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Citation: [The Journal of Chemical Physics](#) **2**, 231 (1934); doi: 10.1063/1.1749455

View online: <http://dx.doi.org/10.1063/1.1749455>

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An X-Ray Study of the *n*-Aliphatic Alcohols, $C_{10}H_{21}OH$ to $C_{18}H_{37}OH$ *

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(Received February 9, 1934)

An x-ray study of the series of *n*-aliphatic alcohols $C_{10}H_{21}OH$ to $C_{18}H_{37}OH$ has been made. Spacings along identity periods perpendicular to the 001 planes (*c* spacings) have been measured at room temperature and at $-50^{\circ}C$. By plotting these *c* spacings against the number of carbon atoms in the chain, it is shown that there are two distinct crystalline modifications, the second appearing only in those members having even numbers of carbon atoms. The common (α) modification is shown to crystallize with

the *c* axis approximately at right angles with the 001 plane while the other (β) has the *c* axis at an angle of approximately $51^{\circ} 55'$ with the 001 plane. The packing at the ends of the molecules is different in these two modifications. A spectrograph to make such x-ray studies at low temperatures has been designed and constructed. These studies are the foundation of a calculation of the intensities of such *c* spacing reflections presented in a following paper.

INTRODUCTION

SERIES of organic compounds, particularly long chain aliphatic compounds, have always yielded results of great interest when studied by x-ray methods.¹ Such series as have been studied in this manner are the straight-chain hydrocarbons, the *n*-aliphatic acids and the saturated aliphatic ketones. Other long chain aliphatic compounds have been studied, for example, unsaturated acids, dicarboxylic acids, esters and soaps, but in these cases, the series have never included more than two or three individual members. The accuracy of this previous work, as regards the spacing along the *c* axis, is open to serious criticism. From the experimental results of Slagle and Ott,² it is known that the observed *c* spacings do not necessarily give the projection of the chain length or double the chain length, as the case may be, of that particular chain present in greatest quantity in the sample but that the observed spacing corresponds to an "average" length of all the various chain

lengths present. Consequently, the presence of neighboring members in a sample of a supposedly pure compound would tend to make the observed value inaccurate as regards the true *c* spacing for that compound. This is undoubtedly the case with some of the values of *c* spacings reported in previous work and accounts for some of the anomalies which have been observed.

In this laboratory, the series of *n*-aliphatic alcohols, $C_{10}H_{21}OH$ to $C_{18}H_{37}OH$, of high purity, were placed at our disposal through the courtesy of Professor Reid.

The *n*-aliphatic alcohols have been studied to some extent by Malkin.³ With a Muller spectrograph and iron $K\alpha$ radiation, the *c* spacings were observed for the *n*-alcohols C_{12} , C_{14} , C_{16} , C_{18} , C_{19} , C_{21} , C_{22} , C_{24} and C_{25} by measuring the reflections from melted and pressed samples on glass plates. It is believed that the present study of the alcohols is justified, because of the high purity of the materials as well as the fact that the available series, although shorter than that at the disposal of Malkin is complete in every member while the other shows many absences of individual compounds.

In connection with the results of Slagle and Ott, mentioned above, concerning known simple and complex mixtures of fatty acids, a similar study of complex mixtures of these alcohols should prove to be of some interest.

* A portion of the thesis submitted by Donald A. Wilson to the Board of University Studies of The Johns Hopkins University in partial fulfillment of the requirements for the degree of doctor of philosophy.

† Pennsylvania state fellow under the National Fellowship Plan; holder of the John Wiley and Sons' fellowship.

¹ Compare Strukturbericht, Leipsig (1931) and S. B. Hendricks, Chem. Rev. 7, 431 (1930).

² Slagle and Ott, J. A. C. S. 55, 4396, 4404 (1933).

³ Malkin, J. A. C. S. 52, 3739 (1930).

EXPERIMENTAL

The alcohols used in this work were prepared by J. D. Meyer,⁴ working under the direction of Professor E. E. Reid and are of a high degree of purity. The melting points were determined with good precision from a time-temperature cooling curve, according to the method introduced by Andrews, Kohman and Johnston.⁵ These "setting point" values are indicative of the purity and are to be found in the work mentioned above.

