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Phase transitions in the antiferroelectric liquid crystal C8 tolane determined by dielectric and electro-optical measurements

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Simultaneous dielectric permittivity measurements and analysis of the first and the second harmonic electro-optical responses have been performed on a 26 μm thick planar oriented sample of the antiferroelectric liquid crystal tolane C8, which has a polymorphism similar to that of MHPOBC. Comparison of these measurements for different frequencies and geometries (in the case of the electro-optical experiment) allows one to determine all the transition temperatures. The high frequency dielectric permittivity exhibits its maximum (depending on the frequency) inside the SmA phase, whereas the electro-optical coefficient is a maximum at the transition SmA–SmC $_{\alpha}^*$ independent of the frequency. A new method for obtaining the temperature dependence of the relaxation frequency in the SmA phase is proposed.

1. Introduction

Since the first discovery of the antiferroelectric liquid crystal MHPOBC [1] many chiral compounds presenting the same mesophases, namely SmC $_{\text{A}}^*$ (antiferroelectric), SmC $_{\gamma}^*$ (ferrielectric), SmC * (ferroelectric) and SmC $_{\alpha}^*$ phases, have been synthesized. The first characterization of these phases was made by switching measurements [1–3] and by conoscopic observations [4–6]. The relaxation processes and phase transitions between these smectic phases have been studied by dielectric [7–11] or electro-optic spectroscopy [12, 13]. Unfortunately, these techniques, as well as conventional X-ray diffraction [14], pyroelectric measurements [15] or calorimetric investigations are not able to give detailed information about the molecular arrangements involved. Therefore several models have been proposed up to now for the microscopic structure of these phases [16–20].

Recently, the first direct structural evidence was obtained by resonant X-ray scattering showing 2-layer, 3-layer and 4-layer superlattices in an antiferroelectric and two ferrielectric phases [21–23]. In the SmC $_{\alpha}^*$ phase, an incommensurate periodicity equivalent to the layer thickness was found [21]. These new results have shown that it is the so-called clock model [18] which is the most consistent with the resonant X-ray scattering observations.

The temperature regions of existence of the SmC $_{\alpha}^*$ and the SmC $_{\gamma}^*$ phases are usually very narrow, typically of the order of 1 K. This makes any experimental identification of these phases difficult, and especially the transitions between them. For example, the second order phase transition SmA–SmC $_{\alpha}^*$ is difficult to observe by a number of experimental techniques because of the strong electro-clinic effect and important fluctuations of the tilt angle [24–26] in the vicinity of this transition. Therefore different (sometimes contradictory) ways of identifying this phase transition can be found in the literature. Usually some anomaly in a physical property is chosen as a criterion for the phase transition determination; this is not always justified and is a source of confusion. The same problem arises for the transitions SmC $_{\gamma}^*$ –SmC $_{\text{A}}^*$ and SmC * –SmC $_{\gamma}^*$.

The aim of this paper is to define a signature for the SmA–SmC $_{\alpha}^*$ transition, based on the anomalous behaviour of the first and the second harmonic electro-optical responses, and on the temperature dependence of the relaxation mode frequency. We also show that the position of the maximum in the temperature dependence of the dielectric constant is strongly frequency dependent and cannot be used for the transition temperature determination [27, 28]. By contrast, the position of this maximum and its variation permits the establishment of a new method of determination of the relaxation frequency and of following the temperature dependence of

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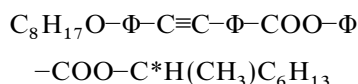
the relaxation frequency. The proposed method has several advantages with respect to the conventional one: (i) it does not need any measurement at frequencies higher than the relaxation, and thus is much less limited in frequency than the conventional method; (ii) the measurement is performed at constant frequency and is not influenced by any spurious frequency-dependent effect.

In this contribution we present *simultaneous* dielectric permittivity measurements and analysis of the first and the second harmonic electro-optical response over a broad frequency range [29]. We use the electro-optical response, which can give more information than dielectric measurements. The first advantage is the sensitivity of the optical analysis which is much higher than that of the dielectric technique. In addition, the change of the optical axis with respect to the polarizers can suppress or enhance the contribution of different modes in the first and the second harmonic optical response.

