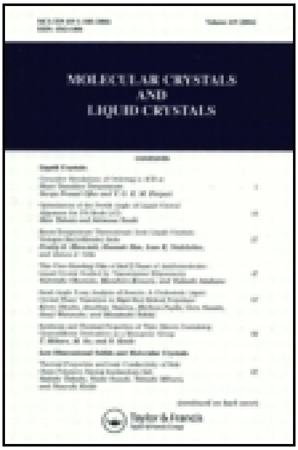

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Polarized Fluorescence Studies of Orientational Order in Some Nematic Liquid Crystals Doped with Stilbene Dye

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Polarized Fluorescence Studies of Orientational Order in Some Nematic Liquid Crystals Doped with Stilbene Dye

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The measurements of the polarized fluorescence intensity for a stilbene guest molecule dissolved in nematic liquid crystals (5CB, 7CB and PCH7) have been used to study the molecular orientational order in thin aligned samples. The temperature dependence of the order parameters $\langle P_2\rangle$ and $\langle P_4\rangle$ have been investigated. The attempt for the explanation of the different behaviour of $\langle P_4\rangle$ parameter in the various liquid crystals has been undertaken. On the basis of the experimental $\langle P_2\rangle$ and $\langle P_4\rangle$ values some information about the orientational distribution of molecules in guest-host mixture have been obtained.

Keywords: nematic liquid crystal, depolarization of fluorescence, absorption measurement, orientational distribution function

INTRODUCTION

The anisotropy of nematics arises because of the tendency of the rod-like liquid crystal molecules to align their long axis along a certain preferred direction, described by "director", $\vec{n}$. At finite temperature the thermal motion of the molecules prevents perfect alignment with $\vec{n}$; the orientation of the molecules is in fact distributed in angle, but with the directors as the most probable, or the most populated, direction. The orientation of any molecule in the director frame can be described using the three Euler angles: α, β and γ. Discussing the orientational order of a collection of molecules it is convenient to introduce a distribution function, $f(\alpha,\beta,\gamma)$. Only uniaxial symmetry around the director is characterized for many liquid crystals, thus no order in the angle α (rotation in the azimuthal direction) is permitted. Morever, if one assumes that the liquid crystal molecules are cylindrically symmetric the rotation around the molecular symmetry axis (angle γ) should not modify the distribution function. Therefore, a consideration of an abbreviated orientation distribution $f(\beta)$ is sufficient, where β is the angle between long molecular axis and director. Knowledge of $f(\beta)$ is of primary importance in liquid crystals research because it completely describes the long range orientational order which gives these substances their unique physical properties.

The distribution function, $f(\beta)$ may be reproduced with accuracy sufficient for most purposes by a truncated series expansion involving the Legendre polynomials, $P_l(\cos\beta)$[1-3].

$$f(\beta) = \sum_{l=0}^{\infty} c_l P_l (\cos\beta). \tag{1}$$

Taking into account that the uniaxial mesophase has a symmetry plane perpendicular to the director only even terms can appear in Equation (1). The coefficients c_l are given by:

$$c_l = \frac{2l+1}{2} \int_{-1}^{1} P_l (\cos\beta) f(\beta) d(\cos\beta) = \frac{2l+1}{2} \langle P_l(\cos\beta)\rangle. \tag{2}$$

The first few terms of the expansion including $\langle\cos^2\beta\rangle$ and $\langle\cos^4\beta\rangle$ are:

$$\langle P_0\rangle = 1, \tag{3a}$$

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

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

The function $f(\beta)$ is then fully described, if all $\langle P_l\rangle$ parameters are known. However, till now only the second- and fourth-rank order parameters and thus $f_4(\beta)$ can be determined from the experiment, where:

$$f_4(\beta) = \frac{1}{2} + \frac{5}{2}\langle P_2\rangle P_2 + \frac{9}{2}\langle P_4\rangle P_4 \tag{4}$$

The average of the second Legendre polynomial, $\langle P_2\rangle$ is equivalent to the liquid crystal order parameter, introduced by Zvetkoff[4] and usually reported as S. However, $\langle P_4\rangle$ gives further information about the orientational order in the sample. The factor $\langle\cos^4\beta\rangle$ allows to determine the molecular fluctuation.[5,6]

