

## CRYSTAL STRUCTURES OF $n$ -HIGHER ALCOHOLS

BY

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### ABSTRACT

The crystal structures of heptadecanol and octadecanol were determined. One of the low-temperature forms ( $\gamma$ ) of octadecanol showed a simple structure similar to that of hexadecanol reported by Abrahamsson *et al.*. While, the low-temperature form ( $\beta$ ) of heptadecanol showed a rather particular structure containing non-equivalent rotational isomers. In either of these low-temperature forms, hydrogen bonds with O to O distances of about  $2.7\text{\AA}$  form infinite chains of hydroxyl groups along  $a$  or  $b$  axis as expected from their dielectric properties. The crystal structures of these substances at higher temperatures were also investigated and two stable monoclinic forms and one metastable trigonal form were found.

### 1. Introduction

High-temperature forms of paraffinic long-chain compounds are thought to have a hexagonal or pseudohexagonal structure with the molecule perpendicular to the plane defined by end groups. So far, investigations by the X-ray method have given merely a broad view of the molecular packing in these crystals, and the crystal structure is still ambiguous in many respects. Only it is sure that the molecule in such a crystal experiences hindered rotation. Fig. 1 shows the transition point between low- and high-temperature forms for the series of  $n$ -alcohols.

In previous papers (1, 2), we reported on the series of  $n$ -alcohols that there were two high-temperature forms different in thermal expansion coefficient. We found also that the tilt angle between the axis of the molecule and the plane of end groups is not always equal to  $90^\circ$ , the inclination becoming more pronounced with increasing molecular length (Fig. 2). Having regard to these facts, there is little hope of success in determining the crystal structure of the high-temperature form by use of the powder method. In the present work, Bragg reflections from a single crystal were studied mainly by the oscillation method. Diffuse scattering, which is important in studying the correlation between rotating molecules, was difficult to measure quantitatively, because the low to high transformation gave rise to twinning inevitably.

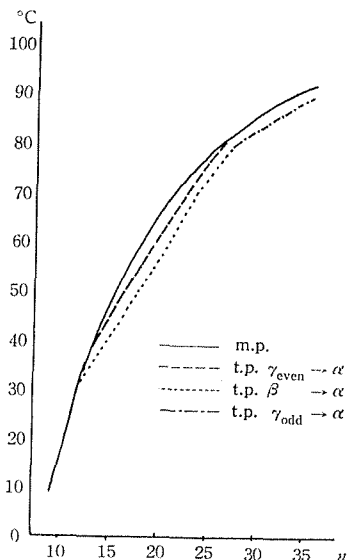


Fig. 1. Melting point (*m.p.*) and transition point (*t.p.*) plotted as functions of carbon number *n*.

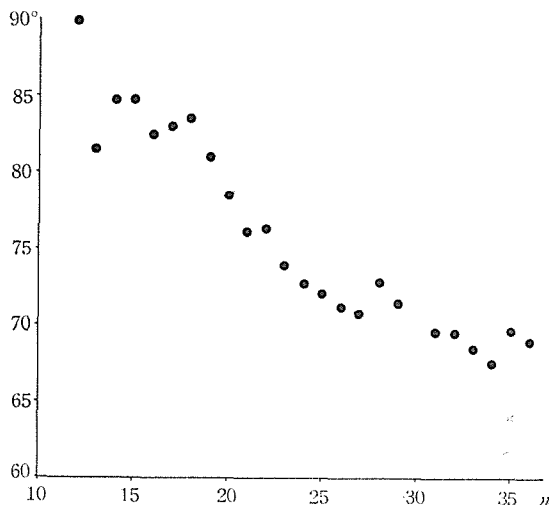


Fig. 2. Variation in the tilt angle of  $\alpha$  form with carbon number *n*.

The high-temperature form of *n*-alcohols has attracted notice for its dielectric anomaly in which hydrogen bonds play an important role (3). X-ray analysis of this form, however, will give little information about its local structure, and it is difficult to prove the presence of hydrogen bonds directly. Instead, a knowledge of the crystal structure at lower temperatures may be available to discuss the situation of end groups. In the first part of this paper, the crystal structures of two important low-temperature forms are given.

## 2. Crystal structures of the low-temperature forms

### (a) $\gamma$ form of octadecanol

An investigation was made on single crystals of  $\gamma$ -form of octadecanol and the results obtained were partly reported in the previous paper (2). Here the data are presented briefly to compare them with those for the other low-temperature form ( $\beta$ ). Recently, Abrahamsson *et al.* (4) published their work on the crystal structure of this form of hexadecanol. Since these crystals are homologous and have quite similar structures, it may be sufficient to refer to their paper for the details of this form.

#### *X-ray data*

Unit cell: monoclinic,

$$a = 8.96 \pm 0.03, \quad b = 4.93 \pm 0.02, \quad c = 99.7 \pm 0.3 \text{ \AA},$$

$$d_{001} = 41.4 \pm 0.15 \text{ \AA} \quad \text{and} \quad \beta = 123^\circ 03' \pm 30';$$

eight molecules per unit cell;

Density calculated:  $0.984 \pm 0.019 \text{ g/cm}^3$ ;

Space group:  $C_{2h}^6 - A2/a$ .

### Structure determined

All the molecules are equivalent and the primitive cell containing four molecules can be taken within a double layer. The molecular arrangement in this form is shown in Fig. 3. The dotted lines in this figure represent hydrogen bonds. They bind O atoms attached to different layers over the center of symmetry and the two-fold axis, forming infinite chains parallel to the *a*-axis.

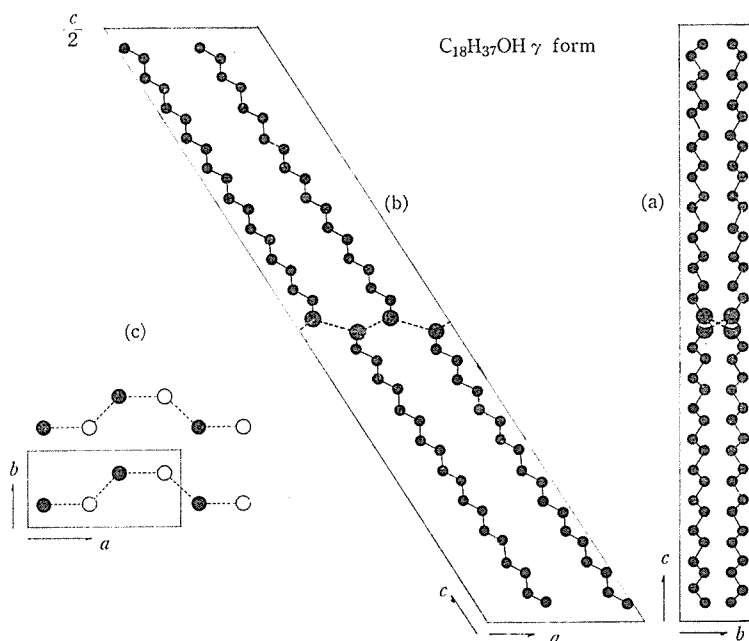


Fig. 3. Molecular arrangement in  $\gamma$  form as viewed along the *a* and *b* axes, large circles representing O atoms. (c) represents O atoms projected perpendicularly to the *a*-*b* plane. Atoms belonging to lower and upper layers are shown by hollow and full circles respectively.

