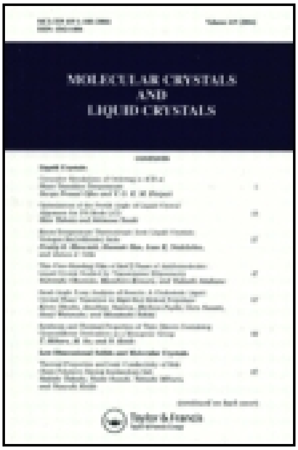

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Dielectric and Optical Measurements for Some Compounds Exhibiting an Is-Ch-SmC* Phase Transition Sequence

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The Isotropic–Cholesteric–Chiral Smectic C–Crystal phase transition sequence for some terminal alkoxy derivatives of 2,2′-dihydroxybenzalazine has been studied. Dielectric and optical measurements for the compounds with $n = 7, 8, 9$ and 10 are reported. The low-frequency dielectric anisotropy is determined for the chiral mesophases and the results are analysed as a function of the terminal chain length. The helical pitch values and tilt angles in the chiral smectic C phases are found to exhibit some peculiar characteristics which are qualitatively different from those of the materials undergoing the more fully studied smectic A–chiral smectic C phase transition.

Keywords: ferroelectric liquid crystals, Ch to Sm C phase transition, dielectric anisotropy measurements, helical pitch measurements*

1. INTRODUCTION

In the last few years the ferroelectric properties of liquid crystal materials with chiral smectic C(Sm C*) phases have attracted increasing interest because of the fast and efficient electro-optical response of these compounds to low external voltages. At the same time, when they are enclosed in very thin cells, a memory effect is found, which makes them potentially useful in optical switching devices.[1,2]

A great part of the investigating effort in this field is directed to the synthesis of new materials with ferroelectric mesophases. In previous work,[3] we have found Sm C* phases in some alkoxy derivatives of the central core unit 2,2'-dihydroxybenzalazine. These compounds with a general chemical formula:

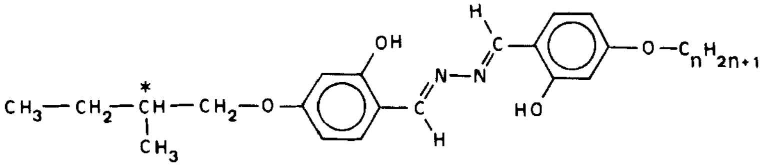

exhibit Sm C* phases for a number of carbons $n \geq 7$ in the righthand terminal chain. The ferroelectric phases with largest range are attained for $n = 7$, 8, 9 and 10 in which cases the Sm C* phase is preceded by a higher temperature cholesteric (Ch) phase. The phase transition sequence is the following

Isotropic (Is) → Ch → Sm C* → Crystal (C)

with crystalline polymorphism in the particular case $n = 7$. So far this kind of phase transition sequence has been scarcely studied due to the difficulty in obtaining properly aligned samples of the Sm C* phase, although the practical potential of these types of material for constructing guest-host cells has recently been pointed out.[4]

In this work we extend the previous thermal and optical microscopic characterization of this series[3] by measurements of the helical pitch and complex permittivity for the compounds with $7 \leq n \leq 10$.

2. EXPERIMENTAL

Cells for dielectric measurements were fabricated with two golden brass-electrodes of diameter 12 mm. The sample was placed between them with an annular teflon ring 0.5 mm thick as spacer. The area of the electrode in contact with the sample was 43 mm^2. Materials were introduced in the Is phase into a shielded sample-holder which allows for high-accuracy dielectric measurements in the audio-frequency region. The temperature can be controlled between -50°C and 250°C with a stability better than 0.1°C by means of a continuous flow of dry nitrogen and a heating element. The whole set-up can be rotated between the poles of an electro-magnet about an axis perpendicular to the magnetic field, in such a way that both homeotropic and homogeneous orientations can be achieved. A detailed scheme of the experimental configuration is shown in Figure 1.

