**Chemistry**. — *Alternations in the Properties of n. Monoalkylmalonic Acids. Some Remarks on* MALKIN's *Views concerning the Alternation Phenomena.* By P. E. VERKADE and J. COOPS Jr. (Communicated by Prof. J. BÖESEKEN).

§ 1. In a previous communication [1]) data were furnished for the melting-points and the solubilities at $25°.0$ in water and in benzene of a series of *n.* monoalkylmalonic acids and some discussion a propos of these data was added. The heats of combustion of these acids had been determined by us at the same time; publication of these data has however so far remained in abeyance as the interpretation of the numerical data collected raised difficulties. We believed that an investigation of these acids by means of *X*-rays could contribute considerably in elucidating our insight into the alternation phenomena occurring with these acids and therefore proposed to Prof. COSTER of Groningen that he should carry out such an investigation. The results of this work of COSTER and VAN DER ZIEL [2]) were published some time ago; hence we have now returned to our investigations on these acids.

§ 2. The results of the measurements carried out by the above mentioned workers *at room temperature* of the long spacings of these acids are reproduced graphically in Fig. 1 as a function of the *term-number* [3]). Beginning with *n.* hexylmalonic acid (term-number 6) the long spacing shows a very definite alternation. On passing up the series large and small increases of this constant alternate with one another and the former occur on passing from an odd to an even term; this alternation is thus *incomplete* and *even* according to the terminology introduced by VERKADE and COOPS [4]). It is noteworthy that the terms with term-number 2—5 on the other hand show no alternation; they form a separate group and neither the series of higher even nor that of the higher odd terms forms a continuation of it. Methylmalonic acid (term-number 1) is left out of consideration here.

§ 3. Particulars of the method of preparation and purification of the acids, of the specimens of acids used and of our measurements of the heats of combustion will be published elsewhere.

Table 1 gives a résumé of the results obtained. The third column contains the isothermal heat of combustion at $19.°5$ and constant volume, per gram, weighed in air with platinum weights. The fifth and sixth columns contain

[1]) Rec. trav. chim. **49**, 568 (1930).
[2]) These Proceedings **35**. 91 (1932).
[3]) Compare VERKADE and COOPS, loc. cit., p. 569.
[4]) loc. cit., p. 570.

the molecular heats of combustion at the temperature given, at constant volume ($Q_v$) and at constant pressure ($Q_p$) respectively; these quantities
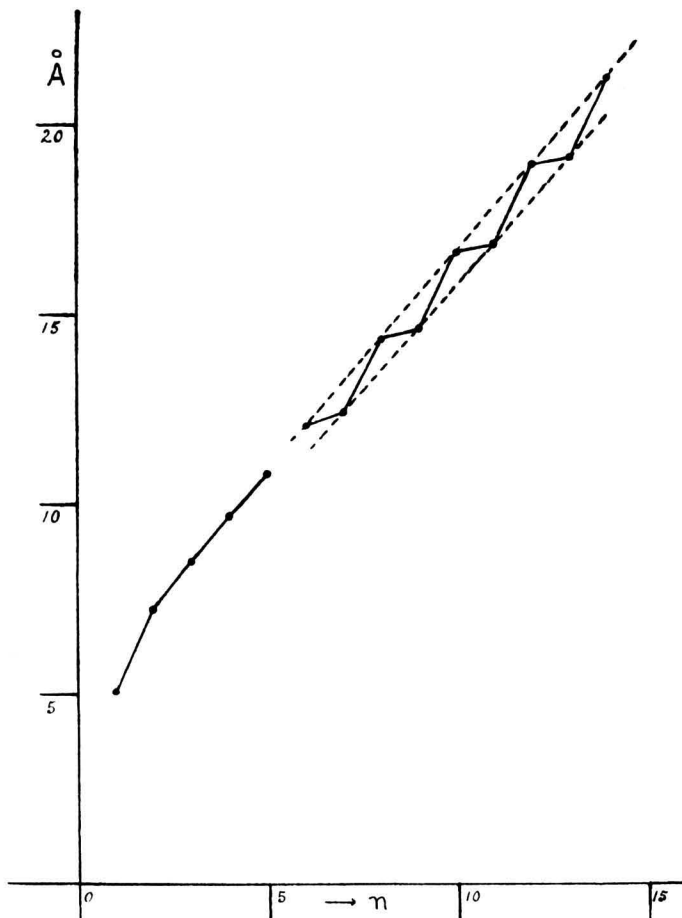


Fig. 1. Long spacings of $n$. monoalkylmalonic acids as a function of their term-number.

have been calculated with the aid of the specific gravities given in the fourth column.

