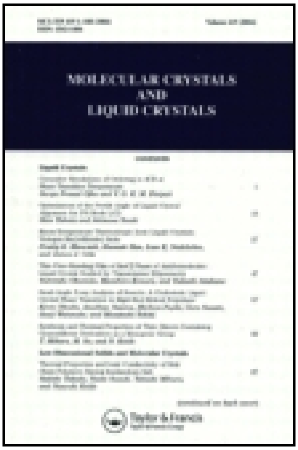

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Thermal, Optical, X-ray, Infrared and NMR Studies on the a-phase of Some Saturated Aliphatic Esters

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Thermal, Optical, X-ray, Infrared and NMR Studies on the α-phase of Some Saturated Aliphatic Esters

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Abstract—The paper reports the results of the investigations carried out from diverse aspects on the α-phase exhibited by ethyl, *n*-propyl and *n*-butyl stearates and mixtures of methyl stearate and palmitate, prior to their solidification into the crystalline β-phase. Optical examination reveals the formation of stepped drops and facetted drops, indicating a high degree of molecular order in the α-phase. From the features observed in X-ray diffraction, it emerges that the α-phase corresponds to the ordered smectic mesophase in which there is hexagonal cylindrical packing of the molecules in the smectic layers. Infrared absorption spectra also show that in the α-phase the zig-zag chains of molecules are fully extended. In the α-phase, the existence of rotational motions of the molecules is revealed both by infrared and proton magnetic resonance studies.

1. Introduction

Many long chain aliphatic compounds while solidifying from the liquid phase are known to undergo a first order transition into a translucent, soft, waxy mass before freezing down into a genuine crystalline solid. This intermediate structure is called the α-form in contradistinction to the more stable crystalline β-form. The condition of the α-form in certain alkyl esters is described by Malkin[1] as typical of the liquid crystalline state. Vold and Vold[2] have remarked that this form is probably identical with what Hermann[3] has called the ordered smectic state. In another paper, Vold and Vold,[4] while stating that the α-phase can be considered as belonging to Bernal and Crowfoot's[5] ordered smectic category of liquid crystals, express the doubt that it may be an anisotropic glassy modification of the solid. Zocher and Machado[6] have concluded from their observations on the solidification of paraffin that it solidifies from the melt in a smectic phase.

Bernal and Crowfoot,[5] from their studies on the various phases exhibited by liquid crystalline compounds, have classified the different phases lying intermediate between the crystalline solid and the liquid. They refer to the particular phase in which there is order within the planes of a smectic structure as " smectic solid: molecules in layers with structure ". They envisage also an effective hexagonal packing arising from the rotations of the molecules about their long axes which are normal to the smectic planes. Hermann,[3] in his classification of the X-ray Debye-Scherrer patterns observed with some cinnamates and benzoates in their different mesophases, describes for some cinnamates a phase for which the pattern consists of two prominent sharp rings. He identifies these rings with the long spacing and side spacing of a smectic structure in which there is hexagonal cylindrical packing of the molecules within the smectic planes (see also Brown and Shaw[7]). Such a structure is referred to as " ordered smectic " to distinguish it from the usual smectic structure which is known to give the diffraction pattern consisting of a long spacing ring and a halo. It is clear that the description given by Bernal and Crowfoot and by Hermann are essentially the same.

Studies from diverse aspects were undertaken to ascertain and understand the nature of the α-phase and in the following we present the results of our investigations on ethyl, n-propyl and n-butyl stearates and mixtures of methyl stearate and palmitate which exhibit the α-phase.

2. Thermal Behaviour

The transition points of the compounds were determined both from heating and cooling curves and by optical examination of the

TABLE 1 Thermal Data
(Temperatures in °C)

Compound	Observed values			Reported values and references		
	s.p.: α[a]	t.p.: $\alpha \rightarrow \beta$[b]	m.p.: β[a]	s.p.: α	t.p.: $\alpha \rightarrow \beta$	m.p.: β
Ethyl stearate $CH_3(CH_2)_{16}COOCH_2CH_3$	31.0	25.6	34.0	31.05[8]	27[8]	33.9[9]
n-Propyl stearate $CH_3(CH_2)_{16}COO(CH_2)_2CH_3$	28.6	22.0	30.3	28.9[9]	—	30–31[10]
n-Butyl stearate $CH_3(CH_2)_{16}COO(CH_2)_3CH_3$	26.1(α_1)	14.8($\alpha_1 \rightarrow \alpha_2$) 11.1($\alpha_2 \rightarrow \alpha_3$)	15.0($\alpha_3 \rightarrow \alpha_1$)	26.1[11](α_1)	13.8[11]($\alpha_1 \rightarrow \alpha_2$) 10.3[11]($\alpha_2 \rightarrow \alpha_3$)	—

[a] The values are from microscopic observations which are considered to be more accurate than those from cooling curves.

[b] The values are from cooling curves.

samples under a polarising microscope equipped with a conventional type of hot stage. For temperature measurements, a calibrated thermometer reading to 0.1 °C was used. For determining the heating and cooling curves, the experimental arrangement consisted of an evacuated double-walled glass vessel (containing the sample) immersed in a thermostatic bath at an appropriate temperature. The cooling (or heating) experiments were carried out over the range of the transitions in about 15 minutes. Table 1 summarizes the thermal data for the compounds studied. In order to keep Table 1 compact, only a few of the earlier reported values are included in it, although more data are available for ethyl stearate[10,12–18] and n-butyl stearate.[10,19,20] From these data as well as from gas-liquid chromatographic estimations, the purity of the substances was ascertained. It was found to be better than 99.7% for all the compounds except n-butyl stearate for which the purity exceeded only 99%.

The cooling curves obtained with all the samples exhibited definite arrests at temperatures corresponding to the liquid $\rightarrow \alpha$ and $\alpha \rightarrow \beta$ transitions. When the compounds were in the α-form they appeared translucent and on changing over to the β-form they turned white and opaque. The α-phase of ethyl and n-propyl stearates were found to be metastable in that they transformed to their β-forms (without cooling), in general, in the course of a few hours, the rapidity of this transformation being greater, the lower the temperature of the material in the α-phase. However, the α-phase of n-butyl stearate was found to be quite stable for several hours, even at the vicinity of the $\alpha \rightarrow \beta$ transition point as evidenced by microscopic and X-ray studies.