The most experimental methods which are used to determine the orientational order in a liquid crystal (optical birefringence of diamagnetic anisotropy measurements, infrared spectroscopy, the dichroism in visible and UV region) allow to estimate only the order parameter $\langle P_2\rangle$. However, both $\langle P_2\rangle$ and $\langle P_4\rangle$ can be simultaneously obtained using X-ray scattering,[7-11] magnetic resonance,[12] Raman spectroscopy[5,6,13-15] as well as fluorescence depolarization of the dye dissolved in liquid crystal.[3,20-27] Although the fairly extensive theory of fluorescence depolarization in liquid crystal,[3,20,22–24,26] there are a little experimental results on $\langle P_2 \rangle$, $\langle P_4 \rangle$ and $f(\beta)$ using this method.[21,24,25,27]

In this paper the fluorescence anisotropy of the stilbene dye dissolved in some nematics has been measured. The results have been used to determine the order parameters, $\langle P_2 \rangle$ and $\langle P_4 \rangle$ as well as the truncated distribution function, $f_4(\beta)$ in order to obtain information about the molecular orientational order in the stilbene-nematic liquid crystal mixtures.

EXPERIMENTAL

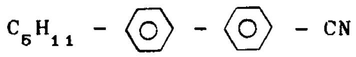
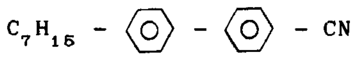
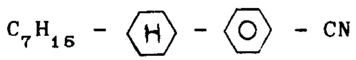
The commercial nematic liquid crystals: 4-n-pentyl-4′-cyanobiphenyl (5CB), 4-n-heptyl-4′-cyanobiphenyl (7CB) and 4-n-heptyl-4′-cyanophenyl-cyclohexane (PCH7) were used without further purification. The molecular structure of these liquid crystals is given in Table I. The stilbene dye was synthesized and purified by chromatograhic method in the Institute of Dyes, Łódź Technical University, Poland. It was dissolved in the liquid crystals at a concentration of 10^{-3} *M*.

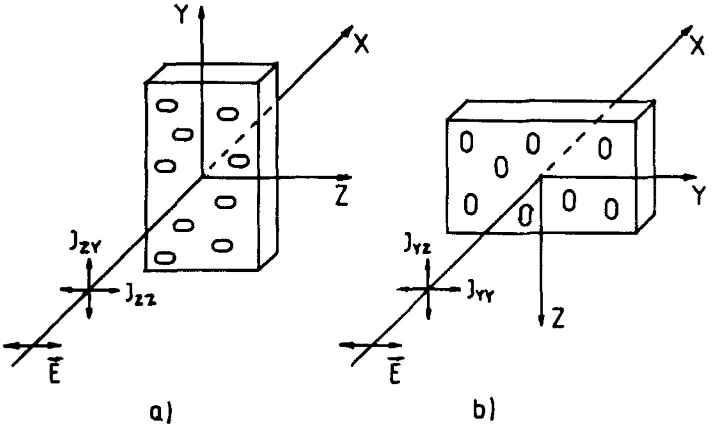
The temperature of the nematic-isotropic phase transition for the pure nematics and doped with the dye was determined by means of a polarizing microscope with an accuracy ±0.05°.

The absorption spectra were measured with a SPECORD M-40 Spectrophotometer (Carl Zeiss Jena) equipped with polarizers. The polarized components of the fluorescence spectra were carried out by means of Π geometry (Figure 1) using a home-made photon-counting fluorimeter. The 436 nm line of the high pressured mercury lamp was used for the excitation of the fluorescence. Corrections of the photomultiplier spectral sensitivity and for the different responses of the device set with various directions of polarization were made. The measurements were made in oriented "sandwich" cells of 20 μm in thickness. The temperature of the cells was regulated and controlled with an accuracy of ±0.1°. The planar orientation of the liquid crystal and dye molecules had been achieved by treatment of the glass surfaces of the cells with polyimide and by the rubbing process additionally. This

TABLE I

Molecular structure and nematic-isotropic transition temperature of liquid crystals investigated.

