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The helical structure of highly ordered smectic phases

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Optical studies of smectic phases have been performed in homogeneously oriented samples of chiral 4-(2′-methylbutyl) phenyl-4′-*n*-octylbiphenyl-4-carboxylate (CE8). The helix structure has been found in smectic phases C, I and J, but not in the smectic G phase. Two chiral phases have been found between S_I^* and S_G phases. Up to now one of them has not been observed. The pitch of the helix has been measured in all of the twisted smectic phases, including the S_J^* phase. The existence of the helix in this phase suggests that the correlations between smectic layers are not very strong.

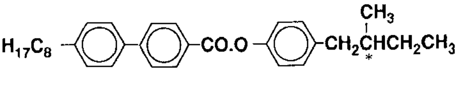
1. Introduction

The smectic A and C are the most extensively studied phases among the known smectic phases. In these phases there is no long range order within the layer plane. The properties of the remaining smectic or smectic-like phases, with various kinds of in-plane order, are not so well known [1]. In six of them (S_I, S_F, S_J, S_G, S_H and S_K) the director is tilted with respect to the smectic layer normal. In principle, when composed of chiral molecules such tilted smectic phases may form helical structures. However, it is believed that in phases with strong correlations between layers (S_J, S_G, S_H and S_K or as they are now denoted J, G, H and K), which in fact are crystal phases, the helix structure is suppressed [1, 2]. Experimental data concerning the helical structures of highly ordered smectic phases (i.e. with in-plane positional long range order) are very limited and sometimes controversial [3–5]. Systematic studies of this problem have not been performed up to now, probably because well oriented samples with thickness many times greater than the pitch are difficult to obtain.

Here, we report the results of studies of the helical structure in the tilted phases of S-4-(2′-methylbutyl)phenyl 4′-*n*-octylbiphenyl-4-carboxylate. In the literature various abbreviations are used for this material (8SI* [3, 4], + 2M4P8BC [5]). In what follows we use the BDH Ltd trade name CE8. This material has five tilted smectic phases and so it is very suitable for the study of highly ordered smectic phases and the transitions between them. By using an appropriate orientation procedure described later homogeneously oriented samples as large as $10 \times 5 \times 0{\cdot}1\ \mathrm{mm}^3$ were obtained. Such large, homogeneous samples prove to be suitable for quantitative studies of the helical structure.

2. Experimental

The CE8 material has the following chemical formula



$$H_{17}C_8-C_6H_4-C_6H_4-CO.O-C_6H_4-CH_2\overset{CH_3}{\underset{*}{C}}HCH_2CH_3$$

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it was obtained from BDH Ltd and used without further purification. We have used the following methods to study CE8: (i) texture observations, (ii) selective reflection measurements, (iii) measurements of the optical rotatory power, and (iv) differential scanning calorimetry. It must be stressed, that during all of these measurements the temperature was changed extremely slowly. This was, in fact, necessary because of the slow kinetics of the phase transitions between the low temperature smectic phases and the slow relaxation of the helix in these phases. Usually, after changing the temperature by only a fraction of a degree, many hours were needed to achieve equilibrium. An example is given in figure 1, where the evolution of a selective reflection band in the S_4^* phase is shown; analogous changes in the smectic I* phase are even slower.

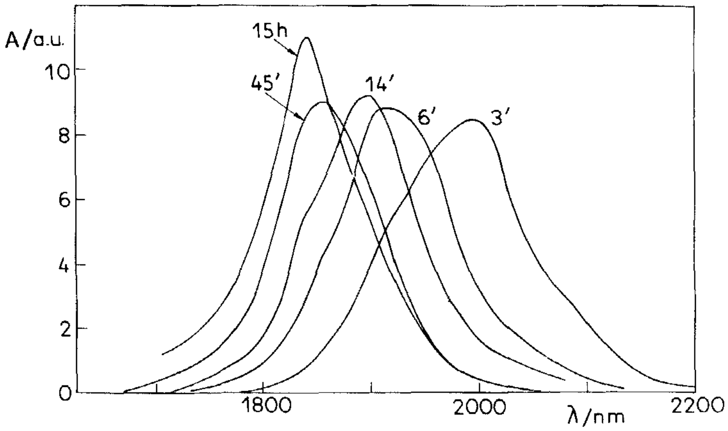

Figure 1. Time evolution of the selective reflection line in the S_4^* phase after a change of temperature.