Although the setting points of α for all the compounds are in agreement with the earlier reported values, the $\alpha \rightarrow \beta$ transition points obtained by different workers for ethyl stearate show some disagreement. From cooling experiments with ethyl stearate which was allowed to age in the α-phase at different temperatures and for different intervals of time, Baker and Smyth[15] found that the value of the transition point is variable and uncertain. We have confirmed that n-propyl stearate also behaves similarly although it is relatively more stable. It appears that the rate of cooling also affects the value of the $\alpha \rightarrow \beta$ transition point.

Malkin[1] has stated that the α-forms of the stearate esters are apparently monotropic since their heating curves show only a single arrest. We could confirm by microscopic studies on the biaxial β-crystals of ethyl and *n*-propyl stearates that they melt without passing through any intermediate phase and that the melting point of β is greater than that of α.

It was reported by Dryden[11] and confirmed by us that *n*-butyl stearate shows three cooling arrests corresponding to the transitions: liquid $\rightarrow \alpha_1(\alpha) \rightarrow \alpha_2(\beta) \rightarrow \alpha_3(\beta')$ the α_2 and α_3 being crystalline solids. Although in the heating curve of solid *n*-butyl stearate (α_2) there could be distinguished only a single arrest at the melting point, optical, X-ray and infrared studies with it reveal that the $\alpha_1 \rightarrow \alpha_2$ transition is reversible.

The presence of homologous impurities are known to increase the stability of the α-state. In particular, the α-phase is induced in methyl stearate by the addition of methyl palmitate, although such a phase is absent in both the pure compounds.[18] It was found that the α-phase in these mixtures is metastable and changes monotropically into the β-phase. A study of the mixtures for compositions varying in steps of 5% by weight was carried out and Fig. 1 shows a plot of the liquid $\rightarrow \alpha$ and $\alpha \rightarrow \beta$ transition points versus the percentage composition. For low impurity contents it was not possible to distinguish from cooling curves the two transition points, owing to their being too close to each other. However, that the α-phase is exhibited by mixtures at percentages as low as 10%, was detected from microscopic examination of the samples.

3. Optical Studies

Although the appearance of the α-form as distinct from the β-form is evident from a macroscopic examination of the solidifying liquids, a number of characteristic features of the α-form are brought out by an examination of the textures under a polarizing microscope equipped with a hot stage. A thin liquid

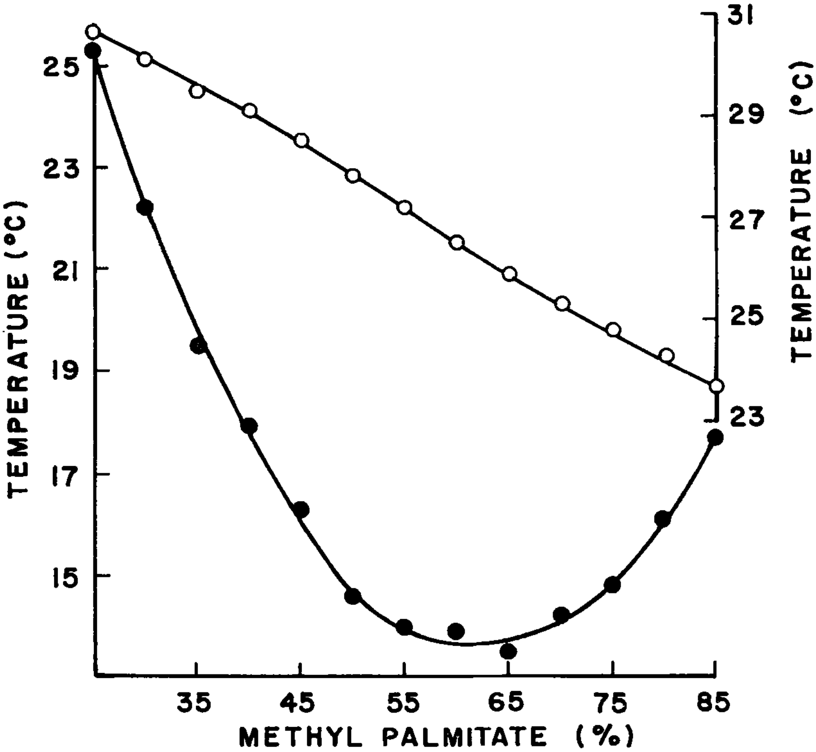

Figure 1. Plot of the transition points versus weight percentage of methyl palmitate in mixtures of methyl stearate and palmitate. Open circles: liquid→α (Temperature scale is on the right side); solid circles: α→β (Temperature scale is on the left side).

film of the material was used between a slide and a cover slip for observing the textures which developed on cooling the liquid slowly at a rate of 0.1 °C per minute or less. When it was required to observe the gradual growth of the texture, it was necessary to control the temperature of the sample to be almost stationary at the setting point of α, as otherwise the textures developed abruptly on crossing the setting point. A slow rate of cooling was adopted to obtain large non-overlapping homogeneous areas for critical examination. It may be mentioned that with a faster rate of cooling the homogeneous areas were small owing to the instantaneous development of minute overlapping α-textures at numerous points. Although it was possible to recognize them as the same characteristic α-textures, they presented a distorted appearance due to their overlap. With both slow and fast cooling the textures which developed at the setting point of α remained unchanged till the onset of α → β transition.

The texture at the onset of α-phase as seen between partially crossed polars consisted of plates with smoothly curved edges lying flat on the supporting surface (Fig. 2). The plates which showed extinction between crossed polars and were apparently isotropic, correspond to the well-known homoeotropic plates in which the long-chain molecules are packed with their long axes perpendicular to the surface. With a high power objective the uniaxial cross could be clearly observed in regions where only homoeotropic plates were present. Using a full-wave retardation plate the optical sign was confirmed to be positive. The homoeotropic plates could be viewed at a small angle to their uniaxial direction by tilting the slide by about 15°. Between crossed polars, the plates now exhibited birefringence, but no colours.

