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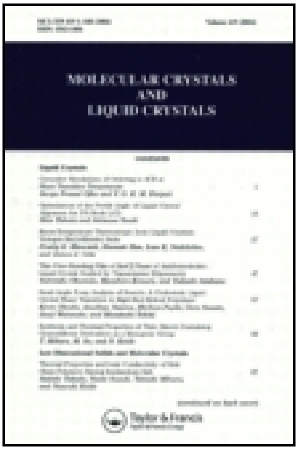

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Structures of the Chiral Smectic C Phase with Selective Reflection in the Wavelength Range of Visible Light. I. Interlayer Distances and Helical Pitches of the (+)-4-n-Alkyloxyphenyl 4-(2″-Methylbutyl)-biphenyl 4′-Carboxylates Series

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Structures of the Chiral Smectic C Phase with Selective Reflection in the Wavelength Range of Visible Light. I. Interlayer Distances and Helical Pitches of the (+)-4-n-Alkyloxyphenyl 4-(2″-Methylbutyl)-biphenyl 4′-Carboxylates Series.†

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Interlayer distances and helical pitches were studied as functions of temperature by X-ray diffraction and transmission spectral measurements for chiral smectic C phases of (+)-4-n-alkyloxyphenyl 4-(2″-methylbutyl)biphenyl 4′-carboxylates, which had selective reflection in the wavelength range of visible light. The relationship between the interlayer distances and the length of the paraffinic chain gives some information about the structure within the layers: the molecular tilt angle (with respect to the normal to the layer plane) is 45-48° and the paraffinic chains form double layers. Interlayer structures and interactions are discussed, in the light of the interlayer distances and the helical pitches.

INTRODUCTION

Recently, various types of smectic phases have been distinguished and characterized at the molecular level.[1] One of them, the chiral smectic C (Sm C*) phase has received considerable attention, since

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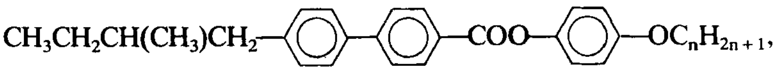
its prediction and discovery in 1970.[2] Bulk properties such as ferroelectricity[3] and characteristic optical properties[4-9] have been investigated, but little information has, however, been obtained about the structure itself.

The (+)-4-n-alkyloxyphenyl 4-(2″-methylbutyl)biphenyl 4′-carboxylates,



form Sm C* phases with selective reflection in the wavelength range of visible light,[10] in contrast to many other Sm C* liquid crystals. One of the members (n = 6) was used for verification of the characteristic features of selective reflection of the Sm C* phase, [7-9] which had been predicted by computer simulation.[6] The molecular tilt angle was estimated to be ~45°. In order to elucidate the precise structures of the Sm C* phases of these compounds, interlayer distances, d, were measured as functions of temperature by X-ray diffraction studies for the n = 6,7,8,9,10,12,14 and 16 compounds. These data give information about the structures within the layers, including indication of tilt angles. In addition, the wavelengths of the selective reflection peaks, λ, of planar textures were obtained from transmission spectral measurements for the even members. The pitch lengths, p, were obtained from the relationship, $\lambda = \bar{n}p$, where $\bar{n}$ is the mean refractive index. The mode of stacking of the layers and interlayer interactions are discussed in terms of d and λ.

EXPERIMENTAL

Materials

All the members were synthesized from commercially available (+)-4-(2″-methylbutyl)-4′-cyanobiphenyl (BDH Chemicals Ltd.) after Gray and McDonnell.[10] 4-Alkoxyphenols were synthesized from hydroquinone and 1-bromoalkanes (Tokyo Kasei K. K.).[11] The 1-Bromoalkanes were used without further purification in the case of an assay > 98%, or after purification by reduced distillation in the case of an assay ≤ 98%. For the members n = 6-10, Sm C*-cholesteric and cholesteric-isotropic liquid transition temperatures were in good agreement with reported values,[10] however, melting points (solid-Sm C*) did not always agree, probably because of polymorphism in the solid states. DSC peaks were sufficiently sharp. The esters n ≥ 14 formed gels with solvents such as alcohols and hexane. However, a

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solid precipitate, although less crystalline, could be obtained from ethanol solution by slow cooling with rapid stirring. Purification was carried out by repeating this procedure until constant transition temperatures were obtained.

