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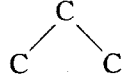(Received February 9, 1934)

Comparison between observed and calculated intensities of c spacings of the α-modification of a series of n-aliphatic alcohols gives excellent values for the coordinates (projected on the c axis) of the constituent atoms.

IN 1925 Shearer[1] published a paper in which he attempted to explain the distribution of intensities of reflection with order from a number of long chain organic compounds. Because of later refinements in the theories of scattering, these calculations offer at best only a qualitative explanation of the phenomena. In the light of some of the observed reflections from long chain compounds used in this work, Shearer's results are actually in error. For these reasons it would seem advisable to use a more modern conception of such scattering and recalculate the intensities of reflection for some of the alcohols used here.

Suppose that instead of using a model such as Shearer proposed, we consider each atom along the chain as a diffracting center. Now if we draw a line parallel to the c axis of the crystal, we may project the centers of the atoms along the molecule on to this line and obtain an arrangement such as shown in Fig. 1. We may deal with this projected row of atomic centers as a row of diffracting centers and by finding the coordinates of each of these points along the line of projection, we may use the regular expression for the structural amplitude and thus calculate the intensities for various orders of the 001 reflections. This simplified arrangement is strictly rigid for such calculations.

In applying this general method to the case of the alcohols, let us see what dimensions or coordinates are unknown. As was previously shown,[2] the projected

$$C - C \quad C$$

distance is 2.54A and hence the projected

$$\underset{C}{\overset{C}{\diagup}}$$

distance is 1.27A for the α-modification which has the molecule chains perpendicular to the 001 plane. This gives us all the necessary dimensions relative to heavy atoms within the projected molecule except the projection of the

$$\underset{C}{\overset{O}{\diagup}}$$

distance. Atomic radii tables give the distance between oxygen and carbon centers as 1.42A.[3] This gives the projection of the

$$\underset{C}{\overset{O}{\diagup}}$$

distance as $1.42/1.54 \times 1.27 = 1.17$A for this linkage, assuming in this case also, the tetrahedral angle. Having these values, we see that there are but two unknown param-

FIG. 1. Showing method of projection of the atoms along the n-alcohol chains.

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[1] Shearer, Proc. Roy. Soc. **A108**, 655 (1925).
[2] D. A. Wilson and Emil Ott, preceding paper, p. 231.
[3] M. L. Huggins, Chem. Rev. **10**, 427 (1932).

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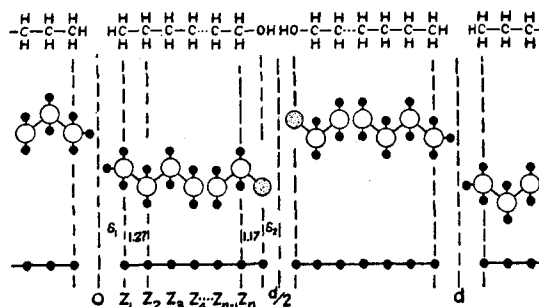eters, δ_1 and δ_2 (their definition is evident from Fig. 1). δ_1 which measures the shift of the entire molecule along this axis of projection is considered unknown, then δ_2 is simply related to δ_1 as follows:

$$d = 2\{\delta_1 + (n-1)1.27 + 1.17 + \delta_2\},$$

where d is the interplanar distance and n is the number of carbon atoms in the molecule.