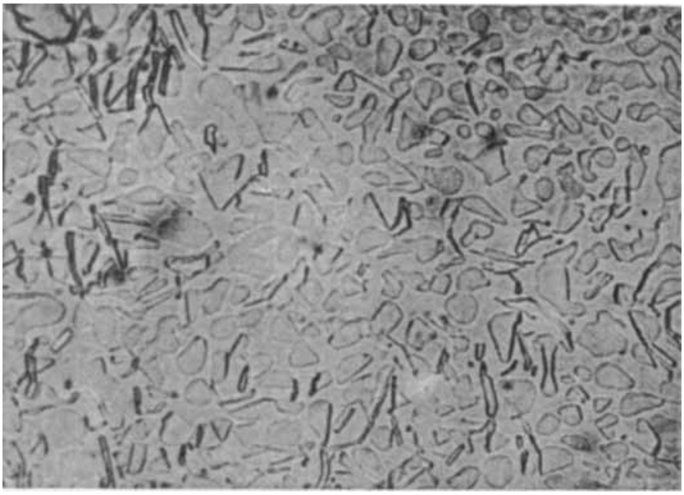

Figure 2. Homoeotropic plates observed with *n*-butyl stearate. Partially crossed polarizers. 310 ×.

However, with also a unit retardation plate between the crossed polars (at 45° to the extinction directions), rotation of the stage revealed changes in the interference colours over the areas of the plates. Such colour changes were not observed in the regions of air-bubbles or liquid. These facts indicate that the plates are several layers thick.

The homoeotropic plates, as observed between partially crossed polars, were seen to grow with time and coalesce with each other. Using a high power objective to get an overall magnification of about 1000, it was found that the plates merged with each other without sharp demarcation lines, except when there took place an upcurving at the meeting edges of the coalescing plates. This upcurving was shown up by the birefringence developed at the meeting edges. It may be mentioned that whenever plates coalesced together without sharp demarcation lines, the existence of weak birefringence at the meeting edges could be confirmed. A full wave plate used between crossed polars served to reveal the slightly different shades of colour at the meeting boundaries, as compared to the uniform colour over the rest of the area of the plates. Only when there occurred over a sufficient area at the coalescing edges, either the upcurving of the edge or a slight deformation or tilt of the surface, was it possible to detect the change in order at the meeting edges.

Almost simultaneously with the appearance of the homoeotropic plates there occurred the growth of birefringent needles which could be observed between crossed (or partially crossed) polars (Fig. 3). A displacement of the cover slip produced curvature of the needles and changed the pattern formed by them, indicating that the needles are flexible. The needles were extinct between crossed polars when their length was along the vibration direction of the polarizer or analyzer. It was confirmed by the use of a quartz wedge that the fast and slow directions of the needles were respectively along the length and breadth of the needles. In other words, the molecules are arranged with their long axes transverse to the length of the needles. The birefringent needles can be seen when the homoeotropic plates present an end on view;

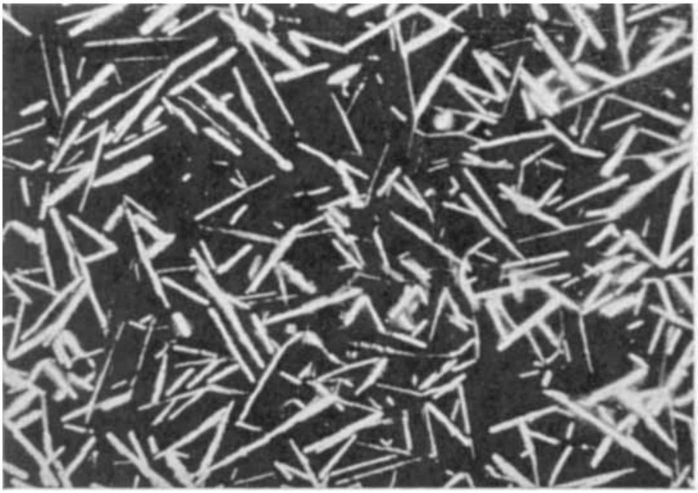

Figure 3. Birefringent needles observed in a mixture of methyl stearate and palmitate (3 : 1). Crossed polarizers. 675 ×.

Figure 4. Polygonal patterns of rolled up borders appearing as birefringent needles in *n*-butyl stearate. Crossed polarizers. 140 ×.

they can also be seen when a rolling up of the borders of homoeotropic plates takes place, as pointed out by Zocher and Machado.[6] Sometimes the needles were observed broad and twisted as in Fig. 5, wherein an end-on view of irregularly twisted homoeotropic plates (now lying vertical to the glass slide) is presented. Sometimes the rolling up of the borders of the homoeotropic plates could be observed and these presented the appearance of needles (Fig. 4). Vorländer and Selke[10] have also described some textures exhibited by the stearates.

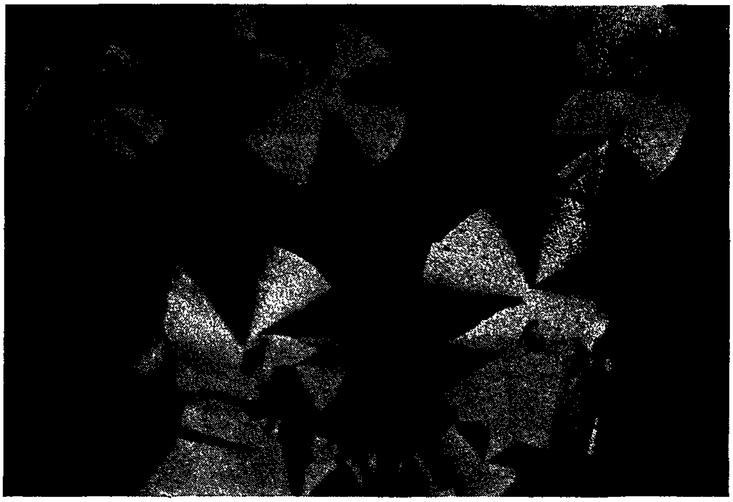

Figure 5. End-on view of twisted homoeotropic plates of *n*-propyl stearate. Crossed polarizers. 635 × .

Figure 6 reproduces a texture similar to that of " oily streaks " observed with liquid crystals of soaps by Rosevear.[21] The oily streaks are formed in the " wake " of air bubbles present in the medium and here again, the molecules are found to be arranged perpendicular to the length of the streaks. It may be remarked that all the textures illustrated here represent the appearance of the homoeotropic plates from different angles and are typical of the compounds and mixtures studied here.

