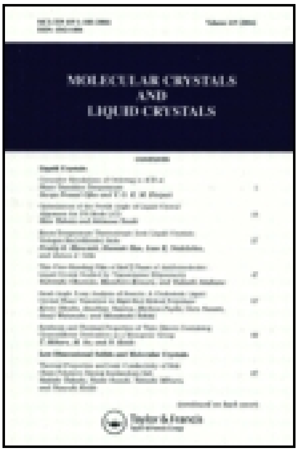

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ELECTROOPTIC SOFT MODE RESPONSE OF COMPOUNDS EXHIBITING THE ANTIFERROELECTRIC PHASE

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Abstract We report measurements on the electrooptic response of thin samples (~2-5 μm) of two antiferroelectric liquid crystals. All the phase transitions in these compounds can be very easily detected using this technique. We have been able to measure such an electrooptic effect for the first time in the antiferroelectric and smectic I* phases of a tolane compound. The response shows a relaxation at high frequencies (~10 KHz) and is attributed to a soft mode which produces an asymmetry in the molecular tilt in successive layers.

INTRODUCTION

In the antiferroelectric liquid crystalline phase chiral molecules tilt essentially in opposite directions in successive layers, leading to a net cancellation of polarization in the medium.[1–4]. However, by applying a sufficiently strong electric field, it is possible to get an antiferroelectric to ferroelectric transition and a trilevel switching which is now being explored for exploitation in display devices. Many compounds which exhibit the antiferroelectric C_A^* phase often exhibit a sequence of other liquid crystalline phases. The prototype compound MHPOBC for example exhibits on cooling the sequence A, C_α^*, C_β^*, C_γ^*, C_A^*, I* and crystalline phases in which A is the smectic A phase, C stands for the various smectic C phases, and I* is the smectic I phase.

Dielectric constant measurements have been used extensively to study the phase transitions in these compounds.[5] The spontaneous polarization gives rise to a large contribution to the dielectric constant in the ferroelectric phase C_β^*, arising from the Goldstone mode. The net polarization is reduced in the ferrielectric (C_γ^*)

phase. Different models have been proposed for the molecular organisation in the ferrielectric phase[6]: (a) the tilt angles of the molecules in a larger number of neighbouring layers are in the same direction than in the opposite direction (3:1 for example), (b) the change in the azimuthal angle between successive layers is between 0 and π radians, (c) the tilt angles of the molecules in different layers may be different. Xray evidence appears to make the last possibility very unlikely. Observations of the Devil's staircase[7] in the field- and temperature-dependence of apparent tilt angle in this phase appear to favour the first model. The net polarization in the antiferroelectric phase is essentially zero and the Goldstone mode does not contribute to the dielectric constant in this phase.

As the tilt angle is the primary order parameter for the smectic C* to smectic A transition, and the polarization is proportional to the tilt angle in a first approximation, there is a corresponding *soft-mode* contribution to the dielectric constant in the ferroelectric phase. However, because of the much stronger contribution from the Goldstone mode, at low frequencies the soft mode contribution to the dielectric constant can be measured easily only near the smectic C_β^* to smectic A transition point.[8]

The electroclinic effect in which an external field induces a tilt in the smectic A phase has been a very useful method of exploring the critical soft mode in the smectic A phase close to the A-C* transition point.[9]. The electrooptic response in the lower temperature tilted phases can also be expected to yield very useful information about the structures and dynamics in these phases. Indeed there have been a couple of electrooptic measurements on some compounds exhibiting antiferroelectric phases.[10,11]. These measurements were made on relatively thick ($\sim 20 \mu$m) samples in which the electrooptic signal was hardly detected in the antiferroelectric phase.

We have made electrooptic measurements on two compounds exhibiting the sequence smectic A - smectic C_α^* - smectic C_β^* - smectic C_γ^* - smectic C_A^* - smectic I* on *cooling* using relatively *thin* samples (2 to 5 μm). We find that we can detect the phase transitions quite clearly using such samples. Indeed in well aligned samples, we could not only get a reasonable electrooptic signal in the antiferroeletric phase, but detect the antiferroelectric to smectic I* transition as well. Moreover the electrooptic response shows a relaxation at frequencies more than 10 KHz in both the antiferroelectric and smectic I* phases. We attribute this response to a soft mode in which molecules in neighbouring layers tilt asymmetrically under the action of the external field.

