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## Liquid Crystals

Publication details, including instructions for authors and subscription information:

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R. Dabrowski; S. Urban

Online publication date: 06 August 2010

**To cite this Article** Dabrowski, R. and Urban, S.(1998) 'Dielectric studies of smectogenic dioxane mixtures revealing a nematic gap', *Liquid Crystals*, 24: 4, 583 – 586

**To link to this Article:** DOI: 10.1080/026782998207055

**URL:** <http://dx.doi.org/10.1080/026782998207055>

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# Dielectric studies of smectogenic dioxane mixtures revealing a nematic gap

by R. DĄBROWSKI

Institute of Chemistry, Military Technical Academy, Warsaw, Poland

and S. URBAN\*

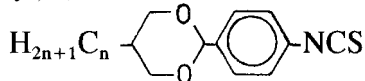
Institute of Physics, Jagellonian University, Reymonta 4, 30-159 Cracow, Poland

(Received 1 October 1997; accepted 6 November 1997)

The results of dielectric studies of two bi-component mixtures of well separated members (fourth and twelfth) of the series of 5-*n*-alkyl-2-(4-isothiocyanatophenyl)-1,3-dioxanes (*n*DBTs) are presented. Pure *n*DBTs exhibit the smectic A phase only, whereas the mixtures of well separated members of the series create a nematic gap. It was found that molecular rotations around the short axes are hindered by a lower activation barrier in the smectic A than in the nematic phase of the mixture, similarly to the situation for many pure substances with the same phase sequence. In the case of the large concentration of the longer component, a crystalline phase is created in which the short component performs uniaxial rotations in cages formed by the long molecules of the second component.

## 1. Introduction

The homologous series of 5-*n*-alkyl-2-(4-isothiocyanatophenyl)-1,3-dioxanes



(*n*DBTs) exhibits only the smectic A<sub>1</sub> (SmA<sub>1</sub>) phase [1]. From the point of view of applications such substances seem not to be interesting because of their much lower ability to give orientation in comparison with nematics. However, binary mixtures composed of well separated members of a series can often create a nematic (N) phase with very useful physical properties [1–3]. In the case of the *n*DBT series, the fourth member, 4DBT, mixed with homologues with  $n \geq 7$  reveals a nematic gap between the isotropic (I) and SmA phases. The temperature range of the N phase reaches a maximum for the 4DBT + 12DBT mixture (as shown in figure 1).

Recently we have performed dielectric studies on pure *n*DBT substances with  $n = 4 \rightarrow 10$  [4]. The relaxation times and the activation enthalpies characterizing the molecular rotations around the short axes show a peculiar behaviour in the SmA phase. In the present paper we report on similar studies performed on two mixtures of the above mentioned compounds. The motivation for these studies was the experimental finding that the activation barriers for molecular rotations around

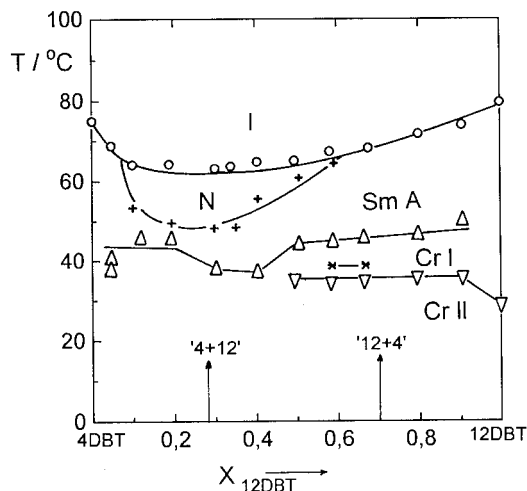


Figure 1. The phase diagram for binary mixtures of 4DBT and 12DBT. The arrows indicate the concentrations at which the present studies were performed.

the short axes are remarkably smaller in the SmA phases than in the N phase [5, 6]. We try here to check this effect for the nematic phase created by the destabilization of the smectic A phase involved when there is a large difference in the molecular lengths of the components.