### (b) $\beta$ -form of heptadecanol

Single crystals of heptadecanol were obtained in thin plates using various volatile solvents. The specimens for X-ray study were cut out with a razor from them. The crystals were rather brittle and hardly suffered from large plastic deformation, which is in contrast with high plasticity of  $\gamma$ -form.

*X-ray data*

Rotation, oscillation and weissenberg photographs were taken about  $a$  and  $b$  axes using  $\text{CuK}\alpha$  radiation. As the diffraction spots appeared at very short intervals, an Ni filter was used in order to avoid confusion. The cell dimensions were determined from powder photographs, and some twinned crystals were used to measure the monoclinic angle.

Unit cell: monoclinic,

$$a=5.03\pm 0.02, \quad b=7.40\pm 0.03, \quad c=94.6\pm 0.3\text{\AA}, \quad \beta=91^\circ 18' \pm 15';$$

eight molecules per unit cell;

Density calculated:  $0.971\pm 0.01\text{ g/cm}^3$ ;

Space group:  $C_{2h}^5-P2_1/c$ .

The intensities of the  $h0l$  and  $0kl$  reflections were estimated visually by multiple-film method. The observed structure factors given in Table 4 are those corrected using the following temperature factors:

$$\exp [-(B \cos \phi + C \sin^2 \phi) \sin^2 \theta / \lambda^2],$$

where  $\phi$  is the angle between the chain axis and the normal of the reflecting plane, and  $B=3.4$ ,  $C=6.2$  for  $a$  projection and 5.0 for  $b$  projection. The effect of absorption and extinction were fully neglected.

*Structure determined*

Strongest reflections showed the presence of a sublattice similar to that in  $\gamma$ -form and in many other paraffinic crystals, but the diffraction pattern of this form was characterized by the presence of the  $0, 2n+1, l$  reflections. The subcell part of this crystal hardly contributes to these reflections because of the extinction law for the space group of the sublattice, and so it is obvious that these reflections are mainly due to anomalous packing of the end groups.

From the  $00l$  synthesis (Fig. 4), it was known straightforwardly that molecules having different conformations are disposed alternatively. One of these

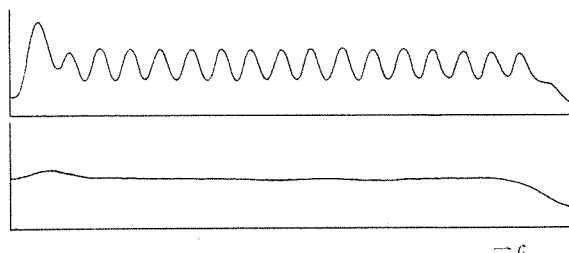


Fig. 4. One-dimensional syntheses for  $\beta$  and  $\alpha$  forms (in arbitrary scale).

conformations is the straight form (the trans form), which is identical with that found in  $\gamma$  form, and the other is such that the oxygen atom and one of the hydrogen atoms attached to the first carbon atom exchange their positions (the gauche form). In arranging the molecules in the unit cell, there are two possible ways, for either end of the molecule can be laid close to the center of symmetry. By analogy with the crystal structures of other paraffinic compounds, it is plausible that the center of symmetry is surrounded by polar groups, but adopting the model of this type, agreement between observed and calculated structure factors could not be obtained. In consequence, such a molecular arrangement as shown in Fig. 5 is the only possible one. Electron-density maps and atomic coordinates

$C_{17}H_{35}OH$   $\beta$ -form

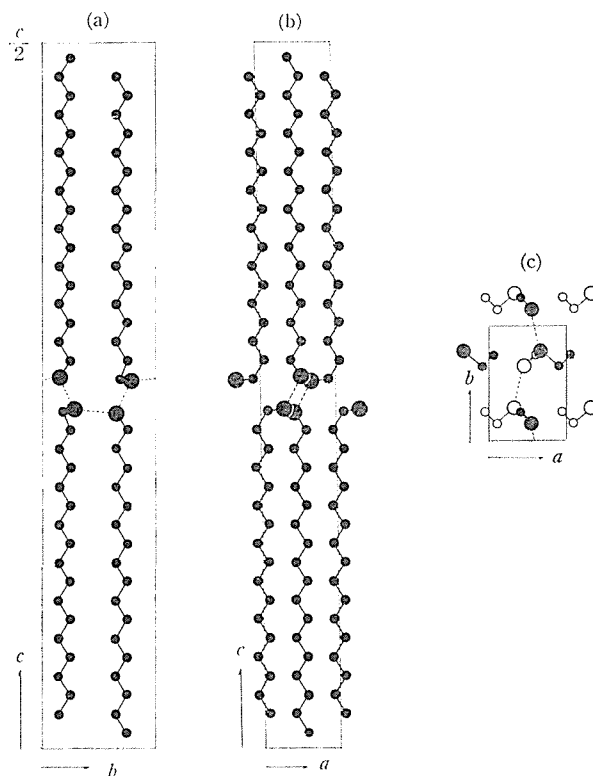


Fig. 5. Molecular arrangement in  $\beta$  form as viewed along the *a* axis (a), the *b* axis (b) and the axis of the molecule (c). Large circles represent O atoms, and full and hollow circles in (c) represent upper and lower layers respectively.

obtained from them are given in Fig. 6 and in Table 1 respectively. Only the coordinates of the overlapped atoms were determined by trial. In Fig. 5 the dotted lines represent the hydrogen bonds forming infinite chains along the screw axes. The O to O distance is 2.73 Å for the intralayer bond and 2.72 Å for the interlayer bond.

In this structure, lamellae are combined by hydrogen bond into double layers, but each double layer, by itself, lacks the center of symmetry and forms a right-handed or a left-handed system. It is an outstanding fact that such systems are regularly stacked under the influence of a rather weak force between them. About hundred crystals were examined, but polytypism was not found at all.

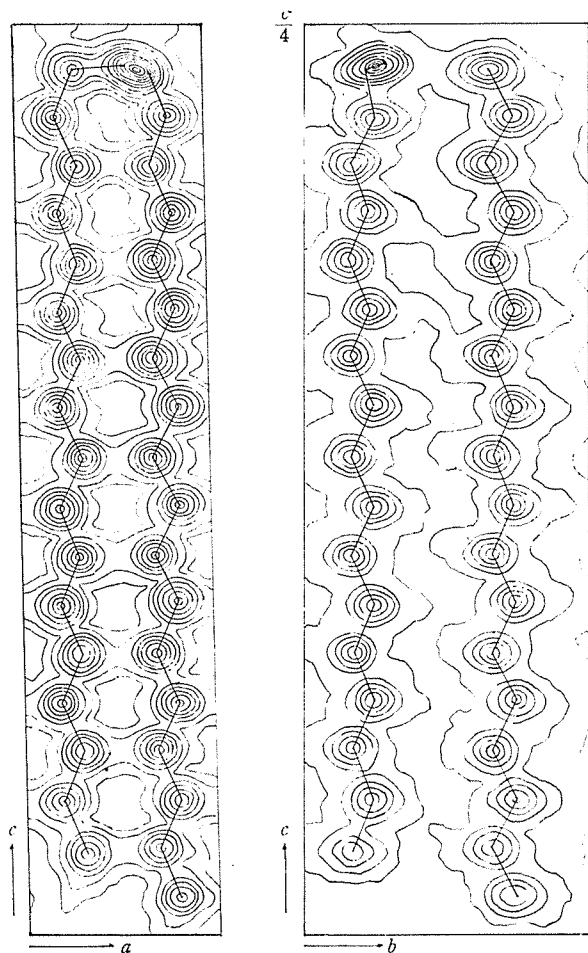


Fig. 6. Electron-density projections along the  $a$  and  $b$  axes for  $\beta$  form.