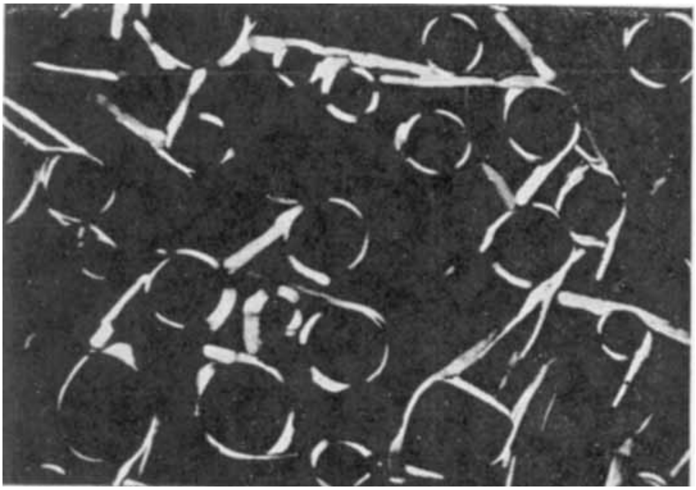

Figure 6. Oily streaks observed with ethyl stearate. Crossed polarizers. 360 × .

Often the homoeotropic plates pile up one above another to form Grandjean terraces, giving rise to the well-known smectic stepped drops—gouttes à gradins (Fig. 7). The contours of steps exhibited by homoeotropic plates in the case of *n*-propyl and *n*-butyl stearates are characteristic of their α-growth process (Fig. 8). Topographs obtained with some open drops (not touching the cover slip) were seen to have plane faces and sharp-meeting edges. A photograph of an open drop as observed in two-beam interference is reproduced in Fig. 9 illustrating this feature. Such facetted drops have been reported by Bernal and Crowfoot[5] for the ordered smectic mesophase of some substances. It was pointed out also by Chandrasekhar[22] that drops with plane faces and possibly sharp edges and corners may be observed when there is translational order in a mesophase. The facts described above from optical studies suggest for the α-phase a high degree of molecular order as in the ordered smectic phase. The absence of focal-conic texture also points to the fact that this phase is distinct from the usual smectic phase. It is surprising however, that these materials do not exhibit any other mesophase between the α-phase and the liquid phase.

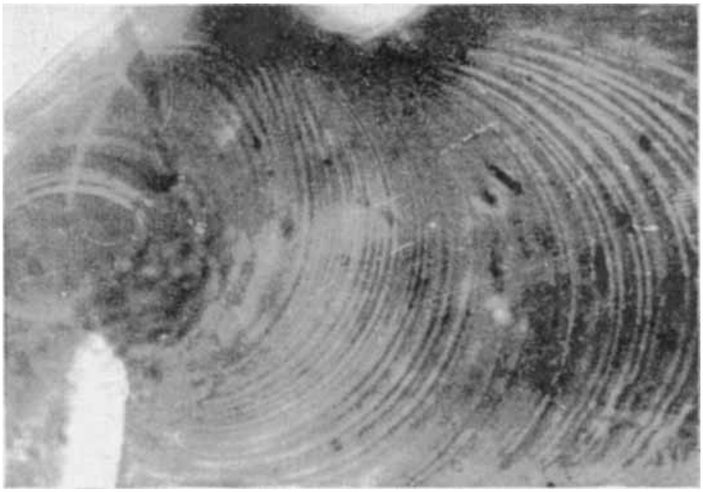

Figure 7. Stepped drop observed with n-propyl stearate. Partially crossed polarizers. Oblique illumination. 1880 ×.

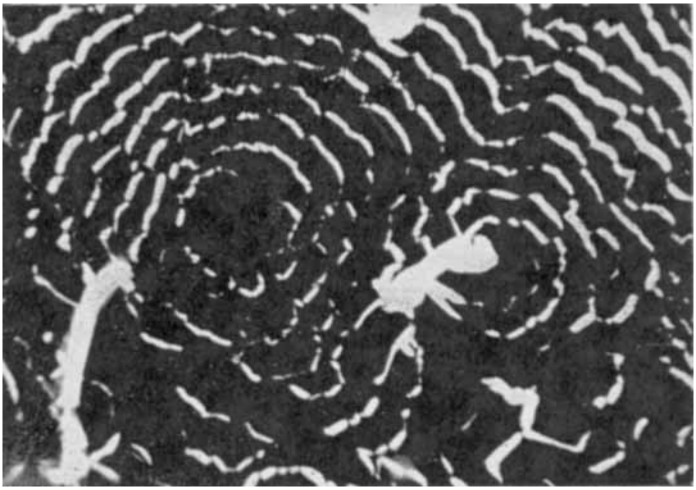

Figure 8. Contours of steps observed with n-propyl stearate. Crossed polarizers. Oblique illumination. 650 ×.

Figure 9. Topograph of a facetted drop of n-butyl stearate observed in two beam interference. 650 ×.

It may be mentioned here that throughout the existence of the α-phase the cover slip over the specimen could be displaced, whereas with the onset of the β-phase the cover slip got rigidly attached. The onset of the β-phase in ethyl and n-propyl stearates was marked by the growth of parallelogram-shaped, biaxial β-crystals at the expense of the material in the α-phase (Fig. 10). With large β crystals their biaxial nature could be confirmed from the isogyres seen between crossed polars. In the case of n-butyl stearate it was not possible to observe any striking change in the α_1-texture or its optical behaviour after the onset of the α_2-phase, *except* for the appearance of a weak birefringence over the originally extinct homoeotropic areas. These areas presented the appearance of a polycrystalline texture. For two mutually perpendicular orientations of any single crystalline grain, extinction was observed between crossed polars. On heating the specimen, this birefringence disappeared at about the same temperature at which it set in. However, the birefringence at the needles remained unchanged. The absence of any striking