Methods

Transition temperatures were measured both with a microscope equipped with a heating stage and by DSC (Seiko Model 580).

X-ray diffraction patterns were obtained using a Rigaku Geigerflex 2001 diffractometer with Cu Kα radiation. Samples were supported on a conventional sample holder with a controlled heater, without any treatment for molecular alignment. The d-values of *trans*-9-octadecenoic acid[12] were used for calibration. Temperature was controlled within ± 0.1 K.

Transmission spectra were measured with a Hitachi 340 spectrophotometer. A sample was sandwiched between a cover glass and a CaF_2 plate. The latter was used to reduce the temperature gradient minimum. The thermal conductivity of CaF_2 is ten times larger than that of glass.[13] Surfaces of the plate and the cover glass were treated with a $CHCl_3$ solution of hexadecyl trimethyl ammonium bromide. Temperature was controlled within ± 0.1 K.

RESULTS AND DISCUSSION

All the members have cholesteric and solid phases above and below the Sm C* phase respectively. The structure of the solid precipitated from solution and that obtained by cooling the Sm C* phase differ from each other, as is often found for mesogenic or long-chain compounds. The X-ray diffraction patterns of the solids obtained from solution show individual characteristics depending on the n-values, but the solid obtained from the Sm C* phases exhibit common features. They have layered structures with a common packing pattern in the layer, as indicated by the presence of the same short spacings of 4.7 and 4.3 Å.

Figures 1 and 2 show the temperature dependence of the interlayer distances, d. The higher temperature limit is the Sm C*-cholesteric transition point (T_{tr}) and the lower one is the solid (from Sm C*)-Sm C* transition point (T_m). The d-values increase linearly with temperature rise in all cases. It appears that the slope, $\Delta d/\Delta T$, increases as n increases. The linear expansion coefficient of the layer thickness, $\Delta d/d\Delta T$, also increases with n, as shown in Figure 3. The values are

