

Phase Transformation of *n*-Higher Alcohols. (II)

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For the members of *n*-higher alcohols from C₁₁ to C₃₇, the crystal structures of solid forms were studied by X-ray method.

A new form, γ_2 , was found out at room temperature in longer odd members. The crystal structure of the form is supposed to be similar to that of γ_1 -form, but the detail is not yet known.

The dependences of lattice spacings on both chain length and temperature were observed and discussed, and stretching of molecules in low temperature forms is concluded. In α -forms, which are known as rotational form, there must be molecular shift in the direction of chain axes as well as molecular rotation to interpret the diffraction patterns.

The dependence of transition points on chain length is also discussed, and it is concluded that there must be some partial order of molecular arrangement in liquid state.

INTRODUCTION

The *n*-higher alcohol is materials of interest for their anomalous dielectric behavior. Several crystal forms are known of some members of the series. Among the forms, crystal structures of α -, β - and γ_1 -forms have already been analyzed¹⁾, but the dependence of the structures on carbon number has not yet been fully studied. Especially, the structure of α -form, which has been called rotational form or hexagonal form, varies with both temperature and carbon number in a complicated way, though the X-ray diffraction patterns of the form are rather simple because of the considerably disordered structure.

The present work was undertaken to investigate the dependences of the crystal structures on temperatures and the chain length by the X-ray method. The results were partly reported in the previous paper,²⁾ but, in the present paper, more precise data are presented for the members covering more wide range of carbon number.

The materials here used were all chemically synthesized and purified by repeated recrystallizations.³⁾ Some of them were recognized to be doubtful in purity by the X-ray method, though their melting points were almost normal. The impurity was supposed to be due to imperfect reactions in the chemical processes, and the data of them are omitted in the discussions.

CRYSTAL FORMS

Hitherto, three forms have been known with the series. A possibility of existence of another new form for longer members was suggested in the

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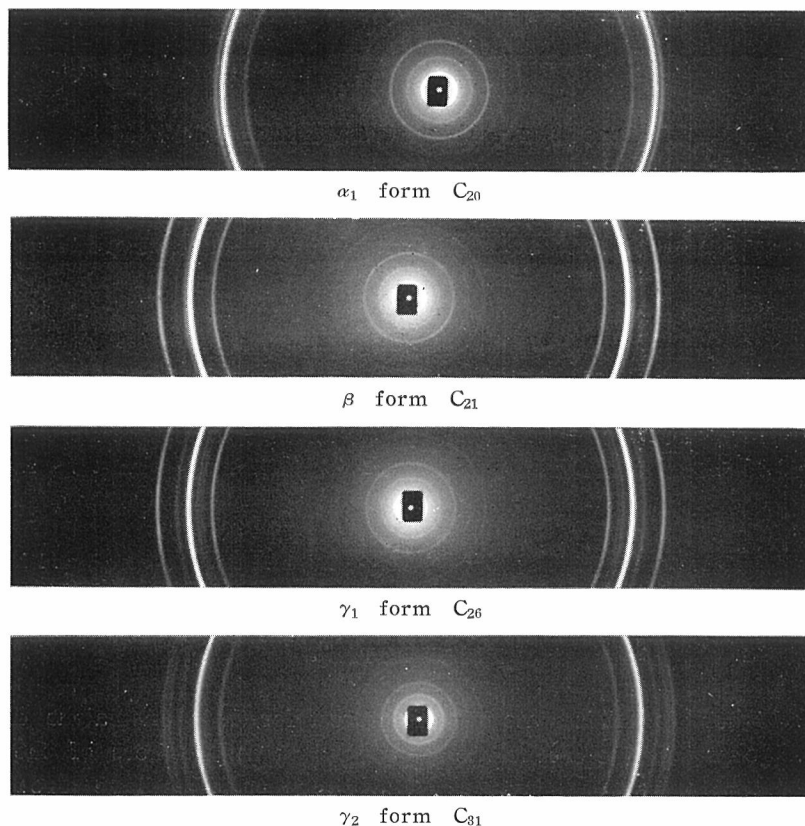


Fig. 1. Diffraction patterns of four typical forms of n -higher alcohols.

previous paper. This expectation was supported by the present investigation, and the new form was designated as γ_2 -form. Accordingly, the γ -form in the previous paper will be described as γ_1 -form hereafter. The typical X-ray powder patterns of the four forms are reproduced in Fig. 1.