Table 1. Atomic coordinates for  $\beta$  form.

| Atom            | $x/a$  | $y/b$ | $z/c$  | Atom            | $x/a$ | $y/b$ | $z/c$  |
|-----------------|--------|-------|--------|-----------------|-------|-------|--------|
| O <sub>1</sub>  | 0.333  | 0.283 | 0.2388 | O <sub>2</sub>  | 0.458 | 0.644 | 0.2369 |
| C <sub>1</sub>  | 0.075  | 0.197 | 0.2375 | C <sub>18</sub> | 0.573 | 0.722 | 0.2245 |
| C <sub>2</sub>  | -0.038 | 0.241 | 0.2242 | C <sub>19</sub> | 0.463 | 0.655 | 0.2112 |
| C <sub>3</sub>  | 0.082  | 0.159 | 0.2113 | C <sub>20</sub> | 0.577 | 0.735 | 0.1984 |
| C <sub>4</sub>  | -0.036 | 0.235 | 0.1976 | C <sub>21</sub> | 0.460 | 0.662 | 0.1984 |
| C <sub>5</sub>  | 0.075  | 0.159 | 0.1844 | C <sub>22</sub> | 0.580 | 0.734 | 0.1715 |
| C <sub>6</sub>  | -0.038 | 0.233 | 0.1708 | C <sub>23</sub> | 0.463 | 0.660 | 0.1580 |
| C <sub>7</sub>  | 0.077  | 0.159 | 0.1844 | C <sub>24</sub> | 0.577 | 0.735 | 0.1444 |
| C <sub>8</sub>  | -0.040 | 0.235 | 0.1440 | C <sub>25</sub> | 0.459 | 0.660 | 0.1580 |
| C <sub>9</sub>  | 0.075  | 0.161 | 0.1305 | C <sub>26</sub> | 0.569 | 0.735 | 0.1176 |
| C <sub>10</sub> | -0.042 | 0.235 | 0.1173 | C <sub>27</sub> | 0.455 | 0.661 | 0.1041 |
| C <sub>11</sub> | 0.069  | 0.159 | 0.1036 | C <sub>28</sub> | 0.563 | 0.735 | 0.1176 |
| C <sub>12</sub> | -0.049 | 0.236 | 0.0904 | C <sub>29</sub> | 0.451 | 0.660 | 0.0773 |
| C <sub>13</sub> | 0.065  | 0.159 | 0.0765 | C <sub>30</sub> | 0.560 | 0.737 | 0.0639 |
| C <sub>14</sub> | -0.052 | 0.233 | 0.0634 | C <sub>31</sub> | 0.450 | 0.660 | 0.0773 |
| C <sub>15</sub> | 0.065  | 0.160 | 0.0498 | C <sub>32</sub> | 0.559 | 0.738 | 0.0371 |
| C <sub>16</sub> | -0.058 | 0.240 | 0.0366 | C <sub>33</sub> | 0.455 | 0.659 | 0.0236 |
| C <sub>17</sub> | 0.062  | 0.163 | 0.0231 | C <sub>34</sub> | 0.560 | 0.741 | 0.0102 |

### 3. Crystal structure at higher temperatures

A single crystal of  $\beta$  or  $\gamma$  form was heated in the diffraction camera and photographs were taken successively while the temperature was raised. The high-temperature form is so soft that it is liable to suffer from distortion during the experiment. To avoid this difficulty the specimen was stuck on the cleavage surface of a LiF crystal. In this way, two types of the high-temperature form were found; one was observed in the earliest stage of the phase transformation and changed irreversibly into the other with the progress of the transition. On cooling, the latter was supercooled to several degrees below the transition temperature, until it reverted directly to the low-temperature form. Accordingly, the former was considered to be metastable, while the latter stable.

#### *Stable $\alpha$ form*

Fig. 7 shows rotation photographs with the normal to the flat face of the crystal as the axis of rotation. In these photographs, the row lines intersect the equatorial line at right angles, showing that the plane of the layer is preserved during the transformation. However, the diffuse layer line in the upper photograph shows through its inclination that the molecule in  $\alpha$  form is not vertical but is inclined. Fig. 8 gives examples of the oscillation photographs showing individual row lines. Comparing the patterns due to different specimens, the

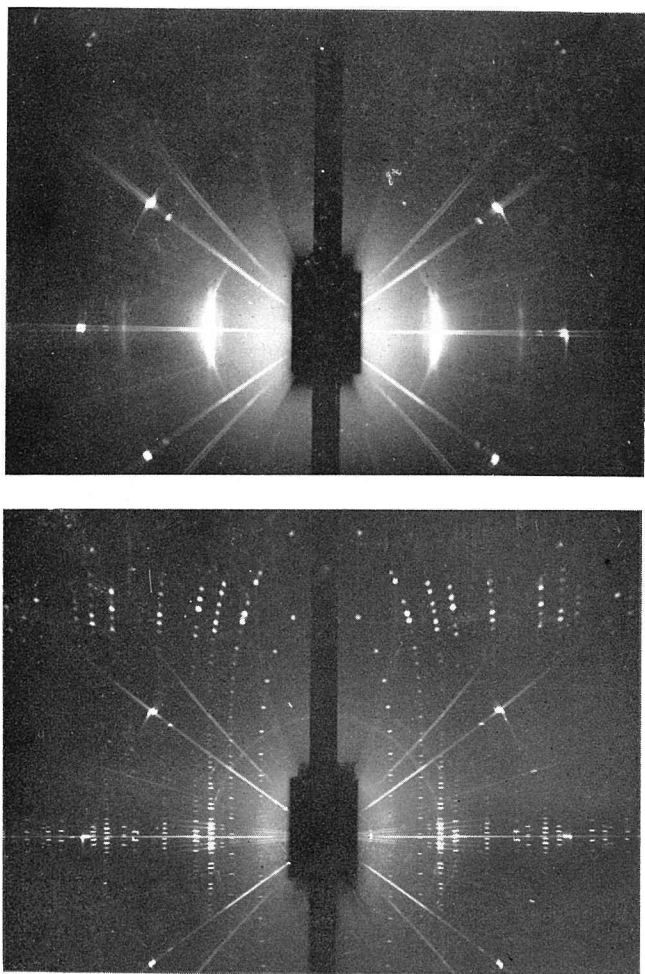


Fig. 7. Rotation photographs of  $\alpha$  and  $\beta$  forms. Radial streaks and spots on them are due to the specimen holder.

