

The Crystal Structure of the Normal Paraffins at Temperatures Ranging from that of Liquid Air to the Melting Points.

By ALEX MÜLLER.

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[PLATES 5, 6.]

Introduction.

The aim of this paper is to give a survey of the structures of the normal paraffins at temperatures ranging from that of liquid air to those in the neighbourhood of the melting points. The paper divides naturally into two parts, one dealing with the thermal expansion, *i.e.*, with the gradual and continuous increase of the lattice dimensions with increasing temperature; the other with the discontinuous structural changes which occur under certain conditions when the substances are subjected to temperature changes.

Chemical Material.

The chemical material was partly that already used in previous work and partly new material. Most of the substances were synthesised in the Davy-Faraday Laboratory. Some of the preparations such as hexane and pentane were bought and carefully purified. The writer is again very much indebted to his colleagues, Dr. H. S. Gilchrist and Mr. E. L. Holmes, who were kind enough to do all the chemical work for him.

Experimental.

The following method for mounting the samples on the X-ray spectrometer was found to be very convenient. Thin-walled glass tubes of, say, $\frac{1}{2}$ to $1\frac{1}{2}$ mms. diameter were partly filled with the substances and then sealed off at both ends. In this form the samples could be kept indefinitely and handled with ease. These glass tubes were made to fit closely into small metal holders and could then be centred accurately on the spectrometer. During the exposure they were rotated. The cooling of these samples was quite a simple matter. For the liquid air investigation the sample holder had the shape of a small cup supported by a stem. The glass tubes were made to fit into a narrow central hole in the stem. The liquid air was conducted through a small glass funnel which ended very close to the sample and near the point where the X-rays

struck the substance. The liquid air flowed along the glass tube into the cup and overflowed or evaporated there. By this method it was possible to keep substances like butane and pentane frozen. The film holder which surrounded the sample was made into a camera sufficiently air-tight to prevent moisture from entering it. No traces of ice lines could be detected on the photographs. Work at higher temperatures was done with the same apparatus except for a few minor alterations. The cup-shaped holder was replaced by a small cylindrical one, and a small platinum heating coil which surrounded the sample closely was put immediately below the point where the X-rays struck the glass tube. Any of the samples investigated here could be kept in a liquid state by sending a small current through the coil. The surface which separated the solid from the liquid phase inside a sample tube could be shifted up and down, and the solid or liquid portion could be brought into the path of the X-rays at will.

The X-ray tube with copper anticathode $\lambda = 1.539 \text{ \AA.U.}$ was run by an induction coil with a Wehnelt interrupter and the radiation was filtered by nickel foil.

I.—*Thermal Expansion.*

Before giving an account of the expansion measurements it is necessary to recall a few facts about the structure of these hydrocarbons. $\text{C}_{29}\text{H}_{60}$ has been previously determined from X-ray measurements on a single crystal.* In the present work there was no necessity to procure single crystals. Powder photographs, examples of which are given at the end of this paper, showed at once that a whole series of these substances have identical structures, *i.e.*, the chain molecules although different in length are arranged in exactly the same manner throughout the series. It will be shown in the second part of this paper that under certain conditions some of these paraffins can form a second structure different from the one mentioned above. It should be remembered that the expansion measurements treated in this section have been carried out on the first, or "normal" structure, *i.e.*, on the one corresponding to $\text{C}_{29}\text{H}_{60}$.

A few words may be said about the way the figures for the expansion were obtained from the photographs. The plan was to find the linear expansion in the direction of the three crystallographic axes. First it was necessary to identify the reflections on the films. The size of the lattice being known, the usual difficulty did not arise. There were three reflections which could always be obtained with comparatively short exposures, namely, the 110, 200 and 020.

* 'Roy. Soc. Proc.,' A, vol. 120, p. 437 (1928).

The first was the strongest, the two others were weaker. The two last reflections were usually the most clearly defined of the three. The spacings corresponding to them gave at once half the length of the two main axes a and b in the basal plane of the crystals. The following table gives the numerical data of the lengths of these two axes as obtained from different substances at different temperatures. With regard to the temperature it will be noted that no figures are given in the table. No attempt is made in this preliminary paper to obtain a high degree of accuracy.

Table I.