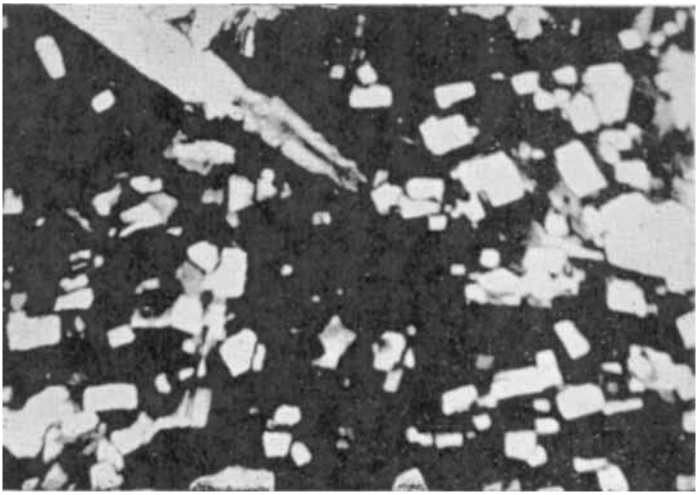

Figure 10. Crystalline texture in the β-phase of ethyl stearate. Crossed polarizers. 300 ×.

change in texture due to the $\alpha_1 \rightarrow \alpha_2$ transformation may be related to the molecular order as shall be discussed in the following section.

4. X-ray Studies

The X-ray diffraction studies made earlier by Malkin,[1,23] Dryden[11] and Lutton and Hugenberg[18] with the different compounds give information regarding the molecular arrangement in the α-phase. However, for the sake of completeness we have reinvestigated the X-ray diffraction by these substances and have obtained data regarding the side spacings in the case of ethyl and *n*-propyl stearates. Also the studies show that the $\alpha_1 \rightarrow \alpha_2$ transition in the case of *n*-butyl stearate is reversible (and not monotropic as hitherto believed).

The diffraction photographs were obtained using a thin film of the sample on a loop of platinum wire which was nearly normal to the X-ray beam. For controlling the temperature of the sample the loop was attached to an aluminium rod in contact

Table 2 X-ray Data

Compound	Short spacings (Å)				Long spacings (Å)			
	Observed		Reported		Observed		Reported	
	α	β	α	β	α	β	α	β
Ethyl stearate	4.15	3.77 4.19	—	3.69[28] 4.08[28]	28.8	25.7	28.6[1]	25.5[1]
n-Propyl stearate	4.13	3.78 4.14	—	—	30.2	26.5	30.1[1]	26.2[1]
n-Butyl stearate	4.10(α_1)	3.71(α_2) 4.20(α_2)	4.10[11](α_1)	3.84[11](α_2) 4.25[11](α_2)	31.6(α_1)	31.6(α_2)	31.7[11](α_1)	31.7[11](α_2)
Methyl stearate + Methyl palmitate (by weight 1 : 1)	4.05 4.03	3.66	—	—	25.7	23.2‡	—	—

‡ Mean values calculated from the rings which appear as close doublets.

Note: The diffraction photographs in the α-phase were obtained with freshly formed samples. To preclude any spurious effects due to the onset of β, a short exposure was given and the sample was melted *in situ*. It was recooled to the original temperature to form the α and the exposure was continued. This procedure was repeated several times.

with a thermostatic bath and a thermocouple was employed to measure the temperature of the specimen. The samples were taken in the form of a liquid film on the loop and cooled to the required phase. The photographs were recorded on flat film for at least two different sample-to-film distances and unfiltered copper radiation was used. Table 2 gives the observed spacings in the different cases.

The diffraction photographs in the α-phase are characterized by a single, sharp intense ring identifiable with the side spacing of the molecular arrangement. Besides, at low angles there appear weaker rings of different orders, the long spacing here corresponding to the length of the molecules (Fig. 11). The low angle rings are weak because of the preferential orientation of homoeotropic plates (see for example Gray[24]). The diffraction pattern of the α-phase clearly corresponds to that of the ordered smectic structure with hexagonal cylindrical packing of the molecules, described in the introductory section. The explanation, that the hexagonal symmetry is due to the rotational motion of the lath shaped molecules about their long axes, was proposed by Müller[25] and

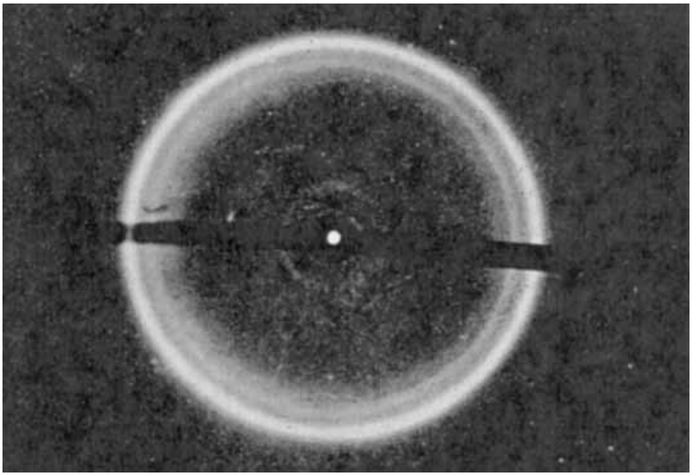

Figure 11. X-ray diffraction in the α-phase of n-propyl stearate. 24 °C.

Bernal[26] to account for the results in the case of a number of long chain compounds. Confirmatory evidence for such motions is available from the proton magnetic resonance studies on several long chain compounds by Andrew.[27]

In the β-phase the photographs exhibit two rings corresponding to the side spacings as also weaker rings at low angles (Fig. 12).

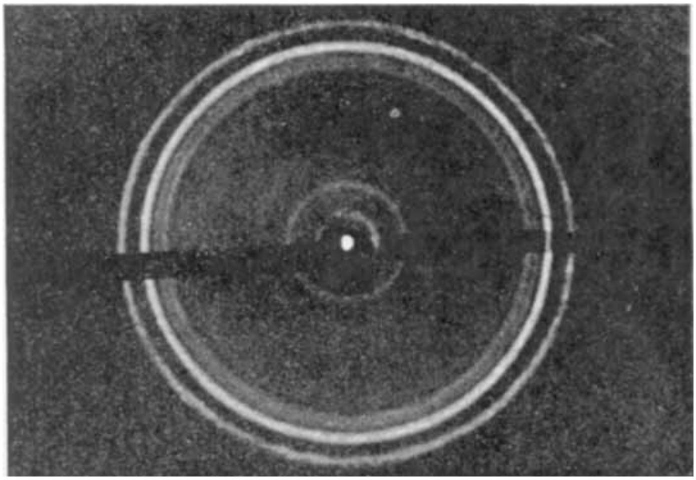

Figure 12. X-ray diffraction in the β-phase of n-propyl stearate. 18 °C.

