rison of the iso electronic systems *Ni* I, *Cu* II, *Zn* III, *Ga* IV and *Ge* V. For *Ni* I the *g*-values interpose between the LANDÉ *g*-values and those calculated according to (*JJ*) coupling, as may be seen from the tables.

The author is indebted to Prof. ZEEMAN for his interest and advice during this investigation.

Laboratory "Physica" of the University.

Amsterdam, Jan. 1932.

Physics. — *An X-ray Investigation of the n-mono-alkyl malonic Acids.* By D. COSTER and A. v. D. ZIEL. (Communicated by Prof. J. G. VAN DER CORPUT.)

(Communicated at the meeting of January 30, 1932.)

As is well known, several series of organic compounds (fatty acids, paraffines) when investigated by *X*-rays, show the existence of a long spacing which increases proportionally to the number of *C*-atoms in the molecule. Very often in those compounds a phenomenon of alternation has been observed: the spacing of the molecules with an odd number of *C*-atoms not lying midway between the spacings of the adiacent molecules with an even number of C-atoms, but those with an even number as well as those with an odd number of C-atoms forming a series of their own. Also as regards other properties: melting point, solubility, heat of combustion, analogous alternating phenomena have been observed [1]).

Prof. VERKADE at Rotterdam proposed us to investigate by means of *X*-rays a series of *n*-mono-alkyl malonic acids used in his own work in order to make sure in how far a parallelism between the change in grating constant in this series and other properties investigated by him exists.

The work was done with a vacuumspectrograph of a slightly modified type. The crystal table was fixed to the cover of the spectrograph. This cover turned with a cone on the body of the spectrograph, its position could be read on a scale with a vernier. The distance from the slit to the axis of the spectrograph or from the axis to the photographic plate was 6,18 cm. The preparation was brought in a thin sheet on a glass strip which was fixed on the crystal table. The thin sheet was made by first dissolving the substance in water (the lower members of the series) or in alcohol, aceton or ether (the higher members) and pouring a little of the solution on the glass strip. The thickness of the sheet which remained after

[1]) See e.g. P. E. VERKADE, H. HARTMAN and J. COOPS, Rec. trav. chim. Pays Bas. **45**, 373, 1926.

P. E. VERKADE, J. COOPS and H. HARTMAN, ibidem **45**, 545, 1926.

P. E. VERKADE and J. COOPS, ibidem **46**, 903, 1927.

P. E. VERKADE and J. COOPS, ibidem **49**, 568, 1930.

the liquid was evaporated was not more than 0,1 mm. This sheet of the preparation works as a reflecting crystal in the BRAGG camera. It was first brought in the axis of the spectrograph, the zero position was determined, then it was turned into the right position for reflection. During the exposure it was oscillated over an angle of about 0,3° on both sides of the angle of BRAGG reflection. As the glass strip was always fixed in the same way on the crystal table, the adjustment as well as the determination of the zero position had only to be done once.

The grating constants were calculated from the first and second order spectral lines at the same side of the direct beam. In order to control the identification of the spectral lines, also the first order reflections on both sides of the direct beam were taken on another plate. The lines were in general less sharp than those obtained by the same method with fatty acids. This means that the individual crystals are not so well oriented with their reflecting planes parallel to the surface of the glass as in the case of the fatty acids. Therefore it was necessary to make the beam of X-rays very narrow (the divergence of the beam was not more than $\frac{1}{2}$ degree) so that the reflection takes place only on a small part of the preparation in the neighbourhood of the axis of the spectrograph.

The results are given in table 1 and Fig. 1.

TABLE 1.

$C_n H_{2n + 1} CH(COOH)_2$	Grating constant	
		Value of HENDERSON
n = 1 methyl	5.07 Å U	
2 ethyl	7.25 „ „	7.36
3n . propyl	8.50 „ „	8.70
4n . butyl	9.71 „ „	9.83
5n . amyl	10.82 „ „	
6n . hexyl	12.09 „ „	
7n . heptyl	12.44 „ „	12.78
8n . octyl	14.38 „ „	
9n . nonyl	14.61 „ „	
10n . decyl	16.64 „ „	
11n . undecyl	16.82 „ „	
12n . dodecyl	18.90 „ „	
13n . tridecyl	19.09 „ „	
14n . tetradecyl	21.15 „ „	

We estimate the accuracy of our numbers to be about 3 $^0/_{00}$ for the members of the series higher than C_5 and about 5 $^0/_{00}$ for the lower ones, where the lines are still more diffuse.