The third column of Table 2 contains the values of $\triangle_{CH_2}$, deduced from the values of $Q_p$, that is to say, the increase of this heat of combustion on regular increase of the term-number by 1 $\left(\dfrac{\triangle Q_P}{\triangle n}\right)$. The picture, which these values of $\triangle_{CH_2}$ show, must now be interpreted in such a way as to be in agreement with the above-mentioned results of COSTER and VAN DER ZIEL.

It has repeatedly been observed that some alternation becomes gradually less noticeable as the series is ascended. For example in the case of the solubility in water and the melting-point [8] of the dicarboxylic acids of the

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[8] FAIRWEATHER, Phil. Mag. **1**, 944 (1926).

## TABLE 1.

| Term-number | R . CH(COOH)$_2$ | Heat of combustion per g (air) (19°.5; v const.) | Spec. grav. | $Q_v$ | $Q_p$ |
|---|---|---|---|---|---|
| 0 | malonic acid[6] | 1991.3 cal$_{15°}$ | 1.62 [5] | 207.0 Cal$_{15°}$ | 206.4 Cal$_{15°}$ |
| 1 | R = methyl | — | 1.45 [7] | — | — |
| 2 | ethyl | 3930.3 ,, | | 518.6 ,, | 518.6 ,, |
| 3 | n. propyl | 4623.7 ,, | | 674.9 ,, | 675.2 ,, |
| 4 | n. butyl | 5186.5 ,, | | 829.6 ,, | 830.2 ,, |
| 5 | n. amyl | 5666.7 ,, | | 985.7 ,, | 986.6 ,, |
| 6 | n hexyl | 6070.3 ,, | 1.21 [5] | 1140.9 ,, | 1142.1 ,, |
| 7 | n. heptyl | 6418.5 ,, | 1 19 [5] | 1296.2 ,, | 1297.7 ,, |
| 8 | n. octyl | 6719.3 ,, | 1.17 [5] | 1451.0 ,, | 1452.8 ,, |
| 9 | n. nonyl | 6984.3 ,, | 1.16 [5] | 1606.1 ,, | 1608.1 ,, |
| 10 | n. decyl | 7218.9 ,, | 1.15 [5] | 1761.4 ,, | 1763.4 ,, |
| 11 | n. undecyl | 7427.6 ,, | 1.14 [5] | 1916.0 ,, | 1918.6 ,, |
| 12 | n. dodecyl | 7613.4 ,, | 1.13 [5] | 2070.5 ,, | 2073.4 ,, |
| 13 | n. tridecyl | 7783.1 ,, | | 2225.6 ,, | 2228.8 ,, |
| 14 | n. tetradecyl | 7936.6 ,, | | 2380.6 ,, | 2384.1 ,, |

## TABLE 2.

| Term-number | $Q_p$ | $\triangle_{CH_2}$ | $\triangle_{C_2H_4}$ Even terms | $\triangle_{C_2H_4}$ Odd terms |
|---|---|---|---|---|
| 0 | 206.4 Cal$_{15°}$ | | | |
| 1 | — | — | 312.2 Cal$_{15°}$ | |
| 2 | 518.6 ,, | — | | |
| 3 | 675.2 ,, | 156.6 Cal$_{15°}$ | 311.6 ,, | |
| 4 | 830.2 ,, | 155.0 ,, | | 311.4 Cal$_{15°}$ |
| 5 | 986.6 ,, | 156.4 ,, | | |
| 6 | 1142.1 ,, | (155.5) ,, | | |
| 7 | 1297.7 ,, | 155.6 ,, | 310.7 ,, | |
| 8 | 1452.8 ,, | 155.1 ,, | | 310.4 ,, |
| 9 | 1608.1 ,, | 155.3 ,, | 310.6 ,, | |
| 10 | 1763.4 ,, | 155.3 ,, | | 310.5 ,, |
| 11 | 1918 6 ,, | 155.2 ,, | 310.0 ,, | |
| 12 | 2073.4 ,, | 154.8 ,, | | 310.2 ,, |
| 13 | 2228.8 ,, | 155.4 ,, | 310.7 ,, | |
| 14 | 2384.1 ,, | 155.3 ,, | | |