EXPERIMENTAL

The samples used in the experiments were the following:

1) MHPOBC:

$$C_8H_{17}O\Phi\Phi COO\Phi COO\ C^*H(CH_3)C_6H_{13}$$

K 30° I* 66° C_A^* 118°.3 C_γ^* 119° C_β^* 120°.7 C_α^* 122° A 156° Iso

2) C8-tolane compound:

$$C_8H_{17}O\Phi C \equiv C\Phi COO\Phi COO\ C^*H(CH_3)C_6H_{13}$$

K 67.6° I* 71.6° C_A^* 95.1° C_γ^* 97° C_β^* 104° C_α^* 105.5° A 135° Iso

Both the samples were synthesised at CRPP, and the transition points correspond to the data from DSC measurements. The samples were homogeneously aligned in the smectic A phase by taking them between two ITO coated glass plates which had been treated with polyimide and rubbed. The sample thickness was typically between 2 to 5 μm and the alignment was generally good in the smectic A phase with a few focal conic defects. The electrooptic set up is quite standard with the sample cell taken in an INSTEC HS1-i hot stage. A helium-neon laser beam polarized at $\pi/8$ radians with respect to the director in the A phase was passed through the cell. The electrooptic signal coming out of an analyser crossed with respect to the polariser was monitored using a PIN photodiode. The 'f' signal at the frequency of the applied voltage was measured using a PAR model 5301A lock-in-amplifier and the DC signal by an HP model 3457A multimeter. The whole experiment was controlled by a computer, using a Spectrum Interface software.

RESULTS AND DISCUSSION

The temperature-runs were made at realtively low frequencies and were used to locate the transition points. The applied voltage was controlled to get a more or less constant optical signal. This ensures that we are generally in the *linear regime.* Thus, the applied voltage is ~0.6 V/μm far above C_α^*-A transition point and comes down to ~15 mV/μm near C_α^* - C_β^* transition point and increases again to ~0.6 V/μm in the antiferroelectric and smectic I* phases. The electrooptic response

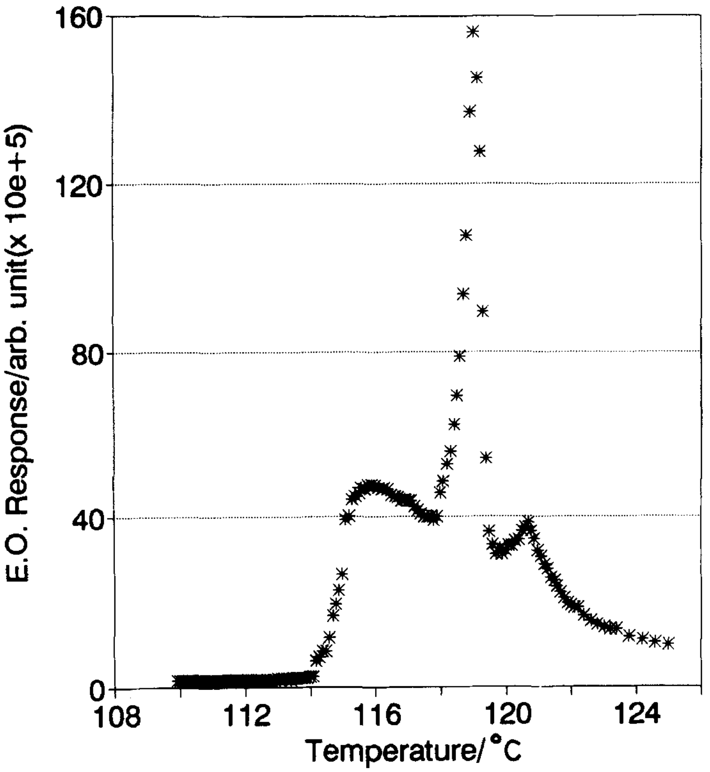

FIGURE 1 Temperature dependence of the electrooptic response (per unit voltage) of a 4.3 μm thick sample of MHPOBC at 752 Hz in the cooling mode.

shown in figures 3 and 4 is given by [f signal/(electric field x DC signal)], while in other figures, where only the qualitative trends are relevant, it is simply the ratio of the f signal to the applied voltage.

