
Comparative Study of Orientational Order of Some Liquid Crystals from Various Homologous Series

N. BIELEJEWSKA, E. CHRZUMNICKA, E. MYKOWSKA,
R. PRZYBYLSKI, M. SZYBOWICZ, K. WŁADYSIAK
AND D. BAUMAN*

Faculty of Technical Physics, Poznań University of Technology
Nieszawska 13A, 60-965 Poznań, Poland

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The long-range orientational order of liquid crystals from homologous series of 4-*n*-alkyl-4'-cyanobiphenyl, 4-*n*-alkoxy-4'-cyanobiphenyl, *trans*-4-*n*-alkyl(4'-cyano-phenyl)-hexane, and 4-(*trans*-4'-*n*-alkylcyclohexyl)-isothiocyanato-benzene was studied by means of classical methods of optical spectroscopy: absorption of the polarized light, fluorescence depolarization, and Raman scattering depolarization. The absorption, emission, and Raman scattering spectra of linearly polarized light were recorded as a function of temperature in the whole range of the mesophase. On the basis of these spectra the order parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$ as well as the orientational distribution function were determined. The results obtained for members of various series with the same number of carbon atom in the alkyl chain were compared. It was found that the orientational order of liquid crystal molecules depends on the structure of the rigid core, on the kind of the terminal group as well as on the alkyl chain length. The odd-even effect for the order parameters, explained as the alteration of interaction between alkyl chains, was observed.

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1. Introduction

In science and technology of liquid crystals the study of the molecular orientation is one of the most significant and inevitable issues, because the degree of order influences the anisotropy of physical properties of these substances [1]. In

*corresponding author

the simplest liquid crystal phase, the nematic phase (N), molecules have preference to orient their long axis along one direction, denoted usually by a unit vector called the director, \mathbf{n} , and the molecular centres of mass are placed randomly. Therefore, in this phase only the long-range orientational order occurs. Smectic liquid crystals possess additionally long-range positional order and molecules show a preference to form a layered structure. In the smectic A (SmA) phase, the director is parallel to the layer normal; in the smectic C (SmC) phase, the director makes some angle with the layer normal. There are many other smectic phases in which the short-range positional order or the bond orientational order develops within the plane of the layers [1, 2].

A complete description of the orientational order in the mesophase can be obtained from the molecular distribution function $f(\alpha, \beta, \gamma)$ which gives the probability density of finding a molecule at a certain position with respect to the director, and α, β, γ are Euler's angles. The molecular distribution function can be expanded in terms of a complete set of orthogonal functions. For uniaxial liquid crystalline phases, by assuming the mesogenic molecules to have $C_{\infty V}$ symmetry, the distribution function depends only on the angle β and can be expanded in terms of Legendre polynomials, $P_L(\cos\beta)$ [3]:

$$f(\beta) = \sum_L^{\infty} \frac{2L+1}{2} \langle P_L(\cos\beta) \rangle P_L(\cos\beta), \quad (1)$$

where

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

are order parameters and β is the angle between the long molecular axis and \mathbf{n} . Thus, the knowledge of $f(\beta)$ in principle provides the order parameters. For non-deformed nematics and non-ferroelectric smectics, $f(\beta)$ is symmetrical to 0. Therefore, the odd terms in the expansion (1) are zero and hence so are the odd parameters.

As the order parameters are key properties for identifying different liquid crystal phases, there has been much interest in determining them experimentally. Common methods for determining $\langle P_2 \rangle$ include optical birefringence and diamagnetic anisotropy measurements, infrared spectroscopy, dichroism in visible and UV region, nuclear magnetic resonance. However, on the basis of electron paramagnetic resonance [4], fluorescence depolarization of a guest probe dissolved in a liquid crystalline matrix [3, 5–7] as well as Raman scattering spectroscopy [8, 9] the parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$ can be simultaneously obtained. The entire distribution function is possible to obtain using X-ray [10] or neutron [11] diffraction.

In the paper we have studied the orientational order of some liquid crystals from homologous series of 4-*n*-alkyl-4'-cyanobiphenyl (*n*CB), 4-*n*-alkoxy-4'-cyanobiphenyl (*n*OCB), *trans*-4-*n*-alkyl(4'-cyano-phenyl)-hexane (*n*PCH), and 4-(*trans*-4'-*n*-alkylcyclohexyl)-isothiocyanato-benzene (*n*CHBT) by using follow-

ing optical spectroscopy methods: dichroism of absorption in the visible spectral region, fluorescence depolarization, and depolarization of Raman scattering. In two former methods liquid crystals were doped with a small amount of a dichroic dye, which acted as the probe reflecting the matrices orientation (“guest-host” effect [12]).

2. Materials and methods

The liquid crystal materials used in the study, namely n CBs for $n = 5-9$, n OCBs for $n = 4-9$, n PCHs for $n = 3-10$ and n CHBTs for $n = 3-9$ were supplied by Prof. R. Dąbrowski from Military University of Technology in Warsaw. The compounds show smectic A (SmA) and nematic (N) phases between the solid (Cr) and isotropic (I) states and their transition temperatures are given in Tables I–IV. 4-dimethylamino-4'-nitrostilbene (DANS), which was used as a fluorescent guest probe, was synthesized and chromatographically purified in the Institute of Dyes at Łódź University of Technology. It was dissolved in the liquid crystals at a concentration of 5×10^{-3} mol/dm⁻³. DANS was 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 [3, 5–7, 13].

