_1$ ,  $d_3$ ,  $d_4$ ,  $d_5$ , are denoted by the term 'side spacings', and it is believed that they are measures of the cross-section of the molecule. The spacings  $d_1$  and  $d_3$ , at least for the even acids remain practically constant throughout the series, their average values being 4.15 and 3.71 ÅU. These spacings are characteristic of many series of long chain compounds. The average value for  $d_4$  is 2.96 and for  $d_5$ , 4.63 ÅU. All the lower acids show side spacings characteristic of both odd and even acids. Of all the side spacings only  $d_5$  is common to both odd and even acids.

If we plot the values of  $d_1$  against the total number of carbon atoms we find that the relation between them is linear. The lower members diverge more or less from this relationship. From my investigations, I cannot agree with Trillat's conclusion which I have mentioned previously (page 14).

Note The complete crystal structure of succinic acid has been worked out by Yardley (Proc. Roy. Soc., 1924, 105, 451). She found a spacing of 4.46 ÅU which is equal to that found by me (4.43 ÅU) and which I have called  $d_2$ . This is a second order reflection, the calculated spacing being 8.9 ÅU, so that succinic acid does not seem to be entirely comparable with the higher members of the series.



Note:- The odd acids are marked in red.



I will consider first the  $d_1$  spacing with special reference to the higher members of the series. As we move up the series this spacing increases, but there is a considerable difference in passing from an odd to the next even acid, than in passing from an even to the next odd acid. The average increment in  $d_1$  for the addition of two  $\text{CH}_2$  groups is  $2.1 \text{ \AA}$  or  $1.05 \text{ \AA}$  for one  $\text{CH}_2$  group. This closely resembles the increment per  $\text{CH}_2$  group -  $1 \text{ \AA}$  - found by Müller in the fatty acid series. Hence it would be permissible to say that the dicarboxylic acids and the fatty acids have the same type of chain structure. The figures in the  $d_1$  column also indicate that only one molecule lies between successive reflecting planes, since the diameter of the carbon atom is  $1.5 \text{ \AA}$ .

$d_1$  considerable  
^ greater.

Let us compare the  $d_1$  spacings of the following three groups of acids. ( $n$  denotes the number of  $\text{CH}_2$  groups).

Acid	$n$	$d_1$	Difference
Adipic	4	690	
Pimelic	5	765	0.75
Suberic	6	905	1.40
Suberic	6	905	
Azelaic	7	956	0.51
Sebacic	8	1119	1.63

Acid	n	d	Difference
Decane dicarboxylic	10	1325	
Brassylic	11	1330	005
Dodecane dicarboxylic	12	1540	210

We see that the increment in  $d_1$  going from an even acid to the next higher odd acid is always less than the increment in going from an odd acid to the next higher even acid. Further, the former increment diminishes as we move up the series, and the latter consequently increases, since the increase for  $2\text{CH}_2$  groups is  $2 \cdot 1\text{ÅU}$ , until we find that Brassylic acid which contains 11  $\text{CH}_2$  groups has approximately the same  $d_1$  spacing as decane dicarboxylic acid, which contains 10  $\text{CH}_2$  groups. This point is interesting in that it shows the parallelism between the results of this X-ray investigation and the physical properties such as melting points and solubilities mentioned in the introduction. It is unfortunate that I do not have a specimen of the acid  $\text{HOOC}(\text{CH}_2)_{11}\text{COOH}$  which has been prepared. An X-ray examination of this acid would, I feel sure, greatly assist in the matter of differentiation between odd and even members.

It would appear that the odd acids have a different chain structure from the even acids. This statement/

statement receives support from the fact that the side spacings of the odd acids differ from those of the even acids, as can be seen from the table of results. The odd acid molecules seem to be more compact, as if a pressure were exerted on them in a vertical direction causing longitudinal contraction with consequent lateral expansion. If we could carry the investigations further, we might have one of three possibilities. Take, for example, the 19 acid. Its  $d_1$  spacing might be equal to or shorter than the  $d_1$  spacing of the 18 acid, or it might be longer by an amount less than the difference in  $d_1$  between the 10 and 11 acids, until in the limit the spacing of an odd acid would be exactly equal to that of the next lower even acid. Unfortunately we cannot verify or refute either of these statements. We have, however, a similar state of affairs in the melting points of these acids. The two curves for odd and even acids may meet and cross each other, or they may meet and run together, or thirdly, they may remain asymptotic. I am inclined to adhere to the last of these possibilities from the character of the curves. From the parallelism between the two properties - length of chain and melting points - I think we can rule out the possibility that the  $d_1$  spacing of an odd acid will ever be smaller than that of the next lower even acid. This leaves/

leaves two alternatives, but, only by continuing investigations by X-rays, of odd acids further up the series, can we hope to decide between the two. The difficulties of preparing such compounds are practically insurmountable.

It has been shown that the chain structure of the odd acids is different from that of the even acids, hence we may say that this is the cause, or at least one of the causes, of the alternation in physical properties.

The melting-point of a crystalline solid may be regarded as being largely determined by the magnitude of the forces of cohesion within the crystal.<sup>1</sup> I take this statement to include forces within the molecule and forces between molecules in the crystal. We would expect the forces within a molecule of an odd acid to differ from those in the molecule of an even acid owing to their difference in chain structure, and this will have an effect on their respective melting points, but I do not think this would account to any appreciable extent for the very pronounced alternation observed in the dicarboxylic acid series. Then let us examine the forces between molecules in a crystal. Garner and his co-workers/

<sup>1</sup> Bragg 'X-rays & Crystal Structure' 4<sup>th</sup> ed.p.191.



co-workers (loc.cit.), from their investigations on heats of crystallisation etc. in the fatty acid series, and assisted by Müller and Shearer's X-ray investigations of these compounds, have given an explanation of alternation in this series. They conclude that the alternation in properties observed in the fatty acid series is entirely due to different arrangements of the carboxyl groups in the odd and even acids. (There is no variation in cross section in this series). This seems a sound explanation on the theory that the melting point is determined by the magnitude of the forces between molecules in a crystal. In the fatty acids there are two molecules between successive reflection planes and they are oriented in opposite directions, the carboxyl group of the one being oriented towards the carboxyl group of the other. Now, if these carboxyl groups have different structures in the odd and even acids, we would expect that the forces of attraction between two molecules would be different in the two cases. Hence the melting points and other physical properties of the odd and even acids would belong to two distinct series. Now let us apply this theory to the dicarboxylic acids. Here there is only one molecule between successive reflecting planes. <sup>cf. p. 46</sup> Nevertheless, there is still a strong/



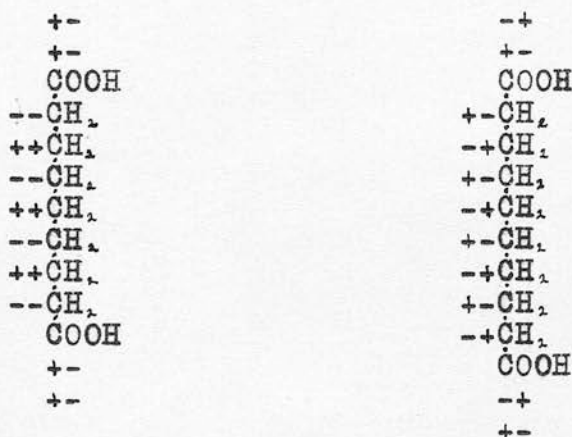
strong attraction between a carboxyl group of one molecule and a carboxyl group of the neighbouring molecule, but owing to the presence of a carboxyl group at each end of a dicarboxylic acid molecule, it is attracted at both ends by a similar molecules (Possibly also, the two carboxyl groups in one molecule have an attraction for each other, which is communicated along the chain of  $\text{CH}_2$  groups.) Hence Garner's theory would apply equally well to the dicarboxylic acid series. As a rider to Garner's theory I would add that the difference in structure of the terminal groups in the odd and even acids is caused by the difference in the nature of the hydrocarbon chain.

To summarise the preceding, alternation is due in part to a difference in the structure of the terminal groups, and in part to difference in the structure of the hydrocarbon chain.

The higher dicarboxylic acids, in spite of their long hydrocarbon chains, are not in the least flaky like the fatty acids, but are quite hard and brittle. The flakiness and greasiness of the fatty acids has been attributed to the fact that the two terminal groups in the double molecule are  $\text{CH}_3$  groups which have very little or no attractive force for other molecules. This/

This fact supports the view of the existence of strong cohesive forces at the terminal groups of the dicarboxylic acids.

In the domain of organic chemistry, Challenor and Thorpe, (*loc.cit.*) while looking for an explanation of the greater chemical reactivity of the odd dicarboxylic acids noticed that the even acids have crossed polarities, while the odd acids have concordant polarities. e.g. azelaic and sebacic acids.



The alternate positive and negative charges induced from the carboxyls at either end on each carbon atom of the chain reinforce each other in the odd members and neutralise each other in the even members. As mentioned by Fairweather (*loc.cit.*), the mutual attraction of the carboxyl groups in the odd series may be diminished by the presence of like charges upon them, in which case their melting points would be lower than those in the/

the even series. He continues, that, on this assumption the decrease in melting point as the even series is ascended may be explained by the fact that as the chain is lengthened, the transmission of the alternate polarity effect is progressively weakened and the terminal carboxyl carbons become gradually free from the influence of the carboxyl group at the other end of the chain. If this view were correct, it would be expected that in compounds in which the chain is very long, there would be little or no difference between the melting points of consecutive odd and even acids, which is the case.

While this view seems to fit the facts, I am inclined to be sceptical about it. The theory of alternate polarities, as used by organic chemists, seems to me to lack a physical basis, and merely provides a convenient notation which serves as a cloak to our comparative ignorance of atomic and molecular structure. In any case, the polarity theory in its present form, has not been employed with any success to compounds containing single bonds only.

Regarding the difference in increment in  $d_1$  in passing from an even to an odd acid and vice versa, Müller and Shearer (loc.cit.) suggested a type of carbon chain which, if placed with its direction of length normal/

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. I do not think, however, that this chain would explain the fact that the even and odd acids <sup>seem to</sup> have <sup>^</sup> different cross-sections.\*

Considering chain structures in general, Müller and Shearer designed their specimen chains on the assumption that the lines joining the centres of adjacent atoms make the tetrahedral angle with each other. It seems to me that this angle is not necessarily found in these hydrocarbon chains. In a molecule in which four identical groups of atoms are attached to a carbon atom by its four valencies, we expect the angle between the valency directions of this carbon atom to be the tetrahedral angle, but in a molecule in which the four groups are not equal we would expect a variation from this angle. Will not the angle between any two valencies of a carbon atom be a function of the relative molecular volumes of the groups attached to it? This is the conclusion arrived at by Ingold in his work on the effect of substituents on reactivity in chemical reactions. For example, take Brassylic acid and consider the 6th or middle carbon atom of the chain. Its four valencies are attached to two hydrogen atoms and/

\* nor would it explain why  $d_1$  for an odd acid approaches  $d_2$  for the next lower even acid as the series is ascended.



and to two  $\text{HOOC}\cdot\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2-$  groups. The angle between the two valencies attached to these two hydrocarbon groups will adopt a definite value, dependent upon the conditions I have mentioned. Now, consider the carbon atom next to the central carbon atom. It is attached to two hydrogen atoms, a  $\text{HOOC}\cdot\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2$  group and a  $\text{HOOC}\cdot\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2$  group. Hence if we regard the centre carbon atom as fixed and attached to the 5th carbon atom at a fixed angle, this 5th carbon atom will make a slightly different angle with the 4th carbon, and so on. This variation would be progressive along the chain. Also the variation would become more pronounced in the low members of a series, and so might serve to explain the deviations in the linear relationship connecting observed spacing with number of carbon atoms in the chain.

I do not suggest that this is the only determining factor in chain formation, but it seems to me that it will determine, to a certain extent, the nature of the chain which an aliphatic compound will adopt. I do not think this theory would be contrary to the observed experimental fact of constant increment in a series of compounds. After all, the so-called constant increment is not absolutely constant. Deviations from steady increment may be attributed to experimental error, such as/



as inaccurate measurement, but we cannot be sure that this is the cause. If my suggestion were the main determining factor then there would be only one type of chain, but no two substances would have exactly the same chain.

To expand this idea and to apply it to any one series would probably lead to conclusions which would be in conflict with the results of its application to other series, for we do not know the effect of other determining factors in chain formation.

In these pages I have brought forward several suggestions, my own and those of others, to explain alternation in properties in the dicarboxylic acid series, and discussed them at some length. It seems that any solution must essentially be entirely theoretical, and while it may be supported by several experimental facts, we cannot hope, in the light of our present knowledge at least, to trace with certainty the chain structure of a substance, nor to write down quantitatively the effects of the various agencies working to produce this chain.