(i) *Texture observations*

The thickness of samples was controlled by spacers within the range 10 to 140 μm. The samples, (i) unoriented and (ii) oriented in such a way that the smectic layers were parallel to the surfaces of the glass plates, were studied with a Leitz polarization microscope or a Biolar (PZO) microscope, both equipped with a Mettler hot stage FP 5/52.

(ii) *Selective reflection*

The sandwich-type samples about 70 μm thick were oriented homeotropically (the smectic layers parallel to the glass plates) in the S_A phase by means of a surfactant, and then slowly cooled. To maintain a good orientation in the low temperature smectic phases the rate of cooling was very low (sometimes lower than 0·1°C/hour). The transmission spectra of samples placed in the Mettler hot stage was measured with a Cary 17 spectrophotometer using unpolarized light in the spectral range 0·4 to 2·5 μm.

(iii) *Optical activity*

The samples, about 120 μm thick, were prepared in a manner similar to that described for selective reflection measurements. The rotation of the plane at polarized light as measured with a Biolar microscope (PZO) using monochromatic light (λ = 546 nm).

(iv) *Differential scanning calorimetry*

The D.S.C. measurements were performed with a Perkin–Elmer DSC-2 calorimeter. These measurements were used mainly to determine the transition temperatures for samples prepared in the standard way.

3. Results

(i) *Textures*

Observations of the optical textures enabled us to determine the transition temperatures (see table) and to gain some information about the optical properties of the phases. During our observations we distinguished six smectic phases lying below the cholesteric phase (i.e. one more than had been reported in the literature [1–6]). Altogether, on increasing the temperature we found the phase sequence

$$\mathrm{C},\ \mathrm{S}_6,\ \mathrm{S}_5^*,\ \mathrm{S}_4^*,\ \mathrm{S}_\mathrm{I}^*,\ \mathrm{S}_\mathrm{C}^*,\ \mathrm{S}_\mathrm{A},\ \mathrm{Ch},\ \mathrm{BPI},\ \mathrm{BPII},\ \mathrm{BPIII},\ \mathrm{I}.$$

By S_6, S_5, S_4 we denote here the three low temperature phases observed in the temperature range in which up to now only two phases, S_G and S_J, were known to exist.

For a rate of change in the temperature of about 0·1°C/min the transition temperatures determined during the heating and cooling process differ remarkably. However, these differences vanish if the rate of change of the temperature is reduced to about 0·01°C/min. Thus, we conclude that the temperature differences observed at faster rates were caused by slow kinetics for the phase transitions and that real supercooling does not take place between the smectic phases. The transition temperatures measured at a very slow cooling rate (nearly stationary conditions) are listed in the table. As shown in the table we have found an additional phase transition. The S_4^*–S_5^* phase transition is distinctly visible under the polarizing microscope (see figure 2(*c*)). In the presence of a slight temperature gradient the settling of phase boundaries can be clearly observed. Both the S_5^* and S_4^* phases exist over a narrow temperature range. Such a narrow temperature range together with the apparent supercooling described here were probably the reasons why the S_5^*–S_4^* phase transitions had not always been observed [1–6].

Transition temperatures (in °C) in CE8; values in parentheses denote the racemate.

Reference	C–S_6	S_6–S_5	S_5–S_4	S_4–S_I	S_I–S_C	S_C–S_A	S_A–Ch(N)	Ch–BP	Ch–I (N–I)
This work	48	63·3	64·7	66·7	69·0	85·0	135·4	140·7	141
BDH	48	61		67	70	87	135		140
[9]	(51·8)	(62·8)		(66·8)	(68·3)	(84·8)	(135)		(139·8)
[5]		(63)		(65)	(70)	(86)	(137)		(141)
[5]		59		61					
[8]	(66)	(64)			(69·5)	(84)	(135)		(141)
[10]	53	60·5		67	72·5	82	138·5	139·5	140
[3]	48·2	61·7		66·5	71·1	81	137·2	138·7	140
[4]		61·7		66·5	70·3	81·0	136·4		141·4
[4]		(62)		(65)	(68·7)	(83·8)	(135·1)		(140·6)
[11]	48	63	65	67	71	81	136	139	140