This paper is organized as follows: In §2 we present the experimental conditions and the electro-optical method for the measurements of the first and the second harmonic electro-optical coefficients. The experimental results are summarized in §3, where special attention is paid to the difference between the high frequency electro-optical and dielectric responses in the SmA phase. This difference is explained in §4. A new method for the determination of the temperature dependence of the relaxation frequency in the SmA phase is presented in §5.

2. Experimental

The liquid crystal studied was the tolane C8 [30], which has the following chemical formula:



where Φ stands for the phenyl ring. This compound shows practically the same polymorphism as MHPOBC. This was proved by texture and dislocation observations in the reflection mode on thin homeotropic samples of both compounds [31].

The samples used in our experiments were of the usual sandwich type, consisting of two parallel glass substrates with inner surfaces covered by ITO. An alignment layer of polyimide was deposited on top. To obtain a good planar alignment, the samples in the ferroelectric phase were submitted for one hour to a low frequency a.c. electric field. The sample thickness defined by mylar spacers was 26 μm .

The phase sequence of the liquid crystal C8 is the following [30]:



(tolane C8 exhibits the same phases as the liquid crystal 10OTBBB1M7 studied in the resonant X-ray scattering experiment [21]).

The temperature was controlled by an Instec heating stage. All the results presented were obtained on continuous cooling at a rate of 0.1 K min^{-1} , except for the measurements involved in the determination of relaxation frequencies which were performed at stabilized temperatures.

The dielectric susceptibility was measured using an impedance analyser (Schlumberger 1260). The measuring field from the impedance analyser served simultaneously as the source field for the measurement of the electro-optical response. The measuring field was kept as small as possible ($E < 0.2$ V per 26 μm). The conventional set-up [32, 33] was used in this experiment. The transmitted light was detected by a photo-diode and the first and the second harmonics were measured by a lock-in amplifier (EG&G, Model 5302).

The analysis of the electro-optical data was performed in the following way. The intensity I of the transmitted light for a homogeneous cell between crossed polarizers is expressed as:

$$I/I_0 = \sin^2(2\alpha) \sin^2(\beta n_a) \quad (1)$$

with

$$\beta = \pi d/\lambda \quad (2)$$

where I_0 is the intensity of the incident light, α is the angle between the smectic layer normal and the direction of the polarizer, n_a is the anisotropy of the refractive indices, d is the sample thickness and λ stands for the wavelength of light. Both α and n_a are modified by an applied electric field:

$$\alpha = \alpha_0 + \Delta\alpha \quad (3)$$

$$n_a = n_{a0} + \Delta n_a \quad (4)$$

where α_0 and n_{a0} are equilibrium values at zero field, and $\Delta\alpha$ and Δn_a are the field induced terms. Using equations (3), (4) and (1), the variation of the intensity ΔI under an electric field ΔE can be expressed up to the second order as proposed in [34]:

$$\Delta I/I_0 = 2 \sin 4\alpha_0 \sin^2(\beta n_a) \Delta\alpha \quad (5a)$$

$$+ \beta \sin^2 2\alpha_0 \sin(2\beta n_a) \Delta n_a \quad (5b)$$

$$+ 4 \cos 4\alpha_0 \sin^2(\beta n_a) (\Delta\alpha)^2 \quad (5c)$$

$$+ \beta^2 \sin^2 2\alpha_0 \cos(2\beta n_a) (\Delta n_a)^2 \quad (5d)$$

$$+ 2\beta \sin 4\alpha_0 \sin(2\beta n_a) \Delta\alpha \Delta n_a. \quad (5e)$$

The detailed discussion of the general physical conclusions from this formula will be published elsewhere [35]. For reasons of symmetry [34], the term Δn_a is

proportional to $(\Delta\mathbf{E})^2$ in the bulk, but when the symmetry is broken, for example by a d.c. biasing electric field or by the influence of boundary conditions, the variation of the birefringence can be a linear function of the field $\Delta\mathbf{E}$. In that case we should take into account all terms in equation (5).