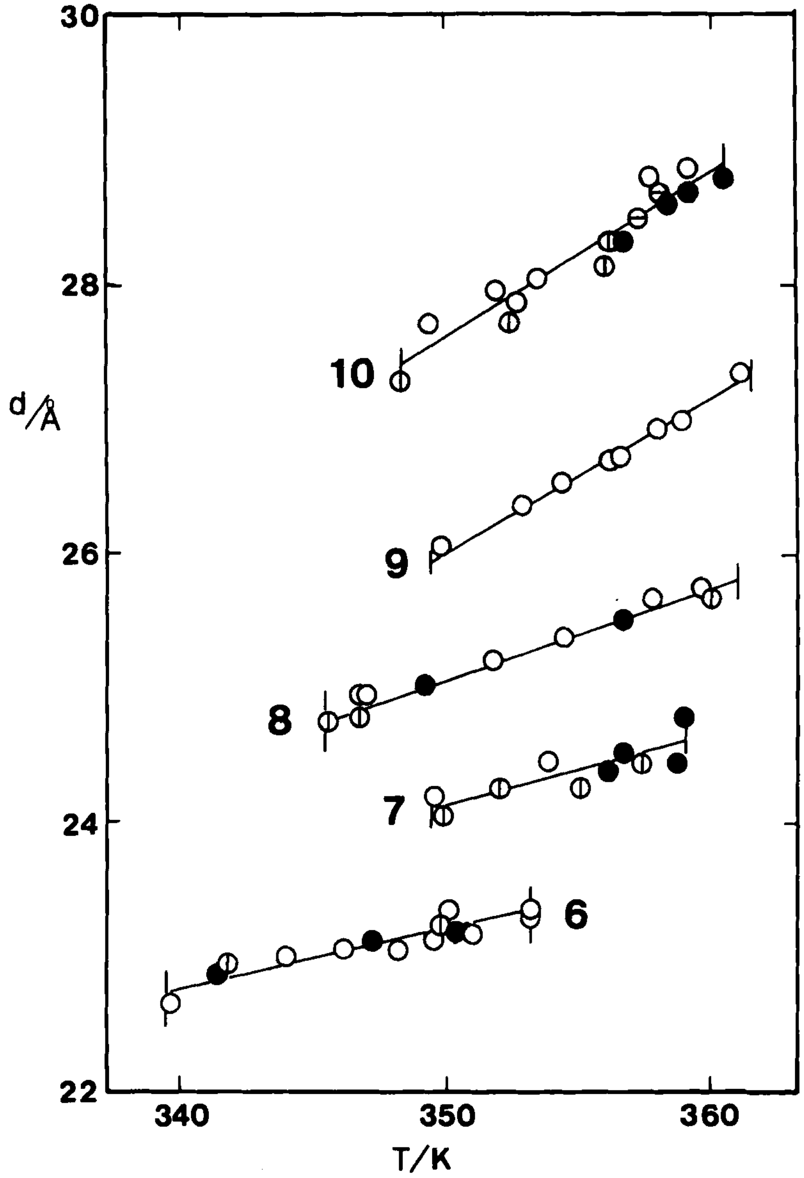

FIGURE 1 Temperature dependence of *d* for the $n = 6-10$ compounds. Different symbols are used for different runs (also in Figure 2).

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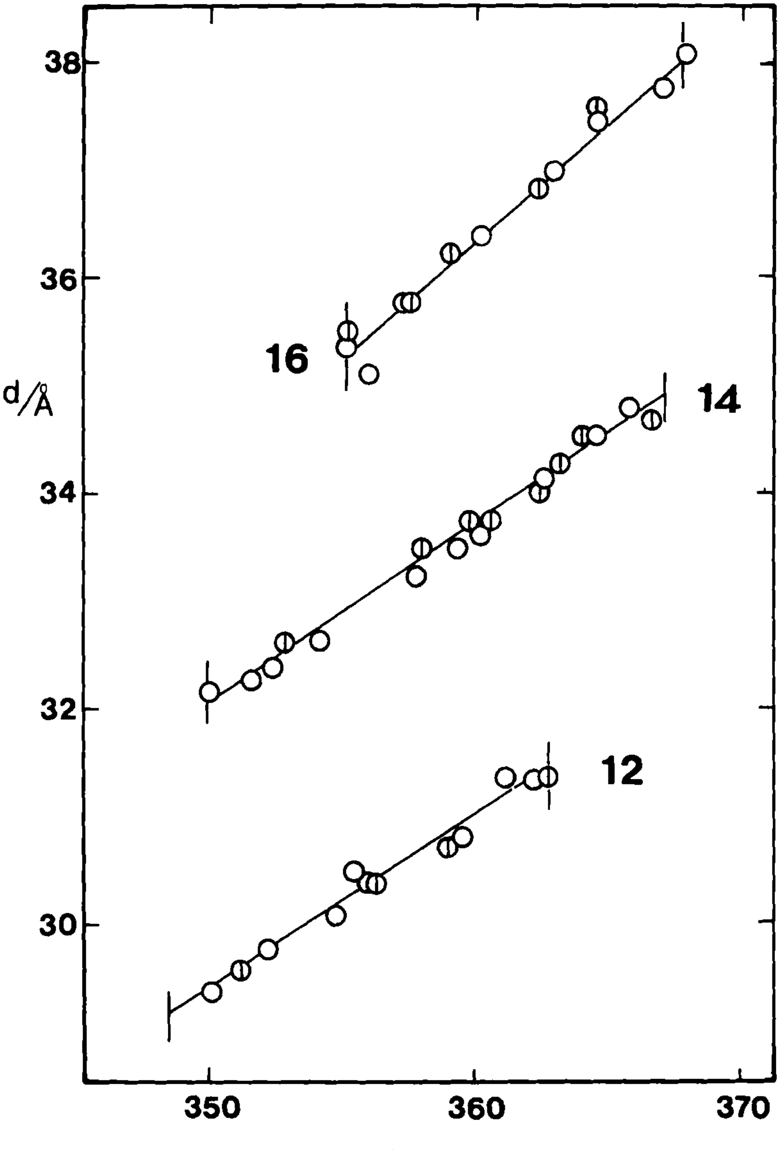

FIGURE 2 Temperature dependence of *d* for the *n* = 12, 14 and 16 compounds.