Number of C atoms.	Liquid air temperature.		Room temperature.		Few degrees C. below melting point.	
	$a/2$.	$b/2$.	$a/2$.	$b/2$.	$a/2$.	$b/2$.
11	3.59	2.46	—	—	—	—
15	3.59	2.47	—	—	—	—
17	3.595	2.445	—	—	3.83	2.51
18	—	—	—	—	3.84	2.50
19	3.58	2.44	3.70	2.49	3.86	2.485
20	—	—	—	—	3.88	2.50
23	3.60	2.45	—	—	—	—
24	3.62	2.45	3.73	2.49	3.80	2.51
29	—	—	3.70	2.47	3.79	2.49
30	—	—	3.74	2.48	—	—

The figures show clearly that the lengths of both axes increases considerably with increasing temperature. We take the figures $a/2$ and $b/2$ for different paraffins at liquid air temperature. They are identical within the limits of experimental error, *i.e.*, $\frac{1}{2}$ to 1 per cent. The average for $a/2$ and $b/2$ at liquid air temperature is:—

$$a/2 = 3.593 \pm 0.004 \text{ \AA.U.}$$

$$b/2 = 2.453 \pm 0.004 \text{ \AA.U.}$$

The relative errors of the averages are thus only a few thousandths. (The absolute values should be correct within, say, $\frac{1}{2}$ per cent.) In the following table the linear expansions of the a and the b axis have been calculated with the aid of the figures in the previous table.

Table II.

Number of C atoms.	Melting points.	Temperature range.	Δ_a in per cent.	Δ_b in per cent.	Δ_a/Δ_b .
	° C.				
17	22	Liquid air—near melting point	6.74	2.32	2.9
18	28	.. —	6.87	1.91	3.6
19	31	.. —room temperature	2.98	1.51	2.0
19		.. —near melting point	7.57	1.30	5.8
20	38	.. —	7.99	1.91	4.2
24	54	.. —room temperature	3.81	1.51	2.5
24		.. —near melting point	5.76	2.34	2.5
29	64	.. —room temperature	3.14	0.77	4.1
29		.. —near melting point	5.48	1.51	3.6
30	66	.. —room temperature	4.01	1.10	3.5

a_l = length of a axis at liquid air temperature.

b_l = length of b axis at liquid air temperature.

a_t = length of a axis at temperature t .

b_t = length of b axis at temperature t .

$$\Delta_a = 100 (a_t - a_l)/a_l; \quad \Delta_b = 100 (b_t - b_l)/b_l.$$

The table shows that the percentage expansions of the a axes are considerably larger than the corresponding ones of the b axes. The average of the figures in the last column of the table gives

$$(\Delta_a/\Delta_b)_{av.} = 3.5 \pm 0.35.$$

In order to get sufficiently accurate data for the change in length of the c axes, it was found necessary to adopt the usual method for mounting the powder samples in which the substances are spread into thin layers on flat glass surfaces. The photographs obtained with the glass tube samples did as a rule show the long spacings corresponding to the c axes, but the definition of the lines was not good enough to allow measurements of small changes. The photographs obtained from these thin layers show very sharp lines, and changes of the order of 1 per cent. could have been detected in the distance of two symmetrical reflections on the films.

The photographs showed no appreciable displacement of the long spacing reflections when taken at different temperatures. In other words: the expansion of the c axis was found to be much smaller than that of the a or b axes; and not to exceed one-tenth of the expansion of the a axis. A reproduction of a photograph which shows this very clearly is given at the end of this paper. The figures obtained in this section will be discussed later on.

II.—The Structural Changes with Temperature.

This second section deals with the discontinuous changes in the structures which take place when some of the substances are subjected to temperature alterations. The fact that such changes can easily be detected by X-ray methods has been shown in an earlier investigation on the paraffins.* It was noted that these changes were reversible. Each of the two crystalline forms which the substances could assume were stable over a certain range of temperatures, and the substance could be made to change from one form into the other by altering the temperature.

In this section of the paper an attempt is made to follow up the earlier investigation by a more detailed study of the phenomena. The substances which are dealt with in this section range from C_5H_{12} pentane to $C_{30}H_{62}$ triacontane.

The lower members of the series being liquids at room temperature had to be kept frozen during the X-ray exposure. These samples were kept in those thin-walled glass tubes mentioned at the beginning. The higher members of the series were either used in the same way or in the form of thin layers on glass.

The following table gives the data for the "long spacings," *i.e.*, those spacings which depend essentially upon the length of the carbon chain in each individual substance.

Table III.

N.	Even numbers.		N.	Odd numbers.	
	d_1 .	d_2 .		d_1 .	d_2 .
6	—	8.55	5	—	7.35
8	—	11.0	7	—	10.0
10	—	13.4	9	—	12.8
16	—	20.9	11	15.9	—
18	25.3	23.3	15	21.0	—
20	27.4	25.4	17	23.6	—
24	32.6	—	19	26.2	—
26	35.2	—	21	28.7	—
30	40.0	—	23	31.0	—
—	—	—	29	38.8	—

The figures of Table III are plotted in fig. 1.