Measurements were performed on slow cooling from the Is phase and the appropriate alignment was induced by means of the magnetic field. Since the molecular rearrangement at a Ch–Sm C* phase transition produces poorly aligned Sm C* samples in the absence of any aligning agent, magnetic fields (about 3–4 KGauss) were maintained during the whole cooling process. These field values are supposed to produce the required alignment without unwinding the helical structures. Actually, dielectric measurements revealed no significant differences when magnetic fields up to 5 KGauss in both parallel and perpendicular directions with respect to the cell-plates were retained or suppressed in the Ch or Sm C* phases. This suggests that although these fields must be enough for alignment purposes (due to the large thickness of the cells[5]), the properties of the materials were not appreciably influenced by them and the helical structure was not distorted. Since the anisotropy of the molecular magnetic susceptibility is expected to be positive in these compounds, the helix axis in the Ch phases is forced to align normal to the applied field direction. On the other hand, the Sm C* helix axis must lie along the magnetic field since the magnetic susceptibility is larger when measured along the helical axis ($\chi_{\|}\cos^2\theta + \chi_{\perp}\sin^2\theta$) than when measured normal to the helix ($\chi_{\|}\sin^2\theta/2 + \chi_{\perp}(1 + \cos^2\theta)/2$) provided that $\cos^2\theta > 1/3$ (θ is the tilt angle and $\chi_{\|}$ and $\chi_{\perp}$ are the parallel and perpendicular molecular susceptibilities).

Both components of the complex permittivity were obtained from the measurement of the complex capacity of the sample. This was achieved by monitoring the X and Y outputs of a two-channel lock-in amplifier which determines the in-phase and quadrature voltages on a high-capacity reference condenser in series with the sample.[6] The whole arrangement was interfaced to a micro-computer for data acquisition. In the present work, two fixed frequencies of 79 Hz and 12 KHz were employed and data were recorded in steps of about

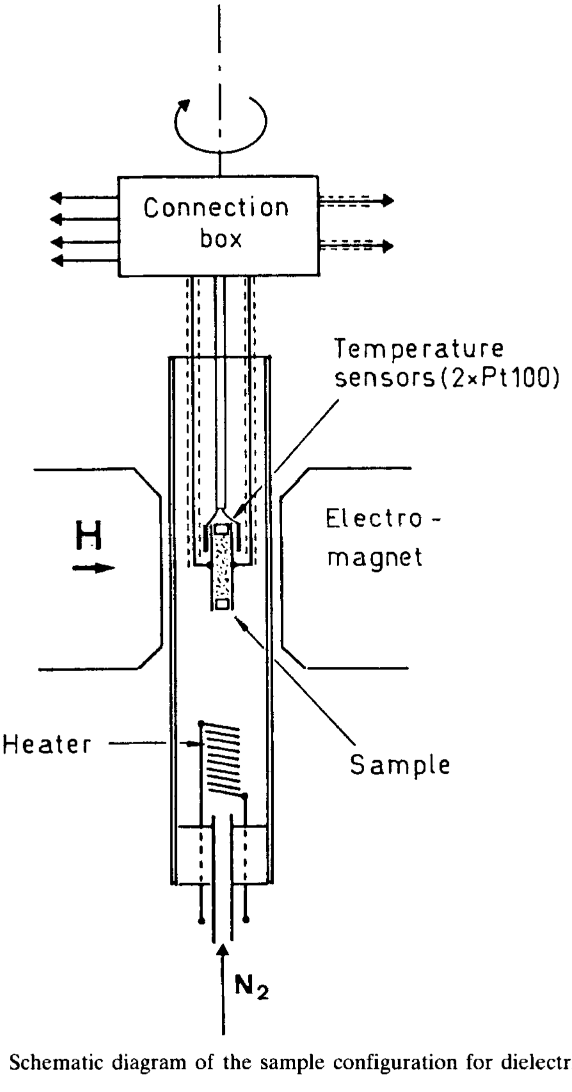

FIGURE 1 Schematic diagram of the sample configuration for dielectric measurements.