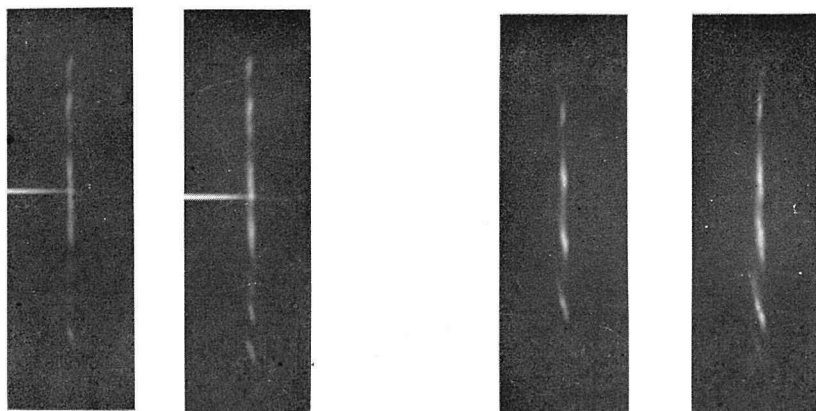


Fig. 8. Oscillation photographs of  $\alpha$  form showing one of the strongest row lines.

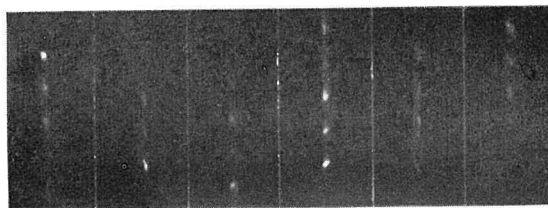


Fig. 9. Oscillation photographs of a small  $\alpha$  crystal. Three strong reflections are seen in each row.

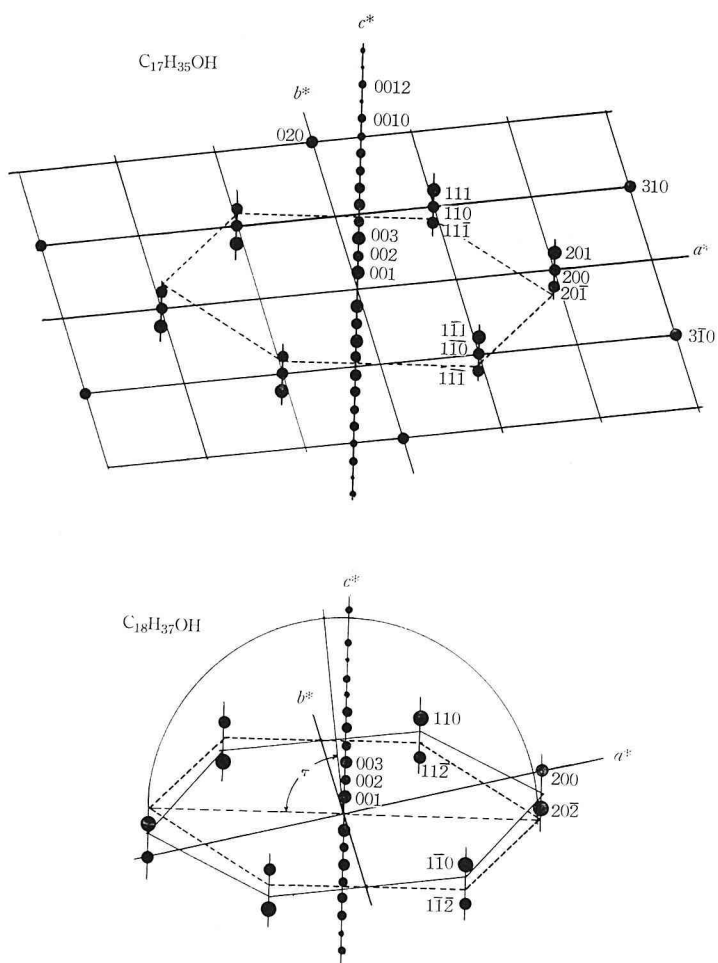


Fig. 10. Weighted reciprocal lattices for  $\alpha$  forms. Dotted lines represent the equatorial plane corresponding to the two-dimensional net work of end groups.

positions of the maxima were the same if only the temperature was fixed, whereas the relative intensities of the maxima varied from specimen to specimen. From this fact it was concluded that the specimen generally consisted of six components with twin relations among them. Fig. 9 shows reflections from a small crystal in which one of the six components predominates over the others. By taking up the maxima due to the same component, reciprocal lattice for this form was obtained as shown in Fig. 10. The direction of the molecular axis can be given as the normal to the plane passing through the center of the intensity distribution on the row line. Together with the cell dimensions the tilt angle of the molecule,  $\tau$ , thus obtained is shown in Table 2. Although the molecule is not perpendicular to the plane of end groups, the two-dimensional net work they make is almost exactly hexagonal.

Table 2. Crystal data for the stable  $\alpha$  form at the transition temperature.

|              | System     | Probable space group | $a$  | $b$  | $c$    | $\beta$ | $\tau$ |
|--------------|------------|----------------------|------|------|--------|---------|--------|
| Heptadecanol | Monoclinic | $C2/m$               | 8.40 | 4.85 | 46.6 Å | 95°20'  | 83°00' |
| Octadecanol  | Monoclinic | $C2/m$               | 8.44 | 4.87 | 49.1 Å | 93°00'  | 83°30' |

Reflections due to (001) plane were observed to the 16th order, and their intensities were measured quantitatively. The absolute values of the structure factors were estimated by comparing them with the data for  $\beta$  form obtained from the same specimen prior to the phase transformation. These spectra were similar to each other except that the temperature factor for  $\alpha$  form decays very rapidly with growing order (Table 3). In the one-dimensional synthesis, the electron-density distribution corresponding to the hydrocarbon chain is smeared out as shown in Fig. 4, but a maximum is still seen at the same position as that of O atoms in  $\beta$  form, showing that some atoms overlap at that position. If all the molecules take the straight configuration as in  $\gamma$  form, overlapping of atoms can be expected only at the center (or the end) of the unit cell at which adjacent molecules are in contact with each other. It is therefore likely that half of the

Table 3. Structure factors of  $\alpha$  and  $\beta$  forms for 00 $l$  reflections.

| $l$        | 1  | 2  | 3  | 4  | 5  | 6  | 7  | 8  | 9   | 10 | 11  | 12   | 13  | 14  | 15  | 16  |
|------------|----|----|----|----|----|----|----|----|-----|----|-----|------|-----|-----|-----|-----|
| $F_\alpha$ | 53 | 20 | 45 | 23 | 31 | 21 | 17 | 21 | 7.8 | 15 | 4.4 | 10   | 0   | 7.2 | 0   | 5   |
| $l$        | 2  | 4  | 6  | 8  | 10 | 12 | 14 | 16 | 18  | 20 | 22  | 24   | 26  | 28  | 30  | 32  |
| $F_\beta$  | 52 | 23 | 42 | 23 | 28 | 22 | 19 | 20 | 5.3 | 16 | 0   | 11.5 | 3.2 | 7.5 | 3.5 | 4.6 |

The values for  $\beta$  form represent the observed values multiplied by an artificial temperature factor  $\exp(-80 \sin^2 \theta / \lambda^2)$ .

molecules are in the gauche form, which suggests the possibility of intralayer hydrogen bonds similar to those in  $\beta$  form.

