

## A non-standard temperature dependence of the order parameter of the 5CB liquid crystal doped with an azo-derivative

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### Abstract

The effects of the *cis* and *trans* form of the 4-OMe-phenylazobenzene at 1% and 7% mole fraction on order, mesophase stability and dynamics of the 5CB liquid crystal were studied using the ESR spin probe technique. The presence of the *trans* azo-derivative induced a downshift of the nematic–isotropic transition temperature  $T_{NI}$  which increased with the concentration but did not change the dependence of the order parameter on the reduced temperature. The *cis* isomer caused even larger  $T_{NI}$  shifts, determining a marked decrease of the order parameter with a peculiar dependence on the reduced temperature, quite different from the standard Haller-type behavior. The spin probe dynamics appeared instead to be essentially unchanged by the presence of the azo-derivative.

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## I. INTRODUCTION

In recent years a great deal of technological interest has been generated by photoresponsive materials formed by a nematic liquid crystal (LC) with a variable amount (usually a few percent) of an azobenzene derivative dissolved. Besides the possible direct applications of these materials, ranging from optical switching to information storage devices [1], systems of this type have also attracted attention as simpler models for the study of the fundamental working principles of photoresponsive polymers [2, 3]. Depending upon the nature of the components, the photomodulation of the nematic phase allows either to modify the LC director orientation (“order–order” change) or to induce a phase transition (“order–disorder” change) [4]. Both these processes can be performed via the well-known azo-derivative *trans–cis* reversible photoisomerization.

In particular, the “order–disorder” change, which is the object of the present study, has been interpreted in terms of a change of the ordered phase stability. The rod-like shape of the para-substituted *trans* isomer, being similar to that of the LC host, has a limited influence on the nematic phase, while the bent, V-shape of the *cis* azo-derivative introduces a large destabilization which causes a marked shift of the nematic–isotropic (N–I) phase transition to a lower temperature. The *trans–cis* photoisomerization leads to a lowering of the nematic–isotropic transition temperature ( $T_{NI}$ ) of the mixture and thus, when the  $T_{NI}$  is reduced below the current sample temperature, the system will effectively undergo an isothermal N–I (“order–disorder”) phase transition.

## II. EXPERIMENTAL

The structure of the 4-OMe-phenylazobenzene (OMPAB) photoactive unit used in this study is shown in Fig. 1.

**Insert Figure 1 here.**

OMPAB was synthesized according to the Mills reaction [5], in which nitrosobenzene combines with primary arylamines in glacial acetic acid to give unsymmetrical azo-derivatives. The compound obtained did not show any LC phase.

The host matrix employed was the LC 4-cyano-4'-n-pentylbiphenyl (5CB), having a nematic range between 295.7 and 308.5 K. It was obtained from Merck KGaA (Darmstadt, Germany) and used without any further purification. To monitor the order and the dynamics of the LC system, we chose the nitroxide spin probe 3 $\beta$ -DOXYL-5 $\alpha$ -cholestane (CSL), purchased from Aldrich. Its size, rigidity and rod-like shape similar to that of the 5CB make this molecule a suitable probe for our purposes [6, 7]. The CSL structure together with the standard choice for the molecular frames and the corresponding definition of the principal components  $D_{\perp}$  (reorientation of the molecular long axis) and  $D_{\parallel}$  (rotation around the long axis) of the rotational diffusion tensor have been presented in a previous work [7].

The samples were prepared by adding OMPAB to a solution of CSL spin probe in 5CB with a concentration of  $6 \times 10^{-4} \text{ g}_{CSL}/\text{g}_{5CB}$ . Two values of the azo-derivative mole fraction were studied:  $x = 1\%$  and  $x = 7\%$ . The good solubility of the spin probe and of the OMPAB in 5CB, at the concentrations studied, made it possible to prepare uniform samples just by mechanical mixing at a temperature slightly above  $T_{NI}$ , without adding any solvent.