In the third column the values found by HENDERSON[1]) are inserted. They differ slightly more from our values than the limit of experimental error for our numbers. Besides HENDERSON has measured C_{18}, for which he finds 25.59 Å, in good agreement with the value 25.67 extrapolated from our numbers. From his data HENDERSON has already drawn the conclusion, that in the case of the n-mono-alkyl malonic acids there is only one molecule between successive reflecting planes. This conclusion is confirmed by table 1. For the higher members of the series the spacing increases on the average with 1,13 Å per CH_2-group, whereas in the case of the fatty acids, where two molecules are supposed to be between two successive identity planes, this increase is about 2,3 Å. From this the conclusion may be drawn that in the case of the n-mono-alkyl malonic acids the two active carboxyl groups of the same molecule are saturated by one
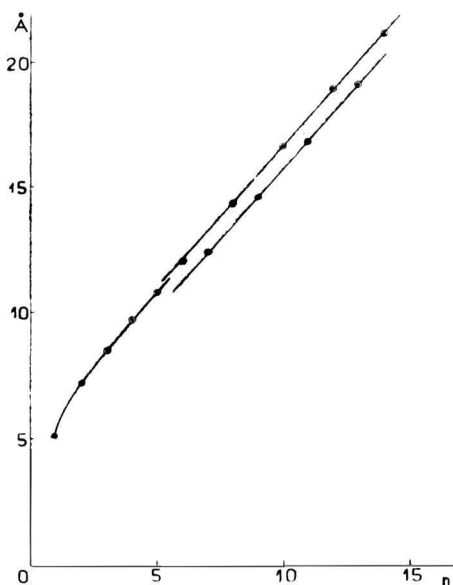

Fig. 1
The grating constant as a function of the number of C-atoms in the alkyl group of the n-mono-alkyl malonic acids.
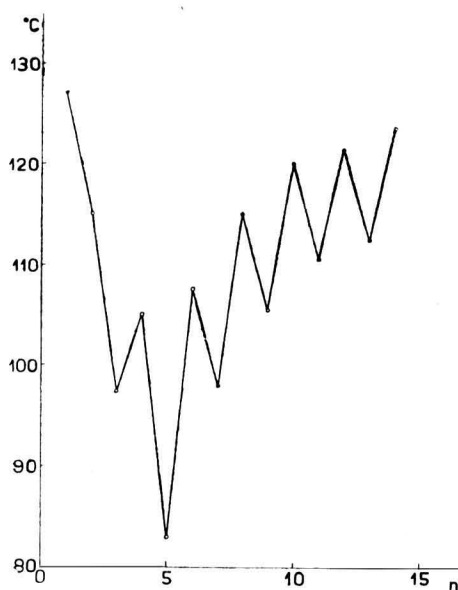
Fig. 2
Melting point of the n-mono-alkyl malonic acids as a function of the number of C-atoms in the alkyl-group.

another, whereas in the case of the fatty acids, where two molecules are placed head-on between the identity planes, the carboxyl groups of two successive molecules are saturated by one another.