The high-temperature form of octadecanol was also studied, and the results obtained are shown in Fig. 10 and Table 2. In this case, the metastable form was not observed. Fig. 11 is a schematical representation of the molecular arrangements in heptadecanol and in octadecanol deduced from the relative intensities of the reflections. In determining these structures it was assumed that they consist of similar double layers as is usual with long-chain compounds having a polar group at a chain end. The most striking difference between these structures is in the way of stacking molecules. Disregarding the shape of the structural unit, the molecular arrangement in heptadecanol can be compared to that in the

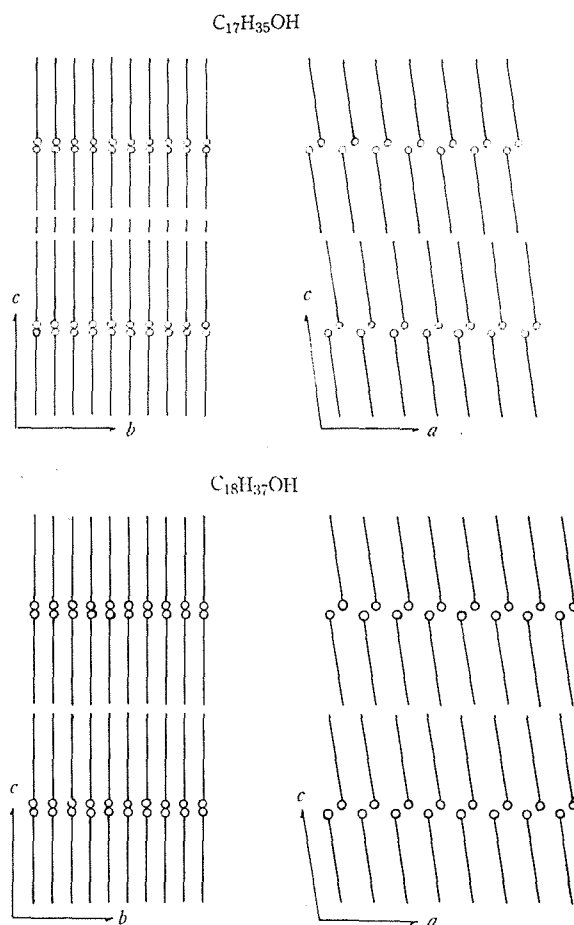


Fig. 11. Schematical representation of the molecular arrangement in  $\alpha$  form.



Table 4. Structure factors for  $\beta$  form of heptadecanol.