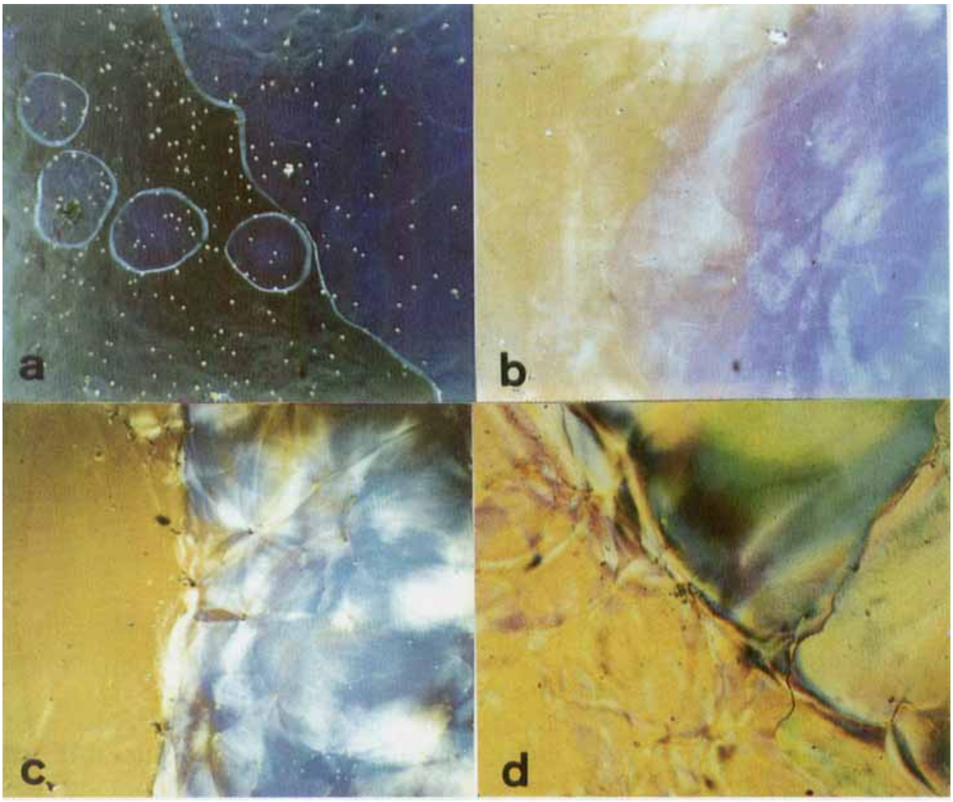

Figure 2. Phase boundaries between different smectic phases of CE8 observed by polarizing microscopy. (*a*) S_C^*/S_I^*, (*b*) S_I^*/S_4^*, (*c*) S_4^*/S_5^*, (*d*) S_5^*/S_6.

As can be seen in figure 2 (*a*), the S_C^*–S_I^* phase transition is first order (sharp phase boundary, phase equilibrium). The D.S.C. measurements confirm this conclusion. The remaining phase transitions between the smectic phases are continuous.

Figure 2 shows that in all of the smectic phases below the S_A phase specific colours caused by optical activity appear. These colours change as the analyser is turned. The only exception is the S_6 phase in which a twist of the plane of polarization is visible but only temporarily after a relatively fast passage from the S_5^* phase; if the temperature is kept constant slightly below the S_5^*–S_6 transition (63·6°C) for several hours, the optical activity vanishes. This disappearance of the optical activity is caused by a slow reorientation process during which the sample becomes homogeneous over large areas (e.g. $10 \times 5\,\mathrm{mm}^2$). Summing up, we conclude that the S_5^*, S_4^*, S_I^* and S_C^* phases are helical, whereas the S_6 phase may reveal some temporary twisting properties due to paramorphosis. The helical structure of the S_5^* phase is not caused by paramorphosis, since after heating from the untwisted homogeneously oriented S_6 phase, it also reveals optical activity.

