*The Synthesis and the Physical Properties of Normal Higher Primary Alcohols. V. Thermal and X-Ray Studies of the Polymorphism of Alcohols of Odd Carbon Numbers from Undecanol to Heptatriacontanol**

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The transition phenomena in the solid state of normal higher alcohols of the even series from dodecanol ($C_{12}H_{25}OH$) to tetratriacontanol ($C_{34}H_{69}OH$) have already been studied by thermal and X-ray examinatons; the results were reported in a preceding paper⁽¹⁾. Since it has been known that, in some of the long chain compounds, transition points as well as melting points differ systematically between the odd and even series, it seems important to extend the study to the odd series of the alcohols in order to gain further knowledge on the transition behavior of the compounds. The present paper deals with the thermal analyses and X-ray pattern meaurements of odd alcohols, including the 14 members from undecanol ($C_{11}H_{23}OH$) to heptatriacontanol ($C_{37}H_{75}OH$). It also includes a discussion of the present results of those of the previous studies of the even series, with reference to their relation to the structure analysis data of the selected compounds.

The syntheses of the alcohols investigated here have previously been described in this Bulletin[2-4]. The experimental porcedures used in this study were essentially the same as those used in the previous study of even alcohols. The definition of the terms was given in a previous paper[1] and will be followed in the present paper as well. The crystal modifications will be interpreted briefly. Four modifications, which are called the β, γ_1, γ_2, and α forms, have been known in solid alcohols, the former three modifications being low temperature forms and the latter a high temperature form. When the material is cooled from the melting point, the α form appears at the freezing point, but this form suddenly changes to a low temperature form on further cooling, to either the β, γ_1 or γ_2 form depending upon the carbon number of the compound. This phase change has also been known to occur in some cases on heating the materials. The α form is of interest because of its unique properties. This form is somewhat more transparent than the low temperature forms. It is believed, judging from the X-ray data, that the crystal is nearly hexagonal, that the hydrocarbon chain is

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* This study has been carried out at the Department of Physics, Faculty of Science, Kyoto University, as a part of a co-operative research project on "The Synthesis and the Physical Properties of Long Chain Compounds".

1) A. Watanabe, This Bulletin, 34, 1729 (1961).

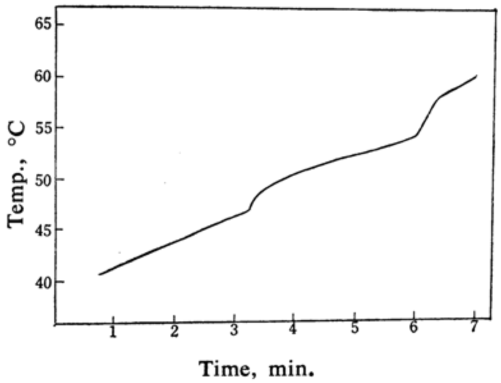
2) A. Watanabe, ibid., 32, 1295 (1959).

3) A. Watanabe, ibid., 33, 531 (1960).

4) A. Watanabe, ibid., 34, 398 (1961).

perpendicular to the plane of the end group, and that the molecules are less tightly packed than in the low temperature forms. A high dielectric constant value has been found in the α form, the molecule being assumed to rotate around the long axis. In the β form, the chain is perpendicular to the plane, while in the γ_1 and γ_2 forms the chain inclines at an angle to the plane. In these low temperature forms, no rotational freedom of the molecule has been found.

Since the present author, as well as previous workers, has found that small amounts of impurities influence the transition phenomena of long chain compounds, not only final products but starting materials were purified with great care in this study. The alcohols used in the present measurements were recrystallized several times or were subjected to high vacuum distillation, followed by recrystallizations, until constant melting points and transition points were obtained. The stored materials were recrystallized again before the measurements were undertaken.



Heating curve for heptadecanol

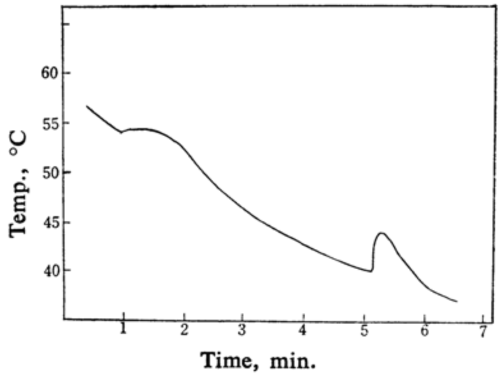


Fig. 1. Cooling curve for heptadecanol.