[5] BILTZ, FISCHER and WÜNNENBERG, Z. physik. Chem., A **151**, 25 (1930).
[6] VERKADE, HARTMAN and COOPS, Rec. trav. chim. **45**, 373 (1926).
[7] TANATAR and TSCHELEBIJEW, Journ. Russ. phys. chem. Ges. **22**, 549 (1890).

oxalic acid series this *damping* of the alternation soon becomes quite pronounced. Now we were originally of the opinion that in the case of the heats of combustion of the *n.* monoalkylmalonic acids we were dealing with such a damping of the alternation which set in quite low down in the series and soon became practically complete.

This hypothesis is nevertheless not tenable. Indeed, on the basis of what COSTER and VAN DER ZIEL brought to light with regard to the long spacings of these acids, the acids with term-number 5 and lower and those with term-number 6 and higher must be considered as quite separate groups. *In the group of the lower terms the heat of combustion shows an unmistakable, though somewhat weak odd alternation. In the group of the higher terms, the values of* $\triangle_{CH_2}$ *are on the other hand constant within the error of observation; no trace of an alternation of the heat of combustion can thus be detected.*

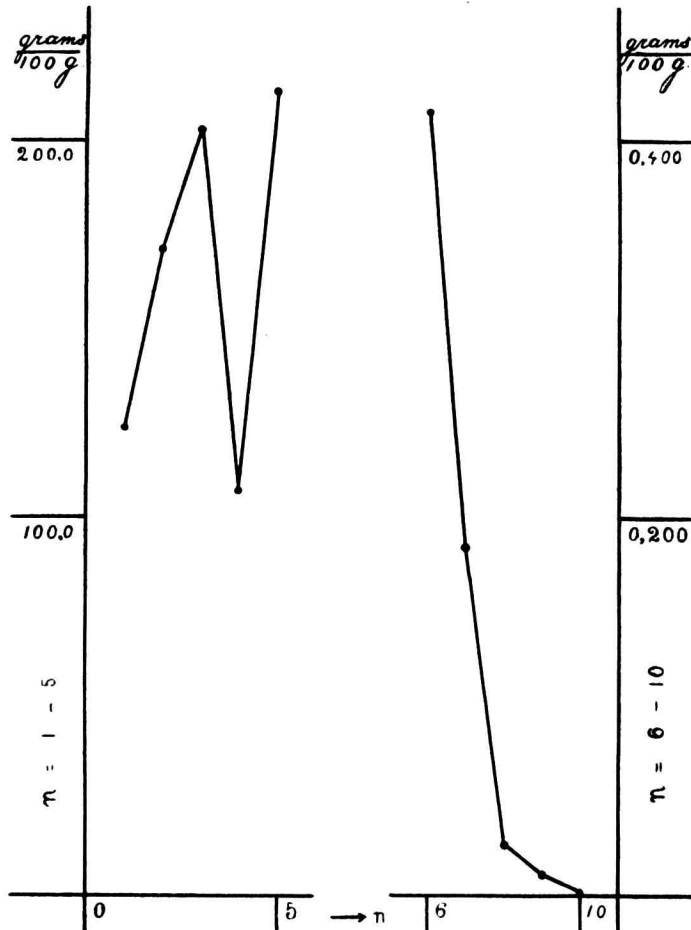§ 4. In our previous communication it was shown that there exists a



Fig. 2. Solubility of *n.* monoalkylmalonic acids in water as a function of their term-number.

quite remarkable contrast between the solubility in water at 25°.0 of the acids with term-number 2—5 and that of the higher acids (comp. Fig. 2). The work of COSTER and VAN DER ZIEL throws some light also on this noteworthy difference in behaviour between the lower and the higher terms of this series.