* 'J. Chem. Soc.,' vol. 127, p. 599 (1925).

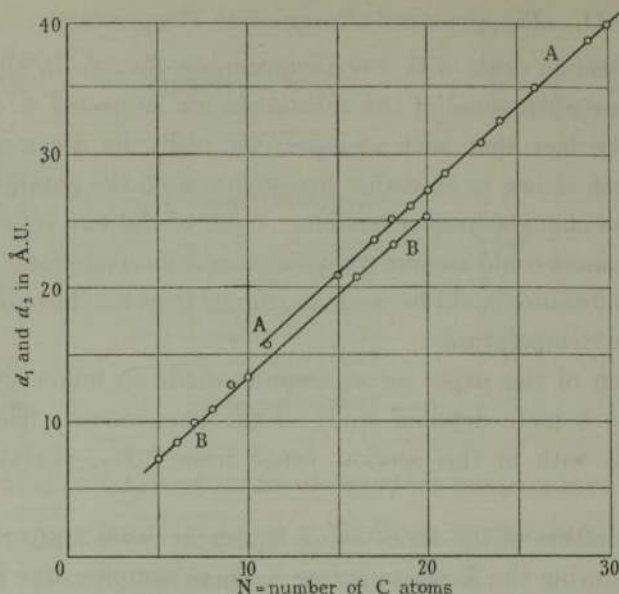


FIG. 1.

The spacings d_1 and d_2 are plotted against the number N of carbon atoms in the chains. Above $N = 20$ the spacings of both the odd and the even numbered substances lie within the limits of experimental error on one straight line AA. The increase of the spacing per carbon atom is 1.25 \AA.U. In the neighbourhood of $N = 20$ the odd and even numbered substances begin to differ in their behaviour. From both $\text{C}_{20}\text{H}_{42}$ and $\text{C}_{18}\text{H}_{38}$ two sets of spacings can be obtained. If the substances are kept near their melting points longer spacings appear which lie on AA. At lower temperatures another set appears, and the spacings now lie on the line BB. Further cooling no longer produces any change and the two spacings still persist at liquid air temperature. $\text{C}_{16}\text{H}_{34}$ gives only one spacing on the lower line, and the same thing is for the still lower members of the even series down to C_6H_{14} . The odd members of the series behave in a different way. $\text{C}_{19}\text{H}_{40}$ gives only one spacing and no change is found when the substance is cooled down to liquid air temperature. The spacing of $\text{C}_{19}\text{H}_{40}$ lies on the upper line AA. The same holds for C_{17} , C_{15} and C_{11} . At C_9H_{20} a change takes place, and the long spacings of the members of the odd series from $N = 9$ downwards approach the straight line BB. This is so far as the long spacings are concerned. The structural changes which both C_{20} and C_{18} can undergo are shown not only by the appearance of the two sets of long spacings but also in the general appearance of the powder photographs.

Particularly when "glass tube samples" are used the two structures give quite different patterns on the photographs. Those on which the longer spacings appear show the features characteristic of the normal form, and similarly, those on which the shorter spacings appear are almost indistinguishable from each other except for the long spacing lines. This second characteristic pattern is not only found with $C_{20}H_{42}$ and $C_{18}H_{38}$ but also with lower members of the even series and can be traced down to C_8H_{18} . Structures which show this second characteristic pattern will from now on be called "second form" in contradistinction to the "normal form." Reproductions showing the difference between the two patterns will be found at the end of this paper. The three strongest lines of the second structure have the spacings 4.56, 3.79, 3.58 Å.U. ($C_{20}H_{42}$ at room temperature).

With regard to the appearance of the second form it may be mentioned that on rare occasions faint traces were found on photographs of $C_{24}H_{50}$ of a line which did not belong to the normal structure. This line coincided with the strongest line of the second form. It is therefore not unlikely that traces of the second form may coexist with the normal form. The writer has not been able to find the exact conditions under which this phenomenon occurs.

An attempt was further made to explore the finer details of the changes in the crystal structure in the immediate neighbourhood of the melting point. A very fine pencil of X-rays had to be used for getting a clear separation of the lines and the temperatures had to be changed in small steps. A sample was first completely melted. The photograph obtained at this stage was the well-known broad ring characteristic of the liquid state. The temperature was then lowered a very little. The X-rays beam was made to strike the spot where the solid and the liquid phase met. The photograph obtained under these circumstances was rather striking. The broad ring had vanished and a very well-defined sharp ring appeared which had the appearance of a normal crystal reflection. The striking fact was that no other reflection of anything like the same order of intensity could be found on the photographs. At a slightly lower temperature more lines appeared, but this line remained without showing any appreciable change in definition or position, and was found to coincide with the 110 reflection of the normal structure. The various stages through which the structures went are shown in the reproductions. The sharp single reflection was found to appear with both even and odd numbered substances.