The source of x-rays used throughout the course of this work was a metal hot filament type x-ray tube with aluminum windows made in the Seemann Laboratories in Freiburg i. Br. A copper anticathode was used and when operated at *ca.* thirty kilovolts and twenty to thirty milliamperes the radiation consisted essentially of copper $K\alpha$ radiation. A nickel filter removed the copper $K\beta$ radiation as well as some of the continuous region. At no time during the course of the spectrographic work was any radiation other than copper $K\alpha$ observed; in particular, the L series of tungsten was absent.

The two spectrographs used were both of the Bragg oscillating crystal type. The material to be studied was placed on a glass plate either by melting, crystallizing from a solvent or pressing the solid crystals. This prepared plate was then mounted upon the crystal table of the spectrograph and the x-ray reflections were recorded photographically. Reflection occurs according to the Bragg formula, $n\lambda = 2d \sin \theta$. According to the usual method, when the crystal plate has been oscillated so that sufficient length of exposure has been afforded the reflections on one side of the primary beam, the crystal table is rotated 180° and the procedure repeated on the other side. Thus, by measuring the distance between corresponding lines on either side of the primary beam, the glancing angle θ can be ascertained, knowing the essential dimensions of the spectrograph. Knowing θ , $\sin \theta$ can be found and since n the order of reflection (obtained definitely by observation of several orders) and λ the wave-length of copper $K\alpha$ radiation are known, the Bragg formula can be solved for d ,

the interplanar distance. The value used for the wave-length of copper $K\alpha$ radiation is 1.538674Å as obtained from Siegbahn⁶ and is the value of the center of gravity of copper $K\alpha_1$ and $K\alpha_2$. The opening of the slit was 0.1 mm throughout the entire work in both spectrographs.

The value of the interplanar distance measured in this manner, when applied to crystal analysis, is not to be confused with the spacing along the c axis of the crystal. It is rather the projection of the spacing along the c axis on a line perpendicular to the glass plate. For this reason, a graphical comparison of these "projection" spacings can be used to show the presence of various modifications when these modifications make characteristic angles with the glass plate. For the purposes of brevity and to follow the usual custom, the projection of the c axis will be referred to merely as the c axis and the observed spacings will be listed as c spacings.

Since the materials used have a melting point range of from 57°C to 5.9°C , it was necessary⁷ to design and construct a spectrograph which would keep the sample cooled sufficiently for the material to remain solid. However, the majority of the x-ray diagrams of the alcohols which melt above room temperatures was taken on a spectrograph which was made in the Seemann Laboratories at Freiburg i. Br. The calibration of this spectrograph is described in the work of Slagle and Ott.²

The design and construction of our low temperature vacuum spectrograph follows. It is essentially a Bragg oscillating crystal spectrograph with the crystal table located at the center of a circle of approximately 18 cm radius and with the first slit located on the circumference and the photographic plate located as the tangent to a point 180° from the slit. The exposed plate area is 1×11 cm which allows reflections up to glancing angle $\theta = 9^\circ$ to be observed on either

⁶ Manne Siegbahn, *Spektroskopie der Röntgenstrahlen*, Berlin, Julius Springer, 1931.

⁷ The construction of the low temperature spectrograph was not absolutely necessary for the study of the alcohol series alone, but was essential for studies of other series with lower ranges of melting points such as the bromides and acetates, which are being made in this laboratory. The present work shows the applicability of this spectrograph to such studies.

⁴ Meyer and Reid, J. A. C. S. 55, 1574 (1933).

⁵ Andrews, Kohman and Johnston, J. Phys. Chem. 29, 914 (1925).

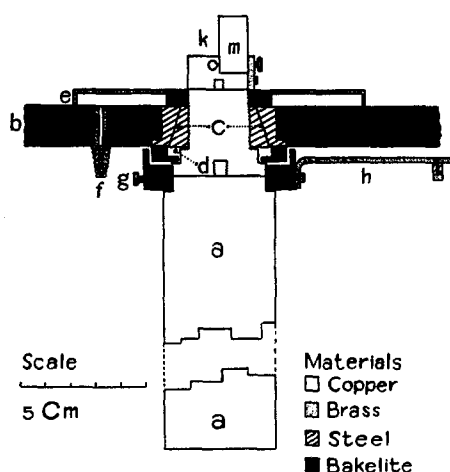


FIG. 1. Scale diagram of crystal table and cooling rod of the low temperature vacuum spectrograph.

side of the primary beam, which is a sufficient range for the purposes of this and following investigations. The arrangement of the recording photographic plate as a tangent does not impair the focussing, since the length of the plate is small as compared with the circumference of the circle. As a collimator, a system of two slits is used, the first being adjustable and made of a hard lead alloy while the second is fixed just in front of the crystal table and is made of steel. The oscillation of the crystal is accomplished by an eccentric cam arrangement driven by an electric motor.