TABLE I
Phase transition temperatures (in °C) for
 n CB series.

n	Cr	SmA	N	I
5	• 24.5		• 35.3	•
6	• 14.5		• 29.0	•
7	• 30.0		• 42.8	•
8	• 19.5	• 32.6	• 40.0	•
9	• 41.0	• 46.8	• 48.9	•

TABLE II
Phase transition temperatures (in °C) for
 n OCB series.

n	Cr	SmA	N	I
4	• 78.0		• 75.5 ^a	•
5	• 48.0		• 68.0	•
6	• 57.0		• 75.5	•
7	• 54.0		• 74.0	•
8	• 54.5	• 67.5	• 81.0	•
9	• 61.3	• 77.5	• 80.0	•

^amonotropic phase.

TABLE III

Phase transition temperatures (in °C) for *n*PCH series.

<i>n</i>	Cr	N	I
3	• 42.0	• 46.0	•
4	• 44.0	• 40.5 ^a	•
5	• 31.0	• 55.0	•
6	• 42.0	• 47.0	•
7	• 30.0	• 59.0	•
8	• 37.0	• 55.0	•
9	• 44.0	• 59.0	•
10	• 43.0	• 59.5	•

^amonotropic phase.

TABLE IV

Phase transition temperatures (in °C) for *n*CHBT series.

<i>n</i>	Cr	N	I
3	• 38.5	• 41.5	•
4	• 34.5	• 32.0 ^a	•
5	• 67.5	• 49.5 ^a	•
6	• 12.5	• 43.0	•
7	• 37.0	• 52.0	•
8	• 28.0	• 48.0	•
9	• 39.0	• 54.0	•

^amonotropic phase.

The absorption spectra of liquid crystals doped with DANS 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 the dichroic dye dissolved in the liquid crystalline matrix the order parameter $\langle P_2 \rangle$ was calculated from the following formula [14]:

$$\langle P_2 \rangle = \frac{A_{\parallel} - A_{\perp}}{A_{\parallel} + 2A_{\perp}}, \quad (3)$$

where A_{\parallel} and A_{\perp} are the absorbances of the light polarized, respectively, parallel and perpendicular to \mathbf{n} .

The fluorescence measurements were carried out by using a photon-counting spectrofluorimeter built in our laboratory and described in detail in Ref. [15]. The

exciting light was a 436 nm line from a high-pressure mercury lamp. The Glan-Thomson polarizers were used in the pathway of the incident and emitted light. 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 [5]. On the basis of fluorescence intensity values, the emission anisotropies, R_1 and R_2 , were determined as follows:

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

$$R_2 = \frac{J_{yz} - J_{yy}}{J_{yz} + 2J_{yy}}. \quad (4b)$$

J_{ij} 's are here 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.

If we assume that the rotation relaxation time, τ_R is much longer than the lifetime, τ_F of the excited state of the fluorescent molecule, then R_1 and R_2 can be related to the order parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$ as follows [16]:

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

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

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

Equations (3), (5a) and (5b) are valid if the angle between the vector of the absorption transition moment and the long axis of a dye molecule is 0° . This assumption is fulfilled in the first approximation for the transition moment of the DANS molecule responsible for the absorption in the visible region [17].

The polarized Raman scattering spectra were recorded by means of the conventional apparatus. Experiments were performed in the back scattering geometry [9] by using two neutral UV polarizers. An ILA-120 Carl Zeiss Jena laser operating at 488 nm was the exciting source. In order to reduce the local heating of the sample by the laser beam, the light power was kept at 20 mW. The scattering anisotropies R_1 and R_2 were determined on the basis of experimental Raman line intensities in analogous way as in fluorescence measurements (Eqs. (4a) and (4b)), where the first subscript denotes now the polarization of the incident light and the second one refers to that of the scattered light in the laboratory frame x, y, z .

In the Raman scattering spectrum it is always possible to find the particular vibration for which the polarizability tensor, $\hat{\alpha}$, related to the molecular frame, has a diagonal form [8]:

$$\hat{a} = \begin{pmatrix} a & 0 & 0 \\ 0 & b & 0 \\ 0 & 0 & 1 \end{pmatrix}. \quad (6)$$

For the uniaxial liquid crystal molecules it is reasonable to assume that $a = b$. This value can be easily determined on the basis of scattering anisotropy measurements in the isotropic phase [8]. In the simplest case $a = b \approx 0$ and then the order parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$ can be directly obtained on the basis of R_1 and R_2 using the following relations:

$$\langle P_2 \rangle = \frac{2 + 7R_1 - 14R_2 + 5R_1R_2}{23 - 14R_1 + R_2 - 10R_1R_2} \quad (7a)$$

and

$$\langle P_4 \rangle = \frac{-12 + 21R_1 - 21R_2 + 30R_1R_2}{23 - 14R_1 + R_2 - 10R_1R_2}. \quad (7b)$$

Equations (7a) and (7b) are valid if the principal axis of the normal mode of vibration lies along the long molecular axis. It should be also noted that they are equivalent to Eqs. (5a) and (5b) for $\delta = 0^\circ$.

All the measurements were made as a function of temperature over the whole mesophase range of an appropriate liquid crystal. The “sandwich” cells of $20 \mu\text{m}$ (absorption and emission measurements) and $20\text{--}40 \mu\text{m}$ (Raman measurements) in thickness were used. The planar molecular orientation was achieved by treatment of cell glass surfaces with polyimide and by additional rubbing process. This procedure gave homogeneous planar molecular orientation which was checked by means of a polarized microscope.