In this paper we present the measurements obtained with a sample 26 μm thick without applying a biasing electric field. In addition as the helical pitch p in all helicoidal phases of the tolane C8 is of the order of 0.5 μm or smaller [30] ($p \ll d$), the influence of the boundary conditions can be neglected, and the results obtained therefore correspond to the bulk measurements. This means that equation (5) can be simplified to the first three terms. Note that their contributions to the linear and non-linear electro-optical responses are quite different: The first one (5a) can be detected in the first harmonic and the two others (5b) and (5c) in the second harmonic response [34]. This theoretical conclusion was verified in the C8 tolane sample for several temperatures above 98 $^\circ\text{C}$ in the SmA and SmC* phases. The first harmonic electro-optical response was measured as a function of the angle α_0 , its explicit angular dependence, and the proportionality (5a) of $\Delta I/I_0$ to $\sin 4\alpha_0$ was confirmed. From this analysis we can conclude that the maximum sensitivity for the first harmonic electro-optical response is obtained for $\alpha_0 = 22.5^\circ$, whereas this maximum for the second harmonic corresponds to the angle $\alpha_0 = 45^\circ$.

3. Experimental results

The electro-optical coefficient e is usually defined in the SmA phase as:

$$e = \Delta\theta/\Delta\mathbf{E} \quad (6)$$

where $\Delta\theta$ is the tilt angle induced by the electric field $\Delta\mathbf{E}$ (the electroclinic effect). In tilted helicoidal phases, the electro-optical response also contains other contributions induced by the optical axis rotation and by the birefringence variation, see equation (5). Hereafter, we shall consider the electro-optical coefficient as the variation of the light intensity under an electric field:

$$e_{1f} = \Delta I/I_0 \Delta E \quad (7a)$$

and similarly for the second harmonic:

$$e_{2f} = \Delta I/I_0 (\Delta E)^2. \quad (7b)$$

The first and the second harmonic low frequency ($f = 10\text{ Hz}$) electro-optic coefficients (e_{1f} and e_{2f}) are presented in figure 1 as a function of temperature. Both curves show practically the same temperature dependence as the thermal variation of the static dielectric constant. In figure 1 the values of the electro-optical coefficients are given in arbitrary units which are not

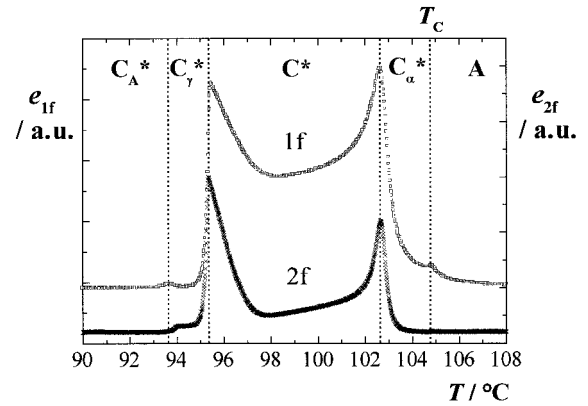


Figure 1. The temperature dependence of the low frequency ($f = 10\text{ Hz}$) electro-optical coefficients for the first and the second harmonic. e_{1f} was measured for $\alpha_0 = 22.5^\circ$, e_{2f} for $\alpha_0 = 45^\circ$.

the same for e_{1f} and e_{2f} . The second harmonic electro-optical signal is more than one order of magnitude smaller. These two measurements were performed at two different values of α_0 in order to obtain the maximum sensitivity for each measurement, see equation (5).