The high temperature forms are observed in a narrow temperature region immediately below the melting points, and they have larger molar volume and higher symmetry compared with other forms. It has been known by the present research that there exists a certain variety in α -forms. The α -form of each member shorter than octadecanol gave the characteristic powder pattern composed of one strong line. This form was designated as α_0 -form.

In the case of longer members, however, the characteristic line splitted into two lines, and it was known from continuous powder patterns that some of the members had two types of α -form, which considerably differed in thermal expansion coefficients. One was observed only when α -form was realized by the phase transformation from β -form, and was considered as a metastable form, while the other was observed more generally. These modifications were designated as α_2 -form and α_1 -form respectively.

The specification of these three α -forms were deduced from the continuous X-ray powder patterns with only a few lines, and the differences among the

patterns are delicate. Accordingly, we do not necessarily expect the existence of the three forms corresponding to the above three forms. In other words, one of the forms might be a mixed system of two crystal structures, or on the contrary, two of the forms might have the same crystal form. However, the conventional model of molecular rotation or orientational disorder,⁴⁾ which has been applied for molecular motion in α -forms, seems to be inadequate considering such complicated behaviors of high temperature forms described above.

There are two types of modifications at low temperature region, one is vertical β -form, and the other is tilted γ -forms. β -form is observed with odd members shorter than C_{29} and even members shorter than C_{18} . The crystal structure is similar to that of an ortho-rhombic paraffin and the molecular axes are almost vertical to the layer plane, but there are two types of molecular configurations as shown in Fig. 2.

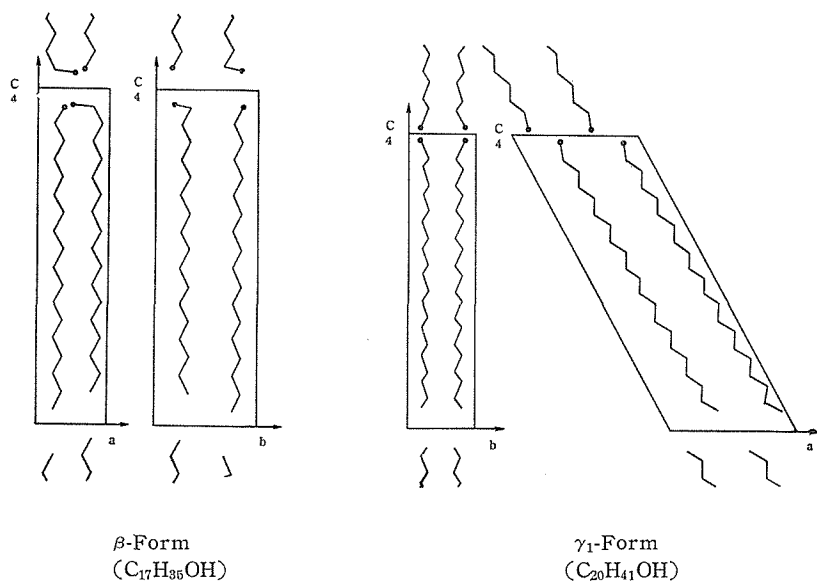


Fig. 2. Crystal structure of β - and γ_1 -forms of *n*-higher alcohols.

γ_1 -form is observed with even members longer than C_{14} . The axes of molecules are tilted at about 60° to the layer plane, but the sub-cell structure⁵⁾ is similar to that of vertical form. γ_2 -form is observed with odd members longer than C_{29} , and the tilt angle is about 60° , too. Though the crystal structure of the form is not yet determined, the obtained powder diffraction patterns of

Table 1. Crystal data.

Form	Space Group	<i>a</i>	<i>b</i>	<i>c</i>	β	τ	N
α (C_{17})	Monoclinic ?	8.34 Å	4.85 Å	46.5 Å	$96^\circ 30'$	84°	4
β (C_{17})	Monoclinic $P2_1/c$	4.96 Å	7.37 Å	94.5 Å	$91^\circ 20'$	89°	8
γ_1 (C_{18})	Monoclinic $A2/a$	8.66 Å	4.94 Å	98.0 Å	$123^\circ 03'$	56°	8

N : Number of molecules in a unit cell.