| <i>hk l</i> | <i>F</i> <sub>obs.</sub> | <i>F</i> <sub>cal.</sub> | <i>hk l</i> | <i>F</i> <sub>obs.</sub> | <i>F</i> <sub>cal.</sub> | <i>hk l</i> | <i>F</i> <sub>obs.</sub> | <i>F</i> <sub>cal.</sub> | <i>hk l</i> | <i>F</i> <sub>obs.</sub> | <i>F</i> <sub>cal.</sub> |
|-------------|--------------------------|--------------------------|-------------|--------------------------|--------------------------|-------------|--------------------------|--------------------------|-------------|--------------------------|--------------------------|
| 00 0        |                          | 1168                     | 01 10       | —                        | -3.1                     | 01 67       | —                        | -6                       | 02 35       | 56                       | 58                       |
|             |                          |                          | 11 13       |                          | 14                       | 68          | 27                       | -24.9                    | 36          | —                        | 4.5                      |
| 00 2        | 50                       | -54                      | 12 31       |                          | 36                       | 69          | —                        | 6                        | 37          | 180                      | 178                      |
| 4           | 24                       | -24                      | 13 14       |                          | 15                       | 70          | 6                        | 3.6                      | 38          | 120                      | 108.4                    |
| 6           | 45                       | -47                      | 14 —        |                          | -3.8                     | 71          | —                        | -4                       | 39          | 77                       | -89                      |
| 8           | 28                       | -27                      | 15 15       |                          | 15.5                     | 72          | 37                       | -38.7                    | 40          | 24                       | 39                       |
| 10          | 35                       | -39                      | 16 40       |                          | 42                       | 73          | —                        | 3                        | 41          | 18                       | -20                      |
| 12          | 31                       | -32                      | 17 15       |                          | -16                      | 74          | 22                       | -7.4                     | 42          | 14                       | -15                      |
| 14          | 27                       | -26                      | 18 2        |                          | -4.2                     | 75          | 8                        | -7.7                     | 43          | 22                       | -26                      |
| 16          | 36                       | -39                      | 19 14       |                          | 15                       | 76          | —                        | -1.4                     | 44          | 24                       | 28                       |
| 18          | 11                       | -12                      | 20 45       |                          | 45                       | 77          | 5                        | -1.3                     | 45          | 13                       | -14                      |
| 20          | 39                       | -39                      | 21 14       |                          | -14.5                    | 78          | 12                       | -9.9                     | 46          | 23                       | -24                      |
| 22          | —                        | 3.2                      | 22 3        |                          | -4                       | 79          | —                        | 0.2                      | 47          | 7                        | -13                      |
| 24          | 42                       | -42                      | 23 12       |                          | 13                       | 80          | 16                       | -15.8                    | 48          | 22                       | 24.5                     |
| 26          | 15                       | 19                       | 24 43       |                          | 44                       | 81          | —                        | -1.2                     | 49          | 11                       | -13                      |
| 28          | 45                       | -44                      | 25 11       |                          | -11.5                    | 82          | 7                        | 0.6                      | 50          | 25                       | -22                      |
| 30          | 27                       | 27                       | 26 4        |                          | -4.0                     | 83          | —                        | 2.0                      | 51          | —                        | -7.0                     |
| 32          | 46                       | -43                      | 27 7        |                          | 10                       | 84          | 11                       | -11.8                    | 52          | 18                       | 22                       |
| 34          | 33                       | 34                       | 28 42       |                          | 40.4                     | 85          | —                        | -3.0                     | 53          | 8                        | -12                      |
| 36          | 45                       | -45                      | 29 7        |                          | -8                       | 86          | 4                        | 0.1                      | 54          | 23                       | -21                      |
| 38          | 37                       | 38                       | 30 3        |                          | -3.0                     | 87          | —                        | 4.0                      | 55          | 7                        | -5.4                     |
| 40          | 40                       | -42                      | 31 3        |                          | 7                        | 88          | 6                        | -7.6                     | 56          | 19                       | 20                       |
| 42          | 41                       | 40                       | 32 39       |                          | 35                       |             | —                        | —                        | 57          | 7                        | -12                      |
| 44          | 36                       | -36                      | 33 3        |                          | -5                       | 02 0        | 375                      | 489                      | 58          | 18                       | -16                      |
| 46          | 38                       | 36                       | 34 3        |                          | -2.2                     | 1           | 185                      | -225                     | 59          | —                        | -4.6                     |
| 48          | 31                       | -29                      | 35 —        |                          | 4                        | 2           | 22                       | 28.5                     | 60          | 20                       | 19                       |
| 50          | 34                       | 31                       | 36 36       |                          | 30.2                     | 3           | 70                       | -77.6                    | 61          | 6                        | -0.2                     |
| 52          | 27                       | -26                      | 37 8        |                          | -7.5                     | 4           |                          | 2.9                      | 62          | 12                       | -10                      |
| 54          | 23                       | 23                       | 38 14       |                          | -14.0                    | 5           | 29                       | -38                      | 63          | —                        | -5.4                     |
| 56          | 22                       | -23                      | 39 —        |                          | 0.2                      | 6           | 27                       | 25.5                     | 64          | 25                       | 22                       |
| 58          | 14                       | 12                       | 40 25       |                          | 19.8                     | 7           | 35                       | -39                      | 65          | 3                        | -7.6                     |
| 60          | 23                       | -21                      | 41 4        |                          | 1.0                      | 8           | 2                        | 4.7                      | 66          | 3                        | -3.9                     |
| 62          | —                        | 1.4                      | 42 4        |                          | -0.3                     | 9           | 12                       | -17                      | 67          | 12                       | -9.7                     |
| 64          | 25                       | -25                      | 43 5        |                          | -2.5                     | 10          | 22                       | -18.6                    | 68          | 29                       | 32                       |
| 66          | —                        | -12                      | 44 12       |                          | 7.5                      | 11          | 20                       | -25                      | 69          | —                        | -0.9                     |
| 68          | 42                       | -37                      | 45 5        |                          | 4.0                      | 12          | 4                        | 7.4                      | 70          | —                        | 4                        |
| 70          | —                        | -20                      | 46 —        |                          | 0.6                      | 13          | 6                        | -9.4                     | 71          | 34                       | -22                      |
| 72          | 135                      | -135                     | 47 8        |                          | -5.5                     | 14          | 13                       | 9.5                      | 72          | 95                       | 89                       |
| 74          | 139                      | -146                     | 48 —        |                          | 1.4                      | 15          | 15                       | -17.5                    | 73          | 30                       | 29                       |
| 76          | 233                      | 233                      | 49 6        |                          | 6                        | 16          | 6                        | 10.5                     | 74          | 81                       | 88                       |
| 78          | —                        | 3.4                      | 50 —        |                          | -1.6                     | 17          | 4                        | -5.3                     | 75          | 142                      | 134                      |
| 80          | 66                       | 71                       | 51 8        |                          | 7                        | 18          | —                        | 1.8                      | 76          | 144                      | -145                     |
| 82          | —                        | 6                        | 52 3        |                          | -5.6                     | 19          | 11                       | -11.1                    | 77          | 35                       | -28                      |
| 84          | 35                       | 32                       | 53 8        |                          | 8                        | 20          | 11                       | 14.3                     | 78          | 10                       | -6.8                     |
| 86          | —                        | 2.4                      | 54 3        |                          | 2.4                      | 21          | —                        | -2.8                     | 79          | 8                        | 10                       |
| 88          | 15                       | 19                       | 55 5        |                          | -8.5                     | 22          | 8                        | -15.4                    | 80          | 41                       | -40                      |
| 01 0        | —                        | 0                        | 56 10       |                          | -11.5                    | 23          | —                        | -6.3                     | 81          | 10                       | -12                      |
| 1           | —                        | -1.5                     | 57 8        |                          | 8.7                      | 24          | 14                       | 17.5                     | 82          | —                        | -0.4                     |
| 2           | —                        | -1.0                     | 58 7        |                          | 3.2                      | 25          | —                        | -0.9                     | 85          | —                        | -0.5                     |
| 3           | 4                        | 5                        | 59 7        |                          | -8.3                     | 26          | 20                       | -26                      | 84          | 19                       | -21                      |
| 4           | 8                        | 13                       | 60 16       |                          | -16.4                    | 27          | —                        | 0.1                      | 85          | —                        | -6.7                     |
| 5           | 9                        | -9                       | 61 7        |                          | 8.5                      | 28          | 16                       | 19                       | 86          | —                        | 2.9                      |
| 6           | —                        | -2.1                     | 62 7        |                          | 3.6                      | 30          | 39                       | -43                      | 87          | —                        | -5.1                     |
| 7           | 10                       | 10.5                     | 63 3        |                          | -8                       | 31          | 11                       | 14.5                     | 88          | 6                        | -14                      |
| 8           | 20                       | 26                       | 64 21       |                          | -6                       | 32          | 17                       | 18                       |             |                          |                          |
| 9           | 12                       | -13.0                    | 65 7        |                          | 8                        | 33          | 6                        | 6.9                      | 03 4        | 12                       | -10                      |
|             |                          |                          | 66 8        |                          | 3.8                      | 34          | 70                       | -68                      | 5           | 13                       | -12.4                    |



Table 4. (continued)