For ethyl and n-propyl stearates the long spacing in the β-phase is less than that for the corresponding rings in the α-phase. This feature is explained as due to the formation of a tilted structure in which the molecules, although parallel to one another, are inclined to the normal to the layers. On the other hand, in the case of n-butyl stearate, the long spacings of α_1 and α_2 forms are the same showing that there is no such tilting. Data are not available regarding the symmetry to which the α_2-form of n-butyl stearate belongs. However, the observation of two side spacings in the α_2-phase excludes the possibility of a hexagonal packing of the molecules. Many long chain paraffins are known to have an orthorhombic or monoclinic layered structure.[4] The monoclinic form may be excluded here since this form is known to consist of tilted chains as in ethyl stearate[28] which is monoclinic. Probably the tilted structure of *n*-propyl stearate also belongs to this system. If the α_2-form of *n*-butyl stearate corresponds to an orthorhombic layered structure the transformation from α_1 to α_2 can occur by a small change in the distance between the chains as in some *n*-paraffins.[25] The absence of any striking change in the α_1-texture of *n*-butyl stearate on passing to the α_2 form is hence understandable, as this type of transformation does not require any drastic molecular reorientation as in ethyl and *n*-propyl stearates. For such an orthorhombic structure the long axes of the molecules correspond to the acute bisectrix. The birefringence is seen in the α_2-phase (at the originally homoeotropic areas of α_1-vide Section 4) because, now for these areas the direction of observation coincides with the acute bisectrix.

It is found by heating the α_2-form to temperatures above the $\alpha_1 \rightarrow \alpha_2$ transition point, that the diffraction pattern consists of only one side spacing ring and the long spacing rings corresponding to the α_1-phase (Fig. 13). Hence the $\alpha_1 \rightarrow \alpha_2$ transition is reversible.

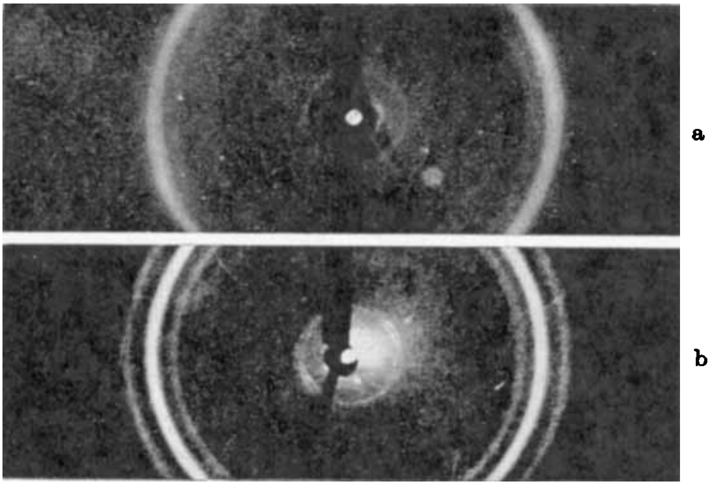

Figure 13. (a) X-ray diffraction in the α_1-phase obtained by heating the α_2-phase of *n*-butyl stearate. 18 °C. (b) X-ray diffraction in the α_2-phase of *n*-butyl stearate. 12 °C.

5. The Infrared Absorption Spectra

The infrared absorption by ethyl stearate in its different phases was reported and briefly discussed earlier by Chapman.[29] No infrared studies appear to have been made on the α-phase of the other compounds under discussion. The infrared absorption spectra were determined for the liquid, α and β-phases of all the compounds; however, since we are mainly concerned with the α-phase, we shall discuss in the following only the salient spectral characteristics of the α-phase. A detailed discussion of the band assignments for the various spectra will be reported elsewhere.

The spectra were recorded with a Perkin-Elmer 137 Infracord spectrophotometer. Thin films of the samples sandwiched between KBr plates were used. As the different phases occur close to the room temperature, by suitable heating or cooling of the cell and by a visual examination of the texture of the sample, it was possible to record the spectra in the different phases. The cooling was done slowly to get large homogeneous areas, so that scattering could be reduced. The temperatures at which the spectra were recorded were not measured when the sample was in the infrared beam, because the beam heated the sample. But, the temperature to which the sample was cooled, was checked before the commencement of the recording. Care was taken to see that the records were obtained without the melting of any portion of the sample. The reproducibility of the character of the spectrum in every case was also checked by repeated runs for short periods with freshly prepared samples.

The compounds studied have the structural formula,

$$CH_3(CH_2)_nCOO(CH_2)_mCH_3,$$

and each molecule consists predominantly of a chain of methylene groups [—$(CH_2)_n$—], with other groups at either end. The crystal structure determinations for some of these and analogous compounds have conclusively shown that in the crystalline β-phase the carbon skeleton of the main chain has an extended, planar, zig-zag geometry.[28,30,31] The C—C and C—H bonds of the main chain are expected to be tetrahedrally arranged so that the CH_2 groups of the chain form an all-trans configuration. As a consequence of this structure of the polymethylene chains, specific dipolar interactions between the various CH_2 groups are expected to set in. Associated with each CH_2 group of the chain there are a set of symmetry modes (e.g., rocking, twisting, wagging, etc.) corresponding to each one of which there should arise a progression of maxima owing to the intermethylene interactions.