The samples not requiring photoisomerization (*trans* isomers) were stored in the dark at room temperature into glass capillaries of 1.8 mm internal diameter, until ESR measurements. To obtain the *cis* isomers, according to the *trans-cis* photoisomerization reaction (see Fig. 1), the samples were exposed to UV-light ( $\lambda=365 \text{ nm}$ ) in a quartz cuvette with a UVGL-58 MINERALIGHT Lamp (UVP). The *trans-cis* photoisomerization was monitored by recording, during the exposure, a series of UV-visible absorption spectra with a Cary 1E (Varian) spectrophotometer. UV-visible spectra were taken before any irradiation and after different times of exposure, dissolving 5CB azo-doped samples in cyclohexane to achieve a concentration of the azo-derivative of  $2.5 \times 10^{-4} \text{ M}$ .

The *trans* isomer spectra exhibited a strong absorption band at about 340 nm, due to  $\pi \rightarrow \pi^*$  transition, and a much weaker band centered at 450 nm, due to  $n \rightarrow \pi^*$  transition. Both these features are characteristic of *trans*-azobenzene type molecules. Irradiation at 365 nm caused a decrease of the  $\pi \rightarrow \pi^*$  band intensity and a build-up of the  $n \rightarrow \pi^*$  band, which was slightly shifted toward shorter wavelengths. This was an indication that the isomerization was taking place. We decided to consider the process successful when we could not observe any further change by comparing two consecutive UV-visible spectra (see Fig. 2). This typically required between 10 and 24 hours, depending on the OMPAB concentration. Immediately after the isomerization, the samples doped with the

*cis* azo-derivative were inserted into the capillaries and ESR spectra were recorded. After the ESR measurements, a further UV-visible absorption spectrum was taken and compared to the last one taken immediately before the ESR measurements. In all the cases, these spectra were essentially identical, indicating that the *cis* isomers did not significantly reverse to the *trans* configuration during the measurements.

**Insert Figure 2 here.**

The ESR spectra were acquired with a Bruker ESP300E spectrometer equipped with an ER 041XG microwave X-band (9.5 GHz) Gunn Diode bridge and a rectangular ER 4102 cavity. The samples were thermostated with a nitrogen flux through a variable temperature unit Bruker B-VT 2000. The temperature, monitored with a calibrated type T thermocouple (Comark Ltd.) located in contact with the capillary containing the sample, showed a stability better than  $\pm 0.05$  K. We recorded ESR spectra on heating taking the samples from the N to the I phase, in a range of about 20 K around the  $T_{NI}$ .

### III. RESULTS AND DISCUSSION

The ESR spectra simulation program adopted was based on a set of Fortran routines implementing the “slow tumbling” theory for a spin probe reorienting in a LC, developed by Freed and collaborators [8–10], combined with a software package [11] that optimizes the fit parameters for a series of spectra at the same time (global target analysis) using the Gauss-Newton-Marquardt non-linear least squares method [12].

We started our analysis by applying the same globalization scheme proposed in previous works [7, 13], where, for each sample, the spectra recorded at different temperatures, within the same phase (N or I), are fitted simultaneously in a global analysis. The ESR spectra of each sample are reproduced considering as variable, not global, fit parameters the orientational order parameter of the probe  $\langle P_2 \rangle$  and the perpendicular component of the probe rotational diffusion tensor  $D_{\perp}$ . To minimize the correlation between the components of this tensor, the ratio  $D_r = D_{\parallel}/D_{\perp}$  was also introduced.

Spectra in the I phase were fitted by keeping the values of  $\langle P_2 \rangle$  fixed to zero and considering  $D_r$  as a global variable. This approach gave stable and uncorrelated values for the

parameters with a  $D_r$  of 9.9. In a series of preliminary fits, the temperature dependence of  $D_r$  in the N phase, for each sample, was described by a Haller-type equation:

$$D_r(T) = D_r^0(1 - T/T_c)^\gamma + D_r^I, \quad (1)$$

where  $T_c$  is the temperature at which the  $\langle P_2 \rangle$  drops to zero,  $D_r^I$  is the diffusion coefficient ratio of the I phase which was kept fixed to the value indicated above, whereas  $\gamma$  and  $D_r^0$ , the limiting deviation of  $D_r$  from the isotropic value at zero temperature, were adjustable global parameters. Unfortunately, this choice for the temperature dependence of  $D_r$  did not help significantly to reduce the correlation among the parameters. A more appropriate approach seemed to be considering  $D_r$  simply independent of the temperature, as done for the I phase.