Liquid crystal	Molecular structure	T_{NI} [K]
5CB		308.4
7CB		316.4
PCH7		330.7



a) b)

FIGURE 1 Experimental geometries for measuring the emission of anisotropies R_1 (a) and R_2 (b). Arrows indicate the vibration direction of the electric vectors of exciting and emitted light.

procedure gives a good homogenous orientation of the molecules in a thin layer what has been controlled with the aid of crossed polarizers.

RESULTS AND DISCUSSION

Phase transition temperature

The values of the nematic-isotropic transition temperature, T_{NI} for pure liquid crystals investigated are listed in Table I. The results are in substantial agreement with data given in literature.[28-30]

The stilbene dye added to the liquid crystal up to concentration 10^{-3} M has no effect on the nematic-isotropic transition temperature of the pure nematic within experimental uncertainties.

Order parameters of nematic liquid crystal

The intensity of fluorescence excited with the light beam polarized in the i-direction and observed after passing the analyser giving the light polarized along j-axis is given by:

$$J_{ij} = \langle M^2_{ai} M^2_{ej} \rangle, \qquad (5)$$

where M^2_{ai} and M^2_{ej} are the squares of the absorption and emission oscillator components projected onto the axes i and j, respectively. The average is made over all molecules in the illumination volume and includes all possible angular positions of the absorption and emission oscillators weighted by the appropriate statistical distribution.

Figure 2 shows the four components of the fluorescence intensity, J_{zz}, J_{zy}, J_{yz}

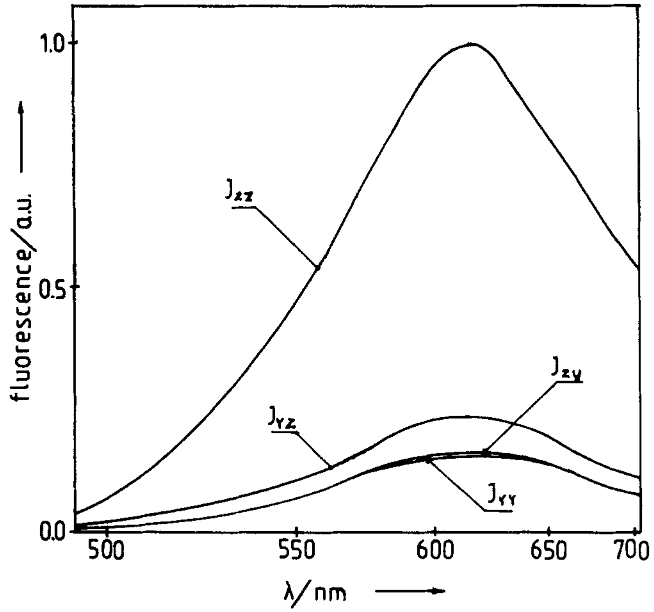


FIGURE 2 Intensity of the polarized fluorescence components for stilbene dye in PCH7 at $T^* = 0.977$.

and J_{yy} measured in the geometries presented in Figure 1 for the stilbene dye in PCH7 at reduced temperature $T^* = 0.977$ ($T^* = T/T_{NI}$).

On the basis of the fluorescence intensity measurements the emission anisotropies were calculated using following expressions:

$$R_1 = \frac{J_{zz} - J_{zy}}{J_{zz} - 2J_{zy}}, \tag{6}$$

for the excitation with the light polarized parallel to the z axis (Figure 1a), and

$$R_2 = \frac{J_{yy} - J_{yz}}{J_{yy} + 2J_{yz}}, \tag{7}$$

for the excitation with the light polarized parallel to the y axis (Figure 1b).