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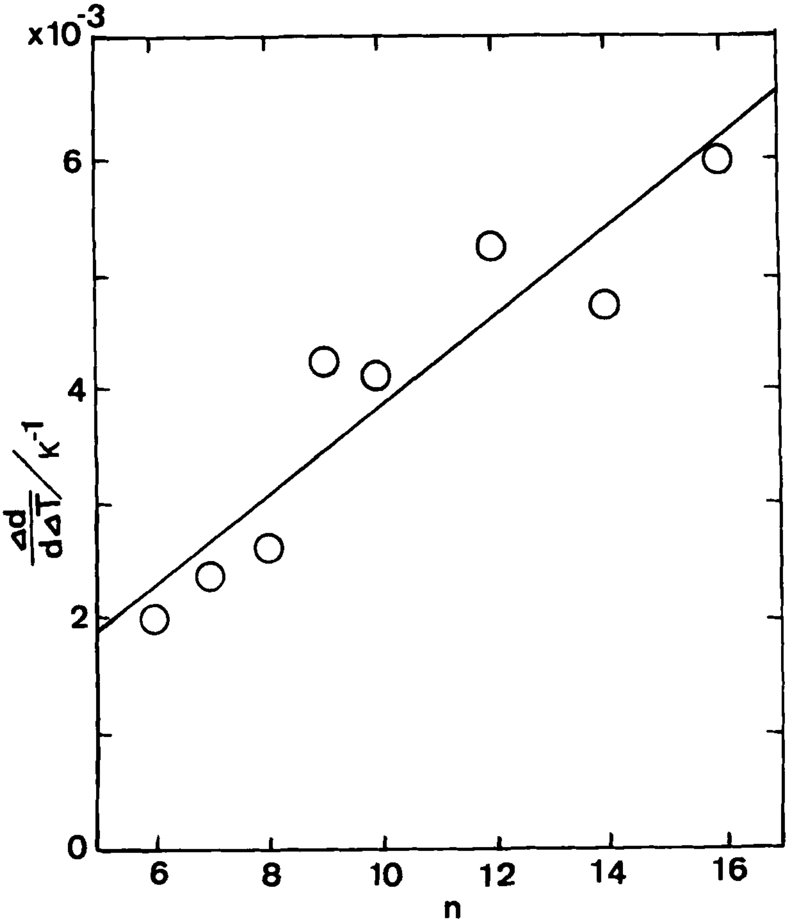

FIGURE 3 The *n*-value dependence of the expansion of *d*.

rather large as compared with those of ordinary isotropic liquids, for example, pentane, which has body expansivity (three times the linear expansivity) of 1.6 × 10^{-3} K^{-1}.[14] Two main factors are considered to contribute to this large expansion: changes of the paraffinic chain conformation and changes of tilt angles of the rather rigid central cores.

Figure 4 shows the relationship of the d-values with n. The d-values at T_{tr} show an excellent linearity, showing that the Sm C* phases in equilibrium with cholesteric phases have a certain common structure regardless of n. On the other hand, a small deviation is observed for the d-values at T_m. This is due to the different temperature ranges

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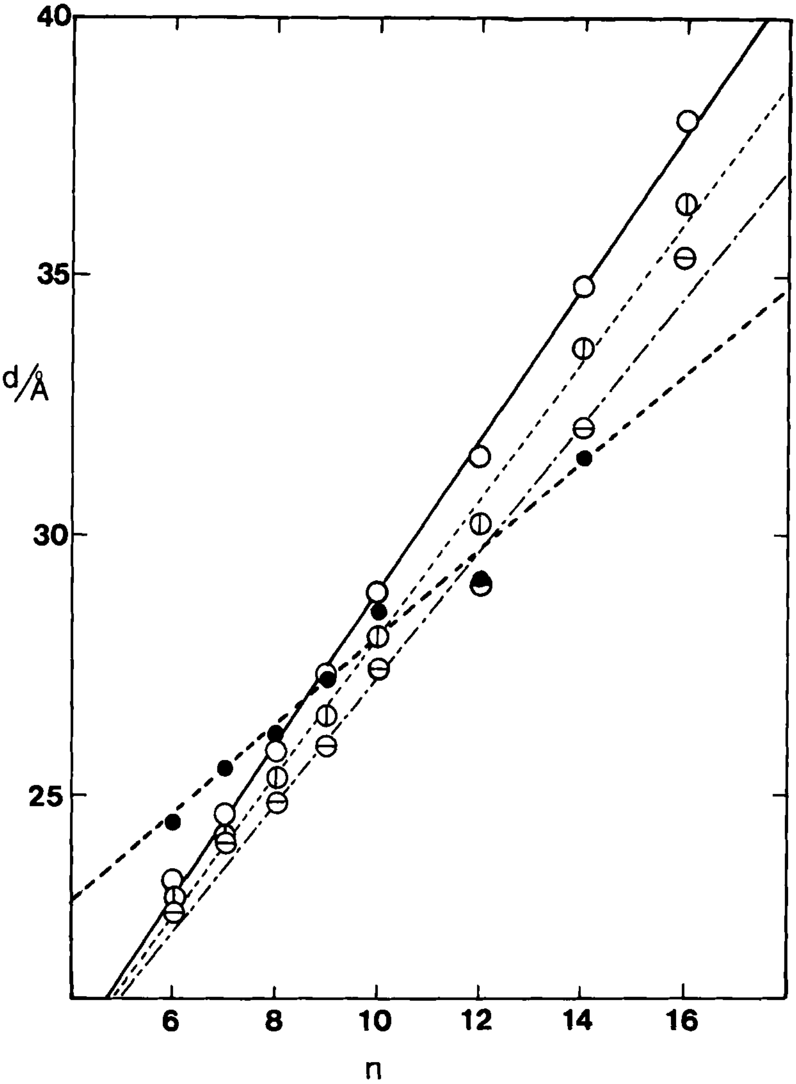