γ_2 -form are quite different from those of γ_1 -form.

The crystal structures of β - and γ_1 -forms and one of the high temperature forms have already been analyzed. (It could not be decided which α -form it corresponds to, because the diffraction patterns of α -forms were very similar to one another.) The crystal data are reported as in Table 1.

LONG SPACINGS

Long spacings of each form were determined by powder method. For high temperature forms, the specimens were prepared by solidification from melts, and accordingly, the observed spacings of longer members are considered to be those of α_1 -form and not of α_2 -form for the reason explained previously. For low temperature forms, specimens were kept at room temperature during the exposure.

The results are tabulated in Table 2, and also plotted in Fig. 3 as a function of carbon number n . The experimental error is at most 0.2 % for each member. The plots for low temperature forms may be regarded as straight lines, while the plot for high temperature form seems to be composed of two parts with different slopes.

By least square method, the experimental formulae of the long spacings in A unit are given as linear functions of n for low temperature forms respectively,

Table 2. Long spacing of n-higher alcohols.

Carbon number	α -form	β -form	γ_1 -form	γ_2 -form
11	28.8 A	32.2 A	— A	— A
12	34.1	34.9	—	—
13	36.1	37.3	—	—
14	38.9	39.63	33.05	—
15	41.3	42.36	—	—
16	43.83	44.90	37.27	—
17	46.34	47.46	—	—
18	48.93	50.23	41.60	—
19	51.11	52.82	—	—
20	53.13	—	45.67	—
21	55.35	57.95	—	—
22	57.74	—	49.89	—
23	59.82	63.12	—	—
24	61.89	—	54.24	—
25	64.03	68.14	—	—
26	66.08	—	58.02	—
27	68.31	73.29	—	—
28	70.65	—	62.60	—
29	73.5	78.4	—	65.5
30	(78.0)	(81.05)	—	—
31	77.2	—	—	69.7
32	79.4	—	71.0	—
33	81.2	—	—	74.2
34	82.8	—	75.1	—
35	86.6	—	—	78.6
36	—	—	—	—
37	90.9	—	—	83.0

The values in parenthesis are doubtful, because the material was impure.

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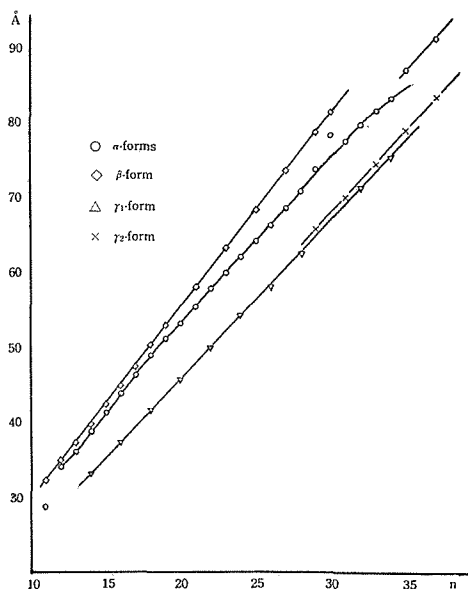


Fig. 3. Long spacings of *n*-higher alcohols.

$$l_{\beta} = 2.567 n + 3.94,$$

$$l_{\gamma_1} = 2.112 n + 3.47,$$

$$l_{\gamma_2} = 2.210 n + 2.25.$$

If molecules are straight in low temperature forms, tilt angles of molecules to the layer plane will be calculated assuming that the molecules in β -form is just perpendicular to the layer plane. The obtained values are,

$$\tau_{\beta} = 90^{\circ}, \tau_{\gamma_1} = 55^{\circ}22' \text{ and } \tau_{\gamma_2} = 59^{\circ}03'.$$

These angles may be considered to be characteristic constants of the respective forms.

As is seen in Fig. 3, long spacings of α -forms cannot be a linear function of *n*, but, roughly speaking, the plot may be divided into two parts at *n*=18, and approximate formulae for these parts are,

$$l_{\alpha_0} = 2.53 n + 3.45 \text{ for shorter members,}$$

$$l_{\alpha_1} = 2.17 n + 9.9 \text{ for longer members.}$$

The above formulae are considered to correspond to α_0 -form and α_1 -form respectively as mentioned previously.