| <i>hk l</i> | <i>F</i> <sub>obs.</sub> | <i>F</i> <sub>cal.</sub> | <i>hk l</i> | <i>F</i> <sub>obs.</sub> | <i>F</i> <sub>cal.</sub> | <i>hk l</i> | <i>F</i> <sub>obs.</sub> | <i>F</i> <sub>cal.</sub> | <i>hk l</i> | <i>F</i> <sub>obs.</sub> | <i>F</i> <sub>cal.</sub> |
|-------------|--------------------------|--------------------------|-------------|--------------------------|--------------------------|-------------|--------------------------|--------------------------|-------------|--------------------------|--------------------------|
| 10 54       | 16                       | 13                       | 20 0        | 410                      | 373                      | 20 30       | —                        | -2.8                     | 30 60       | 14                       | -16                      |
| 56          | 7                        | -2.6                     | 2           | 45                       | -41                      | 32          | 6                        | 11                       | 30 2        | 7                        | -18                      |
| 58          | 19                       | 20                       | 4           | 3                        | -7.8                     | 34          | —                        | -6.2                     | 4           | —                        | -0.8                     |
| 60          | 6                        | -7                       | 6           | 5                        | 8.2                      | 36          | 17                       | 8.6                      | 6           | —                        | -10                      |
| 62          | 23                       | 23                       | 8           | 33                       | -32                      | 38          | 16                       | -10                      | 8           | —                        | -1.5                     |
| 64          | 9                        | -10                      | 10          | 8                        | 2.4                      | 40          | —                        | -0.6                     | 10          | —                        | -0.2                     |
| 55          | 28                       | 25                       | 12          | 43                       | -42                      | 42          | —                        | 2.6                      | 12          | —                        | 0.2                      |
| 68          | 12                       | -14                      | 14          | 13                       | 10                       | 44          | —                        | 1.6                      | 14          | —                        | 2.7                      |
| 70          | 32                       | 25                       | 16          | 48                       | -44                      | 46          | 5                        | 11                       | 16          | —                        | -5.4                     |
| 72          | —                        | -17                      | 18          | 15                       | 13                       | 48          | 4                        | -2.2                     | 18          | —                        | 9.7                      |
| 74          | 12                       | -6.5                     | 20          | 48                       | -46                      | 50          | 6                        | 11                       | 20          | 11                       | -7.9                     |
| 76          | 37                       | -28                      | 22          | 16                       | 16                       | 52          | 8                        | -12                      | 22          | 17                       | 17                       |
| 78          | 22                       | 19                       | 24          | 42                       | -45                      | 54          | 6                        | 10                       | 24          | 19                       | -18                      |
| 80          | 22                       | -17                      | 26          | 14                       | 14                       | 56          | 14                       | -13                      | 26          | 23                       | 22                       |
| 82          | —                        | 12                       | 28          | 33                       | -38                      | 58          | 7                        | 5.6                      | 28          | 30                       | -26                      |
|             |                          |                          | 30          | 9                        | 13                       | 60          | 19                       | -18                      | 30          | 34                       | 27                       |
| 10 2        | 7                        | 4.4                      | 32          | 22                       | -27                      | 62          | —                        | 2.2                      | 32          | 54                       | -52                      |
| 4           | 50                       | -51                      | 34          | 5                        | 7                        | 64          | 28                       | -28                      | 34          | 50                       | 34                       |
| 6           | 15                       | 14                       | 36          | 14                       | -18                      | 66          | —                        | 13                       | 36          | 180                      | -191                     |
| 8           | 52                       | -55                      | 38          | 17                       | 19                       | 68          | 41                       | -37                      | 38          | 92                       | -104                     |
| 10          | 21                       | 21                       | 40          | —                        | -7.3                     | 70          | —                        | -8.1                     | 40          | 124                      | 117                      |
| 12          | 45                       | -48                      | 42          | —                        | 3.1                      | 72          | 59                       | -83                      | 42          | 32                       | 6.8                      |
| 14          | 24                       | 27                       | 44          | —                        | -1.9                     | 74          | 100                      | -108                     | 44          | 38                       | 44                       |
| 16          | 41                       | -40                      | 46          | —                        | -3.1                     | 76          | 110                      | 125                      | 46          | —                        | 10                       |
| 18          | 23                       | 24                       | 48          | 6                        | 1.4                      | 78          | 30                       | 20                       | 48          | 21                       | 25                       |
| 20          | 34                       | -35                      | 50          | —                        | -4.6                     | 80          | 13                       | 18                       | 50          | —                        | 9.6                      |
| 22          | 18                       | 24                       | 52          | 6                        | 4.6                      | 30 0        | 5                        | 0.4                      | 52          | 11                       | 16                       |
| 24          | 27                       | -34                      | 54          | 4                        | -8.1                     | 2           | 13                       | -21                      | 54          | —                        | 6.8                      |
| 26          | 16                       | 23                       | 56          | 7                        | 5.9                      | 4           | 7                        | 3                        | 56          | 6                        | 11                       |
| 28          | 23                       | -29                      | 58          | 5                        | -10                      | 6           | 16                       | -17                      |             |                          |                          |
| 30          | 14                       | 17                       | 60          | 10                       | 5                        | 8           | 10                       | 9.2                      | 40 0        | 60                       | 42                       |
| 32          | 35                       | -36                      | 62          | 4                        | -15                      | 10          | 17                       | -19                      | 40 2        | 27                       | 20                       |
| 34          | 21                       | 17                       | 64          | —                        | 0.7                      | 12          | 12                       | 10                       |             |                          |                          |
| 36          | 193                      | -168                     | 66          | —                        | -12                      | 14          | 17                       | -20                      | 50 32       | 24                       | 19                       |
| 38          | 80                       | -78                      | 68          | —                        | -10                      | 16          | 10                       | 10                       | 34          | 35                       | -21                      |
| 40          | 124                      | 106                      | 70          | 16                       | -13                      | 18          | 15                       | -18                      | 36          | 220                      | 197                      |
| 42          | 2                        | -22                      | 72          | 89                       | -87                      | 20          | 6                        | 8.8                      | 38          | 42                       | -40                      |
| 44          | 59                       | 58                       | 74          | 53                       | -58                      | 22          | 14                       | -13                      | 40          | 70                       | -60                      |
| 46          | —                        | -5.6                     | 76          | 130                      | 146                      | 24          | —                        | 9.5                      | 42          | 25                       | 4.8                      |
| 48          | 47                       | 45                       | 78          | —                        | 13                       | 26          | 14                       | 8.0                      | 44          | 45                       | 43                       |
| 50          | 6                        | -6.9                     | 80          | 31                       | 29                       | 28          | —                        | 13                       | 46          | —                        | 6.4                      |
| 52          | 35                       | 41                       | 82          | 16                       | 10                       | 30          | 12                       | -5.2                     | 48          | 22                       | 25                       |
| 54          | 8                        | -8.8                     | 20 2        | 28                       | 40                       | 32          | —                        | 2.5                      |             |                          |                          |
| 56          | 30                       | 34                       | 4           | 35                       | -28                      | 34          | 14                       | 9.5                      | 50 32       | 35                       | -32                      |
| 58          | 8                        | -7.2                     | 6           | 18                       | 2.0                      | 36          | 223                      | 251                      | 34          | 43                       | 13                       |
| 60          | 20                       | 27                       | 8           | 4                        | -7.9                     | 38          | —                        | 3.1                      | 36          | 80                       | -122                     |
| 62          | 5                        | -4.6                     | 10          | 14                       | -5.9                     | 40          | 98                       | -99                      | 38          | 135                      | 138                      |
| 64          | 20                       | 21                       | 12          | 4                        | 2.3                      | 42          | 36                       | 17                       | 40          | 100                      | 110                      |
| 66          | —                        | -2.0                     | 14          | 11                       | -11                      | 44          | 61                       | -62                      | 42          | 32                       | 2.4                      |
| 68          | 17                       | 19                       | 16          | 7                        | 9.3                      | 46          | 20                       | 21                       | 44          | 24                       | 43                       |
| 70          | —                        | -13                      | 18          | 9                        | -10                      | 48          | 38                       | -44                      | 46          | —                        | 12                       |
| 72          | 25                       | 11                       | 20          | 8                        | 12                       | 50          | 20                       | 22                       |             |                          |                          |
| 74          | 29                       | -25                      | 22          | 7                        | -8.7                     | 52          | 27                       | -32                      | 60 0        | 120                      | 111                      |
| 76          | 27                       | -16                      | 24          | 8                        | 12                       | 54          | 13                       | 24                       |             |                          |                          |
| 78          | 6                        | 5.0                      | 26          | —                        | -5.8                     | 56          | 19                       | -22                      |             |                          |                          |
| 80          | 9                        | -4.8                     | 28          | 8                        | 12                       | 58          | 9                        | 17                       |             |                          |                          |

Since the specific volume of this form is nearly equal to that of stable form, the rotation of the molecule is obviously hindered one, but the correlation between molecules in this form must be less than that in the stable form.

