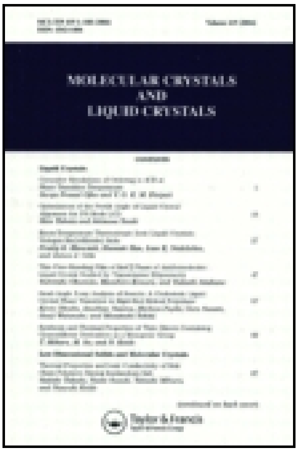

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Molecular Orientation and Odd-Even Effect in Nematogenic Homologous Series of 4-Cyanophenyl-4′-N-Alkylbenzoate

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Molecular Orientation and Odd-Even Effect in Nematogenic Homologous Series of 4-Cyanophenyl-4′-*N*-Alkylbenzoate

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The orientational behavior of liquid crystals from homologous series of 4-cyanophenyl-4′-n-alkylbenzoate ($C_nH_{2n+1}PhCOOPhCN$) *doped with dichroic dyes was investigated by means of optical spectroscopy methods: electronic absorption and fluorescence. The absorption and emission spectra of linearly polarized light were recorded as a function of temperature in whole range of the mesophase. The second- and fourth-rank order parameters* ($<P_2>$, $<P_4>$) *and molecular distribution function were determined.The odd-even effect for the order parameter, explained as the alternation of interaction between alkyl chains, was observed. An influence of the dye molecular structure on the orientational order of the liquid crystal/dye mixture was reported.*

Keywords Dichroic dye; electronic absorption; fluorescence; liquid crystal; odd-even effect; order parameter

1. Introduction

Liquid crystal displays (LCDs) have been used in various electronic products and their expansion has been supported by the progress of newly synthesized compounds in order to obtain good LCD performance. Most of the research in this field has been done with nematic liquid crystals (NLCs) which are the simplest liquid crystalline phase formed by elongated molecules that, in average, are oriented parallel to each other [1]. Many of the anisotropic physical properties associated with use in devices are closely related to the orientational order of the system. To quantify the molecular orientation, it is necessary to define an orientational model. For nematogens, a uniaxial orientation of mesogenic molecules with respect to the preferred direction is generally considered.

Long-range orientational order in liquid crystalline phases arises because of tendency of the rod-like molecules to align their long axes along a certain preferred direction, described by director, **n**, treated as a vector, the both directions of which,

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+**n,** and –**n**, are equivalent. The simplest complete description of the orientational order is the orientational distribution function, f(α,β,γ), integrated over all possible translations [2], where α, β, and γ are Euler angles. Only uniaxial symmetry around the director is characterized for many liquid crystals, thus no order in the angle α is permitted. If the mesogenic molecules are cylindrically symmetric ($C_{\infty h}$), rotation around molecular symmetry axis (angle γ) cannot modify the distribution function. Assuming an uniaxial orientation of the mesogen with respect to the preferred direction, **n**, the orientation distribution of the long molecular axes, f(β), can be characterized by using a truncated series of Legendre polynomials, $P_L(\cos\beta)$ [3,4]:

$$f(\beta) = \sum_{L=0}^{\infty} \left(\frac{2L+1}{2}\right) \langle P_L \rangle P_L(\cos\beta), \tag{1}$$

where the normalization term (2L+1)/2 ensures the convergence of the series. The coefficients $<P_L>$ are the orientation factors determined experimentally:

$$\langle P_L \rangle = \frac{\int_0^{\pi} P_L(\cos\beta) f(\beta) \sin\beta \, d\beta}{\int_0^{\pi} f(\beta) \sin\beta \, d\beta}, \tag{2}$$

where β is the angle between the long molecular axis and **n**. Thus, the knowledge of f(β) in principle provides the order parameters. Only the even terms in Legendre expansion of f(β) are nonzero, as due to equivalence of **n**, and –**n** one has f(π-β) = f(β).

The order parameter $<P_2>$ can be measured by techniques probing a second order tensor property [5], such as diamagnetic anisotropy, optical birefringence, nuclear magnetic resonance, dichroism in visible and UV region. Both $<P_2>$ and $<P_4>$ can be simultaneously obtained on the basis of X-ray diffraction [6], electron paramagnetic resonance [7], fluorescence depolarization of a guest probe dissolved in liquid crystalline matrix [4,8,9] as well as polarized Raman scattering [10–12].