It is probably not an accidental coincidence that the solubility of these acids in benzene at 25°.0 shows a maximum just at *n*. amylmalonic acid (term-number 5). (See Fig. 3).
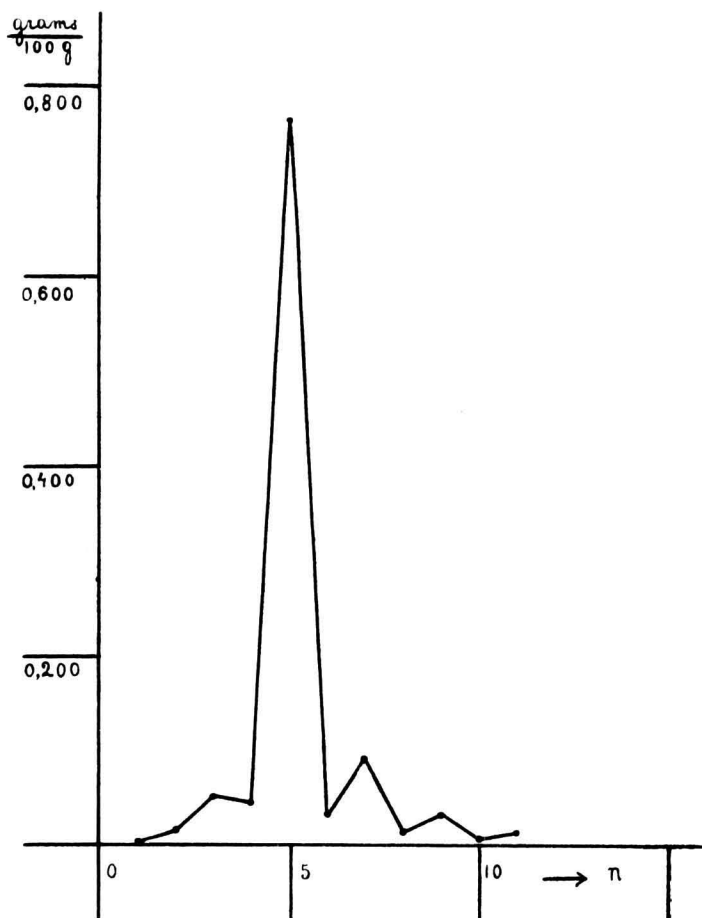


Fig. 3. Solubility of *n*. monoalkylmalonic acids in benzene as a function of their term-number.

COSTER and VAN DER ZIEL also draw attention to the melting-point curve (Fig. 4) which shows a minimum at the same term. It is however not at all certain a priori that all these acids retain the same crystal structure during heating from room temperature up to the melting-point and it is consequently dangerous to combine the long spacings found at room temperature with the melting-points.