Considering the fact that in some simple crystals such as Co and ZnS crystals, hexagonal and cubic forms often coexist, it is interesting that a definite mode of layer stacking was seen in this metastable form in which the molecule is randomly rotating.

Let an isolated lamella be composed of rotating long-chain molecules. Then, the axis of the molecule can be thought as a sixfold axis. In fitting two such lamellae face to face, there are, of course, two equivalent ways. Once a double layer is formed, however, the molecule will interact through the end group with three molecules lying in the other lamella, and axis of the molecule is no longer sixfold axis but only threefold one. In adding the third lamella, two possible ways of fitting are, therefore, not equivalent, and hence further adding of lamellae will produce a regular lattice, namely a hexagonal or a trigonal one, provided that the torsional motion of the molecule does not exceed a certain limit. When the thermal motion of the molecule is such that the ends of the molecule rotate independently, this ordering effect will vanish. Thus we may conclude that even in the metastable form, both ends of the molecule rotate in phase.

#### 4. Discussions

From the crystallographic point of view, it is proper that the even and the odd members of a paraffinic homologous series should be treated as distinct series, because crystals of these substances generally show an alternation effect in many properties such as melting point, specific volume, etc.. When the molecule is perpendicular to the plane of layer, the alternation effect may not be so striking, but crystals of odd and even series are still expected to be different in symmetry. In the high-temperature form of *n*-alcohols, this effect was observed rather clearly. In so far as  $\beta$  form is concerned, however, the X-ray patterns of odd and even members are so similar that they are not easy to distinguish from each other without careful analysis, and the low-temperature forms with vertical molecules are here denoted by  $\beta$  irrespective of odd and even. Probably, the structure of  $\beta$  form for even series will be obtained from that for odd series by adding one  $\text{CH}_2$  group to (or removing it from) each molecule without altering the packing of polar groups and by translating the double layer by a small distance to allow nonpolar end groups to fit one another as before. The change in molecular arrangement as a result of this operation is not important, because the stable arrangement is confined by the spatial requirement that molecules of

different effective length must be in contact with one another at their chain ends.

So far  $\beta$  form, which, in reality, is monoclinic, was often supposed to be an orthorhombic form by the reasons that its subcell is of usual type and that the molecule is almost vertical to the plane of end groups. Amelinckx (5), however, has found in his study on growth patterns that one of the low-temperature forms ( $\alpha$  by his nomenclature) of *n*-alcohols showed fourfold interlaced patterns indicating monoclinic symmetry of the crystal. His result is quite natural if the crystal he observed was  $\beta$  form here described.

*Hydrogen bonds in the low-temperature forms*

Both of the low-temperature forms,  $\gamma$  and  $\beta$ , contain infinite chains of hydrogen bonds. In the case of  $\gamma$  form, every hydrogen bond appears to be symmetrical, but as Abrahamsson *et al.* pointed out, the O to O distance of about 2.7 Å corresponds with that of the asymmetric hydrogen bond. Accordingly, the apparent symmetry can be explained by a disordered distribution of protons. While in the crystal of  $\beta$  form, although the hydrogen bonds are apparently asymmetric, the O to O distances, 2.72 Å (interlayer) and 2.73 Å (intralayer), are nearly equal to the values for  $\gamma$  form (2.74 and 2.69 Å by Abrahamsson *et al.*), and so at ordinary temperatures, disorder in the proton distribution may also be expected. Such a disorder in the hydrogen bond chain can be related to the dielectric anomalous dispersion in the low frequency region observed by Meakins (6), Asai (7) and other researchers. Asai reported similar dispersions on both of the low-temperature forms.

If the valence of the O atom is always satisfied, then there are two possible directions of polarization for each of the hydrogen bond chains. With  $\gamma$  form, these directions must be equivalent at ordinary temperatures. If the apparent symmetry of this form come from disorder, there is a possibility that restoration of order at low-temperatures may cause an anomalous effect such as ferro or antiferro electricity. With  $\beta$  form, on the other hand, the possible directions of polarization are not equivalent, so that the resultant polarization will vanish at low-temperatures on account of the presence of the center of symmetry. Comparison of dielectric properties of these forms at low-temperatures is to be desired.

*Relative stability of the low temperature forms*

There is a tendency that  $\beta$  form becomes unstable as the molecule increases in length. Even members longer than eicosanol ( $C_{20}H_{41}OH$ ) have not  $\beta$  form, and odd members longer than pentacosanol ( $C_{25}H_{51}OH$ ) have another form with the molecule inclined just as  $\gamma$  form of even members. This tendency is to be

expected from the difference in crystal structure between  $\beta$  and  $\gamma$  forms. These forms are crystallographically homologous, and so the contribution to the cohesive energy from the end group packing including hydrogen bond energy will not alter largely, if the number of carbon atoms in the molecule is changed. Consequently, the difference in subcell structure may be responsible for the dependence of the relative stability on carbon number. Roughly speaking,  $\beta$  and  $\gamma$  have similar subcells, but the subcell of the former departs slightly from the usual structure having the space group, Pnam, and its volume is larger by 2% than that of the latter. Such a strain in the subcell part of  $\beta$  form may be considered as an elastic one caused by the formation of the intralayer hydrogen bonds. Since the elastic energy stored in the subcell part surely becomes important with increasing carbon number,  $\beta$  form is expected to be unstable for molecules long enough.

*Temperature dependence of the monoclinic angle of  $\alpha$  form*

As already mentioned, the tilt angle for  $\alpha$  form is not constant but varies with carbon number, that is to say,  $\alpha$  form is not strictly homologous. The inclination of the molecule seems to be related to the degree of rotational disorder by the following reason. In a highly ordered state, the tilt angle may have a certain value not equal to  $90^\circ$ , because the molecule itself is asymmetric about its axis. On the contrary, the molecule in a perfectly disordered state is symmetric on an average, and there is no reason for the molecule to incline in a particular direction. Therefore, the tilt angle will vary between the two extreme values according to the degree of order. If the ordering energy is roughly proportional to the length of the molecule the degree of order will also increase with molecular length. From this point of view, the tilt angle of  $\alpha$  form may depend on temperature as well as on molecular length.

Though the temperature range of observation was fairly narrow, lattice parameters of  $\alpha$  form varied appreciably with temperature. Fig. 7 contains oscillation photographs of heptadecanol taken at  $51^\circ$  and  $46^\circ\text{C}$ . The conditions other than temperature were the same, but these photographs gave values of monoclinic angle different by about  $40'$ . From several examples, it was known that the monoclinic angle gradually approaches to  $90^\circ$  with increasing temperature. Such an observation of the change in the lattice parameter was not made on octadecanol and on other members because of the difficulty in obtaining suitable single crystals. The change observed in the monoclinic angle of heptadecanol, however, is parallel with the expected change in tilt angle, and it seems to support the view of the variable tilt angle mentioned above.

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