FIGURE 4 The n-value dependence of d, ⦶ at T_{tr}, ⊖ at $0.98T_{tr}$ and ○ at T_m in the Sm C* phases and ● in the solid states obtained from Sm C* phase.

of the Sm C* phases for different n. Since the mean value of T_m is $0.962T_{tr}$, the d-values at $0.98T_{tr}$ are also plotted as middle point values. Applying the equation, $d = d_r + nd_m$, to each of these three straight lines yields the thickness of one methylene group, d_m, and the thickness of the remaining part of the molecule other than the

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normal alkyl chain, d_r. The results shown in Table I reveal that the large expansion of the Sm C* phase is attributable to the normal alkyl chain part, whilst the thickness of the remaining part decreases slightly with increasing temperature. This result may be compared with that shown by smectic A phases. Here, two distinct effects have been observed. In one case, the layer thickness decreases with increasing temperature and this behavior is interpreted as a spreading of the alkyl chains at the interface between layers.[15] In the other case, where the layer thickness increases slightly with increasing temperature, it has been concluded that the molecular structure within the layer is almost constant.[16]

The part other than the normal alkyl chain includes the 2-methylbutyl group. A molecular model in Figure 5 shows that the length of this part is estimated to be 21.3 Å, on average, regardless of various conformations of the bulky 2-methylbutyl group. On the basis of this model, the tilt angle of the rather rigid core is calculated to be as shown in Table I. This result is consistent with the previous measurements by a conoscopic observation:[17] the tilt angle is about 45°, independent of temperature, for smectics C adjacent to nematics.

The large increase in d_m-values with increasing temperature indicates that large changes occur in the arrangement of the normal alkyl chains. It is not likely that the chains are shortened by the presence of more *gauche* conformations at lower temperatures and/or extended by the creation of more *trans* conformations at higher temperatures. It is more reasonable to assume that they are, as a whole, more tilted at lower temperatures and less tilted at higher temperatures. Furthermore, d_m-values themselves suggest an interesting arrangement of the normal alkyl chains. The values at T_{tr}, 1.470 Å, is remarkably larger than the increment of one methylene group in its most stretched conformation, 1.26 Å. Moreover, d_m-values at T_m, 1.226 Å, are also larger than those expected for largely tilted chains. Therefore, the normal alkyl chains are considered to have bilayer arrangement shown in Figure 6. A similar arrangement of alykyl chains has been previ-

TABLE I

Molecular parameters in the Sm C* phase

	d_r/Å	d_m/Å	θ/deg
T_{tr}	14.20	1.470	48
$0.98T_{tr}$	14.65	1.342	46
T_m	15.12	1.226	45