The essential features of the cooling arrangement and crystal table are shown diagrammatically in Fig. 1. *a* is a solid copper rod which extends up through the floor *b* of the spectrograph and which is surrounded by a cooling mixture contained in a Dewar flask. The cooled portion is insulated as much as is possible with Bakelite parts. A lubricated steel on steel ground joint *c* affords the vacuum tight mechanism by means of which the oscillating motion is transmitted to the crystal table. The lubricating medium which is best suited for the carbon dioxide temperatures at which this work was being done is a mixture of a light aviation grade motor oil and a good grade gasoline in the ratio of 9 to 4. It is contained in the Bakelite reservoir *d* which acts in addition as a further protection against leakage. A brass shield *e* has the two-fold

purpose of protecting the body of the spectrograph against oil seepage and to keep any air which might leak through the ground steel joint in as close contact as possible to the outlet *f* which leads to an ordinary oil vacuum pump. The crystal table *k* is so constructed that a solid block of copper *m* is forced against the ledge *o* by means of a set-screw holding the crystal plate tightly between the block and the ledge. Here, the plate is cooled by the copper block *m* which is in contact with the cooling rod *a*. *h* is the rocking arm which leads to the cam mechanism not shown here.

A mixture of CO₂ snow and acetone was found to produce a temperature of approximately -50°C at the surface of the sample. On account of this low temperature, it was necessary to keep moisture from collecting on the surface of the crystal in some manner and this, in addition to reduced conduction of heat, was the reason for building the spectrograph with its vacuum feature. Under ordinary conditions of running, the amount of moisture which would collect on the crystal surface during a 16 hour period was barely noticeable. This, of course, is not sufficient to interfere seriously with ordinary x-ray reflection.

In order to know the temperature obtained in this manner, as well as to observe the constancy of this temperature with time, several cooling curves were plotted. The temperature was measured with a copper-constantin thermocouple, one junction of which was cemented to the surface of the crystal plate by means of universal wax. The cooling curves were made under as nearly as possible the same conditions as were met with in ordinary running. These curves proved that by refilling the Dewar cooling vessel at 2 hour intervals, a temperature constant to $\pm 1^\circ$ was kept for any desired length of time.

It was necessary of course to calibrate the spectrograph, but it was impossible to do this in the same manner as was used to calibrate the Seemann spectrograph previously described, because the range of the glancing angle θ (0° - 9°) observable on the plate is small and too close to the primary beam. This means that even with silver radiation and the mica 001 face, an insufficient number of reflections would be observed for accurate calibration. This difficulty

was surmounted by using as standard several long chain organic compounds whose spacings had been determined with known accuracy on the Seemann spectrograph in this laboratory. Three compounds were used, the C_{15} *n*-aliphatic acid, determined by Slagle and Ott² and the C_{17} and C_{18} *n*-aliphatic alcohols determined during the course of this work. The combination of these three substances gave a series of 19 points on the calibration curve, plotting distance in millimeters between corresponding lines on the film against the glancing angle θ . All fall accurately on a very smooth calibration curve which is nearly a straight line. The calibration curve is curved somewhat, since the photographic plate was placed as a tangent to the circle of focus rather than exactly on the circumference. The frame of the spectrograph is so insulated from the crystal table that its dimensions remain sufficiently constant under all running conditions. The entire work of calibration was performed at room temperature and so all of the spacings determined at the low temperature are referred to the calibration at room temperature. This fact allows comparisons to be made between spacings observed at -50°C and at room temperature and thus allows us to show the existence or non-existence of an expansion coefficient along the c axis.

The main body of the spectrograph was constructed of brass, with the exception of the floor which is of Bakelite and all the joints between brass and brass and brass and Bakelite were made vacuum tight with universal wax. The cover of the spectrograph and the brass plateholder were both cemented on with universal wax and were removed with lifting screws after air had been allowed to enter the spectrograph. The cover of the spectrograph was provided with a red glass window directly above the crystal table by means of which the rotation of the crystal could be observed. The 180° -rotation is accomplished by loosening the set-screw g (Fig. 1) and applying a specially constructed wrench to the cooling rod a .