§ 5. Although on the one hand the work of COSTER and VAN DER ZIEL has brought positive enlightenment, yet on the other hand the alternation
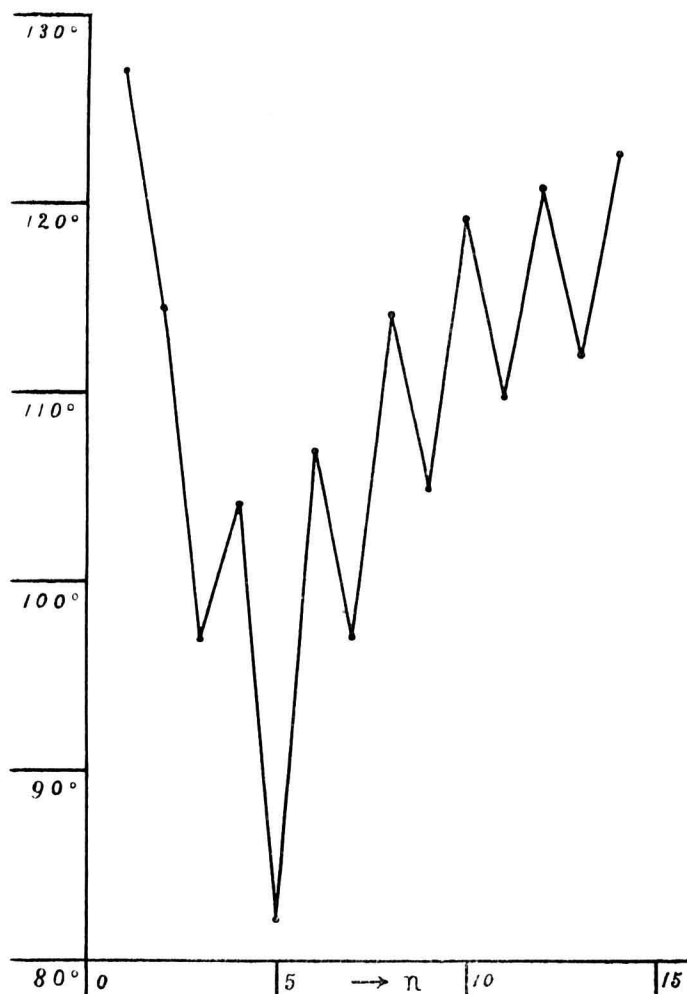


Fig. 4. Melting point of *n*. monoalkylmalonic acids as a function of their term-number.

phenomena occurring with these acids now appear to be more complicated than one would suppose a priori. In what follows we develope some further ideas about these phenomena.

a. In the small group of the *lower* acids an alternation of the long spacings is not observed. (See Table 3). As appears immediately from an examination of a model, *in the absence of such an alternation the zigzag chains of methylene groups must be perpendicular to the planes formed by the terminal groups.* If the value 1.54 Å is taken for the diameter of the carbon atom and the tetrahedral angle 109° 28' is retained in the chains, the length of a vertical zigzag chain will increase by 1.26 Å per methylene

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TABLE 3.

| Acid | Long spacing | $\frac{d}{n}$ |
|---|---|---|
| Ethylmalonic | 7.25 Å | |
| | | 1.25 Å |
| n. propylmalonic | 8.50 Å | |
| | | 1.21 Å |
| n. butylmalonic | 9.71 Å | |
| | | 1.11 Å |
| n. amylmalonic | 10.82 Å | |

group. In a number of series with non-alternating long spacing the experimentally found increase is somewhat greater because, as is commonly assumed, the angle is somewhat greater than 109° 28'; examples of this are furnished by the ethyl esters of the fatty acids (MALKIN [9])), the normal primary alcohols (MALKIN [10])), the acid potassium salts of the fatty acids (PIPER [11])), the ketones (SAVILLE and MÜLLER [12])), etc. The hypothesis does not seem to us to be too risky that *the members of the group of n. monoalkylmalonic acids in question possess a vertical chain* ; the increase in length of the chain per methylene group (see Table 3) is in favour of this hypothesis.

This group of acids does meanwhile show an alternation of the solubility in water and in benzene at 25°.0, of the energy-content at 19°.5 and also of the melting-point. We consider this fact somewhat more closely in § 6 ; it is in our opinion definitely interesting in connection with the views of MALKIN on the cause of the alternation phenomena. The acids with the groups —$CH_3$ and —$CH(COOH)_2$ in the *cis*-position with respect to the chain of methylene groups — on applying the terminology suggested by us, these are the even acids — have the relatively smaller energy-content, the smaller solubility in water and benzene and the higher melting-point.

*b.* The long spacings found for the group of the *higher* acids show a marked alternation (Fig. 1). *The zigzag chains of methylene groups are thus tilted with respect to the terminal planes.* From the data of COSTER and VAN DER ZIEL it can be calculated that the long spacing increases for each two methylene groups in the even acids by 2.26 Å on the average and in the odd acids by 2.21 Å on the average. The angle of tilt of the chains calculated from these data on the before-mentioned premises amounts to about 63½° and about 61½° respectively. We need not concern ourselves here with this possible difference in angle of tilt in the odd and even terms, which also occurs in other series.