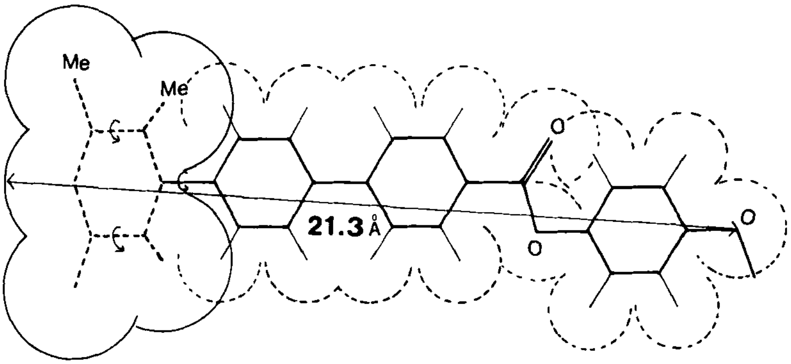

FIGURE 5 A molecular model for the part except the normal alkyl chain. Each part is not necessarily coplanar.

ously suggested for smectic A phase in the 4-acetyl-4′-n-alkanoyloxyazobenzene series.[16]

As mentioned above, the solids obtained from Sm C* have layered structures. The interlayer distances increase linearly with increasing n, for all the members, indicating that they have a common structure. A similar consideration of the d-values for the solids gives d_r = 19.50 Å and d_m = 0.846 Å. The former gives a tilt angle of the part except the normal chain to be 24°. The latter gives a tilt angle of the normal chain to be 48°, if the chains are assumed to have monolayer arrangements, because it is not necessary to assume bilayers in this case, and if the chains are assumed to be composed of almost only *trans*-conformations, as is usual in the solid states. A possible model is shown in Figure 6. The angle between the core and the normal chain is estimated to be 24°. This value is consistent with the value estimated from a molecular model in its most extended conformation. The solids obtained from melts are not the quenched states of the Sm C* phases. This is also indicated by the first-order phase transition which occurs between the two phases.

On the other hand, the stacking pattern of the layers is also an interesting problem of layered structures, as well as intralayer structures. A Sm C* phase is composed of layers stacking with slight deviation from layer to layer resulting in a helical arrangement. Selective light reflection is a direct consequence of periodicity of a helical arrangement and the peak wavelength, λ, is related to a helical pitch, p, by an equation, $\lambda = \bar{n}p$, where $\bar{n}$ is mean refractive index. The λ-values shifted to longer wavelength range with temperature increase. The variation of λ with temperature showed a slightly concave

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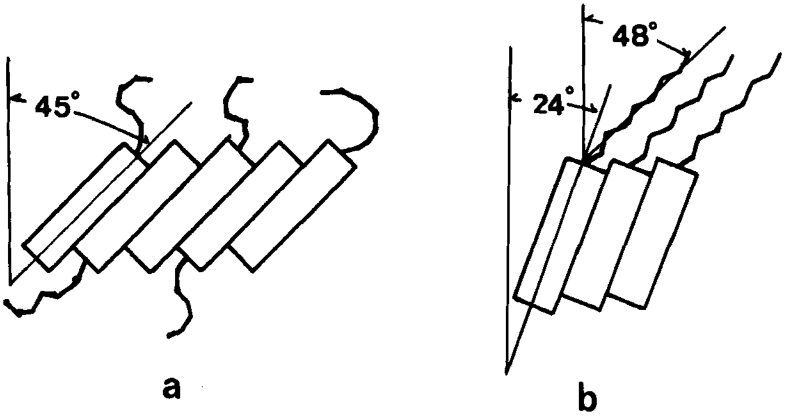

FIGURE 6 Possible molecular arrangements in the layer, (a) for the Sm C* phase and (b) for the crystalline solid obtained from the Sm C* phase.

curve for all the members as was shown in the case of n = 6.[10] No indications of the divergence of the λ-values at T_{tr} were apparant. For n = 6, the λ-values agreed with those reported[10] within 200 Å. Figure 7 shows the λ-values at T_m and T_{tr}. They shifted to longer wavelength range, as the n-values, and the interlayer distances, increase. In contrast the λ-values of the cholesteric phases at T_{tr} were almost constant, about 5500 Å, for all the members. For n = 6, the reported value was 5700 Å.[18]

