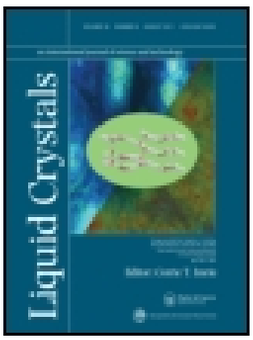

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Nonlinear optical properties of dye-doped E7 liquid crystals at the nematic–isotropic transition

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This work shows the influence of a 2,1,3-benzothiadiazole-based dye in the nonlinear optical refraction and nonlinear optical absorption of the thermotropic liquid crystal E7 at the nematic–isotropic transition in the ms time-scale using the Z-scan technique. The addition of dye does not modify the critical exponent of the nonlinear birefringence observed for the undoped sample at the transition, confirming the tricritical character. Also, the order parameter based in the nonlinear absorption shows, for the samples with higher dopings, a critical exponent that deviates from the expected value in the tricritical hypothesis.

Keywords: dye; phase transition; Z-scan technique; thermal lens; nonlinear absorption; nonlinear refraction

1. Introduction

The presence of dye molecules in a liquid crystal host leads to new phenomena in the field of nonlinear optics due to the complex guest–host interactions, depending mainly on the geometry and structure of both, the dye and the liquid crystal.[1] The optical properties of dyes and their interactions with the liquid crystal molecules and fields find practical applications as the production of efficient dye-doped polymer dispersed liquid crystals [2] or dye-integrated cholesteric photonic luminescent solar concentrators. [3] From a basic point of view, an enhancement of the orientational optical nonlinearity due to an intermolecular torque of photo-excited dye molecules [4–6] and a surface-assisted optical nonlinearity were observed.[7,8] A possible mechanism behind the last effect would be photo-induced charges at the irradiated surface.[9] Also, a pretransitional enhancement of the nonlinear optical properties has been reported at the Nematic (N)–Isotropic (I) transition.[10] On the other hand, the addition of a dye to a liquid crystal usually changes its physical properties like the order parameter and the transition temperatures.[11]

In previous works, the nonlinear optical refraction and nonlinear optical absorption of the undoped E7 liquid crystal at the N–I transition was studied by the Z-scan technique. The nonlinear optical refraction index displayed an enhancement at the N–I transition, while the nonlinear birefringence decreased, vanishing to zero in the isotropic phase with a critical exponent $\beta = 0.28 \pm 0.03$.[12] On the other hand, by defining the parameter S_{NL} in terms of the nonlinear optical absorption in analogy to the order parameter based in the anisotropy of the optical absorption,[13] we obtained that S_{NL} also reaches zero at the N–I transition, with a critical exponent $\beta = 0.22 \pm 0.05$ corresponding to a tricritical character of the phase transition.[14] So the behaviour of both the nonlinear birefringence and S_{NL} is compatible with the tricritical hypothesis of the N–I transition.[15]

In this paper, we present experimental results on the nonlinear optical refraction and absorption of the E7 liquid crystal doped with a 2,1,3-benzothiadiazole-based dye at the N–I phase transition. It will be shown that the nonlinear optical refraction presents the general behaviour observed in the undoped liquid crystal, but the nonlinear optical absorption shows new and interesting findings. Also, the addition of this dye shifts the N–I transition temperature in an unexpected direction. This report is organised as follows: in Section 2, the samples and the Z-scan technique are described. In Section 3, the results and the discussion are presented. Finally, in Section 4,the conclusions are given.

2. Experimental details

The liquid crystal E7 is a mixture consisting of several types of cyanobiphenyls, mainly 5CB, and triphenyl in less quantity. It exhibits a nematic phase in the temperature interval from -10°C till the transition to the isotropic phase at $T_{NI} = 58.1$°C. In this work, we used comercial E7 (Merck) without further purification. The dye employed was the 4,7-bis{2-[4-(4-decylpiperazin-1-yl)phenyl]ethynyl}-[2,1,3]-benzothiadiazole.[16,17] The optical absorption of the dye is