Fig. 1 reveals a new interesting fact: beginning with C_6 the higher

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[1]) E. HENDERSON, Proc. Roy. Soc. of Edinburgh 48, 20, 1927—'28.

members of the series show the phenomenon of alternation in grating constant for the odd and even numbers as discussed above. The lower members, however, do not show such alternation; they form a series of their own which is different from the odd as well as from the even higher members. It is a very curious fact that the lower members of the series cannot be regarded as a continuation of the higher members, the latter forming a series beginning with C_6. The same feature is also shown by other physical properties. This is clearly brought out by the figures 2, 3 and 4. The data with the help of which these figures were constructed are taken from the work of VERKADE and COOPS[1]). Fig. 2 shows an alternating series with a melting point increasing on the average for the higher members beginning with C_6, whereas the lower members form a series of their own with a melting point decreasing on the average as the number of C-atoms increases.
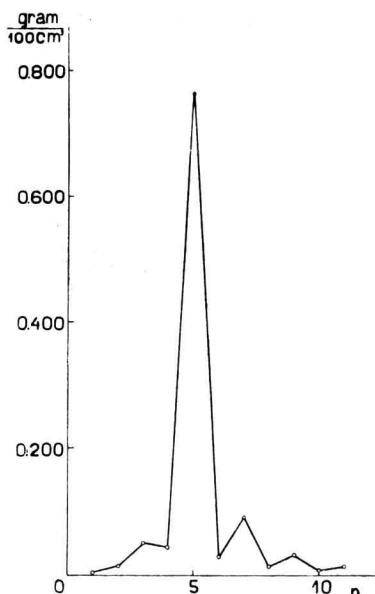

Fig. 3

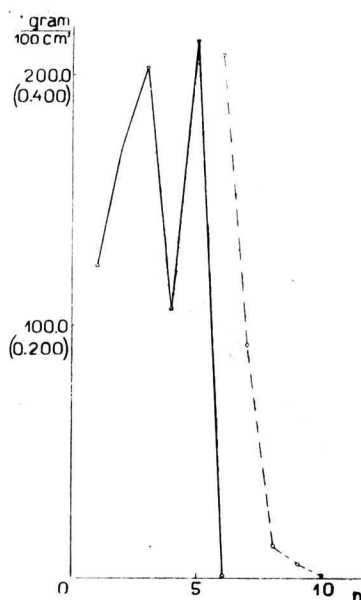Solubility of the n-mono-alkyl malonic acids in benzene as a function of the number of C-atoms in the alkylgroup.

Fig. 4

Solubility of the n-mono-alkyl malonic acids in water as a function of the number of C-atoms in the alkyl group, As the solubility for the higher members beginning with C_6 is very small, for these the curve is drawn on a larger scale (dotted line).

An analogous aspect is met in Fig. 3. The higher members form an alternating series beginning with C_6 with on the average decreasing solubility in benzene as the number of C-atoms increases. With the lower mem-

1) P. E. VERKADE and J. COOPS, Rec. trav. chim. Pays Bas **49**, 568, 1930.

bers, however, on the average the solubility increases as the number of C-atoms increases. An anomalously large maximum is shown by C_5.

A slightly different behaviour for the solubility in water is shown in Fig. 4. Here the phenomenon of alternation is not shown by the higher members, but they behave also quite differently from the lower members in as much as the solubility is very great for the latter ones and very small for the former ones.

As is seen from Fig. 1 the grating constant of methyl malonic acid is smaller than the value obtained by a linear extrapolation from the con-stants for the acids C_2, C_3, C_4 and C_5. Also in other respects C_1 behaves different from the other lower members of the series. From Fig. 2 e. g. we see that in general the lower as well as the higher members alternate in melting point. If C_1 should do the same, its melting point had to be lower than that of C_2 whereas as a matter of fact it is higher. An analogous con-clusion may be drawn as regards the solubility (see Fig. 3 and 4). It therefore seems, that C_1 hardly belongs to the series of the lower mem-bers, but that this series only begins with C_2.

The preparations of Prof. VERKADE appeared to be very pure. At any rate, in general, no other long spacings were found than those inserted in table 1. An exception will be discussed further on. The lines which appeared most clearly on the plates were the copper $K\alpha$ and $K\beta$ lines (a copper antikathode was used in the X-ray tube). As a tungsten hot wire kathode was used and the tungsten was sputtered on the antikathode, also the $L\alpha$ and $L\beta$-lines of tungsten appeared on the plates but usually rather weak. The lines are clearly seen on the photometercurves (see Fig. 5). Because of the small dispersion the $L\alpha$-line of tungsten is not separated from the Cu $K\alpha$ line; it is only seen as an asymmetry in the latter [1]. For the same reason the $L\beta_1$ and $L\beta_2$ line of tungsten could not be separated. The large blackening to the right is the direct beam. Between this and the lines already referred to, very often another group of lines of variable intensity is found. They point at a grating constant about two times as large as those of table 1.