As expected, the presence of the azo-derivatives induced a decrease of  $T_{NI}$ , as reported in Table I. We also observed that the temperature transition downshift increased with the solute concentration and was larger for the *cis*-doped samples.

**Insert Table I here.**

In samples containing the *trans* isomer, at both concentrations, the temperature dependence of the  $\langle P_2 \rangle$  (on the reduced temperature,  $T^* = T/T_{NI}$ ) and of the dynamics (on the absolute temperature) were essentially identical to those observed in the pure 5CB.

Unfortunately, in samples doped with the *cis* isomer, despite the apparent good fit of the experimental spectra (not shown), the globalization scheme presented above did not seem to be able to recover reasonable parameters. In particular, at 1% *cis* there was only a slight decrease of the order parameter, with respect to the pure 5CB, across almost the whole nematic phase but not in a range of temperatures close to  $T_{NI}$ , where the deviation was significantly larger and the  $\langle P_2 \rangle$  seemed to approach the N-I phase transition in a continuous fashion, despite its first order nature. At 7% *cis* the orientational order was significantly reduced, showing, toward the end of the N phase, an almost linear dependence on the  $T^*$ , quite peculiar for an order parameter, and no transition at all. Finally, the recovered parameters for the rotational dynamics were also difficult to rationalize exhibiting unusual correlations and unreasonably large errors.

Altogether, these results suggested that the adopted model was not appropriate to describe the *cis*-doped samples whose behavior turned out to be more complex than expected (see below). In fact, LC mixtures containing non-mesomorphic solutes can be affected not only by a downshift of the  $T_{NI}$ , as we have seen in our samples, but also by a broadening of the transition temperature, due to the onset of a biphasic (N/I) region as the system approaches the  $T_{NI}$  [14, 15]. In the biphasic region, the nematic and the isotropic phases coexist in equilibrium and the solute is distributed between them, according to its activity coefficients.

A more detailed examination of the ESR spectra relative to the *cis*-doped samples, acquired near the  $T_{NI}$ , indeed suggested that those line shapes could be related to the superposition of a nematic and an isotropic spectrum. The presence of a biphasic region was then confirmed with a polarizing microscope, by observing the temperature behavior of the samples throughout the N phase up to the N–I transition. The cholestane partitioning between the two phases could in principle affect the analysis of the ESR spectra, and thus the recovery of meaningful parameters, particularly if the probe concentration in the nematic (or isotropic) phase became so low to hinder the detection of the corresponding contribution to the spectra. However, here we did not encounter this problem: in fact, all the ESR spectra relative to the biphasic regime clearly showed the features characteristic of both the phases, including the line positions that determine the order parameters (see Fig. 3). We thus expect the CSL spin probe to be partitioned essentially uniformly between the phases, reporting the LC behavior of the ordered nematic and the isotropic environment.

In the final fits, we adopted, therefore, a different globalization scheme where the spectra corresponding to a biphasic system were fitted to a weighted sum of two spectra, one for each phase, modeled with the same set of parameters described above but keeping, for the nematic contribution,  $D_r$  fixed to 7.1, the value obtained for the pure 5CB, to further minimize the correlation. For consistency, nematic spectra that did not show phase coexistence, were also fitted by keeping  $D_r$  fixed to 7.1. Isotropic spectra were fitted as described in the previous globalization scheme. The good agreement between the experimental and the calculated spectra is shown in Fig. 3.

**Insert Figure 3 here.**

In Fig. 4 we show the results relative to the probe orientational order, plotted against the reduced temperature  $T^*$  to easily compare the behavior of the pure LC and the ones relative to the azo-doped samples. The  $\langle P_2 \rangle$  temperature dependence of the pure 5CB and of the *trans*-doped samples, at both concentrations (Fig. 4 (a)), was found to be, as expected, identical to the one obtained with the first globalization scheme. The reduced temperature dependence of the  $\langle P_2 \rangle$  of *cis*-doped samples (Fig. 4 (b)) showed a discontinuity at the  $T_{NI}$ , typical of a first order transition.