Until now in this group of acids there has moreover been encountered

[9]) Journ. Chem. Soc. 1931, 2796.
[10]) Journ. Amer. Chem. Soc. **52**, 3739 (1930).
[11]) Journ. Chem. Soc. 1929, 234.
[12]) Ibid, **127**, 591 (1925).

besides an alternation of the melting-point an alternation of the solubility in benzene at $25°.0$ and of the molecular volume at 16—18° [5]). The acids with the groups $—CH_3$ and $—CH(COOH)_2$ in the *cis*-position possess the relatively longer spacing, the relatively larger molecular volume and furthermore, as in the case of the group of lower acids, the smaller solubility in benzene and the higher melting-point. In other homologous series the picture presented by the sum total of the types of alternation in these constants can be different; in the dicarboxylic acids of the succinic acid series, for example, the acids with the relatively longer spacing — in this case the even acids with the — COOH-groups in the *trans*-position [13]) — have the relatively smaller molecular volume at 25° [14]), the smaller solubility in benzene at $25°.0$ [15]) and the higher melting-point. A detailed knowledge of the crystal structures of the odd and even terms of a given homologous series will probably be able to contribute much to a better understanding of the type of each alternation phenomenon in this series and thereby of the connection between these phenomena. Little or nothing can at present be said on this question without falling into very speculative discussions. An indirect proof of this is furnished by the contents of the publication of MALKIN [16]), presently to be discussed. *Conversely the knowledge of the alternation phenomena occurring in a homologous series will meanwhile perhaps be able sometimes to be of service in the interpretation of the results of crystallographic or röntgenographic investigation of this series.*

It is a curious fact that, on the other hand, no alternation whatever is observed in the solubility in water at $25°.0$ and in the heat of combustion of these higher acids. The increase in the heat of combustion on passing from one even term to the next even term ($\triangle_{C_2H_4}$) amounts to *310.5* $Cal_{15°}$ on the average; in the odd acids this increase amounts to *310.4* $Cal_{15°}$ (see Table 2). The excellent constancy of $\triangle_{C_2H_4}$ leads one to a conclusion with regard to the *latent heats of fusion* of these acids which will be dealt with in a publication to appear elsewhere.

§ 6. As a result of their own work and of a critical survey of the literature VERKADE, COOPS and HARTMAN [17]) were the first to express the conviction *that such alternation phenomena only occur in constants which are related to the crystalline state.* This conception was acknowledged straight away to be correct by other investigators of these phenomena. Only NEKRASSOV [18]) — apparently unaware of the above

13) TRILLAT, Comptes rendus, **180**, 1329 (1925); HENDERSON, Proc. Roy. Soc. Edin. **48**, 20 (1927—1928).
14) BILTZ and BALZ, Z. anorg. Chem. **170**, 335 (1928).
15) VERKADE and COOPS, Rec. trav. chim. **49**, 578 (1930).
16) Nature, **127**, 126 (1931); Journ. Chem. Soc. 1931, 2796.
17) Rec. trav. chim. **45**, 585 (1926).
18) Z. physik. Chem. **128**, 203 (1927).

mentioned paper — still in 1927 illustrated his interesting views with the aid of — pretended — alternations in series of *liquid* homologues. In a private conversation with one of us (VERKADE) in July 1928 SCHILOW, under whose supervision NEKRASSOV worked, frankly acknowledged the correctness of the former's conception.

The results of the work on monomolecular layers of long chain compounds and of the X-ray investigation of such crystalline substances have soon afterwards led to somewhat more profound theories concerning the cause of the alternation phenomena. They showed that with regular increase of the term-number of a series of crystalline homologues the terminal groups are alternately in the *cis* and the *trans* position with respect to the zigzag chains of methylene groups. *Some workers now see in this fact the cause of the alternation phenomena.* Besides the work of NEKRASSOV [18] that of MÜLLER [19] must be cited ; reference may also be made to the paper of PAULY [20] which bears evidence of a prophetic insight. It is not necessary for our purpose to discuss the relevant literature here.