The temperature run on a 4.3 μm sample of MHPOBC in the cooling mode is shown in figure 1 at a frequency of 752 Hz. The peak at the highest temperature corresponds to the A-C_α^* phase transition. We assume that the ferrielectric phase consists of a repeating unit of $(m + n)$ layers having m successive layers oriented with one sign of tilt and the next n successive layers with the opposite sign of tilt. Using this model, it can be shown that the chiral interactions can give rise to the change of handedness between C_β^* and C_γ^* phases and lead to a variation of pitch depending on the values of m and n. In particular we can get true ferroelectric and antiferroelectric phases, i.e., without any helical arrangement of the unit cells in the bulk sample for $m=3$, $n=1$ and $m=2$, $n=2$ respectively. We attribute the broad peak in the electrooptic response in the ferrielectric phase to the variation of pitch with m and n as the temperature is decreased. Experimentally,[12] the pitch in MHPOBC is usually ≥ 1 μm and changes sign across the C_β^* to C_γ^* transition. It is also found to diverge in the antiferroelectric phase. Hence our sample which is $\simeq$ 4.3 μm thick can be expected to be in an *unwound* state at least in the antiferroelectric range.[13] The highest peak presumably corresponds to C_α^* to C_β^* transition. Our results can be compared with the earlier data of Glogarova *et al.*[10] on MHPOBC studied using 25 to 50 μm thick samples. The transition from smectic A to C_α^* and C_α^* to C_β^* were marked by changes in slope in their experiments.

We also measured the frequency dependence of the electrooptic response to find the relaxation frequencies (see figure 2) in the smectic A, ferroelectric and ferrielectric phases. Unlike in the studies of Glogarova *et al.*,[10] who found a step-wise decrease of the relaxation frequency as the temperature was lowered across

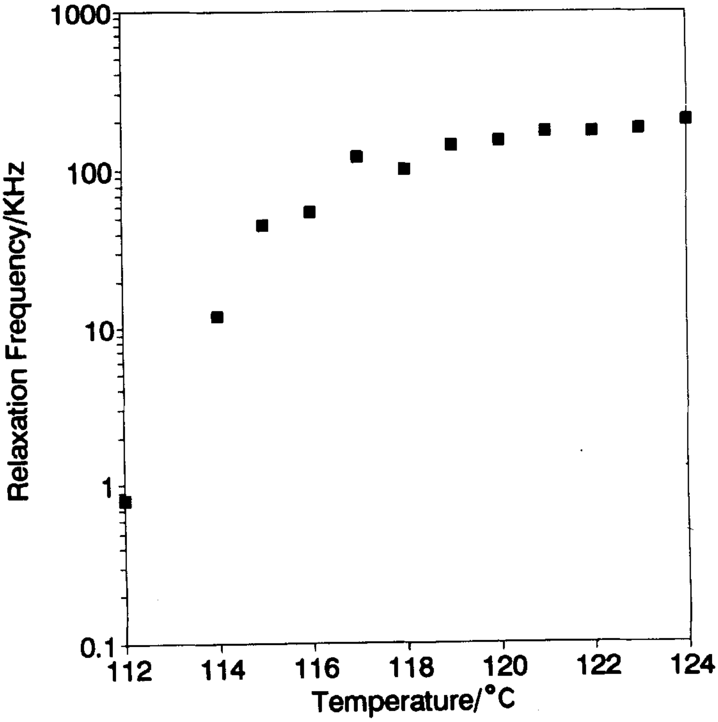

FIGURE 2 Temperature dependence of the relaxation frequency of the electrooptic signal of MHPOBC.