3. Results

Figure 1 presents the polarized components of absorption and fluorescence spectra of DANS oriented in 8CB at $T = 28^\circ\text{C}$ in smectic A (SmA) and $T = 39^\circ\text{C}$

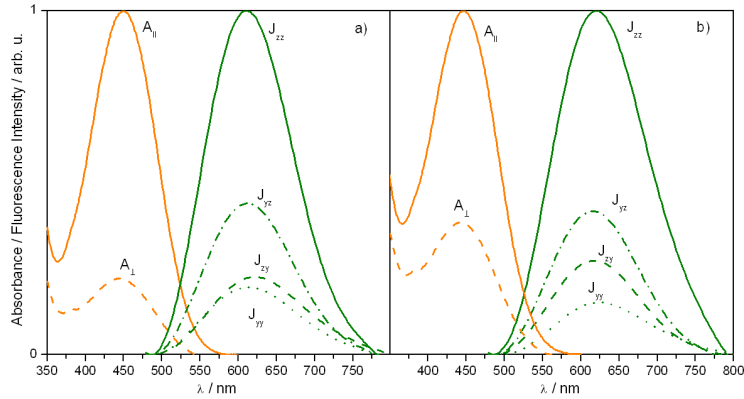


Fig. 1. Spectra of polarized components of absorption ($A_{||}$ and A_{\perp}) and fluorescence (J_{zz} , J_{zy} , J_{yz} , and J_{yy}) for DANS in 8CB in: (a) smectic A ($T = 28^\circ\text{C}$) and (b) nematic ($T = 39^\circ\text{C}$) phases.

in nematic (N) phases, as an example. In the visible spectral region DANS exhibits one absorption band with the maximum at $\lambda_A \approx 445$ nm and one fluorescence band with the maximum at λ_F between 600 and 625 nm, depending on the liquid crystal and temperature.

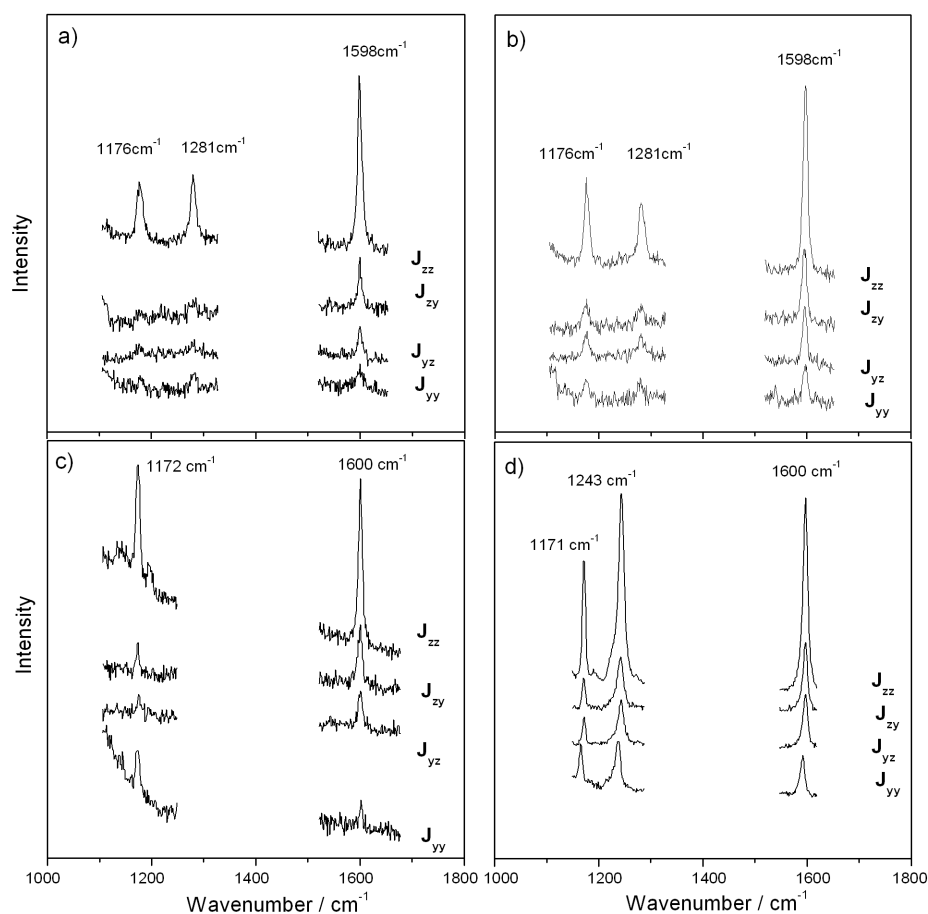


Fig. 2. Polarized components of Raman scattering spectra (J_{zz} , J_{zy} , J_{yz} , and J_{yy}) of (a) 8CB ($T = 26^\circ\text{C}$ — SmA phase), (b) 8OCB ($T = 57^\circ\text{C}$ — N phase), (c) 6PCH ($T = 32^\circ\text{C}$), (d) 7CHBT ($T = 42^\circ\text{C}$).

Figures 2a–d show polarized components of Raman scattering spectra for liquid crystals 8CB ($T = 26^\circ$), 8OCB ($T = 57^\circ$), 6PCH ($T = 32^\circ$), and 7CHBT ($T = 42^\circ$). The spectra obtained for all the liquid crystals investigated at various temperatures consist of several distinctly separated lines with different intensity. Using a fitting procedure by means of the Lorentz curve and making the analysis of the spectra, the individual bands were attributed to appropriate vibrations. The Raman spectra of all liquid crystals contain the band lying 1590–1600 cm^{-1}

away from the exciting line. This band is assigned to the C–C stretching mode of benzene ring [18]. The spectra of the members of *n*CB and *n*OCB series reveal the presence of a band at 1281 cm^{-1} related to the C–C stretching vibration of the biphenyl ring [18]. Moreover, the less intensive bands at $1155\text{--}1176\text{ cm}^{-1}$ related to the aromatic C–H in plane deformation [18] can be seen in the Raman spectra of the liquid crystals under investigation. For the liquid crystals from *n*CHBT series the band connected with the aromatic ring vibration (at $1239\text{--}1255\text{ cm}^{-1}$) [18] is also observed.