Discussion.

The data in the first part of this paper show that the hydrocarbons are strongly anisotropic. The average coefficient of expansion between the temperature of liquid air and the melting points of all the substances investigated is 6.8 per cent. in the direction of the *a* axes and 1.9 per cent. for the *b* axes. The average ratio of the two is 3.5 ± 0.35 , *i.e.*, the coefficient of expansion of the *a* axis is about three to four times as large as the one of the *b* axis. Compared with these expansions of the two axes in the basal plane, the expansion

in the direction of the third long axis of the higher members of the series is very small. In the photograph which is shown at the end of the paper there is no displacement detectable in the long spacing reflections at liquid air temperature and at room temperature. This photograph was obtained from $C_{19}H_{40}$. The above facts are illustrated in fig. 2.

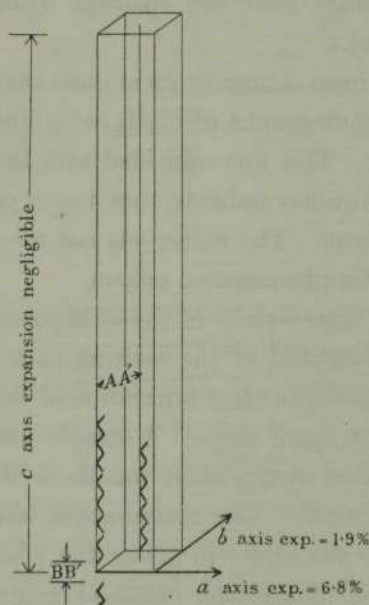


FIG. 2.

In this diagram is shown a zig-zag line indicating the position of the chain molecules in the unit cell. The distances and arrangement of the chains in the crystals and the structure of the chain itself have been discussed in detail in the previous paper on $C_{29}H_{60}$ (*loc. cit.*).

The expansion data show that the chain axes move apart from each other as the temperature increases, *i.e.*, the distance *AA'* becomes larger when the crystal is heated. The expansion of the length of the *c* axis depends upon two factors. One is the moving apart of the end groups, *i.e.*, the increase of *BB'* with temperature. The second is the expansion of the chain molecule itself. The expansion or possible contraction of *BB'* is unlikely to differ in magnitude from the lateral change in distance of the chain axes. If, therefore, it is found that the total expansion of the *c* axis is negligible compared with this lateral expansion, the conclusion is that the molecule itself has a negligible expansion in the direction of its axis. This simply indicates that the forces which hold the atoms together in the molecule are different in magnitude from those which keep the molecules apart from each other. The chemical conception of the

entity of the molecule is thus confirmed for the solid state. This in itself is not surprising, but the fact that the investigation is now brought within the range of numerical treatment opens interesting possibilities. By increasing the accuracy of the measurements it will undoubtedly be feasible to obtain the expansion of the chain itself, and so to compare the intramolecular with the intermolecular cohesion.

The expansion ratio 3.5 of the a and b axis confirms what has been found in the structure investigation of the paraffins, namely, that the chain molecule has no radial symmetry about the chain axis.

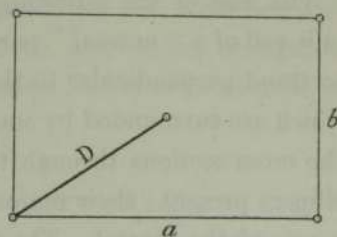


FIG. 3.

It is interesting to see how the distance of nearest approach of two adjacent chain axes alters when the temperature is raised. This distance D is shown in fig. 3.

Take the measurements for $C_{19}H_{40}$ which melts at $31^\circ C$.

Temperature.	D .
	Å.U.
Liquid air	4.35
Room temperature	4.5
Near melting point { Solid	4.6
{ Molten.....	4.6

The last figure refers to the substance in the liquid state when the temperature is not far from the melting point. The X-ray reflection on the photograph is a broad ring, and the spacing corresponding to this ring cannot be calculated with the same degree of accuracy as those which appear when the substance is in the solid state. It seems, however, that there is no appreciable discontinuity in the figures. By measuring the width of the ring it is therefore possible to get an approximate measure of the distance of nearest approach of the chain axes when the substance is a liquid.