Thus we see that in an aliphatic alcohol containing n carbon atoms, the carbon atoms are located at $\pm\delta_1$, $\pm(1.27 + \delta_1)$, $\pm\{2(1.27) + \delta_1\}$, $\pm\{3(1.27) + \delta_1\}$, $\cdots$ $\pm\{(n-1)(1.27) + \delta_1\}$ and the oxygen atom is located at $\pm\{(1.27)(n-1) + \delta_1 + 1.17\}$. These values are obtained by finding the distance along the axis of projection of each diffracting center from the origin, placed at a center of symmetry of the "double molecule" for convenience. However, in the expression for the structural amplitude, it is necessary that these coordinates be expressed as fractions of d along the z axis and hence we must transform these coordinates to $\pm u$, $\pm\{1.27/d + u\}$, $\pm\{2(1.27)/d + u\}$, $\pm\{3(1.27)/d + u\}$, $\cdots$ $\pm\{(n-1)(1.27)/d + u\}$ for the carbon atoms and $\pm\{[(n-1)(1.27) + 1.17]/d + u\}$ for the oxygen atom when $u = \delta_1/d$. In all these considerations, the hydrogen atoms in each $-CH_2-$ group are considered as being projected to the same point on the axis of projection. This is merely done for convenience, since as is readily seen, the calculation remains rigid for 001 reflections. The $-OH$ group is treated as a single diffracting center while the end hydrogen on the hydrocarbon chain is neglected. This simplification can certainly introduce but a minor error.

These coordinates are then substituted in the expression for the structural amplitude,

$$S = 2 \sum_n F_n e^{2\pi i r z_n} = (A - iB),$$

where

$$A = 2 \sum_n F_n \cos 2\pi r z_n,$$

and

$$B = 2 \sum_n F_n \sin 2\pi r z_n,$$

where z_n is the fractional coordinate of the nth atom along the z axis, r is the order of reflection and F_n is the scattering factor for the nth atom.

However, it is most reasonable to assume that the two alcohol molecules are arranged symmetrically about the origin, which is the center of the "double molecule" and corresponds to a center of symmetry in this case, since the molecule beyond the origin is the precise image of the one before it. The intensity is proportional to the square of the absolute value of the structural amplitude and is therefore proportional to $A^2 + B^2$. However, now the term $B^2 = 0$ and so the intensity,

$$I \propto A^2 \propto (2 \sum_n F_n \cos 2\pi r z_n)^2$$

and because $B^2 = 0$ only cosine values need be considered and only positive values of the coordinates z_n are necessary. Nothing quantitative is known about the scattering factors for the carbon and oxygen atoms at such small values of θ, so as a first approximation, this factor was taken to be proportional to the atomic number, or 8 for the $-CH_2-$ groups and 9 for the $-OH$ group.

The F_n values for oxygen and carbon[4] in this region of small glancing angles actually do change and although the shape of the curve is not known accurately, we find that apparently to the first approximation it may be compared satisfactorily in our region with the curve of the function $1/\sin\theta$. With the rotating crystal method of analysis used in this work, it is necessary to introduce a correction factor $\sin\theta$ in calculating intensities since the area of crystal surface intercepting the x-ray beam increases as $\sin\theta$ and the energy striking the crystal surface must increase as that function. Consequently, it was thought that the value of this calculation would not be seriously impaired if these two corrections were allowed to cancel and only the relative heights of the two F_n curves for oxygen and carbon be applied as the scattering factors.

The intensity is then proportional to A^2 or to $(A/2)^2$, since any constant factor does not need to be included in a relative calculation and is equal to $f(\theta)(A/2)^2$ where $f(\theta)$ is a function of θ including the polarization, Lorentz and absorption factors. The value of $f(\theta)$ used is given

[4] R. W. G. Wyckoff, *The Structure of Crystals*, Chem. Cat. Co., (1931).

by Wyckoff[4] and can be shown to be valid for this type of calculation.

Since this calculation is based on the assumption that the alcohol molecules crystallize in pairs with the polar −OH groups adjacent it is perhaps necessary to justify this viewpoint. This idea has been held by organic chemists for some years as applicable to all such cases of long chain molecules bearing a polar group on one end. X-ray researches with fatty acids and particularly in the case of lauric acid,[5] have further justified this point of view, at least with the case of the acids. That the alcohols present an analogous case can be seen by comparing the forces of molecular cohesion,[6] that of the acids being about 8970 cal. per mole and that of the alcohols being about 7250 cal. per mole. Shearer[1] has presented a more complete justification of this assumption as a preface to his calculations. At any rate, the success of the present calculations gives evidence strongly in support of this primary assumption.