The temperature dependences of the dielectric permittivity ϵ and of the first harmonic electro-optical coefficient e_{1f} were measured simultaneously. Figure 2 shows the results of these measurements for the frequency $f = 1\text{ kHz}$. Both dependences are again very similar (as was the case for $f = 10\text{ Hz}$). It should be stressed that at low frequencies the electro-optical as well as the dielectric responses increase below $T = 98^\circ\text{C}$ and exhibit a significant maximum at the transition SmC*–SmC $^*_\gamma$. In this region the appearance of dechiralization lines is observed by polarizing microscopy [36]. The density of these lines increases with decreasing temperature and they disappear at the transition SmC*–SmC $^*_\gamma$ where the sharp drop in the low frequency responses is observed.

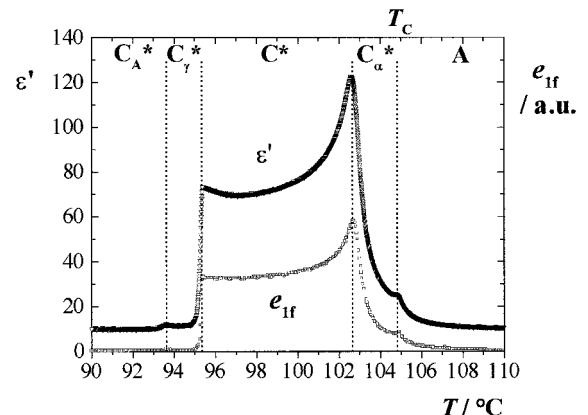


Figure 2. The dielectric permittivity ϵ' and the first harmonic electro-optical coefficient e_{1f} as a function of temperature measured simultaneously at a frequency $f = 1\text{ kHz}$.

This maximum is not observed for frequencies higher than 1 kHz. This means that in this temperature region another mode contributes to both responses, with a relaxation frequency smaller [36] than the relaxation frequency of the Goldstone mode (f_G is about 5 kHz over the whole temperature region of the SmC* phase [27]). As we are concentrating in this paper on the determination of the transition temperatures of tolane C8, we discuss this new mode (having its origin in a thickness variation of a surface layer) in detail in [36, 37].

It has been shown above that the low frequency electro-optical and dielectric responses exhibit the same temperature dependence. This is not the case for the high frequency $e_{1f}(T)$ and $\varepsilon'(T)$ (figure 3). The maximum of $\varepsilon'(T)$ has been found inside the SmA phase, whereas $e_{1f}(T)$ has the maximum at the transition temperature T_c (SmA–SmC* $_{\alpha}$).

For the exact determination of the transition temperature T_c between the SmA and the SmC* $_{\alpha}$ phase we have put together the results of four different measurements in the same plot (figure 4). Comparison of these data will show that not all of the measured characteristics undergo an anomalous change at the transition temperature.

Curve (1) presents the low frequency ($f = 120$ Hz) second harmonic electro-optical response $e_{2f}(T)$ measured for $\alpha_0 = 45^\circ$. At the transition temperature T_c it shows a sharp maximum. This measurement was completed by a simultaneous texture study using polarizing optical microscopy. At this temperature, corresponding to the maximum of $e_{2f}(T)$, a slight variation in the texture was observed. The same behaviour was found for MHPOBC antiferroelectric liquid crystal samples [38].

Curve (2) in figure 4 represents the temperature dependence of $(\Delta\varepsilon')^{-1}$ ($\Delta\varepsilon'$ is the dielectric strength of

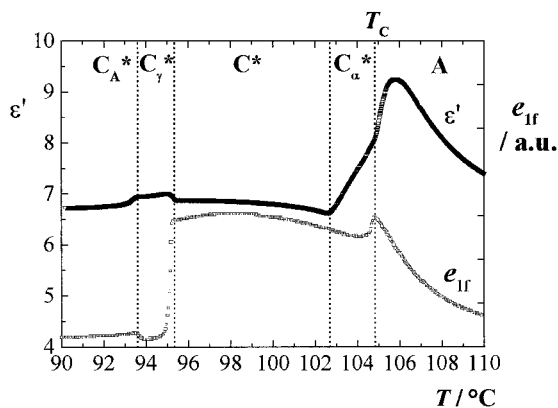


Figure 3. The temperature dependence of the dielectric permittivity ε' and the first harmonic electro-optical coefficient e_{1f} measured simultaneously at a frequency $f = 80$ kHz.