Since the reflection loss at the cell-sample interface is anisotropic, the correction factor is incorporated to obtain the above scattering anisotropies from the recorded intensities J^{exp} as follows[5]:

$$R_1 = \frac{J_{zz}^{exp}C_n - J_{zy}^{exp}}{J_{zz}^{exp}C_n + 2J_{zy}^{exp}}, \tag{8}$$

$$R_2 = \frac{J_{yy}^{exp} - C_nJ_{yz}^{exp}}{J_{yy}^{exp} + 2C_nJ_{yz}^{exp}}, \tag{9}$$

where:

$$C_n = [(n_g + n_e)/(n_g + n_o)]^2; \tag{10}$$

here n_g is the refractive index of the glass plate, and n_o and n_e represent, respectively, the ordinary and extraordinary indices of a liquid crystal at given temperature and wavelength of exciting light.

In our consideration we assume that the fluorescent molecule (trans-stilbene[31] under conditions of our experiment) has cylindrical symmetry and that this symmetry is not changed in the excited state. As a consequence the emission and absorption transition dipole moments are parallel to each other and almost parallel to the molecular long axis. It is further assumed, that the rotational relaxation time, τ_R is much longer than the lifetime, τ_F of the excited state of the fluorescent molecule and the effect of rotational motion on the emission anisotropy can be neglected.

Under such assumption the R_1 and R_2 values can be related with $\langle\cos^2\beta\rangle$ and $\langle\cos^4\beta\rangle$ as follows[19]:

$$R_1 = \frac{3\langle\cos^4\beta\rangle - \langle\cos^2\beta\rangle}{2\langle\cos^2\beta\rangle}, \tag{11}$$

$$R_2 = \frac{3 - 10\langle\cos^2\beta\rangle + 7\langle\cos^4\beta\rangle}{3 + 2\langle\cos^2\beta\rangle - 5\langle\cos^4\beta\rangle}, \tag{12}$$

and formulae for the order parameters $\langle P_2\rangle$ and $\langle P_4\rangle$ are identical as those obtained from resonance Raman scattering[6,18]:

$$\langle P_2\rangle = \frac{2 + 7R_1 - 14R_2 + 5R_1R_2}{23 - 14R_1 + R_2 - 10R_1R_2}, \tag{13}$$

$$\langle P_4\rangle = \frac{-12 + 21R_1 + 21R_2 - 30R_1R_2}{23 - 14R_1 + R_2 - 10R_1R_2} \tag{14}$$

Nevertheless, the assumption applied here gives only the roughly estimated order parameters, however we are interested in the investigation of the difference of the orientation for the various liquid crystals rather than in the absolute $\langle P_2\rangle$ and $\langle P_4\rangle$ values.

The $\langle P_2\rangle$ parameter can also be evaluated using the absorption dichroic ratio, D of the dye dissolved in a liquid crystal, from the formula:

$$\langle P_2\rangle = \frac{D - 1}{D + 2}. \tag{15}$$

$D = A_{\parallel}/A_{\perp}$, where $A_{\parallel}$ and $A_{\perp}$ are the polarized absorption components, measured in parallel and perpendicularly to the long molecular axis of a liquid crystal.

In principle, both from the fluorescence depolarization and absorption dichroic ratio only the orientational order parameter of the soluted guest molecule in nematic liquid crystal can be determined, as the guest-host interaction can cause the perturbation in the molecular alignment. Assuming, however, that the size and the shape of a dye molecule are similar to those of nematic host, no significant difference between order parameters of pure liquid crystal and of guest in liquid crystal matrix can be expected, as it was shown by Blinov *et al.*[32] For our experiment we choose the stilbene dye, which molecular length calculated from the known bond lengths and configuration in molecules[33] including the van der Waals radii of the terminal atoms[34] is about 17Å. The molecular length of monomeric liquid crystal used in this paper and calculated in the same way with regard of the flexibility of alkyl chain is almost the same (≈18 Å, taking number of carbon in alkyl chain n = 3[35,36]). For these reasons the stilbene dye is often utilized as a fluorescent probe in determination of orientational order of liquid crystal[3,24,37]. Moreover, the order parameters of the stilbene dye in 5CB, 7CB and PCH7 obtained from absorption measurements ($(\langle P_2\rangle_G)$) and those of pure liquid crystals ($(\langle P_2\rangle_H)$) are equal to each other at the same reduced temperature within experimental uncertainties (for example for 5CB at $T^* = 0.967$ $\langle P_2\rangle_H = 0.58$[38], $\langle P_2\rangle_G = 0.57$ from Figure 3). It is also worth noting that the concentration of the dye used in this work is so low (10^{-3} M ≈ 0.03% wt) that the concentrational depolarization can be neglected.[24] Therefore we assume that in our experiment $\langle P_2\rangle_H = \langle P_2\rangle_G$.