However, attention should be paid to the fact that the constant term in the latter of the above formulae is 9.9, which is too large to be attributed to the packings of end groups, CH_3 and OH , and it is likely to consider that the linearity of the plot is merely apparent. The crystal structures of the high temperature forms will be discussed later.

SIDE SPACINGS

As is concluded in the preceeding section, tilt angles of low temperature forms are constants, and the side packings of the molecules resemble each

other as were seen in the diffraction patterns. The crystal structures of those forms may be specified by lattice constants a and b , and also by tilt angle τ .

The lattice constant b obtained by X-ray powder method was almost independent of n throughout the observed members. The lattice constant a cannot be deduced from the observed spacings unless the axial angle β is known, which is not generally equal to tilt angle. If c -axis is chosen so that the difference between β and τ is as small as possible, as shown in Fig. 4, the following relation will hold,

$$l (\cot \beta - \cot \tau) = p,$$

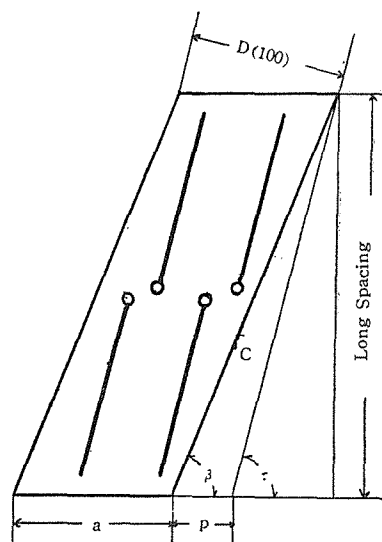


Fig. 4. Relation of β and τ .

Table 3. Calculated lattice constants.
(β -form)

Carbon number	Long spacing ($c \sin \beta$)	$a \sin \beta$	β	a	b	c	D
11	32.2 A	5.07 A	91°27'	5.07 A	7.37 A	32.2 A	5.07 A
12	34.9	5.08	91 25	5.08	7.40	34.9	5.08
13	37.3	5.07	91 24	5.07	7.38	37.3	5.07
14	39.63	5.05	91 23	5.05	7.37	39.64	5.05
15	42.36	5.04	91 22	5.04	7.37	42.38	5.04
16	44.90	5.04	91 21	5.04	7.38	44.92	5.04
17	47.46	5.04	91 20	5.04	7.39	47.48	5.04
18	50.28	5.03	91 19	5.04	7.39	50.30	5.03
19	52.82	5.03	91 18	5.03	7.40	52.84	5.03
20	—	—	—	—	—	—	—
21	57.95	5.01	91 17	5.01	7.38	56.97	5.01
22	—	—	—	—	—	—	—
23	62.12	5.00	91 16	5.00	7.37	62.14	5.00
24	—	—	—	—	—	—	—
25	67.84	5.00	91 15	5.00	7.38	67.87	5.00
26	—	—	—	—	—	—	—
27	73.0	4.99	91 15	4.99	7.39	73.0	4.99
28	—	—	—	—	—	—	—
29	79.0	4.98	91 14	4.98	7.41	79.0	4.98

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 (γ_1 -form)

Carbon number	Long spacing ($c \sin \beta$)	$a \sin \beta$	β	a	b	c	D
16	37.27 A	7.23 A	52°31'	9.11 A	4.94 A	46.95 A	7.50 A
18	41.60	7.25	52 48	9.10	4.94	51.85	7.49
20	45.67	7.25	53 02	9.08	4.93	57.15	7.47
22	49.89	7.28	53 13	9.09	4.95	62.30	7.48
24	54.24	7.30	53 23	9.09	4.94	67.58	7.48
26	58.02	7.30	53 31	9.08	4.94	72.16	7.47
28	62.60	7.33	53 39	9.10	4.94	77.73	7.49
30	—	—	—	—	—	—	—
32	71.0	7.34	53 51	9.09	4.94	89.0	7.48
34	75.1	7.34	53 56	9.08	4.94	92.9	7.47
36	—	—	—	—	—	—	—

$P=2.841$ A, $\tau=55^\circ 22'$ and $\beta=52^\circ 48'$ for C_{18} calculated from Table 1, because the values $a \sin \beta$ above are spacings d (101) in single crystal data.