The twist angle per layer, ϕ, was obtained from the equation, $\phi = 2\pi \times d/p = 2\pi \times d\bar{n}/\lambda$, where $\bar{n}$ is assumed to be 1.5. The ϕ-values at both phase transition temperatures are also shown in Figure 7. They decrease as the n-values increase. It is considered that interactions between the chiral centers in adjacent layers reduce as the thickness of intervening layers composed of melting paraffinic chains increases. The ϕ-values decrease also with temperature rise. Temperature increase causes expansion of d, and hence, reduction of ϕ. The contribution of this effect is, however, estimated to be less than 1/5, even in the case of the largest increase in the d-values. The greater part of the effect probably originates in the 'loosening' of the structure as temperature rises. The twist angle may be regarded as a kind of order parameter. The ratio of the value at T_{tr} to the one at T_m is 0.75–0.80 for all the members. This is comparable with those obtained for other smectics C. For example, the ratio of line splittings at T_{tr} and T_m is calculated to be 0.86 from the data by Poldy et al.[19] for the smectic C phase of 4, 4′-dioctadecyloxyazoxybenzene, which is adjacent to an isotropic phase. The ratios of DMR line splittings

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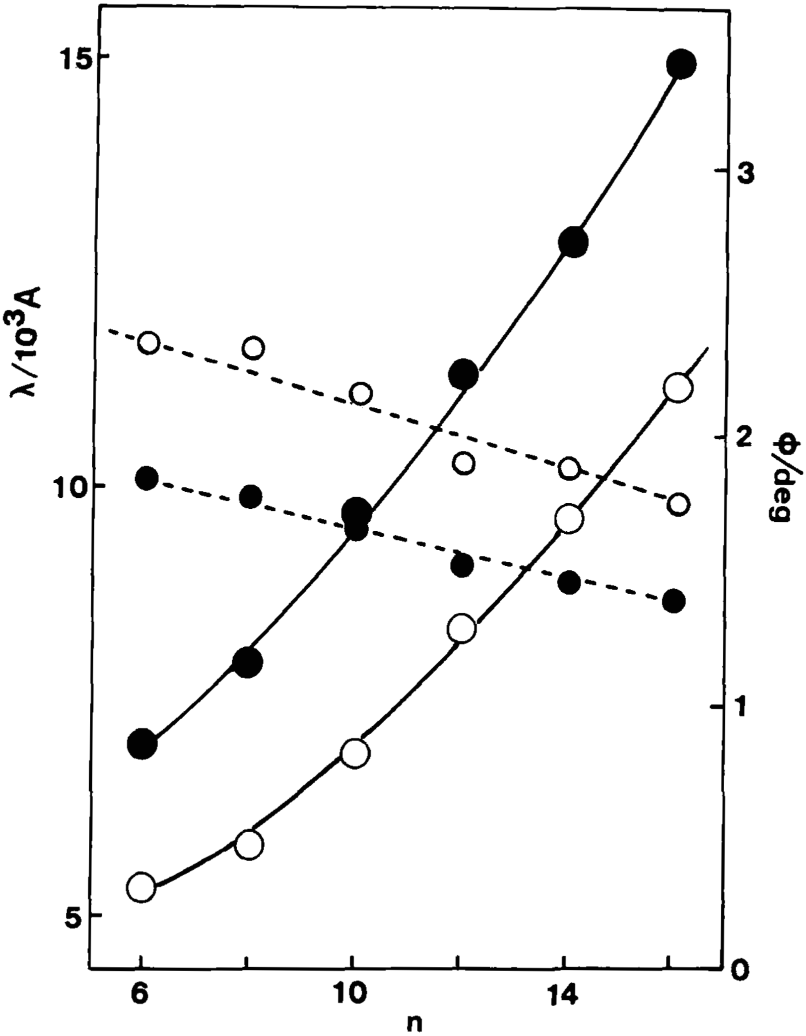

FIGURE 7 The n-value dependence of λ and φ. Large circles are for λ and small circles for φ. Solid circles are for the values at T_{tr} and open circles are for those at T_m.

are calculated to be 0.76–0.89 for various parts of molecules from the data by Deloche et al.[20] for the smectic C phase of deuteriated TBBA, which is adjacent to a smectic A phase.

It is concluded that in the Sm C* phase of (+)-4-n-alkyloxyphenyl 4-(2″-methylbutyl)biphenyl 4′-carboxylates, the tilt angle of the rather ridgid core is 45–48°, and is almost constant over the whole temperature range. The long paraffinic chains, which are considered to form double layers, radically change their conformations, as temperature increases. There is a slight reduction of the twist angle per layer with temperature rise.

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