Rings of this nature have been obtained by several investigators; the interest of the above figures lies in the fact that they suggest a more definite interpretation of the significance of this ring than has been obtained hitherto.

A few words may be said about the rather unexpected phenomenon of the

single sharp reflection which appeared when the substances were investigated in the immediate proximity of the melting point. The phenomenon will have to be studied in more detail before a definite explanation can be given. It is perhaps not out of place, however, to discuss the subject to some extent.

The first of the following diagrams represents a cross-section through the unit cell of a "normal" paraffin crystal. The chain axes, which are supposed to stand perpendicular to the plane of the paper, intersect this plane in points which are surrounded by small ellipses in the drawing. These ellipses represent the cross-sections through the chain molecules. There are two sets of these ellipses present; their major axes are placed symmetrically with regard to the a axis of the crystal. The positions of the molecules indicated in fig. 4 have to be regarded as average positions at a given temperature.

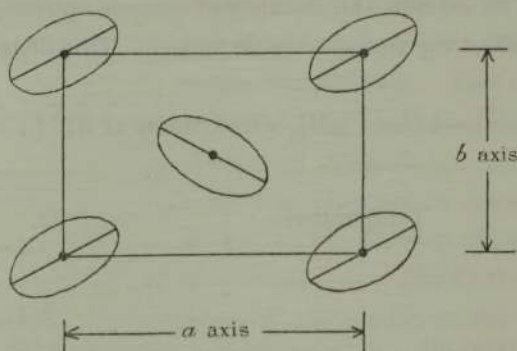


FIG. 4.

Apart from a change in proportions the above arrangement is found to exist until the temperature reaches very nearly the melting point.

At this juncture the arrangement of the molecules in the crystal seems to alter. The X-ray photographs change their appearance. The 200 reflection becomes very faint compared with 110 line, and seems to disappear completely when the photograph is taken at a slightly higher temperature. Yet the 110 line does not alter appreciably in sharpness and only disappears when the substance turns into the liquid state. The broad ring which then appears has a distinctly different spacing, 4.6 \AA.U. compared with 4.2 \AA.U. of the 110 reflection.

A photograph with a single sharp reflection would be obtained from a layer structure, *i.e.*, from an arrangement in which groups of molecules are placed in equidistant layers. Each group would have to contain a sufficiently large number of molecules to give sharp reflections. The groups themselves taken as a whole could be oriented at random. The question arises as to whether

the normal structure can be transformed into a layer structure in a simple way. This seems to be so. The oscillations of the molecules round their chain axes, one possible mode of thermal agitation, must increase as the temperature rises. These oscillations may become so strong that some of the first set of molecules turn into positions occupied by the other set, and *vice versa*. The step from such an arrangement to one where groups of molecules are arranged in layers is then easily made. This is illustrated in fig. 5.

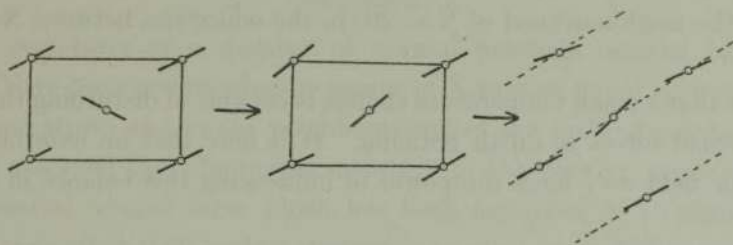


FIG. 5.

Without the knowledge of the nature of the intermolecular forces it is obviously impossible to see why just this layer arrangement should have a certain stability. Further investigation will show whether the explanation of this sharp single line is correct. If this is so, then observations taken in the neighbourhood of the melting points are of particular interest, for they are likely to reveal the strongest bonds between the molecules.

The following part of the discussion will deal with the abrupt changes in the structures of some of the paraffins. The essential facts have already been given in an earlier part of this paper. The experiments show that there is a marked difference in the behaviour of the odd and even numbered substances. This general observation is hardly surprising, for it has been shown in a previous note* that such differences may almost be regarded as geometrical consequences of the zig-zag chain structure. The interest lies in the manner in which these differences reveal themselves. A qualitative explanation can easily be found.