We can now state our complete expression for the calculation of intensities.

$$I = f(\theta)(A/2)^2,$$

$$I = \frac{1 + \cos^2 2\theta}{\sin 2\theta} \left[\sum_n F_n \cos 2\pi r z_n \right]^2. \quad (1)$$

This expression can be criticized only from the point of view that the Darwin "extinction coefficient" of absorption has been neglected. The extinction coefficient does not become appreciable until we deal with reflections which lie exceedingly close to the primary beam, such as the first, second and possibly the third orders of reflection as observed in this work. This fact is used later to explain slight disagreements between observed and calculated intensities in the first two or three orders.

The C_{17} alcohol was chosen first for calculation for two reasons; first because reflections from this alcohol have been observed to higher orders than for any of the others and secondly because the c spacing obtained for this member is "average" in that the value falls accurately on the curve,

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[5] *Strukturbericht*, Leipzig, (1931).

[6] K. H. Meyer and H. Mark, *Der Aufbau der Hochpolymeren Organischen Naturstoff*, Leipzig, (1930).
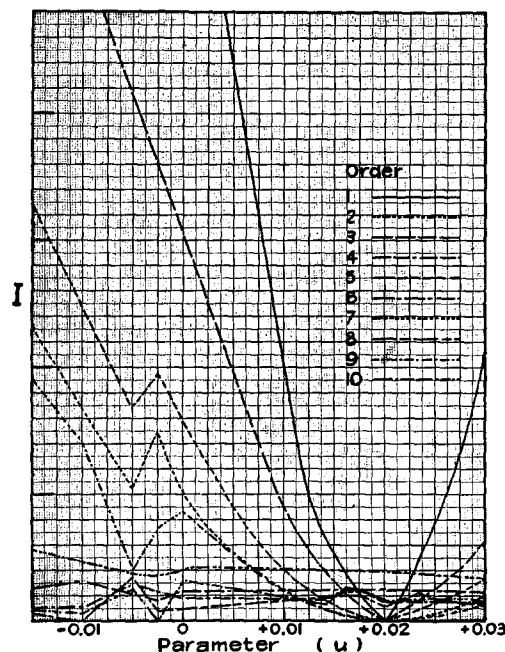

FIG. 2. Calculated intensities plotted against parameter values for the C_{17} alcohol.

plotting c spacings against the number of carbon atoms.[2] (See Fig. 2.)

The coordinates of each carbon and oxygen atom in the chain are found in the manner presented. The −CH_2− groups can be placed at

u, $(0.02692 + u)$, $(0.05385 + u)$, $(0.08078 + u)$,

$(0.10771 + u)$, $(0.13464 + u)$, $(0.16157 + u)$,

$(0.18850 + u)$, $(0.21543 + u)$, $(0.24237 + u)$,

$(0.26929 + u)$, $(0.29622 + u)$, $(0.32315 + u)$,

$(0.35008 + u)$, $(0.37701 + u)$, $(0.40394 + u)$,

$(0.43087 + u)$ and the −OH group at $(0.45568 + u)$. Thus $u = \delta_1/d$ is the only unknown parameter. It was determined by making preliminary calculations of the intensities, by using values of u increasing regularly on each side of the origin. Having obtained in this way a series of calculated intensities varying with the parameter u, the next step was to plot these calculated intensities against the parameter u for each order. That value of u which was found to give the proper sequence of relative intensities for the various orders, as compared with the experimental data, was found to be a singular value at $u = +0.027$.

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TABLE I. *Calculated and observed intensities.**

Order of reflection	$C_{18}H_{37}OH$		$C_{17}H_{35}OH$		$C_{16}H_{33}OH$		$C_{15}H_{31}OH$		$C_{14}H_{29}OH$		$C_{13}H_{27}OH$	
	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.
1	1614	500	1241	625	1180	320	1020	300	849	460	1161	385
2	312	250	349	200	354	165	371	150	419	230	251	200
3	526	500	385	500	355	320	300	300	246	460	341	350
4	155	150	224	175	225	160	183	120	246	200	150	150
5	255	250	200	225	161	160	81	250	127	230	176	190
6	155	50	146	200	121	115	66	90	137	140	120	150
7			124	125	99	100	104	60	48	90	98	70
8			150	175	168	165	161	120	181	185	114	115
9			72	50							54	60
10			174	175								

* The observed intensities listed here were estimated by direct visual observation. The error in such a method is about one part in ten and greater accuracy than this is not claimed.