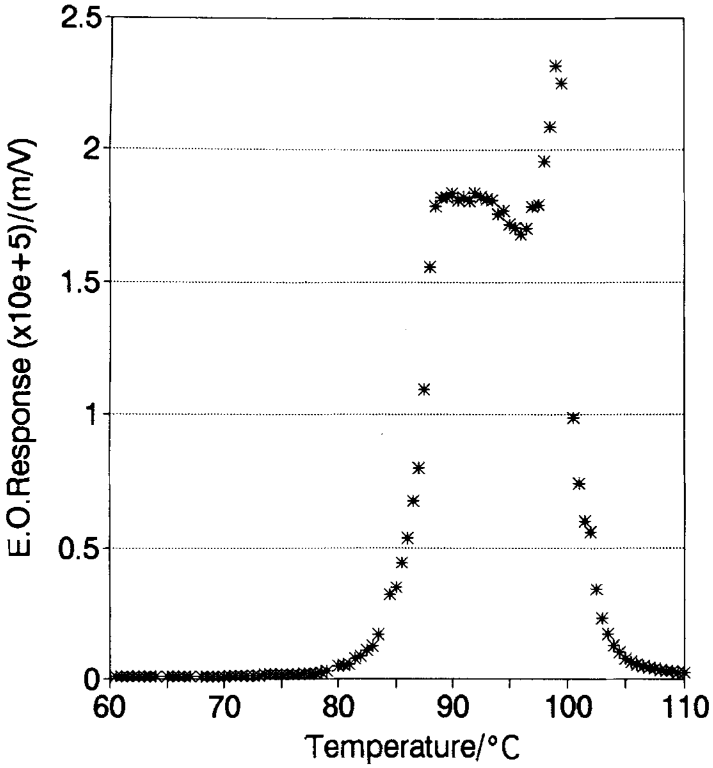

FIGURE 3 Temperature dependence of the normalised electrooptic signal (see text) of a 3.3 μm thick sample of the tolane compound at 754 Hz on cooling.

the smectic A, ferroelectric and ferrielectric phases, we find a more gradual decrease as the temperature is lowered in the tilted phases. Further, we find a measurable signal even in the antiferroelectric phase which showed a relaxation at relatively high frequencies (~10 KHz).

We conducted more detailed experiments on the tolane compound. A temperature run at 754 Hz on a 3.3 μm thick sample is shown in figure 3 and that on a 5.2 μm thick sample in figure 4. The temperature variation is very similar to that on MHPOBC. The thicker sample has a sharper drop in the vicinity of ferri- to antiferroelectric transition. The run in the vicinity of A to C_α^* transition is shown in detail in figure 5 for the 3.3 μm thick sample, which shows the phase transition very clearly. There is recent evidence that in MHPOBC the C_α^* phase has antiferroelectric and ferrielectric characteristics as the temperature is lowered.[14] The reduction in the electrooptic signal immediately below the A to C^*_α phase transition point and the subsequent increase at lower temperatures is consistent with the possibility that C8-tolane compound may also have a similar sequence. We have also studied a 2.2 μm thick sample which had an exceptionally good alignment. The electrooptic signal (figure 6) in this case was relatively high in the antiferroelectric phase and further the antiferroelectric to smectic I* transition at ~70°C and the smectic I* to smectic J* (a 3D-crystal) transition at ~64°C could be very clearly located. The signal drops by a large factor at the antiferroelectric to smectic I* transition which indicates that the hexatic I* phase also has an antiferroelectric order in this compound. The peak at the smectic I* to crystal transition probably indicates that the antiferroelectric order may be relaxed in the crystalline phase.

As the sample was heated over several days, it slowly deteriorated. It is interesting that the smectic A to C^*_α phase transition became weaker and eventually