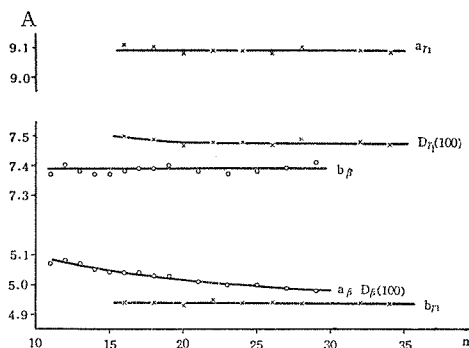


Fig. 5. Side spacing of β - and γ -forms at 20°C .

where p is a parameter dependent only on the relative positions of neighboring end groups.

Assuming that p is independent of chain length, all the lattice constants can be determined for the members of a form, using the calculated values of p from single crystal data in Table 1, and using also tilt angles deduced in the preceding section. The obtained values are shown in Table 3 and Fig. 5. Here we used $\tau_\beta=88^\circ 55'$ from single crystal data instead of $\tau_\beta=90^\circ$.

If β - and γ_1 -forms are both strictly homologous series in the sense described by Vand,⁵⁾ the constants to be kept independent of chain length are a , b and τ . Of course, the distance between the molecules in a layer, which can be derived from these constants, is also independent. In order to compare the side packings of both forms, the distance D between the next neighboring molecules in a - c projection are calculated from the following equation,

$$D = a \sin \tau,$$

and D thus obtained are also given in Table 3 and Fig. 5. The values of a , b and D of γ_1 -form can be considered as constants, throughout the observed region of carbon number n , while considerable dependences of those parameters a and D on n are seen for β -form. Accordingly, γ_1 -form is a strictly homologous series, but β -form is not.

As is seen in Fig. 3, high temperature forms are not a homologous series,

and appreciable temperature dependence of side spacings were also observed. The plots of side spacings of α -forms against carbon number are shown in Fig. 6 (a). Considerable fluctuations of the plots are presumably a result of rough control of temperature of observation. The specimens during the exposure were kept at an appropriate temperature in α -regions, but they were not adjusted systematically with chain length, and accordingly temperature dependence of spacings could not be excluded accurately. In the diffraction pattern of α_0 -form, there was only one strong line. With longer members, the second diffraction line was observed at a little larger Bragg angle than the first, and the intensity was about 10 % of the stronger. The lines other than the above were too weak to be observed. The plots in Fig. 6 (a) are those of two spacings corresponding to the observed diffraction lines. Roughly speaking, these side spacings of α -forms increase with carbon number. This would be due to thermal agitation because the temperature of observation was higher for longer members. The thermal expansion coefficients of the side spacings above of $C_{23}H_{47}OH$ are 6.57×10^{-4} for the former and 10.5×10^{-4} for the latter. If the coefficients were kept constant for every member and at all temperatures, extrapolated values of above spacings at a given temperature may be calculated. The values at $30^\circ C$ thus obtained are plotted in Fig. 6 (b). That is to say, if α -form of every member were brought to a fixed temperature, the former spacing would be nearly constant, and the latter spacing would rather decrease with increasing chain length.

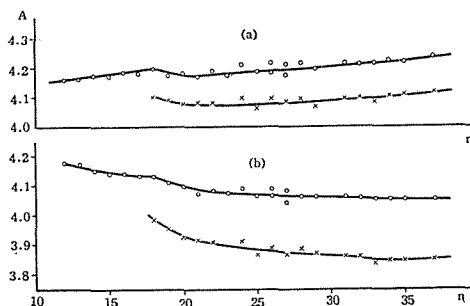


Fig. 6. Side spacing of α -form.
(a) Observed spacing.
(b) Extrapolated spacing (at $30^\circ C$).

However, the spacings could not be determined accurately enough, because the diffraction lines were diffuse, and above results is not available for further detailed discussions.

TRANSITION AND MELTING POINTS

The transition points determined by continuous powder method are tabulated in Table 4, which were partly reported in the previous paper together with the experimental procedure.

The transition temperatures of a member in heating process were a little

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Table 4. Transition and melting points (in °C).