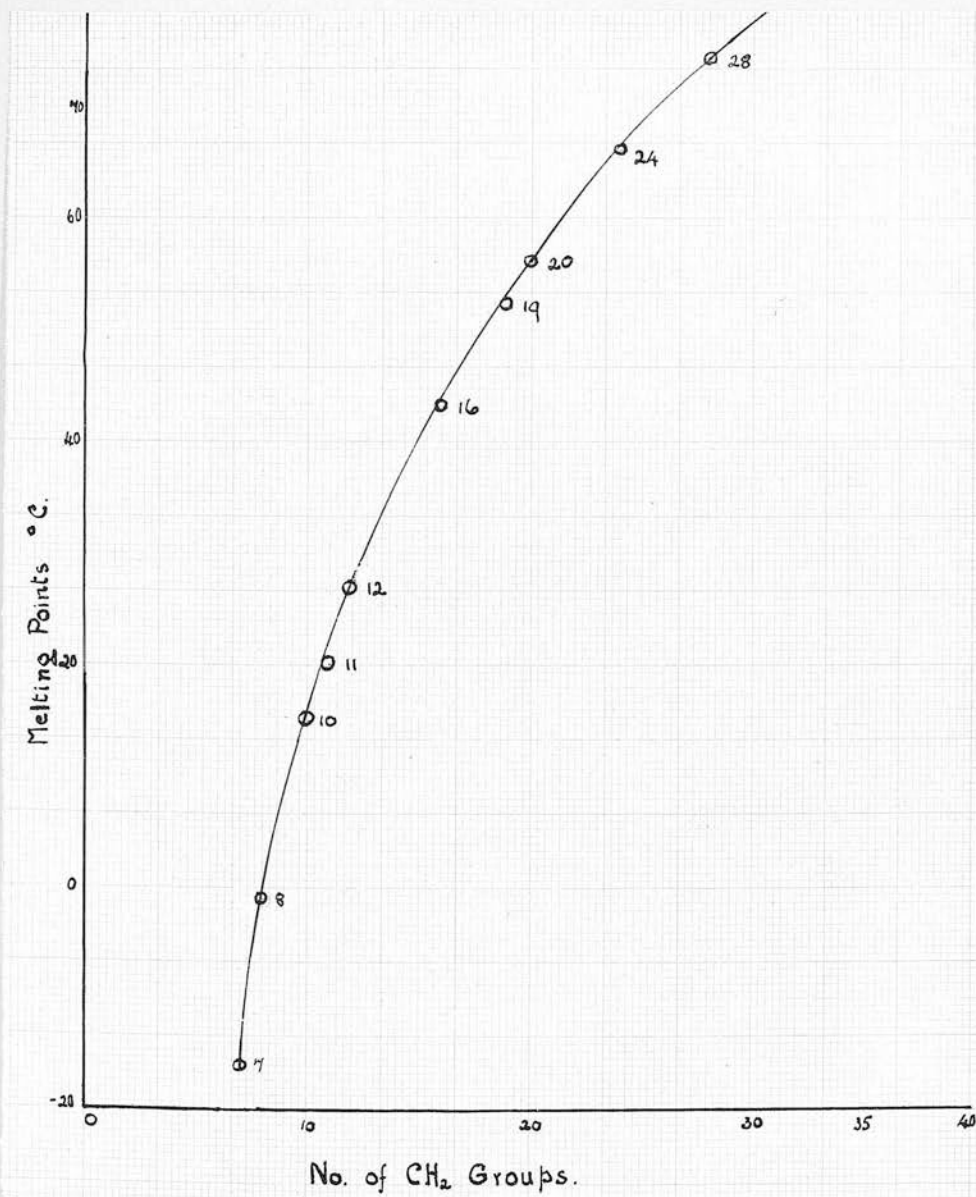
The Diethyl Esters of the Dicarboxylic Acids.

We come now to the series of diethyl esters of the dicarboxylic acids. Several of these were prepared in the pure state by Fairweather (loc.cit.), and their melting points determined. In these compounds there is no terminal polar group, and the melting-points show no alternation whatever; they rise in quite a normal manner as the series is ascended, odd and even members alike lying on the same smooth curve.

Following is a list of their melting-points:-

Esters.	n	M.P.°C.
$\text{CH}_3\text{OOC}(\text{CH}_2)_7\text{COOCH}_3$	7	-16
$\text{CH}_3\text{OOC}(\text{CH}_2)_8\text{COOCH}_3$	8	-1
$\text{CH}_3\text{OOC}(\text{CH}_2)_{10}\text{COOCH}_3$	10	15
$\text{CH}_3\text{OOC}(\text{CH}_2)_{11}\text{COOCH}_3$	11	20
$\text{CH}_3\text{OOC}(\text{CH}_2)_{12}\text{COOCH}_3$	12	27
$\text{CH}_3\text{OOC}(\text{CH}_2)_{16}\text{COOCH}_3$	16	43
$\text{CH}_3\text{OOC}(\text{CH}_2)_{19}\text{COOCH}_3$	19	52
$\text{CH}_3\text{OOC}(\text{CH}_2)_{20}\text{COOCH}_3$	20	56
$\text{CH}_3\text{OOC}(\text{CH}_2)_{24}\text{COOCH}_3$	24	66
$\text{CH}_3\text{OOC}(\text{CH}_2)_{28}\text{COOCH}_3$	28	74
$\text{CH}_3\text{OOC}(\text{CH}_2)_{32}\text{COOCH}_3$	32	80

In this graph the melting points are plotted against the number of  $\text{CH}_2$  groups in the hydrocarbon chain:-



Note. Since writing this, I have found in a recent paper (Helv. Chim Acta 1926 p 264) that a very slight alternation is found in the M.P.'s of these odd and even esters.

The esters for which  $n = 7, 8,$  and  $10$  could not be investigated by means of X-rays with the apparatus already described unless a special cooling chamber were employed, as they are liquid at ordinary temperatures.

In this series the following results were obtained:-

	M.P. <sup>o</sup> C.	$d_1$	$d_2$	$d_3$	$d_4$	$d_5$
$(CH_2)_{11}(COOCH_2)$	20	22.7	-	-	-	463
$(CH_2)_{12}(COOCH_2)$	27	23.7	409	364	-	-
$(CH_2)_{13}(COOCH_2)$	43	28.5	408	356	-	-
$(CH_2)_{14}(COOCH_2)$	56	33.6	414	370	-	463
$(CH_2)_{15}(COOCH_2)$	74	43.7	410	369	-	453
$(CH_2)_{16}(COOCH_2)$	80	49.0	417	371	-	463

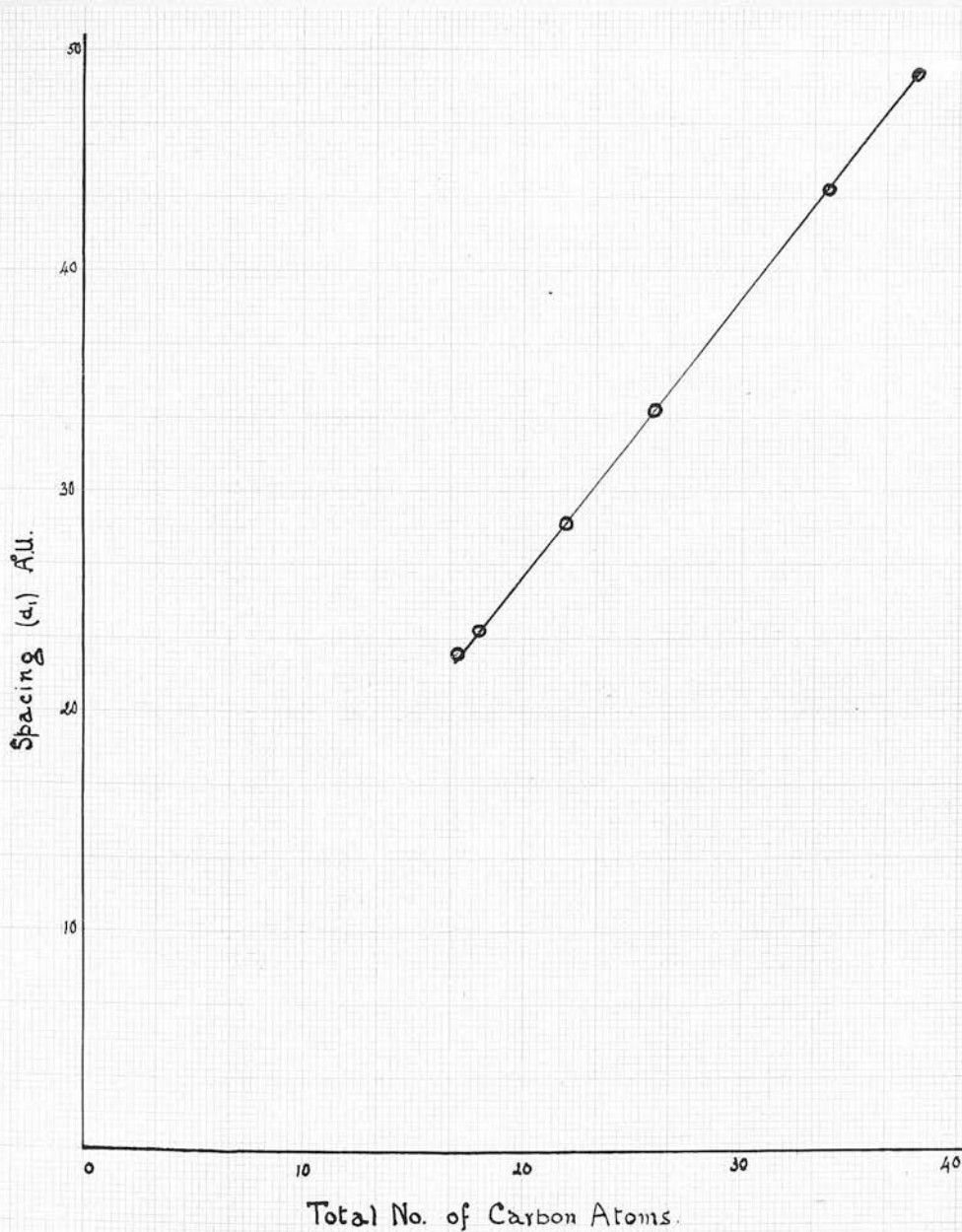
As before,  $d_1$  is the spacing associated with the length of the chain. The average increment per  $CH_2$  group is  $1.21\text{\AA}$ , and the figures indicate that only one molecule lies between successive reflecting planes. This is as we should expect, owing to the inactivity of the terminal groups. The  $d_2, d_3,$  and  $d_5$  spacings are roughly the same as in the dicarboxylic acid series, but the  $d_4$  spacing is entirely missing. The odd ester examined seems to fall into line with the even esters, and this is of interest in connection with the fact that the melting points of odd and even esters lie on one curve. I do not place too much reliance, however, on/

on this result, as the photograph obtained is not very good on account of the low melting point of the substance. Spacings corresponding to 22.7 and 23.9 ÅU. were obtained. More odd esters would require to be examined before I could venture to draw conclusions from the suspected parallelism between melting points and spacings. The arguments as to chain structure employed in connection with the dicarboxylic acids will apply equally well to this series. In dealing with the terminal groups we cannot say, nor have we any means of finding out, in what manner the esterification of the carboxyl group will affect its structure. As far as the results go the odd esters do not seem to differ materially from the even esters, but it is a significant fact that the  $d_2$  and  $d_3$  spacings are missing from the one odd ester examined. Whether this be due to the unstable state of the substance during examination or to some difference in the structure of the molecule, I cannot tell. The melting point curve would seem to indicate that odd and even esters have the same structure, and as this is not refuted by the X-ray measurements, I must conclude that they have roughly the same type of structure.



33(a)./

If we plot the  $d_1$  values against the total number of carbon atoms we find that all the points lie on a straight line:-



Mono-Ethyl Esters of the Dicarboxylic Acids.

Only two mono-ethyl esters of the dicarboxylic acids were available for X-ray investigation, but these are sufficient to determine the structure of the crystals.

The results are as follows:-

Ester.	M.P.°C.	$d_1$	$d_2$	$d_3$
$\text{CH}_3\text{OOC}(\text{CH}_2)_{12}\text{COOH}$	55	421	414	366
$\text{CH}_3\text{OOC}(\text{CH}_2)_{16}\text{COOH}$	71	505	412	366

The odd order reflections from the  $d_1$  planes are much stronger than the even order reflections.

If we consider a molecule of one of these compounds we see that it consists of a chain of  $\text{CH}_2$  groups having at one end an esterified carboxyl group and at the other a free carboxyl group. As we might expect in a crystal built up from this type of molecule, the values obtained for  $d_1$  are in agreement with the assumption that the reflection planes associated with  $d_1$  are separated by a distance approximating to twice the length of the molecule. The increment in  $d_1$  per  $\text{CH}_2$  group is 2.1 ÅU or 1.05 ÅU per molecule. The  $d_2$  and  $d_3$  spacings are the same as are found in the dicarboxylic acids and their diethyl esters. The  $d_4$  and  $d_5$  spacings are missing. These half esters resemble the fatty acids in their flakiness and greasiness, which might serve as an indication that the carboxyl group is not free in the crystal.

The Distribution of Intensity in the X-ray Spectra  
of the Normal Saturated Dicarboxylic Acids, their  
Diethyl and Mono-Ethyl Esters.

Owing to the relatively large spacing of the principal plane and hence the relatively small displacement of the first order reflection from the principal plane, from the centre of the photographic plate, I was able to observe several successive orders of reflection. I propose in this section to discuss the intensity distribution among these several orders of reflection with a view to verifying the molecular structures, and the arrangement of the molecules in the crystals.

In order to be able to calculate the intensity distribution, it is necessary to know the distribution of scattering matter between the successive planes. The carbon chain which, with its attached hydrogens, forms the greater part of these molecules, is regarded as a uniform distribution of scattering material. At the ends of the chain, and in the diethyl and mono-ethyl esters, at points along the length of the chain, there are divergences from this uniform distribution. If we assume that the scattering power is approximately proportional to the mass, then a COOH group will have a greater/

greater scattering power than the average scattering power of the chain while in the esters, the ketonic oxygen attached to a carbon atom in the chain will give rise to an increase in scattering power at this point.

Take first the general case, and let  $f(x)$  denote the scattering power at a distance  $x$  from one plane. It was shown by Shearer<sup>1</sup> that if the crystal is set for reflection at the  $r^{\text{th}}$  order and if the wave falling on the first plane be represented by  $A \sin(2\pi ct/\lambda)$ , then the wave scattered by an element  $dx$  at a distance  $x$  from this plane will be -

$$A f(x) \sin(2\pi ct/\lambda + 2\pi rx/d) dx.$$

where  $d$  is the spacing of the plane,  $\lambda$  is the wavelength and  $2\pi r$  represents the phase difference between the waves scattered from successive planes. The resultant wave reflected from the interval between successive reflecting planes will be -

$$\int_0^d A f(x) \sin(2\pi ct/\lambda + 2\pi rx/d) dx.$$

or

$$A \sin(2\pi ct/\lambda) \int_0^d f(x) \cos(2\pi rx/d) dx + A \cos(2\pi ct/\lambda) \int_0^d f(x) \sin(2\pi rx/d) dx \quad (1)$$

The amplitude is given by -

$$A (I_1^2 + I_2^2)^{1/2}$$

where  $I_1$  and  $I_2$  are the values of the two integrals in the/

<sup>1</sup> Proc. Roy. Soc. A. 108, 1925.

the above expression. The intensity of the reflected wave is proportional to the square of the amplitude or to

$$A^2(I_1^2 + I_2^2)$$

In the special case where there are two molecules end to end in opposite directions (1) becomes

$$\int_0^{d/2} A f(x) \sin(2\pi ct/\lambda + 2\pi rx/d) dx + \int_{d/2}^d A f(x) \sin(2\pi ct/\lambda + 2\pi rx/d) dx.$$

and after simplification

$$2A \sin(2\pi ct/\lambda) \int_0^{d/2} f(x) \cos(2\pi rx/d) dx.$$

The amplitude is given by

$$2A \int_0^{d/2} f(x) \cos(2\pi rx/d) dx. \quad (2)$$

I will now take up the case of the normal saturated dicarboxylic acids -  $\text{HOOC}(\text{CH}_2)_n\text{COOH}$ . Fig.(1) shows diagrammatically the distribution of scattering power along the length of the molecule. Here discontinuities occur only at the ends of the chain.