On the basis of the polarized absorption, fluorescence, and Raman scattering spectra the order parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$ at various temperatures in the

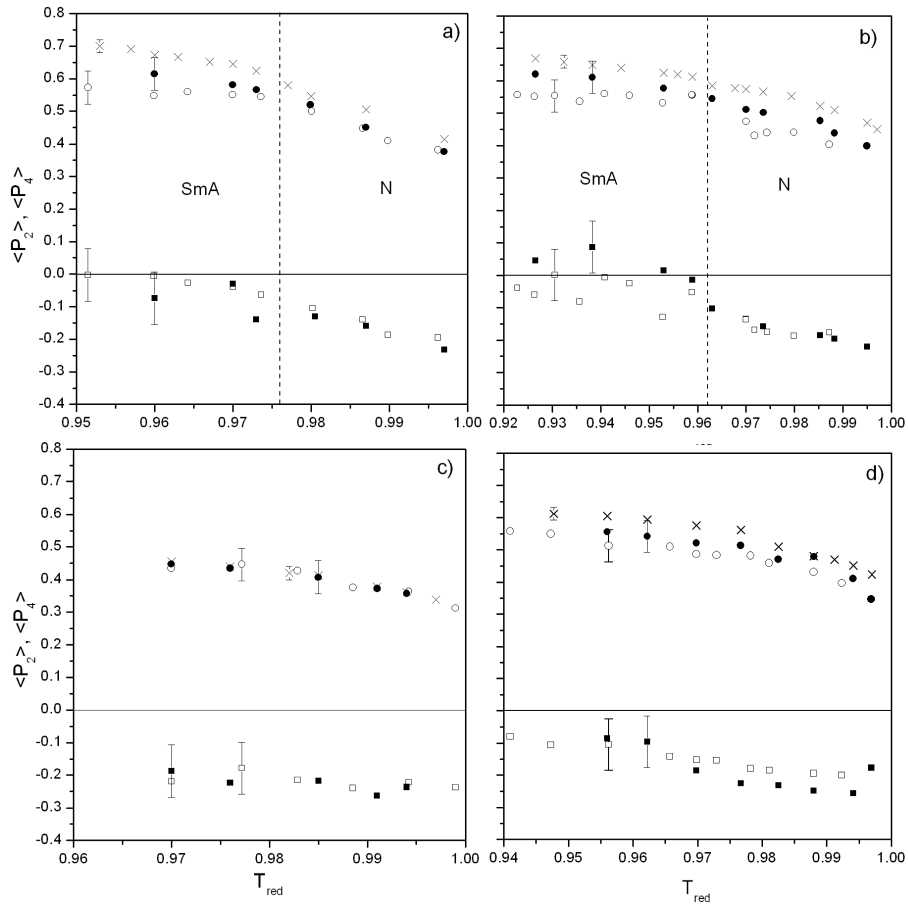


Fig. 3. Dependence of order parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$ on reduced temperature $T_{\text{red}} = T/T_{\text{NI}}$ for liquid crystals (a) 8CB, (b) 8OCB, (c) 6PCH, (d) 6CHBT doped with DANS determined from absorption (\times — $\langle P_2 \rangle_{\text{A}}$ only) and fluorescence measurements (\bullet — $\langle P_2 \rangle_{\text{F}}$, \blacksquare — $\langle P_4 \rangle_{\text{F}}$) and for respective liquid crystals obtained from Raman scattering measurements (\circ — $\langle P_2 \rangle_{\text{R}}$, \square — $\langle P_4 \rangle_{\text{R}}$).

mesophase were calculated by using Eqs. (3), (5), and (7), respectively. For calculations, the values of the absorbance as well as of fluorescence and Raman scattering intensities were taken at the wavelength (or wavenumber) corresponding to the maximum of the appropriate band. The angle δ which is needed to evaluate the order parameters from Eqs. (5a) and (5b) was assumed to be 17° , as it was given in Ref. [3]. For calculations of $\langle P_2 \rangle$ and $\langle P_4 \rangle$ from the Raman scattering spectra the various bands were taken into account. For all the bands the a value was small comparing to 1, and therefore, we assumed $a = 0$ in our consideration. We assumed also that the angle between the long molecular axis and the principal axis of the normal mode of the vibration is equal to 0° , which seems to be reasonable for the vibration C–C in the benzene ring because the largest element of the polarizability tensor for this vibration is α_{zz} [19]. For other vibrations this assumption is fulfilled only in the first approximation. Therefore, in the following the results for the band at $1590\text{--}1600\text{ cm}^{-1}$ are presented only.

Figures 3a–d present the dependences of $\langle P_2 \rangle$ and $\langle P_4 \rangle$ on the reduced temperature, T_{red} , for liquid crystals 8CB, 8OCB, 6PCH, and 6CHBT, as examples. $T_{\text{red}} = T/T_{\text{NI}}$, where T_{NI} is the nematic–isotropic transition temperature and T is the temperature of the measurement in K.