Although the point has not been tried, there is no reason to doubt that the spectrograph could be used to investigate the behavior of long chain compounds through a wide range of temperatures by substituting for the CO_2 -acetone cooling

mixture anything from liquid air to a thermostatic arrangement for temperatures not too high above room temperature. It would only be necessary in each case to find the correct lubricant for the rotating joint. The constancy of the temperature at the surface of the sample suggests that the spectrograph could be used to investigate behavior near melting points, the phenomenon of molecular rotation or in general, transition points of all kinds.

The general method of calculating the c spacings from the films has been previously outlined. The distance l between corresponding lines on either side of the primary beam was measured by a micro-comparator in the case of the strong reflections and with a millimeter rule in the case of the weaker reflections. It was generally possible to measure the first, third and sometimes the fifth orders with the comparator. In each case, five separate readings were made of each order and the average taken as the final average l . Since plates were used in the low temperature spectrograph, it was not necessary to correct for shrinkage, but in the case of the Seemann spectrograph, which required films, this was necessary. The correction was made by making parallel scratches on the film before exposure, a known distance apart and then measuring the distance between these scratches just before measuring. The average l was then corrected, proportional to the amount of this shrinkage.

Having l , the distance between corresponding lines, accurately measured for several orders, it remains to find the glancing angle θ . The calibration curves for the two spectrographs were made by plotting l against θ and so θ is obtained simply by reading from the calibration curve. Now, knowing θ for a variety of orders, $\sin \theta$ can be found and by knowing n the order of reflection, from observation, $(\sin \theta)/n$ is found which reduces the sine values of the reflections from higher orders down to $n=1$. The variation in these values of $(\sin \theta)/n$ then gives us the maximum error in the calculation of d , the interplanar distance, which is obtained simply by substituting the average $(\sin \theta)/n$ value in Bragg's formula. Since $(\sin \theta)/n$ is averaged over several orders, the maximum deviation from the mean which is given in connection with the

TABLE I. Calculations of *c* spacings.*

Order of reflection	Seemann spectrograph				Low temperature spectrograph			
	$C_{15}H_{31}OH$ (α)		$C_{18}H_{37}OH$ (β)		$C_{12}H_{25}OH$ (α)		$C_{13}H_{27}OH$ (α)	
	$\frac{\sin \theta}{n}$	Deviation (%)	$\frac{\sin \theta}{n}$	Deviation (%)	$\frac{\sin \theta}{n}$	Deviation (%)	$\frac{\sin \theta}{n}$	Deviation (%)
1	0.01825	-0.05	—	—	0.02252	+0.044	—	—
2	0.01828	+0.075	0.01876	-0.107	—	—	0.02081	-0.144
3	0.01826	0.00	0.01876	-0.107	—	—	0.02083	-0.048
4	0.01828	+0.075	0.01882	+0.212	0.02264	+0.57	0.02087	+0.144
5	0.01826	0.00	0.01878	0.00	0.02242	-0.38	0.02085	+0.048
6	0.01826	0.00	0.01881	+0.10	0.02246	-0.22	0.02083	-0.048
7	—	—	0.01878	0.00	—	—	—	—
8	0.01827	+0.05	—	—	—	—	—	—
Average $\frac{\sin \theta}{n}$	0.01826		0.01878		0.02251		0.02084	
$d = c$	42.12 \pm 0.05		40.96 \pm 0.10		34.17 \pm 0.32		36.91 \pm 0.05	

* It must be remembered that the *c* spacings calculated in this manner are not to be confused with the regular *c* spacings along the crystallographic *c* axes. The two are identical only when the *c* axis is perpendicular to the glass plate and hence to the 001 plane. These *c* spacings are a measure of the projection of the true *c* spacings on a line perpendicular to the 001 plane which appears to be parallel with the plane of the glass plate.

determination of *d* is probably much greater than the average error or the most probable error. However, in this work, it was thought best to give the variation in terms of the maximum deviation rather than the error, since the number of observations is relatively small.