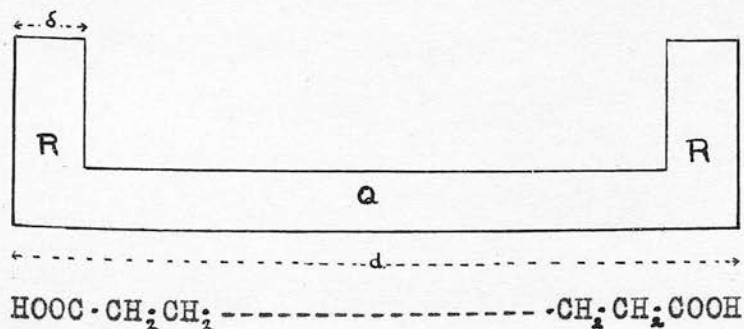


Fig.(1).



If we consider COOH as a single group occupying a length  $\delta$ , this series is practically analogous to (that of) the hydrocarbon series which was worked out by Shearer. The successive planes are separated by the length of a single molecule, whose length we will represent by  $d$ , and we may write  $f(x) = R$  from  $x = 0$  to  $x = \delta$ , and from  $x = d - \delta$  to  $x = d$ ;  $f(x) = Q$  from  $x = \delta$  to  $x = d - \delta$ .

Now we have to evaluate the two integrals found above.

$$I_1 = \int_0^d f(x) \cos(2\pi r x / d) dx.$$

$$I_2 = \int_0^d f(x) \sin(2\pi r x / d) dx.$$

$$\begin{aligned} I_1 &= \int_0^{\delta} f(x) \cos(2\pi r x / d) dx \\ &+ \int_{\delta}^{d-\delta} R \cos(2\pi r x / d) dx + \int_{d-\delta}^d Q \cos(2\pi r x / d) dx \\ &= \frac{Rd}{2\pi r} \sin(2\pi r \delta / d) + \frac{Rd}{2\pi r} \sin(2\pi r \delta / d) - \\ &\quad \frac{Qd}{2\pi r} \sin(2\pi r \delta / d) - \frac{Qd}{2\pi r} \sin(2\pi r \delta / d) \end{aligned}$$

$$\therefore I_1 = \frac{(R-Q)d}{\pi r} \sin(2\pi r \delta / d)$$

and similarly -

$$\begin{aligned} I_2 &= \int_0^{\delta} f(x) \sin(2\pi r x / d) dx \\ &= \frac{-Rd}{2\pi r} \cos(2\pi r \delta / d) + \frac{Rd}{2\pi r} - \frac{Rd}{2\pi r} + \frac{Rd}{2\pi r} \cos(2\pi r \delta / d) - \\ &\quad \frac{Qd}{2\pi r} \cos(2\pi r \delta / d) - \frac{Qd}{2\pi r} \cos(2\pi r \delta / d) \end{aligned}$$

$$\therefore I_2 = 0$$

Hence the intensity of the  $r^{\text{th}}$  order reflection is proportional to

$$I_1^2 + I_2^2$$

i.e.  $\propto \frac{(R-Q)^2 d^2}{\pi^2 r^2} \sin^2(2\pi r \delta / d).$  (3)

From (3), the lower members of the series where  $\delta/d$  is relatively large ought to show a more rapid decrease of intensity with increase of order than the higher members where  $\delta/d$  is small. In my investigations this is found to be the case. As is to be expected from the greater value of  $\delta$ , the falling off in intensity is more rapid than for hydrocarbons of a similar length of chain.

Since I am only concerned with the intensities of the various orders of reflection of each member of the series separately, and not with any relationship among the orders of reflection of the acid series as a whole, the formula (3) reduces for the purposes of calculation to

$$\frac{\sin^2(2\pi r \delta/d)}{r^2} \quad (4)$$

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#### Calculations.

Assuming that the length occupied by a  $\text{CH}_2$  group is 1 unit and the length occupied by a  $\text{COOH}$  group  $1\frac{1}{2}$  units, the total length of the molecule ( $d$ ) =  $n + 3$  where  $n$  is the number of  $\text{CH}_2$  groups in the chain.

Hence/

Hence for the acid  $\text{HOOC}(\text{CH}_2)_4\text{COOH}$  we have -

$$d = n + 3 = 7$$

$$\delta/d = 3/14.$$

r	$2\pi r\delta/d$	$\sin 2\pi r\delta/d$	$\sin^2 2\pi r\delta/d$	$\frac{\sin^2 2\pi r\delta/d}{r^2}$	<u>Relative Intensity</u>
1	$77^\circ$	.9744	.9495	.9495	100
2	$154^\circ$	.4384	.1921	.0480	-
3	$231^\circ$	-.7771	.6039	.0671	-
4	$308^\circ$	-.7880	.6209	.0388	-
5	$385^\circ$	.4226	.1786	.0071	-
6	$462^\circ$	.9781	.9567	.0266	-

$\text{HOOC}(\text{CH}_2)_5\text{COOH}$      $d = 8$

$$\delta/d = 3/16.$$

1	$67^\circ 30'$	.9239	.8536	.8536	100
2	$135^\circ$	.7071	.4999	.1250	15
3	$202^\circ 30'$	-.3827	.1464	.0163	-
4	$270^\circ$	-1.0000	1.0000	.0625	-
5	$337^\circ 30'$	-.3827	.1464	.0059	-
6	$405^\circ$	.7071	.4999	.0140	-

$\text{HOOC}(\text{CH}_2)_6\text{COOH}$      $d = 9$

$$\delta/d = 1/6$$

1	$60^\circ$	.8660	.7500	.7500	100
2	$120^\circ$	.8660	.7500	.1875	25
3	$180^\circ$	0.0000	0.0000	0	-
4	$240^\circ$	.8660	.7500	.0470	-
5	$300^\circ$	.8660	.7500	.0300	-
6	$360^\circ$	0.0000	0.0000	0	-

HOOC(CH<sub>2</sub>)<sub>7</sub>COOH    d = 10

$\delta/d = 3/20$

r	$2\pi r\delta/d$	$\sin 2\pi r\delta/d$	$\sin^2 2\pi r\delta/d$	$\frac{\sin^2 2\pi r\delta/d}{r^2}$	<u>Relative Intensity</u>
1	54°	.8090	.6542	.6542	100
2	108°	.9511	.9045	.2261	35
3	162°	.3090	.0955	.0106	3
4	216°	-.5878	.3456	.0216	-
5	270°	-1.0000	1.0000	.0400	-
6	324°	-.5878	.3456	.0096	-

HOOC(CH<sub>2</sub>)<sub>8</sub>COOH    d = 11

$\delta/d = 3/22$

1	49°	.7547	.5696	.5696	100
2	98°	.9903	.9807	.2352	43
3	147°	.9205	.8473	.0941	17
4	196°	-.2756	.0760	.0048	-
5	245°	-.9063	.8213	.0329	-
6	294°	-.9135	.8345	.0232	-

HOOC(CH<sub>2</sub>)<sub>10</sub>COOH    d = 13

$\delta/d = 3/26$

1	41° 32'	.6630	.4395	.4395	100
2	83° 4'	.9926	.9855	.2464	56
3	124° 36'	.8231	.6777	.0753	17
4	166° 8'	.2396	.0574	.0036	-
5	207° 40'	-.4643	.2156	.0086	-
6	249° 12'	-.9348	.8737	.0243	-

42./

HOOC(CH<sub>2</sub>)<sub>11</sub>COOH    d = 14 $\delta/d = 3/28.$ 

r	$2\pi r\delta/d$	$\sin 2\pi r\delta/d$	$\sin^2 2\pi r\delta/d$	$\frac{\sin^2 2\pi r\delta/d}{r^2}$	<u>Relative Intensity</u>
1	38°34'	.6234	.3887	.3887	100
2	77° 8'	.9749	.9506	.2377	61
3	115°42'	.9011	.8117	.0902	23
4	154°16'	.4342	.1885	.0118	3
5	192°50'	-.2221	.0493	.0019	-
6	231°24'	-.7815	.6110	.0170	-

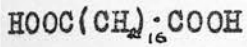
HOOC(CH<sub>2</sub>)<sub>12</sub>COOH    d = 15 $\delta/d = 1/10$ 

1	36°	.5878	.3455	.3455	100
2	72°	.9511	.9045	.2261	65
3	108°	.9511	.9045	.1005	29
4	144°	.5878	.3455	.0368	10
5	180°	-	-	-	-
6	216°	-.5878	.3455	.0096	-

HOOC(CH<sub>2</sub>)<sub>14</sub>COOH    d = 17 $\delta/d = 3/34$ 

1	31°46'	.5265	.2772	.2772	100
2	63°32'	.8952	.8013	.2003	72
3	95°18'	.9957	.9913	.1101	40
4	127° 4'	.7980	.6368	.0398	14
5	158°50'	.3611	.1304	.0052	2
6	190°36'	-.1840	.0339	.0009	-

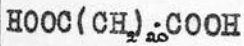




$d = 19$

$\delta/d = 3/38$

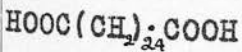
$\theta$	$2\pi r \delta/d$	$\sin 2\pi r \delta/d$	$\sin^2 2\pi r \delta/d$	$\frac{\sin^2 2\pi r \delta/d}{r^2}$	<u>Relative Intensity</u>
1	$28^{\circ}25'$	·4759	·2265	·2265	100
2	$56^{\circ}50'$	·8371	·7008	·1752	77
3	$85^{\circ}15'$	·9966	·9035	·1104	49
4	$113^{\circ}40'$	·9159	·8388	·0524	23
5	$142^{\circ}5'$	·6145	·3778	·0151	7
6	$170^{\circ}30'$	·1650	·0272	·0008	-



$d = 23$

$\delta/d = 3/46$

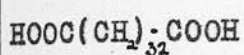
1	$23^{\circ}28'$	·3982	·1586	·1586	100
2	$46^{\circ}56'$	·7306	·5339	·1335	84
3	$70^{\circ}24'$	·9421	·8876	·0986	62
4	$93^{\circ}52'$	·9977	·9955	·0622	39
5	$117^{\circ}20'$	·8883	·7888	·0315	20
6	$140^{\circ}48'$	·6320	·3994	·0111	7



$d = 27$

$\delta/d = 1/18$

1	$20^{\circ}$	·3420	·1170	·1170	100
2	$40^{\circ}$	·6428	·4130	·1033	88
3	$60^{\circ}$	·8660	·7498	·0833	71
4	$80^{\circ}$	·9848	·9700	·0606	52
5	$100^{\circ}$	·9848	·9700	·0388	33
6	$120^{\circ}$	·8660	·7498	·0208	18



$$d = 35$$

$$\delta/d = 3/\lambda_0$$

r	$2\pi r\delta/d$	$\sin 2\pi r\delta/d$	$\sin^2 2\pi r\delta/d$	$\frac{\sin^2 2\pi r\delta/d}{r^2}$	<u>Relative Intensity</u>
1	1526'	.2662	.0709	.0709	100
2	3052'	.5130	.2631	.0658	93
3	4618'	.7230	.5226	.0581	82
4	6144'	.8808	.7758	.0485	68
5	7710'	.9751	.9506	.0380	54
6	9236'	.9990	.9983	.0277	39

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The following table shows the results calculated for each acid investigated, together with the results actually obtained by observation of the photographic plates:-

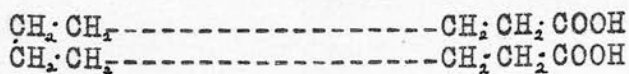
Table I      Relative Intensity.

Order	n = 6	n = 7	n = 8	n = 10	n = 11	n = 12	n = 14	n = 16	n = 20	n = 24	n = 32
	obs.	calc.	obs.	calc.	obs.	calc.	obs.	calc.	obs.	calc.	obs.
1	100	100	100	100	100	100	100	100	100	100	100
2	20	25	40	35	30	43	40	56	40	56	60
3	-	-	10	3	10	17	20	17	30	23	30
4	-	-	-	-	10	3	-	14	10	23	39
5	-	-	-	-	-	-	-	2	-	7	20
6	-	-	-	-	-	-	-	-	-	7	39

n represents the number of CH<sub>2</sub> groups.

The principle I have adopted is to make the first observed line, i.e. the strongest line in this case, equal to 100 units, and the intensities of the remaining orders of reflection have been estimated roughly by eye, relative to this strongest line. It will be noticed that, say in the case of the 32 acid, the first six orders should be comparatively strong, and yet only the first five orders were observed on the plate. This could probably be rectified by increasing the time of exposure. My main object, however, is to show how the observed and calculated results agree as regards relative intensity and not as regards absolute intensity. The agreement is good in every case.

I have assumed that the dicarboxylic acids consist of a single chain with a carboxyl group at both ends, and the observed intensity distributions are found to be in agreement with such an assumption. It has been suggested that the molecule is folded back on itself, as it were, and that the actual formula is one in which the two COOH groups are close to one another; thus:-



If such were the case in the solid, then the spacing observed/

observed would be that corresponding to two molecular layers, oppositely oriented owing to the presence of the COOH groups at one end, and the actual measurement of the spacing would be approximately the same for both arrangements. In the second case, however, the intensities of successive orders would be such that the even orders would be weak compared with the odd orders, and would not fall off in the observed manner. In addition the  $d_2$ ,  $d_3$ , and  $d_4$  spacings would probably be different if they are really connected with the cross-section of the molecule. The conclusion is, therefore, that the X-ray results are in agreement with the single-chain molecule.

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Diethyl Esters -  $\text{CHOOC}(\text{CH}_2)_2\text{COOCH}_2$

There is only one molecule between successive reflecting planes, so we may represent the distribution of scattering matter thus:-

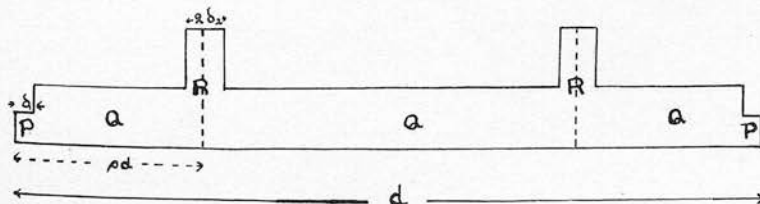


Fig.(2).