0.3°C. The dielectric permittivity was measured in both parallel ($\epsilon_{\parallel}$) and perpendicular ($\epsilon_{\perp}$) directions to the magnetic field. It should be noted that none of these measured quantities corresponds to the permittivities along and perpendicular to the molecular director. Moreover, in view of the orthogonal relationship between the helical axis in the Ch and Sm C* phases, $\epsilon_{\parallel}$ and $\epsilon_{\perp}$ are the permittivities parallel and normal to the helix axis only in the Sm C* phases. The opposite situation applies to the Ch phases.

The helical pitch for the Sm C* phases was determined by measuring the distance between consecutive fringes in the stripe pattern exhibited by a homogeneously aligned cell under a polarizing microscope. The values obtained were checked by observing the diffraction pattern of a He–Ne laser beam perpendicularly incident to the sample. No significant differences were found.

Cells were made of tin-oxide-coated glass plates on which a thin film of poly(hexamethylene-nonanediamide) was deposited as described in Ref. 7. Only one plate was rubbed so as to achieve maximum planar alignment.[8,14] Cells were glued after surface treating and the cell gap was maintained by teflon spacers. Prior to the filling process they were kept at 150°C for an hour in order to allow the glue to out-gas and force it to undergo the irreversible expansion processes that usually take place in epoxy resins. Sample thicknesses were about 60 μm in all cases. The sensitivity of the helical pitch to the surface anchoring condition and sample thickness[9] was overcome by using the method described in Ref. 10 to get the free value of the helical pitch in thin samples with strong surface treatment.

3 RESULTS AND DISCUSSION

3.1 Dielectric Results

Figures 2 to 5 show the low-frequency (79 Hz) dielectric behaviour for the compounds with $n = 7, 8, 9$ and 10 respectively. The data for the real part of the permittivity measured along ($\epsilon_{\parallel}'$) and perpendicular ($\epsilon_{\perp}'$) to the direction of the magnetic field are represented. The dielectric losses are also included in these figures through the imaginary part of the permittivity in the parallel direction ($\epsilon_{\parallel}''$).

The different phases and transition temperatures were identified from the anomalies in the dielectric behaviour together with comparison with previous DSC data and texture observations using the polarizing microscope. Transition temperatures corresponding to the parallel direction are labelled in the figures. In all cases, the temperatures for the Sm C*–C phase transition were found to depend on the alignment direction. The different phases and transition temperatures are summarized in Figure 6 for all the compounds studied.

A significant feature of the dielectric results is that the Is–Ch phase transition is characterized in all cases by a noticeable change in the temperature dependence of the imaginary component of the permit-

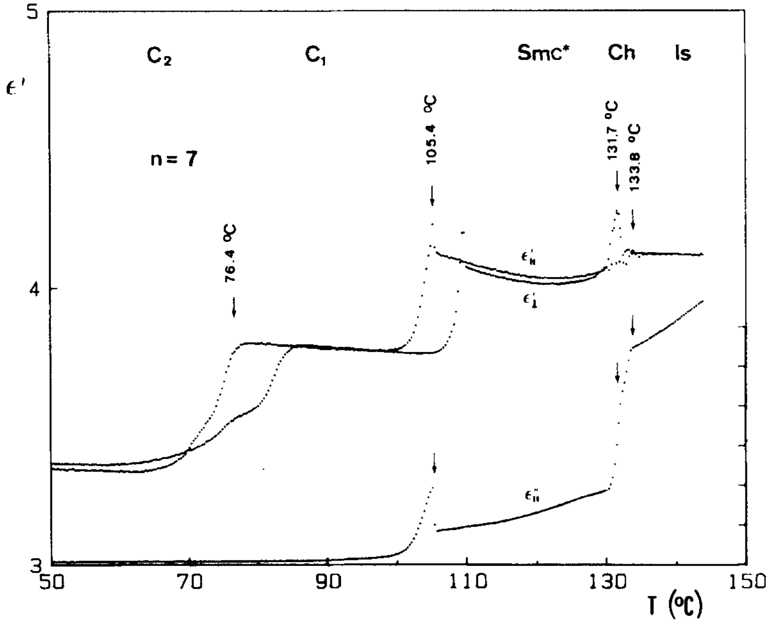

FIGURE 2 Dielectric permittivity as a function of temperature for the compound with $n = 7$ (79 Hz).