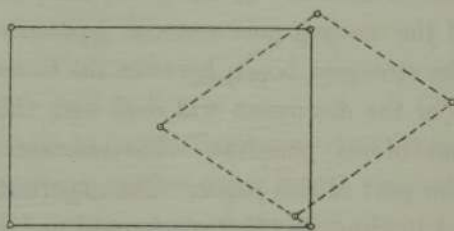
Supposing first we deal with paraffin crystals which contain very long chains. The influence of the groups at the ends of these chains upon their mutual arrangement must then be very small, and the chains will arrange themselves in their own typical fashion. Both odd and even numbered substances will practically have the same structure, as is shown in the case of the paraffins which have more than 20 carbon atoms. But supposing the chains become

* 'Roy. Soc. Proc.,' A, vol. 124, p. 317 (1929).

shorter. The discontinuity in the structure of the chains at their ends, or in other words the end groups, will then increase their relative influence. At a certain chain length they may become preponderant and a complete change in the crystal structure may be the result. It is here that we expect to see a difference in the behaviour of the odd and the even numbered substances. The orientation of the end groups relative to each other being different in the odd and the even series there is no reason why these groups should act alike. This is what actually happens. The change of the structure in the even series occurs in the neighbourhood of $N = 20$, in the odd series between $N = 9$ and $N = 11$.

The fact that a small temperature change is capable of disturbing the balance of the internal forces is worth noticing. It is here that an external electric or magnetic field may have the power of influencing this balance in a similar way.

A problem the complete solution of which has been postponed is the determination of the structure of the second form. The powder photographs suggest that the cross section of the unit cell of this form is no longer rectangular. From the three strongest reflections a cross section can be calculated. The result is shown in fig. 6 in correct proportions.



Scale of 1 Å.U.

FIG. 6.

The figure in full lines represents the cross-section of the normal structure. The figure in dotted lines refers to the other. The transformation of the normal section into the second one is easily obtained by a small distortion. It is, however, not unlikely that the base of the second form is a multiple of that which corresponds to the cross section in the diagram. In this case the molecules of second structure would have to be oriented in alternate directions.

The figures given in Table III show that the long spacings of the second form are shorter than the corresponding spacings of the normal form. The reason

for this may either be a shortening of the molecule itself which would involve an alteration of the chain structure, or it may be a tilt of the normal chain relative to the base of the unit cell, or it may be the result of a re-arrangement of the end groups accompanied by a contraction in the direction of the chain axes, or, of course, a combination of these changes. A change in the chain structure itself is, however, not likely to occur. A further investigation will decide which of the explanations is the correct one.

Summary.

1. The structures of a number of normal paraffins ranging from C_5H_{12} to $C_{30}H_{62}$ have been investigated by means of X-rays at liquid air temperature, room temperature, and in the neighbourhood of the melting points.
2. It is observed that the higher members of the paraffin series crystallise in the so-called normal form which has been described in an earlier paper, irrespective whether their carbon content is an even or an odd number. This normal form is found to be stable between the melting points and liquid air temperature.
3. The linear expansion within these temperature limits has been investigated, and it is shown that the coefficient of expansion of the a axes is three to four times larger than the one of the b axes. The coefficient of expansion of the c axes is very much smaller than the one of either the a or the b axes. It was, in fact, too small to be measured in the present experiments.
4. Differences in the behaviour of the even and the odd members begin to show when the carbon content of the substances decreases. $C_{20}H_{42}$ and $C_{18}H_{38}^*$ both exist in two alternative structures. Within a small range of temperatures near the melting points the normal form is found to be stable for either substance. At lower temperatures a second crystal structure appears. The change from one form into the other is reversible for $C_{20}H_{42}$ and $C_{18}H_{38}$. The change from the normal form into another one occurs also in the series of the odd members. The transition takes place between $C_{11}H_{24}$ and C_9H_{20} .
5. Observations taken in the immediate neighbourhood of the melting point indicate that these substances tend to form layer structures.
6. The conclusions drawn from the experiments are given in the last section of the paper.

The writer wishes to express his best thanks to Sir William Bragg for the friendly interest which he has taken in this work, also to Dr. H. S. Gilchrist