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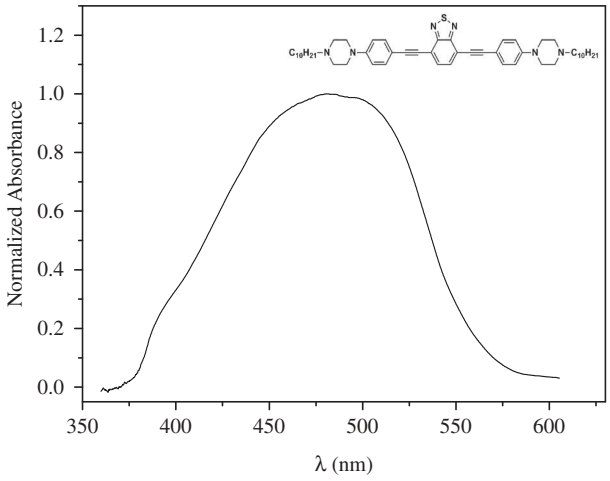

Figure 1. Non-polarised and normalised absorbance of the 4,7-bis{2-[4-(4-decylpiperazin-1-yl)phenyl]ethynyl}-[2,1,3]-benzothiadiazole. The inset shows the molecular structure of the dye.

shown in Figure 1, and the molecular structure of the dye is shown in the inset of Figure 1. As can be seen, the maximum absorbance is about 481 nm. The molecule of the dye is twice the size of the molecules of the E7 liquid crystal and has a permanent electric dipole moment. The dye exhibits a liquid crystal behaviour with a nematic phase between 228.3°C and 300°C, decomposing above this temperature. The dye-doped E7 liquid crystal samples were prepared with three different molar concentrations of dye: 0.025% w, 0.075% w and 0.2% w, labelled S1, S2 and S3 for convenience, respectively. It corresponds to 4000, 1333 and 500 molecules of the E7 liquid crystal for one molecule of the dye, respectively. The higher concentration of dye is close to the limit of solubility. A fourth sample without doping, labelled S0, was used for comparison. Samples were conditioned in parallel glass cells, separated by 20 μm-thick spacers. The glass plates were coated with polyvinyl alcohol (PVA) and buffed for homogeneous planar alignment of the liquid crystal. The transition temperatures of the samples were determined using a polarised light microscope (Olympus) and the temperature was controlled via a hot stage (Instec) with a precision of 0.2°C between 20°C and T_{NI}.

The Z-scan technique exploits the formation of a lens in a medium when a Gaussian-profile laser beam impinges on it (TEM_{00}).[18] For a nonlinear medium and under the incidence of a beam of intensity I, the refraction index and the absorption coefficient can be written as $n = n_o + n_2 I$ and $\alpha = \alpha_o + \alpha_2 I$, respectively, where n_o is the linear refraction index, n_2 is the nonlinear refraction index, α_o the linear absorption coefficient, and α_2 the nonlinear absorption coefficient. A

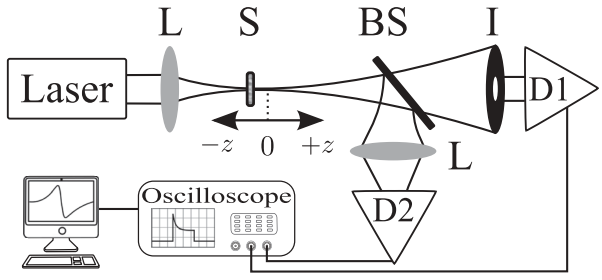

Figure 2. Sketch of the set-up for the simultaneous implementation of the closed-aperture and open-aperture Z-scan techniques: L (lens), S (sample), I (iris), BS (beam splitter), and D (photodetector). D_1 is used for the closed-aperture Z-scan and D_2 for the open-aperture Z-scan.