With this value, the calculated intensities are found to be the values shown in Table I, where they may be compared with the experimental values.

The calculation is made simply by performing the designated operations in Eq. (1) for the intensity, summing the cosine values first over all the carbon atoms, then over the one oxygen atom, multiplying by the appropriate scattering factor F_n, completing the sum and squaring. The complete mathematical expression for the intensity of the C_{17} alcohol is

$$I = \frac{1+\cos^2 2\theta}{\sin 2\theta} \{8(\cos 2\pi r\, 0.027 + \cos 2\pi r\, 0.05392 + \cos 2\pi r\, 0.08085 + \cos 2\pi r\, 0.10778$$

$$+ \cos 2\pi r\, 0.13471 + \cos 2\pi r\, 0.16164 + \cos 2\pi r\, 0.18857 + \cos 2\pi r\, 0.21550 + \cos 2\pi r\, 0.24243$$

$$+ \cos 2\pi r\, 0.26973 + \cos 2\pi r\, 0.29629 + \cos 2\pi r\, 0.32322 + \cos 2\pi r\, 0.35051 + \cos 2\pi r\, 0.37708$$

$$+ \cos 2\pi r\, 0.40401 + \cos 2\pi r\, 0.43094 + \cos 2\pi r\, 0.45787) + 9(\cos 2\pi r\, 0.48268)\}^2.$$

It is necessary to solve this equation for each order since r is the order of reflection and θ, the glancing angle, depends upon the order of reflection.

In order to compare these with the observed intensities, in Fig. 3 are shown diagrammatic representations of the calculated and observed intensities, with the absolute scale of each changed so that they are made to coincide insofar as possible. One will note that the agreement is very good indeed, particularly in the higher orders. It would be surprising if the first two or three orders were to coincide exactly because we have, as mentioned previously, neglected the "extinction coefficient" of absorption which becomes increasingly important in the low orders lying very close to the primary beam.

Let us see what this calculation tells us about the structure of this α-modification. In the first place, we have assumed that the chain axis was perpendicular or very nearly so with the 001 plane. The success of this calculation tends to substantiate this assumption. Since we have found $u = 0.027$ in this manner and since $u = \delta_1/d$, we can find δ_1 which turns out to be 1.273A. This value is the distance from the origin to the center of the first carbon atom projection, which tells us that the projections of two molecules along the c axis have a distance of 2.55A between projections of the carbon centers on the ends opposite the hydroxyl groups. Solving for δ_2 then gives us the distance between the projection of the hydroxyl group and the point $d/2$. This value of δ_2 is subject to some variation due to inaccuracies in
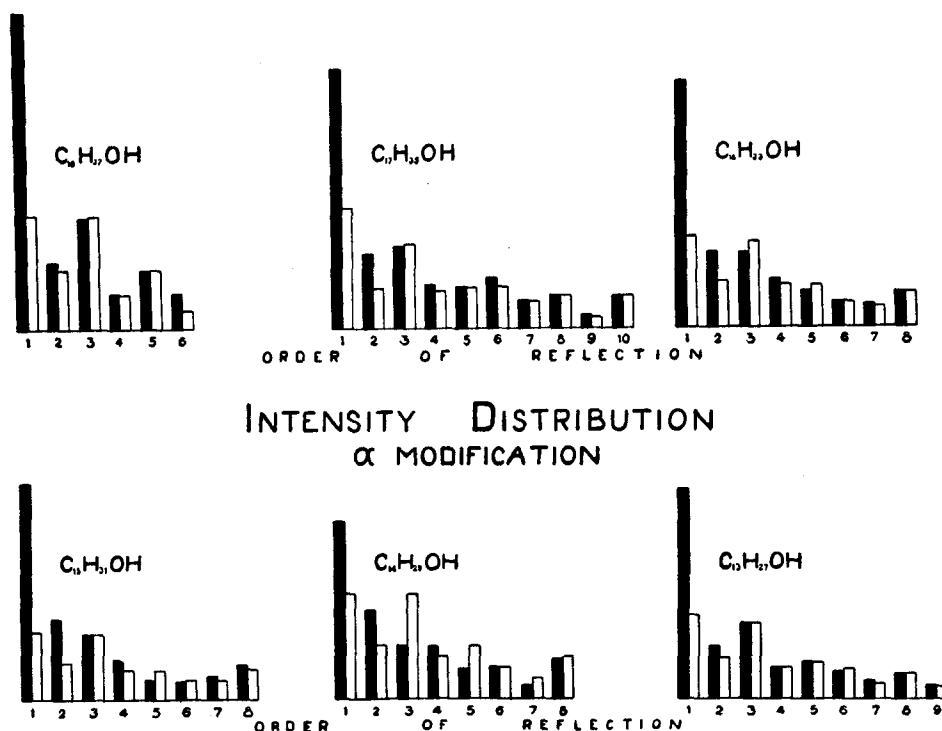
FIG. 3. Calculated intensities compared with observed intensities. The shaded values indicate calculated intensities.