In this paper the orientational properties of homologous series of 4-cyanophenyl-4′-*n*-alkylbenzoate (C_nH_{2n+1}PhCOOPhCN, n = 4–10) by means of optical spectroscopy methods: absorption in visible region and depolarization of fluorescence were investigated. The liquid crystals were doped with a small amount of fluorescent dye or two azo-dyes with various molecular structure. The absorption and emission spectra of linearly polarized light were recorded as a function of temperature in the nematic phase. To investigate ordering properties of liquid crystals of the homologous series of C_nH_{2n+1}PhCOOPhCN, the second-and fourth-rank order parameters ($<P_2>$, $<P_4>$) and the molecular distribution function were determined. The results of the study of the influence of the dye molecular structure on the order parameter and the effect of the dichroic dye presence on the mesophase range of the liquid crystalline matrix are presented.

The conformation of the end chain causes pronounced alternations in certain physical properties as the number of carbon atoms in an alkyl chain varies from odd to even in liquid crystal molecules. This effect is known as the odd-even effect [13]. Here, this effect in nematogenic homologous series of C_nH_{2n+1}PhCOOPhCN was determined experimentally. The variations of the order parameter $<P_2>$ with the increase of the alkyl chain length at various temperatures in the whole range of the nematic phase were estimated.

2. Experimental Methods

The molecular structure of the compounds investigated is given in Table 1.

The liquid crystal materials used in the study, namely 4-cyanophenyl-4′-n-alkylbenzoates ($C_nH_{2n+1}PhCOOPhCN$) for n = 4–10, were synthesized and chromatographically purified at the Institute of Chemistry, Military University of Technology, Warsaw, Poland. The temperatures of the phase transitions are shown in Table 2.

There were observed monotropic transition into nematic phase for n = 4 and n = 5, and into smectic A phase for n = 10, while cooling. Other compounds of the series are enantiotropic materials having stable crystalline, nematic, and isotropic phases during heating and cooling. We used two azo-dyes (R1 and R2) of various phases molecular sizes and shapes in order to study an influence of molecular structure of the dye on the order parameter of the guest-host mixtures and the effect of

Table 1. Molecular structure of compounds investigated

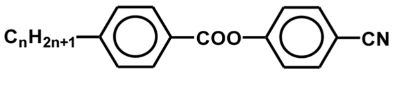
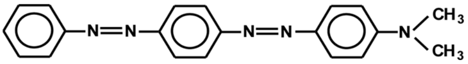
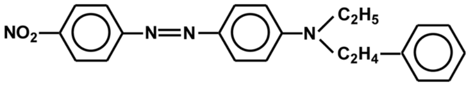
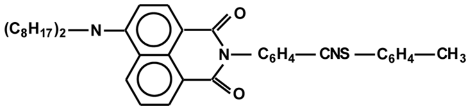
Compound	Molecular structure
	LIQUID CRYSTALS
nCPB n = 4–10	
	DYES
R1	
R2	
NDBA	

Table 2. Mesophase range of liquid crystals investigated

Liquid crystal	T_{CN}/°C	T_{SN}/°C	T_{NI}/°C
4CPB	52.2	–	(42.9)
5CPB	61.5	–	(57.9)
6CPB	45.0	–	48.6
7CPB	29.0	–	57.7
8CPB	40.5	–	54.5
9CPB	44.9	–	60.9
10CPB	59.5	(55.5)	60.0

() – monotropic phase.

dye presence on the mesophase range. The naphthalene derivative of bicarboxylic acid (NDBA) was used as a fluorescent probe. NDBA is known as a dye of high orientation ability in the liquid crystalline matrices [11,14]. The molecular structure of dyes is shown in Table 1. All the dyes were synthesized and chromatographically purified at the Institute of Polymer Technology and Dyes at Łódź University of Technology and were dissolved in the liquid crystals at concentration of $2 \cdot 10^{-2}\,\mathrm{mol/dm^3}$.

The textures and phase transition temperatures, both of pure liquid crystals and dye-liquid crystals mixtures, were studied with a polarizing microscope (PZO, Warsaw, Poland) equipped with a heating stage.

For precise characterization of the nematic-isotropic phase transition of the compounds, Raman spectra were recorded with the resolution of about $2\,\mathrm{cm^{-1}}$ by means of inViaRenishaw system. A Raman microscope, equipped with argon ion laser operating at 488 nm, was used to measure the backscattered light from the liquid crystals sample. The laser beam was tightly focused through an Leica 50x microscope objective.

The polarized light absorption of the guest-host mixtures was measured in the visible spectral region by means of a spectrophotometer CARY 400. The setup was possible to be equipped with UV dichroic polarizers for registration of polarized components of the spectra. On the basis of polarized absorption spectra of the dichroic dye dissolved in the liquid crystalline matrix, the order parameter $<P_2>$ was calculated from the following equation [15]:

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

where A_z and A_y denote the components of the absorbance polarized parallel and perpendicular to the director, and φ is the angle between the absorption transition dipole moment, $\boldsymbol{\mu}_\mathbf{A}$ and the long axis of the dye molecule.