medium characterised by $n_2>0$ ($n_2<0$) behaves like a positive (negative) lens. The magnitude and sign of n_2 and α_2 can be obtained unambiguously by means of a simultaneous implementation of the closed-aperture and open-aperture Z-scan technique (Figure 2). In the closed-aperture set-up, the normalised transmittance of the iris at the far field is affected by both, the nonlinear refraction and nonlinear absorption of the sample. On the contrary, in the open-aperture set-up, only the nonlinear absorption is put in evidence. The normalised transmittance as a function of the z position in the former configuration, $\Gamma(z)_c$, defined by $\Gamma(z) = \frac{S(z)}{S(z\to\infty)}$, where $S(z)$ is the transmittance of the sample at position z, is given by [18,19]:

$$\Gamma_c = 1 - \frac{4\Phi\left(\frac{z}{z_o}\right)}{\left[1+\left(\frac{z}{z_o}\right)^2\right]\left[9+\left(\frac{z}{z_o}\right)^2\right]} - \frac{\Theta\left[\left(3+\left(\frac{z}{z_o}\right)^2\right)\right]}{\left[1+\left(\frac{z}{z_o}\right)^2\right]\left[9+\left(\frac{z}{z_o}\right)^2\right]}, \quad (1)$$

where z_o is the Rayleigh range of the beam, $\Phi = k n_2 I_o L_{ef}$, k is the wave number, $L_{ef} = [1 - exp(-\alpha_o L)]/\alpha_o$ is the effective thickness of the sample, I_o is the irradiance at the beam waist of the laser, and $\Theta = \alpha_2 I_o L_{ef}$.

In the open-aperture configuration, the total intensity transmitted by the sample as a function of the position along the z-axis is measured. The normalised transmittance in this configuration, Γ_o, is given by [18,19]:

$$\Gamma_o = 1 - \frac{1}{2}\frac{\Theta}{\left[1+\left(\frac{z}{z_o}\right)^2\right]}. \quad (2)$$

The arrangement shown in Figure 2 allows the simultaneous determination of n_2 and α_2 and uses a CW laser ($\lambda = 532$ nm, Ventus, Laser Quantum) with power in the range of $3 - 40$ mW. The beam waist at focus was about 26 μm, and data acquisition was made *via* a digital oscilloscope (Tektronix). The polarisation of the laser beam ($\mathbf{E}$) was set either parallel or perpendicular to the nematic director ($\mathbf{n}$) induced by the surface treatment; therefore, reorientation of the nematic director by an optical torque $\left(\mathbf{\Gamma}_{\text{opt}} = \mathbf{D} \times \mathbf{E}\right)$ is not expected to occur. Under incidence of a CW laser beam with moderate power, and for relative orientation between the nematic director and the polarisation of the beam, the nonlinearity in a nematic liquid crystal is essentially from thermal origin due to the temperature dependence of the order parameter S. It is said that the laser induces a thermal lens and the intensity of this effect is proportional to the thermooptical coefficient $\mathrm{d}n/\mathrm{d}T$ [20] i.e. the refraction index can be written as $n = n_0 + (\mathrm{d}n/\mathrm{d}T)\Delta T$, where ΔT is the temperature variation.[21] Although the diffusion of heat leads to a phase variation of the laser beam, which does not exactly match the spatial profile of the intensity, for samples with low absorption and low thermal conductivity, it was shown that the Sheik-Bahae model for the Z-scan experiment, based in a purely local effect, gives a good description of the transmittance. [22] In this case, it is possible to write that $\mathrm{d}n/\mathrm{d}T \propto n_2$, where n_2 and $\mathrm{d}n/\mathrm{d}T$ are the fitting parameters of the Sheik-Bahae' s model [18] and the Thermal Lens model,[20] respectively.

3. Results and discussions

The measured transition temperatures of the S0, S1, S2 and S3 were 58.1°C, 59.0°C, 59.4°C and 60.1°C, respectively. As can be seen, the addition of the dye increases T_{NI}. It was shown that the clearing temperature of binary liquid crystal mixtures depends on the percentages and type of the molecules [23], and for nonmesogenic impurities, the transition temperatures decrease,increasing the perceincreasing the percentage of the dontage of the doping. [15] Also, the observed shift of the transition temperature does not seem to correspond to a previously obtained result by Bauman et al. [24]. In our case, we cannot foresee the values of T_{NI} due to the fact that the liquid crystal E7 is a mixture of many components.