Carbon number	T($\beta \rightleftharpoons \alpha$)	T($\gamma_1 \rightleftharpoons \alpha$)	T($\gamma_2 \rightleftharpoons \alpha$)	T($\alpha \rightleftharpoons \text{lig}$)	T($\beta \rightleftharpoons \text{lig}$)	T($\gamma_1 \rightleftharpoons \text{lig}$)
11	11.7(10)	—	—	13 (13)	—	—
12	—(18)	—	—	—(22)	23(—)	—
13	—(25)	—	—	—(29)	—	—
14	37.5(32)	—	—	37.9(37)	—	38(—)
15	39 (35)	—	—	44 (40)	—	—
16	42 (41)	46 (—)	—	49 (48.5)	—	—
17	48 (42)	—	—	53 (51)	—	—
18	49 (46)	52 (—)	—	58 (55)	—	—
19	54 (48)	—	—	62 (60)	—	—
20	—	63 (58)	—	66 (63)	—	—
21	60 (54)	—	—	68 (65)	—	—
22	—	67 (61)	—	72 (67)	—	—
23	68 (60)	—	—	73 (69)	—	—
24	—	72 (65)	—	75 (74)	—	—
25	72 (67)	—	—	77 (76)	—	—
26	—	77 (72)	—	79 (77)	—	—
27	75 (70)	—	—	80 (78)	—	—
28	—	—(75)	—	—(80)	—	82(—)
29	79 (72)	—	—	73 (80)	—	—
30	81* (75)*	—	—	85* (82)*	—	—
31	—	—	81 (76)	86 (85)	—	—
32	—	—(83)	—	—(86)	—	88(—)
33	—	—	85 (80)	89 (87)	—	—
34	—	—(86)	—	—(88)	—	90(—)
35	—	—	85 (80)	90 (89)	—	—
36	83* (82)*	—	—	91* (89)*	—	—
37	—	—	88 (85)	92 (90)	—	—

* Doubtful because of impurity in the specimen. The values in parenthesis are those in cooling processes

higher than those in cooling process, but the difference of them was nearly constant regardless of the carbon number of the material or the transformations between a pair of forms,

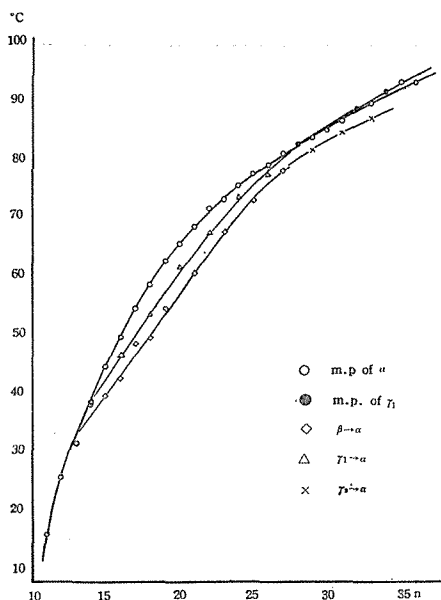
$$T(\alpha \rightarrow \text{liq.}) - T(\text{liq.} \rightarrow \alpha) = 2^\circ\text{C},$$

$$T(\beta \rightarrow \alpha) - T(\alpha \rightarrow \beta) = 6^\circ\text{C},$$

$$T(\gamma_1 \rightarrow \alpha) - T(\alpha \rightarrow \gamma_1) = 6^\circ\text{C},$$

$$T(\gamma_2 \rightarrow \alpha) - T(\alpha \rightarrow \gamma_2) = 5^\circ\text{C},$$

where $T(A \rightarrow B)$ means the temperature of transformation from A to B . Here, we denoted three α -forms only ' α -form' simply, because the difference among the diffraction patterns of these α -forms were delicate and we could not distinguish them strictly. These are the values observed in the processes in which heating and cooling speeds were $1 \sim 3^\circ\text{C}/\text{min}$. When the temperature of material varies very slowly, the differences of transition temperatures in both processes will be smaller. If the differences are due to super-cooling, the transition temperatures in cooling processes will be raised, while those in heating processes will be kept nearly constant. However, the differences of the transition points $T(\alpha \rightleftharpoons \beta)$ or $T(\alpha \rightleftharpoons \gamma)$ may, in part, be due to the existence of two α -forms of different stabilities such as α_1 and α_2 . These forms were really observed near the transition points in heating and cooling processes with longer members, and there is a possibility that shorter members may also have more than one α -form which could not be distinguished by powder method. The observed transition points in heating process are plotted in Fig. 7.