Such progressions of absorption maxima have been observed in the spectra of many long chain crystalline compounds[32–34] in the rocking-twisting, twisting-rocking and wagging regions, viz., 9.43–13.89, 7.63–8.55 and 7.07–8.55 μ respectively. In fact, the infrared absorption spectra, in the crystalline phase of all the compounds studied by us, exhibit the rocking-twisting and wagging progressions in the respective regions (see e.g., Fig. 14). It is presumed here that as in fatty acids[32] the twisting-rocking progression is masked by the stronger absorption maxima of the wagging progression. In the liquid phase, on account of the possible rotations around the C—C bonds, the molecules can acquire numerous conformations and hence the interactions

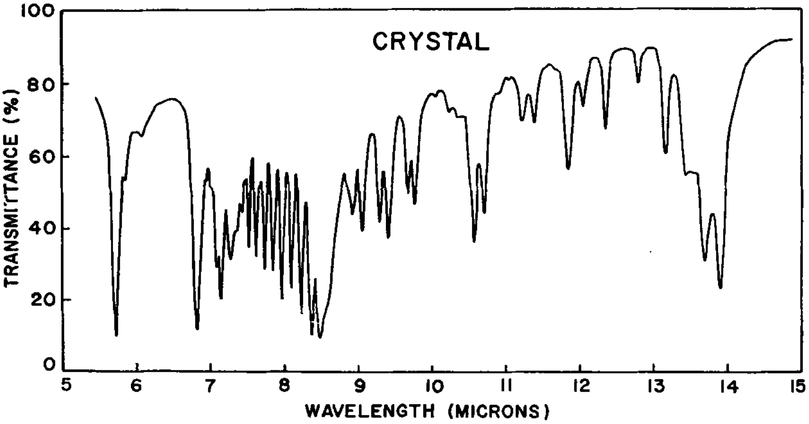

Figure 14. Infrared absorption spectrum of n-butyl stearate in the α_2-phase.

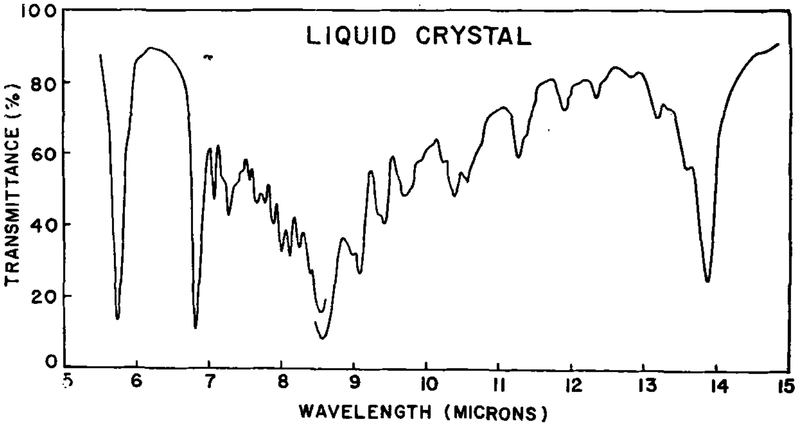

Figure 15. Infrared absorption spectrum of *n*-butyl stearate in the α_1-phase.

between the methylenes of the chain become indefinite and the progressions of maxima are no longer observable (Fig. 16). A study of the development of these maxima in the α-phase indicates the degree of rotation and flexing present in the molecule. In the α-phase the progressions of maxima are present but are somewhat less pronounced than in the β-phase (Fig. 15). In fact, the maxima

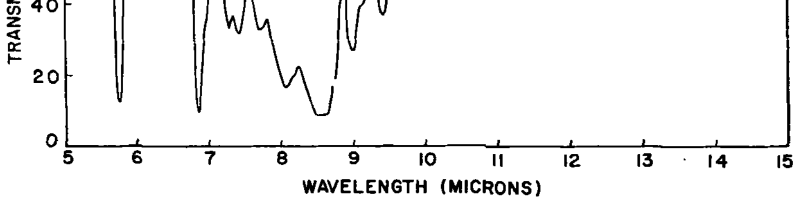

Figure 16. Infrared absorption spectrum of *n*-butyl stearate in the liquid phase.

of the progressions are found to be better developed at lower temperatures of the α-phase. It is clear that in the β-phase and the α-phase the polymethylene chain of the molecule has an extended zig-zag conformation. The greater flexibility of the chains in the α-phase is probably responsible for the less pronounced character of the progressions in this phase. The appearance of X-ray diffraction rings at low angles corresponding to the long spacing of the molecules, is in agreement with the picture of the extended chains in the structure.

It may be pointed out here that the intense rocking-twisting band near 14μ in the liquid phase appears at the same position as in the α-phase as a single peak, whereas in the crystalline phase it has split into a doublet. This splitting arises due to intermolecular coupling in the crystal. The absence of splitting in the α-phase indicates that there are no enduring intermolecular interactions and this is in agreement with the view that in the α-phase the molecules are executing rotational motions about their long axes. The absence of splitting of the 14μ band in the α-phase served as a criterion for checking that the β-phase had not set in. With the aid of this criterion it was confirmed that the α_2-phase of *n*-butyl stearate passes over into the α_1-phase on heating, as remarked in Section 4.

The spectra obtained with mixtures of methyl stearate and palmitate also show similar features. In fact, in an earlier paper[35] we have reported the infrared absorption of a sample of methyl stearate which exhibited the α-phase. It is now confirmed that the sample contained homologous impurities; however, our conclusions regarding the differences observed in the spectra for different phases remain unaltered.

6. Proton Magnetic Resonance

In order to explain the appearance of only a single side-spacing diffraction ring in the α-phase, it was stated in Section 4 that the molecules are performing rotational motions about their long axes. It is well established that molecular motions strikingly influence the width of the proton resonance signal.[27] Wide-line proton magnetic resonance studies undertaken by us confirm the existence of molecular motions in the α-phase. Such studies have been reported earlier for ethyl stearate by Grant and Williams.[36]

The wide-line proton resonance curves were recorded using a Varian Associates spectrometer. The frequency of the R. F. oscillator was kept constant at 15.0 Mc/s (in some cases 7.5 Mc/s) and the magnetic field was varied across the resonance value. The temperature variation and control was accomplished using a Varian heat exchanger unit. About 2 ml of sample was used for investigation.