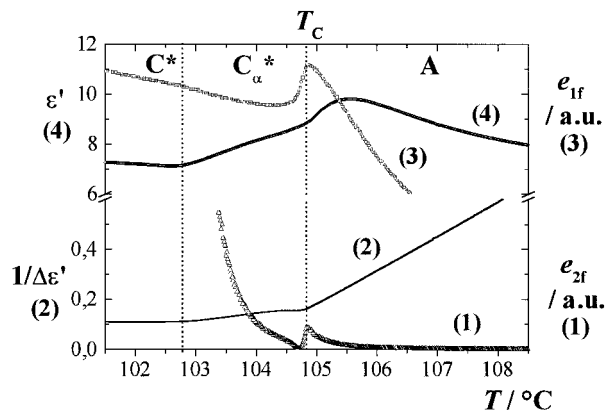


Figure 4. The transition temperature T_c between the SmA and the SmC* $_{\alpha}$ phases has been determined by comparing four different measurements. Curves (1–4) are the temperature dependences for: (1)—the low frequency ($f = 120$ Hz) second harmonic electro-optic response; (2)— $1/\Delta\varepsilon'$ measurements, where $\Delta\varepsilon'$ is the difference between the static dielectric permittivity and the high frequency dielectric permittivity far in the SmA phase; (3)—the high frequency ($f = 53$ kHz) electro-optical response e_{1f} with a maximum at T_c ; (4)—the high frequency ($f = 53$ kHz) dielectric constant ε' , the maximum of ε' is inside the SmA phase.

the soft mode) confirming the Curie–Weiss law for the SmA phase. The relaxation frequency of the soft mode in the SmA phase determined from the first harmonic electro-optical response shows the same linear dependence. The minimum frequency at the transition SmA–SmC* $_{\alpha}$ was found to be 20 kHz (see figure 5).

Curve (3) in figure 4 corresponds to the temperature dependence of the first harmonic high frequency ($f = 53$ kHz) electro-optical response $e_{1f}(T)$ showing a distinct maximum at the transition temperature T_c .

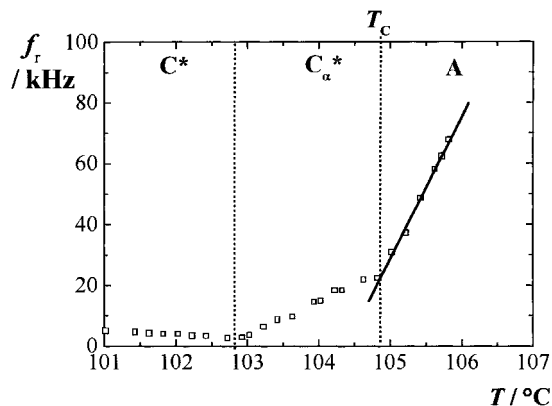


Figure 5. The relaxation frequency of C8 tolane obtained from electro-optical experiments. In the SmA phase, the relaxation frequency f_r is a linear function of the temperature (soft mode) which is in good agreement with the Curie–Weiss law found for $1/\Delta\varepsilon'$, curve (2) in figure 4.

Curve (4) is for the high frequency ($f = 53$ kHz) dielectric constant $\varepsilon'(T)$. One can also see a maximum for this dependence, but this maximum is situated inside the SmA phase.

The relaxation frequency $f_r(T)$ presented in figure 5 was obtained at stabilized temperatures by fitting the first harmonic electro-optical response $e_{1f}(f)$ with a Debye relaxator. In the ferroelectric phase, f_r corresponds to the relaxation frequency of the Goldstone mode.

In order to show that the maximum of the high frequency dielectric constant $\varepsilon'(T)$ does not correspond to the phase transition SmA–SmC $_{\alpha}^*$, in figure 6 we have plotted $\varepsilon'(T)$ for different frequencies. The maxima of these curves show an important variation in the range from 50 to 400 kHz. This experimental fact proves that the position of the maximum in the ε' dependence should not be taken as the temperature of the SmA–SmC $_{\alpha}^*$ transition, contrary to the maximum of the electro-optical response. In the next section we clarify this difference.