Now it is well known that many organic acids are decomposed under the influence of light [2]. Malonic acid e.g. decomposes into acetic acid and carbon dioxide [3]. To test this point for the acids in this paper we mounted a strip of glass with a certain preparation, say C_8, in the X-ray spectrograph and determined the spectrum. Then the preparation was exposed to the mercury arc or to sunlight, and again an X-ray spectrum was taken. To make sure that the same part of the preparation was responsible for the X-ray spectrum before and after the treatment by light, the cover of the spectrograph with the crystal table was taken from the

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[1] Naturally the dispersion is far too small to separate the two components of the $K\alpha$-line.
[2] See KISTIAKOWSKY "Photochemical Processes" The Chemical Catalog Co. Inc. New York 1928, p. 146, 229.
[3] VOLMAR, Compt. Rend. **180**, 1172, 1925.

X-ray spectrograph for this treatment and care was taken that nothing in the adjustment of the glass strip with the preparation was changed. The Fig. 5, 6, 7 and 8 are photometercurves taken from spectra made with the same preparation C_8 in the same position but respectively exposed to sunlight or the light of the mercury arc.

From the Fig. 5, 6, 7 and 8 it is clearly shown that the n-mono-alkyl malonic acid C_8 gradually changes by photochemical reaction into another substance with much larger grating constant. A comparison of Fig. 7 and Fig. 8 shows that sunlight with a lower limit of wave-length of about 3300 Å works equally well as the mercury quartz arc in which much shorter wave-lengths play an important part. The rather small difference between fig. 5 and 6, though a vigorous treatment with light took place before the spectrum 6 was taken, is a little surprising at first. The same we observed in all other cases, where we studied the photochemical reaction in this way: In the beginning the change takes place very slowly, if once however, the new spacing is a little stronger, then it grows more intense in a comparitivily short time. It seems to us that this peculiarity is caused by the method itself. We may assume that in the beginning the photo-chemical reaction will take place at random throughout the preparation just were a light quantum happens to be absorbed. But by the method of X-ray reflection no single molecule can be detected but only crystalline aggregates of several thousands of molecules of the same kind. We thus understand why in the beginning the new grating appears so slowly; it is because there are perhaps many single molecules but not enough crystalline aggregates to give good reflections.

On the other hand it is a curious fact, indeed, that the lines of the anomalous large spacing as well as of the old normal spacing are rather sharp on fig. 7 and 8. From this we may conclude that the individual crystals which give rise to the reflections in question must not be too small (say at least hundred reflecting planes). This curious fact proves that the molecules with anomalous large grating are not distributed at random between the original molecules, but are more or less concentrated in rather large aggregates. So far as we see, this may be explained in two different ways: It is possible that they are formed at random throughout the substance and by diffusion combine to larger aggregates. Or it might be that the new molecule acts as a kind of catalyser for the photochemical reaction in question. The first supposition seems us to be the most probable.

The same photochemical process was studied in the same way with C_{13}, C_{12} and C_{11}. As the results were *mutatis mutandis* the same, we need not to go into further detail. As the cause of the appearance of the anomalous large grating now was known, we worked with the preparations in the dark. In this case we really succeeded in getting photographs without the anomalous large spacings.