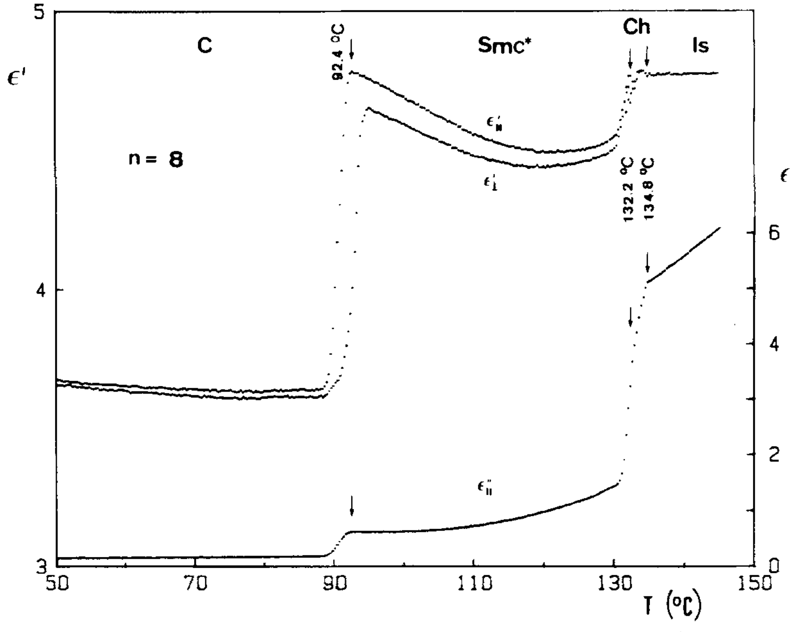

FIGURE 3 Dielectric permittivity as a function of temperature for the compound with $n = 8$ (79 Hz).

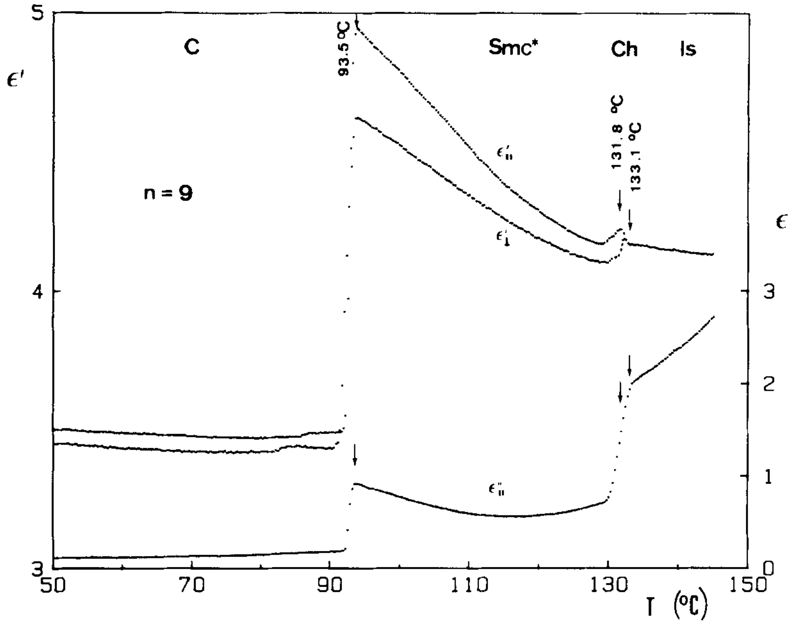

FIGURE 4 Dielectric permittivity as a function of temperature for the compound with $n = 9$ (79 Hz).