A few derivative curves for *n*-propyl stearate are reproduced in Fig. 17. The signal for the liquid phase is extremely sharp and for the solid phase, at low temperatures, it is quite broad, as is to be expected. When the molten sample was slowly cooled to the α-phase, the signal showed a broad component overlapping a strong sharp component, as shown in Fig. 17(b). The recordings for the α-phase were made within a few minutes to preclude any spurious effects due to the onset of the β-phase. It may be mentioned that the broad component for the sample in the

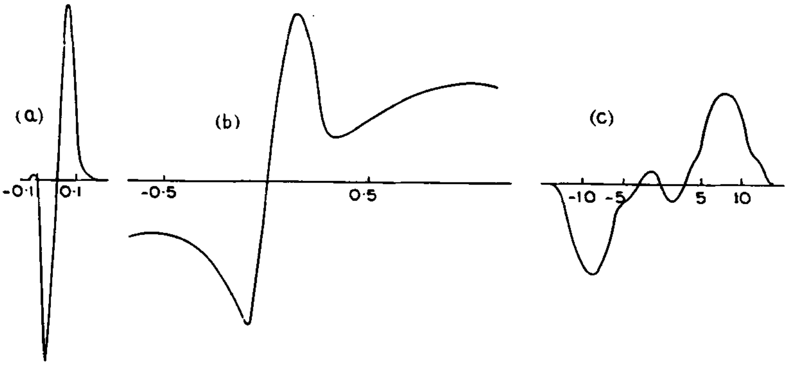

Figure 17. Derivative curves of proton magnetic resonance absorption observed with *n*-propyl stearate. (a) liquid (40 °C); (b) α-phase (26 °C); (c) solid (– 50 °C). Values shown along *x*-axis are in gauss. Value of R.F. was 15 Mc/s.

α-phase was not recorded right up to the base line because the scanning rate was too slow.

The second moments of the curves for the solid samples were calculated in the usual way using Simpson's method of numerical integration. The second moment data are given in Table 3. For ethyl stearate these have been given earlier by Grant and Williams[36] for various temperatures. They have calculated the theoretical rigid lattice second moment for ethyl stearate to be about 27.5 gauss^2 and for all the compounds studied here, this is about the value to be expected. However, the studies of Grant and Williams as well as the present study clearly show that, with increasing temperature, the experimental second moment becomes progressively smaller than the theoretical rigid-lattice value.

TABLE 3. Proton Magnetic Resonance Data

Compound	Temperature °C	Phase	Experimental second moment (gauss^2)
Ethyl stearate	− 77	β	25.8[a]
	0	β	24.3[a]
	24	β	21.0[a]
	28	α	6.6[a]
n-Propyl stearate	− 50	β	27.8
	0	β	21.8
	15	β	18.0
n-Butyl stearate	0	α_3	20.1
Methyl stearate (35% by weight) + Methyl palmitate (65% by weight)	15	β	17.2

[a] Data of Grant and Williams.[36]

It has been recognized, in the case of many long chain compounds, that the contour of the derivative curve at very low temperatures (corresponding to the rigid lattice) is broad, with no evident fine structure; with increasing temperature there develops a fine structure which becomes more pronounced as the melting point is approached.[27] This behavior is shown up as a pair of sharp positive and negative peaks at the centre of the derivative curve, indicating thereby the presence of a sharp resonance peak at the centre of the absorption line profile. In the case of *n*-paraffins, Andrew[27] has explained the central peak as possibly arising due to the methyl end groups. The equilateral triangular assemblage of protons of a CH_3 group gives rise to a resonance spectrum containing a central component. In a rigid lattice, inter and intramolecular proton interactions cause a large broadening of the absorption and hence the central component is considered to become indistinct. However, when the molecules rotate or oscillate with large amplitudes, the broadening due to neighbours considerably diminishes and the central component is resolved. Further, the intensity of the central component becomes slightly enhanced when the CH_3 group rotates.

The above explanation for the observation of a separate central maximum can be extended also to the case of esters, where the molecules have at one end an ester group and at the other a CH_3 group. Malkin[1] has shown that at ordinary temperatures the ether-oxygen linkage in the molecules is flexible, so that a facile rotation of the ester group is possible. Therefore, in the α-phase of the esters, the two terminal groups can rotate independently of the polymethylene—$(CH_2)_n$— chain. The molecule as a whole also can rotate about the chain axis, about which the moment of inertia is small. As mentioned in Section 5, there is to be expected a slight overall flexibility of the chain. Besides, there is the possibility of molecular motion in lattice defects.[37] As a consequence of these different motions, the resonance line width generally narrows very much and the central component due to the terminal groups becomes well-resolved. As may be observed from Fig. 17(b), the fine structure on the derivative curve for the α-form of *n*-propyl stearate is almost liquid-like in sharpness and width, and is resolved from the broad component. With *n*-butyl stearate, in the α_1-phase only a sharp liquid-like signal was observed, the broad component being presumably too weak. An analogous situation has been reported by Andrew[27] for anthracene at 184 °K where the line-width narrows to liquid-like value. It has been explained that the broad component is probably too weak to be detected and has wide extensions on either side.

The fine structure referred to above is not visible in the rigid-lattice resonance line of *n*-propyl stearate at − 50 °C. It may be mentioned that at 15 °C also no fine structure peaks were evident. However, with *n*-butyl stearate the signal revealed the fine structure at 0 °C. The α and β-forms of the mixture of methyl stearate and palmitate behaved similar to *n*-propyl stearate except that the β-form of the mixture showed the fine structure at 15 °C.

For the α and β forms of ethyl stearate, Grant and Williams[36] report fine structure of the type discussed above. Whereas they explain the sharp component observed in the β-phase as due to molecular motion in lattice defects, they attribute a similar sharp component in the α-form to the existence of liquid-like zones of disorder in the medium. The liquid-like zones are said to gradually become part of an ordered structure where molecular motion is more restricted. They arrive at this conclusion because, in their measurements of the spin-lattice relaxation time for the α-phase by the pulse technique, they found that at 28 °C the first pulse decay decreased in intensity to half the initial value after 30 minutes and to a quarter after 50 minutes. They report that there was no change in the appearance of the sample and that the sample was definitely in the α-phase. However, we find that a sample of molten ethyl stearate when kept at 28 °C immediately forms the α-form, which on microscopic examination reveals the growth of a few β-crystals within 15 minutes. The size of the β-crystals and their number increase with efflux of time. They have a melting point higher than that of the α-form, as usual. Evidently, there are no liquid-like zones in the medium which slowly transform to the α-structure, but it is the α which slowly changes over to the β. However, the studies of Grant and Williams, also confirm the existence of rotational motions of the molecules in the α-state.

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