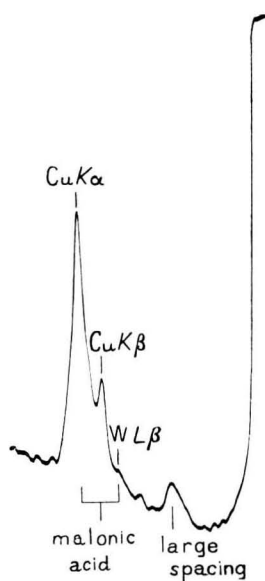Another question is, if the X-rays themselves show a photochemical

Fig. 5

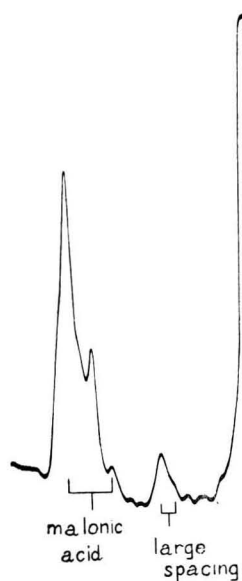Before the treatment with light. The anomalous long spacing is visible, but rather weak.

Fig. 6

Exposed during 5 hours to sunlight. The anomalous long spacing is a little stronger, but not much.
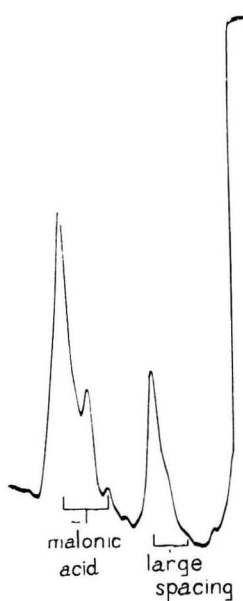
Fig. 7

Again exposed during 6 hours to the light of the mercury arc. The anomalous long spacing is much stronger.
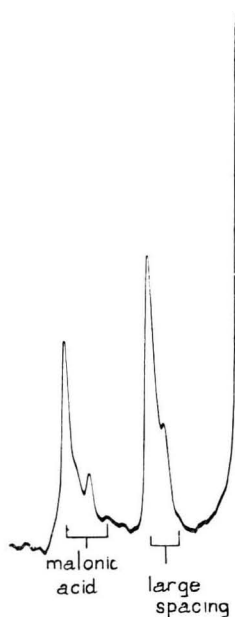
Fig. 8

Again exposed during 10 hours to sunlight. The anomalous long spacing gives now by far the strongest reflection. The normal spacing gives much weaker reflections than in the former figures.

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action on the alkyl malonic acids. To decide this question we used a preparation of C_{11} which showed in addition to the normal spacing also the large spacing. The preparation was strongly exposed during 8 hours to X-rays. A new X-ray spectrum clearly showed 'an increase of the intensity of the long spacing. To make sur that no other unknown effect might cause the chemical reaction in question, the preparation was afterwards kept during 15 hours in the dark. An X-ray spectrum now taken showed no perceptable increase of the intensity of the long spacing.

During one single exposition of an X-ray spectrum, however, the photochemical action of the X-rays is too small to give a perceptable effect. The time of exposure is only 2 hours, whereas the X-rays strike the preparation at an angle of about 1—3 degree. Therefore we estimate the total intensity only about 5 per cent of the intensity in the above case in which a change caused by the X-rays was clearly observed.

Now the question arises into which substances the n-mono-alkyl malonic acids are converted by the action of light. As the new substance has a spacing about two times as large as the corresponding alkyl malonic acid, it seems to be most probable that this should be a fatty acid. This seems to be most reasonable also from a chemical point of view. So we might suppose that the octyl malonic acid C_8 is converted into caprinic acid C_{10} and carbon dioxide.

Unfortunately there are some serious difficulties in testing this question by a measurement of the spacings. As is well known the fatty acids occur in at least 3 different modifications with widely varying grating constants [1]). Furthermore it seems that the grating constant can be easily changed to a perceptable amount by small impurities or by mechanical treatment of the preparation. Now the values found for the large spacings, which arise from the treatment with light, differ more from the spacings of the fatty acids than the limit of experimental error. In general they are about 10 per cent too small. For the moment we cannot explain this discrepancy but we intend to investigate this point in a continuation of our work.

In conclusion, we wish to express our thanks to Prof. P. E. VERKADE of Rotterdam for supplying the substances investigated in this paper.

Groningen, Natuurkundig Laboratorium der Rijks-Universiteit.

[1]) G. M. DE BOER, Nature 119, 634, 1927.