3.1. *Nonlinear optical refraction*

Figure 3 shows the typical closed-aperture Z-scan trace, obtained with S2 at $T = 25$°C (nematic phase) for $\mathbf{n} \| \mathbf{E}$. The error bars correspond to the standard error of the mean value for at least 10 measurements in each z-position, and the solid line is the best fitting to Equation 1. As can be seen, for $\mathbf{n} \| \mathbf{E}$, the samples exhibit the valley-peak configuration corresponding to a negative nonlinear refraction coefficient $\left(n_{2\|}<0\right)$ and the small asymmetry of the trace is due to the presence of a simultaneous small negative nonlinear optical absorption. On the other hand, for $\mathbf{n} \perp \mathbf{E}$, the samples exhibit positive nonlinear refraction $(n_{2\perp}>0)$ (figure not shown). After an incident laser beam impinges on the sample, the transmittance reaches a stationary value after about 35 ms. This is a typical value of the formation time of a thermal lens in a medium. So our results are consistent with a nonlinear optical response of thermal origin. Besides the linear optical absorption of pure E7 to be low at the visible range, it is measurable and produces a nonlinear optical response of thermal origin, i.e. the formation of a thermal lens by a nonradiative relaxation process. The addition of the dye just increases the linear absorption of the sample at the laser wavelength [17] being larger for a polarisation of the laser beam parallel to the nematic director. An increase of temperature leads to a wider angular distribution of the long molecular axis around the nematic director. So, the effective molecule seen by the laser beam is shorter along the molecular axis and thicker in a perpendicular direction, resulting in a diminution of the extraordinary refraction index and an increase of the ordinary refraction index, respectively. We have also checked the nonlinear optical response of the empty glass cell with PVA coating: for the intensities of the laser beam used in our experiment, the cell does not show any nonlinear optical

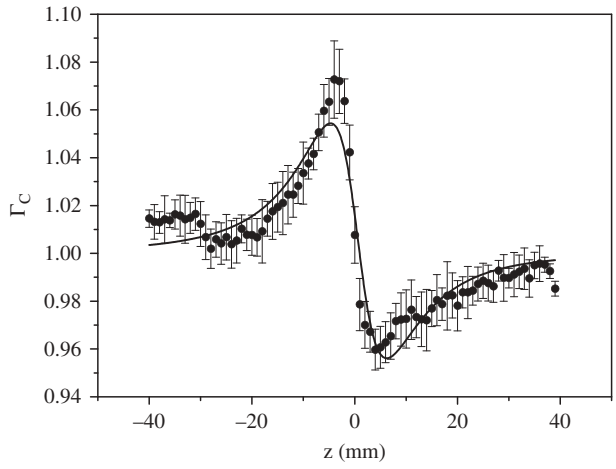

Figure 3. Typical Z-scan curve obtained for $\mathbf{n} \| \mathbf{E}$ with closed-aperture configuration Z-scan technique ($T = 25$°C). The solid line shows the fitting to Equation 1.

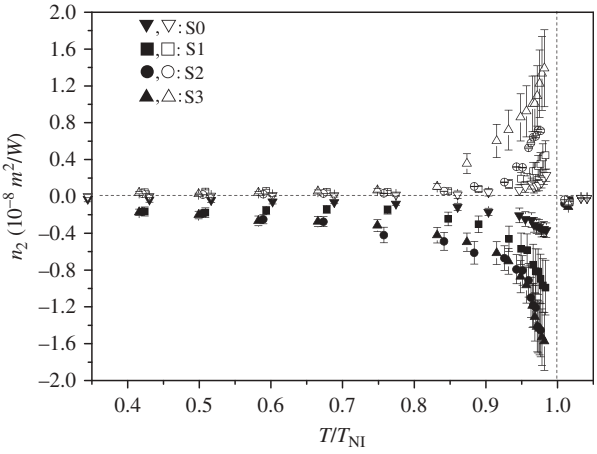

Figure 4. Nonlinear refraction coefficient as a function of temperature in the nematic and isotropic phases, for both configurations between the nematic director and the polarisation of the incident beam: $\mathbf{n}\|\mathbf{E}$ (full symbols) and $\mathbf{n}\perp\mathbf{E}$ (empty symbols).