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

$$f_4(\beta) = \frac{1}{2} + \frac{5}{2} \langle P_2(\cos \beta) \rangle P_2(\cos \beta) + \frac{9}{2} \langle P_4(\cos \beta) \rangle P_4(\cos \beta). \quad (8)$$

Examples of $f_4(\beta)$ function for compounds under investigation are given in Figs. 4 and 5. Figure 4 shows $f_4(\beta)$ for DANS in 8OCB and 9CB obtained from fluorescence measurements in SmA and N phases, whereas Fig. 5 presents $f_4(\beta)$ deter-

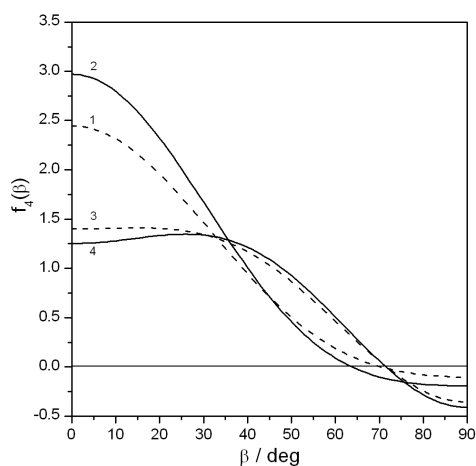


Fig. 4. Distribution function $f_4(\beta)$ in SmA (1,2) and N (3,4) phases for liquid crystals 8OCB ($T_{\text{red}} = 0.94$ (1) and 0.962 (3)) and 9CB ($T_{\text{red}} = 0.984$ (2) and 0.994 (4)) doped with DANS determined from fluorescence measurements.

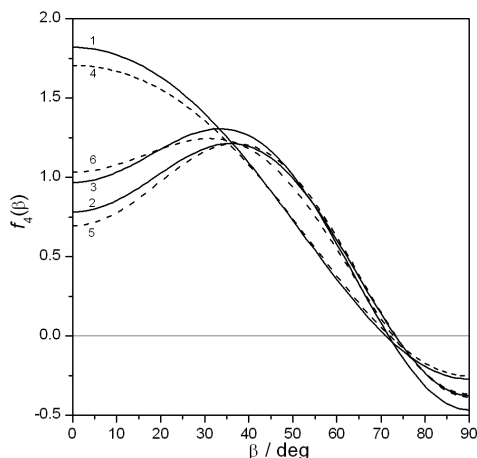


Fig. 5. Distribution function $f_4(\beta)$ for liquid crystals 8CB (1), 6PCH (2), and 6CHBT (3) doped with DANS determined from fluorescence measurements and liquid crystals 8CB (4), 6PCH (5), and 6CHBT (6) obtained from Raman scattering measurements at $T_{\text{red}} = 0.97$.

mined on the basis of $\langle P_2 \rangle_{\text{F}}$ and $\langle P_4 \rangle_{\text{F}}$ for 8CB, 6PCH, and 6CHBT doped with DANS (solid curves) and from $\langle P_2 \rangle_{\text{R}}$ and $\langle P_4 \rangle_{\text{R}}$ for pure liquid crystals (dashed curves).

4. Discussion

From the results shown in Figs. 3a–d as well as obtained for other liquid crystals it follows that the character of changes of the order parameter $\langle P_2 \rangle$ with the temperature does not depend on the liquid crystal but on the kind of the mesophase. In the whole SmA phase $\langle P_2 \rangle$ is only weakly dependent on temperature, whereas in N phase it significantly depends on temperature, especially in the vicinity of the clearing point. It should be, however, noted that the run of the temperature dependence of $\langle P_2 \rangle$ is different for various liquid crystals, which indicates the different resistance of compounds investigated on the thermal fluctuations. The character of changes of $\langle P_2 \rangle$ is also independent of the method used, although the absolute values differ somewhat. The values of the order parameter $\langle P_2 \rangle$ obtained for DANS-liquid crystal mixtures from fluorescence measurements are usually lower than those obtained from absorption measurements, especially at higher temperatures. This may be due to the assumption that $\tau_{\text{R}} \gg \tau_{\text{F}}$. Meanwhile, as the temperature increases, the values of both times become almost comparable. This can lead to a considerable misinterpretation of the fluorescence data and cause the difference between $\langle P_2 \rangle_{\text{A}}$ and $\langle P_2 \rangle_{\text{F}}$. Raman scattering, like fluorescence, is a two-photon process, and the only difference occurs in the scale of time: while the lifetime of the molecule in the excited state is of the order of 10^{-9} – 10^{-7} s, the Raman scattering process takes place almost immediately

($\approx 10^{-12}$ s) after absorption of the light. The values of $\langle P_2 \rangle$ and $\langle P_4 \rangle$ obtained in our experiments by using Raman scattering spectroscopy are quite similar to those determined from fluorescence measurements (within an experimental uncertainty), but $\langle P_2 \rangle_R$ values are usually smaller than those estimated on the basis of absorption spectra. In some cases it can be connected with a different thickness of the probe used in absorption and Raman scattering measurements [9].

TABLE V
Order parameter $\langle P_2 \rangle_A$ for all the liquid crystals investigated at four reduced temperatures.