Observations of wedge shaped samples provide an additional confirmation of the helical structure of the S_5^*, S_4^*, S_I^* and S_C^* phases. Figure 3 shows that dislocations of

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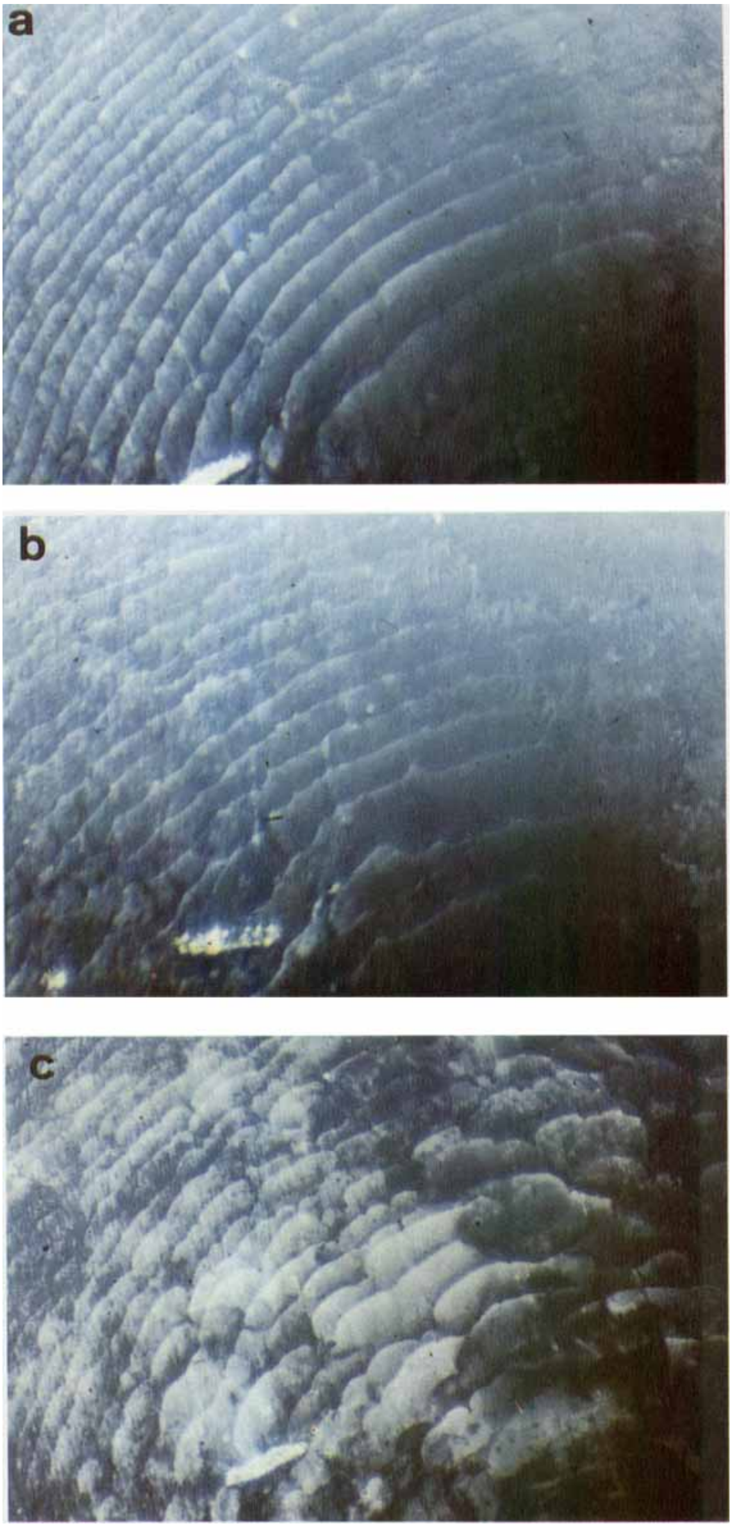
Figure 3. Microphotographs of Grandjean–Cano rings of a wedge shaped smectic CE8 sample (placed between a convex lens and a glass plate), these show a helical structure in the (*a*) S_I^*, (*b*) S_4^*, and (*c*) S_5^* phases.


a
b
c

the Grandjean–Cano type, characteristic of helically twisted phases, appear in all of these phases.