The fluorescence measurements were carried out by using a photon–counting spectrofluorimeter constructed in our laboratory. The details of this setup were described in [16]. The fluorescence spectra were recorded in B 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 [14,17]. On the basis of fluorescence intensity values, the emission anisotropies, R_1 and R_2 were calculated in the following way:

$$R_1 = \frac{J_{zz} - J_{zy}}{J_{zz} + 2J_{zy}}, \tag{4a}$$

$$R_1 = \frac{J_{yz} - J_{yy}}{J_{yz} + 2J_{yy}}. \tag{4b}$$

J_{ij}'s are here the reduced fluorescence intensities regarding corrections for instrumental, concentration and volume factors. The first factors 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 is the plane of the sample and the director coincides with the z axis.

On the assumption that the fluorescence lifetime, τ_F is much less than rotational diffusion times, τ_R of emitting molecule ($\tau_F << \tau_R$), the order parameters can be determined from the following system of equations [17–19]:

$$R_1 = \frac{\frac{1}{3}\langle P_2\rangle\, P_2[\cos(\delta-\varphi)] + A + B\langle P_2\rangle + 6C\langle P_4\rangle}{\frac{1}{3}+\frac{2}{3}\,\langle P_2\rangle\, P_2(\cos\,\varphi)}, \tag{5a}$$

$$R_2 = \frac{\frac{1}{3}\langle P_2\rangle P_2[\cos(\delta-\varphi)] - \frac{1}{2}\,(2A\ +\ 7C\langle P_4\rangle)}{\frac{1}{3}\langle P_2\rangle P_2(\cos\varphi) + A - B\langle P_2\rangle + C\langle P_4\rangle}, \tag{5b}$$

where A, B, C are some functions depending only on the angle δ and φ; δ is the angle between the absorption and the emission oscillators. The relation $\delta = \varphi + \theta$ is valid, where θ denotes the angle between the long molecular axis and the emission transition moment, $\boldsymbol{\mu}_{\mathbf{e}}$.

The measurements of the liquid crystal/dye mixtures were carried out in "sandwich" cells of 10 Φm in thickness. The glass surface of the cells was coated with polyimide layer, and, next, they were subjected to rubbing procedure. As a result of anchoring forces on the polyimide layers, a uniform planar orientation of the mesogenic and nonmesogenic molecules was obtained of the samples. The temperature of the cells was determined with an accuracy of ∀0.1EC by use of a Scientific Instruments temperature controller, model 9700.

3. Results and Discussion

3.1. *Order Parameters*

Figure 1 presents parallel, A_z and perpendicular, A_y components of polarized absorption spectra and four components of polarized fluorescence, J_{zz}, J_{zy}, J_{yz}, J_{yy} for 8CPB/NDBA, as an example.

On the basis of such spectra the order parameters $<P_2>$ and $<P_4>$ at various temperatures in the mesophase were calculated by using Eqs. (3), (5a), and (5b), respectively. For calculations, the values of absorbance and fluorescence intensity were taken at the wavelength corresponding to the maxima of absorption and emission bands.

Figure 2 shows the order parameter $<P_2>_A$ as a function of the reduced temperature, $T_{red} = T/T_{NI}$, where T is the temperature of measurement, T_{NI} is the temperature of nematic-isotropic transition in K. The $<P_2>_A$ was calculated for dyes R1, R2 and NDBA in 8CPB. For comparison, the Figure 2 presents also the appropriate results for the liquid crystal/DANS mixture. The data for dyes R1, R2 and NDBA in 8CPB were normalized to the points of the 8CPB/DANS mixture at $T_{red} = 0.927$. DANS has been often utilized as the probe in the determination of calamitic liquid crystals order due to the molecular structure similar in size and shape to that of mesogenic molecules. Thus, one can assume that this dye reflects well the orientation of liquid crystals. The data for 8CPB/DANS mixture is taken from Ref. [20].