Figures 3–5 present $\langle P_2\rangle$ and $\langle P_4\rangle$ parameters estimated on the basis of the

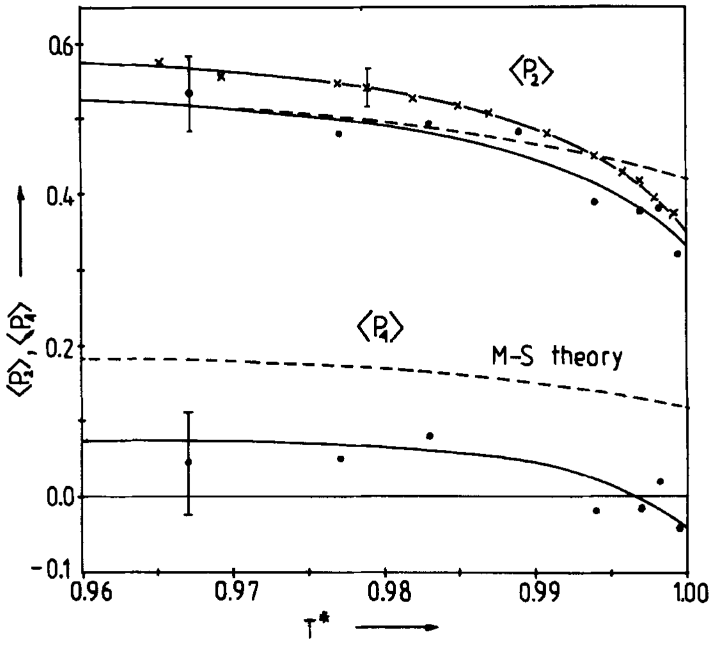


FIGURE 3 Order parameters *versus* reduced temperature for 5CB with stilbene dye: —×—×— $\langle P_2\rangle$ evaluated from absorption dichroic ratio; —•—•— $\langle P_2\rangle$ and $\langle P_4\rangle$ evaluated from fluorescence measurements; dashed curves: $\langle P_2\rangle$ and $\langle P_4\rangle$ from Maier-Saupe theory.

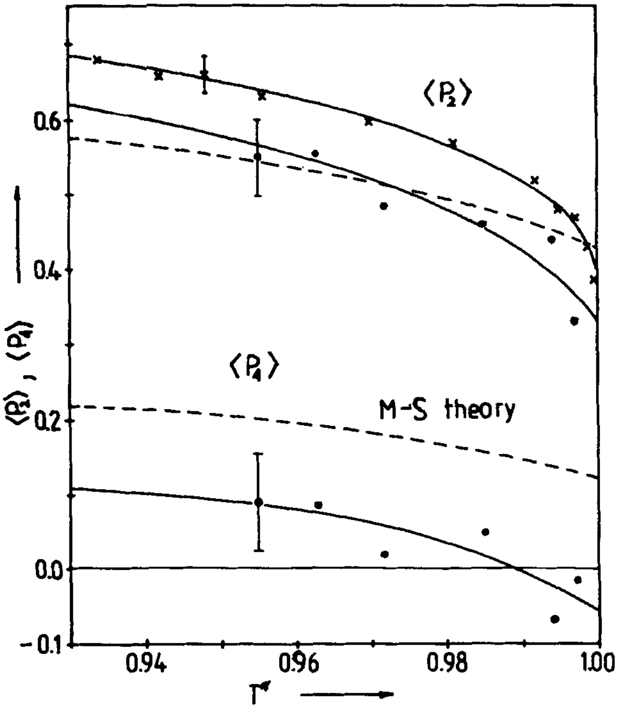


FIGURE 4 Order parameters *versus* reduced temperature for 7CB with stilbene dye: —×—×— $\langle P_2\rangle$ evaluated from absorption dichroic ratio; —•—•— $\langle P_2\rangle$ and $\langle P_4\rangle$ evaluated from fluorescence measurements; dashed curves: $\langle P_2\rangle$ and $\langle P_4\rangle$ from Maier-Saupe theory.