the experimental determination of d, but when calculated for all the available alcohols in the α-modification, the results shown in Table II are found.

TABLE II. *Calculated values of δ_2.*

Alcohol	C_{18}	C_{17}	C_{16}	C_{15}	C_{14}	C_{13}	C_{12}	C_{11}	C_{10}
δ_2	0.737	0.877	0.807	0.837	0.877	0.753	0.667	0.497	0.497

Average $\delta_2 = 0.73A$

$2\delta_2$ is, of course, the distance between the projections of neighboring $-OH$ groups. The fact that all the variation due to experimental error in the determination of d seems to appear in the value of δ_2, is only apparent, because the calculation could just as easily have been made using the point $d/2$ as the origin which would have caused δ_2 to appear invariant. It is readily seen that the same experimental error is inherent both in δ_1 and δ_2.

So far we have derived all these quantities from the parameter found by calculating in-

tensities for only the one alcohol $C_{17}H_{35}OH$. Precisely the same calculation, by using the same parameter values, should be applicable to the other members of the α-modification. The possibility of a change in the packing of the end groups from one member to another is quite remote, because not only do the c values all fall quite accurately on the same straight line[2] but the observed intensities all show the same type of alternation (Fig. 3). Thus, if we use the parameter $\delta_1 = 1.273$ with $\delta_2 = 0.73$ and apply the calculation to other members of this series and if the calculated intensities again check the experimental, this would offer good evidence in support of the theory. Such calculations have been made for the C_{13}, C_{14}, C_{15}, C_{16} and C_{18} members which give the calculated intensities shown in Table I and when the comparison of the intensities is shown diagrammatically as in Fig. 3, the results are good; in fact the agreement is even better in some cases than with the C_{17} alcohol.

Work is now in progress in this laboratory attempting to calculate intensities in a similar manner for the β-modification. The results are

promising but the calculations are complicated by the presence of two parameters, one measuring the angle of rotation of the molecule around its long axis as well as the one measuring the position of the projection of the molecule on the perpendicular. This new parameter arises from the fact that the c axis of the β-modification is tilted with respect to the 001 plane and consequently the projections of the individual atoms along the chain change their relative positions as the molecule is rotated.

It should be possible to extend the theory here presented to the calculation of intensities of reflection for all the long chain compounds, although many of the others offer complications which are not present in the case of the alcohols such as tilt, double bonded oxygens and so on. However, if the proper assumptions are made, it should be possible to extend this or a similar calculation to all cases.