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Study of Orientational Order of $\overline{8}S5$ in Nematic and Smectic Phases by means of Optical Spectroscopy Methods

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The long-range orientational order of 4-n-pentylphenylthio-4′-n-decyloxybenzoate ($\overline{10}S5$) doped with a dichroic dye was studied as a function of temperature in the nematic, smectic A, smectic C and smectic J phases by means of two optical spectroscopy methods: dichroism of absorption in the visible spectral region and fluorescence depolarization. On the basis of absorption and fluorescence spectra the order parameters $<P_2>$ and $<P_4>$ as well as the orientational distribution function were determined. The discontinuous change of both $<P_2>$ and $<P_4>$ parameters at the smectic A – nematic phase transition for dye/ $\overline{10}S5$ mixtures was observed, in an agreement with the microscopic theory proposed by McMillan. An influence of the dye molecular structure on the orientational order of the dye/ $\overline{10}S5$ mixture was observed. The correlation between the order parameter values and the shift of the phase transitions temperatures due to the dye addition was confirmed.

Keywords: dichroic dye; light absorption and emission; orientational order; phase transition; thermotropic liquid crystal

1. INTRODUCTION

The long-range orientational order is the most characteristic and the most important order for the liquid crystalline phases. It occurs both in the nematic and smectic phases. In the nematic (N) phase of rod-like molecules, the long axes of molecules have preference to orient along one direction, denoted usually by a unit vector called the director, **n**,

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and the molecular centres of mass are placed randomly. Therefore, in this phase only the orientational order exists. Smectic phases possess additionally long-range positional order, in that molecules show a preference to form a layered structure. There are a number of such phases, but two important are smectic A (SmA) and smectic C (SmC) phases. In the SmA phase the director is parallel to the layer normal; in the SmC phase, the director makes an angle with the layer normal [1,2].

For optically uniaxial smectic phases, *e.g.*, SmA phase, the orientational order can be determined from any of methods used for the nematic phase, *i.e.*, from the anisotropy of the refractive index, dielectric constant, diamagnetic susceptibility, or by using a wide variety of spectroscopic methods.

In this paper we present results of the study of the long-range orientational order of the liquid crystal 4-*n*-pentylphenylthio-4'-*n*-decyloxybenzoate ($\overline{10}$S5) doped with different dichroic dyes (push-putt substituted stilbene, bisazobenzene and anthraquinone derivative) using two methods of polarized light spectroscopy: electronic absorption and fluorescence measurements. The aim of the investigations was the determination of the orientational order parameters on the basis of absorption and emission spectra recorded as a function of temperature in the N, SmA, SmC, and SmJ phases. The smectic C and J phases are optically biaxial phases and therefore we were able to estimate the orientational order only in some approximation. However, an influence of the dye molecular structure on the order parameter values of the dye/liquid crystal mixtures in all the phases was detected. The results obtained in this study were compared with previously obtained results for $\overline{8}$ S5 [3].

2. THEORETICAL BACKGROUND

The orientational order of an ensemble of biaxial molecules in biaxial phases can be described by four order parameters [4]:

$$S = \frac{1}{2}\langle 3\cos^2\beta - 1\rangle, \tag{1}$$

$$D = \frac{3}{2}\langle 3\sin^2\beta\cos 2\gamma\rangle, \tag{2}$$

$$P = \frac{3}{2}\langle 3\sin^2\beta\cos 2\alpha\rangle, \tag{3}$$

$$C = \frac{3}{2}\langle (1-\cos^2\beta)\cos 2\alpha\cos 2\gamma - 2\cos\beta\sin 2\alpha\sin 2\gamma\rangle, \tag{4}$$

where α, β, and γ are Euler's angles between the laboratory-fixed and molecule-fixed coordinate systems.

S is the usual Maier-Saupe parameter [4] and characterizes the orientation of the molecular axis with respect to the optical axis of the uniaxial phase, while D is a measure for the deviation from a rotationally symmetrical distribution of molecules (biaxiality parameter). P represents the anisotropy of the nematic-type fluctuations projected on the laboratory plane perpendicular to the director **n**. C has no simple interpretation in its full form. In uniaxial phases, the rotation of the sample with the angle α does not influence the probability for a molecule to have a specific orientation. Therefore $P = C = 0$. For the simplest case of uniaxial molecules having $C_{\infty V}$ symmetry in a uniaxial phase, only S is different from 0. It is equivalent to $<P_2(\cos\beta)>$, where P_2 is second-rank Legendre polynomial and β is the angle between the long molecular axis and the director. The order parameter $<P_2(\cos\beta)>$, together with the fourth-rank order parameter $<P_4(\cos\beta)>$, allow one to determine the truncated distribution function in the following way [5]:

$$f_4(\beta) = \frac{1}{2} + \frac{5}{2}\langle P_2(\cos\beta)\rangle P_2(\cos\beta) + \frac{9}{2}\langle P_4(\cos\beta\rangle P_4(\cos\beta), \qquad (5)$$

where $<P_4(\cos\beta)>$ is defined as follows:

$$\langle P_4(\cos\beta\rangle = \frac{1}{8}\left\langle 35\cos^4\beta - 30\cos^2\beta + 5\right\rangle. \qquad (6)$$

From the electronic absorption measurements it is possible to obtain only the order parameter $<P_2(\cos\beta)>$, whereas on the basis of fluorescence measurements one can calculate both $<P_2(\cos\beta)>$ and $<P_4\ (\cos\beta)>$ parameters.

3. MATERIALS AND METHODS

The liquid crystal 4-*n*-pentylphenylthio-4′-*n*-decyloxybenzoate ($\overline{10}$S5) with the following phase sequence: isotropic → nematic → smectic A → smectic C → smectic J (monotropic) → crystal was supplied by Dr. A. Żywociński from Institute of Physical Chemistry, Polish Academy of Sciences, Warsaw. Three dichroic dyes of the different molecular structure were used as guest species. The chemical formulas of the compounds investigated are shown in Figure 1. We used the dyes from various groups (push-putt substituted stilbene, bisazobenzene and anthraquinone derivative) in order to check an influence of the molecular structure of the guest on the order parameters of the

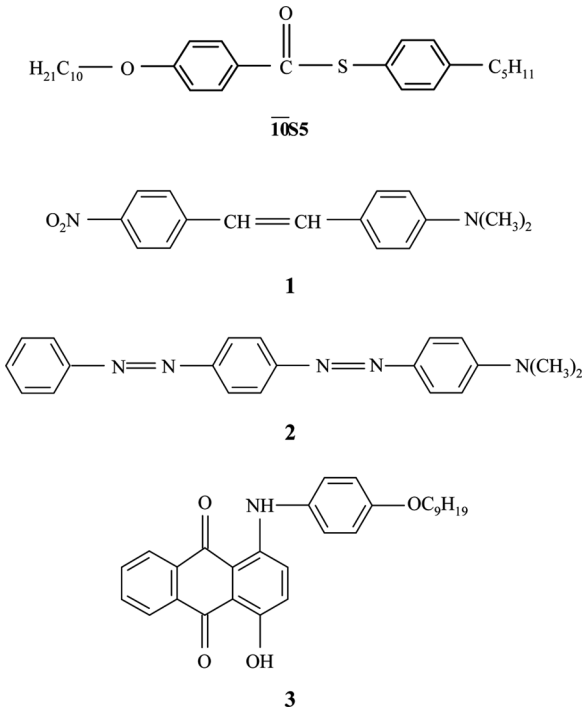

FIGURE 1 Molecular structure of liquid crystal and dyes under investigation.

guest/host mixture. All the dyes were synthesized and chromatographically purified in Institute of Dyes at Łódź University of Technology. Dyes **1** and **2** were dissolved in the liquid crystals at a concentration of $5 \cdot 10^{-3}$mol/dm^3, while the concentration of dye **3** was $4.5 \cdot 10^{-2}$ mol/dm^3 because of its significantly lower extinction coefficient as compared with the other dyes. Only dye **1** could be used in the fluorescence experiment because of satisfactory fluorescence quantum yield.

The temperatures of the phase transitions, both for pure $\overline{10}$S5 and for dye-liquid crystal mixtures, were determined with an accuracy of ± 0.1 K by means of a polarizing microscope (PZO, Warsaw, Poland) equipped with a heating stage. The temperature was stabilized with a practical accuracy of ± 0.1 K using a Temperature Controller 660 (UNIPAN, Warsaw, Poland).

The absorption spectra of the dye/$\overline{10}$S5 mixtures were recorded in the visible spectral region by means of a spectrophotometer CARY 400 equipped with Glan-Thomson polarizers. On the basis of polarized

absorption spectra of a dichroic dye dissolved in a liquid crystalline matrix, the order parameter $<P_2>$ can be calculated from the following formula [6]:

$$\langle P_2 \rangle = \frac{A_\parallel - A_\perp}{A_\parallel + 2A_\perp}, \tag{7}$$

where $A_\parallel$ and $A_\perp$ are the absorbances of the light polarized, respectively, parallel and perpendicularly to **n**.

The polarized fluorescence spectra were recorded by using a homemade photon-counting spectrofluorimeter described in detail in Ref. [7]. The exciting light was 436 nm line from a high-pressure mercury lamp. Glan-Thomson polarizers were used in the pathway of the incident and emitted light. The fluorescence was measured in the π geometry, *i.e.*, the exciting light beam was perpendicular to the cell surface and the fluorescence light was monitored perpendicularly from the same side of the cell [8]. On the basis of fluorescence intensity values, the emission anisotropies, R_1 and R_2 for excitation with the light polarized, respectively, parallel and perpendicularly to the director **n** were determined from the formula:

$$R_{1,2} = \frac{J_{\parallel\,1,2} - J_{\perp\,1,2}}{J_{\parallel\,1,2} + 2J_{\perp\,1,2}}, \tag{8}$$

where $J_{\parallel\,1,2}$ and $J_{\perp\,1,2}$ are reduced fluorescence intensities (regarding corrections for instrumental, concentration and volume factors) polarized, respectively, parallel and perpendicularly to **n**.

Assuming that the rotation relaxation time, τ_R is much longer than the lifetime, τ_F of the excited state of the fluorescent molecule, R_1 and R_2 can be related to the order parameters $<P_2>$ and $<P_4>$ as follows [9]:

$$R_1 = \frac{\left[\frac{2}{5} + \frac{11}{7}\langle P_2\rangle + \frac{36}{35}\langle P_4\rangle\right] P_2(\cos\delta)}{1 + 2\langle P_2\rangle}, \tag{9a}$$

$$R_2 = \frac{\left[\langle P_2\rangle - \frac{2}{5} - \frac{21}{35}\langle P_4\rangle\right] P_2(\cos\delta)}{1 - \langle P_2\rangle + 2\left[\frac{1}{5} - \frac{2}{7}\langle P_2\rangle + \frac{3}{35}\langle P_4\rangle\right] P_2(\cos\delta)}. \tag{9b}$$

δ is here the intramolecular angle between the absorption and emission oscillators.

Equations (7), (9*a*), and (9*b*) are valid only for a uniaxial phase and in the case when the angle between the vector of the absorption transition moment and the long axis of a dye molecule is equal to 0°. The latter assumption is fulfilled at the first approximation for the

transition moment responsible for the absorption in the visible region for all three dyes under investigation [10,11].

4. RESULTS AND DISCUSSION

Both $\overline{10}$S5 molecules as well as molecules of the dyes investigated can be treated as having the cylindrical symmetry with ability to free rotation. In this case the order parameters D and C (Eqs. (2) and (4)) are assumed to be zero. In the N and SmA phases the order parameter P (Eq. (4)) is also equal to zero. In the biaxial SmC and SmJ phases the orientation of molecules is dependent on the angle α and therefore, in general, $P \neq 0$. The results presented in Ref. [12] gave, however, evidence that this order parameter for the homologues of $\overline{n}$S5 series is at most 1% of the value of $S \equiv <P_2>$ (Eq. (1)). Thus, in this paper we determined the orientational order of $\overline{10}$S5 doped with dyes **1**, **2**, or **3** in all the liquid crystalline phases by the order parameter $S \equiv <P_2>$ only. Additionally, the $<P_4>$ values for **1**/$\overline{10}$S5 mixture were estimated.

Fig. 2 shows the polarized components of absorption ($A_{\parallel}$ and $A_{\perp}$) and fluorescence ($J_{\parallel 1}$, $J_{\parallel 2}$, $J_{\perp 1}$, and $J_{\perp 2}$) spectra of **1** in $\overline{10}$S5 at $T = 75^{\circ}C$, *i.e.*, in the SmA phase, as examples. On the basis of such spectra, the order parameters were calculated: $<P_2>_A$ from Eq. (7), and $<P_2>_F$ and $<P_4>_F$ on the basis of Eqs. (9*a*) and (9*b*). For calculations, the values of the absorbance and the fluorescence intensity were taken at the wavelengths corresponding to the maxima of absorption and emission bands, respectively. The angle δ between the absorption and emission oscillators of **1**, which is needed to the calculation of the order parameters from fluorescence measurements was taken as 12° on the basis of data given in Ref. [13]. The results obtained are presented in Figures 3 and 4. Figure 3 shows the order parameters $<P_2>_A$ (crosses), $<P_2>_F$ (squares) and $<P_4>_F$ (circles) as a function of the reduced temperature $T_{red} = T/T_{NI}$ (T – temperature of the measurement, T_{NI} – temperature of the nematic-isotropic transition in K) for dye **1** in $\overline{10}$S5 in the whole mesophase region, whereas Figure 4 presents the temperature dependence of $<P_2>_A$ values for **2**/$\overline{10}$S5 (squares) and **3**/$\overline{10}$S5 (triangles) mixtures.

In the SmC and SmJ phases the director **n** makes the temperature dependent angle θ with the light polarization direction. The data presented in Figures 3 and 4 do not take this fact into account. However, we had showed in our previous paper [3] that the influence of the angle θ on the results obtained is not very large. Even when one assumes that directions of the inclination of molecules in the tilted phases are fully ordered, $<P_2>_A$ changes at most of 2%.

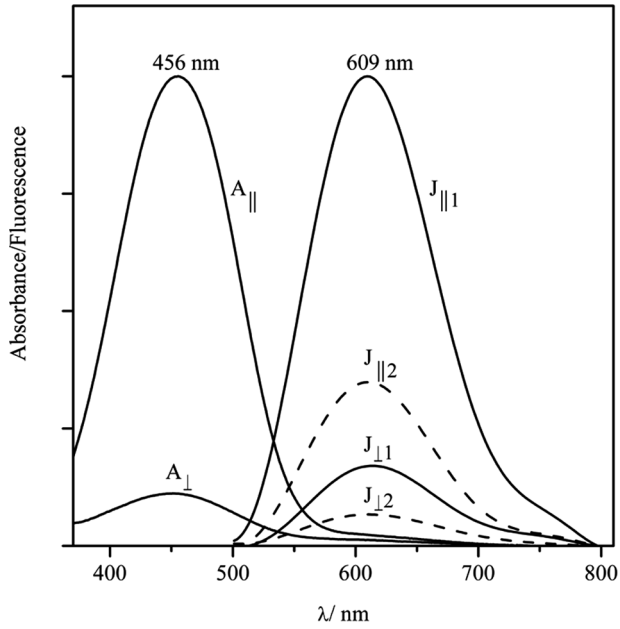

FIGURE 2 Polarized components of absorption ($A_{\parallel}$ and $A_{\perp}$) and fluorescence ($J_{\parallel 1}, J_{\parallel 2}, J_{\perp 1},$ and $J_{\perp 2}$) spectra of dye **1** in $\overline{10}$S5.

From Figure 3 results that the values of the order parameter $<P_2>$ estimated from absorption measurements are in good agreement (within experimental uncertainties) with those obtained from fluorescence studies in the N and SmA phases. In the tilted phases some differences between $<P_2>_{\mathrm{A}}$ and $<P_2>_{\mathrm{F}}$ are observed. They indicate that in the fluorescence measurements the influence of the angle θ on the results obtained cannot be neglected. Moreover, one should keep in mind that, in general, the fluorescent dye molecule is excited at a certain orientation and is observed after a time t at another orientation. Therefore, the error in the estimation of the order parameters from fluorescence measurements is greater than that determined on the basis of absorption spectra. Especially, it is very high for $<P_4>_{\mathrm{F}}$.

Now, let us compare the temperature dependence of $<P_2>_{\mathrm{A}}$ for all dye/$\overline{10}$S5 mixtures. Results presented in Figures 3 and 4 show that the character of changes of $<P_2>_{\mathrm{A}}$ with the temperature is similar for all the mixtures investigated. In the nematic phase, $<P_2>_{\mathrm{A}}$ decreases with rising temperature to a certain value and jumps to zero at the clearing point. At the transition from the nematic to the

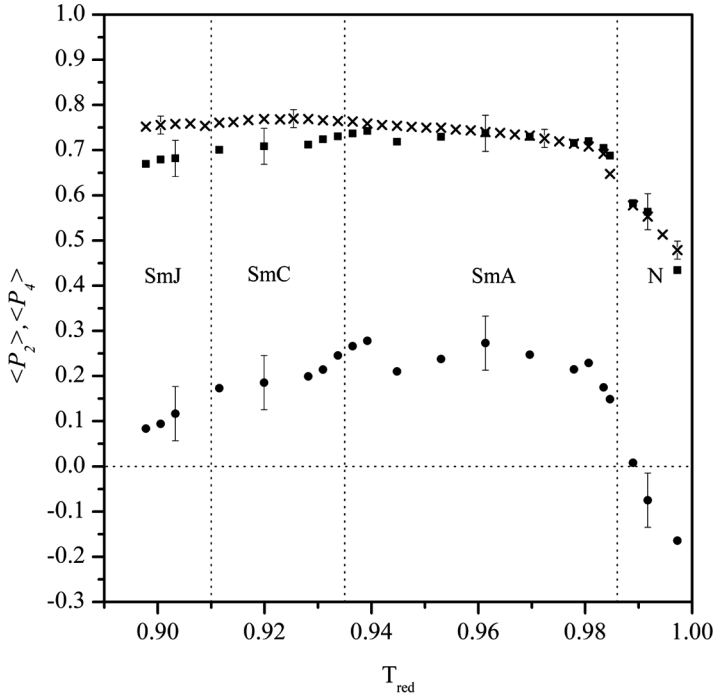

FIGURE 3 Dependence of order parameters $<P_2>$ and $<P_4>$ on reduced temperature $T_{red} = T/T_{NI}$ for $\overline{10}S5$ doped with dye **1** determined from absorption (crosses – $<P_2>_A$) and fluorescence (squares – $<P_2>_F$, circles – $<P_4>_F$) measurements.

smectic A phase, the distinct discontinuity in the $<P_2>_A(T)$ curve is observed. However, the transitions SmA-SmC and SmC-SmJ are very difficult to be identified. We plotted additionally the temperature dependence of $\partial <P_2>_A/\partial T$, but this procedure did not give clearly discernible results for all the mixtures under investigation. The transition temperatures indicated by dashed lines in Figure 3 and by arrows in Figure 4 were estimated on the basis of both $\partial <P_2>_A/\partial T$, curve analysis and texture observations by means of polarizing microscope.

From the results shown in Figures 3 and 4 follows that $<P_2>_A$ value at given temperature is different for various mixtures, which means that it depends strongly on the molecular structure of the dye doped to the liquid crystal. For dye **3** extremely low order parameter is observed. Such a low optical order parameter can arise either from the direction of the electronic transition dipole moment which cannot

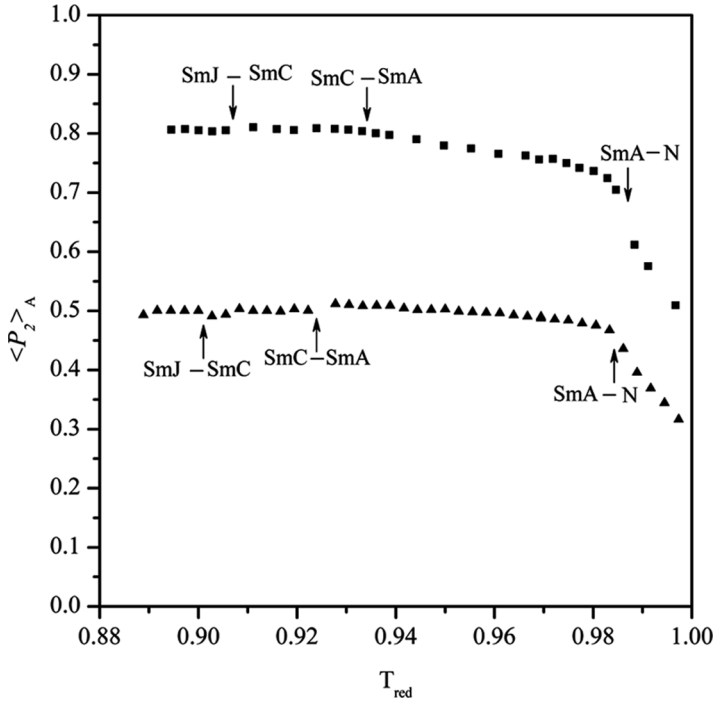

FIGURE 4 Dependence of order parameters $<P_2>$ on reduced temperature $T_{red} = T/T_{NI}$ for $\overline{10}$S5 doped with dyes **2** (squares) and **3** (triangles) determined from absorption measurements.

be assumed as parallel to the long molecular axis of a dye or from the incomplete alignment of dye molecules with respect to the orientation axis of a liquid crystal. The molecular structure of **3** suggests that one can expect non-zero angle between the transition moment and the long axis of the molecule, however, this deviation is rather small and cannot cause so strong decrease in the value of the order parameter obtained from absorption measurements. It seems that steric effects due to the presence of the long chain connected to the main molecular core are of crucial importance here. They are the source of the short-range repulsive forces which reduce the guest-host van der Waals interaction by preventing close alignment of the dye and liquid crystal molecules. As a result, the order parameter grows smaller. This statement can be confirmed by the significant influence of the dye addition on the phase transition temperatures of $\overline{10}$S5, which becomes noticeable in Table 1. In this table the phase transition temperatures of $\overline{10}$S5 and its mixtures with the dyes are given. It is seen that dye **3**

TABLE 1 Phase Transition Temperatures of Compounds Investigated

Compound	Phase transition temperature/°C					
	Cr → SmC	Cr ← SmJ	SmJ ← SmC	SmC ↔ SmA	SmA ↔ N	N ← I
$\overline{10}$S5	62.0	48.0	53.0	65.0	82.8	88.5
1/$\overline{10}$S5	62.1	50.3	56.2	64.9	83.7	88.8
2/$\overline{10}$S5	62.2	50.2	55.2	65.0	83.8	88.9
3/$\overline{10}$S5	57.2	46.3	50.9	59.5	81.1	86.8

decreases significantly the temperatures of all the phase transitions of $\overline{10}$S5. Meanwhile, the influence of dyes **1** and **2** is not so strong. Both these dyes even increase somewhat the transition temperatures, and their mixtures with $\overline{10}$S5 are characterized by very high order parameter. This can be a confirmation of the fact that there exists strong correlation between the order parameter and the shift of the phase transition temperatures of the dye/liquid crystal mixture with respect to that of the pure liquid crystal. Such correlation had been found previously for many dye/liquid crystal systems [3,11,14–16] and allows one to ascertain that the determination of phase transition temperatures can be sufficient to state whether the given dye is able to adopt the same anisotropic orientation as the liquid crystalline host or not. The lack of the shift or a very small change in the transition temperature after the dye addition suggest a very good correlation of the orientation between guest and host molecules. In such cases (*e.g.*, dyes **1** and **2** in $\overline{10}$S5, it is possible to obtain information about the molecular arrangement from the polarized absorption spectra of a dye dissolved in a liquid crystal and Eq. (7) can be successfully used for the determination of the order parameter of a liquid crystalline host.

Figure 5 shows the comparison of $<P_2>_A$ for $\overline{10}$S5 and $\overline{8}$S5 doped with dye **2** in the vicinity of the N-SmA transition. In the abscissa axis T/T_{AN} is given, where T_{AN} is the temperature of the N-SmA transition in K. At the transition temperature, the order parameter value of **2**/$\overline{10}$S5 mixture changes of about 0.1, whereas for **2**/$\overline{8}$S5 mixture the change is 5-fold smaller and is equal to 0.02. Similar results for the mixtures with dyes **1** and **3** were obtained. Such behavior of $<P_2>$ seems to be easily explained if one takes into account changes of the enthalpy for $\overline{10}$S5 and $\overline{8}$S5 at the N-SmA phase transition. For $\overline{10}$S5, $\Delta H = 1.05\,kJ/mol$, and for $\overline{8}$S5 it is about 9-fold smaller ($\Delta H = 0.12\,kJ/mol$) [17]. The transition from the nematic to the smectic A phase for $\overline{8}$S5 is of the second order, whereas for $\overline{10}$S5 it is weakly first order. Such difference in the nature of the SmA-N transition for $\overline{8}$S5 and $\overline{10}$S5 was found previously by other authors studying

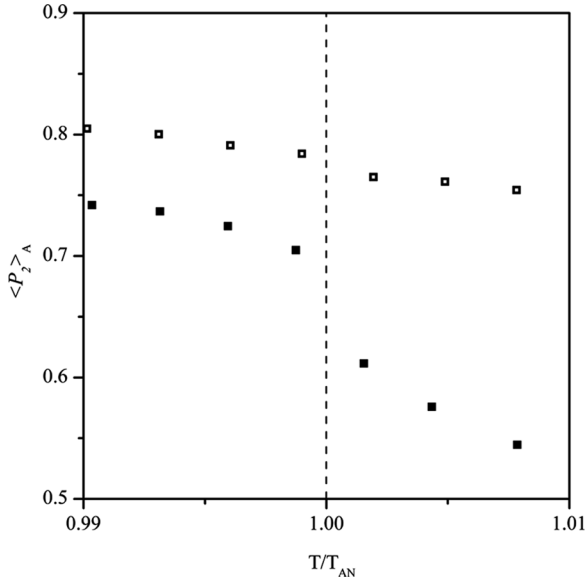

FIGURE 5 Dependence of order parameters $<P_2>_A$ on reduced temperature T/T_{AN} for $\overline{10}S5$ (filled squares) and $\overline{8}S5$ (open squares) doped with dye **2** in the vicinity of SmA-N transition.

birefringence [18], heat capacity and X-ray diffraction [19] as well as molar volume [20,21] of these liquid crystals. The results obtained are in agreement with the microscopic theory given by McMillan [22]. From this theory follows that when T_{AN}/T_{NI} ratio is increasing (the nematic range is decreasing), the nematic order parameter is less saturated and its coupling with the smectic order parameter is enhanced because of increasing susceptibility [1,22]. It leads to the transition change from continuous to discontinuous. McMillan had determined that when $T_{AN}/T_{NI} > 0.87$, the first order behavior of the transition should be observed. Experimentally, because of molecular fluctuations, it occurs at higher value of this ratio [23]. For example for $\overline{8}S5$, where $T_{AN}/T_{NI} = 0.936$, the transition is still of the second order [3,20].

The order parameter $<P_4>$ depends on the higher power of the angle β (Eq. (6)), thus it is more sensitive to the molecular fluctuations and decreases rapidly when the molecular orientation is perturbed. It can be seen distinctly in Figure 3 at the SmA-N transition. In all the smectic phases the order parameter $<P_4>_F$ is positive and in the SmA phase it is constant, within the experimental uncertainty. In the nematic phase the values of $<P_4>_F$ are very low and even negative.

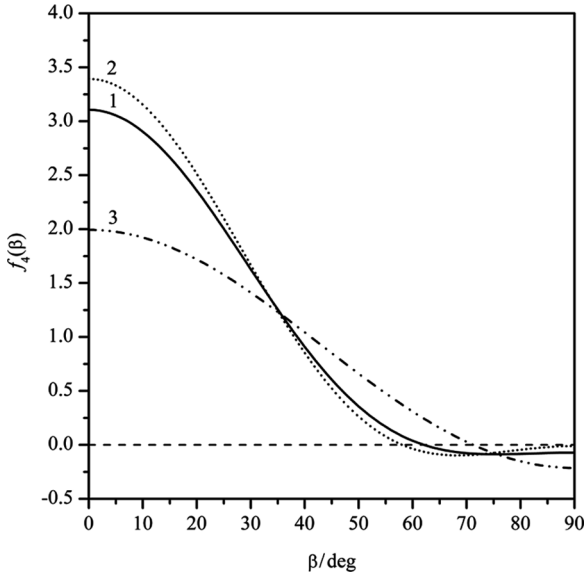

FIGURE 6 Distribution function f_4 (β) in SmC (1), SmA (2), and N (3) phases for liquid crystals $\overline{10}$S5 doped with dye **1** determined from fluorescence measurements at T = 58.8°C (1), 70.7°C (2), and 83.7°C (3).

Meanwhile, any theory of the nematic phase [5,24] does not predict the negative value of $<P_4>$ parameter. However, such behavior of $<P_4>$ had been observed experimentally by many authors studying the orientational order of nematics using fluorescence [9,13,25–27] and Raman scattering [27–31] depolarization methods.

As it was mentioned previously, the experimental error in the estimation of $<P_4>_F$ parameter is very large. Therefore it cannot be used to the identification of the SmA-SmC and SmC-SmJ phase transitions. The systematic decreasing of this parameter below SmA-SmC transition temperature, together with the decreasing $<P_2>_F$ parameter, can be yet some indication of the transition to the tilted phases. The SmJ phase is most ordered than SmC phase, and the transition enthalpy of SmC-SmJ transition for $\overline{10}$S5 is about 4-fold larger than that of N-SmA transition [17]. Thus, the order parameter should rise distinctly below SmC-SmJ transition temperature. However, in the SmJ phase the results obtained did not allow to calculate the order parameter adequate, because on cooling from the SmC phase the total absorbance and fluorescence intensity decreased somewhat as a result of crystallization (SmJ phase is in fact a soft crystal [2]).

In any way, the temperature dependence of $<P_4>_F$ in the N, SmA and SmC phases, obtained in this study for $\mathbf{1}/\overline{10}$S5 mixture, seems to be reasonable and thus, one is able to follow the behavior of the molecular distribution function in these phases. Figure (6) presents $f_4(\beta)$, calculated from Eq. (6), at various temperatures, corresponding to the SmC (1), SmA (2), and N (3) phases. The broadening of $f_4(\beta)$ function with the rise of temperature is observed, especially in the nematic phase, where $<P_4>_F$ value is negative. This means that this parameter affects strongly the shape of the distribution function. The determination of this function is of primary importance for both theoretical and experimental aspects, as well as for the technical application of liquid crystals.

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