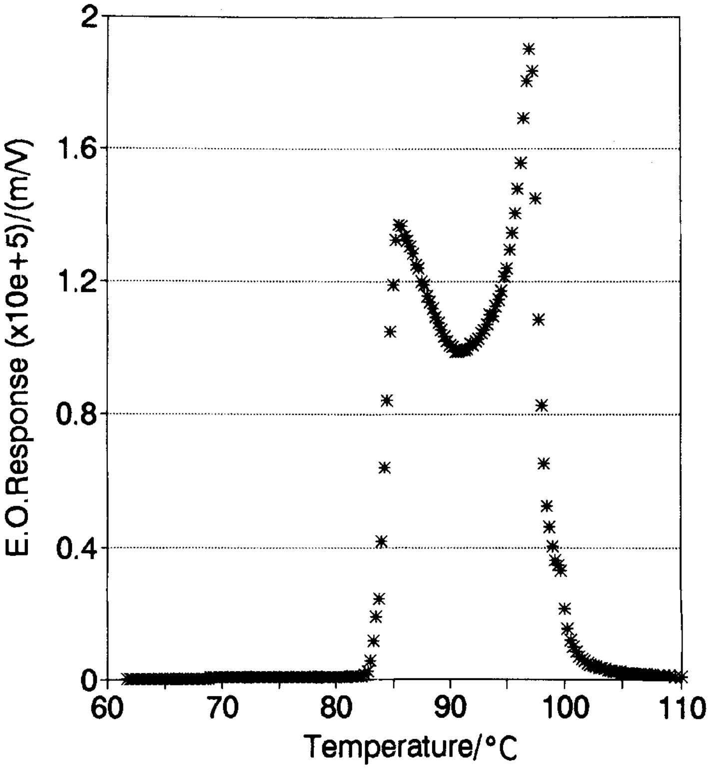

FIGURE 4 Temperature dependence of the normalised electrooptic signal of a 5.2 μm thick sample of the tolane compound at 754 Hz on cooling.

undetectable as the deterioration worsened. Further, the range of the ferrielectric phase appeared to widen at the expense of the antiferroelectric phase.

We have made detailed frequency dependent measurements on the tolane compound. As is seen in figure 7, the electrooptic signals at different frequencies drop rapidly in the ferrielectric range. The relaxation frequency is ~500-600 Hz in these phases, typical of the Goldstone mode.[8]

As the temperature is lowered in the antiferroelectric phase (fig.8), the signal level gradually decreases, but more interestingly, there appear to be two relaxations: one at a few 100 Hz, the frequency of which also decreases with decrease of temperature and another at high frequencies (~20 KHz). In the lowest temperature ranges of the antiferroelectric phase (see fig.8 and 9), only the high frequency relaxation is visible. In the smectic I* phase (fig.9), the signal decreases further compared to that in the antiferroelectric phase and the relaxation frequency decreases to ~ 10,000 Hz. (At the highest frequencies, we had to apply ~3 V/μm to

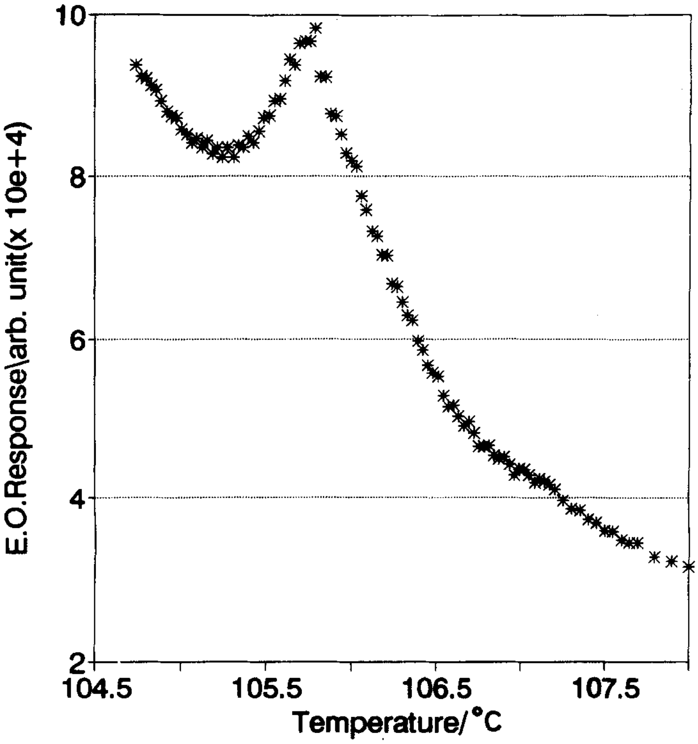

FIGURE 5 A detailed temperature run of a relatively pure tolane compound near the smectic A - C_α^* transition.