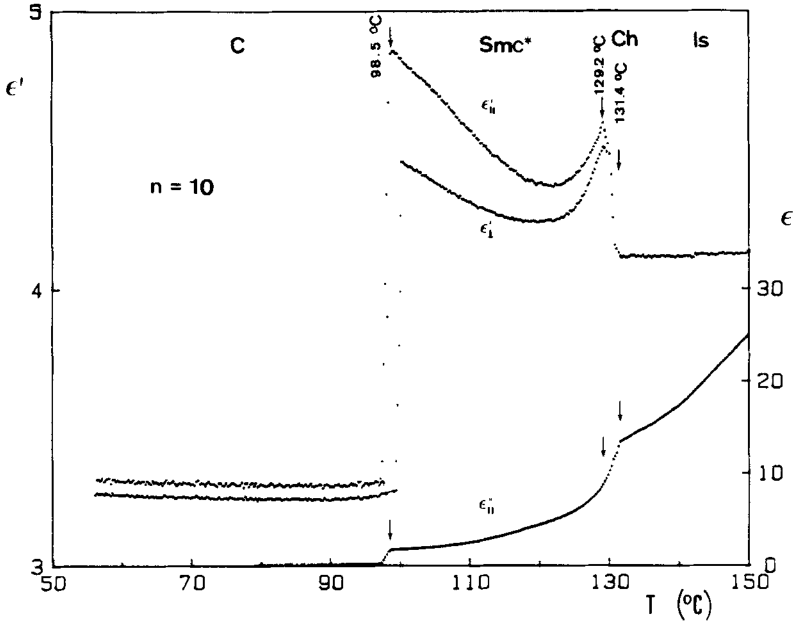

FIGURE 5 Dielectric permittivity as a function of temperature for the compound with $n = 10$ (79 Hz).

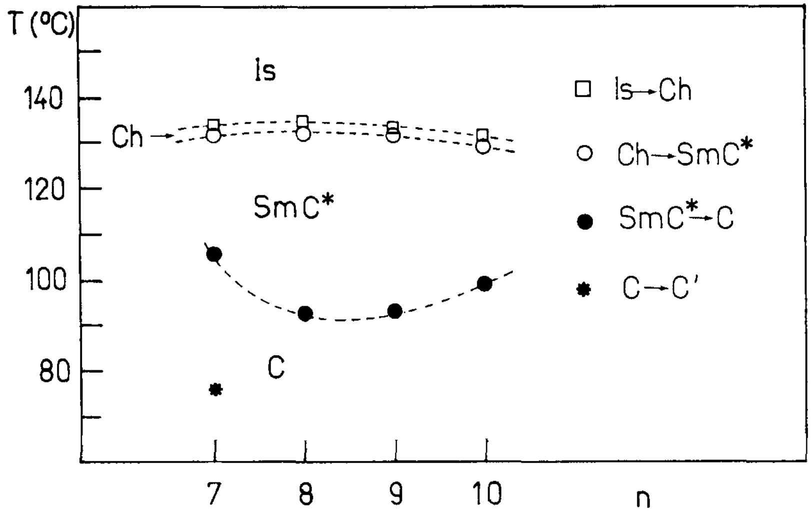

FIGURE 6 Phase transition sequence for S-4'-*n*-alkoxy-2,2'-dihydroxy-4-(2-methylbutoxy)benzalazines as a function of the terminal chain length.

tivity. This change almost disappears when the frequency is raised, which suggests a great difference in the conductivity behaviour of both phases in contrast with the weak anomalies found in the real component of the permittivity.

Figure 7 shows the high frequency (12 KHz) dielectric permittivity of the four compounds around the Ch–Sm C* phase transition as a function of $T-Tc$. We consider that this frequency is high enough to eliminate the low-frequency effects associated with the helical structure.[11] The Ch phases could not be readily identified from these measurements because of their narrow temperature range of stability, and the Is–Ch phase transition temperatures were taken from data in Figures 2–5. However the Ch phases seemed to be associated with a progresive increase in the difference $\epsilon'_{\parallel}-\epsilon'_{\perp}$ from the Is to the Sm C* phase. The Sm C* phase is characterized by the presence of dielectric anisotropy. However, the difference $\epsilon'_{\parallel}-\epsilon'_{\perp}$ presents a rather small value. This can be explained in terms of the weak polar character of these compounds and the average induced by the helicoidal structure in the observable dielectric anisotropy. If $\Delta\epsilon'_u$ denotes the dielectric anisotropy of the unwound structure, the actually measured difference $\epsilon'_{\parallel}-\epsilon'_{\perp}$ is easily shown to be

$$\epsilon'_{\parallel}-\epsilon'_{\perp} = \Delta\epsilon'_u\,(3\cos^2\theta - 1)/2$$