Some time ago a different conception with regard to the cause of these phenomena was put forward by MALKIN [16]. The view above mentioned demands in principle the occurrence of alternation phenomena in all the terms of all homologous series. MALKIN sees a difficulty in this, since, according to him, series exist which show no alternation phenomena ; he mentions as such, without any illustration, the normal paraffins, the methyl ketones, the normal primary alcohols and the ethyl esters of the fatty acids. These series are those, in which vertical chains have been observed (see § 5). *According to* MALKIN *it is now a characteristic of a series with alternation phenomena that it possesses a tilted chain, while a vertical chain should be present in a series without alternation phenomena.* That is to say *"alternation is caused by some effect resulting from a tilted chain"* ; the supposed nature of this effect is then indicated.

We would now make some remarks with regard to this conception of MALKIN:

1⁰. The long spacing increasing by an amount of about 1.3 Å per methylene group, from which one concludes that the compounds possess a vertical chain, was met with in the X-ray investigation of the *higher* terms of the series mentioned by MALKIN. For example, the term-number of the terms in question of the series of ethyl esters of the fatty acids amounted to 17—21 [9] and with the alcohols it lay between 12 and 25 [10]), with the paraffins [21] between 17 and 35. Is now absence of an alternation of the long spacing in the affected forms of these high terms attended by the absolute absence of alternation in other physical constants which also relate to the crystalline state ? MALKIN may have made such a connection

19) Proc. Roy. Soc. London, A **124**, 317 (1929).
20) Z. anorg. Chem. **119**, 271 (1922).
21) MÜLLER and SAVILLE, Journ. Chem. Soc. **127**, 599 (1925).

the starting-point of his deductions, it has not in the least been proved ; he himself even makes no attempt in this direction. Precision measurements of constants of these high terms suitable for settling the existence or non-existence of this connection were, as far as we know, not available in the literature and have not been carried out by MALKIN.

A careful investigation dealing with several physical constants for the purpose of answering the question put forward above seems to us to be of quite definite importance.

$2^0$. MALKIN's statement that no alternation phenomena occur in the above mentioned homologous series is incorrect and is most probably a consequence of careless editing of his paper with regard to this point. For example, the lower paraffins show an alternation of the zero-point volume ("Nulpunktsvolumen") [22]) and the alcohols up to and including term-number 11 a definite melting-point alternation [23]) ; FRANCIS, PIPER and MALKIN [24]) found a clearly alternating long spacing in that form of the ethyl esters of the fatty acids which is stable below the transition point. It can however be conceded that data available in the literature, mostly however not at all accurate, concerning the *melting-points* of the *higher* terms of these series strongly suggest the absence of an alternation in this constant. Very probably this fact merely has been in MALKIN's thoughts and is the actual and as yet rather uncertain basis of his arguments.

One cannot however in any way draw the conclusion from the absence of alternation in a single constant that alternation phenomena are entirely absent in the homologous series in question. Indeed it appears for example from our investigation of the group of the *higher* monoalkylmalonic acids that in this case some constants show a definite alternation, others on the contrary no noticeable alternation.

$3^0$. Neither MALKIN nor MÜLLER mention a single word about *the possibility that the dimensions of the cross-section of the molecule are different in the case of cis- or trans-position of the terminal groups.* Such a possibility appears to us to be in every way conceivable. One could then expect that the dimensions of the cross-section alternate in the homologous series. It needs no further exposition that in such an alternation in the density of packing of the chains may lie a source of alternation in other physical constants (molecular volume, melting-point, etc.), even if the odd and even terms of the series in question possess a vertical chain.

It is definitely of interest to refer in this connection to the values reproduced in Table 4 of short spacings $d_3$ and $d_4$ found by HENDERSON [25]) in an X-ray investigation of odd and even terms of the succinic acid series. These short spacings show a definite alternation. It must however be

[22]) BILTZ, FISCHER and WÜNNENBERG, loc. cit.; HEUSE, Z. physik. Chem., **147**, 266 (1930).

[23]) VERKADE and COOPS, Unpublished observations.