get a measurable signal in the I* phase.) We have confirmed that even in the 5.2 μm sample the electrooptic signal has a relaxation at frequencies comparable to those in the thinner samples at similar temperatures in the antiferroelectric range. However, the electrooptic response is roughly half that of 3.3 μm sample. The pitch of C8-tolane compound has been recently measured as a function of temperature (private communication from Bordeaux group). The helical sense reverses between the ferroelectric and antiferroelectric phases. The highest pitch is ~0.6 μm in the antiferroelectric phase. Hence it is unlikely that even in our thinnest sample there would be a full unwinding of the helix. However, for thin cells, the surface anchoring of the director which suppresses the helical arrangement near the glass plates effectively enhances the electrooptic effect. It is interesting to note that in none of the earlier studies on thicker samples the electrooptic signal had been observed deep in the antiferroelectric phase, and hence the high frequency relaxation in the C_A^* and I* phases is a new result.

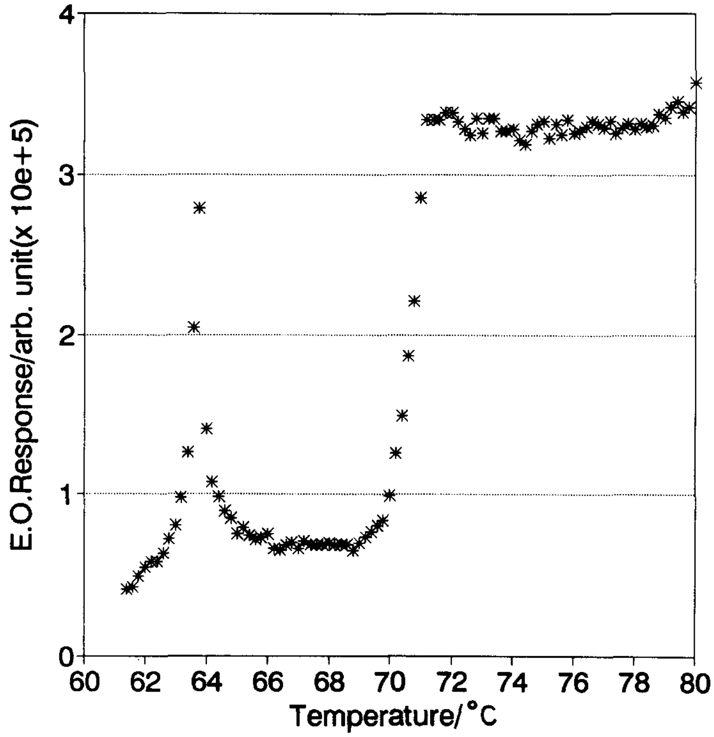

FIGURE 6 Electrooptic signal at 754 Hz in the lower temperature range of a 2.2 μm thick tolane sample showing the C_A^* to I* and the I* to crystal transitions.

The electrooptic response on the same compound has been measured by Gisse *et al.*[11] on a 23 μm thick sample. They argue that the strongest peak (see figures 3 and 4) is within the C^*_β phase rather than at the transition point between C^*_β and C^*_α phases and corresponds to the minimum in the Goldstone mode relaxation frequency. They also observed a fairly sharp peak at the C^*_β - C^*_γ transition while we see only a sharp change in the slope which probably occurs in the C^*_γ range for reasons discusssed earlier. Further, they mention that below 93°C in the antiferroelectric phase of the tolane compound they could not observe any relaxation in the dielectric constant between DC and 1 MHz.