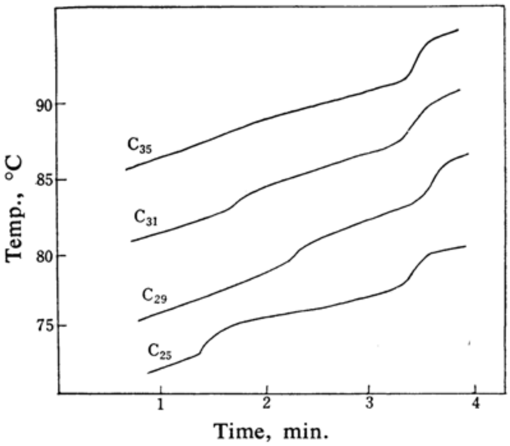


Fig. 2. Heating curves for C_{25}, C_{29}, C_{31} and C_{35} alcohols.

Results and Discussion

In Fig. 1 the time is plotted against increasing and decreasing temperature for heptadecanol ($C_{17}H_{35}OH$). The forms of the curves are general for all members of the series. As may be seen in the figure, there is a super cooling at the transition point which could not be avoided even though the sample was cooled very slowly. This made it difficult to determine accurately, the transition temperature on cooling. For undecanol, and Reid7) found no arrest of the time-temperature curve on cooling. This was confirmed by the present thermal studies, in which it was also indicated that this compound does not show the transition on heating. The transition in tridecanol ($C_{13}H_{27}OH$) is not reversible. The heating curve shows that no phase change occurs until the temperature reaches the melting point, while the cooling curve clearly indicates the existence of the transition. The high temperature form, which was confirmed to be the α form by X-ray5) and dipolemment6) measurements, showed such a stability that no tendency to change to a more opaque, low-temperature form was observed in visual examination over a 10 hr. period. In the alcohols from pentadecanol ($C_{15}H_{31}OH$) to hentriacontanol ($C_{31}H_{63}OH$), the transition is reversible, appearing both on cooling and heating. The transitions in tritriacontanol ($C_{33}H_{67}OH$) and higher compounds were observed only on cooling. Identification of the phases was made by X-ray pattern measurements, according to which, in the alcohols up to C_{27}, the transition is $\beta \rightleftarrows \alpha$, while in the alcohols above C_{29}, it is $\gamma_2 \rightleftarrows \alpha$. Typical photographs are reproduced in Fig, 3. The data on the transition phenomena for the C_{15}, C_{17} and C_{19} alcohols

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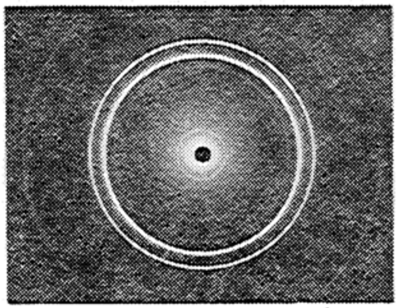
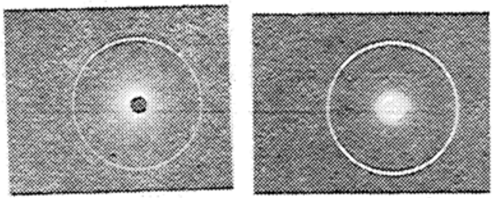
5) K. Tanaka, T. Seto and T. Hayashida, *Bull. Inst. Chem. Res., Kyoto. Univ.*, **35**, 123 (1957).

6) K. Asai, unpublished.

7) J. D. Meyer and R. E. Reid, *J. Am. Chem. Soc.*, **55**, 1574 (1933).

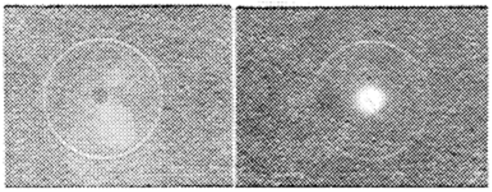


β-Form of heptadecanol



β-Form of heptacosanol

α-Form of pentatriacontanol



γ_2-Form of pentatriacontanol

α-Form of heptadecanol

Fig. 3.

TABLE I. MELTING POINTS AND TRANSITION POINTS OF *n*-HIGHER ALCOHOLS

C, No.	M. p., °C	Tr. p., °C on heating	Tr. p., °C on cooling
11	14.0	—	—
12	24.0	—	—
13	30.0	—	25.0
14	38.0	36.2	33.5
15	45.5	41.5	36.0
16	49.5	45.7	43.0
17	54.5	47.5	42.0
18	58.5	54.5	52.5
19	62.0	58.0	53.0
20	65.0	63.5	58.2
21	68.5	60.5	54.5
22	70.5	67.6	63.5
23	73.2	66.5	60.5
24	75.5	72.8	71.5
25	77.5	73.0	67.5
26	79.3	78.1	73.5
27	80.5	76.5	72.0
28	82.5	—	77.5
29	83.3	81.0	74.0
31	86.5	82.0	77.0
32	88.5	—	86.2
33	88.5	85.0	81.2
34	91.0	—	—
35	91.0	85.0	82.5
37	91.2	87.5	86.0

The values of C_{30} and C_{36} are omitted because of doubtfulness.