From results presented in Figure 2 it can be seen that character of $<P_2>_A$ changes with temperature is similar for all the mixtures investigated. It should be, however, noted that the liquid crystal/dyes mixtures investigated are differently resistant to thermal fluctuations. Moreover, if one considers the same reduced

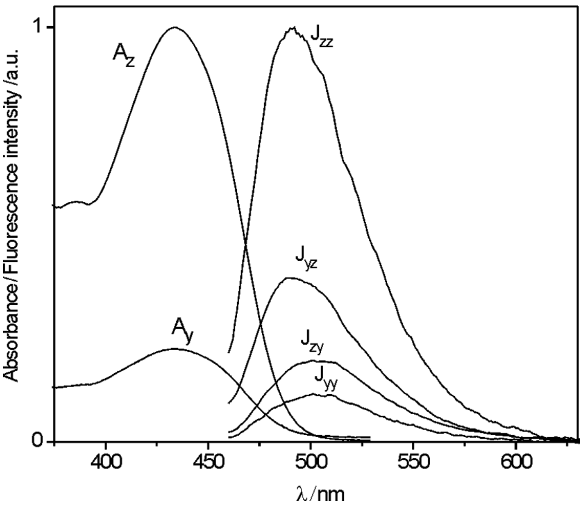


Figure 1. Spectra of polarized components of absorption (A_z, A_y) and fluorescence (J_{zz}, J_{zy}, J_{yz}, J_{yy}) for 8CPB/NDBA at $T_{red} = 0.95$.

temperature, the values of the order parameter are different for various 8CPB/dyes mixtures, indicating strong influence of the molecular structure of the dye doped to the liquid crystal on the orientational order. For 8CPB/R1 as well as for 8CPB/NDBA mixtures $<P_2>_A$ is greater than the order parameter for 8CPB/DANS, which suggests that the elongated molecules of dyes can improve the molecular

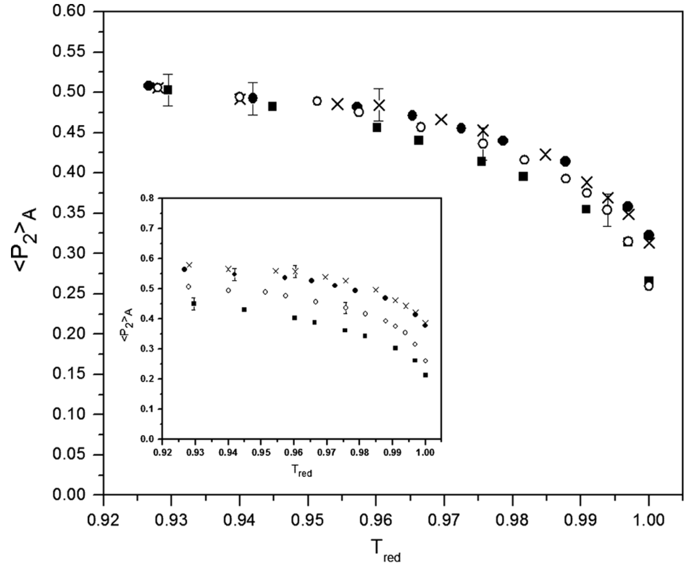


Figure 2. Dependence of order parameter $<P_2>$ (normalized to the points of the 8CPB/DANS at $T_{red} = 0.927$) on reduced temperature $T_{red} = T/T_{NI}$ for 8CPB/dye mixtures determined from absorption measurements (X– R1, ■–R2, x–NDBA, B-DANS [20]). The inset indicates the data unnormalized to the DANS points.

Table 3. Temperatures of nematic-isotropic phase transition for liquid crystals investigated and their mixtures with dyes R1, R2 and NDBA

	T_{NI}/°C				ΔT_{NI}/°C		
LC	LC	LC/R1	LC/R2	LC/NDBA	LC/R1	LC/R2	LC/NDBA
4CPB	42.2	42.9	41.8	43.4	+0.7	−0.4	+1.2
5CPB	56.7	57.0	56.5	58.2	+0.3	−0.2	+1.5
6CPB	48.5	48.8	48.4	49.1	+0.3	−0.1	+0.6
7CPB	59.0	59.5	58.3	59.5	+0.5	−0.7	+0.5
8CPB	55.2	55.5	55.0	55.9	+0.3	−0.2	+0.7
9CPB	61.0	61.2	60.5	62.1	+0.2	−0.5	+1.1
10CPB	60.0	60.5	59.8	61.7	+0.5	−0.2	+1.7

orientation in guest-host mixture. This means that these dyes have a good compatibility with the liquid crystals, *i.e.*, the correlation between the mutual parallel alignment of the dye and liquid crystals molecular long axes is very strong. However, the presence of the additional benzene ring in the end group of the dye R2 causes the decrease of $<P_2>_A$. This can be due to the non-zero angle between the long molecular axis and the electronic transition dipole moment or to incomplete alignment of the dye molecules with respect to the orientation axis of a liquid crystal [21]. The results obtained from absorption measurements were confirmed by influence of the dye addition on the nematic-isotropic phase transition temperature, T_{NI} of the $C_nH_{2n+1}PhCOOPhCN$ homologous series (Table 3). In this table, the temperatures of the nematic-isotropic transition for pure liquid crystals and their mixtures with azo dyes as well as with NDBA are given. ΔT_{NI} is difference between T_{NI} of the mixture and that of pure liquid crystal.