4. Comparison between dielectric and electro-optical measurements

The soft mode contribution to the static dielectric susceptibility in the SmA phase can be expressed as (obtained from classical Landau theory, see [39]):

$$\chi_s = \frac{\varepsilon^2 C^2}{Kq_0^2 + a(T - T_c)} \quad (8)$$

where ε is the high temperature dielectric permittivity in the SmA phase and C is the constant of bilinear coupling between the polarization and the tilt; K is the elastic constant and q_0 is the wave vector of the helical modulation; $a(T - T_c)$ is the coefficient of the quadratic term of the order parameter in the Landau free energy expansion.

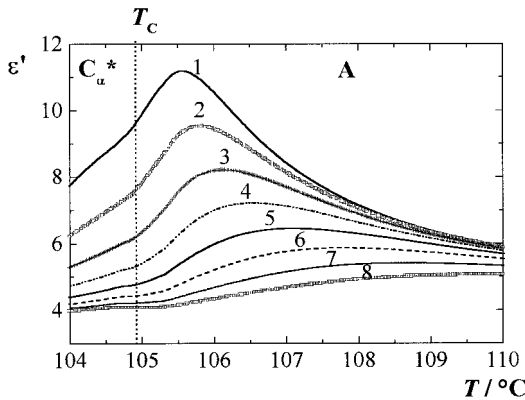


Figure 6. The temperature dependence of the dielectric permittivity ε' for different frequencies: 1—53 kHz, 2—70 kHz, 3—93 kHz, 4—123 kHz, 5—163 kHz, 6—216 kHz, 7—286 kHz, 8—378 kHz.

Similarly for the first harmonic electro-optical coefficient:

$$e_s = \frac{\varepsilon C}{Kq_0^2 + a(T - T_c)}. \quad (9)$$

As discussed in the previous section, the contribution to the first harmonic electro-optical coefficient e_{1f} is given only by the $\Delta\alpha$ contribution (5a). In the paraelectric SmA phase, $\Delta\alpha$ is equal to $\Delta\theta$ which is the tilt angle induced by the electric field (electroclinic effect) and proportional to the induced polarization $\Delta\mathbf{P}$. Then it follows that the dielectric permittivity ε should be proportional to the first harmonic electro-optical coefficient e_{1f} due to the relations: $\varepsilon = \Delta\mathbf{P}/\Delta\mathbf{E}$ and $e_{1f} = \Delta\theta/\Delta\mathbf{E}$. This is true for complex ε^* and e_{1f}^* . But for practical reasons, in dielectrics the real and imaginary parts of the complex dielectric permittivity are measured, whereas in optics, it is the module and the phase shift of the complex electro-optical coefficient which are detected.

Assuming that the dynamics of the soft mode are described by a simple Debye relaxator, the real part of the dielectric susceptibility is expressed as:

$$\chi = \chi_s \left(1 + \frac{f^2}{f_r^2}\right)^{-1} \quad (10)$$

and the module of the first harmonic electro-optical coefficient as:

$$e_{1f} = e_s \left(1 + \frac{f^2}{f_r^2}\right)^{-1/2} \quad (11)$$

where f_r is the relaxation frequency of the soft mode:

$$f_r = \frac{Kq_0^2 + a(T - T_c)}{2\pi\gamma} \quad (12)$$

with γ the viscosity coefficient. This linear dependence $f_r(T - T_c)$ is experimentally verified for $T > T_c$ as can be clearly seen in figure 5. The relaxation frequency f_r was obtained by fitting the electro-optical coefficient $e_{1f}(f)$ to the simple Debye relaxator (11). The measurements of $e_{1f}(f)$ were performed at stabilized temperatures. From the linear dependence $f_r(T - T_c)$ in the SmA phase the slope was found to be $a/2\pi\gamma = 46.6$ kHz K $^{-1}$.