$\delta_1$  represents the length occupied by end hydrogen atom  
 $2\delta_2$  " " " " " carbonyl group  
 $d$  " " " of one molecule.

The centre of the carbonyl group is distant  $\rho d$  from the end of the molecule or of the reflecting plane.

It is assumed that the oxygen of the ester group plays the part of  $\text{CH}_2$  as regards scattering power, and that the  $\text{CH}_2$  groups in the  $\text{CH}_2$  ends are of approximately the same scattering power as the  $\text{CH}_2$  groups in the principal chain.

Let  $f(x) = P$  from  $x = 0$  to  $x = \delta_1$ , and from  $x = d - \delta_1$  to  $x = d$

$f(x) = Q$  from  $x = \delta_1$  to  $x = \rho d - \delta_2$  and from  $x = \rho d + \delta_2$  to  $x = d - \rho d - \delta_2$  and from  $x = d - \rho d + \delta_2$  to  $x = d - \delta_1$ .

$f(x) = R$  from  $x = \rho d - \delta_2$  to  $x = \rho d + \delta_2$  and from  $x = d - \rho d - \delta_2$  to  $x = d - \rho d + \delta_2$ .

We have to evaluate the two integrals obtained above:-

$$I_1 = \int_0^d f(x) \cos(2\pi r x/d) dx$$

$$I_2 = \int_0^d f(x) \sin(2\pi r x/d) dx$$

$$\begin{aligned}
 I_1 &= \int_0^{\delta_1} P \cos(2\pi r x/d) dx + \int_{d-\delta_1}^d P \cos(2\pi r x/d) dx \\
 &+ \int_{\delta_1}^{\rho d - \delta_2} Q \cos(2\pi r x/d) dx + \int_{\rho d + \delta_2}^{d - \rho d - \delta_2} Q \cos(2\pi r x/d) dx + \int_{d - \rho d + \delta_2}^{d - \delta_1} Q \cos(2\pi r x/d) dx \\
 &+ \int_{\rho d - \delta_2}^{\rho d + \delta_2} R \cos(2\pi r x/d) dx + \int_{d - \rho d - \delta_2}^{d - \rho d + \delta_2} R \cos(2\pi r x/d) dx \\
 &= \frac{Pd}{2\pi r} \left[ \sin(2\pi r \delta_1/d) - \sin 2\pi r \cos(2\pi r \delta_1/d) + \cos 2\pi r \sin(2\pi r \delta_1/d) \right]
 \end{aligned}$$

$$\begin{aligned}
& + \frac{Qd}{2\pi r} \left[ \sin 2\pi r (\rho d - \delta_2)/d - \sin(2\pi r \delta_1/d) + \sin 2\pi r \cos(2\pi r (\rho d + \delta_2)/d) \right. \\
& \quad - \cos 2\pi r \sin(2\pi r (\rho d + \delta_2)/d) - \sin 2\pi r (\rho d + \delta_2)/d \\
& \quad + \sin 2\pi r \cos(2\pi r \delta_1/d) - \cos 2\pi r \sin(2\pi r \delta_1/d) \\
& \quad \left. - \sin 2\pi r \cos(2\pi r (\rho d - \delta_2)/d) + \cos 2\pi r \sin(2\pi r (\rho d - \delta_2)/d) \right] \\
& + \frac{Rd}{2\pi r} \left[ \sin(2\pi r (\rho d + \delta_2)/d) - \sin(2\pi r (\rho d - \delta_2)/d) + \sin 2\pi r \cos(2\pi r (\rho d - \delta_2)/d) \right. \\
& \quad - \cos 2\pi r \sin(2\pi r (\rho d - \delta_2)/d) - \sin 2\pi r \cos(2\pi r (\rho d + \delta_2)/d) \\
& \quad \left. + \cos 2\pi r \sin(2\pi r (\rho d + \delta_2)/d) \right] \\
= & \frac{Pd}{2\pi r} [2 \sin(2\pi r \delta_1/d)] \\
& + \frac{Qd}{2\pi r} [2 \sin(2\pi r (\rho d - \delta_2)/d) - 2 \sin(2\pi r \delta_1/d) - 2 \sin(2\pi r (\rho d + \delta_2)/d)] \\
& + \frac{Rd}{2\pi r} [2 \sin(2\pi r (\rho d + \delta_2)/d) - 2 \sin(2\pi r (\rho d - \delta_2)/d)] \\
= & \frac{Pd}{2\pi r} [2 \sin(2\pi r \delta_1/d)] \\
& + \frac{Qd}{2\pi r} [-2 \sin(2\pi r \delta_1/d) - 4 \cos 2\pi r \rho \sin(2\pi r \delta_2/d)] \\
& + \frac{Rd}{2\pi r} [4 \cos 2\pi r \rho \sin(2\pi r \delta_2/d)] \\
= & \frac{(P-Q)d}{\pi r} \sin(2\pi r \delta_1/d) + \frac{2(R-Q)d}{\pi r} \cos 2\pi r \rho \sin(2\pi r \delta_2/d)
\end{aligned}$$

Similarly

$$\begin{aligned}
I_2 & = \int_0^{\delta_1} P \sin(2\pi r x/d) dx + \int_{d-\delta_1}^d P \sin(2\pi r x/d) dx \\
& + \int_{\delta_1}^{\rho d - \delta_2} Q \sin(2\pi r x/d) dx + \int_{\rho d + \delta_2}^{d - \rho d - \delta_2} Q \sin(2\pi r x/d) dx + \int_{d - \rho d + \delta_2}^{d - \delta_1} Q \sin(2\pi r x/d) dx \\
& + \int_{\rho d - \delta_2}^{\rho d + \delta_2} R \sin(2\pi r x/d) dx + \int_{d - \rho d - \delta_2}^{d - \rho d + \delta_2} R \sin(2\pi r x/d) dx \\
= & - \frac{Pd}{2\pi r} [\cos(2\pi r \delta_1/d) - \cos 0^\circ + \cos 2\pi r - \cos(2\pi r (d - \delta_1)/d)] \\
& - \frac{Qd}{2\pi r} [\cos(2\pi r (\rho d - \delta_2)/d) - \cos(2\pi r \delta_1/d) + \cos(2\pi r (d - \rho d - \delta_2)/d) \\
& \quad - \cos(2\pi r (\rho d + \delta_2)/d) + \cos(2\pi r (d - \delta_1)/d) - \cos(2\pi r (d - \rho d + \delta_2)/d)] \\
& - \frac{Rd}{2\pi r} [\cos(2\pi r (\rho d + \delta_2)/d) - \cos(2\pi r (\rho d - \delta_2)/d) + \cos(2\pi r (d - \rho d + \delta_2)/d) \\
& \quad - \cos(2\pi r (d - \rho d - \delta_2)/d)] \\
= & - \frac{Pd}{2\pi r} [\cos(2\pi r \delta_1/d) - \cos(2\pi r \delta_1/d)] \\
& - \frac{Qd}{2\pi r} [\cos(2\pi r (\rho d - \delta_2)/d) - \cos(2\pi r \delta_1/d) + \cos 2\pi r \cos(2\pi r (\rho d + \delta_2)/d) \\
& \quad + \sin 2\pi r \sin(2\pi r (\rho d + \delta_2)/d) - \cos(2\pi r (\rho d + \delta_2)/d) + \cos(2\pi r \delta_1/d) \\
& \quad - \cos 2\pi r \cos(2\pi r (\rho d - \delta_2)/d) - \sin 2\pi r \sin(2\pi r (\rho d - \delta_2)/d)]
\end{aligned}$$

$$\begin{aligned}
& - \frac{Rd}{2\pi r} \left[ \cos(2\pi r(\rho d + \delta_2)/d) - \cos(2\pi r(\rho d - \delta_2)/d) + \cos 2\pi r \cos(2\pi r(\rho d - \delta_2)/d) \right. \\
& \quad + \sin 2\pi r \sin(2\pi r(\rho d - \delta_2)/d) - \cos 2\pi r \cos 2\pi r(\rho d + \delta_2)/d) \\
& \quad \left. - \sin 2\pi r \sin(2\pi r(\rho d + \delta_2)/d) \right] \\
= & - \frac{Qd}{2\pi r} \left[ \cos(2\pi r(\rho d - \delta_2)/d) - \cos(2\pi r \delta_1/d) + \cos(2\pi r(\rho d + \delta_2)/d) \right. \\
& \quad \left. - \cos(2\pi r(\rho d + \delta_2)/d) + \cos(2\pi r \delta_1/d) - \cos(2\pi r(\rho d + \delta_2)/d) \right] \\
& - \frac{Rd}{2\pi r} \left[ \cos(2\pi r(\rho d + \delta_2)/d) - \cos 2\pi r(\rho d - \delta_2)/d) + \cos(2\pi r(\rho d - \delta_2)/d) \right. \\
& \quad \left. - \cos(2\pi r(\rho d + \delta_2)/d) \right] \\
= & 0
\end{aligned}$$

Now, if we assume that  $(P-Q) = (Q-R)$  and  $\delta_1 = \delta_2$

$$\begin{aligned}
I_1 &= \frac{(P-Q)d}{\pi r} \sin(2\pi r \delta_1/d) - \frac{2(P-Q)d}{\pi r} \cos 2\pi r \rho \sin(2\pi r \delta_1/d) \\
&= \frac{(P-Q)d}{\pi r} \sin(2\pi r \delta_1/d) \{1 - 2\cos 2\pi r \rho\}
\end{aligned}$$

and  $I_2 = 0$

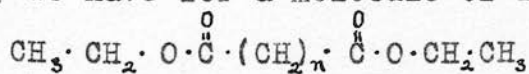
Intensity  $\propto (I_1^2 + I_2^2)$

i.e.  $\propto \frac{(P-Q)^2 d^2}{\pi^2 r^2} \sin^2(2\pi r \delta_1/d) \{1 - 2\cos 2\pi r \rho\}^2$

For the purposes of calculation, this reduces to

$$\frac{\sin^2(2\pi r \delta_1/d)}{r^2} (1 - 2\cos 2\pi r \rho)^2$$

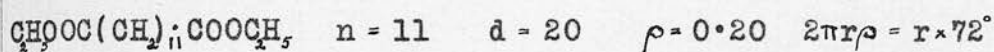
If we take a  $\text{CH}_2$ , CO, or chain oxygen as occupying one unit of length and allow one half unit for final hydrogens, we have for a molecule of formula



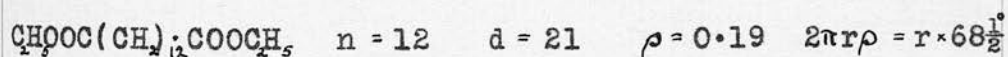
$$d = n+9$$

distance from end of molecule to centre of carbonyl group = 4 units

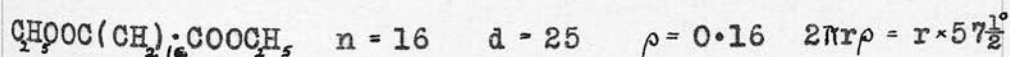
$$\therefore \rho = \frac{4}{n+9}$$

Calculations.

r	$2\pi r \rho$	$2 \cos 2\pi r \rho$	$1 - 2 \cos 2\pi r \rho$	$(1 - 2 \cos 2\pi r \rho)^2$	$\frac{\sin^2 2\pi r \rho / d}{r^2}$	I	$I_{100}$
1	$72^\circ$	0.62	0.38	0.14	1.00	0.14	2
2	$144^\circ$	-1.62	2.62	6.90	9.775	6.74	100
3	$216^\circ$	-1.62	2.62	6.90	9.36	6.45	96
4	$288^\circ$	0.62	0.38	0.14	8.83	0.12	2
5	$360^\circ$	2.00	-1.00	1.00	8.2	0.82	12
6	$432^\circ$	0.62	0.38	0.14	7.4	0.10	2

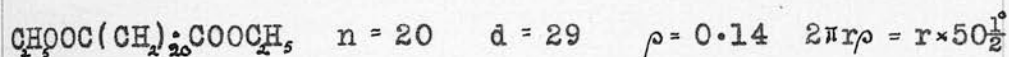


1	$68\frac{1}{2}^\circ$	0.73	0.27	0.07	1.00	0.07	1
2	$137^\circ$	-1.46	2.46	6.10	9.78	5.96	81
3	$205\frac{1}{2}^\circ$	-1.80	2.80	7.80	9.46	7.38	100
4	$274^\circ$	0.14	0.86	0.74	8.96	0.66	9
5	$342\frac{1}{2}^\circ$	1.91	-0.91	0.83	8.33	0.69	9
6	$411^\circ$	1.26	-0.26	0.07	7.66	0.05	1

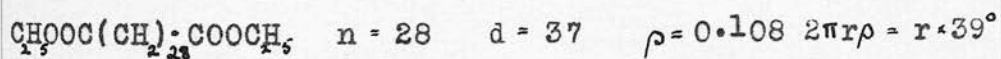


1	$57\frac{1}{2}^\circ$	1.07	-0.07	0.005	1.00	0.005	0
2	$115^\circ$	-0.84	1.84	3.38	9.87	3.34	39
3	$172\frac{1}{2}^\circ$	-1.98	2.98	8.90	9.62	8.56	100
4	$230^\circ$	-1.29	2.29	5.20	9.24	4.81	56
5	$287\frac{1}{2}^\circ$	0.60	0.40	0.16	8.79	0.14	2
6	$345^\circ$	1.93	-0.93	0.86	8.28	0.71	10

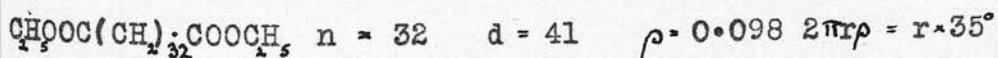




r	$2\pi r \rho$	$2\cos 2\pi r \rho$	$1 - 2\cos 2\pi r \rho$	$(1 - 2\cos 2\pi r \rho)^2$	$\frac{\sin^2 2\pi r \rho / d}{r^2}$	I	I <sub>100</sub>
1	$50\frac{1}{2}^\circ$	1.27	-0.27	0.07	100	0.07	1
2	$101^\circ$	-0.38	1.38	1.90	988	1.88	24
3	$151\frac{1}{2}^\circ$	-1.76	2.76	7.60	970	7.37	96
4	$202^\circ$	-1.85	2.85	8.10	943	7.63	100
5	$252\frac{1}{2}^\circ$	-0.60	1.60	2.56	910	2.37	31
6	$303^\circ$	1.09	-0.09	0.01	870	0.01	0



1	$39^\circ$	1.54	-0.54	0.29	100	0.29	3
2	$78^\circ$	0.42	0.58	0.34	992	0.34	4
3	$117^\circ$	-0.91	1.91	3.65	980	3.58	44
4	$156^\circ$	-1.83	2.83	8.07	964	7.78	96
5	$195^\circ$	-1.93	2.93	8.59	942	8.09	100
6	$234^\circ$	-1.18	2.18	4.75	917	4.36	54



1	$35^\circ$	1.64	-0.64	0.41	100	0.41	5
2	$70^\circ$	0.68	0.32	0.10	995	0.10	1
3	$105^\circ$	-0.52	1.52	2.31	985	2.28	27
4	$140^\circ$	-1.53	2.53	6.40	972	6.22	73
5	$175^\circ$	-1.99	2.99	8.94	955.5	8.54	100
6	$210^\circ$	-1.73	2.73	7.45	933	6.95	81
7	$245^\circ$	-0.85	1.85	3.42	912	3.12	36



Comparing the observed and calculated results we find that the agreement is satisfactory.