The data reported in Table 3 for T_{NI} are in agreement with the results obtained by means of Raman scattering spectroscopy. Figure 3 shows Raman scattering spectrum of the liquid crystal 5CPB, as an axample, recorded at a room temperature.

We analyzed two main bands: at 1604 $cm^{-1}$and 2229 cm^{-1}. The first band is assigned to the C=C stretching vibration in the aromatic ring, and the latter one to the stretching vibration of the terminal group C≡N [22,23]. The nematic-isotropic phase transition for nCPB is manifested by change of the integral intensity of the Raman bands. Figure 4 shows the integral intensity of the C=C and the C≡N Raman band as a function of temperature.

With the decrease of temperature from 75EC to 60EC the constant value of the integral intensity (within experimental uncertainties, 5%) is observed. In the vicinity of 60EC, the temperature dependence of the integral intensity of Raman band for the C=C stretching mode as well as for the C≡N losses the linear character, becoming discontinuous at the point of the phase transition.

According to the data presented in Figure 2 and Table 3, it can be concluded that there exists correlation between the order parameter and the shift of the phase transition temperature of a liquid crystal/dye mixture with respect to that of pure liquid crystal. Such correlation had been found previously [21,24].

The $<P_2>$ order parameter gives only approximate information about the orientational distribution of cylindrical molecules in a uniaxial phase. More precise description is possible if the $<P_4>$ is known.

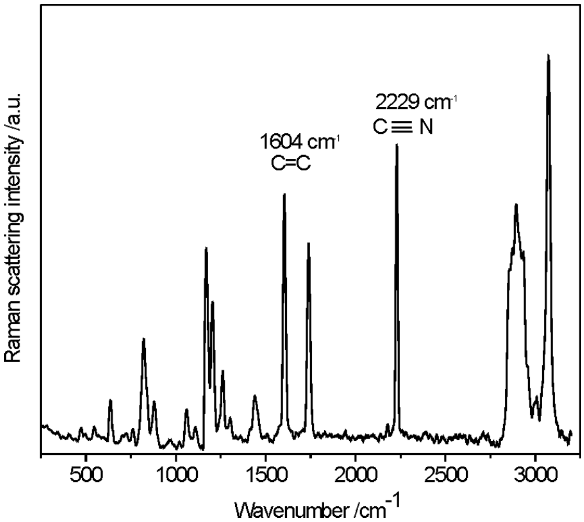


Figure 3. Depolarized Raman scattering spectrum of an unoriented 5CPB at room temperature.

Figure 5 shows the order parameters $<P_2>_A$, $<P_2>_F$, and $<P_4>_F$ as a function of T_{red} for NDBA in 7CPB in the nematic phase, whereas Figure 6 presents, the temperature dependence of $<P_2>_A$, $<P_2>_F$, and $<P_4>_F$ values for NDBA/10CPB/NDBA mixture in the smectic A and nematic phases. For calculation the angle φ for NDBA molecule was determined from absorption and fluorescence experimental data at the lowest temperature used in experiment, where $\tau_F << \tau_R$ can be assumed. Thus, the order parameters calculated independently from the absorption ($<P_2>_A$) and from emission ($<P_2>_F$) anisotropies should be equal to

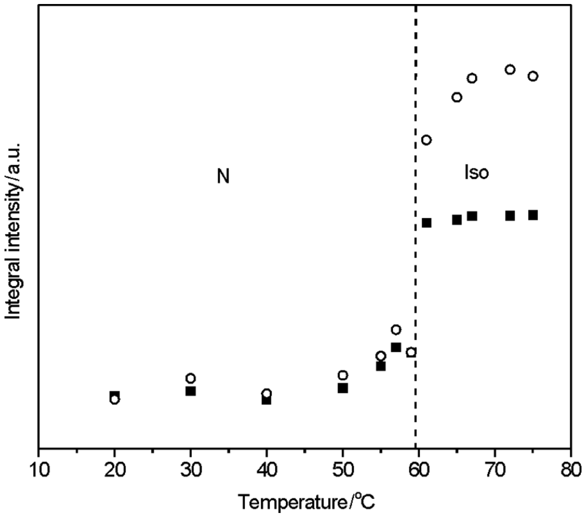


Figure 4. Integral intensity of Raman bands vs. temperature for 5CPB (B – 2229 cm^{-1}, ■–1604 cm^{-1}), $\Delta I_{\infty} = 5\%$.