From relations (10) and (11), it follows that the real part of the dielectric susceptibility is proportional to the module of the electro-optical coefficient at low frequencies ($f \ll f_r$) (cf. figure 2). This is not the case for $f > f_r(T_c)$.

For frequencies higher than $f_r(T_c)$ one can find from equation (10), using (12), that the dielectric susceptibility exhibits a maximum inside the SmA phase. The temperature T_{\max} corresponding to this maximum can be

calculated from (10):

$$T_{\max} = T_c - \frac{Kq_0^2}{a} + \frac{2\pi\gamma}{a}f. \quad (13)$$

The frequency dependence of T_{\max} is demonstrated in figure 6. One can note that all curves exhibit a small change in the slope at the temperature T_c . In order to check the linear dependence (13), T_{\max} was plotted as a function of f (see figure 7). Two regions of this dependence can be clearly distinguished. The line describing the dependence in the region close to T_c , line (a) can be expressed as $T_{\max} = 0.0225f + 104.6$, and the other, line (b), responsible for the relaxation frequency behaviour over a wide temperature region of the SmA phase, as $T_{\max} = 0.0125f + 105.1$, where the frequencies are given in kHz. The two slopes differ approximately by a factor of 2. This behaviour will be briefly discussed in § 6.

Using equation (12) in equation (11) one can easily show that $de_{1f}/dT < 0$; the module of the high frequency electro-optical coefficient is thus monotonous in the SmA phase and the extremum of e_{1f} does not depend on the frequency, and corresponds to the transition temperature T_c .

5. Determination of the relaxation frequency

It has been shown in the previous section that at low frequencies the electro-optical coefficient (more precisely its module) e_{1f} is proportional to the real part of the dielectric constant ϵ' in the SmA phase. However, the high frequency permittivity ϵ' exhibits a maximum inside this paraelectric phase at a temperature $T_{\max} > T_c$ in contrast with the module of e_{1f} . A comparison of expressions (12) and (13) shows that the frequency for which ϵ' is maximal, is the relaxation frequency f_r corresponding to the temperature $T = T_{\max}$, i. e. f can be replaced in (13) by f_r and T_{\max} by T . Therefore figure 7 can be taken

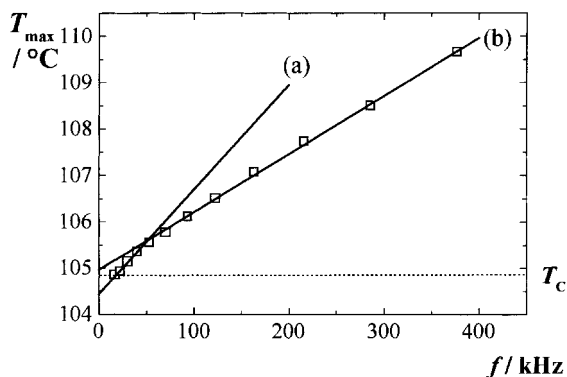


Figure 7. The temperature T_{\max} at which $\epsilon'(T)$ exhibits a maximum in the SmA phase as a function of the frequency. The experimental data were obtained from the measurements of $\epsilon'(T, f)$ (see figure 6).

as another equivalent presentation of the temperature dependence of the soft mode relaxation frequency in the SmA phase.

Using equation (13), we have calculated from the slope of line (a) in figure 7 that $a/2\pi\gamma = 44.5 \text{ kHz K}^{-1}$, in good agreement with the value found from figure 5. This fact confirms again that figure 7 represents the temperature dependence of the relaxation frequency.

The experimental determination of $T_{\max}(f)$ therefore provides a new method to obtain the temperature dependence of the relaxation frequency in the SmA phase. The traditional method is based on measurements of the dielectric or electro-optical response as a function of frequency. Analysis of the spectra obtained allows the determination of the relaxation frequency, for example from the maximum of the dielectric losses ϵ'' . The disadvantage of this technique is the fact that it also needs data at frequencies sufficiently higher than f_r . This requirement limits considerably the region of available f_r values for many reasons. These are: (i) at high frequencies the measured values can be influenced by some spurious effects; (ii) it is well known from dielectric permittivity measurements that the impedance of a liquid crystal sample with ITO electrodes is influenced at high frequencies by the resistance of these electrodes [40]; (iii) in the electro-optical experiment it is the characteristic of the amplifier which limits the frequency region.