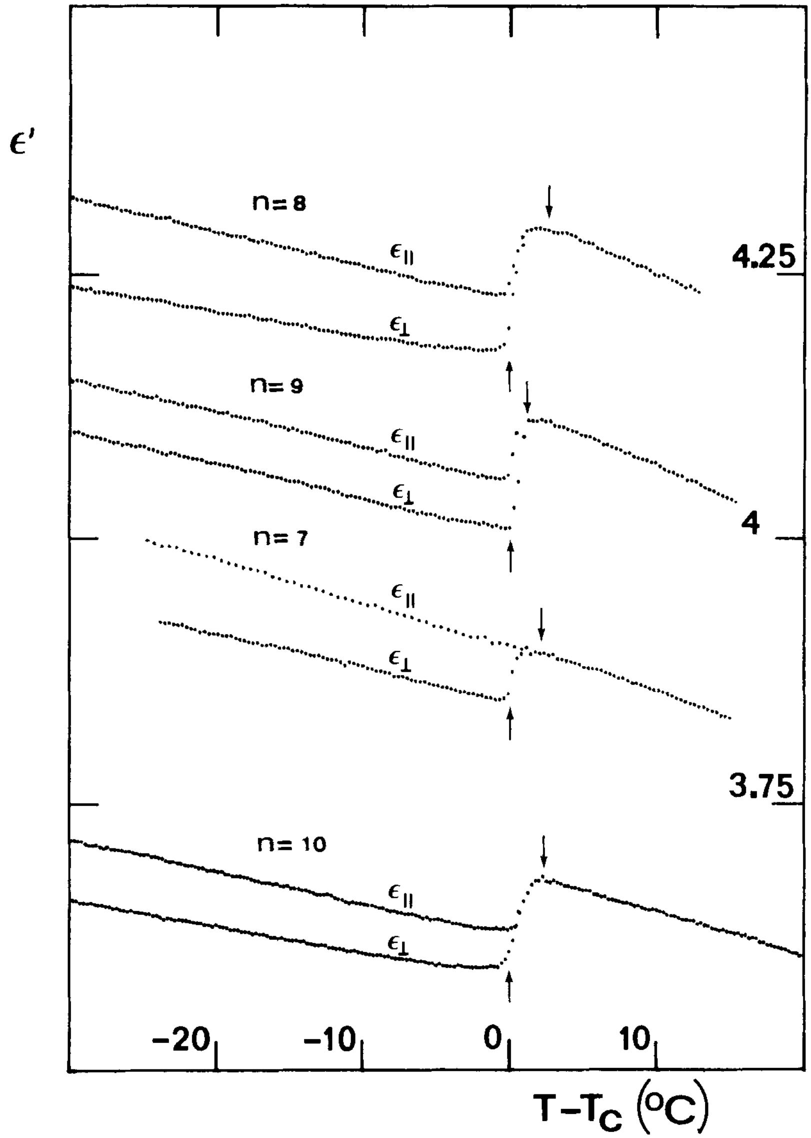

FIGURE 7 Dielectric permittivity at 12 KHz showing the anisotropic behaviour in the Ch and Sm C* phases. Transition temperatures are indicated by arrows.

where θ is the tilt angle. As will be shown below, $\theta \simeq 45°$ in our case, which implies a resulting $\epsilon_{\|}'-\epsilon_{\perp}'$ value four times smaller than the anisotropy of the unwound structure.