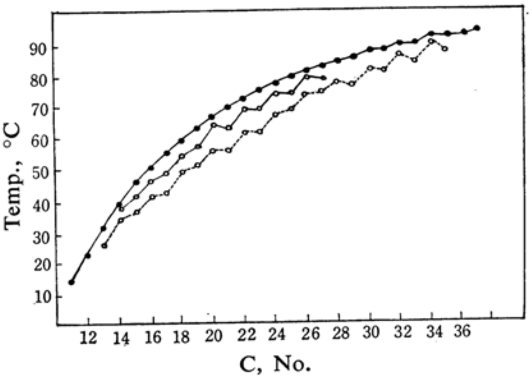


Fig. 4. Melting and transition points of *n*-higher alcohols.

—●— Melting points
—○— Transition point on heating
- -○- - Transition point on cooling

were found to agree with those of thermal analyses by Phillips and Mumford[8], while those for other compounds have not yet been reported, except for the X-ray data[9] reported previously from this laboratory. However, some discrepancies were found between the results of the present thermal analyses and those of the X-ray pattern measurements[9]. The X-ray data revealed that the C_{33}, C_{35} and C_{37} alcohols exhibit the transition on heating as well as on cooling. To examine this phenomenon further, pentatriacontanol ($C_{35}H_{71}OH$) was resynthesized and purified, and then the transition was studied with the greatest possible care. The results, however, were identical with those in the previous measurements. It is, therefore, assumed that the appearance of the heating transition can not be ascribed to the presence of impurities. A possible interpretation for the phenomenon is that the γ_2 to α transition is so gradual that it escapes observation in the thermal analyses. This theory is supported by the fact that the inflexion of the heating curve in C_{29} and C_{31} is less sensitive than those in the shorter members, a decrease in the energy barrier at the transition being indicated in the higher members (Fig. 2).

The melting and transition points of the alcohols, including all the odd and even members investigated, are given in Table I and, graphically, in Fig. 4. As may be seen in Fig. 4, the transition points show a definite

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[8] J. W. C. Phillips and S. Mumford, *J. Chem. Soc.*, **1931**, 1732.

[9] K. Tanaka, T. Seto, A. Watanabe and T. Hayashida, *Bull. Inst. Chem. Res., Kyoto. Univ.*, **37**, 281 (1959).

alternation in the compounds from C_{13} to C_{37}, the transition points of even members lying on an upper curve. On the contrary, the melting points lie on a smooth curve in the series from C_{11} to C_{29}, but, beginning with C_{29}, the higher series exhibit an alternation relationship.

This melting and transition behavior, with the number of carbon atoms, may be interpreted from the structural point of view. Müller[10] and Malkin[11] interpreted the melting behaviors of normal paraffins with relation to the tilted structure of hydrocarbon chains and to the planes of the end groups. In general, the inclination of the chains to the planes is indicated by the long spacing values, the shorter spacings meaning the more tilted structures, as has already been reported by Malkin[12] for the relatively shorter members of higher alcohols. The series were recently extended in this laboratory with more detailed investigations[9]. The data are represented here in Table II and Fig. 5, from wihch it may be seen that vertical (β) and tilted (γ_1) structures appear alternatively in the series up to C_{29}, the vertical form appearing in odd members and the tilted form in even members. Accordingly, considering the fact that the transition points of even members lie on an upper curve, the tilted structure seems to be more stable than the vertical structure in low temperature forms. This is analogous to the previous observation[1] that, in hexadecanol ($C_{16}H_{33}OH$), the transition point of the γ_1 form was slightly higher than that of the β form. In contrast to the low temperature forms, no difference in structure between the odd and even members seemed to exist in the high temperature forms (Fig. 3). Therefore, it is plausible that the alternation does not appear in the melting points.

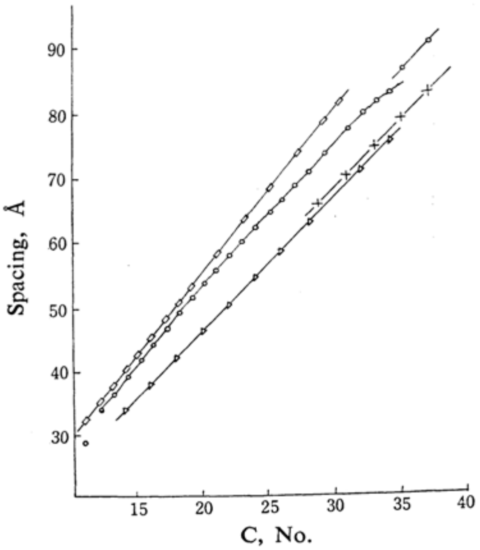

Fig. 5. Long spacing of *n*-higher alcohls.