## 2. Experimental and results

Two mixtures were prepared: one with a concentration of 0.28 mole fraction of 12DBT (abbreviated as '4 + 12'), corresponding to the maximum of the nematic gap

\* Author for correspondence.

(figure 1), and the second with a concentration of 0.30 mole fraction of 4DBT (abbreviated as '12+4'). Their transition temperatures obtained on cooling are

'4+12' I-64.5-N-49-SmA-35-Cr (°C)

'12+4' I-69-SmA-52-Cr<sub>I</sub>-35-Cr<sub>II</sub> (°C).

The substances were synthesized in the Institute of Chemistry of the Military Technical Academy, Warsaw. The measurements of the complex dielectric permittivity,  $\varepsilon^*(\nu) = \varepsilon'(\nu) - i\varepsilon''(\nu)$ , were performed in the frequency range 1 kHz–13 MHz using a HP 4192A impedance analyser. A parallel-plate capacitor ( $A \approx 2 \text{ cm}^2$ ) was calibrated with the use of standard liquids; the distance between the electrodes was 0.2 mm. The samples were aligned by a magnetic field ( $B \approx 0.7 \text{ T}$ ). All measurements were performed on cooling the samples, temperature was stabilized within  $\pm 0.1 \text{ K}$ .

Figure 2 presents the static permittivity  $\varepsilon_s$  as a function of temperature for both mixtures. In the case of the '4+12' mixture, the transition I–N was accompanied by a considerable increase (parallel orientation,  $\mathbf{B} \parallel \mathbf{E}$ ), or decrease (perpendicular orientation,  $\mathbf{B} \perp \mathbf{E}$ ) of the permittivity ( $\mathbf{E}$  being the measuring electric field). The parallel component,  $\varepsilon_{\parallel}$ , reaches maximum a few degrees above the N–SmA transition and then smoothly decreases through the transition point and into the smectic phase (the open points in figure 2 come from two independent runs). The perpendicular alignment always failed a few degrees above the transition to the smectic phase. The transition I–SmA in the case of the '12+4' mixture was always accompanied by a stepwise decrease of the permittivity, similarly to that in the studies of the pure substances [4]. However, the static

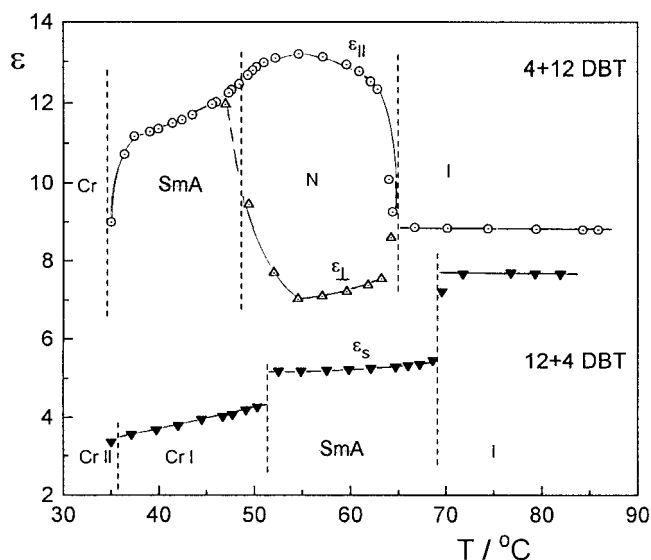


Figure 2. Temperature dependence of the static permittivities of the two binary mixtures.

permittivity does not decrease to the high frequency value  $\varepsilon_{\infty}$  at the SmA–crystalline (Cr<sub>I</sub>) phase transition as for the pure compounds: this happens at the second, Cr<sub>I</sub>–Cr<sub>II</sub>, phase transition.

The dielectric relaxation spectra were analysed with the Cole–Cole equation

$$\frac{\varepsilon^*(\omega) - \varepsilon_{\infty}}{\varepsilon_s - \varepsilon_{\infty}} = \frac{1}{1 + (i\omega\tau)^{1-\alpha}}, \quad (1)$$

where  $\tau$  is the relaxation time and the parameter  $\alpha$  characterizes the distribution of the relaxation times. Figure 3 presents the dispersion and absorption spectra which are representative for particular phases of both mixtures. The lines are the fits of the imaginary part of equation (1) to the spectra. The relaxation times were calculated from the frequency of the maximum of the losses  $\varepsilon''_{\max}$ :  $\tau = (\omega_{\max})^{-1} = (2\pi\nu_{\max})^{-1}$ . They are presented in figure 4 in the form of the Arrhenius plots.