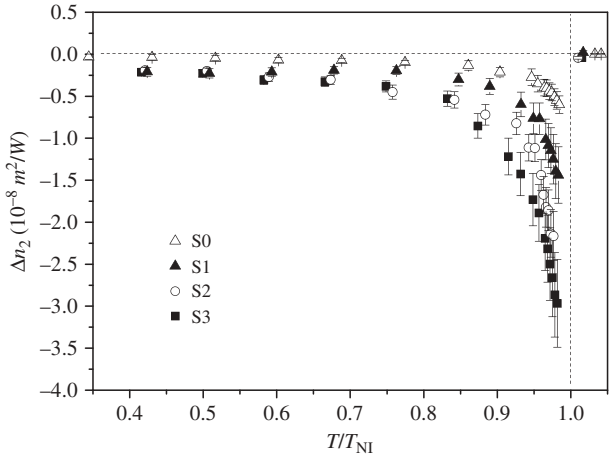

Figure 5. Nonlinear birefringence Δn_2 of the samples as a function of temperature. Vertical dashed line indicates T_{NI}.

response. Bechtold et al. have shown that the rubbing process of the PVA coating onto the glass to induce a planar orientation of the liquid crystal matrix in the cell does not induce superficial static charges.[26] This is ascribed to the the fact that the OH groups of the PVA polymeric chains are good conductors, allowing that the charges produced by the rubbing process leak out of the surface.

Figure 4 shows the nonlinear refraction coefficients n_2 of all the dye-doped liquid crystal samples, and of the undoped liquid crystal for reference purpose, in the nematic and isotropic phases for both relative orientations between the nematic director and the polarisation of the laser, as a function of the normalised temperature T/T_{NI}.

For each sample, a different power (P) of the laser beam was used due to the different values of optical absorptions. As shown by Equation 1, the amplitude of the transmittance curve in the Z-scan technique is proportional to $\Phi \propto n_2 I_o$, where I_o is proportional to P for a laser beam with a Gaussian-intensity profile. So, the value of n_2 is independent of the incident power on the sample, as we could check. In the full nematic region, for $\mathbf{n}\|\mathbf{E}$, the samples display a self-defocusing effect $(n_{2||}<0)$, and for $\mathbf{n}\perp\mathbf{E}$, the samples display a self-focusing effect $(n_{2\perp}>0)$. Approaching T_{NI} from below, the modulus of n_2 diverges for both relative orientations between the polarisation of the optical beam and the nematic director. Still, the temperature dependence of the refraction indices leads to a critical-like behaviour of the thermooptical coefficient $\frac{dn}{dT}$ at the nematic–isotropic phase transition.[27] Figure 5 shows the nonlinear birefringences $\Delta n_2 = n_{2||} - n_{2\perp}$ of the samples as a function of temperature.

As observed, the magnitude of the nonlinear birefringence diverges at T_{NI} when approached from below and is zero at the isotropic phase. Although in the nematic phase, far from T_{NI}, the birefringence of all the samples is rather similar, close to T_{NI}, the higher the doping of dye, the bigger the birefringence. As the dye absorption is dominant over the liquid crystal E7 at 532 nm, the thermal nonlinear optical response measured here comes mainly from the dyes, and that explains the nonlinear birefringence behaviour with the dye concentration. It was shown previously that the nonlinear birefringence can be written as

$$\Delta n_2 \propto \left[1 - \frac{T}{T^{\dagger}}\right]^{\beta-1}, \tag{3}$$

where β is the critical exponent of the order parameter and $T^{\dagger}$ is the temperature of the effective second-order transition seeing from below T_{NI}.[12] Figure 6 shows a ln–ln plot of $|\Delta n_2|$ as a function of the reduced temperature $1-\frac{T}{T^{\dagger}}$ for S3, assuming $T^{\dagger} = T_{NI}$.

Similar plots were obtained for the other samples. To perform the best fitting, we proceeded to vary $T^{\dagger}$ at regular steps in the temperature range $[T_{NI}, T_{NI} + 0.4°C]$ for each sample and the weighted averages of the effective critical exponents β are summarised in Table 1 (column β (Δn_2)).