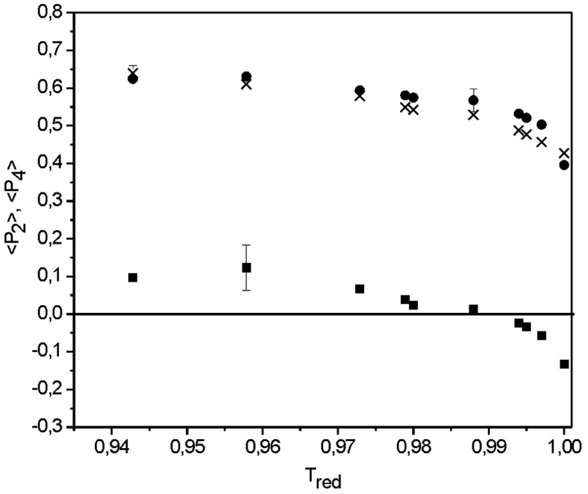


Figure 5. Dependence of order parameters $<P_2>$ and $<P_4>$ on reduced temperature $T_{red} = T/T_{NI}$ for 7CPB/NDBA mixture (x–$<P_2>_A$, X–$<P_2>_F$, ■–$<P_4>_F$).

each other. The angle $\delta = 28E$, $\varphi = 12E$ was taken from [17]. Under such assumption, the calculations give $\varphi = 12E$ for NDBA in 10CPB and $\varphi = 6E$ in 7CPB. As the angle φ is molecular parameter, it should be independent on the liquid crystalline host. Meanwhile, from Table 4 follows that the value of the angle φ for NDBA oriented in various members of nCPB is different. The difference, however, does not exceed the accuracy of the angle φ determination ($\Delta\varphi = \forall 5E$ [17]).

From the results presented in Figures 5 and 6 as well as in Table 4 it can be seen that at given temperature the order parameter determined for nCPB/NDBA mixtures from the absorption measurements is in very good agreement with the

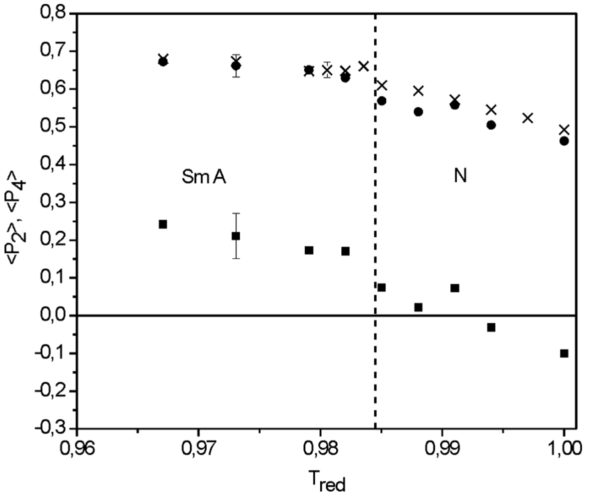


Figure 6. Dependence of order parameters $<P_2>$ and $<P_4>$ on reduced temperature $T_{red} = T/T_{NI}$ for 10CPB/NDBA mixture (x–$<P_2>_A$, X–$<P_2>_F$, ■–$<P_4>_F$).

Table 4. Angle between the long molecular axis and absorption transition moment, ϕ and order parameters $<P_2>$ and $<P_4>$ for liquid crystal/NDBA mixtures at two temperatures

		Lowest temperature			$T_{red} = 0.98$		
LC	$\varphi/^o$	T/°C	$<P_2>_A = <P_2>_F$	$<P_4>_F$	$<P_2>_A$	$<P_2>_F$	$<P_4>_F$
4CPB	9	33	0.56	0.05	0.52	0.53	−0.01
5CPB	8	50	0.55	0.01	0.53	0.53	0.004
6CPB	5	32	0.62	0.14	0.54	0.56	0.02
7CPB	5	40	0.64	0.12	0.54	0.58	0.05
8CPB	9	40	0.58	0.07	0.55	0.56	−0.04
9CPB	4	40	0.73	0.30	0.62	0.65	0.18
10CPB	12	50	0.68	0.24	0.64	0.66	0.19

order parameter obtained from fluorescence measurement ($\Delta<P_2>_A = \pm 0.02$, $\Delta<P_2>_F = \pm 0.03$), when the appropriate values of the φ are taken into account. The similar run of the $<P_2>_A$ and $<P_2>_F$ versus temperature indicate that the condition $\tau_F << \tau_R$ is good fulfilled in the whole temperature range of the mesophase of the liquid crystals investigated. The character of temperature dependence of $<P_2>$ is similar for all members of the homologous series of nCPB.