n	$T_{\text{red}} = 0.960$				$T_{\text{red}} = 0.972$			
	$n\text{CB}$	$n\text{OCB}$	$n\text{PCH}$	$n\text{CHBT}$	$n\text{CB}$	$n\text{OCB}$	$n\text{PCH}$	$n\text{CHBT}$
3	–	–	–	–	–	–	–	–
4	–	0.47	–	–	–	0.44	0.48	0.51
5	–	0.42	0.57	–	0.47	0.38	0.55	0.53
6	–	0.46	–	0.60	–	0.43	0.45	0.56
7	–	0.49	0.55	0.62	0.50	0.44	0.52	0.58
8	0.67 ^a	0.62 ^a	0.53	0.58	0.63 ^a	0.58	0.48	0.54
9	–	0.63	0.50	0.63	–	0.62	0.48	0.59
10	–	–	0.54	–	–	–	0.50	–
n	$T_{\text{red}} = 0.980$				$T_{\text{red}} = 0.991$			
	$n\text{CB}$	$n\text{OCB}$	$n\text{PCH}$	$n\text{CHBT}$	$n\text{CB}$	$n\text{OCB}$	$n\text{PCH}$	$n\text{CHBT}$
3	–	–	–	0.52	–	–	0.41	0.47
4	–	0.41	0.46	0.50	–	0.36	0.43	0.45
5	0.44	0.36	0.52	0.52	0.40	0.33	0.46	0.47
6	0.45	0.41	0.43	0.52	0.39	0.34	0.37	0.47
7	0.46	0.38	0.51	0.56	0.40	0.32	0.45	0.50
8	0.54	0.55	0.46	0.51	0.47	0.50	0.40	0.44
9	0.75 ^a	0.60	0.45	0.56	0.69 ^a	0.48 ^a	0.41	0.47
10	–	–	0.47	–	–	–	0.42	–

^aSmA phase.

For the comparison of the orienting properties of various liquid crystals used in our studies, in Table V the values of $\langle P_2 \rangle_A$ at four reduced temperatures are gathered. From the results presented in this table it follows that the molecular structure of the liquid crystal significantly influences the orientational order of molecules. Considering only nematogens it is seen that for a given n the following relation occurs:

$$\langle P_2 \rangle(n\text{CHBT}) > \langle P_2 \rangle(n\text{PCH}) > \langle P_2 \rangle(n\text{CB}) > \langle P_2 \rangle(n\text{OCB}), \quad \text{for } n \leq 7.$$

It means that the orientation ability of liquid crystals depends on the terminal po-

lar group ($-\text{NCS}$ or $-\text{CN}$) and the kind of the rings in the molecular core (aromatic or aliphatic rings). The addition of the oxygen atom to the alkyl chain causes the decreasing of the order parameter which can also be observed in Figs. 6 and 7 for liquid crystals 8CB and 8OCB as well as 9CB and 9OCB. The results presented in Fig. 7 indicate additionally that the same observation for $\langle P_2 \rangle_{\text{F}}$ and $\langle P_4 \rangle_{\text{F}}$, both in SmA and N phases, may be seen.

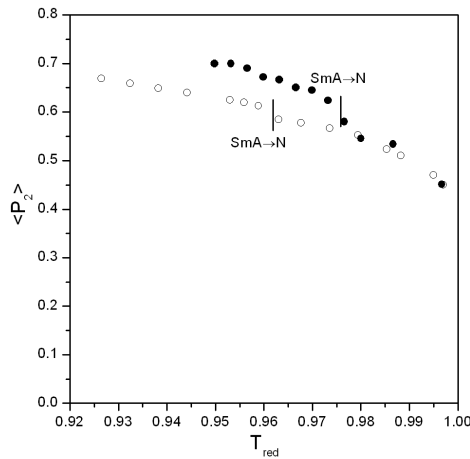


Fig. 6. Comparison of the order parameter $\langle P_2 \rangle_{\text{A}}$ for 8CB (\bullet) and 8OCB (\circ).

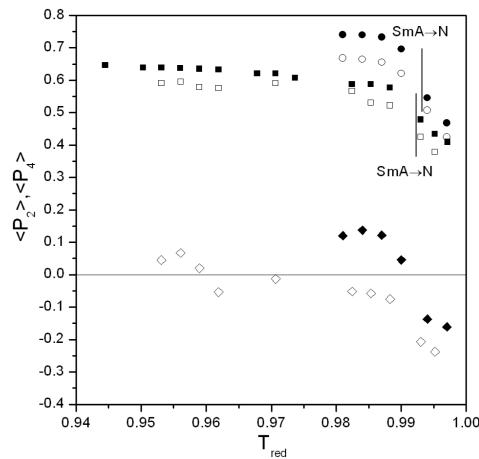


Fig. 7. Comparison of the order parameters $\langle P_2 \rangle_{\text{A}}$ (\bullet , \blacksquare), $\langle P_2 \rangle_{\text{F}}$ (\circ , \square), and $\langle P_4 \rangle_{\text{F}}$ (\blacklozenge , \diamond) for 9CB (\bullet , \circ , \blacklozenge , \diamond) and 9OCB (\blacksquare , \square , \blacklozenge , \diamond).

Smectogenic molecules are usually better oriented than nematogenic ones, and this is valid over the whole mesophase region. Therefore, at $T_{\text{red}} = 0.994$,

when all the compounds under investigation are in N phase, the following relation is fulfilled:

$$\langle P_2 \rangle(n\text{CB}) \gtrsim \langle P_2 \rangle(n\text{OCB}) > \langle P_2 \rangle(n\text{CHBT}) > \langle P_2 \rangle(n\text{PCH}), \quad \text{for } n \geq 8.$$

The $\langle P_4 \rangle$ values obtained in our study for all the liquid crystals investigated are very low. They are positive only for 9CB, 8OCB, and 9OCB in SmA phase, whereas in N phase always the negative values of $\langle P_4 \rangle$, determined both from fluorescence and Raman scattering depolarizations, are observed. The low values of $\langle P_4 \rangle$ influence the shape of the molecular distribution function $f(\beta)$, as it is illustrated in Figs. 4 and 5. From Fig. 4 it follows that in SmA phase the probability of finding the molecule at a very small angle with respect to the director, \mathbf{n} , is significantly greater than in N phase. However, a comparison of the solid curves with the dashed ones in Fig. 5 allow us to ascertain that the presence of DANS in the liquid crystal matrix has only small influence on the statistical distribution of molecules around \mathbf{n} . This confirms the assumption about the compatibility of liquid crystals under investigations and DANS molecules.