(ii) *Selective reflection*

The wavelengths, λ_R, of light selectively reflected from the CE8 samples in various phases are plotted in figure 4. The incident beam of light was parallel to the helical axis. In the S$_5^*$ phase the selective reflection wavelength decreases with increasing temperature down to a value of 1·8 μm at the S$_5^*$–S$_4^*$ phase transition. In the vicinity of the S$_5^*$–S$_6$ phase transition measurements were impossible to perform because of strong absorption and a broadening of the selective reflection band. However, observations of the textures indicate that at the S$_5^*$–S$_6$ transition the selective reflection wavelength diverges. If we assume that the refractive index along the helix axis is about 1.5, then the helical pitch of the S$_5^*$ phase at the S$_5^*$–S$_4^*$ transition should be about 1·2 μm. The value of the helical pitch in the S$_4^*$ phase is almost temperature independent within the whole range of this phase.

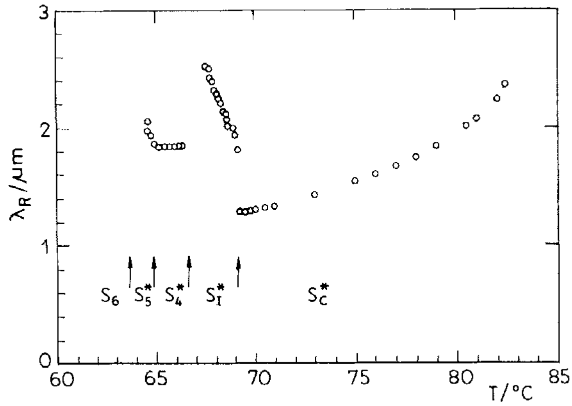


Figure 4. Wavelength of maximum selective reflection versus temperature for the smectic phases of CE8; sample thickness 71 μm.

The temperature dependence of the helical pitch in the S$_I^*$ phase is similar to that observed in the S$_5^*$ phase; it also decreases with increasing temperature. Within the range over which the measurements could be performed this dependence is approximately linear. The temperature dependence of the helical pitch in the S$_C^*$ phase is typical, i.e., the pitch increases with increasing temperature. This dependence can be described with very good accuracy by

$$\lambda_R = A(1 - T/T^*)^{-1/2}, \tag{1}$$

with $T^* = T_{S_C^*S_A^*} + 3{\cdot}3\,\mathrm{K}$ and $A = 292\,\mathrm{nm}$. In the vicinity of the S$_C^*$–S$_A^*$ phase transition measurements could not be performed because of strong absorption.

A time dependence of the selective reflection wavelength was observed after a change in temperature of the sample. In the S$_C^*$ phase these transitions are very fast and in practice we did not observe any relaxation of the pitch. However, in the S$_I^*$ phase the equilibrium value of the pitch is obtained only after many hours. Before reaching equilibrium, the selective reflection line is broad and distorted; this indicates a distribution of pitch values within the sample. In the S$_4^*$ and S$_5^*$ phases the equilibrium value of the selective reflection wavelength is attained more rapidly; practically one hour after changing the temperature the position of the band is already constant (figure 1).

(iii) *Optical rotatory power*

The results of the measurements of the optical rotatory power are presented in figure 5. It shows that the rotatory power diverges at the S_5^*–S_6 phase transition. It should be mentioned that the pitch of the S_5^* phase begins to diverge in the same temperature range (cf. figure 4). This behaviour is different from that observed for the variation of the pitch and optical rotatory dispersion in cholesterics and may be due to the special structure of the S_5^* plane. At the S_5^*–S_4^*, S_4^*–S_I^* and S_I^*–S_C^* transitions we observed jumps in the rotation. The discontinuities of the optical rotation at phase transitions are also clearly visible in the photographs shown in figure 2(*a*), (*b*), (*c*). In the S_C^* phase the value of the rotation angle decreases linearly with increasing temperature and vanishes at the S_C^*–S_A transition.