[24]) Proc. Roy. Soc. London, A **128**, 224 (1930).

[25]) Proc. Roy. Soc. Edin, **48**, 20 (1927—1928).

remarked that it is not certain whether these spacings are really connected with the cross-section of the molecule.

$4^0$. In § 5 it was demonstrated that the members of the group of *lower n*. monoalkylmalonic acids most probably possess a vertical chain. *In conflict with* MALKIN's *conception, a definite alternation has now been observed here in the solubility in water and in benzene at 25°.0, in the energy-content at 19°.5 and also in the melting-point.* It appears highly improbable to us that these alternations are to be attributed to a difference in the density of packing of the chains in the cis- and trans-acids. Investigation of a model shows immediately that this possibility can be safely left out of consideration, if one of the two terminal groups is a methyl group; thus, for example, in the acids in question and in the homologous series mentioned by MALKIN.

TABLE 4.

| Term-number | $d_3$ | | $d_4$ | |
|---|---|---|---|---|
| | even | odd | even | odd |
| 5 | | 3.78 Å | | 3.38 Å |
| 6 | 3.65 Å | | 2.98 Å | |
| 7 | | 3.87 | | 3.28 |
| 8 | 3.75 | | 2.99 | |
| 10 | 3.77 | | 2.98 | |
| 11 | | 3.93 | | 3.21 |
| 12 | 3.71 | | 2.97 | |

It may here be mentioned that HENDERSON [25]) found no contrast between the short spacings observed with ethyl- and *n*. butylmalonic acid on the one hand and *n*. propylmalonic acid on the other.

$5^0$. An explanation for the alternation phenomena in these acids might also be sought in the hypothesis that in the case of such low term-numbers the two terminal groups of the molecule still exert a powerful influence upon one another and to a different extent in the cis-position than in the trans-position. However, such an explanation seems to us to be unacceptable, partly because one of the terminal groups is a so little reactive, non-polar methyl group, partly because of the fact that in this case also the long spacings ought to show alternation.

$6^0$. *In our opinion these alternation phenomena occurring in the lower monoalkylmalonic acids definitely make still more improbable the already insufficiently experimentally founded views of* MALKIN. MALKIN's ideas are too naive; they cannot in any way embrace the very complicated whole of

these phenomena. This appears once more when we subject to a critical examination that part of MALKIN's paper in which he discusses the alternation phenomena occurring in homologous series with tilted chains and states to what cause in his opinion these are to be attributed. As a consequence of his views on the subject — reference may be made to the original paper for these — MALKIN deduces certain rules with regard to the connection between the types of alternation occurring in various physical constants. The *odd* terms — we will not yet go into the question of what MALKIN understands by this — should possess the lower melting-point, the larger spacing and the less tilted chain. If MALKIN's views were correct, these rules ought to possess a quite general validity. However, there is no question of this. Already the series of higher alkyliodides investigated by MALKIN[9]) himself furnishes a clear exception : the odd terms here have the higher melting-point and the shorter spacing. As follows from what has been stated in the preceding § the monoalkylmalonic acids and the dicarboxylic acids of the succinic acid series for example do no more satisfy these rules.

*The properties of the odd and even terms of a homologous series are to a preponderating degree determined by the nature of the two terminal groups*; these latter are therefore also of influence on the alternation phenomena occurring in this series. This is an obvious fact which cannot be tampered with. *It is now just the fault of ideas such as those of* MALKIN *and also of those of* MÜLLER[19]) *that the nature of these terminal groups is completely left out of the argument.*

7[0]. Finally it may incidentally be remarked that it is certainly quite wrong, as MALKIN does, — at least we believe that we are justified in deducing this from his paper ; it is nowhere stated expressly — to consider the physical properties as functions of the *total number of carbon atoms* in the molecule, inclusive thus of those of the terminal groups. The application of a system of numbering the successive terms such as that suggested by NEKRASSOV[18]) or by VERKADE and COOPS[3]) appears to us to be so much more rational.

*Rotterdam, Laboratory of the Dutch Commercial University,*
Dec. 1932.