Table (II) - Relative Intensity.

	n = 11		n = 12		n = 16		n = 20		n = 28		n = 32	
Order	obs.	calc.	obs.	calc.	obs.	calc.	obs.	calc.	obs.	calc.	obs.	calc.
1	10	2	5	1	10	0	5	1	-	3	-	5
2	100	100	100	81	60	39	20	24	-	4	-	1
3	100	96	100	100	100	100	100	96	50	44	50	27
4	10	2	10	9	50	56	100	100	100	96	100	73
5	10	12	-	9	10	2	20	31	100	100	100	100
6	-	2	-	1	-	10	-	-	50	54	100	81
7	-	-	-	-	-	-	-	-	-	-	?	36

Note: The observed values for the 28 and 32 esters are only very roughly approximate as the photographs obtained were not very good. I conclude from the above data that the structure attributed to the diethyl esters is the correct one.

Mono-Ethyl Esters -  $\text{CHOOC}(\text{CH}_2)_2\text{COOH}$ .

The case of the mono-ethyl esters presents an entirely different aspect to the preceding. As was mentioned above, I concluded from the X-ray investigation that there are two molecules between neighbouring reflection planes. The distribution of scattering matter may be represented thus:-

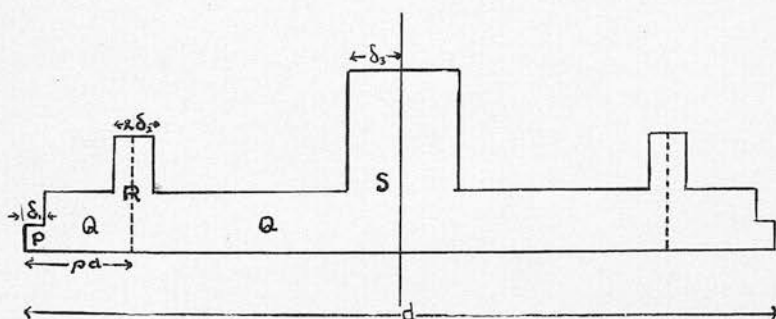


Fig.(III).

In the calculation of the relative intensities of the various orders in this series, I will make use of the following notation:-

- $d$  = combined length of the two molecules.
- $\delta_1$  = length occupied by end hydrogen atom.
- $\delta_2$  = " " " carboxyl group.
- $2\delta_2$  = " " " carbonyl group, and the centre of this group is distant  $\rho d$  from the end of the molecule.

Let  $f(x) = P$  from  $x = 0$  to  $x = \delta_1$ ,

Let/

Let  $f(x) = Q$  from  $x = \delta_1$  to  $x = \rho d - \delta_2$  and from

$$x = \rho d + \delta_2 \text{ to } x = d/2 - \delta_3$$

$$f(x) = R \text{ from } x = \rho d - \delta_2 \text{ to } x = \rho d + \delta_2$$

$$f(x) = S \text{ from } x = d/2 - \delta_3 \text{ to } x = d/2.$$

from formula (2), the amplitude is proportional to:-

$$\int_0^{d/2} f(x) \cos(2\pi r x/d) dx$$

i.e. it is proportional to:-

$$\int_0^{\delta_1} P \cos(2\pi r x/d) dx + \int_{\delta_1}^{\rho d - \delta_2} Q \cos(2\pi r x/d) dx + \int_{\rho d + \delta_2}^{d/2 - \delta_3} Q \cos(2\pi r x/d) dx$$

$$+ \int_{\rho d - \delta_2}^{\rho d + \delta_2} R \cos(2\pi r x/d) dx + \int_{d/2 - \delta_3}^{d/2} S \cos(2\pi r x/d) dx.$$

$$\text{i.e. } \propto \frac{Pd}{2\pi r} [\sin(2\pi r x/d)]_0^{\delta_1} + \frac{Qd}{2\pi r} [\sin(2\pi r x/d)]_{\delta_1}^{\rho d - \delta_2} + \frac{Qd}{2\pi r} [\sin(2\pi r x/d)]_{\rho d + \delta_2}^{d/2 - \delta_3}$$

$$+ \frac{Rd}{2\pi r} [\sin(2\pi r x/d)]_{\rho d - \delta_2}^{\rho d + \delta_2} + \frac{Sd}{2\pi r} [\sin(2\pi r x/d)]_{d/2 - \delta_3}^{d/2}$$

$$\propto \frac{Pd}{2\pi r} [\sin(2\pi r \delta_1/d)]$$

$$+ \frac{Qd}{2\pi r} [\sin(2\pi r(\rho d - \delta_2)/d) - \sin(2\pi r \delta_1/d) + \sin(2\pi r(d/2 - \delta_3)/d) - \sin(2\pi r(\rho d + \delta_2)/d)]$$

$$+ \frac{Rd}{2\pi r} [\sin(2\pi r(\rho d + \delta_2)/d) - \sin(2\pi r(\rho d - \delta_2)/d)]$$

$$+ \frac{Sd}{2\pi r} [\sin(2\pi r(d/2)/d) - \sin(2\pi r(d/2 - \delta_3)/d)]$$

$$\propto \frac{Pd}{2\pi r} [\sin(2\pi r \delta_1/d)]$$

$$+ \frac{Qd}{2\pi r} [-2 \cos 2\pi r \rho \sin(2\pi r \delta_2/d) - \sin(2\pi r \delta_1/d) + \sin(2\pi r(d/2 - \delta_3)/d)]$$

$$+ \frac{Rd}{2\pi r} [2 \cos 2\pi r \rho \sin(2\pi r \delta_2/d)]$$

$$+ \frac{Sd}{2\pi r} [\sin \pi r - \sin(2\pi r(d/2 - \delta_3)/d)]$$

$$\propto \frac{(P-Q)d}{2\pi r} \sin(2\pi r \delta_1/d) + \frac{(R-Q)d}{2\pi r} 2 \cos 2\pi r \rho \sin(2\pi r \delta_2/d) + \frac{(Q-S)d}{2\pi r} \sin(\pi r - 2\pi r \delta_3/d)$$

now when  $r$  is odd

amplitude

$$\propto \frac{(P-Q)d}{2\pi r} \sin(2\pi r \delta_1/d) + \frac{(R-Q)d}{2\pi r} 2 \cos 2\pi r \rho \sin(2\pi r \delta_2/d) + \frac{(Q-S)d}{2\pi r} \sin(2\pi r \delta_3/d)$$

and when  $r$  is even

amplitude

$$\propto \frac{(P-Q)d}{2\pi r} \sin(2\pi r \delta_1/d) + \frac{(R-Q)d}{2\pi r} 2 \cos 2\pi r \rho \sin(2\pi r \delta_2/d) - \frac{(Q-S)d}{2\pi r} \sin(2\pi r \delta_3/d)$$

If we assume that  $(P-Q) = (Q-S) = (Q-R)$  then the amplitude is proportional to

$$\frac{(P-Q)d}{2\pi r} \left[ \sin 2\pi r \delta_1/d - 2 \cos 2\pi r \rho \sin(2\pi r \delta_2/d) \pm \sin(2\pi r \delta_3/d) \right]$$

according as  $r$  is odd or even;

and putting  $\delta_1 = \delta_2 = \delta_3/2$  we have:-

$$\text{amplitude} \propto \frac{(P-Q)d}{2\pi r} \sin(2\pi r \delta_1/d) \left[ 1 - 2 \cos 2\pi r \rho \pm 2 \cos(2\pi r \delta_1/d) \right]$$

according as  $r$  is odd or even.

Since in these compounds  $\delta_1/d$  is very small, we may

$$\text{put} \quad 2 \cos(2\pi r \delta_1/d) = 2$$

$$\text{Hence amplitude} \propto \frac{(P-Q)d}{2\pi r} \sin(2\pi r \delta_1/d) \{ 3 - 2 \cos 2\pi r \rho \}$$

when  $r$  is odd

$$\propto \frac{(P-Q)d}{2\pi r} \sin(2\pi r \delta_1/d) \{ 1 + 2 \cos 2\pi r \rho \}$$

when  $r$  is even, so that the intensity is proportional

$$\text{to} \quad \frac{\sin^2(2\pi r \delta_1/d)}{r^2} (3 - 2 \cos 2\pi r \rho)^2 \quad \text{when } r \text{ is odd}$$

$$\frac{\sin^2(2\pi r \delta_1/d)}{r^2} (1 + 2 \cos 2\pi r \rho)^2 \quad \text{when } r \text{ is even.}$$

In calculating the relative intensities, I will neglect

the factor  $\frac{\sin^2(2\pi r \delta_1/d)}{r^2}$  It involves a gradual

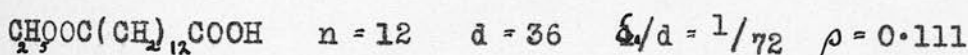
decrease in the values given below as  $r$  increases.

If  $n$  is the number of  $\text{CH}_2$  groups in the principal chain and we take a  $\text{CH}_2$ , CO, or chain oxygen atom as occupying one unit of length and allow one half unit for final hydrogen, the total length of the molecule is/

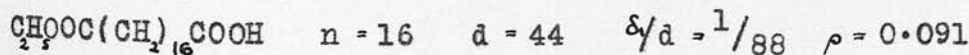
is  $n+6$ , and since  $d$  now represents double the length of the molecule  $d = 2n+12$ ,  $\delta_1 = \frac{1}{2}$  and  $\rho d = 4$ .

Hence  $\rho = \frac{4}{2n+12}$

Calculations.



$r$	$2\pi r \rho$	$2\cos 2\pi r \rho$	$\sqrt{I}$	$I$	$I_{100}$
1	$40^\circ$	1.53	1.47	216	10
2	$80^\circ$	0.35	1.35	1.82	8
3	$120^\circ$	-1.00	4.00	16.00	70
4	$160^\circ$	-1.88	0.88	0.77	3
5	$200^\circ$	-1.88	4.88	23.81	100
6	$240^\circ$	-1.00	0.00	0.00	0
7	$280^\circ$	0.35	2.65	7.02	28
8	$320^\circ$	1.53	2.53	6.41	24
9	$360^\circ$	2.00	1.00	1.00	3



1	$33^\circ$	1.68	1.32	1.74	7
2	$66^\circ$	0.81	1.81	3.28	14
3	$99^\circ$	-0.31	3.31	10.96	45
4	$132^\circ$	-1.34	0.34	0.12	1
5	$165^\circ$	-1.92	4.92	24.40	100
6	$198^\circ$	-1.90	0.90	0.81	3
7	$231^\circ$	-1.26	4.26	18.20	75
8	$264^\circ$	-0.21	1.21	1.46	6
9	$297^\circ$	0.91	2.10	4.40	18

It is seen that the even orders are very weak compared with the odd orders, as is actually found by experiment. Such a distribution of intensity is of common occurrence, and is shown by the fatty acid series and the/



the alcohols which were investigated by Shearer.

The agreement between observed and calculated results is good, as is shown by the following table:-

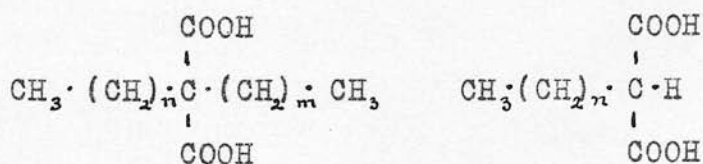
Table (III) - Relative Intensity.

Order	n = 12		n = 16	
	obs.	calc.	obs.	calc.
1	20	10	?	7
2	10	8	10	14
3	90	70	60	45
4	10	3	0	1
5	100	100	100	100
6	0	0	1	3
7	20	28	55	75
8	10	24	0	6
9	0	3	10	18

Note: In the 16 ester the first order reflection was obscured by the blackness produced on the plate by the undeflected X-rays.

The assumption, based on the results of the measurement of the spacings, that there are two molecules between successive reflecting planes and that these two molecules are oppositely oriented leads to intensity distributions which are in good agreement with those actually found, thus affording strong evidence in favour of Shearer's theory.

Following the completion of the work on the dicarboxylic acids and their esters, it was suggested that I should study the crystal structure of some acids of a different type. Up to the present I have investigated series of compounds in which the distance between the terminal carboxyl groups has been increased, in going up the series, by the introduction of  $\text{CH}_2$  groups, one at a time. In this later work it was thought to expand the molecule laterally instead of longitudinally, i.e. to increase the size of the molecule without altering appreciably the distance between the terminal carboxyl groups. With this object in view I prepared a number of mono and di-alkyl malonic acids.



where m and n have the values 0, 1, 2, 3, 4, and 7.

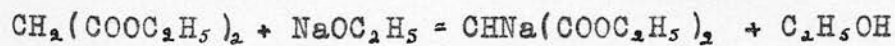
All the acids were prepared by the same general method with modifications in certain cases. The method employed was the well known 'Malonic Ester Synthesis' which was devised by Conrad.<sup>1</sup>

The details are as follows:-

Sodium ethoxide was first prepared by dissolving sodium/

<sup>1</sup>Annalen, 1880, 204, p. 134.

sodium in absolute alcohol in the proportion 23 grams Na to 250 grams alcohol. Whilst the product was still slightly warm one molecular proportion of diethyl malonate was added. After a time a white crystalline body (sodium ethyl malonate) separated out and the whole solidified. To the solid mass was added excess of alkyl iodide. The mass softened and soon completely liquified with evolution of heat. The product was heated on a water-bath and became turbid from the separation of NaI in the form of a fine powder. When the liquid ceased to be alkaline the reaction was complete (about  $1\frac{1}{2}$  hours). The alcohol was distilled off from a brine-bath. On the addition of water to the residue the NaI dissolved and an oil separated out. This was extracted with ether, dehydrated over  $\text{CaCl}_2$  and distilled.