emission anisotropies from Equations (13–14) as well as $\langle P_2\rangle$ determined from the absorption dichroic ratio (Equation 15) as a function of the reduced temperature for the stilbene dye in the liquid crystals used. For calculation of the order parameters the values of J_{ij} and A_k ($k = \|, \perp$) were taken at the wavelengths corresponding to the maxima of the fluroescence intensity and absorption, respectively. The dashed lines are calculated on the basis of the Maier-Saupe mean field theory.[39] The $\langle P_2\rangle$ values for 5CB and 7CB estimated from the fluorescence measurements are slightly lower than those determiend from the absorption dichroic ratio. This difference can be due to the neglecting of the effect of the rotational depolarization in our consideration. Additionally, the intermolecular energy transfer processes can also depolarize the emission in an unpredictable manner. However, the temperature dependences of the $\langle P_2\rangle$ as well as $\langle P_4\rangle$ parameter in this paper are very close to the results obtained by other authors for 5CB,[6,13,14,16,18,19] 7CB[14,18] and PCH7[15] using Raman scattering measurements. This fact confirms our assumption that guest and host order parameters are approximately the same.

A comparison of our results with those derived from Maier-Saupe model indicates that $\langle P_4\rangle$ values for 5CB and 7CB are much lower than predicted by theory and they become negative near the nematic-isotropic transition. The $\langle P_4\rangle$ parameter for PCH7 approaches rather close to the value which is expected from mean field theory and stays positive throughout the nematic phase. The non-typical behav-

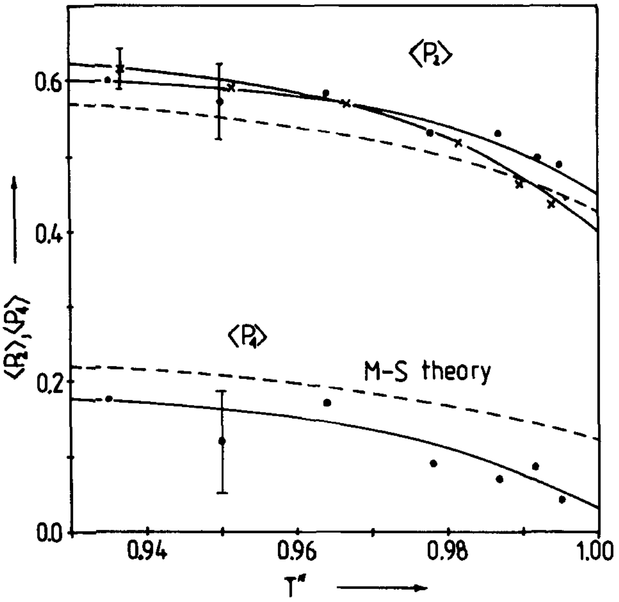


FIGURE 5 Order parameters *versus* reduced temperature for PCH7 with stilbene dye: —×—×— $\langle P_2 \rangle$ evaluated from absorption dichroic ratio; —•—•— $\langle P_2 \rangle$ and $\langle P_4 \rangle$ evaluated from fluorescence measurements; dashed curves: $\langle P_2 \rangle$ and $\langle P_4 \rangle$ from Maier-Saupe theory.

iour of the $\langle P_4 \rangle$ parameter for 5CB and 7CB has also been noticed by other authors studying the orientational order of these nematics by Raman scattering method.[13-19] If the all systematical experimental errors are estimated (as it was done in this work using the appropriate geometry and incorporating the optical corrections) then three reasons of the deviation of the experimentally obtained $\langle P_4 \rangle$ values from the Maier-Saupe theory are possible: 1) molecular flexibility, especially due to the alkyl chain of liquid crystal,[14,16,17] 2) anisotropy of the molecular local field[15-17] and 3) molecular association ("dimerization") due to the strongly polar —CN group of the nematics under consideration.[16-18]

The theoretical model of Maier-Saupe assumes rigid molecules of liquid crystals, what is not correct, but the molecular flexibility cannot explain the difference between $\langle P_4 \rangle$ values for 7CB and those for PCH7 as these two liquid crystals have the same alkyl-chain length.