In Table I are placed the calculations of films obtained from $C_{15}H_{31}OH$ and $C_{18}H_{37}OH$, respectively, by using the Seemann spectrograph. They represent one of the least and one of the most favorable cases and are typical of the accuracy obtained and the type of calculation. Likewise, Table I contains similarly representative calculations made from diagrams obtained on the low temperature spectrograph. These are $C_{12}H_{25}OH$ and $C_{13}H_{27}OH$, respectively. The table of calculations is self-explanatory.

In order to show the sharpness of reflection with which we are dealing and the type of films obtained, Fig. 2 shows several representative films made on the two spectrographs. The low temperature films, while easily measurable, do not reproduce well.

The final calculated values for the *c* spacings of all these aliphatic alcohols are given in Table II. In this table are also included Malkin's values for comparison. As will be seen later,

these values indicate two distinct modifications of the *n*-alcohols. Quite arbitrarily, that modification which gives the longer spacing is called the α -modification whereas the one with the shorter spacing is called the β -modification.

DISCUSSION

If we compare *c* spacings as obtained from pressed samples with those obtained from crystallized or melted samples, we see that occasionally the agreement is not good. Of the two values, the spacing obtained from the pressed sample is likely to be in error. This is because the pressed sample is thicker, presents a more uneven surface, and as Slagle and Ott² have shown is likely to give spacings varying with the amount of pressure put upon the sample. As will be seen in Table II, the spacings observed in this work do not always agree with those published by Malkin³ even within the maximum experimental deviation. This is probably not due to an inherent error in the methods used in the two investigations (although it is believed that the accuracy has been increased in this laboratory) but can be attributed to the presence of impurities in the alcohol in question. As explained before, the purity of the alcohols used in this

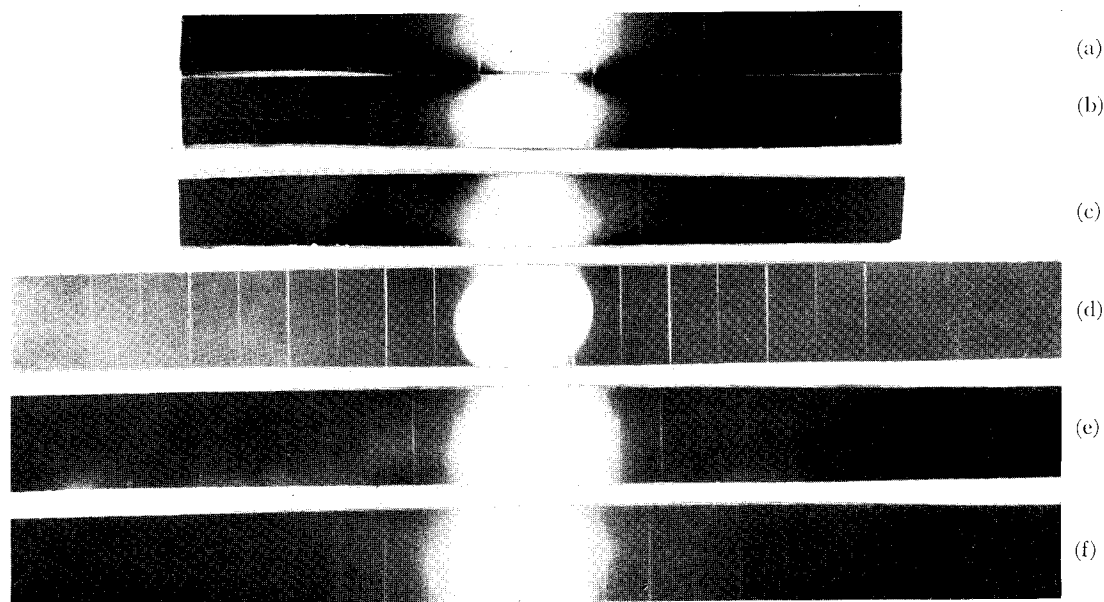


FIG. 2. X-ray diagrams taken on the two spectrographs used in this work. Diagrams (a), (b) and (c) were taken on the low temperature spectrograph while diagrams (d), (e) and (f) were taken on the Seemann spectrograph.

- | | |
|--|---|
| (a) $C_{14}H_{28}COOH$ —room temperature | (d) $C_{16}H_{32}OH$ — β -modification |
| (b) $C_{14}H_{28}COOH$ — $-50^{\circ}C$ | (e) $C_{15}H_{31}OH$ — α -modification |
| (c) $C_{17}H_{35}OH$ — $-50^{\circ}C$ — α -modification | (f) $C_{14}H_{28}OH$ — α -modification |

work is unusually high and consequently the values given here are considered the more correct.