We attribute the high frequency relaxation which we have observed to a *soft* mode involving variations of the tilt angle. As the polarization directions in neighbouring layers are antiparallel, an external field can be expected to produce an asymmetric change in the tilt angles due to the electroclinic effect (fig.10). We feel that this mode can be easily excited in the antiferroelectric phase, as in a linear

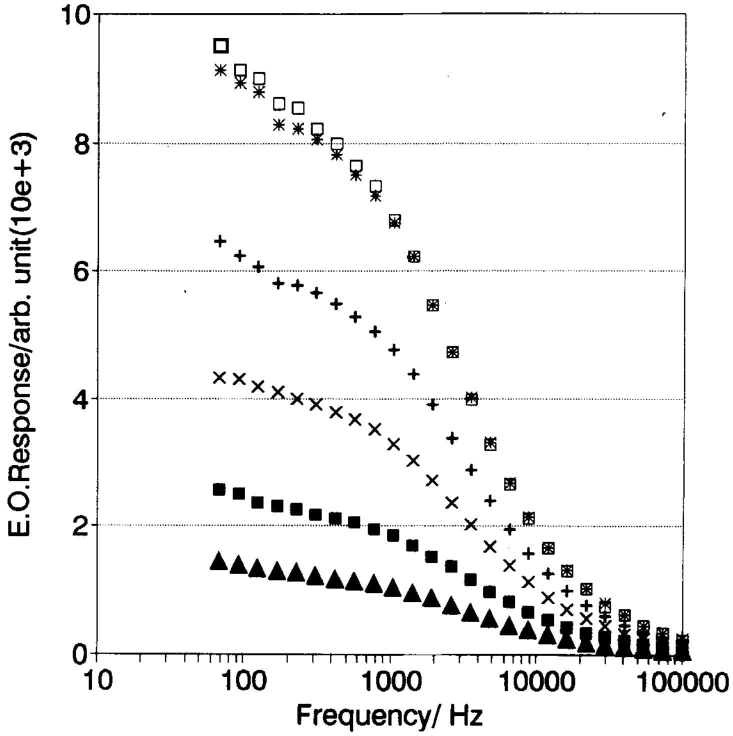

FIGURE 7 Frequency dependence of the electrooptic response at various temperatures in the ferrielectric range. □ (90°C), ★ (88°C), + (87°C), x (86°C), ■ (85°C), ▲ (84°C).

approximation the change in the tilt angle and hence in the layer thickness of neighbouring layers is equal, but opposite, i.e., there is no net change in the thickness of a *pair* of layers.

If the tilt angle in the field free case is θ_o and $\Delta\theta$ is the additional tilt introduced by the field, taking into account the fact that both θ_o and $\Delta\theta$ have opposite signs in successive layers, a simple calculation shows that the transmission coefficient in the experimental geometry is given by

$$I = I_o + eE(.707)\sin|2\theta_o| \qquad (1)$$

where e is an *electroclinic* coefficient, and I_o is the transmitted intensity in the absence of the field E. Since $I - I_o$ changes sign with that of E, we get an electrooptic signal at the frequency of the applied field.

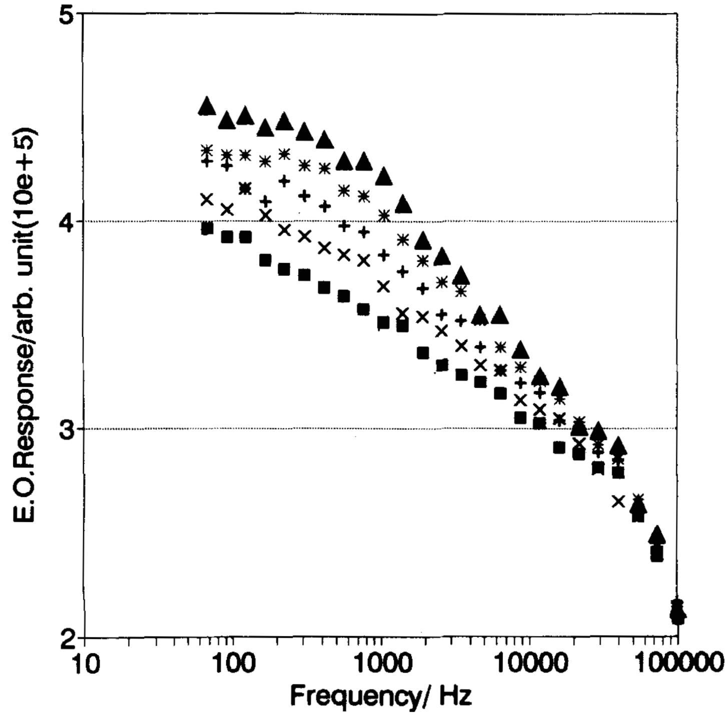

FIGURE 8 Frequency dependence of the electrooptic response at various temperatures of the C_A^* phase. ▲ (77°C), ★ (76°C), + (75°C), × (74°C) and ■ (73°C) (note the difference in scale compared to that in Fig.7).