The negative values of $\langle P_4 \rangle$ are in disagreement with theoretical predictions [20, 21]. Nevertheless, the nontypical behaviour of this parameter was observed by many other authors studying the orientational order in the nematic phase using Raman scattering [8, 9, 22–25] and fluorescence depolarization [3, 5–7] methods. Although many attempts were undertaken in order to explain the deviation of the experimentally obtained $\langle P_4 \rangle$ values from the theories [22–27], up to now no satisfactory explanation was found. In our present study we checked the influence of the angle between the absorption transition moment and the long axis of a dye molecule, φ , on $\langle P_4 \rangle$ values obtained from fluorescence measurements as well as on $\langle P_2 \rangle_A$ and $\langle P_2 \rangle_F$. By calculating the order parameters from Eqs. (3) and (5) we assumed always that this angle is equal to 0° . This assumption is, however, valid only in the first approximation. Therefore, we tried to check how the order parameter values are changing when φ is small, but different from 0° . In order to attain this, we used the calculation method proposed by Wolarz [28]. The exemplary results obtained for $\varphi = 5^\circ$ and 10° are listed in Table VI. It is seen that the changes of $\langle P_2 \rangle_A$ and $\langle P_2 \rangle_F$ values are not very significant ($\leq 7\%$ for $\langle P_2 \rangle_A$ and $\leq 20\%$ for $\langle P_2 \rangle_F$ at $0^\circ \leq \varphi \leq 10^\circ$). A different situation is found for the $\langle P_4 \rangle_F$ order parameter, which is very sensitive for the variation of the φ angle. For example, the increase in the φ value from 0° to 10° causes the alteration of the $\langle P_4 \rangle_F$ sign from negative to positive values, both in the smectic and nematic phases of the liquid crystals investigated.

Previously it was found that the nematic–isotropic transition temperature and other physical properties of some homologous series show the odd–even effect [29–32]. Such behaviour was explained as the alteration of interaction between alkyl chains [33]. Figures 8 and 9 present the order parameters $\langle P_2 \rangle_A$, $\langle P_2 \rangle_F$, and $\langle P_4 \rangle_F$ for all the series investigated: for *n*CBs and *n*OCBs at $T_{\text{red}} = 0.994$

TABLE VI

Experimental (for $\varphi = 0^\circ$) and simulated (for $\varphi = 5^\circ, 10^\circ$) values of $\langle P_2 \rangle_A$, $\langle P_2 \rangle_F$ and $\langle P_4 \rangle_F$.

Liquid crystal	T °C	$\varphi = 0^\circ$			$\varphi = 5^\circ$			$\varphi = 10^\circ$		
		$\langle P_2 \rangle_A$	$\langle P_2 \rangle_F$	$\langle P_4 \rangle_F$	$\langle P_2 \rangle_A$	$\langle P_2 \rangle_F$	$\langle P_4 \rangle_F$	$\langle P_2 \rangle_A$	$\langle P_2 \rangle_F$	$\langle P_4 \rangle_F$
8CB	28	0.67	0.61	-0.07	0.68	0.69	0.30	0.70	0.71	0.44
	32	0.62	0.57	-0.14	0.63	0.64	0.23	0.65	0.67	0.36
	36	0.51	0.45	-0.16	0.51	0.51	0.03	0.53	0.52	0.15
	39	0.41	0.38	-0.23	0.42	0.42	-0.07	0.43	0.42	0.05
8OCB	56	0.67	0.62	0.05	0.67	0.67	0.24	0.69	0.69	0.35
	65	0.62	0.58	0.02	0.63	0.63	0.19	0.65	0.65	0.32
	68	0.58	0.54	-0.10	0.59	0.59	0.07	0.61	0.60	0.19
	77	0.51	0.44	-0.20	0.47	0.47	-0.05	0.53	0.48	0.06
8PCH	42	0.54	0.53	-0.07	0.54	0.55	0.04	0.56	0.57	0.18
	47	0.51	0.50	-0.10	0.51	0.52	0.01	0.53	0.54	0.14
	52	0.46	0.46	-0.23	0.47	0.47	-0.13	0.48	0.49	-0.01
	54	0.44	0.43	-0.17	0.44	0.44	-0.07	0.46	0.46	0.06
8CHBT	30	0.61	0.56	-0.11	0.61	0.63	0.08	0.63	0.63	0.21
	36	0.56	0.54	-0.12	0.56	0.58	0.06	0.58	0.61	0.20
	42	0.48	0.49	-0.26	0.49	0.51	-0.10	0.51	0.54	0.02
	45	0.43	0.43	-0.11	0.43	0.45	0.05	0.45	0.49	0.17