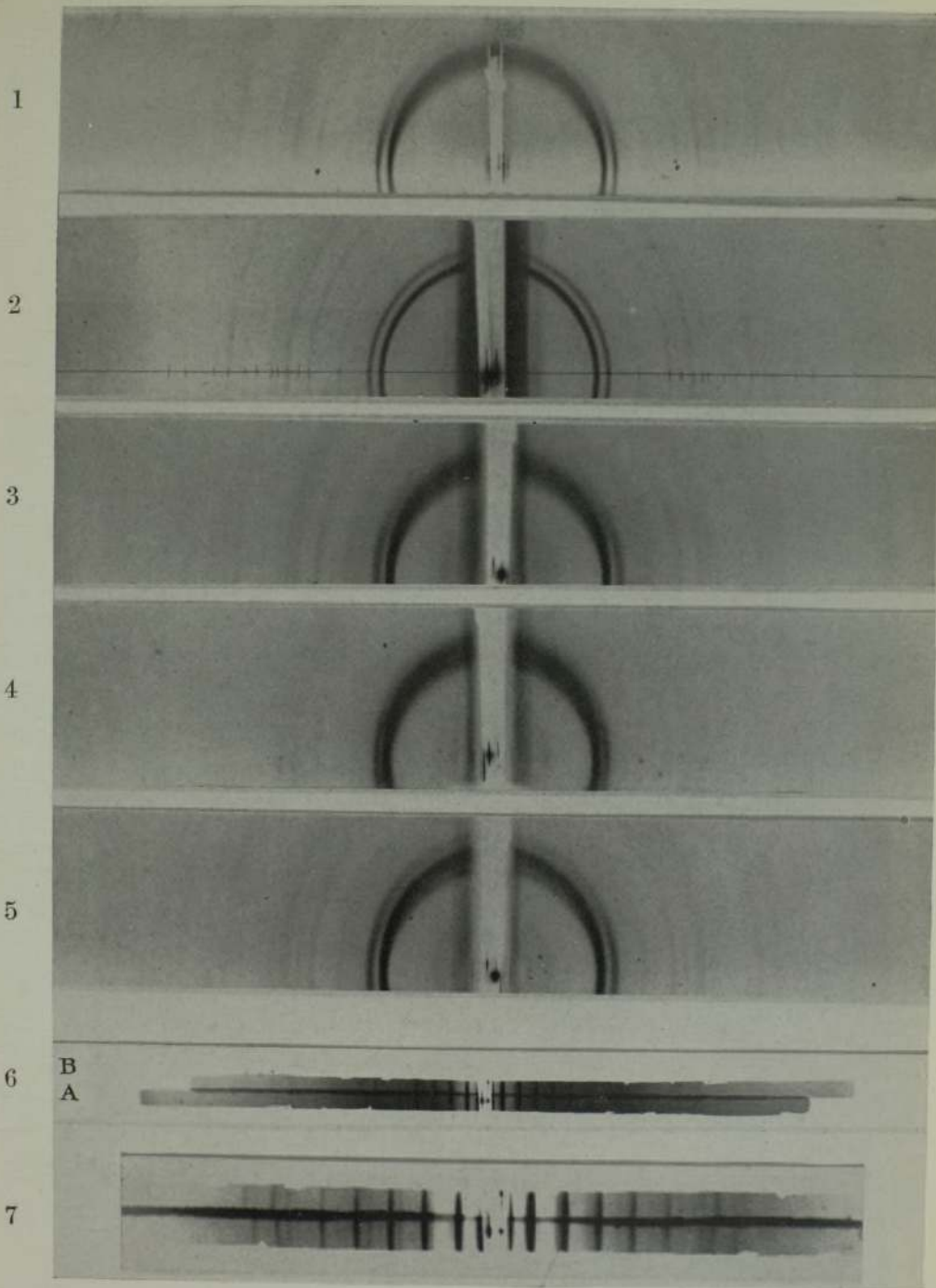
* *Note added in proof*—The missing $C_{22}H_{46}$ has been investigated by the writer since this paper was sent in. C_{22} behaves like C_{18} and C_{20} , *i.e.*, it shows the two forms.