Figure 8 shows the $\epsilon_{\|}'-\epsilon_{\perp}'$ values at 79 Hz in the chiral phases. The

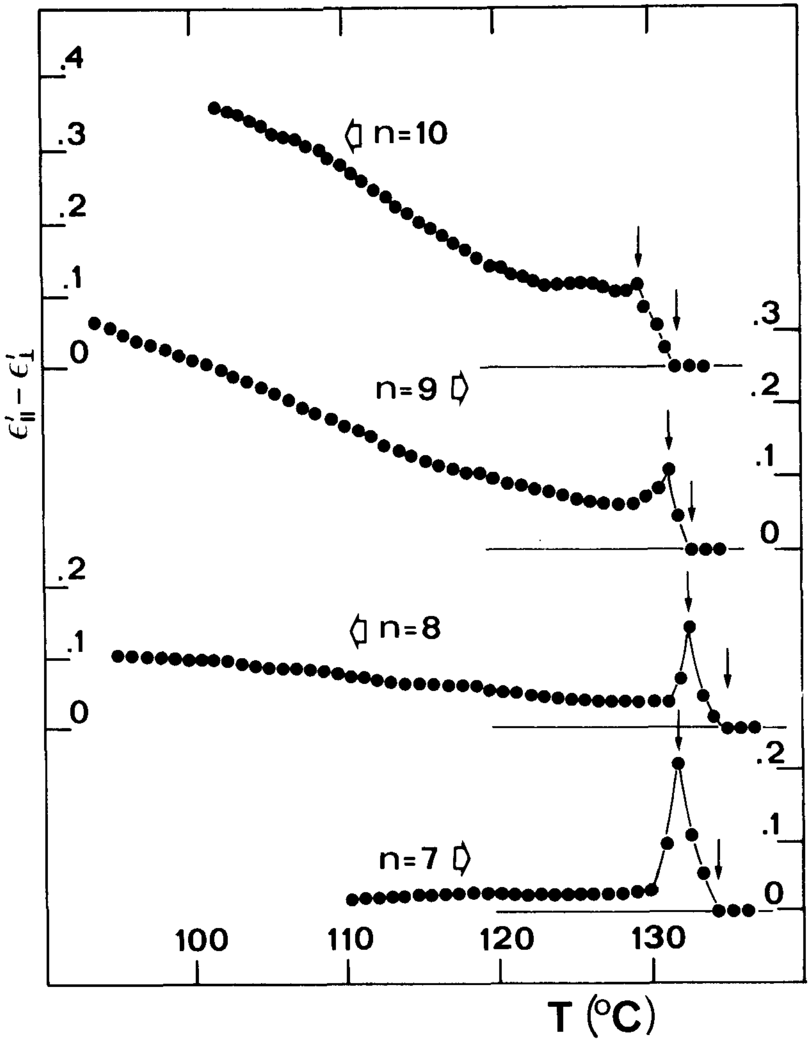

FIGURE 8 $\epsilon'_{\parallel}-\epsilon'_{\perp}$ values at 79 Hz for the Ch and Sm C* phases for the four materials studied. Transition temperatures are indicated by arrows.

Ch to Sm C* phase transition is characterized by a peak, which presumably arises from the 90° rotation of the helical axis at the transition point.[4] In any case, this anomalous behaviour is only present at very low frequencies and must probably be associated with the chiral structures of these phases. In contrast with the results at 12 KHz, $\epsilon'_{\parallel}-\epsilon'_{\perp}$ values for the Sm C* phases exhibit a clear dependence on both T and n. For $n = 7$ the observed anisotropy is smaller than its high-frequency value. This fact shows that the perpendicular component of the permittivity has a relaxation larger than the parallel component as can be expected from the chiral smectic structure,[12] in spite of its weak dipolar transverse moment. This effect decreases and reverses as the terminal chain length becomes larger. Thus $\epsilon'_{\parallel}$ relaxes more strongly for longer molecular lengths in this frequency range. This behaviour resembles that found in some nematics[13] and hides the contribution arising from the smectic helical structure which can only be detected for the compounds with shorter chains in this series.

3.2 Optical Results

Cells used for optical measurements were filled by capillarity in the Is phase and cooled slowly down to the Sm C* phase under a strong electric field. When the field was removed, most areas of the sample were aligned with an angle between the pitch bands and the rubbing axis close to 45°. This angle, which shows no appreciable variation with temperature, is the tilt angle if the molecular long axes align along the rubbing direction. The same result has also been found[14] for other materials which also exhibit Ch to Sm C* phase transitions. More accurate measurements of the tilt angle for these compounds are presently being carried out in our laboratory.