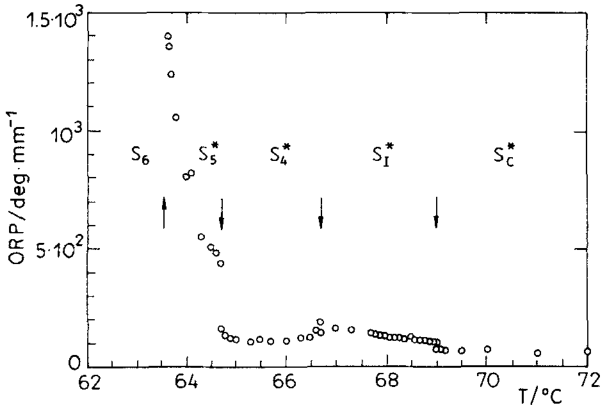


Figure 5. Optical rotatory power versus temperature of the smectic phases of CE8; sample thickness 118 μm.

Based on the sign of the rotation of the plane of polarization we have determined the handedness of the helix; using a method described in [7]. In all of the twisted smectic phases a right handed helix was found.

4. Discussion

(i) *Phase sequence*

Identification of the highly ordered smectic phases of CE8 has its own history. In 1979 Goodby and Gray [8] observed only one phase below the S_I^* phase, it was then called S_H. In 1984 Brand and Cladis [3, 4] observed two phases below the S_I^*. On the basis of systematic X-ray and miscibility studies Budai *et al.* [5] classified these phases at S_J and S_G.

The optical studies reported here suggest that there are not two but three smectic phases in CE8 below the S_I^* phase. However, a complete identification of these phases cannot be made on the basis of optical measurements alone. For this reason we are not able to assign code letters to the S_4^*, S_5^* and S_6 phases. The results of Budai *et al.*

[5] allow us to decide that two of them are the J and G phases, but it is impossible to tell which is which. Comparison of the transition temperatures does not help much because of the large discrepancies in the literature (see the table). For example, the data on the S_G–S_J transition temperature vary from 59 to 63°C. Similarly, those for S_J–S_I transition range from 61 up to 67°C. The analysis of data in the table can only tell us that the S_6 phase is probably the S_G phase (which has been named the smectic X by Brand and Cladis [3, 4]), whereas one of the S_4^* and S_5^* phases must necessarily be of the S_J^* type. (If S_5^* is of S_J^* type then S_4^* could be S_F^*.) On the other hand, large discrepancies in the transition temperatures reported in the literature suggest that quite possibly various authors were observing S_6–S_5, or, S_5–S_4 phase transitions identifying it always as the S_G–S_I transition. Both the S_4^* and S_5^* phases exist over a relatively narrow range of temperature (1–2°C), and if the rate at which the temperature is changed is not sufficiently low the phase transition S_4^*–S_5^* could easily be overlooked.

Could it be that what we have observed is not a new phase but only an artifact of the pretransitional effect of the S_J^*–S_G transition? Indeed, below 64·7°C both λ_R and the optical rotatory power display divergences; these might give rise to such a suspicion. However, a sharp discontinuity observed in the optical rotatory power at 64·7°C excludes this possibility. This conclusion is strongly supported by observations of the texture. At 64·7°C we observe a clear phase boundary, cf. figure 2 (*c*), at both sides of which different colours (stemming from different optical activities) are seen.

Numerical analysis of the optical rotatory power (ORP) for the S_5^* phase shows that it displays a critical behaviour which can be fitted well with the power law

$$\mathrm{ORP} = C(T/T^* - 1)^{\beta}, \tag{2}$$

where $C = 1{\cdot}32\,\mathrm{deg/mm}$, $T^* = 336{\cdot}22\,\mathrm{K}$ (63·06°C) and $\beta = -1{\cdot}09$. Extrapolating equation (2) into the temperature range of the S_I^* phase we find that the optical rotatory power of the latter fits it with surprisingly good accuracy, see figure 6. This indicates that critical fluctuations in the S_I^* and S_5^* phases are of the same nature and that structures of the two phases are similar. Among all of the smectic phases, S_J^* is most similar to S_I^* (they differ only in the strength of the interlayer correlations). Thus, it is quite probable that the S_5^* phase is of the S_J^* type. On the other hand, as seen in figure 6 the optical rotatory power data for the S_4^* phase do not follow equation (2).