As in the case of the fatty acids, it is evident that the alcohol molecules crystallize in a double arrangement of some kind, probably with the hydroxyl groups adjacent to each other. The lengths of the c spacings as well as the increase observed for consecutive members of the series are much too great to be explained in any other manner. This viewpoint is supported by evidence in the paper following calculating intensities of reflection from assumed atomic arrangements.

Some of the diagrams show the presence of two modifications. This is clearly brought out if we plot the c spacings against the number of carbon atoms, in the usual manner. The graph, shown in Fig. 3, is made up of the c spacings obtained both by Malkin and the present authors. It therefore serves as a comparison of the two sets of values. The modification giving values which fall on the upper line is the α -modification while values which fall on the lower line belong to the β -modification.

It is interesting to note that in all of this work, there have been only two modifications

observed as contrasted with the case of the fatty acids which show four and possibly five different modifications² in either even or odd series. In all cases the reflection from the α -modification is the more pronounced, when both appear on the same film. However, in the case of some preparations of the C_{16} and C_{18} alcohols, the presence of the β -modification only was observed. Reference to Fig. 3 will show that the β -modification has appeared only in the cases where the alcohol has an even number of carbon atoms. This is probably due to some difference in the ease of packing for even and odd molecules. That there is a difference in the packing of the α - and β -modification is indicated by a quite different relation between intensity and order of reflection.

Meyer and Reid⁴ working with this same series of alcohols have obtained evidence from cooling curves which they interpret as showing the existence of two modifications of both even and odd members of the series. Our failure to obtain two modifications in the case of the odd members may be due to one of two reasons; either in our method of preparing the sample

TABLE II. Observed *c* spacings in *A* of *n*-aliphatic alcohols.*

No. of carbon atoms	Crystallized from ether	Pressed	Results of Malkin	
			Melted	Pressed
Room Temperature				
13	36.88±0.07 (α)	36.89±0.07 (α)		
14	39.67±0.07 (α)	39.38±0.46 (α)		39.7 (α)
15	42.12±0.05 (α)	42.13±0.08 (α)		
16	44.62±0.05 (α) 36.97±0.03 (β)	44.70±0.25 (α) 36.95±0.30 (β)	44.9 (α) 37.4 (β)	
17	47.16±0.14 (α)	46.99±0.25 (α)		
18	49.54±0.12 (α) 40.96±0.10 (β)	41.25±0.09 (β)	50.2 (α)	41.35 (β)

No. of carbon atoms	Crystallized from ether	Melted	Pressed	
-50° Centigrade				
10		28.74±0.34 (α) 22.41±0.06 (β)		
11		31.28±0.36 (α)		
12		34.17±0.32 (α)		
13			36.91±0.05 (α)	
14			39.38±0.19 (α)	
15			42.16±0.25 (α)	
16			44.84±0.11 (α) 36.84±0.20 (β)	
17	46.93±0.03 (α)			
18	49.57±0.12 (α) 40.96±0.08 (β)			

* See note below Table I regarding *c* spacings.

the cooling was so rapid that the transition point was passed without any appreciable change and at the low temperature, the rate of transition is so slow as not to give the second modification in any appreciable quantity, or this second transition point is due to a change in the rotation of the molecule only which would have no effect on our x-ray diagrams but which would have a marked effect upon the specific heat. Which of these two explanations is the correct one can only be decided after further work.

From our series of values of *c* spacings, we can calculate the average increase in length as the number of carbon atoms increases. This value is 2.53Å for the α-modification and 2.00Å for the

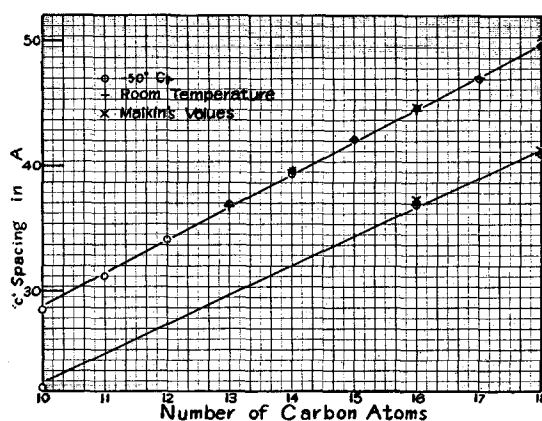


FIG. 3. Graph plotting *c* values against the number of carbon atoms in the hydrocarbon chain.