The values of β for all the samples are approximately the same and seem to confirm the tricritical character of the phase transition.[15] From a previous work, it was observed that the dye order parameter increases in the range of concentration investigated here [17] so it is possible to conclude that the critical

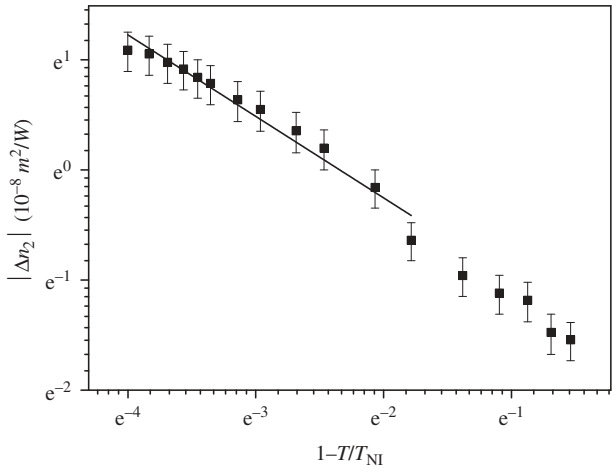

Figure 6. ln–ln plot of the absolute value of Δn_2 as a function of the reduced temperature $1 - T/T_{NI}$. Solid line represents a typical linear fitting of data.

Table 1. Critical exponents of the samples at the N–I transition.

Sample	β (Δn_2)	β (S_{NL})
S0	0.28±0.03	0.22±0.05
S1	0.22±0.04	0.24±0.02
S2	0.23±0.03	0.19±0.02
S3	0.22±0.03	0.29±0.02

exponent β is not directly affected by changes in the molecular order parameter. This can be probably linked to the fact that the addition of dye molecules, which are approximately twice as big as the molecules of the E7 liquid crystal, increases density fluctuations at the N–I transition.

3.2. *Nonlinear optical absorption*

Figure 7 shows a typical open-aperture *Z*-scan trace, obtained with S2 at $T = 25°C$ (nematic phase) for $\mathbf{n} \| \mathbf{E}$, and the continuous line is the fitting to Equation 1.

The error bars correspond to the standard error of the mean value for at least 10 measurements in each z position. As can be seen, for $\mathbf{n} \| \mathbf{E}$, the sample exhibits saturable absorption (SA), i.e. the open-aperture transmittance of the sample increases when approaching the focal point $(\alpha_{2\|} < 0)$. On the other hand, for $\mathbf{n} \perp \mathbf{E}$, the samples exhibit positive nonlinear absorption $(\alpha_{2\perp} > 0)$, i.e. the open-aperture transmittance decreases when approaching the focal point. It is worth to mention that the empty PVA-coated cells do not exhibit any nonlinear optical absorption.

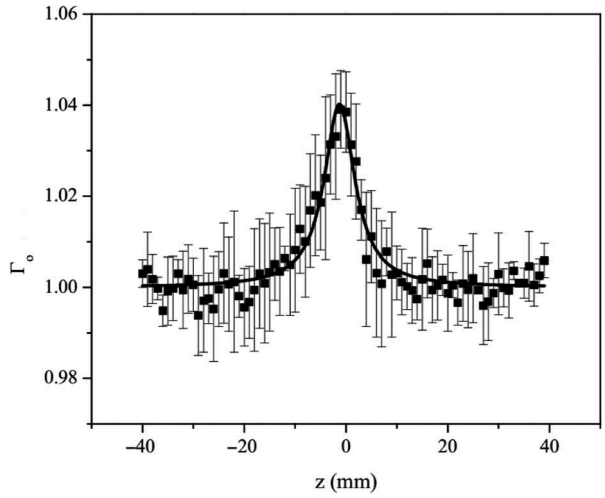

Figure 7. Typical *Z*-scan curve obtained for $\mathbf{n} \| \mathbf{E}$ with the open-aperture configuration Z-scan technique ($T = 25°C$). Solid line shows the fitting to Equation 2.