Fig. 7. Transition points of n -higher alcohols.

The difference between the melting point and setting point would be also due to the existence of some α -forms, but here we consider them to be due to super-cooling mainly. Accordingly, the equilibrium temperature of α -forms and liquid state is regarded to be the melting point of each member.

If both latent heat and entropy of transformation are given by linear functions of carbon number n , as is described in usual discussions of transformation of long chain compounds,⁶⁾

$$\Delta E = E_0 + \varepsilon n,$$

$$\Delta S = S_0 + \sigma n,$$

transition temperature T in absolute scale is given as

$$T = \frac{\Delta E}{\Delta S} = \frac{\varepsilon}{\sigma} - \frac{\frac{\varepsilon}{\sigma} \left(\frac{S_0}{\sigma} - \frac{E_0}{\varepsilon} \right)}{n - \frac{S_0}{\sigma}}$$

The observed melting points of n -higher alcohols can be expressed in the following form approximately,

$$T = 406 - \frac{n+1.6}{1450}$$

giving the ratios $\varepsilon/\sigma = 403$, $S_0/\sigma = 1.6$ and $E_0/\varepsilon = -2.0$. For n -paraffins, according to King *et al.*,⁷⁾ the melting points are given as,

$$T = 408.5 - \frac{2281}{n+2.71}$$

and $\varepsilon/\sigma = 408.5$, $S_0/\sigma = 3.5$ and $E_0/\varepsilon = -2.87$. Because crystal structures of n -paraffin and n -alcohol at the temperature immediately below the melting points are similar to each other, it may be expected that each value of σ and ε is much the same for both series.

Comparing the end effects in both cases, the existence of OH group in alcohol molecules raises the latent heat a little, but lowers appreciably the entropy of fusion, which might be expected to increase for the additional OH group. This requires such a picture that the interaction between OH groups remains even in liquid state at temperatures near the melting point. Therefore, we may expect a partially ordered arrangement of molecules in liquid.

DISCUSSIONS

(a) Stretching of Molecules in Low Temperature Forms

Referring to the experimental formula of long spacing for β -form,

$$l_{\beta} = 2.567n + 3.94,$$

coefficient of linear term, 2.567, which represents the length per two CH_2 groups, is larger than the usually accepted value, 2.54 Å, and the difference is beyond the region of experimental error. From single crystal analysis, it was reported that the tilt angles of low temperature forms are,

$$\tau_{\beta} = 88^{\circ}55' \text{ for } C_{17} \text{ and } \tau_{\gamma_1} = 55^{\circ}48' \text{ for } C_{18},$$

which are in good agreement with the values derived from our data, $\tau_{\beta} = 90^{\circ}$ and $\tau_{\gamma_1} = 55^{\circ}22'$ respectively. Accordingly, it is considered that $(\text{CH}_2)_n$ chains are stretched in low temperature forms. Such an elongation of molecules was reported with the series of silver salts of fatty acids.⁵⁾ This would be caused by the compression perpendicular to the chain axes by the cohesive force.

The length of the molecules may contract with increasing temperature because of the loosening of side packing by thermal motion, if such an assumption is correct. In order to obtain some information on this problem, the variations of spacings of β -form with increasing temperature was observed for $\text{C}_{23}\text{H}_{47}\text{OH}$ (Fig. 8). The negative thermal expansion coefficient of long spacing was observed, and it seems to suggest the decrease of molecular length with