**Insert Figure 4 here.**

At the larger concentration of 7% (Fig. 4 (b)), for  $T^* > 0.98$ , the  $\langle P_2 \rangle$  values showed a peculiar behavior, quite different from the standard Haller-type decrease of the order parameter, normally observed. This can be explained considering that approximately at  $T^* = 0.98$  the system enters the biphasic region, where the azo-derivative is distributed between the two coexisting phases, resulting in a decrease of its concentration in the N phase. A lower concentration of the azo-derivative will reduce the destabilization of the N fraction, causing the observed small increase of the  $\langle P_2 \rangle$ . As the system approaches the phase transition, the  $\langle P_2 \rangle$  behavior is therefore determined essentially by two effects: a further decrease of the concentration of the azo-derivative in the N phase and the increase of the temperature. The first effect would increase the order of the N phase even further but the second will, of course, act in the opposite direction, resulting in the observed peculiar behavior of the  $\langle P_2 \rangle$ .

The dynamics appeared essentially independent of the nature, the configuration and the concentration of the azo-derivative, while was found to have a different trend in the N and in the I phase. In fact, the temperature dependence of the tumbling diffusion coefficient  $D_{\perp}$  of the spin probe is well represented by an Arrhenius-type behavior, ( $D_{\perp} = D_0 \times \exp[-E/RT]$ ), with  $D_0 = (6 \pm 2) \times 10^7 \text{ ns}^{-1}$  and  $E = 53 \pm 2 \text{ kJ/mol}$  for the N and  $D_0 = (3 \pm 1) \times 10^5 \text{ ns}^{-1}$  and  $E = 41 \pm 2 \text{ kJ/mol}$  for the I phase.

## IV. CONCLUSIONS

The presence of the azo-derivative, even at the lower mole fraction of 1%, induces a shift of the nematic–isotropic transition to a lower temperature. The shift increases, as expected, with the concentration of the azo-derivative and is always larger for the *cis* isomer.

A comparison of the reduced temperature dependence of  $\langle P_2 \rangle$  for each sample reveals that at 1% and 7% *trans* (Fig. 4 (a)) and 1% *cis* (Fig. 4 (b)), the destabilization caused by the azo-derivative results essentially in a shift of the whole phase diagram to a lower temperature. In fact, in these cases, the  $\langle P_2 \rangle$  dependence on  $T^*$  is identical to that of the pure 5CB and it begins to show only a small decrease for the *cis* at 1%. At 7% *cis* (Fig. 4 (b)), instead, the order of the phase is clearly lower than that of the pure 5CB, indicating that the shift of the phase diagram to a lower temperature is no longer able to compensate the destabilization introduced by the azo-derivative.

Moreover, in this case the system shows a region of phase separation which begins approximately at  $T^* = 0.98$ . The occurrence of a biphasic region within what was supposed to be a purely N phase, is suggested by a peculiar ESR line shape which looks significantly different from a typical nematic one and is confirmed by the polarizing microscope observations. The fit of the biphasic spectra is then successfully carried out using the second model proposed. The  $\langle P_2 \rangle$  dependence on  $T^*$  shows a peculiar behavior where the order parameter slightly increases as the system enters the biphasic region. In the cases studied, the spin probe dynamics in the presence of the azo-derivative is essentially unchanged with respect to that observed in the pure 5CB. A more systematic study of the effects of different azo-derivatives on the order, the mesophase stability and the occurrence of a biphasic region in 5CB is under way.

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## TABLES

Table I: Nematic–isotropic phase transition temperatures ( $T_{NI}$ ) and corresponding shifts with respect to the pure 5CB ( $\Delta T_{NI} = T_{NI,5CB+OMPAB} - T_{NI,5CB}$ ) for the liquid crystal samples doped with *trans* or *cis* 4-OMe-phenylazobenzene (OMPAB) at the two concentrations studied (1% and 7%).