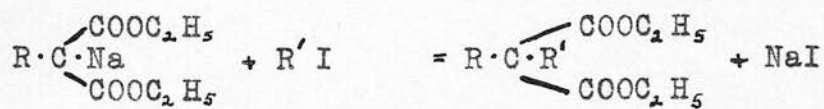
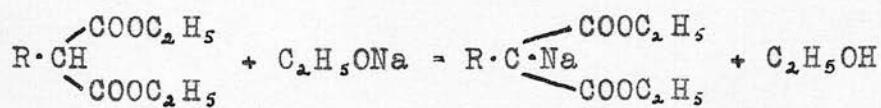


R represents an alkyl radical.

Hydrolysis. The esters prepared as above were hydrolysed with strong aqueous KOH. The product was diluted with water neutralised with conc. HCl. and the free acid precipitated as the calcium salt with a strong solution of  $\text{CaCl}_2$ . This was filtered off, dissolved in conc. HCl. and the free acid extracted with/

with ether. The ether extract was dehydrated over anhydrous  $\text{Na}_2\text{SO}_4$ , and the ether evaporated off leaving the acid in the form of a syrup which solidified when cooled. This was redissolved in water, boiled with animal charcoal to remove colouring matter, and evaporated to a syrupy consistency. The colourless acid crystallised on cooling. The acids were purified by repeated crystallisation from benzene, ligroin etc. until they gave a sharp melting point.

The dialkyl malonic acids were prepared by the same method, the starting substances being sodium ethoxide, a mono-alkyl malonic diethyl ester and an alkyl iodide.



Following is a list of the acids prepared together with their melting points:-

<u>Acid</u>	M.P.°C.
Methyl Malonic Acid	131-2
Ethyl " "	112
Dimethyl " "	192
n-Propyl " "	94.5
Isopropyl/	

<u>Acid.</u>	<u>M.P.°C.</u>
Isopropyl Malonic Acid	86.5
Methyl Ethyl " "	118.5
n-Butyl " "	101.5
Isobutyl " "	105.5
Diethyl " "	127
Methyl Propyl " "	101.5
Ethyl Propyl " "	114
Dipropyl " "	155.5
Ethyl Butyl " "	114
n-Heptyl " "	96.25
Dibutyl " "	160

In addition to these I have been able to investigate specimens of mono and di-octadecyl malonic acids through the kindness of Mr. N. K. Adam.

Mono-octadecyl malonic acid 121-122.5

di-octadecyl malonic acid 93.5

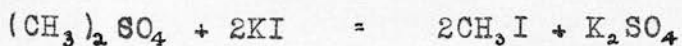
The acids containing a methyl group were the most difficult to prepare. The methyl group did not enter readily into the molecule, and only a partially methylated product was obtained. For example, in preparing methyl malonic acid from diethyl malonate and methyl iodide, the final product before hydrolysis consisted of a mixture of malonic ester and methyl malonic ester in which the first of these was /



was in excess. The two esters could not be separated by fractional distillation as their boiling points were practically identical. The reason for the non-entrance of the methyl group into the molecule seemed to be that the heat produced by the incipient action of the  $\text{CH}_3\text{I}$  on the malonic ester expelled the remaining  $\text{CH}_3\text{I}$  from the flask in spite of the fact that the reaction was performed under reflux. Methyl iodide is of course extremely volatile. To ensure a fully methylated product the ester was treated several times with excess of methyl iodide. This method proved satisfactory.

In evaporating off the ether from the acid in the final stages of the preparation, care had to be taken not to overheat, since alkyl malonic acids tend to decompose into fatty acids with evolution of  $\text{CO}_2$ .

Methyl Iodide was prepared by the double decomposition of Potassium Iodide and dimethyl sulphate.



Ethyl, Propyl, and Butyl iodides were prepared from the alcohol, red phosphorus, and iodine - the usual laboratory method.

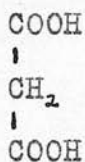
n-heptyl iodide was prepared by passing pure dry hydriodic acid into n-heptyl alcohol.

The melting points of the pure compounds were determined/

determined with accurate thermometers.

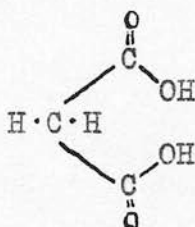
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In the section dealing with the dicarboxylic acids I mentioned malonic acid and succinic acid. These two, and particularly malonic acid, show little resemblance in their X-ray photographs to the other members of the dicarboxylic acid series. The malonic acid photograph shows 20 lines of different intensity. It is obviously impossible by an examination of this plate to say which line corresponds to a certain atomic distance in the crystal. Only a complete analysis of the malonic acid crystal could enable us to determine its exact internal arrangement. If we represent malonic acid, as a member of the dicarboxylic acid series, thus:-



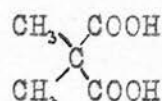
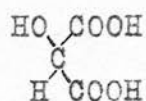
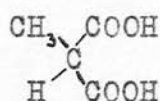
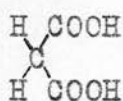
we would expect its crystal structure to resemble that of the other members of the series. We can be reasonably certain, both from X-ray results and also from the physical and chemical nature of the substance itself, that it does not have the above structure. Its melting point does not lie on the curve for the odd dicarboxylic acids. The two carboxyl groups are only/

only separated by one  $\text{CH}_2$  group, hence we would expect that any attractive force which one carboxyl group may exert on the other will be much stronger than in the case of the higher dicarboxylic acids. This attraction will tend to deform the molecule from the structure of the dicarboxylic acid series. In addition, when malonic acid is heated it decomposes, one of the products of decomposition being carbon suboxide  $\text{C}_3\text{O}_2$ . This involves the splitting off of two molecules of water. For this to take place the molecule would require to be compact and something of this nature



in three dimensions. Considerations such as these show the futility of trying to correlate spacings obtained from the photographic plate with atomic distances in the crystal. Although malonic acid is not comparable with the dicarboxylic acids, I thought I might be able to obtain some idea of its structure by comparing its X-ray photograph with those of some closely related compounds such as tartronic acid (Hydroxy malonic acid), methyl malonic acid, and dimethyl malonic acid. In the following table I give/

give the spacings calculated from the lines observed on the photographs of each of these substances. To the eye their photographs do not resemble that of malonic acid in the slightest. The introduction of a simple group into the malonic acid molecule seems to destroy its structure completely. Neither do the three last-mentioned substances resemble each other to any great extent.



5 71 ÅU  
 5 35  
 5 13  
4 79  
 4 44  
 4 29  
 4 18  
3 97  
 3 85  
 3 77  
3 60  
 3 56  
 3 32  
 3 00  
 2 86  
 2 78  
 2 73  
 2 70  
 2 53  
2 35

5 14  
 4 65  
 4 46  
 4 40  
 4 02  
 3 69  
 3 53  
3 32

5 45  
5 24  
 4 41  
3 77  
 3 44  
 3 36  
 3 24  
3 04  
 2 99  
 2 84  
 2 73  
2 69

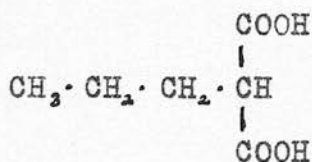
6 62  
6 00  
 4 97  
4 72  
 4 45  
 4 05  
 3 88  
3 41  
 3 06  
 2 99  
 2 84  
 2 77  
 2 64  
 2 48  
 2 31

The strongest lines are underlined.

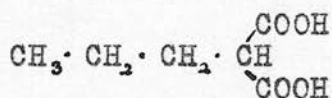
As will be seen from these values, there is very little similarity among the four substances. Among so many lines it is impossible to pick on any one and attribute/

attribute it to a certain atomic distance in the crystal. A spacing of about 4.4 ÅU seems to be common to all four substances.

I will now consider the mono-alkyl malonic acids, taking as my example propyl malonic acid.

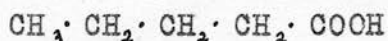


What will be the effect of the introduction of a propyl group into the malonic acid molecule? First of all, the distance between the two carboxyl groups has not been materially affected. They are still in a position to attract each other, hence it seems reasonable to assume that the molecule will be of this nature.



in three dimensions.

Now if we replace one of the carboxyl groups by a hydrogen atom we obtain the molecule

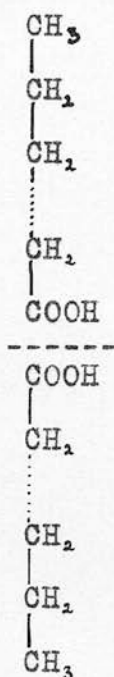


This is obviously a member of the fatty acid series, namely, Valeric Acid. The lower members of the fatty acid series were investigated by Gibbs,<sup>1</sup> who found/

<sup>1</sup> J.C.S. 1924, vol. 125, p.2622.



found that they have the crystal structure character:  
 istic of the higher members of the series, examined  
 by Müller (loc.cit.). In the fatty acid series,  
 successive reflection planes are separated by the  
 length of two molecules which are oppositely oriented  
 thus:-



The molecules are held together by the attraction of  
 the chemically active carboxyl groups. Propyl  
 malonic acid as we formulate it on paper differs only  
 slightly from valeric acid, and we might expect that  
 its crystal structure would be similar and its prin:  
 :cipal spacing would be very nearly equal to that of  
 valeric acid, assuming that both compounds have the  
 same chain arrangement. Further, in virtue of the  
 two carboxyl groups attached to the end carbon atom  
 in/

in propyl malonic acid, we might say that the attraction of one molecule for a second molecule would be even stronger than in the case of the fatty acids. On the other hand the two carboxyl groups in one molecule may mutually satisfy each other and so successive reflection planes will be separated by the length of one molecule only.

The results of the X-ray investigations of the n-mono-alkyl malonic acids are as follows:-

Acid	M.P.°C.	$d_1$ ÅU.	$d_2$	$d_3$	$d_4$	$d_5$
$C_2H_5CH(COOH)_2$	112	7.36	4.09 4.00	4.42	2.94	4.31
$C_3H_7CH(COOH)_2$	94.5	8.70	4.02 3.93	4.42	2.93	4.31
$C_4H_9CH(COOH)_2$	101.5	9.83	3.99	4.44	-	4.33
$C_7H_{15}CH(COOH)_2$	96.25	12.78	4.16	-	-	4.67
$C_{18}H_{37}CH(COOH)_2$	121-122.5	25.59	4.25	3.69	-	-

Many lines other than those given above were obtained on the plates but these are the most prominent. In every case the  $d_1$  line is the strongest. The  $d_1$  spacing increases with the number of  $CH_2$  groups present, and the increase per  $CH_2$  group is 1.0-1.3 ÅU. I submit, therefore, that this spacing is a measure of the length of the molecule, and that there is only one molecule between successive reflection planes. This receives support from a comparison of the  $d_1$  values given above with the  $d_1$  values of the corresponding fatty/

fatty acids.

Acid	$d_1$	$d_2$	$d_3$	$d_4$
$C_2H_5 \cdot CH_2 \cdot COOH$	9.65	4.09	3.65	3.45
$C_3H_7 \cdot CH_2 \cdot COOH$	10.10	-	-	-
$C_4H_9 \cdot CH_2 \cdot COOH$	14.60	4.14	3.65	3.47
$C_7H_{15} \cdot CH_2 \cdot COOH$	22.90	4.22	3.71	3.48
$C_{18}H_{37} \cdot CH_2 \cdot COOH$	about 43.30	-	-	-

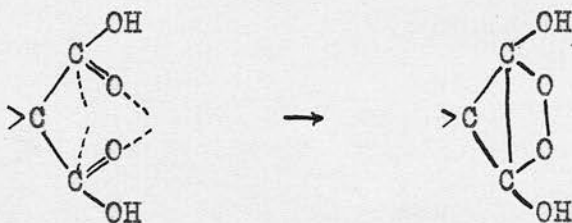
It would appear that the malonic acids have a different chain arrangement from the fatty acids. It is possible that the mutual attraction of the two carboxyl groups at the end of the malonic acid molecule tends to cause the hydrocarbon chain to straighten out as compared with the fatty acid chain, in the low members at least.\* As the substituent group becomes greater the molecule will adopt the characteristic chain structure. This would account for the diminution of the value of  $\frac{\delta d}{\delta n}$  as we move up the series. It would seem that my suggestion that the two carboxyl groups mutually satisfy each other is correct. This brings us to the question of the nature of the chemical activity of a carboxyl group. The carboxyl group is termed an unsaturated group, or, in other words, the valencies of the constituent atoms of a carboxyl group are not completely satisfied. Hence in the fatty acids one molecule is attached to the contiguous molecule/

\* or inclination of chain to normal to cleavage planes is smaller, and increases as we go up the series.

molecule by these partial valency forces, or, to use a more modern expression, the molecules are held together by the forces of residual affinity.