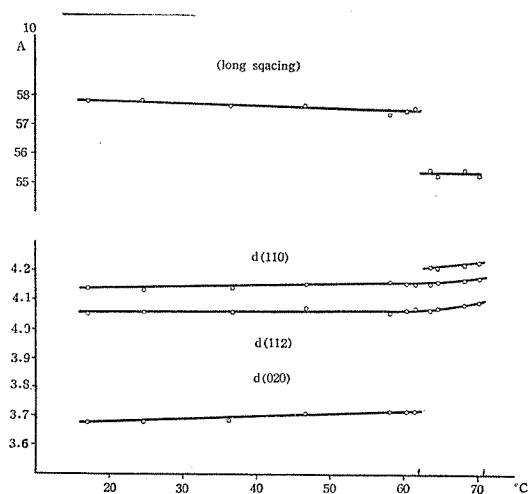


Fig. 8. Temperature dependence of spacings of $\text{C}_{23}\text{H}_{47}\text{OH}$.

increasing temperature, because τ_β is almost 90° , so a small variation in tilt angle about this value will not bring any appreciable change in observed long spacing. If the decrease in long spacing is caused by shrinkage of molecules, the value of long spacing observed immediately below the transition point will give a proper length for the considerably stress-free molecule. Long spacing of $C_{23}H_{47}OH$ at transition point was 57.37 Å. Assuming that both inter-layer packings and tilt angle of molecules are kept unchanged, the distance between the atoms of next nearest neighbor in a $(CH_2)_n$ chain is calculated to be 2.544 Å, which is in good agreement with the expected value.

In α -form of shorter members, the increment of long spacing was 2.53 Å. If the distance between the carbon atoms of next nearest neighbor in a chain is the same as that in low temperature forms, (2.567 Å) tilt angle is calculated to be 80° . While, if the interatomic distance of next nearest neighbor is 2.54 Å, the tilt angle is estimated to be 84° , which is rather in good agreement with the value 84° from single crystal data. Probably, the molecules in α -form are considered to be stress-free, and 2.54 Å would be acceptable for the interatomic distance of next nearest neighbor in a chain.

(b) Molecular Configuration in α -Forms

As is mentioned before, the plot of long spacing of α -forms against carbon number n may be roughly approximated to two lines with different slope, and the experimental formulae are,

$$l_{\alpha 0} = 2.53n + 3.45 \text{ for shorter members,}$$

$$l_{\alpha 1} = 2.17n + 9.9 \text{ for longer members.}$$

However the usual model of α -form will be applicable for shorter members, the constant term in the formula for longer members is 9.9, which is too large to be attributed to the packings of end groups. Therefore, it is unnatural that the molecules of longer members in α -form are tilted at a constant angle deduced from the slope of the plot, as is true for low temperature forms.

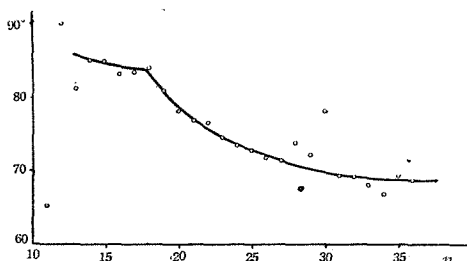


Fig. 9. Dependence of tilt angle of α -form on carbon number.

Accordingly, the tilt angle is considered to decrease gradually with increasing carbon number. Fig. 9 gives the dependence of tilt angle on molecular length assuming the above scheme. To explain the large constant term, some other models are considered, but they are difficult to be accepted. In fact, it is recognized from diffraction patterns of single crystal that the tilt angle of molecules in α -form depends on temperature, and it is natural to expect the

dependence of tilt angle on chain length.

(c) Degree of Freedom of Molecules along the Axes

In the preceeding paragraph, it is concluded that the molecules in α -forms tilt against the layer plane, and the tilt angle depends on chain length and temperature. As Schoon noticed,⁸⁾ the tilt angle in low temperature forms is confined to some definite angles on account of periodic structure of periodic structure of $(CH_2)_n$ chain, while the tilt angle of α -form varies gradually with chain length covering considerably wide range of angle. This means that, in α -form, neighboring molecules are allowed to shift relatively to each other in the direction of chain axes.

In X-ray diffraction patterns of α -form, the intensity of long spacing reflections decreases rapidly with increasing order of reflection, and there can hardly be observed such higher order reflections as corresponding to the spacings smaller than 5 Å. That is to say, long spacing reflections shows the existence of discrete layers clearly, but gives little information about the positions of atoms. Accordingly, molecules in α -form may have freedom not only of rotation or twisting around the chain axes but also of shift along the axes, and probable order of shift is estimated to be comparable with C-C distance in a chain.

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