### 3. Discussion

In ref. [4] we analysed the electric structure of DBT molecules, concluding that their net dipole moment  $\mu \approx 4.1 \text{ D}$  and is inclined from the *para*-axis of the benzene ring by  $\beta \approx 31^\circ$ . The static permittivity in the isotropic phase,  $\varepsilon_{is}$ , gradually decreases with  $n$  which indicates that the effective dipole moment becomes 'dissolved' in the longer alkyl chains. In the case of the mixtures under study, the static permittivity of the isotropic phase is 8.0 for the '4+12' and 7.7 for the '12+4' mixture (figure 2). Taking into account the actual concentrations of the components and  $\varepsilon_{is}$  values measured for the pure substances (10.7 for 4DBT and 6.7 for 12DBT), one can conclude that the dipole moments exhibit antiparallel correlations in the isotropic phase of the mixtures.

#### 3.1. '4+12' Mixture

The large value of the dielectric anisotropy,  $\Delta\varepsilon = \varepsilon_{\parallel} - \varepsilon_{\perp} \approx 6$ , observed in the nematic phase of the '4+12' mixture is characteristic for strongly polar substances and is comparable with the anisotropies obtained for other isothiocyanato compounds [7–10]. The parallel component survives to some extent to the smectic phase, whereas the perpendicular one could not be kept stable from a few degrees above the N–SmA transition (figure 2). The  $\varepsilon_{\parallel}^*$  relaxation spectra of the nematic phase show some distribution of the relaxation times ( $\alpha \sim 0.1$ ). After cooling to the SmA phase these spectra exhibit a small distortion at the low frequency side which is better seen in the Cole–Cole plot (figure 5). This suggests that the rotations of molecules of particular components about the short axes become separated in the SmA phase. However, the spectrum is dominated by the rotations of the shorter 4DBT molecules (compare figures 3 and 5),