In the malonic acids where there are two carboxyl groups attached to one carbon atom we would expect something of this nature:-

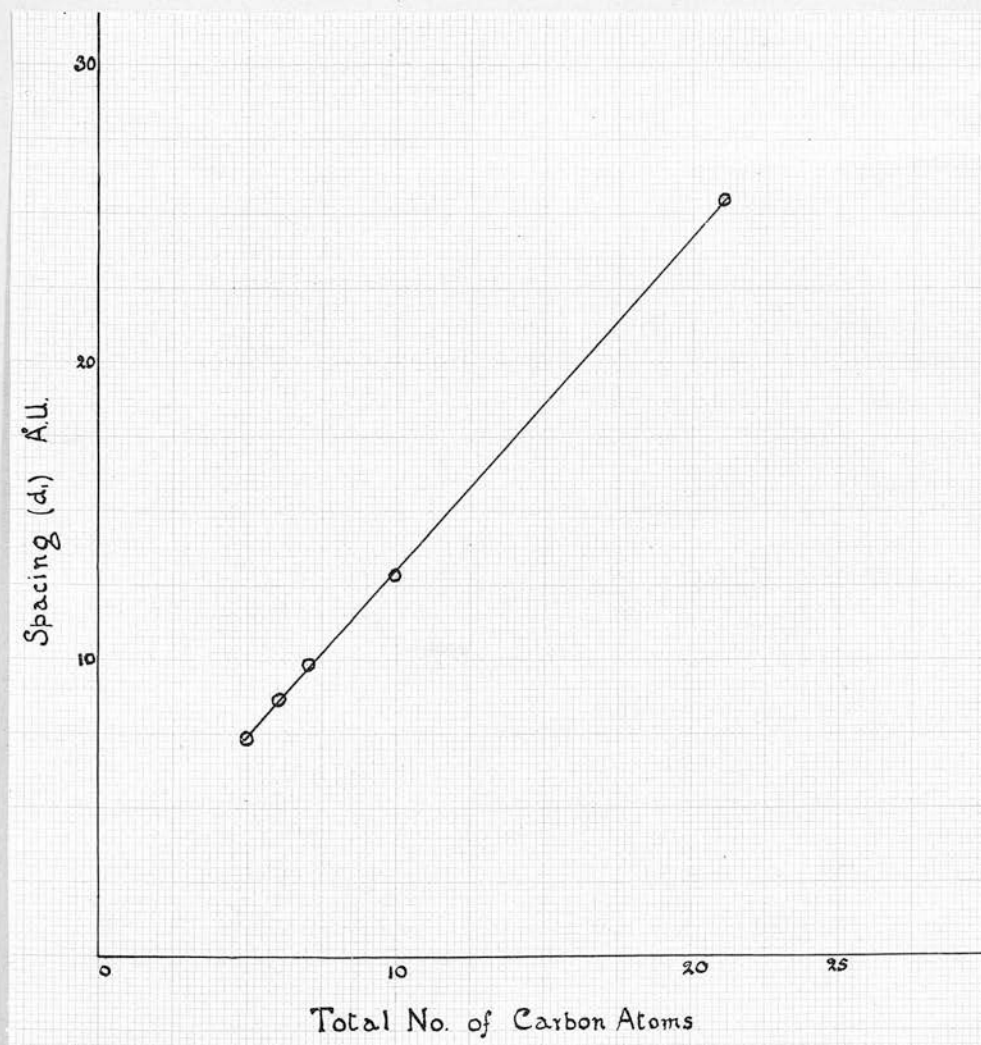


I do not suggest that these formulae depict what really takes place, but I have formulated them on the lines of the recent ideas of chemists. Formulae of this type, however, serve my present purpose, which is to attempt to give an explanation of the fact that in the fatty acids there are two molecules and in the malonic acids only one molecule between successive reflecting planes. It seems reasonable to conclude that the terminal carboxyl arrangement in the malonic acids will be different from that in the fatty acids.

The  $d_2$ ,  $d_3$ ,  $d_4$ , and  $d_5$  spacings remain constant in the lower members. The photograph of octadecyl malonic/

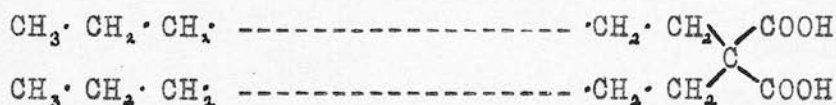


malonic acid is much simpler than the lower members of the series and its side spacings differ from those of the lower members. This is not surprising, since we would expect the chain to undergo a quite appreciable change in passing from the lower members of a series to the higher members. In the following graph, the  $d_1$  values are plotted against the total number of carbon atoms in the molecule.

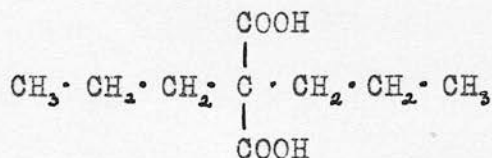




The X-ray photograph of dioctadecyl malonic acid is almost identical with that of mono-octadecyl malonic acid. The  $d_1$  spacing is exactly the same, but the side spacings are slightly different. Also the distribution of intensity in the several orders of reflection from the long spacing planes in the two photographs is slightly different. It would appear then that in the dioctadecyl malonic acid molecule the two  $C_{18}H_{37}$  groups are parallel to each other, thus:-



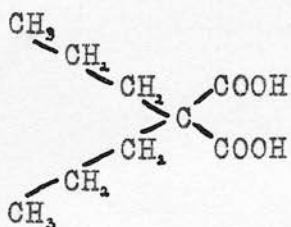
In the consideration of other possible structures I will take as my example dipropyl malonic acid.



The molecule as given above is a normal hydrocarbon with a chain of 7 carbon atoms in which the two hydrogens attached to the central carbon atom are replaced by carboxyl groups. If this were the structure of the molecule in the crystalline state, then the spacing associated with the length of the molecule would be comparable with that of n-heptane

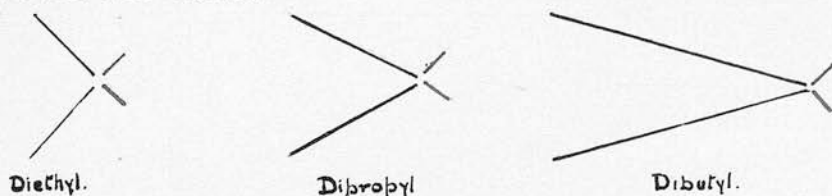
$CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_3$ . The higher members of the hydrocarbon series have been investigated by Müller (loc.cit.) who found that successive reflection planes/

planes are separated by the length of one molecule and that the increment in  $d_1$  for the addition of one  $\text{CH}_2$  group was on the average  $1.3 \text{ \AA}$ . n-Heptane, being liquid at ordinary temperatures, was not one of those investigated. From the  $d_1$  spacing of the higher members, however, we can arrive at a rough idea of what the  $d_1$  spacing of heptane should be - about  $10 - 11 \text{ \AA}$ . As the results will show, there is no spacing in the dipropyl malonic acid crystal as large as this. Further, on this reasoning, dioctadecyl malonic acid should have a  $d_1$  spacing of about  $50 \text{ \AA}$  - which is not observed. Hence this cannot be the structure of the dialkyl malonic acids. The presence of the two carboxyl groups attached to the same carbon atom would, I think, preclude the possibility of such a structure. The two carboxyl groups in virtue of their residual affinity will attract each other. What will be the effect of this attraction on the remaining two valencies of the carbon atom to which they are attached? My suggestion is that the structure of dipropyl malonic acid will be of this nature:-



and/

and since the length of dioctadecyl malonic acid is equal to that of mono-octadecyl malonic acid, I would add that the angle between the alkyl groups will diminish as their volume increases. For example, diethyl, dipropyl, and dibutyl malonic acids may be represented thus:-



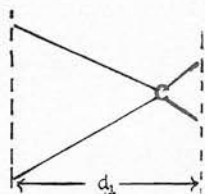
(The carboxyl groups are marked in red and the alkyl groups in black).

In the following table are given the principal spacings for the disubstituted malonic acids in which the two alkyl groups are the same:-

<u>Acid</u>	$d_1$	$d_2$
(Dimethyl malonic acid	4.97	4.45)
Diethyl " "	6.02	5.30
Dipropyl " "	7.90	6.50
Dibutyl " "	9.21	7.72
Dioctadecyl " "	25.59	-

The  $d_1$  spacing for dipropyl malonic acid was very faint. Apart from this one exception the  $d_1$  and  $d_2$  lines are of almost equal intensity in every case. It will be seen that both spacings increase as we go up the series, and, further, they increase by an amount which/

which leads me to conclude that they are directly connected with the length of the molecule. It is impossible to say with certainty what crystal spacings  $d_1$  and  $d_2$  really represent, but it is reasonable to assume, in virtue of the magnitude of the  $d_1$  spacing, that  $d_1$  is a measure of the total length of the molecule.



The interpretation of the  $d_2$  spacing is a matter of considerable difficulty, for we do not know the nature of the packing of the atoms in the crystal molecule, nor do we know the angles between the four groups attached to the central carbon atom (marked in red). The increase in  $d_2$  from diethyl to dipropyl malonic acid is  $1.2 \text{ \AA}$  and from dipropyl to dibutyl  $1.22 \text{ \AA}$ , hence from the equality of the two values  $d_2$  may be connected with the length of the alkyl group. The increase in  $d_1$  as we go up the series is not constant. This is what we would expect if my suggestion that it represents the length of the molecule is correct, for in the lower dialkyl malonic acids the angle between the alkyl groups will vary from compound to compound. Also, from the structures I have given to the three dialkyl acids (page 75) we would expect that the difference in  $d_1$  between mono and di-ethyl malonic acid would be greater than/

than that between mono and di-propyl malonic acids, which in turn would be greater than that between mono and di-butylmalonic acids. This is actually what is found.

<u>Acid</u>	<u>d, AU</u>	<u>difference</u>
Ethyl Malonic Acid	7.36)	
Diethyl " "	6.02)	1.34
Propyl " "	8.70)	
Dipropyl " "	7.90)	0.80
Butyl " "	9.83)	
Dibutyl " "	9.20)	0.63

The  $d_2$  spacing, characteristic of these low members of the series of dialkyl malonic acids, has disappeared by the time we reach dioctadecyl malonic acid, in which the angle between the alkyl groups seems to be practically zero, i.e. from the equality of the  $d_1$  spacings of mono and dioctadecyl malonic acids.

To summarise the preceding, in the dialkyl malonic acids successive reflection planes are separated by the length of one molecule. In the higher members of the series the two alkyl groups are parallel to each other but in the low members they diverge. The smaller the alkyl groups, the greater the angle between them.

I have prepared several di-alkyl malonic acids in which the two alkyl groups are different, and investigated them by means of X-rays. In the following table the results of this investigation are given, together with those/



those of the dialkyl malonic acids in which both alkyl groups are the same. I have included the principal spacings of methyl malonic acid whose photograph resembles the members of this series. If we regard it as methyl hydrogen malonic acid it may be included under the heading of disubstituted malonic acids. These acids seem to fit into the scheme outlined above.

<u>Acid.</u>	$d_1$ ÅU	$d_2$
Methyl Malonic	4.65	4.40
Dimethyl "	4.97	4.45
Methyl ethyl "	5.50	4.95
Methyl propyl "	5.84	4.95
Diethyl "	6.02	5.30
Ethyl propyl "	6.40	5.78
Ethyl butyl "	6.94	6.17
Dipropyl "	7.90	6.50
Dibutyl "	9.20	7.72

As before the angle between the alkyl groups will vary with their respective volumes. The side spacings obtained from the plates, as would be expected from the nature of the substances, show little regularity, and no advantage could be obtained by their inclusion in this thesis.

I do not think I would be justified in attempting a further discussion of the meaning of the  $d_2$  spacing. The information obtainable from the photographs of the low members of the dialkyl malonic acid series is not sufficient to permit me to arrive at a definite conclusion. We can be reasonably certain, however, that

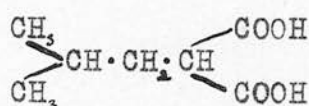
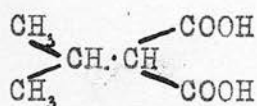
$d_1$  and  $d_2$  are connected with the length of the molecule and the results obtained are in agreement with what was suspected from the examination of dioctadecyl malonic acid, namely, that successive planes are separated by the length of one molecule.

A similar situation was experienced by Gibbs in his investigation of the lower members of the fatty acid series. He found it difficult to distinguish the  $d_1$  line from the other lines on the plate, and it is quite possible that the  $d_1$  values given for the lowest members of the series are not really a measure of the length of the double molecule.

Before leaving this problem, I would refer to an interesting point. If we consider the melting points of the dialkyl malonic acids, it will be seen that the acids in which the two alkyl groups are the same, have much higher melting points than those in which the two alkyl groups are different. The acids in which the two alkyl groups are the same will be symmetrical in character, while the others will be in a distorted condition. This lends support to the view that the melting point is determined <sup>both</sup> by the forces within the molecule and the forces between molecules.

I have investigated two branched chain mono-alkyl malonic acids - namely isopropyl and isobutyl malonic acids -/

acids -

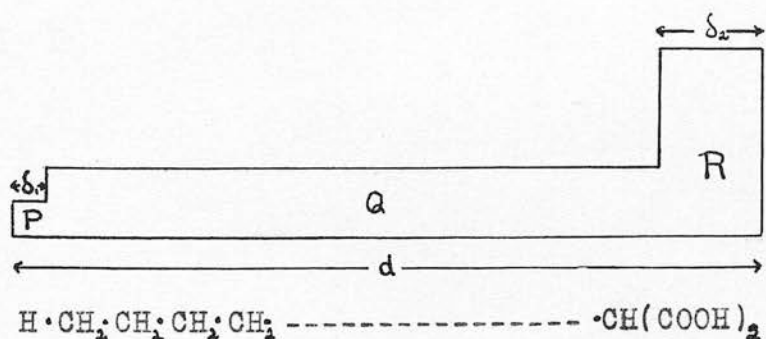


It might be considered that these two substances belong to the series of mono-alkyl malonic acids and that  $d_1$  for isopropyl and isobutyl malonic acids would be less than for the corresponding n-propyl and n-butyl acids. This is not the case, however. The photographs of the two iso-acids do not resemble those of the mono-alkyl acids in any way. Neither do they resemble each other. In the isopropyl malonic acid photograph there are four distinct orders of reflection from the principal spacing planes, and their intensities follow the order 1st > 2nd > 3rd > 4th. These lines correspond to a spacing in the crystal of 10.90 Å. The  $d_1$  spacing of normal propyl malonic acid is 8.70 Å, hence it would seem that if 10.90 Å is a measure of the length of the chain, it represents the length of two molecules. The principal line on the isobutyl malonic acid plate corresponds to a spacing of 4.64 Å. These two results, while conveying little in themselves, establish the fact that the structure of the crystals of the iso-compounds is very different from that of the normal compounds.

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The Distribution of Intensity in the X-ray Spectra  
of the Mono and Di-alkyl Malonic Acids.

In the succeeding pages I will apply Shearer's Theory of Intensity Distribution to the mono and di-alkyl malonic acid series. These series are different from any that have been previously investigated. In their distribution of scattering power they resemble the fatty acids with the difference that, in the present problem, successive reflection planes are separated by the length of one molecule only.



(Fig. 4.)