The order parameter $<P_4>_F$ is positive at lower temperatures and decreases at approaching to T_{NI}. The error in the estimation of the fourth-rank order parameter from fluorescence measurements is very high, $\Delta<P_4>_F = \forall 0.06$. However, the order parameter $<P_4>$ may be useful in determining the phase transition temperature, especially for the smectic A-nematic transition. It can be seen in Figure 6 for 10CPB/NDBA mixture. The data indicate that discontinuity of $<P_2>$ is small. On contrary, $<P_4>_F$ changes very distinctly. In the smectic A phase, $<P_4>_F$ is positive and constant within the experimental accuracy. From results shown in Figures 5 and 6, it (porozdzielac) can be seen that, in the nematic phase, the values of $<P_4>_F$ are very low or even negative. These results are in disagreement with theoretical calculations [25,26]. However, non-typical behavior of this parameter was also observed by the authors studying the orientational order in the nematic phase using Raman scattering [10,11,27] and fluorescence depolarization [4,11,28] method.

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

$$f_4(\beta) = \frac{1}{2} + \frac{5}{2}\langle P_2\rangle P_2(\cos\beta) + \frac{9}{2}\langle P_4\rangle P_4(\cos\beta). \tag{6}$$

Figure 7 presents the orientational distribution function $f_4(\beta)$ for 10CPB/NDBA mixture determined from fluorescence measurements.

Curve 1 represents the molecular distribution of 10CPB doped with NDBA in the smectic A phase at $T_{red} = 0.973$, whereas curve 2 represents the molecular distribution for the same probe in the nematic phase at $T_{red} = 0.985$. The examples illustrate clearly the relation between values of the order parameter, $<P_4>_F$ and the function characterizing the orientational distribution of NDBA molecules in the

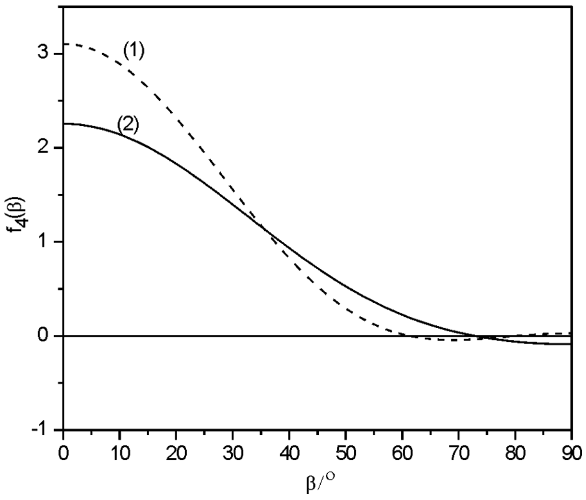


Figure 7. Distribution function $f_4(\beta)$ for 10CPB/NDBA mixture determined from fluorescence measurements at $T_{red} = 0.973$ (1 – smectic A phase), and $T_{red} = 0.985$ (2 – nematic phase).

liquid crystalline matrix. For the smectic A phase the values of $<P_4>_F = 0.21 \pm 0.06$ and in nematic phase $<P_4>_F = 0.08 \forall 0.06$, respectively. The low value of $<P_4>$ influences significantly the breadth of the molecular distribution function.

3.2. *Odd-Even Effect*

It was previously found that small changes of the structure of liquid crystals can result in significant change in the thermal properties of the mesophase. A classical demonstration is the so called "odd-even" effect, which corresponds to alternation in properties and in T_{NI} phase transition temperature, in particular for homologous series containing an alkyl chain, as the number of carbon atoms, n, varies from even to odd [13,29,30]. The molecular anisotropy described by the angle between C-C bond and molecular long axis causes this alternation. A large number of C-C bonds essentially increases the number of the conformations and the increased flexibility dampens the differences between odd and even members [13].

According to the data reported in Table 1 for the $C_nH_{2n+1}PhCOOPhCN$ series, the odd-even effect for nematic-isotropic transition temperatures is observed. For even members of the series, T_{NI} is smaller than for the previous odd members. On the basis of the theoretical studies for the similar homologous series of 4-*n*-alkyl-4′-cyanobiphenyl ($C_nH_{2n+1}PhPhCN$) [31], it can be concluded that in even members of the $C_nH_{2n+1}PhCOOPhCN$ series, the anisotropy of the molecule decreases because the final C-C bond of an alkyl chain makes on average a large angle with the long axis of the molecule, for odd members the final methyl segment is oriented nearly parallel to the long axis of the molecule.