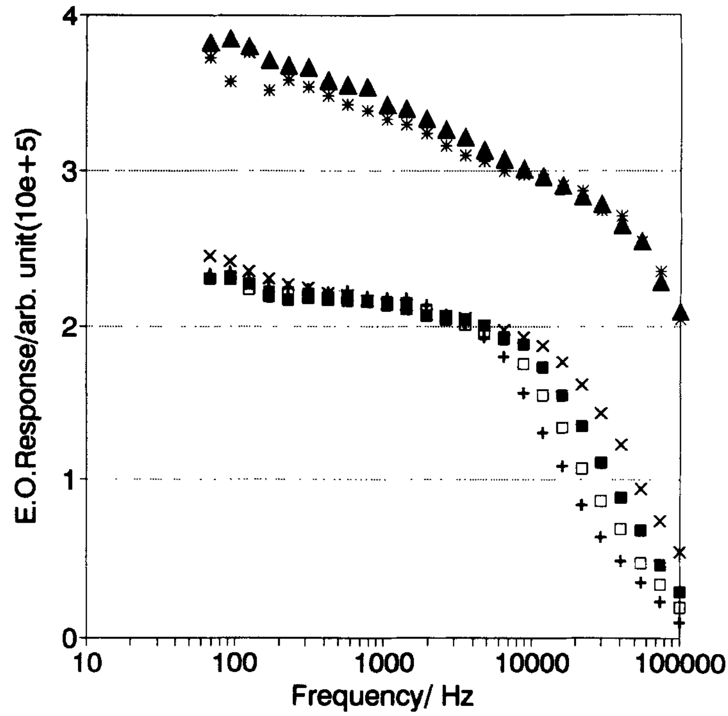

FIGURE 9 Frequency dependence of the electrooptic signal in (a) the C_A^* phase: ▲ (72°C), ★ (71°C) and (b) the I* phase: × (69°C), ■ (68°C), □ (67°C) and + (66°C). Note the relaxation at high frequencies.

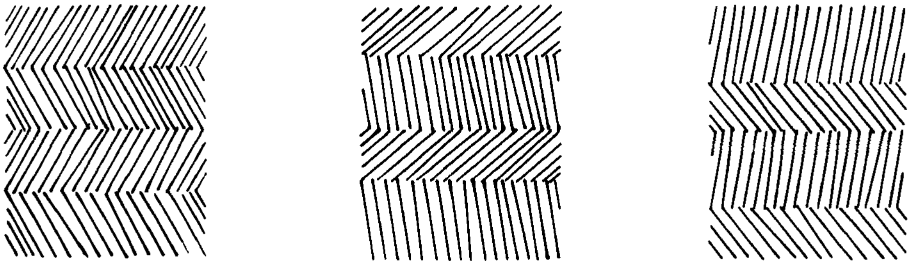

FIGURE 10 Proposed model of the soft mode in the C_A^* phase which can give rise to the high frequency relaxation shown in Fig.9. (left): the symmetric tilt of the molecules in successive layers for zero field; (middle): the asymmetric tilt of the molecules in successive layers for one sign of the electric field applied normal to the plane of the paper; (right): the asymmetric tilt for the opposite field compared to the previous case.

In summary, we have observed a new electrooptic mode which has a relatively high relaxation frequency (~10 KHz) in both the antiferroelectric C_A^* and the smectic I* (antiferroelectric) phases of the tolane compound. We have argued that it can arise from the electroclinic *soft* mode which produces an asymmetric tilt in successive layers of the antiferroelectric phases. We are now conducting Xray measurements to look for a direct evidence for this effect, and are also working out a theoretical model for this mode.

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