Table II presents the values of the optical birefringence, Δn and the dielectric anisotropy, $\Delta\varepsilon$ for the liquid crystals investigated at the same reduced temperature, $T^* = 0.977$. As can be seen PCH7 is optically and dielectrically less anisotropic than 5CB and 7CB. Thus, one can expect that the regard of the local field effects is necessary to obtain the right values of the order parameter from the emission anisotropies. However, Dalmolen *et al.*[16,17] have found that anomalously low values of $\langle P_4 \rangle$ occur also in compounds with a low Δn and *vice versa*—a mean field like behaviour of $\langle P_4 \rangle$ is observed for liquid crystals with fairly high Δn.

It seems, that most probable reason of the differences in the $\langle P_4 \rangle$ values obtained for the various liquid crystals studied in this paper is dipole-dipole interaction

TABLE II

Δn and $\Delta\varepsilon$ values for the liquid crystals studied at $T^* = 0.977$.

Liquid crystal	Δn	$\Delta\varepsilon$
5CB	0.172[a]	10.41[b]
7CB	0.158[c]	10.02[c]
PCH7	0.084[d]	6.85[e]

[a] from[38], [b] from[40], [c] from[41], [d] from[42], [e] from[43]

TABLE III

Kirkwood factor, g and dimer fraction, x_D in the isotropic state of the nematics studied.

Liquid crystal	g	x_D
5CB	0.475[a]	0.356[a]
7CB	0.484[b]	0.348[b]
PCH7	0.637[c]	0.222[c]

[a] from[40], [b] from[41], [c] from[43]

leading to the molecular association of these compounds. Dalmolen eat al.[18] studying the order parameter in homologous series of alkylcyanobiphenyls gave some evidences that the anomalously low values observed for $\langle P_4 \rangle$ in some nematics might be related to dimerization. In our previous paper[40,43] the Kirkwood factor, g[44] and the dimer fraction, x_D for the nematics were calculated. These values are listed in Table III.

All the g values presented in Table III are lower than unity what indicates antiparallel dipole association into dimers. Such an association can influence the measured order paramter because of steric interactions which lead to non-parallelism of the long axis of a dimer and that of a neighbouring monomer. The aggregation of PCH7 molecules is much weaker in comparison with the aggregation of the very similar 5CB and 7CB molecules, what could explain the different behaviour of the $\langle P_4 \rangle$ parameter of these nematics. However, the situation becomes complicated, when one takes into account the experimental values of $\langle P_4 \rangle$ for liquid crystal MBBA obtained from Raman spectroscopy[15] and fluorescence depolarization study.[3] The degree of aggregation of this compound is much smaller (g = 0.769, x_D = 0.131[45]) than that of the nematics studied in this paper. Nevertheless, $\langle P_4 \rangle$ parameter is much lower than that predicted by theory and behaves similarly to that of 5CB and 7CB. From the other hand Feng *et al.*[46] taking into account the anisotropic steric interactions between monomeric molecules showed using theoretical calculations that a stable phases of MBBA requires $\langle P_4 \rangle$ to be negative at and near the nematic-isotropic transition. This leads to the conclusion that the problem of the non-typical behaviour of $\langle P_4 \rangle$ parameter for some nematics is much more complicated than it could arise from the assumption of the molecular association only. The low value of $\langle P_4 \rangle$ is probably a result of the different kind of molecular interactions. The association of the mesogenic molecules into dimers seems to be the important factor, but not the only one.