β-modification. Careful work with the hydrocarbons has shown that the increase in *c* spacing with the addition of two carbon atoms to the molecule is 2.54Å. Since, in the modification of the hydrocarbons referred to, the *c* axis is perpendicular to the 001 plane, the correspondence between this value and our value would indicate that in the α-modification, the *c* axis is perpendicular to the 001 face. Likewise, the value of 2.00Å increase per carbon atom found for the β-modification, when compared with 2.54Å shows that the β-modification has the *c* axis tilted with respect to the 001 face. It is evident that the packing at the ends of the molecule would have no influence on this projected increase. Hence we can calculate the angle that the *c* axis makes with the 001 face in the case of the β-modification. If γ is this angle of tilt, simple geometrical considerations show that $\sin \gamma = 2.00/2.54 = 0.787$ and $\gamma = 51^\circ 55'$, provided that we assume the chains in the case of the β-modification to be also parallel to each other. This would seem to be a reasonable assumption since the chains must be closely parallel to each other in the case of the α-modification. This is shown by the close check between the observed and calculated maximum increase along the *c* axis.

The tilt of the β-modification, when calculated in this manner, can then be used to show that the type of packing at the ends of the molecules must be different in the two modifications. This view, borne out further by the fact that the

relationship of the intensities of reflection is different in the two cases, has not hitherto been proposed. We know from the c spacing, the length of the projection of the total "double molecule." From the angle of tilt, we can easily calculate the value c would have for the β -modification, if the chain axis were perpendicular to the 001 face. This calculated c spacing should be the same as the c spacing for the α -modification if the packing were the same. The calculated c spacings for the β -modification are 46.99Å and 52.04Å for the C_{16} and C_{18} alcohols, respectively, while the corresponding c spacings for the α -modification which is perpendicular to the 001 plane are 44.62Å and 49.54Å. Although the experimental error in the determination of the c spacings is magnified in the value of $\sin \gamma$, we believe that this difference is real and not apparent and that it tends to strengthen our view that the packing is different in these two modifications.

If, in Table II we compare the c spacings obtained at room temperature with those obtained at -50°C , we fail to detect any difference, outside the experimental error. This means that the coefficient of expansion of these alcohols in the c direction is negligible. This compares favorably with the results obtained by Müller⁸ in the case of the hydrocarbons. However, one acid was investigated in this manner and a change in the c spacing was observed. The C_{15} n -aliphatic acid, which was measured by Slagle and Ott² and used in the calibration of the low temperature spectrograph, gave a value at -50°C of $35.19 \pm 0.10\text{Å}$ as compared with $35.65 \pm 0.05\text{Å}$ at room temperature. This is well

⁸ Müller, Proc. Roy. Soc. **A127**, 417 (1930).

outside the experimental error and gives a value for the coefficient of expansion of 0.00015Å per Å per $^\circ\text{C}$. Although this shift in the c spacing with temperature lies outside the experimental error, the calculated coefficient of expansion should only be considered significant in order of magnitude because the experimental error is so large compared with the observed shift.

Because these alcohols are extremely simple as compared with other long chain compounds in regard to the possible number of modifications, they lend themselves very nicely to the study of mixtures and solid solutions. Some work along this line has been done by the authors but because of the fundamental nature of the problem, it was considered advisable to expand this work and publish it in a following paper.

SUMMARY

(1) The c spacings of the series of n -alcohols $C_{10}H_{21}OH$ to $C_{18}H_{37}OH$ have been studied with improved accuracy.

(2) The n -alcohols crystallize in "double molecules" and the members with even numbers of carbon atoms exist in two distinct crystal modifications.

(3) These two modifications are shown to crystallize with the c axis making angles of 90° and $51^\circ 55'$, respectively, with the 001 planes and with the packing at the ends of the molecules likewise different in the two cases.

(4) A special spectrograph designed to permit such x-ray studies at temperatures below room temperature has been constructed.

(5) The results presented here are used in a following paper to determine atomic arrangements from intensity calculations.