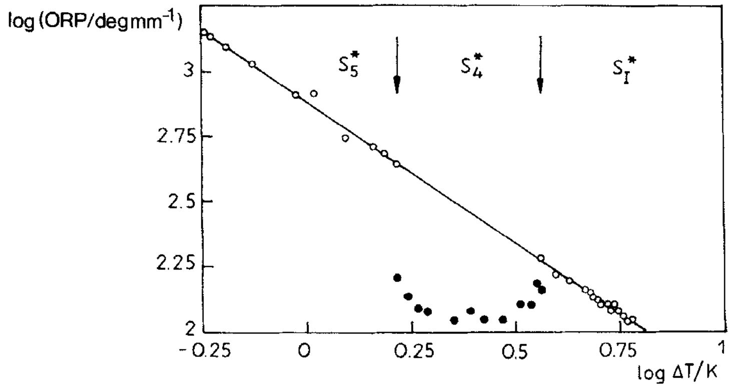


Figure 6. Optical rotatory power of the low temperature smectic phases of CE8 versus log ΔT, where ΔT is the temperature difference with respect to the S_I^*/S_C^* transition. The solid line is calculated from equation (2).

The assumption that the S_4^* phase is of the S_F type, would be in agreement with this observation.

D.S.C. measurements we have performed do not show any anomaly at the S_4^*–S_5^* transition. This, however, cannot be taken as an argument against the existence of the S_4^*–S_5^* phase transition. First of all, the enthalpy of a second order phase transition can be undetectably small [5]. Secondly, the D.S.C. method is inherently dynamic. Thus, if a phase exists over a narrow temperature range and can apparently be supercooled (as in our case), its detection with this method may be practically impossible.

Summing up, it seems to us that at 64·7°C there is a phase transition and the list of phases observed in CE8 should be augmented by one. Recent X-ray experiments performed by Gierlotka *et al.* [11] establish the following sequence of smectic phases in CE8: S_G, S_J^*, S_F^*, S_I^*, S_C^*, S_A. The transition temperatures they determined agree very well with our results. Thus, the S_6, S_5^*, S_4^*, phases which we have described in this paper can be identified, respectively, as S_G, S_J^* and S_F^*.

(ii) *Helical structure*

Our studies have shown that the smectic phases S_I^*, S_4^* (S_F^*) and S_5^* (S_J^*) exhibit a helical structure with a pitch larger than 1·2 μm. All of the phases mentioned exhibit selective reflection of light, optical rotation and Cano-type disclinations (see figures 2–5). In any case, the S_J^* phase also exhibits a helical structure with a relatively short period. The helical structure of this phase was also observed by Brand and Cladis [4], while Budai *et al.* [5] did not observe it. However, Budai *et al.* studied samples 1 μm thick, i.e. thinner than the value of pitch in this phase. In such a thin sample the helical structure is not able to develop.

The existence of the helix indicates that the interlayer correlations in the smectic J* phase are not complete or that the chiral interactions between molecules placed in adjacent layers are still significant despite the crystal-like order of the S_J^* phase. It cannot be excluded (although according to us it is hardly possible) that helix formation in the S_J^* phase is a pretransitional effect caused by the presence of the adjacent helical phase. In the S_I^* phase the interactions between layers are weaker than in both S_4^* and S_5^*. This conclusion is supported by the observation, that after changing the temperature a very long time (of the order of hours) is needed to achieve the equilibrium value of helical pitch. Possibly, at the transition to the S_I^* phase the helix is divided into short uncorrelated regions which explains the broadening and deformation of the selective reflection band and its time dependence (cf. figure 1).

5. Conclusions

Evidence for the existence of an additional smectic phase in CE8 has been found. The values of the helical pitch in the highly ordered smectic phases S_J^*, S_F^* and S_I^* have been determined for the first time. It is concluded that the S_J^* phase also exhibits a helical structure; this implies that the correlations between smectic layers in this phase are not very strong. On the other hand, in the S_6 phase which is of S_G type [11] a helical structure has not been observed. Thus, various orientations of the tilt direction with respect to the edge of a unit cell do not seem to be the only difference in structures of the S_G and S_J^* phases.

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