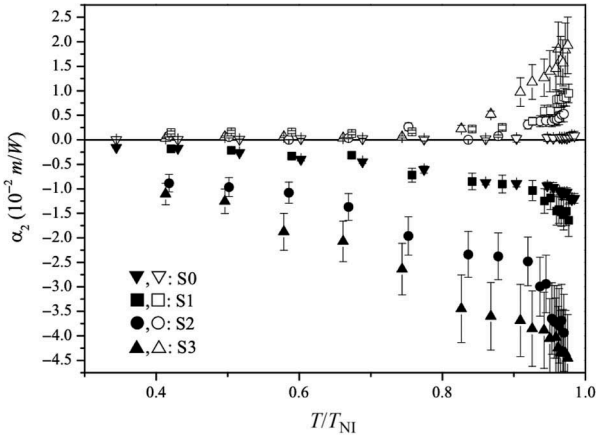

Figure 8. Nonlinear optical absorption of the samples as a function of the normalised temperature T/T_{NI} for both configurations between the nematic director and the polarisation of the incident beam: $\mathbf{n} \| \mathbf{E}$ (full symbols) and $\mathbf{n} \perp \mathbf{E}$ (empty symbols).

Figure 8 shows the nonlinear optical absorption of the samples in the nematic range and close to the N–I transition as a function of the normalised temperature T/T_{NI}.

The modulus of α_2 increases when T approaches T_{NI} for both configurations between the nematic director and the polarisation of the incident beam. The linear optical absorption of liquid crystals containing saturated and unsaturated phenyl is relevant only in the UV spectral region, involving the $\pi \rightarrow \pi^*$ electronic transitions [28], although the optical absorption in the visible range is low but measurable [25]. Also, the optical absorption of the dye is rather low for the wavelength employed here (see Figure 1).

[17] Thus, in this study, a two-photon absorption process can be ruled out due to the low intensities employed. A similar study by the Z-scan technique in a planar-oriented sample of 5CB and using the $\lambda =$ 514.5 nm line of an Ar^{+} laser of similar power did not show any kind of nonlinear optical absorption in nematic phase or in the N-I transition region.[29] Nonresonant stimulated scattering processes, such as Stimulated Raman Scattering (SRS), Stimulated Brillouin Scattering (SBS), Stimulated Orientational Scattering (SOS), and Stimulated Thermal Scattering (STS), observed previously in thermotropic liquid crystals [30] must also be discarded. In a measure of the nonlinear absorption, those processes can not give a transmission curve of the kind of reverse satured absorption (α_2>0) because in addition to producing a forward beam they also originate a small amount of backscattered radiation. A more likely source of the nonlinear absorption observed in our samples could be a laser-induced reorientation of absorbing species as seen in a 50 μm-thick homeotropically oriented sample of dye-doped 5CB.[31] The orientational distribution of excited molecules deviates from the thermodynamical equilibrium. In polarised light, the probability of an electronic transition to an excited state is proportional to $\cos^2\psi$, where ψ is the angle between the electric field vector of the light beam and the transition dipole moment. An optical field exerts an optical torque due to the induced dipole moment proportional to the dielectric anisotropy $\Delta\varepsilon$.[32] From the balance between the elastic torque and the optical torque, under hard-boundary and small director-reorientation conditions, it can be shown that the maximum molecular reorientation $\theta_{\max}$ for an extraordinary ray in a nematic is proportional to $\Delta\varepsilon/K_1$, where K_1 is the elastic constant for splay distortion and I is the intensity of the laser beam. Since $\Delta\varepsilon \propto S$ and $K_1 \propto S^2$, where S is the order parameter, the maximum reorientation in the nematic phase satisfies $\theta_{\max} \propto S^{-1}$. Assuming that close to the N–I transition $S \propto \left(1 - \frac{T}{T^{\dagger}}\right)^{\beta}$,[33] it follows that $\theta_{\max}$ increases as T approaches T_{NI} from below. In this way, the molecules tend to align along the polarisation direction of the incident beam when approaching T_{NI}, leading to a saturation effect (α_2<0). In the case of an ordinary ray, the threshold intensity for director reorientation is proportional to $K_3/\Delta\varepsilon \propto S$, where K_3 is the elastic constant for bend distortion, i.e., the threshold intensity diminishes as T approaches T_{NI}. Moreover, Alliprandini et al. observed that the degree of order in the nematic sample increases by increasing the concentration of dye until 0.2% w, and, in the same proportion, increases the dichroic ratio of the optical absorption parallel and perpendicular.[17] Hence, the nonlinear absorption observed in the E7 liquid crystal below T_{NI} could be due to the reorientation of absorbing species, like the molecules of the liquid crystal and of the dye.