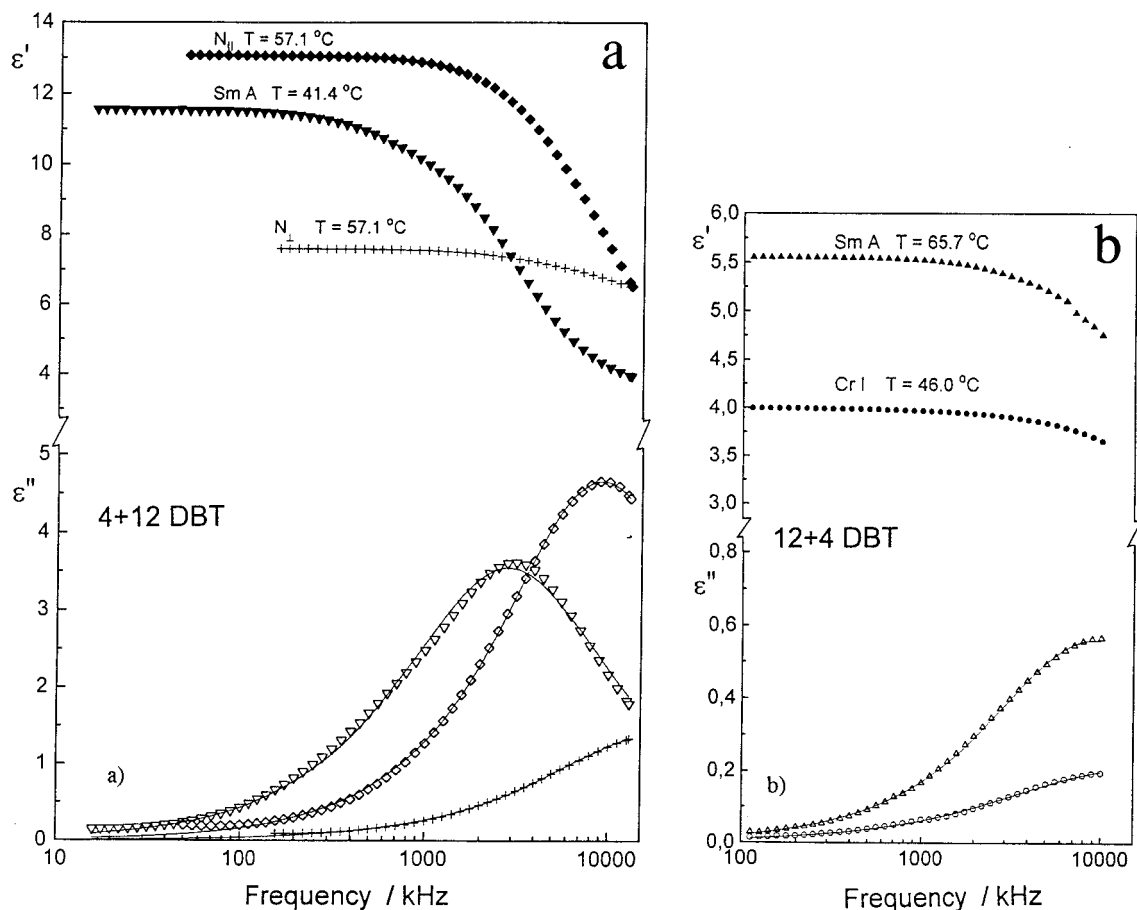


Figure 3. Dispersion and absorption spectra in different phases of mixtures: (a) '4+12', (b) '12+4'. Solid lines are the fits of the imaginary part of equation (1) to the experimental spectra.

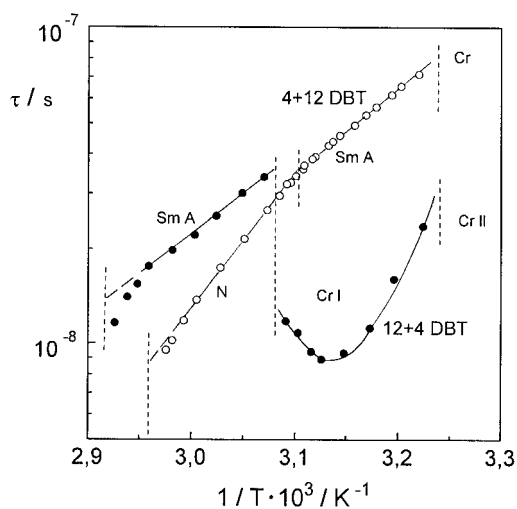


Figure 4. Arrhenius plots for the two mixtures in different phases. The deviations from the straight lines of the points close to the clearing temperatures are probably caused by the two phases regions.

and we assume that the average relaxation time  $\tau_{\parallel}$  calculated from the position of the maximum of the losses (figure 3) well characterizes the relaxation of this component. The activation enthalpies calculated from the Arrhenius equation,  $\tau_{\parallel} = \tau_0 \exp(\Delta H_{\parallel}/RT)$ , are equal to  $78.5 \pm 3 \text{ kJ mol}^{-1}$  in the N phase and  $51.1 \pm 2 \text{ kJ mol}^{-1}$  in the SmA phase (this latter value is  $10 \text{ kJ mol}^{-1}$  smaller than that for pure 4DBT in the SmA phase [4]). Thus, the energy barrier hindering the molecular rotations about the short axes is markedly lower in the SmA than in the N phase of the '4+12' mixture; this is similar to the behaviour observed for many pure substances with nematic and smectic polymorphism [5, 6]. For the perpendicularly oriented nematic sample, the relaxation spectra are shifted to distinctly larger frequencies (see figure 3).