On the basis of $\langle P_2 \rangle$ and $\langle P_4 \rangle$ parameters the truncated distribution function, $f_4(\beta)$ was obtained from Equation (4). Figures 6 and 7 show $f_4(\beta)$ *versus* β for 5CB, 7CB and PCH7 determined from $\langle P_2 \rangle$ and $\langle P_4 \rangle$ values obtained in our experiment as well as for MBBA, calculated on the basis of data given by Chapoy *et al.*[3] at two different reduced temperatures. We also show in the same figures $f_4(\beta)$ curves derived from Maier-Saupe model. As it is seen, our results for PCH7 are the most close to the predictions of the mean field theory, whereas the other examples reveal the signficant deviations, especially near the nematic-isotropic transistion. This means that 5CB, 7CB and MBBA molecule have stronger tendency to be tipped away from the director, n than PCH7 molecules. Therefore, one can suppose that the interactions inducing splay on a microscopic scale, e.g. pair correlations in which neighbouring molecular axes are not parallel, play a greater role for the former liquid crystals than for the later one. Moreover, it is worth noting that only the replacement of one benzene ring by a cyclohexane ring causes significant change in the molecular orientational order, what is clearly seen by comparison the results for 7CB and PCH7.

To summarize, although the problem of the different behaviour of the $\langle P_4 \rangle$ parameter and the different widths of the distribution function for various liquid crystals have not been finally resolved in this paper, we have shown that the

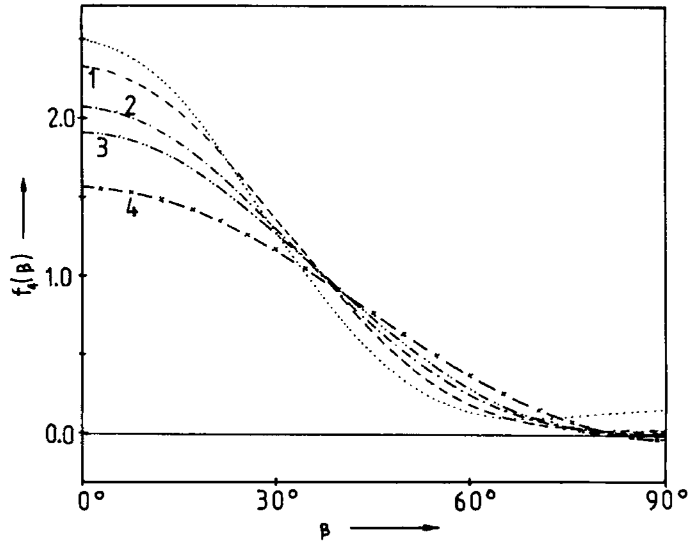


FIGURE 6 The molecular distribution function, $f_4(\beta)$ at $T^* = 0.977$ for: 1—PCH7, 2—5CB, 3—7CB, 4—MBBA (on the basis of data from[3]); small dots: from Maier-Saupe theory.

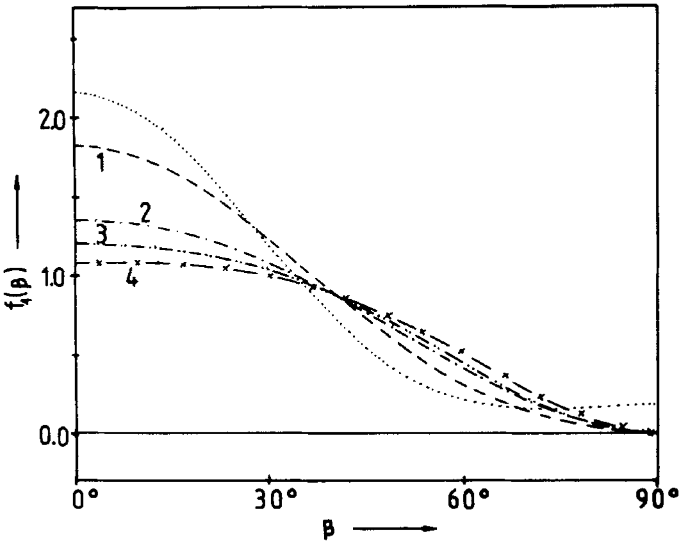


FIGURE 7 The molecular distribution function, $f_4(\beta)$ at $T^* = 0.998$ for: 1—PCH7, 2—5CB, 3—7CB, 4—MBBA (on the basis of data from[3]); small dots: from Maier-Saupe theory.

fluorescence depolarization of guest molecule can give information on the orientational ordering in liquid crystals. The investigation will be continued.

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