—○— α-form —△— γ_1-form
—□— β-form —×— γ_2-form

TABLE II. LONG SPACING OF *n*-HIGHER ALCOHOLS

C, No.	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	—	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
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
37	90.9	—	—	83.0

Beyond the interpretation made from the long spacing data, a more elaborate interpretation of the phenomena is possible based on the configurations which were determined by the X-ray structure analysis of heptadecanol by Dr. Seto and of eicosanol synthesized by the present author. (For the use of the data the author is indebted to him.) The structures of two compounds are illustrated in Fig. 6. The alcohols form a monoclinic structure made up of a double layer of molecules. The unit cell contains eight molecules in two layers, in which the chains are parallel to one another. The structure of the β form appears to be somewhat unique. The layer of the hydroxyl groups contains methylene groups adjacent to oxygen atoms as may be seen in the figure, the atoms being packed more compactly than in the γ_1 form. The value of the O–O distance in the β form is slightly shorter than that in the γ_1 form. On the contrary, the distance between adjacent hydrocabon

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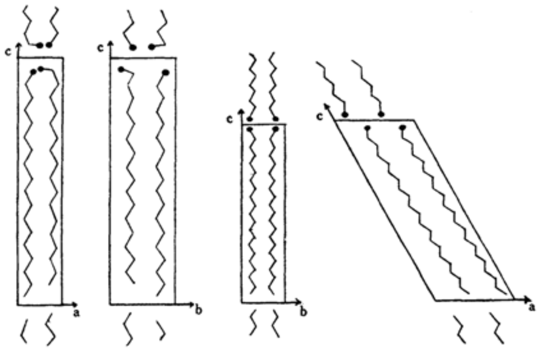
[10] A. Müller, *Proc. Roy. Soc.*, **124**, 317 (1929).

[11] T. Malkin, *Nature*, **127**, 126 (1931).

[12] T. Malkin, *J. Am. Chem. Soc.*, **47**, 1930 (1930).



$C_{17}H_{35}OH$ (β-Form) $C_{20}H_{41}OH$ (γ_1-Form)

Fig. 6. Crystal structure of *n*-higher alcohols. Black circles represent O atoms.

chains is greater in the β form than in the γ_1 form. These structures suggest that in the β form the layer of the ends takes the more stable arrangement, while the hydrocarbon chains are arranged more stably in the γ_1-form. Accodingly, it seems reasonable that in those shorter members in which the end groups predominate over the hydrocarbon chains (C_{12} and C_{14}), the β structure proves to be favorable, while in longer members, in which the chains predominate over the end groups, the γ_1 structure tends to be favorable. Presumably, a similar interpretation may be given of the existence of the tilted form (γ_2) in the higher members of the odd alcohols, although the structure of this form has not yet been determined.

The properties of the α form in odd alcohols were found to change gradually with an increase in the chain length, as was observed in even alcohols. For example:

1. The inflexions at the transition points in the time-temperature curves become smaller. (Fig. 2)
2. The opacity of the α phase increases.
3. The spacings of α form split into two lines. (Fig. 3)
4. Long-spacing variations with chain length indicate that the hydrocarbon chains increase their inclination to the planes of the ends. (Fig. 5)

These facts would suggest that, as the chain length increases, the structure of the α form increases its deviation from the hexagonal structure found in shorter members and gradually changes to structures similar to those of the low temperature form.

The alteration in the melting point appearing in the series from nonacosanol ($C_{29}H_{59}OH$) to heptatriacontnol ($C_{35}H_{71}OH$) may be ascribed to the difference in the phases existing just below the melting point.

Summary

On the phase transition of *n*-higher alcohols with odd carbon atoms from undecanol (C_{11}) to heptatriacontanol (C_{37}), thermal analyses and X-ray pattern measurements were made, with the following results:

1. Tridecanol (C_{13}) shows an irreversible transition which appers only on cooling. A reversible transition sets in at pentadecanol (C_{15}) and continues to the end member of the series (C_{37}).
2. X-Ray pattern measurements indicated that, in the alcohols up to nonacosanol (C_{29}), the transtition is β to α, while in the alcohols above C_{29} the transition is γ_2 to α.
3. Presumably, the γ_2 to α transition is gradual.
4. The properties of the α forms change gradually with an increase in the chain length.
5. The results of the present study and those of previous studies with the even series have been discussed from the configurations of the β and γ_1 forms, as determined by X-ray structure analyses.

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