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A SMECTIC A PHASE OF POSITIVE AND NEGATIVE DIELECTRIC ANISOTROPY

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Abstract A smectic A phase exhibiting positive dielectric anisotropy at low frequency and negative dielectric anisotropy at high frequency of applied field has been found for the first time.

During the past few years several dielectric reorientation[1,2,3,4] effects have been found in smectic A liquid crystals. However, all the effects have to be reversed by heating the smectic phase into the nematic phase so that the reorientation into the initial state (defined by the surface alignment) can occur when the nematic phase is cooled back into the smectic phase.

It has been known for many years that the dielectric anisotropy ($\Delta\varepsilon$) of nematic liquid crystals is dependent on the frequency of the applied field used to measure it. In recent years a small number of compounds have been found[5] which exhibit large changes in dielectric anisotropy with changing frequency in the nematic phase. They are usually dialkyl diesters, having a $\Delta\varepsilon$ of about +1 to +4 at low frequency but exhibiting a small negative dielectric anisotropy at high frequency. These compounds are said to be two-frequency nematics and the frequency at which the dielectric anisotropy changes sign is called the cross-over frequency. This cross-over frequency is very temperature dependent, typically changing by as much as 1 kHz/^{o}C. Why this effect is shown by some compounds and not by others is not yet fully understood.

Although the dielectric properties of nematic phases have been extensively studied, little is known about the dielectric properties of smectics presumably due to lack of commercial interest and the difficulty of reliably aligning them. Also very little has been reported on the change in dielectric anisotropy with changing frequency of the applied field.

If some or all of the known smectic A dielectric orientation effects are to be reversible a smectic material exhibiting a two frequency effect is required.

We have examined several homologues from a class of compounds which show a two frequency nematic phase. The higher homologues show a smectic as well as a nematic phase. Most of the compounds examined had cross-over frequencies above the range of our oscillator (100 kHz). However, the material with the lowest S_A-N temperature showed a cross-over frequency in the low kilohertz range. This communication is the first published report of such a two-frequency material.

EXPERIMENTAL

The cell used in these measurements consisted of two thin, indium-tin oxide coated glass plates which were treated with lecithin in hexane, and held apart by a 19 μm spacer. The cell was filled with a liquid crystal in the nematic phase which aligned homeotropically, and on cooling into the smectic phase the homeotropic alignment remained. The temperature of the cell was controlled by a Mettler hot stage to within 0.1°C and the cell was viewed through a polarising microscope. An a.c. signal of about 20 V (well above threshold) was applied to the liquid crystal when in the nematic phase. At low frequencies, when the phase was exhibiting a positive $\Delta\varepsilon$ no change in texture could be seen, but at higher frequency, when the phase was exhibiting a negative $\Delta\varepsilon$ a random homogeneous texture occurred. The cross-over frequency was determined by observing the change from homeotropic to homogeneous texture in the nematic phase (or to focal conic when in the smectic A phase). This occurred over a frequency band of about 200 Hz. Williams domains were also seen occasionally during the nematic texture change.

The experiment was repeated for various temperatures, and the effect was followed into the smectic A phase. This required much higher voltages (100-200 V) than in the nematic phase. At these voltages, the maximum frequency of the oscillator was about 40 kHz. The texture obtained in the smectic phase above the cross-over frequency was random focal-conic (birefringent) which could be converted back to a homeotropic texture (non-birefringent) by applying a field of frequency lower than the cross-over frequency. Thus the effect was electrically reversible.

RESULTS

4-n-Pentylphenyl 2'-chloro-4'(6-n-hexyl-2-naphthoyloxy) benzoate[6] has the constants C-N, 68.6°; (S_A-N, 52.5°); N-I, 178.9°. The monotropic smectic A phase of this diester was found to exhibit both positive and negative dielectric anisotropies at low and high frequencies respectively. The cross-over frequency as a function of temperature is shown in Fig. 1. The cross-over frequency is very temperature dependent in the nematic phase. At the S_A-N transition this dependence is much reduced. In the S_A phase it increases again but not to the same extent as in the nematic phase.