The proposed method is free from these problems because the measurement is performed at constant frequency. The measured value is the temperature at which *this frequency is the relaxation frequency*. The position of the maximum (temperature T_{\max}) is not influenced by the above-mentioned spurious frequency-dependent effects.

We were able, using this method, to determine the relaxation frequency in the SmA phase in a temperature interval of width 4.5 K (figure 7). With the conventional method the width of the accessible temperature range is about 1 K (figure 5).

6. Discussion and conclusions

A new method for relaxation frequency determination has allowed us to increase the interval studied above T_c and to find two regions in which f_r is a linear function of temperature. Generally, liquid crystals exhibiting SmC_z^* phase show a strong electroclinic effect in the SmA phase and important order parameter (tilt angle) fluctuations close to the SmA– SmC_z^* transition. For the tolane C8, strong fluctuations have been found by Raman spectroscopy [24]. Accurate measurements of the birefringence of tolane C8 have also revealed these fluctuations [41]. For this reason we suggest an explanation of the existence of two regions in the SmA phase in this context. The relaxation process close to

Table. A synopsis of the anomalies found in the dielectric and electro-optical responses for different transitions in tolane C8.

Transition	Low freq. ϵ'	High freq. ϵ'	Low freq. e_{1f}	High freq. e_{1f}	Low freq. e_{2f}
A-C α^*	C. W. law in the A phase	Change of the slope	C. W. law in the A phase	Maximum	Maximum
C α^* -C*	Maximum	Minimum	Maximum	Small maximum	Maximum
C*-C γ^*	Maximum, sharp drop in the C γ^*	Change of the slope	Maximum, sharp drop in the C γ^*	Sharp drop	Maximum
C γ^* -CA*	Small maximum	Change of the slope	Small maximum	Small maximum	Change of the slope

T_c is mainly given by the fluctuations of the tilt or of the polarization [42], figure 7 line (a), whereas inside the SmA phase the contribution comes from the soft mode.

We have paid special attention to the determination of T_c , the temperature of transition between the SmA and SmC α^* phase. This temperature can be used as a reference temperature for the determination of the other transitions in the phase sequence of the anti-ferroelectric liquid crystal tolane C8 under consideration. The anomalies of the dielectric and electro-optical responses of this liquid crystal have been compared with the intervals of existence of different phases found by DSC [30]. The results of this comparison are summarized in the table. The temperature regions of existence of all phases found in this work do not differ very much from these found by DSC. The difference is at most 0.5 K, and this is not surprising if we take into account the difference in experimental conditions (boundary conditions, cooling rate) in the two experiments.

We do not comment in this work on the transition between the two ferroelectric phases present in the tolane C8, as only very sensitive measurements of the second harmonic electro-optical response can reveal this transition, identified by a small sharp peak. This transition, characterized by a change in the helical sign, has been discussed in [43, 44].

The comparison of different experimental methods permits us to clarify the determination of the phase transition temperatures in substances of the MHPOBC family. The most important conclusions are: (1) the high frequency dielectric permittivity exhibits its maximum (depending on the frequency) inside the SmA phase; (2) the phase transition SmC*-SmC α^* is characterized by a strong maximum for all low frequency dielectric and electro-optical responses; (3) a similar maximum is observed at the transition SmC γ^* -SmC*.

Below the temperature $T = 98^\circ\text{C}$ a new low frequency mode contributes to the low frequency dielectric and electro-optical signals, resulting in a remarkable maximum at the SmC γ^* -SmC* transition. The texture observations reveal that this mode is related to the appearance of dechiralization lines. The detailed study of this contribution will be published in [36, 37].

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