	$T_{NI} / \text{K}$				$\Delta T_{NI} / \text{K}$			
	<i>trans</i>		<i>cis</i>		<i>trans</i>		<i>cis</i>	
	1%	7%	1%	7%	1%	7%	1%	7%
5CB + OMPAB	308.3	307.5	306.0	289.5	-0.2	-1.0	-2.5	-19.0
pure 5CB	308.5							

## FIGURE CAPTIONS

Fig. 1 Chemical structure of 4-OMe-phenylazobenzene (OMPAB) together with the *trans-cis* photoisomerization scheme.

Fig. 2 Typical absorption spectra recorded after different times of UV exposure for 5CB doped with 4-OMe-phenylazobenzene (OMPAB) dissolved in cyclohexane (see text for details).

Fig. 3 Typical experimental ESR spectra (dashed line) and fits (solid line) obtained with the second model proposed. For each spectrum, the temperature, the azo-derivative concentration, the isomer type and the corresponding phase are indicated. Spectra labeled 7% *cis* were recorded at temperatures close to the N-I phase transition where the N and the I phase coexist (see text for details).

Fig. 4 Order parameter  $\langle P_2 \rangle$  of the spin probe against reduced temperature  $T^*$  for the samples doped with (a) the *trans* and (b) the *cis* 4-OMe-phenylazobenzene (OMPAB) at 1% and 7% mole fractions, compared to the pure 5CB. The results shown were obtained with the second model considered (see text for details).

## FIGURES

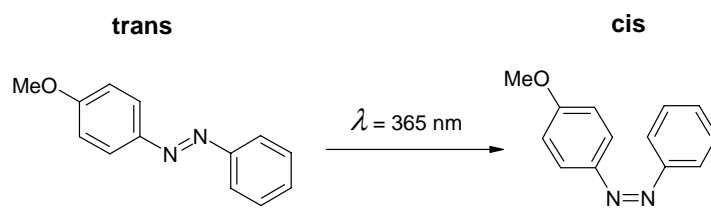


Figure 1:

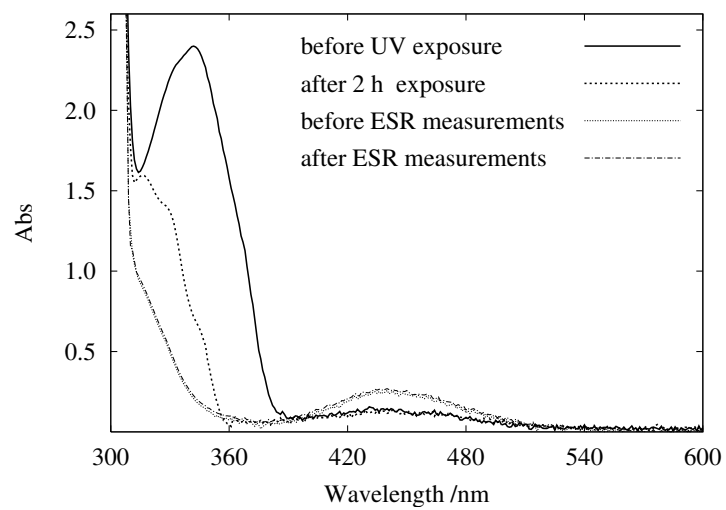


Figure 2:

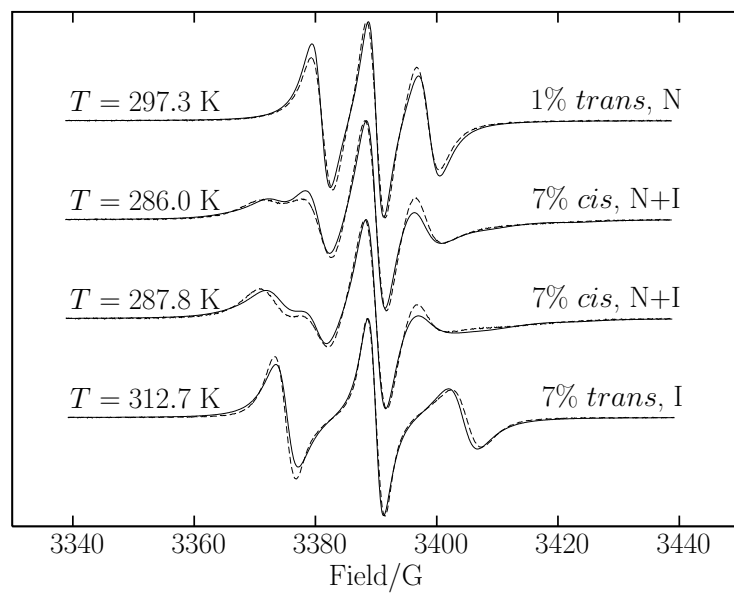


Figure 3:

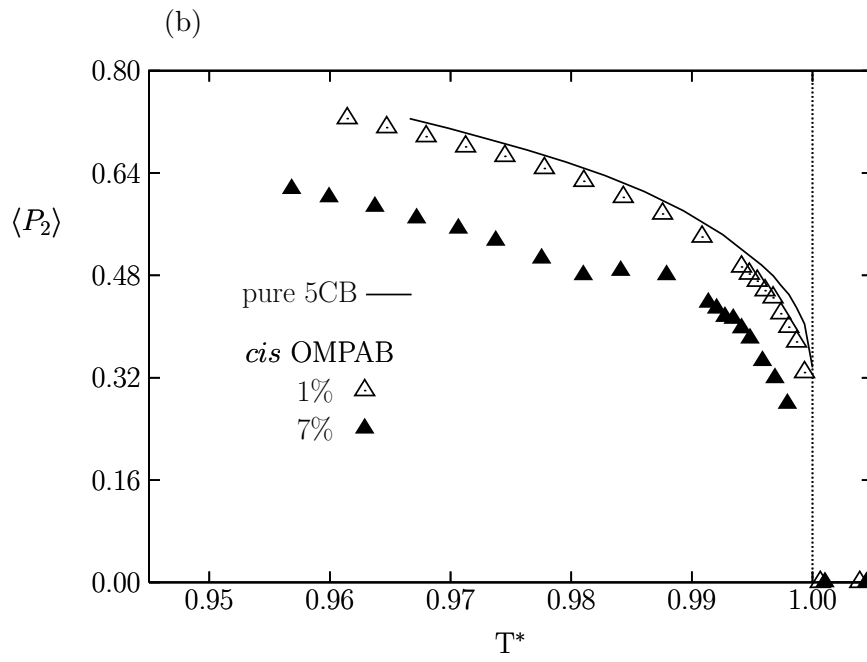
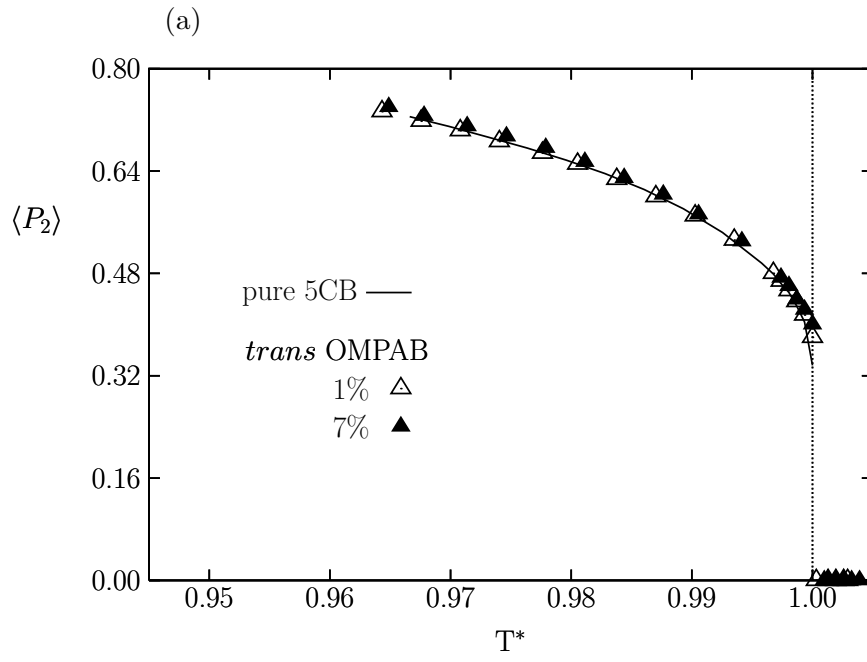


Figure 4: