Orientational Behaviour of some Novel Fluoro-Substituted Liquid Crystals as Studied by Optical Spectroscopy Methods

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The long-range orientational order of eight newly synthesized fluoro-substituted liquid crystals, two with a positive dielectric anisotropy and six with a negative dielectric anisotropy, was studied by means of the optical spectroscopy methods: electronic absorption and fluorescence. The liquid crystals were doped with small amount of the fluorescent dichroic dye. The absorption and emission spectra of linearly polarized light were recorded as a function of temperature in the whole range of the mesophase. The results obtained allow to determine the order parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$ as well as the orientational distribution function. An importance of the molecular structure of the liquid crystal on the orientational order was ascertained and discussed.

Key words: Fluorinated Liquid Crystals; Dichroic Dyes; Order Parameter; Electronic Absorption; Fluorescence.

1. Introduction

In spite of a rapid progress in the research and development of many modern technologies used in construction of display devices, liquid crystal displays (LCDs) are up to now the most common display technology and still find wide commercial application. The progress of LCDs technology would not be possible without the design and production of novel liquid crystal materials with suitable physical properties. In last years, the fluourinated liquid crystals have received much attention. The replacement of one or several hydrogen atoms by fluorine atoms leads to resulting materials with unique and peculiar properties [1 – 3]. The great advantages of these materials are good stability, extended mesophase temperature range, low viscosity, low electric conductivity, and low threshold voltage. Thus, the materials are suitable for applications in the mixtures for twisted nematic (TN) or supertwisted nematic (STN) liquid crystal displays, especially with the use of thin film transistor (TFT) technology [4, 5]. The laterally fluoro-substitution of mesogenic molecules is particularly interesting because it often leads to the nematic liquid crystalline materials with a negative dielectric anisotropy, suitable for utilization in displays operating in the vertical alignment (VA) mode [5]. As the most physical properties of liquid crystals are strongly dependent on the molecular orientation, the knowledge of the degree of order of newly synthesized substances is of primary importance in applications and understanding of various aspects of physics of liquid crystalline materials.

Here, we present the results of the study of the long-range orientational order of eight fluourinated liquid crystals. Two of them are substituted in the lateral position with the fluorine atom, but due to the presence of the strongly polar cyano-group, their dielectric anisotropy is positive. Six other liquid crystals, having two fluorine atoms in lateral positions, are characterized by a negative dielectric anisotropy. The liquid crystalline compounds were doped with a small amount of the fluorescent dichroic dye which plays a role of the probe of the orientational order in the nematic host. The absorption and emission of the linearly polarized light were measured as a function of temperature in the whole range of the nematic phase existence. On the basis of the spectra obtained, the order parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$ as well as the orientational distribution function were determined. The aim of our study was to find the influence of the molecular structure of the liquid crystal, in particular the substitution of the fluorine atom, on the orientational order in the nematic phase.

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2. Experimental

The molecular structure of the compounds investigated is given in Figure 1. The liquid crystals **1**–**8** were synthesized at the Institute of Chemistry, Military University of Technology in Warsaw, Poland. All they possess only the nematic (N) phase between the crystalline (Cr) and isotropic (I) states. The liquid crystals **1**–**2** are characterized by the positive dielectric anisotropy, and **3**–**8** by the negative one. Two dyes, 4-dimethylamino-4′-nitrostilbene (DANS) and naphthalene derivative of bicarboxylic acid (NDBA), were used as fluorescent guest probes. They were synthesized and chromatographically purified at the Institute of Polymer Technology and Dyes, Łódź University of Technology, and were dissolved in the liquid crystals at a concentration of $2 \cdot 10^{-2}$ mol dm^{-3}. DANS has been often utilized as a probe in the determination of the calamitic liquid crystal order because of the molecular structure similar in size and shape to that of the host [6–9], whereas NDBA is known as a dye of high orientation ability in the liquid crystalline matrices [10, 11].

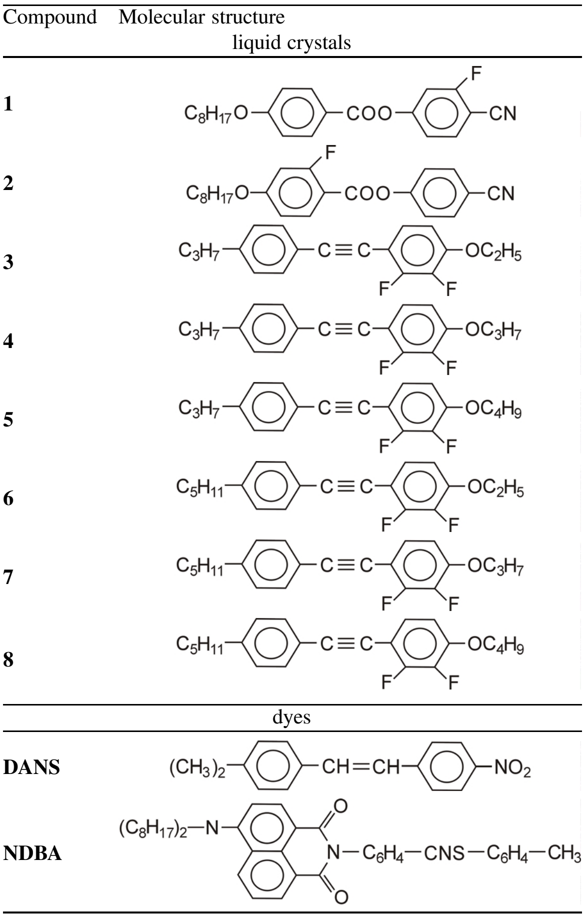

Fig. 1. Molecular structure of the compounds investigated.

The temperature of the phase transitions for the liquid crystals and their mixtures with the dye was determined on the basis of textures observed by means of a polarizing microscope (PZO, Warsaw, Poland) equipped with a heating stage.

The absorption spectra of the dyes dissolved in the liquid crystal were recorded in the visible spectral region by means of a spectrophotometer CARY 400. The fluorescence measurements were carried out by using a home-made photon-counting spectrofluorimeter, described in detail in [12]. The measurements were made in sandwich cells of 10 μm in thickness. A homogeneous planar orientation of the dye and liquid crystal molecules was obtained by treating the glass surfaces of the cells with polyimide and additional rubbing. In order to record the polarized spectra of the dye/liquid crystal mixtures, both the spectrophotometer and the fluorimeter were equipped with neutral UV polarizers. The fluorescence spectra were recorded in 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 [11].

In determination of the phase transitions and in the spectroscopic measurements, the temperature of the sample was stabilized with the use of a Scientific Instruments temperature controller, model 9700, with an accuracy of ±0.1 °C.

3. Orientational Order of Calamitic Liquid Crystals in Uniaxial Phases

The calamitic liquid crystalline molecules, due to their distinctive shape, undergo stronger attractive forces when arranged parallel to one another. Therefore, the molecules tend to align themselves along a certain preferred direction, described by director $\hat{n}$. For an uniaxial phase of the cylindrically symmetric molecules, the orientational order is described by the distribution function which can be reproduced with an accuracy sufficient for many purposes by the following series expansion of even Legendre polynomials $P_{2L}(\cos\beta)$ [6],

$$f(\beta) = \sum_{L=0}^{\infty} \frac{4L+1}{2} \langle P_{2L}(\cos\beta) \rangle P_{2L}(\cos\beta), \quad (1)$$

where $\langle P_{2L}(\cos\beta) \rangle$ are order parameters.

Two leading order parameters are $\langle P_2(\cos\beta)\rangle$ and $\langle P_4(\cos\beta)\rangle$,

$$\langle P_2(\cos\beta)\rangle = \frac{1}{2}\left\langle 3\cos^2\beta - 1\right\rangle, \tag{2}$$

$$\langle P_4(\cos\beta)\rangle = \frac{1}{8}\left\langle 35\cos^4\beta - 30\cos^2\beta + 5\right\rangle. \tag{3}$$

A knowledge of the two order parameters $\langle P_2\rangle$ and $\langle P_4\rangle$ allows one to obtain the truncated distribution function $f_4(\beta)$, where

$$\begin{aligned} f_4(\beta) = {} & \frac{1}{2} + \frac{2}{5}\langle P_2(\cos\beta)\rangle P_2(\cos\beta) \\ & + \frac{9}{5}\langle P_4(\cos\beta)\rangle P_4(\cos\beta). \end{aligned} \tag{4}$$

The two order parameters $\langle P_2\rangle$ and $\langle P_4\rangle$ can be simultaneously obtained using experimental methods such as electron spin resonance [13], Raman scattering spectroscopy [9, 14], and fluorescence depolarization of a dye probe dissolved in an anisotropic matrix [6, 8 – 11]. Doping the liquid crystal with a fluorescent probe and utilizing the 'guest-host' effect [15], we determine, in principle, the order parameters of the guest. However, by choosing the probe with a molecular structure similar to that of the liquid crystal molecule, no significant difference in the orientational order of the host and guest molecules is expected and the assumption that the dye probe reflects the orientation of the matrix is well satisfied.

From the fluorescence intensity measurements, the following emission anisotropies can be determined:

$$R_1 = \frac{J_{zz} - J_{zy}}{J_{zz} + 2J_{zy}}, \tag{5a}$$

$$R_2 = \frac{J_{yz} - J_{yy}}{J_{yz} + 2J_{yy}}. \tag{5b}$$

J_{ij}'s are here the reduced fluorescence intensities, regarding corrections for instrumental, concentration, and volume factors. The first subscript denotes the direction of the incident light and the second one refers to the direction of the emitted light in the laboratory frame x, y, z. The light beam incidents along the x-axis, the yz-plane is the plane of the sample, and the director coincides with the z-axis.

Table 1. Phase transition temperatures for liquid crystals investigated and their mixtures with dye.

Substance	T_{CrN}/°C	T_{NI}/°C	ΔT_{NI}/°C
1	53.5	56.4	–
1 + DANS	–	56.1	−0.3
1 + NDBA	–	57.2	0.8
2	58.4	65.4	–
2 + DANS	–	65.8	0.4
2 + NDBA	–	65.9	0.5
3	68.8	(64.1)	–
3 + DANS	–	(64.0)	−0.1
3 + NDBA	–	(65.5)	1.4
4	46	(39.5)	–
4 + DANS	–	(39.4)	−0.1
4 + NDBA	–	(40.2)	0.7
5	34.7	50.2	–
5 + DANS	–	50.2	0.0
5 + NDBA	–	51.4	1.2
6	57.4	60.9	–
6 + DANS	–	61.1	0.2
6 + NDBA	–	62.3	1.4
7	35.6	44.5	–
7 + DANS	–	44.4	−0.1
7 + NDBA	–	45.1	0.6
8	34.4	54.0	–
8 + DANS	–	54.1	0.1
8 + NDBA	–	54.7	0.7

( ) – monotropic phase.

The method allowing to calculate the order parameters $\langle P_2\rangle$ and $\langle P_4\rangle$ from the polarized fluorescence measurements had been developed on the basis of the theory given by Zannoni [16] and is described in details in [11]. The equations, from which the order parameters can be calculated, are solvable if the angle δ between the absorption and the emission oscillators and the angle φ between the absorption transition moment and the long molecular axis of the dye are known. The value of δ can be easily obtained from another experiment, e. g. from the fluorescence measurements of a dye embedded in an isotropic solid solvent. Additionally, the optical absorption anisotropy measurements need to be used, where the relation between the order parameter $\langle P_2\rangle$ and the angle φ is as follows:

$$\langle P_2\rangle = \frac{A_z - A_y}{A_z + 2A_y}\,\frac{2}{(3\cos^2\varphi - 1)}. \tag{6}$$

A_z and A_y denote here the components of the absorbance polarized parallel and perpendicularly to the director, respectively.

4. Results

Table 1 presents the temperatures of the crystal-nematic (T_{CrN}) and nematic-isotropic (T_{NI}) phase transitions for pure liquid crystals and their mixtures with DANS and NDBA. ΔT_{NI} is the difference between T_{NI} of the mixture and that for pure liquid crystal.

Table 2. Angles between the long axis and absorption (φ) and emission (θ) transition moments of NDBA molecular and order parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$ for dye/liquid crystal mixtures at two temperatures.

Liquid crystal	φ/°	θ/°	Lowest temperature			$T_{\mathrm{red}} = 0.98$		
			T/°C	$\langle P_2 \rangle_{\mathrm{A}} = \langle P_2 \rangle_{\mathrm{F}}$	$\langle P_4 \rangle_{\mathrm{F}}$	$\langle P_2 \rangle_{\mathrm{A}}$	$\langle P_2 \rangle_{\mathrm{F}}$	$\langle P_4 \rangle_{\mathrm{F}}$
1	1	−27	31	0.66	0.15	0.56	0.56	−0.01
2	3	−25	44	0.68	0.29	0.58	0.53	−0.03
3	5	−23	57	0.58	0.03	0.57	0.55	−0.02
4	6	−22	36	0.45	−0.12	0.45[a]	0.45[a]	−0.12[a]
5	4	−24	34	0.63	0.09	0.58	0.57	−0.03
6	4	−24	38	0.67	0.14	0.59	0.57	−0.05
7	1	−27	30	0.59	0.00	0.55	0.57	−0.02
8	2	−26	36	0.67	0.12	0.60	0.59	0.00

$\Delta\varphi = \pm 5°$, $\Delta\langle P_2 \rangle_{\mathrm{A}} = \pm 0.02$, $\Delta\langle P_2 \rangle_{\mathrm{F}} = \pm 0.03$, $\Delta\langle P_4 \rangle_{\mathrm{F}} = \pm 0.06$.

[a] The lowest T_{red} for NDBA/**4** is 0.989.

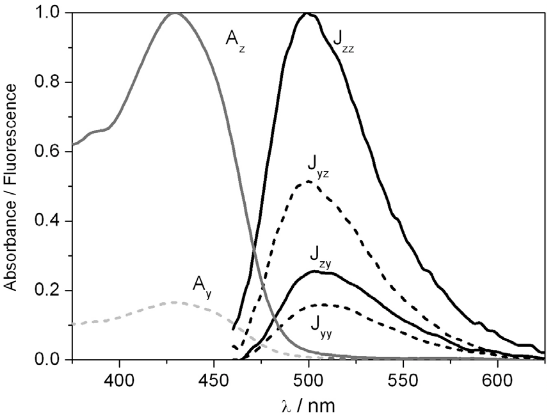

Fig. 2. Spectra of polarized components of absorption (A_z and A_y) and fluorescence (J_{zz}, J_{zy}, J_{yz}, and J_{yy}) for NDBA/**5** mixture at $T_{\mathrm{red}} = 0.95$ (34 °C).

Figure 2 shows, as an example, the polarized components of absorption and fluorescence spectra of dye NDBA oriented in liquid crystal **5** at the reduced temperature $T_{\mathrm{red}} = T/T_{\mathrm{NI}}$ equals to 0.95 (34 °C). On the basis of such spectra the order parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$ were calculated at various temperatures in the mesophase for all the dye/liquid crystal mixtures. For the calculations, the values of the absorbance as well as of fluorescence intensity were taken at the wavelength corresponding to the maximum of the appropriate band.

The angle φ between the absorption transition moment and the long molecular axis for DANS molecule is equal to 0° [7], thus the order parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$ could be obtained on the basis of the fluorescence measurements only [11]. However, the fluorescence intensity of DANS in all the liquid crystals under investigation was very low, indicating a strong quenching of the radiation of this dye in the presence of the fluorine atom in the host molecule. Hence, the order parameters obtained from the fluorescence spectra were estimated with large uncertainty. Therefore, in the following only the results of the absorption measurements for DANS/liquid crystal mixtures are given. On contrary, the fluorescence intensity of NDBA dissolved in the liquid crystals **1**–**8** was high enough and the determination of the order parameters both from the absorption and fluorescence measurements was possible.

The angle φ for NDBA molecules was calculated on the basis of the experimentally obtained absorbance and fluorescence intensity values of the appropriate polarized components for dye/liquid crystal mixtures measured at the lowest temperature used. We supposed that at this temperature, the thermal molecular motions are strongly hindered and the rotational relaxation time τ_{R} is much longer than the lifetime of the excited state of the fluorescent dye molecule τ_{F}. Therefore, the order parameter $\langle P_2 \rangle$ obtained from the fluorescence measurements is equal to that determined on the basis of the polarized absorption spectra and calculated from (7). The angle $\delta = 28°$ between the absorption and emission oscillators of NDBA was taken from [11]. The values of angles φ and $\theta = \delta - \varphi$ for NDBA in liquid crystals **1**–**8** are listed in Table 2. The sign minus at the angle θ means that the emission transition moment lies at the opposite side of the long molecular axis of NDBA than the absorption transition moment.

In the following it was assumed the angles φ and δ to be constant in our experimental temperature range, and the order parameters as a function of temperature were determined independently from the absorption ($\langle P_2 \rangle_{\mathrm{A}}$) and fluorescence ($\langle P_2 \rangle_{\mathrm{F}}$ and $\langle P_4 \rangle_{\mathrm{F}}$) measurements. Figure 3 shows the dependences of $\langle P_2 \rangle$ and $\langle P_4 \rangle$ on the reduced temperature T_{red} for liquid crystal **1** doped with NDBA, as an example, whereas in Table 2 the order parameters for all the NDBA/liquid

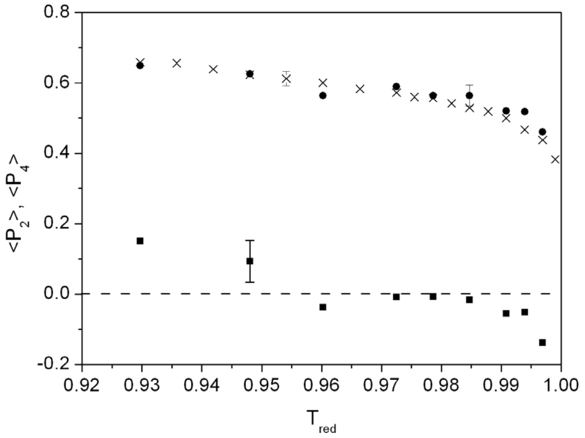

Fig. 3. Dependence of order parameters $\langle P_2\rangle$ and $\langle P_4\rangle$ on reduced temperature $T_{\text{red}} = T/T_{\text{NI}}$ for NDBA/**1** mixture determined from absorption (× — $\langle P_2\rangle_{\text{A}}$ only) and fluorescence measurements (● – $\langle P_2\rangle_{\text{F}}$, ■ – $\langle P_4\rangle_{\text{F}}$).

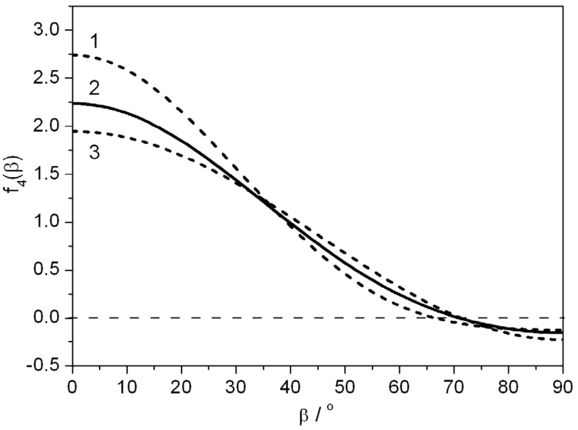

Fig. 4. Distribution function $f_4(\beta)$ for NDBA/**8** mixture at $T_{\text{red}} = 0.94$ (1), 0.96 (2), and 0.98 (3).

crystal mixtures determined at the lowest possible temperature and at $T_{\text{red}} = 0.98$ are presented. Knowing the order parameters $\langle P_2\rangle$ and $\langle P_4\rangle$ it is possible to obtain the truncated distribution function $f_4(\beta)$ from (4). Examples of $f_4(\beta)$ for liquid crystal **8** at $T_{\text{red}} = 0.94$, 0.96, and 0.98 are plotted in Figure 4.

Figure 5 presents the order parameter $\langle P_2\rangle_{\text{A}}$ calculated from (6) on the basis of the absorption spectra of liquid crystals **1** and **2** doped with DANS and NDBA and in Table 3 the values of the order parameter $\langle P_2\rangle_{\text{A}}$ of liquid crystals **1**–**8** doped with both dyes at three different reduced temperatures, are listed. Additionally in Figure 5 the data from [17] for nematogenic non-substituted 4-cyanophenyl-4′-n-octylbenzoate, 8CPB, are given for comparison.

Table 3. Order parameters $\langle P_2\rangle_{\text{A}}$ of dye/liquid crystal mixtures at three reduced temperatures.

Substance	$\langle P_2\rangle_{\text{A}}$		
	$T_{\text{red}} = 0.945$	$T_{\text{red}} = 0.975$	$T_{\text{red}} = 0.99$
1 + DANS	0.54	0.46	0.40
1 + NDBA	0.63	0.56	0.50
2 + DANS	0.61	0.53	0.47
2 + NDBA	0.67	0.59	0.52
3 + DANS	–	0.58	0.53
3 + NDBA	–	0.58	0.53
4 + DANS	–	–	0.43
4 + NDBA	–	–	0.44
5 + DANS	0.64	0.57	0.51
5 + NDBA	–	0.59	0.54
6 + DANS	0.61	0.55	0.49
6 + NDBA	0.64	0.60	0.55
7 + DANS	0.62	0.55	0.49
7 + NDBA	–	0.56	0.51
8 + DANS	0.64	0.57	0.50
8 + NDBA	0.66	0.61	0.56

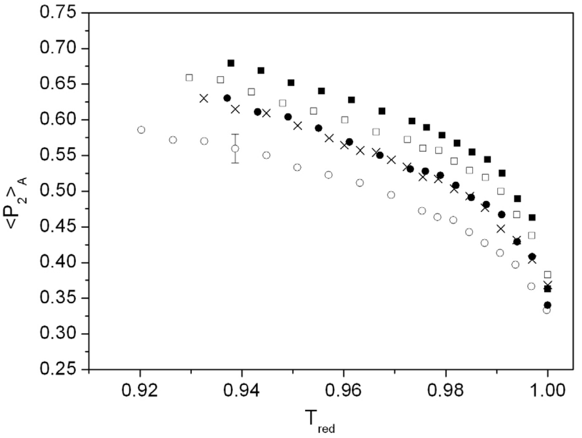

Fig. 5. Order parameter $\langle P_2\rangle$ determined from absorption measurements as a function of reduced temperature $T_{\text{red}} = T/T_{\text{NI}}$ for liquid crystals **1** (open symbols) and **2** (filled symbols) doped with DANS (circles) and NDBA (squares). Crosses mean the data for non-substituted 4-cyanophenyl-4′-n-octylbenzoate, 8CPB [17].

5. Discussion

5.1. Phase Transition Temperatures

Results presented in Table 1 indicate that the crystal-nematic and nematic-isotropic phase transition temperatures as well as the range of the mesophase region strongly depend on the molecular structure of the liquid crystals under investigation. For the liquid crystals with a positive dielectric anisotropy, which differ in the place of the fluorine atom substitution, we observed an increase of the T_{CrN} and T_{NI} temperatures as well as the extension of the mesophase region of liquid crystal **2** with respect to liquid crystal **1**. In the case of the liquid crystals with a negative dielectric anisotropy, the length of both the alkyl and alkoxy chains influences the T_{NI} temperature and the range of the mesophase region. The length of the alkoxy chain affects also the temperature T_{CrN}. For the clearing temperature of liquid crystals **3**–**5** and **6**–**8** odd-even effect [9, 18] can be noticed: T_{NI} of the compounds with the odd number of carbons in the alkoxy chain is lower than that of the compounds with the even number of carbons. The mesophase temperature range of liquid crystals **1**–**8** is not very broad (it is narrower than 10 °C, except for **5**), but at slow cooling of the substance it is possible to obtain the overcooled nematic phase down to 40 °C for liquid crystal **2**, and even below 30 °C in the case of all other liquid crystals. It is worth noting here that compounds analogous to liquid crystals **3**–**8** but without triple bonds between benzene rings, either do not exhibit mesophase region or have only virtual nematic phase with the NI transition below 0 °C [3].

The addition of the dichroic dye does not influence noticeably the T_{CrN} temperature of liquid crystals **1**–**8**, but some changes of the T_{NI} temperature are observed. The effect of DANS is rather small: this dye only slightly decreases or increases T_{NI}, depending on the host compound. In the case of liquid crystal **5** no change of T_{NI} has been found. On contrary, NDBA affects significantly the temperature T_{NI} causing its increasing for all the liquid crystals. The influence of the dichroic dye on the nematic-isotropic transition was extensively investigated previously [19–23] and it was found that the direction and the magnitude of the shift in the T_{NI} temperature of the liquid crystal after the dye addition is strictly related to the molecular geometry of the guest and its compatibility with the anisotropic host [22]. The small T_{NI} shift in the presence of DANS indicates good compatibility of this dye with the liquid crystals under investigation, similarly as it was observed for other calamitic liquid crystals [9, 22, 23]. However, the elongated molecules of NDBA cause the increase of T_{NI}, which is also in agreement with previous results [10].

5.2. Order Parameters

From results shown in Figure 3 as well as presented in Table 2 it can be seen that at given temperature the order parameter $\langle P_2\rangle_{\mathrm{A}}$, obtained for a given NDBA/liquid crystal mixture in the use of the absorption measurements, is in good agreement (within an experimental uncertainty) with the order parameter $\langle P_2\rangle_{\mathrm{F}}$, determined from fluorescence measurements, when the appropriate values of the angles φ and θ are taken into account. These angles calculated for NDBA oriented in various liquid crystals differ somewhat, but the difference does not exceed the accuracy of the determination ($\pm 5°$). The character of the temperature dependence of $\langle P_2\rangle$ is similar for all the liquid crystals investigated. It is characteristic for nematogens and is in agreement with the mean-field theories of the nematic phase [24, 25]. However, with the rise of temperature, $\langle P_2\rangle$ varies somewhat differently for various mixtures, which indicates their different resistance on the thermal fluctuations.

The order parameter $\langle P_4\rangle_{\mathrm{F}}$ is positive at lower temperatures and decreases at approaching to T_{NI}, reaching for some liquid crystals even small negative values. Such results are not in agreement with the theories [24, 25] which do not predict the negative value of the $\langle P_4\rangle$ parameter. For many nematogenic liquid crystals, however, the low and sometimes negative values of $\langle P_4\rangle$ were noted by the authors studying the orientational order in the mesophase using both fluorescence depolarization [6, 9, 11, 23] and Raman scattering methods [9, 14, 26]. Many attempts were undertaken in order to explain these discrepancies and in recent years the careful analysis of the experimental data has shown that the calculation procedure is very sensitive to the choice of the fitting parameters [9, 27–30]. In the case of the fluorescence depolarization, the crucial role plays the angle φ, which cannot be here obtained with accuracy better than $\pm 5°$. Meanwhile, in [9, 27] it was demonstrated that already the change of φ of 5° can cause the alteration of the $\langle P_4\rangle$ sign. The order parameter $\langle P_4\rangle$ strongly influences the distribution function $f_4(\beta)$ because it depends on $\cos^4\beta$ and thus is more sensitive on the molecular fluctuations than the order parameter $\langle P_2\rangle$. This is good illustrated in Figure 4. The broadening of the distribution function, seen with the increasing temperature, points out for a greater tendency of molecules to tip away from the director $\hat{n}$.

Let us now analyze the results presented in Figure 5 and in Table 3. First of all, it is seen that, except for liquid crystals **3**, the order parameter $\langle P_2\rangle$ for NDBA/liquid crystal mixtures is always higher than that for DANS/liquid crystal mixtures. Although in our experiment the order parameter of the dye is being measured, not the order parameter of the liquid crystal, it is reasonable to assume that the structure of DANS, which resembles the structure of the liquid crystals, is aligned so effectively that it reflects very well the orientation of the nematic host. But it is not unusual for the dye to be better ordered than the liquid crystal as it is observed here in the case of NDBA. It is worth noting that the order parameter of the DANS/liquid crystal and NDBA/liquid crystal mixtures is very good correlated with the shift of the T_{NI} temperature after the dye addition (see previous section).

Comparing the order parameter of liquid crystals **1** and **2** (Fig. 5) it is seen that the position of the fluorine atom influences the molecular orientation. For the DANS/**2** mixture almost the same values of $\langle P_2\rangle$ have been obtained as for 8CPB doped with the same dye [17]. This means that the lateral substitution of the fluorine atom to the benzene ring at the alkoxy chain does not disturb the orientational order. This can result from the possibility of the free rotation of the benzene ring with connected fluorine atom in liquid crystal **2** around the long molecular axis, i. e. around the cyano-group axis. In the case of compound **1** the fluorine atom is substituted in the *ortho*-position, rigid with respect to the cyano-group. The presented data show that in such a case the orientational ability of the mesogenic molecules is reduced with respect to that of compound **2**. Furthermore, as clearly results from the data presented in Figure 5, NDBA added to the nematic host more improves the orientation of the less oriented liquid crystal **1** than that of liquid crystal **2**. Such an effect was observed previously for other dyes [31, 32] and is in a good correlation with ΔT_{NI} values (Table 1).

The values of the order parameter itself and the temperature dependences of the order parameter for liquid crystals with a negative dielectric anisotropy, except for liquid crystal **4**, are not markedly different. At the lowest possible temperature $\langle P_2\rangle$ is above 0.6 and closely to T_{NI} decreases only to ≈ 0.5. However, the odd-even effect is observed: at the same T_{red}, the order parameter for the liquid crystals with the odd number of carbon atoms in alkoxy chain (**3**, **5**, and **6**, **8**) is higher than that for the liquid crystals with the even number of carbons (**4** and **7**). For liquid crystal **4** surprisingly low values of $\langle P_2\rangle$ (and also $\langle P_4\rangle$) were obtained, both for the mixtures with DANS and NDBA. As the influence of the dye addition on the temperature T_{NI} is similar to that for other liquid crystals, it seems that our finding for liquid crystal **4** results rather from poor orientation of the liquid crystal molecules themselves than from the fact that the dye molecules do not good reflect the order of the liquid crystal molecules in the mixtures. Note that for this liquid crystal the monotropic mesophase region is quite narrow – it is ≈ 10 °C – in comparison, e. g., to the 35 °C for the second monotropic compound, liquid crystal **3**.

In final conclusion, it must be emphasized that the results of our study are quite convincing in revealing that most of the liquid crystals under investigation, can be consider as promising candidates to utilize them in technologically important mixtures, because of the convenient range of the existence of the nematic phase as well as of the high order parameter in the whole mesophase region.

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