Looking at the results of T_{NI} listed in Table 3 and presented additionally in Figure 8a it is seen that the nCPB/azo dyes mixtures express the odd-even effect very distinctly.

The odd members have larger values of nematic-isotropic transition temperature T_{NI} than even members. Moreover, as the chain length is increased the alternation

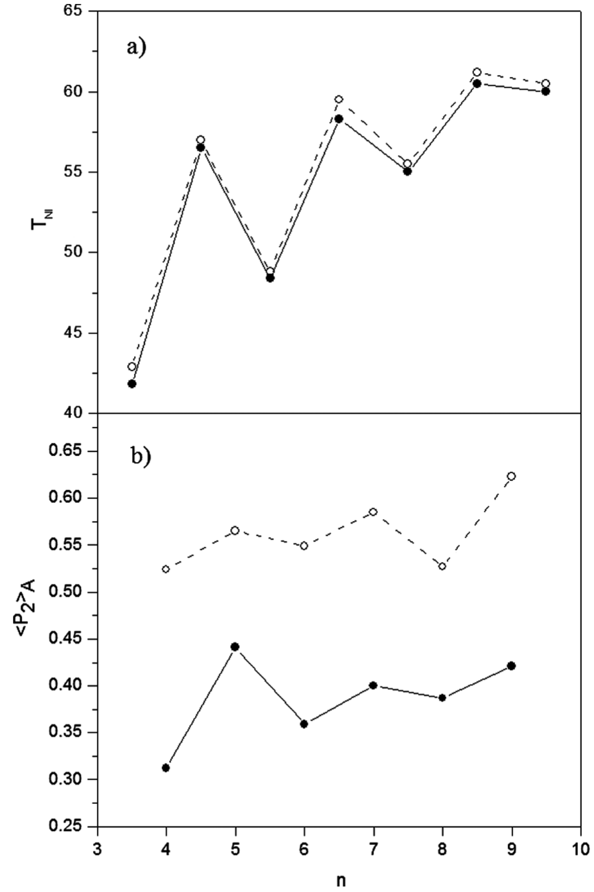


Figure 8. Phase transition temperature T_{NI}. a) and order parameter $<P_2>$ determined from :absorption measurements at $T_{red} = 0.965$. b) as a function of carbon atoms number for nCPB/R1 (B) and nCPB/R2 (X) mixtures.

of T_{NI} decays progressively. It can be concluded that further increase in the length of the alkyl group does not accounts for end-chain interaction between the molecules.

Figure 8b presents the order parameter $<P_2>_A$ as a function of the number of carbon atoms, for dyes R1 and R2 in $T_{red} = 0.965$. Similarly to results reported for the nematic -isotropic transition temperatures, T_{NI} the ordering of both azo-dyes exhibits an odd-even alternation along the C_nH_{2n+1}PhCOOPhCN series. However, character of the changes of the $<P_2>_A$with the number of carbon atom is different for nCPB/R1 and nCPB/R2. According to the data reported in Table 3 and Figure 2, it can be concluded that this effect is connected also with the relation between the sizes of the guest and host molecules.

4. Conclusions and Perspectives

The ordering ability of liquid crystals from homologous series of 4-cyanophenyl-4′-n-alkylbenzoate (C_nH_{2n+1}PhCOOPhCN) for n = 4–10 was studied by means of optical spectroscopy methods using the linearly polarized light: absorption in the visible spectral region and fluorescence depolarization. The dyes with various molecular structures were used as the guest probes. The strong individual molecular interaction of azo dyes R1 and R2 with the liquid crystal host was confirmed. Moreover, it was found that azo dye R1 and naphthalene derivative of bicarboxylic acid, NDBA causes improvement of the orientation of the liquid crystalline hosts under investigation.

Introduction of the dyes into the liquid crystalline matrix resulted in the change of the nematic-isotropic transition temperature. The good correlation between the order parameter values and the shift of the phase transition temperature T_{NI} after dye addition, was found. It was shown that the order parameter $<P_4>_F$, obtained from fluorescence measurements, can be helpful in recognizing the smectic A-nematic phase transition temperature.

The study reveals that the molecular structure of the liquid crystal (the length of the alkyl chain) influences its orienting properties. Moreover, the odd-even effect for the order parameter of the members of the homologous series of nCPB can be distinctly observed. The molecular anisotropy differences between the consequent members causes alternations of the order parameter of nCPB/R1 and nCPB/R2 mixtures as well as T_{NI} phase transition temperature. In the even members of the series, the anisotropy of the molecule decreases on account of the final C-C bond of the alkyl chain creating a large angle with the long molecular axis, whereas bond seen in the odd members is oriented practically parallel to it.

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