Following the procedure shown elsewhere, [14] we calculated the order parameter S_{NL} defined by

$$S_{NL} = \frac{R_{NL} - 1}{R_{NL} + 2}, \tag{4}$$

where $R_{NL} = \left|\frac{\beta_{\parallel}}{\beta_{\perp}}\right|$. Figure 9 shows the values of S_{NL} along the nematic phase for all the samples, and the inset shows the closest points to the N–I transition. The general behaviour of S_{NL} depicted in Figure 9 is in consonance with the dependence of the molecular ordering on the content of dye previously reported. [17] Along the nematic phase, S0 shows bigger variation and smaller values of S_{NL}. On the other hand, for all the samples, S_{NL} reaches zero at $T = T_{NI}$. We fitted $S_{NL}\left(\frac{T}{T^{\dagger}}\right)$ close to the phase transition under the assumption that $S_{NL} \propto \left(1 - \frac{T}{T^{\dagger}}\right)^{\beta}$, where β is the critical exponent and $T^{\dagger}$ is the virtual second-order transition seen below T_{NI} which is different from the spinodal temperature, the absolute limit of the nematic phase upon heating. Usually, $T^{\dagger} - T_{NI} \simeq 0.2$°C. [34] The results of the fitting (column $\beta(S_{NL})$) are shown also in Table 1. The exponent for S1 is rather similar to that of S0 but, for S2 and S3, obtained exponents differ from that corresponding to a phase transition of tricritical character. The ori-

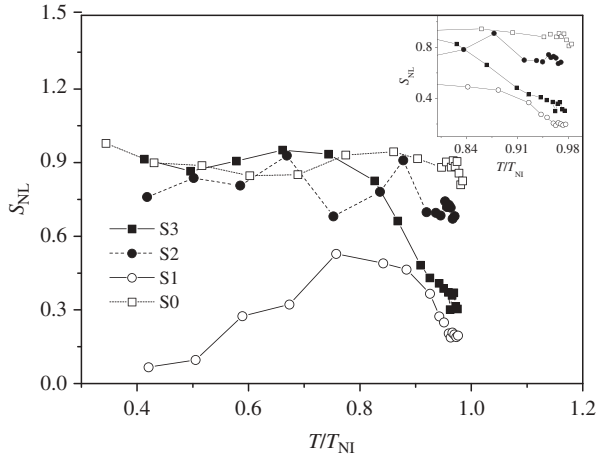

Figure 9. Plot of S_{NL} for all the samples as a function of the normalised temperature T/T_{NI}. The inset shows the points closest to $T/T_{NI} = 1$. The lines are a guide for the eye.

gin of this disagreement for the higher values of doping could be assigned to the effect on the nonlinear absorption of the increasing disorder of the dyes observed at higher doping concentrations.[17]

4. Conclusions

To summarise, we investigated the nonlinear optical response of the E7 liquid crystal doped with a 2,1,3-benzothiadiazole-based dye using the Z-scan technique. Along the nematic phase, the signals of the nonlinear optical refractions are $n_{2||}<0$ and $n_{2\perp}>0$, and those of the nonlinear absorption are $\alpha_{2||}<0$ and $\alpha_{2\perp}>0$, respectively, with modules that increase when approaching T_{NI} from below. The nonlinear birefringence Δn_2 diverges at N–I transition with a critical exponent typical of a tricritical transition for all the values of the doping, and going to zero in the isotropic phase. Finally, the parameter S_{NL} is less than 1 in the nematic phase and goes to zero into the isotropic phase, discontinuously at the transition temperature, with a critical exponent typical for a tricritical transition just for the minor value of doping.

Disclosure statement

No potential conflict of interest was reported by the authors.

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