The observed fringe lines were sharp, but not completely straight, and they were most clearly visible when the polarizer direction was parallel to the smectic planes. All these facts indicate[11,15] that they must correpond to a set of disclination lines which arrange the planar surface condition with the bulk helicoidal structure.

The pitch data are shown in Figure 9. It is clear that the helical pitches are not significantly dependent upon temperature, although in all cases they seemed to increase abruptly at the very point of the Sm C*–Ch phase transition (not shown in Figure 9). The temperature interval where this effect takes place was not determined due to the limited accuracy (0.25°C) of the temperature control in our microscope stage.

Critical fields to suppress the helicoidal structure were found to range between 10 and 100 KV/cm for all the compounds studied. These high values confirm the weak polar character of this family in agreement with the dielectric results. Actually, our results for the tilt angle θ, the helical pitch L and the critical field E_c indicate that the spontaneous polarization values P_s must be one or two orders of magnitude lower than those of the well-studied ferroelectric liquid

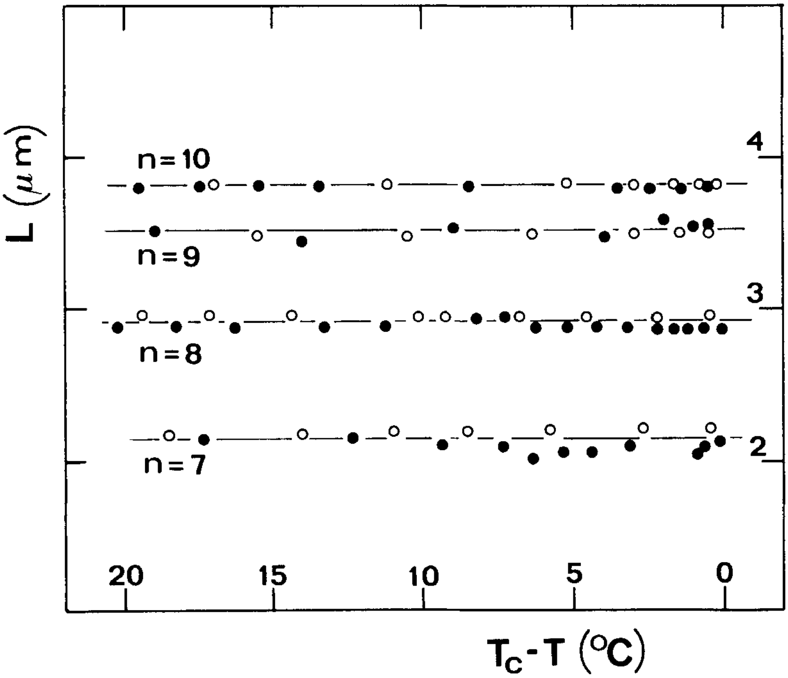

FIGURE 9 Helical pitch values as a function of reduced temperature for the Sm C* phases. Closed circles represent the results from microscopic observations and open circles the values obtained by the diffraction technique.

crystal DOBAMBC. This can be shown from the equation[16]

$$P_s = \pi^4 K\theta^2/(4E_c L^2)$$

assuming a typical value $K = 10^{-12}$ N for the twist elastic constant.

The disappearance and reappearance of pitch lines under increasing and decreasing electric fields were found to display a moderate field hysteresis which was present even in the vicinity of the Sm C*–Ch phase transition. A similar effect has recently been reported for DOBAMBC,[17] although in this case the difference between unwinding and rewinding fields tends to zero as the temperature approaches the Sm C*–Sm A transition point. This effect may be justified in terms of a difference between the activation energies for the processes of annihilation and creation of disclination lines.[18] Nevertheless no comprehensive theory to explain this point seems to be yet available.

Finally, we would like to remark that in order to achieve a more quantitative discussion of the experimental results in this paper a theoretical approach accounting for the Ch–Sm C* phase transition would be necessary. This work would be useful both in fundamental research and in future practical applications.

Acknowledgments

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