### 3.2. '12+4' Mixture

In the case of this mixture the dielectric properties of the SmA phase are similar to those observed for the pure substances [4]. The large value of  $\epsilon_{\infty} \approx 4.3$  suggests that in this case too the high frequency relaxation

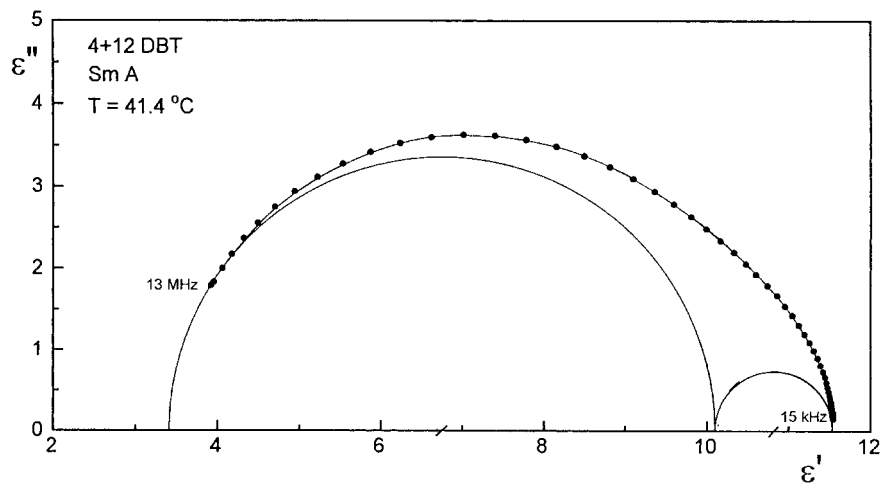


Figure 5. Cole-Cole plot for the spectrum of the SmA phase of the '4+12' mixture shown in figure 3(a). The semi-circles are the fits of two Debye-type processes.

process connected with the rotations of molecules around the long axes exists. After cooling the sample, the next two transitions were observed (see figures 2 and 4). In the high temperature crystalline phase ( $Cr_I$ ), a relaxation process was still observed, however its amplitude (increment  $\delta\varepsilon = \varepsilon_s - \varepsilon_\infty$ ) diminished with cooling and at the second transition it disappeared. The calculated relaxation times show a very strange temperature dependence (see figure 4).

As can be seen in figure 4, the relaxation time behaves normally in the SmA phase only, whereas in the  $Cr_I$  phase its temperature dependence is rather unexpected in spite of a prolonged temperature stabilization. The unusual shortening of  $\tau$  at the SmA- $Cr_I$  phase transition, its further decrease and then increase, as well as a systematic decrease of the dielectric increment  $\delta\varepsilon$  with lowering of the temperature in the  $Cr_I$  phase, can be explained as follows. The '12+4' mixture is dominated by the longer 12DBT component which affects the dielectric spectra rather slightly—compare figure 5 (pure 12DBT in the SmA phase exhibited very small dispersion and the relaxation spectra were broad). Therefore, the observed relaxation process in the SmA phase of the mixture is caused by the distinctly shorter 4DBT molecules which are dissolved in the 'cages' formed by the longer 12DBT molecules. In such a situation, the reorientations of 4DBT molecules are limited to the long axis (uniaxial rotation). This causes a stepwise decrease of the permittivity at the transition due to the smaller value of the perpendicular component of the dipole moment (figure 2), and a considerable decrease in the relaxation times (figure 4). In the course of the cooling process, the ordering of the host 12DBT molecules facilitates the molecular rotations, but beginning at some temperature, the 'cages' become too narrow and the reorientations disappear. This causes a considerable increase in  $\tau$  and a decrease in  $\delta\varepsilon$  which reaches almost

zero close to the  $Cr_I$ - $Cr_{II}$  transition (a real transition point was seen due to disappearance of the losses).

Concluding, we can say that the dielectric relaxation studies give important information about the molecular dynamics in bi-component mixtures of well separated members of the same homologous series. The activation barrier hindering the molecular rotations around the short axes in the mixture exhibiting the nematic and smectic A polymorphism behaves similarly to the case for pure substances with the same phase sequence. A large concentration of the longer component leads to a crystalline phase in which the short component performs uniaxial rotations in cages formed by the long molecules of the second component.

This work was supported by the Polish Research Project No. 2 P03B 059 13, coordinated by KBN.

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