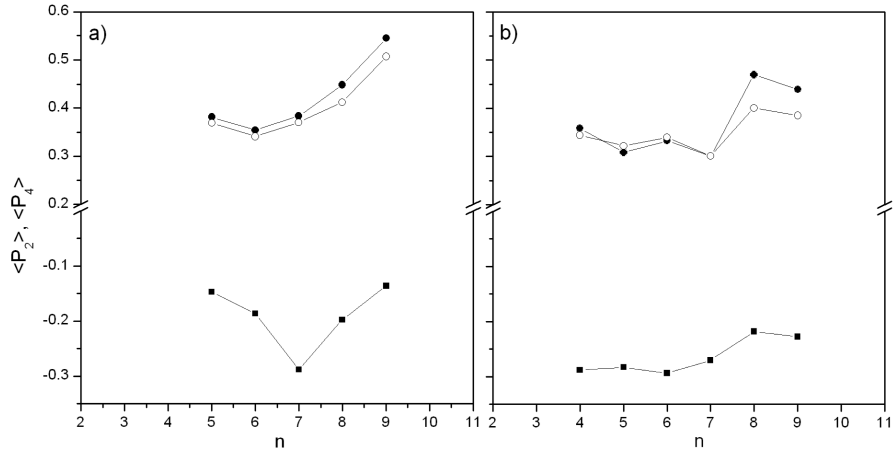


Fig. 8. Order parameters $\langle P_2 \rangle_A$ (\bullet), $\langle P_2 \rangle_F$ (\circ), and $\langle P_4 \rangle_F$ (\blacksquare) at $T_{\text{red}} = 0.994$ (N phase) as a function of the number of carbon atoms in the alkyl chain for (a) n CB and (b) n OCB series.

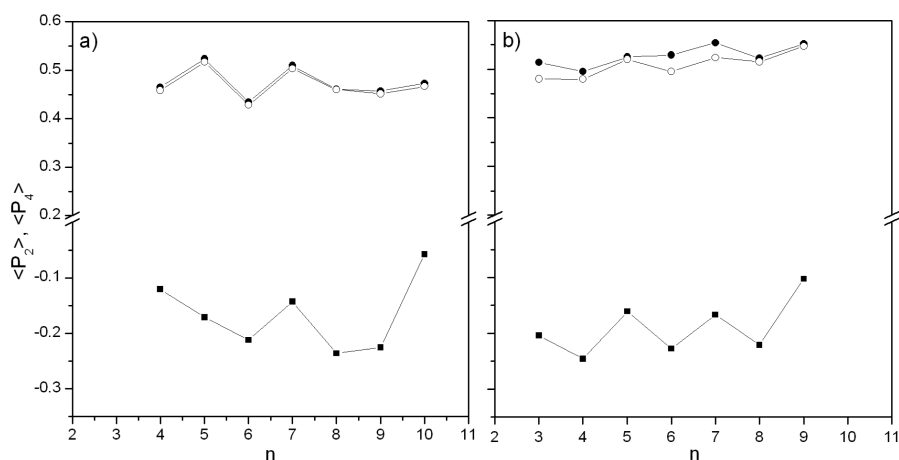


Fig. 9. Order parameters $\langle P_2 \rangle_A$ (●), $\langle P_2 \rangle_F$ (○), and $\langle P_4 \rangle_F$ (■) at $T_{\text{red}} = 0.98$ (N phase) as a function of the number of carbon atoms in the alkyl chain for (a) n PCH and (b) n CHBT series.

and for n PCHs and n CHBTs at $T_{\text{red}} = 0.98$. The odd–even effect for the order parameters of n PCH and n CHBT series is revealed very distinctly, especially for low number of carbon atoms in the terminal chain: the odd members have higher values of $\langle P_2 \rangle$ and $\langle P_4 \rangle$ than the previous even members of the series. When n rises, the flexibility of the long chain can cause that the odd–even effect is not further observed. For n OCB series the opposite behaviour to that of n PCHs and n CHBTs is observed, which is due to the presence of the oxygen atom making change in the alignment alteration of the carbon atom in the chain. In the case of n CB series the odd–even effect is very small and observed only for $n \leq 7$. 8CB and 9CB are characterized by significantly higher order parameters in comparison with the previous members of the series because of the SmA phase occurring for these compounds.

5. Conclusions

The orientational behaviour of the liquid crystals from the homologous series of 4- n -alkyl-4'-cyanobiphenyl (n CB) for $n = 5–9$, 4- n -alkyloxy-4'-cyanobiphenyl (n OCB) for $n = 4–9$, *trans*-4- n -alkyl(4'-cyanophenyl)-hexane (n PCH) for $n = 3–10$ and 4-(*trans*-4'- n -alkylcyclohexyl)-isothiocyanato-benzene (n CHBT) for $n = 3–9$ was studied by means of three optical spectroscopy methods using the linearly polarized light: absorption in the visible region, and depolarization of fluorescence and of Raman scattering. In two former methods the dichroic dye DANS was used as the guest probe. It was found that this dye reflects very well the orientational order of the liquid crystalline hosts under investigation.

The order parameters values obtained in this study reveal that the molecular structure of a liquid crystal (the length of the alkyl chain, the structure of the rigid

core as well as the kind of the terminal polar group) influences its orientational order. The odd–even effect for the order parameter of the members of homologous series investigated was observed.

The absolute values of order parameters estimated by using various methods differ somewhat. There can be many reasons of such differences. The most important one, beside the influence of the rotational motion on the fluorescence depolarization, seems to be connected with the assumptions made in order to obtain the appropriate formulae allowing us to calculate $\langle P_2 \rangle$ and $\langle P_4 \rangle$. In this paper we showed that the order parameters $\langle P_2 \rangle_A$, $\langle P_2 \rangle_F$, and $\langle P_4 \rangle_F$ are sensitive to the value of the angle between absorption oscillator and the long molecular axis of the guest molecule. Especially sensitive is $\langle P_4 \rangle_F$: even a small change of this angle causes the significant change in the $\langle P_4 \rangle_F$ value. The same finding can probably be valid for $\langle P_4 \rangle$ determined on the basis of Raman scattering spectra: the assumption that C–C vibration takes place along the long molecular axis can influence the $\langle P_4 \rangle_R$ values causing that they are negative.

Nevertheless, all the methods used in this study allow us to ascertain and to compare the orienting ability of various liquid crystals under investigation, which is a very important information from the technological point of view, especially in the case of novel synthesized substances.

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