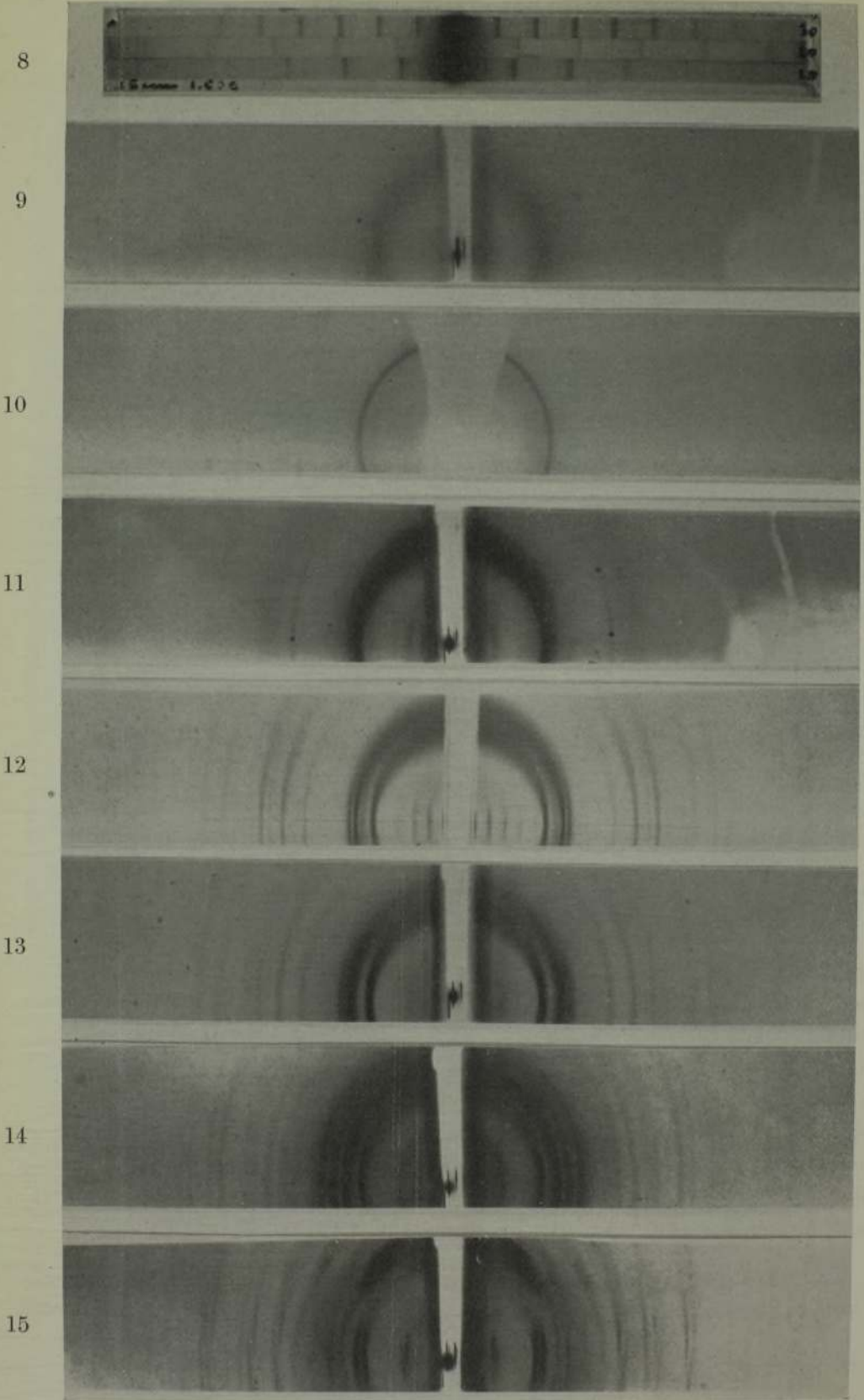
and Mr. E. L. Holmes for their unfailing and enthusiastic help. He feels also much obliged to the managers of the Royal Institution for the opportunities given to him for carrying out this work at the Davy-Faraday Laboratory.

EXPLANATION OF PLATES 5, 6.

The X-ray photographs 1-5 and 9-15 in the table are taken with "glass tube" samples of normal paraffins. Radiation: copper rays and Ni filter. Film radius, 3.79 cms. (1 mm. = 1.510°). Reproduction, natural size.

- No. 1. $C_{30}H_{62}$ room temperature.
 - No. 2. $C_{29}H_{60}$ room temperature.
 - No. 3. $C_{24}H_{50}$ liquid air temperature.
 - No. 4. $C_{17}H_{36}$ room temperature near melting point.
 - No. 5. $C_{17}H_{36}$ liquid air temperature.
 - No. 9. $C_{29}H_{60}$ liquid.
 - No. 10. $C_{29}H_{60}$ near melting point.
 - No. 11. $C_{20}H_{42}$ near melting point (normal form).
 - No. 12. $C_{20}H_{42}$ second form.
 - No. 13. $C_{20}H_{42}$ liquid air temperature.
 - No. 14. C_6H_{14} liquid air temperature.
 - No. 15. C_5H_{12} liquid air temperature.
 - No. 6. $C_{19}H_{40}$ same distance and radiation as before, but substance spread into thin layer on glass. Top, liquid air temperature; bottom, room temperature.
 - No. 7. Enlargement of No. 6.
 - No. 8. Photograph taken on plate at 15.00 cms. distance. Copper radiation. Top, $C_{30}H_{62}$ room temperature; middle, $C_{20}H_{42}$ second form; bottom, $C_{20}H_{42}$ normal form. Substances spread into layer on glass plate (by melting).
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