The distribution of scattering power in both series may be represented as in the above diagram. The only difference in the two series, i.e. mono and di-alkyl acids, will be the value of the ratio  $\frac{P-Q}{Q-R}$

Let  $d$  represent the total length of the molecule

"  $\delta_1$  represent the length occupied by end hydrogen atom

"  $\delta_2$  represent length occupied by the 2 COOH groups.

The method of procedure is the same as in the case of/

of the dicarboxylic acids and their esters. We have to evaluate the two integrals given previously.

$$I_1 = \int_0^d f(x) \cos(2\pi r x/d) dx$$

$$I_2 = \int_0^d f(x) \sin(2\pi r x/d) dx$$

let  $f(x) = P$  from  $x = 0$  to  $x = \delta_1$ ,

"  $f(x) = Q$  "  $x = \delta_1$  to  $x = d - \delta_2$

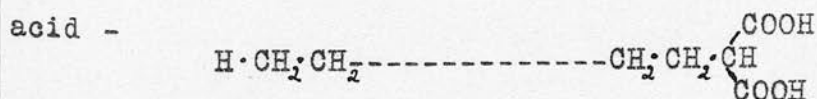
"  $f(x) = R$  "  $x = d - \delta_2$  to  $x = d$

$$\begin{aligned} I_1 &= \int_0^{\delta_1} P \cos(2\pi r x/d) dx + \int_{\delta_1}^{d-\delta_2} Q \cos(2\pi r x/d) dx + \int_{d-\delta_2}^d R \cos(2\pi r x/d) dx \\ &= \frac{Pd}{2\pi r} \sin(2\pi r \delta_1/d) + \frac{Qd}{2\pi r} \sin(2\pi r(d-\delta_2)/d) - \frac{Qd}{2\pi r} \sin(2\pi r \delta_1/d) - \frac{Rd}{2\pi r} \sin(2\pi r(d-\delta_2)/d) \\ &= \frac{Pd}{2\pi r} \sin(2\pi r \delta_1/d) - \frac{Qd}{2\pi r} \sin(2\pi r \delta_2/d) - \frac{Qd}{2\pi r} \sin(2\pi r \delta_1/d) + \frac{Rd}{2\pi r} \sin(2\pi r \delta_2/d) \\ &= \frac{(P-Q)d}{2\pi r} \sin(2\pi r \delta_1/d) - \frac{(Q-R)d}{2\pi r} \sin(2\pi r \delta_2/d) \end{aligned}$$

$$\begin{aligned} I_2 &= \int_0^{\delta_1} P \sin(2\pi r x/d) dx + \int_{\delta_1}^{d-\delta_2} Q \sin(2\pi r x/d) dx + \int_{d-\delta_2}^d R \sin(2\pi r x/d) dx \\ &= -\frac{Pd}{2\pi r} \cos(2\pi r \delta_1/d) + \frac{Pd}{2\pi r} - \frac{Qd}{2\pi r} \cos(2\pi r(d-\delta_2)/d) + \frac{Qd}{2\pi r} \cos(2\pi r \delta_1/d) \\ &\quad - \frac{Rd}{2\pi r} + \frac{Rd}{2\pi r} \cos(2\pi r(d-\delta_2)/d) \\ &= -\frac{Pd}{2\pi r} \cos(2\pi r \delta_1/d) + \frac{Pd}{2\pi r} - \frac{Qd}{2\pi r} \cos(2\pi r \delta_2/d) + \frac{Qd}{2\pi r} \cos(2\pi r \delta_1/d) \\ &\quad - \frac{Rd}{2\pi r} + \frac{Rd}{2\pi r} \cos(2\pi r \delta_2/d) - \frac{Qd}{2\pi r} + \frac{Qd}{2\pi r} \\ &= \frac{(P-Q)d}{2\pi r} (1 - \cos(2\pi r \delta_1/d)) + \frac{(Q-R)d}{2\pi r} (1 - \cos(2\pi r \delta_2/d)) \end{aligned}$$

It now remains to decide the relative values of  $P-Q$  and  $Q-R$ , and also of  $\delta_1$  and  $\delta_2$ .

Consider first an acid such as octadecyl malonic



$$P-Q = 1-14 = 13$$

$$Q-R = 14-90 = 76$$

The excess of scattering matter at the one end of the molecule/



molecule is about 6 times the deficit at the other.

In the dicarboxylic acids, the length of the terminal carboxyl group was made equal to  $1\frac{1}{2}$  units. This value, of course, is quite an arbitrary one.

Let us assume that in the present problem  $5(P-Q) = (Q-R)$  and  $\delta_2 = 4\delta_1$

$$\text{Then } I_1 = \frac{(P-Q)d}{2\pi r} [\sin(2\pi r\delta_1/d) - 5 \sin(8\pi r\delta_1/d)]$$

$$I_2 = \frac{(P-Q)d}{2\pi r} [6 - \cos(2\pi r\delta_1/d) - 5 \cos(8\pi r\delta_1/d)]$$

To simplify the working I will substitute  $x$  for  $2\pi r\delta_1/d$  then  $8\pi r\delta_1/d = 4x$ .

$$I_1^2 = \frac{(P-Q)^2 d^2}{4\pi^2 r^2} [\sin^2 x - 10 \sin x \sin 4x + 25 \sin^2 4x]$$

$$I_2^2 = \frac{(P-Q)^2 d^2}{4\pi^2 r^2} [36 - 12 \cos x - 60 \cos 4x + \cos^2 x + 25 \cos^2 4x + 10 \cos x \cos 4x]$$

$$I_1^2 + I_2^2 = \frac{(P-Q)^2 d^2}{4\pi^2 r^2} [62 - 12 \cos x - 60 \cos 4x + 10 (\cos x \cos 4x - \sin x \sin 4x)]$$

$$= \frac{(P-Q)^2 d^2}{4\pi^2 r^2} [62 - 12 \cos x - 60 \cos 4x + 10 \cos 5x]$$

$$= \frac{(P-Q)^2 d^2}{2\pi^2 r^2} [31 - 6 \cos x - 30 \cos 4x + 5 \cos 5x]$$

Intensity is proportional to  $I_1^2 + I_2^2$ , i.e.

$$\text{Intensity} \propto \frac{(P-Q)^2 d^2}{2\pi^2 r^2} [31 - 6 \cos x - 30 \cos 4x + 5 \cos 5x]$$

For purposes of calculation this reduces to

$$\frac{31 - 6 \cos(2\pi r\delta_1/d) - 30 \cos(8\pi r\delta_1/d) + 5 \cos(10\pi r\delta_1/d)}{r^2}$$

If we allow 1 unit for a  $\text{CH}_2$  group,  $\frac{1}{2}$  unit for final hydrogen, and 2 units for the terminal double carboxyl group/

group, then for Heptyl Malonic Acid  $\text{CH}_3(\text{CH}_2)_6\text{CH}(\text{COOH})_2$

$$d = 10\frac{1}{2} \quad \delta/d = 1/21, \quad 2\pi r\delta/d = r \times 17^\circ 8', \quad 8\pi r\delta/d = r \times 68^\circ 32',$$

$$10\pi r\delta/d = r \times 85^\circ 40'.$$

r	$2\pi r\delta/d$	$6\cos 2\pi r\delta/d$	$30\cos 8\pi r\delta/d$	$5\cos 10\pi r\delta/d$	I	$I_{100}$
1	$17^\circ 8'$	5.734	10.98	0.38	14.67	100
2	$34^\circ 16'$	4.959	-21.96	-4.94	10.76	73
3	$51^\circ 24'$	3.744	-27.05	-1.13	5.91	40
4	$68^\circ 32'$	2.196	2.16	4.77	1.96	13
5	$85^\circ 40'$	0.454	28.63	1.85	0.15	-
6	$102^\circ 48'$	-1.329	18.80	-4.50	0.25	-

Octadecyl Malonic Acid  $\text{CH}_3(\text{CH}_2)_{17}\text{CH}(\text{COOH})_2$   $d = 21\frac{1}{2}$ ,  $\delta/d = 1/43$

$$2\pi r\delta/d = r \times 8^\circ 22' \quad 8\pi r\delta/d = r \times 33^\circ 28', \quad 10\pi r\delta/d = r \times 41^\circ 50'$$

1	$8^\circ 22'$	5.937	25.03	3.73	3.76	100
2	$16^\circ 44'$	5.746	11.75	0.55	3.51	93
3	$25^\circ 6'$	5.434	-5.42	-3.18	3.09	82
4	$33^\circ 28'$	5.006	-20.78	-4.88	2.62	70
5	$41^\circ 50'$	4.472	-29.27	-4.37	2.06	55
6	$50^\circ 12'$	3.842	-28.04	-1.71	1.48	39

Comparing these calculated results with the results observed from the plates, it is seen that the successive orders are in the correct order of intensity, if not of the exact relative magnitude. The agreement is sufficiently good, however, to justify the structure which I have attributed to the acids.

Heptyl Malonic Acid.Octadecyl Malonic Acid.

Order.	Obs.	calc.	obs.	calc.
1	100	100	100	100
2	40	73	90	93
3	5	40	70	82
4	-	13	30	70
5	-	-	10	55
6	-	-	10	39

Consider, now, dioctadecyl malonic acid. The same diagram (Fig. 4.) will represent the distribution of scattering power. The relation between  $\delta_1$  and  $\delta_2$  will be practically the same as in the mono alkyl malonic acids, but the ratio P-Q:Q-R will be different. The first part of the calculation is the same as before, and we obtain

$$I_1 = \frac{(P-Q)d}{2\pi r} \sin(2\pi r \delta_1/d) - \frac{(Q-R)d}{2\pi r} \sin(2\pi r \delta_2/d)$$

$$I_2 = \frac{(P-Q)d}{2\pi r} (1 - \cos(2\pi r \delta_1/d)) + \frac{(Q-R)d}{2\pi r} (1 - \cos(2\pi r \delta_2/d))$$

let us assume that  $2(P-Q) = (Q-R)$  and  $\delta_2 = 4\delta_1$ ,

$$\text{then } I_1 = \frac{(P-Q)d}{2\pi r} [\sin(2\pi r \delta_1/d) - 2\sin(8\pi r \delta_1/d)]$$

$$I_2 = \frac{(P-Q)d}{2\pi r} [3 - \cos(2\pi r \delta_1/d) - 2\cos(8\pi r \delta_1/d)]$$

$$I_1^2 = \frac{(P-Q)^2 d^2}{4\pi^2 r^2} [\sin^2 x - 4\sin x \sin 4x + 4\sin^2 4x]$$

$$I_2^2 = \frac{(P-Q)^2 d^2}{4\pi^2 r^2} [9 - 6\cos x - 12\cos 4x + \cos^2 x + 4\cos^2 4x + 4\cos x \cos 4x]$$

$$I_1^2 + I_2^2 = \frac{(P-Q)^2 d^2}{4\pi^2 r^2} [14 - 6\cos x - 12\cos 4x + 4(\cos x \cos 4x - \sin x \sin 4x)]$$

$$= \frac{(P-Q)^2 d^2}{2\pi^2 r^2} [7 - 3\cos x - 6\cos 4x + 2\cos 5x]$$

Intensity is proportional to  $I_1^2 + I_2^2$ , i.e.

$$\text{Intensity} \propto \frac{(P-Q)^2 d^2}{2\pi^2 r^2} [7 - 3\cos x - 6\cos 4x + 2\cos 5x]$$

For/



General Conclusion.

The results of the X-ray investigation of these five series of compounds have yielded additional support to our general conceptions of the nature of aliphatic organic compounds. While the experimental method which has been used shows strikingly that these aliphatic compounds exist in the crystal in the form of long chains, it does not tell us the exact structure of the compounds.

We do not know the structure of the chain of  $\text{CH}_2$  groups, nor of the terminal groups. Different series would appear to have different chain structures, but it is difficult to see why two compounds of different series, both consisting in the main, of a chain of carbon atoms, should differ so appreciably in their chain structure. From a review of my own work and that of others, I consider that, in spite of the observed differences in  $\frac{\Delta d_i}{\Delta n}$  for different series, there is one general type of chain which is common to all series. I do not think that the tetrahedral angle is rigorously preserved in these compounds, but that the angle between the lines joining the centres of adjacent atoms will vary progressively along the chain, the variation being very gradual. A possible reason for this is given in the text (page 27.). On this view the increment in  $d_i$  per  $\text{CH}_2$  group (1.3 Å) in the hydro-carbon series is not so strange as was thought at first. In addition, the idea, conceived by Müller and Shearer, that/



General Conclusion. Contd.

that the inclination of the molecules to the cleavage planes is different for different series, seems to me to be an excellent one. A combination of these two ideas would seem to govern the observed facts in all the series of long chain compounds so far investigated.

The case of the fatty acid esters is not quite comparable since the chain of  $\text{CH}_2$  groups is broken by the insertion of an oxygen atom. In this series the acid part seems to have a different chain arrangement from the ester part and it is most reasonable to attribute this to the oxygen atom in the chain.

The interpretation of the photographs of the low members of a series is much more difficult than that of the higher members owing to the increased complexity of the photographs and a departure from the structure characteristic of the higher members of a series. This is particularly the case with the lower members of the dialkyl malonic acids which contain two hydro-carbon chains. The main interest in the two series of malonic acids is the fact that we have molecules possessing chemically active terminal groups, and yet successive reflection planes are separated by the length of one molecule only.

Summary.

Five series of compounds have been investigated by X-rays; in the series of normal saturated dicarboxylic acids successive reflection planes are separated by the length of one molecule. In the diethyl esters of these acids there is only one molecule between successive reflection planes, while in the monoethyl esters the distance between successive reflection planes corresponds to the length of two molecules. In the series of mono and di-alkyl malonic acids successive reflection planes are separated by the length of one molecule. The first mentioned series and the last two are of particular interest in view of the fact that though they possess chemically active terminal groups, they consist of mono-molecular layers. An explanation of this is given. From the X-ray results an approximate structure has been attributed to each series. Shearer's theory of 'Intensity Distribution' has been applied to each series in turn, on the basis of these structures. The intensity distribution among the several orders of reflection from the  $d_1$  planes, thus calculated, has been compared with the intensity distribution actually observed from the plates, and the agreement is found to be satisfactory, thus confirming the structures postulated.

An attempt has been made to explain the different increment/

increment in  $d_s$  per  $\text{CH}_2$  group, observed from series to series. It is concluded that all series have the same type of chain but no two substances belonging to the same or different series have exactly the same chain; also that the angle which the chain of carbon atoms makes with the normal to the cleavage planes is approximately constant for any one series but is different for different series.