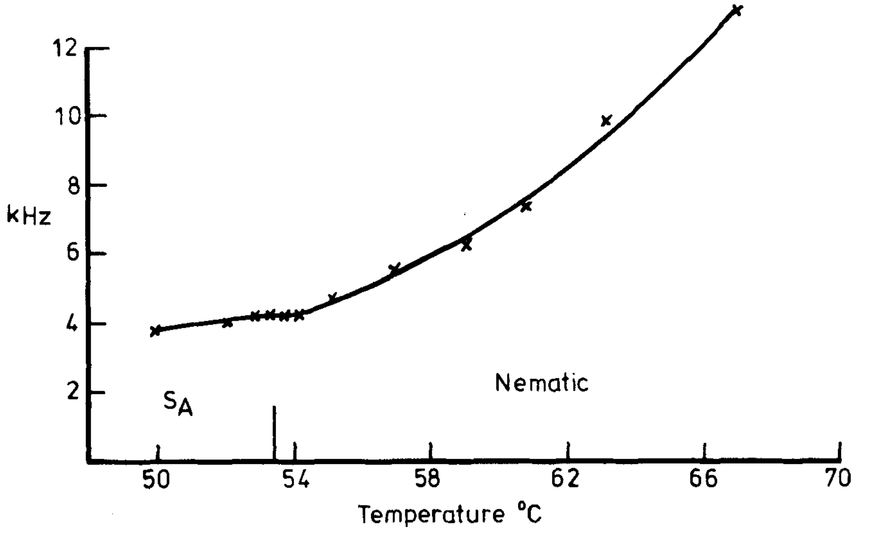

Figure 1 Cross-over frequency vs temperature for 4-n-pentylphenyl 2'-chloro-4'-(6-n-hexyl-2-naphthoyloxy) benzoate.

It is advantageous to mix other esters with the naphthoyl diesters so that a smectic A phase of wider temperature range and lower cross-over frequency is obtained. Figure 2 shows a plot for a tertiary mixture containing substantially 4-n-pentylphenyl 2'-chloro-4'-(6-n-hexyl-2-naphthoyloxy) benzoate.

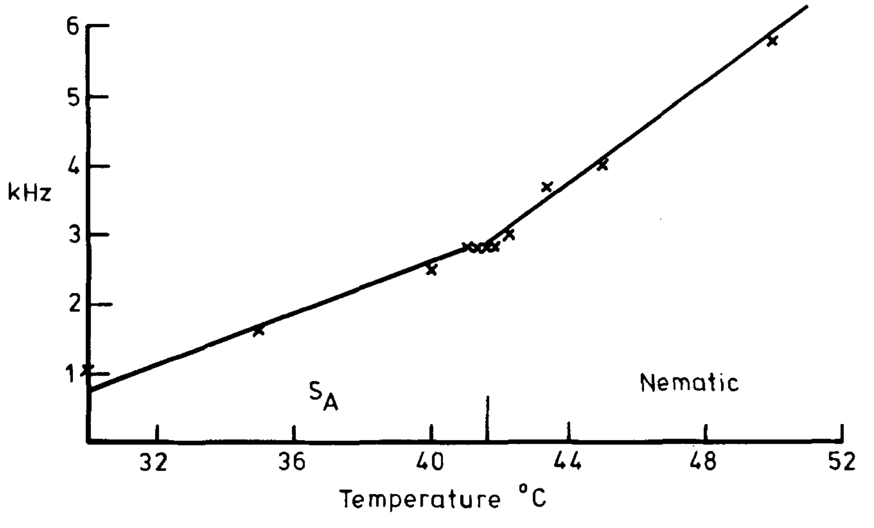

Figure 2 Cross-over frequency vs temperature for a tertiary mixture of esters.

The cross-over frequency dependence on temperature of the ester mixture (Fig. 2) is very similar in general shape to that of Fig. 1 except that both the cross-over frequencies and the temperature are lower.

We have therefore shown that smectic A phases can exhibit both positive and negative dielectric anisotropy and that the frequencies at which the change from positive $\Delta\varepsilon$ to negative $\Delta\varepsilon$ takes place can be quite low.

Some of the electro-optic effects known in smectic A liquid crystals are in principle therefore reversible.

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