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Order Parameters in Some Nematics Determined from Optical Spectroscopy

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Order Parameters in Some Nematics Determined from Optical Spectroscopy

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The measurements of the polarized absorption and fluorescence spectra of stilbene-derivative guest molecules dissolved in some nematic liquid crystals have been used for studies of the long-range orientational order in thin aligned samples. The temperature dependence of the order parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$ has been investigated. The influence of the molecular structure on the orientational order in nematics has been discussed.

Keywords: nematic liquid crystal, guest probe, absorption, fluorescence, phase transition

1. INTRODUCTION

Liquid crystal displays (LCDs) are today the fastest growing display technology because of many advantages of LCDs such as flatness, low power consumption, viewability in bright light and low cost. LCDs have found many various applications. Initially, they were used almost exclusively in watches, calculators and measuring instruments. In recent years LCDs have been applicated in telecommunications, cars, computers, TV and other devices with high information contents. Such a rapid progress of the LCD technology was possible among others due to development made in new liquid crystal materials technology. The electro-optical parameters of nematics important for LCD in addition to the anisotropy of the molecular properties are strongly dependent on the anisotropy in optical, electrical, magnetic and elastic properties. These properties are the result of the long-range orientational order occurring in the liquid crystalline state. Therefore in order to obtain LCD with the optimal performance it is necessary to know the order parameters in liquid crystal matrix.

In this paper we have studied the orientational behaviour of some nematic liquid crystals of different molecular structure. We have used the method based on the

polarized absorption and fluorescence spectra measurements for the guest probe dissolved in the nematic host.

2. EXPERIMENTAL

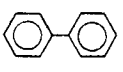
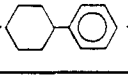
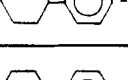
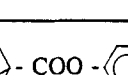
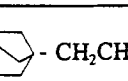
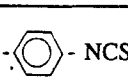
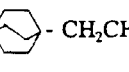
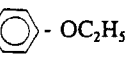
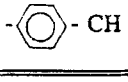
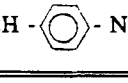
Materials

The chemical formulae of nematogenic molecules used in these studies are given in Table I. The compounds show only nematic phase between the solid and the isotropic states.

Liquid crystal I (K18) was obtained from BDH, Ltd. and all other substances were kindly supplied by Prof. R. Dąbrowski from Military Technical Academy, Warsaw, Poland. 4-Dimethylamino-4'-nitrostilben (DANS), which was used as a fluorescent guest probe, was synthesized and chromatographically purified in Institute of Dyes, Łódź Technical University, Poland. It was dissolved in the liquid crystals at a concentration of 5×10^{-3} M.

TABLE I

Chemical formulae of compounds investigated

N_0	Molecular structure
I	C_6H_{13} -  - CN
II	C_6H_{13} -  - CN
III	C_6H_{13} -  - NCS
IV	C_6H_{13} -  - NCS
V	C_6H_{13} -  - COO -  - NCS
VI	C_6H_{13} -  - CH_2CH_2 -  - NCS
VII	C_6H_{13} -  - CH_2CH_2 -  - OC_2H_5
DANS	$(CH_3)_2N$ - - CH = CH - - NO_2

Apparatus

The temperature of the phase transitions, both for the pure nematics and doped with DANS were determined by means of a polarizing microscope connected with a heating stage, which allows to change the temperature with an accuracy of $\pm 0.1°$.

The polarized absorption spectra were recorded using a SPECORD M-40 spectrophotometer (Carl Zeiss Jena). The polarized components of the fluorescence spectra were obtained using a home-made photon-counting fluorimeter. The 436 nm line of the high pressure mercury lamp was used for the excitation of fluorescence. Further experimental details were reported elsewhere.[1,2] Both in the absorption and fluorescence experiments the UV polarizers from Carl Zeiss Jena were used.

The measurements of absorption and fluorescence intensity as a function of temperature were made in "sandwich" cells of 20 μm in thickness. The temperature of the cells was regulated and controlled with the accuracy of $\pm 0.1°$. The planar molecular orientation was achieved by treatment of the glass surfaces of the cells with polyimide and by additional rubbing process. This procedure gives a good homogeneous orientation of the liquid crystal and guest molecules in a thin layer, what has been controlled with the aid of crossed polarizers.

3. ORDER PARAMETERS IN NEMATIC PHASE

The classical methods of optical spectroscopy are well suited to the study of the long-range orientational order which is characteristic for the nematic liquid crystalline state. Doping the liquid crystal matrix with a fluorescent probe and utilizing the "guest-host" effect[3,4] the information about the order can be obtained both from polarized absorption and fluorescence measurements. In principle, by these methods only the degree of order for the guest molecules may be determined. Due to the structural dependence of the guest-host interaction causing the perturbation in the molecular alignment of the host, the order of the host does not need to be the same as that of the guest. Choosing, however, the probe with the molecular structure similar in size and shape to that of liquid crystal and using low guest concentration, no significant difference in the orientational order for the pure mesophase and for the guest dissolved in the nematic host is expected and the assumption that the orientation of the guest reflects the orientation of the matrix is well satisfied. We have chosen to our experiment the stilbene derivative dye DANS, which was often utilized as a fluorescent probe in the determination of the liquid crystal order.[1,5–7] Here it is worth noting, that even if the absolute values of the degree of order cannot be obtained from the polarized absorption and fluorescence measurements, the results obtained allow to compare the orienting ability of the liquid crystals investigated, what is the very important information from the technological point of view.

In our paper we have assumed for simplicity that the molecules of the liquid crystals investigated are both rigid and possess $C_{\infty v}$ symmetry even though no nematogen conforms to this ideal. Further, we have considered the fluorescence probe which is fairly rigid, at least in the ground state and has effective cylindrical

symmetry (i.e. the parameters which quantify the deviation from uniaxiality are negligibly small)[8] with transition moments possibly tilted away from the effective symmetry axis. Such assumptions, although satisfied only in the first approximation, allow to simplify the problem considerably and give possibility to obtain from the fluorescence measurements not only the second-rank order parameter $\langle P_2 \rangle$, but also the fourth-rank order parameter $\langle P_4 \rangle$, which provides further information about the orientation as it is more sensitive for the molecular fluctuations. $\langle P_2 \rangle$ and $\langle P_4 \rangle$ are, respectively, the second and fourth Legendre polynomials, which constitute a set of order parameters for the anisotropic matrix[9] and are defined as follows:

$$\langle P_L \rangle = \frac{\int_0^{(\pi/2)} P_L(\cos\theta) f(\theta) \sin\theta \, d\theta}{\int_0^{(\pi/2)} f(\theta) \sin\theta \, d\theta}, \quad L = 2, 4. \tag{1}$$

θ denotes here the deviation of a molecular axis about which rotational symmetry has been assumed with respect to the director. The director is the symmetry axis of the orientational molecular distribution function $f(\theta)$.

The emission anisotropies, R_1 and R_2 for excitation with light polarized in parallel and perpendicularly to the orientation axis, respectively, can be calculated from the following formula:

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

$J_\parallel$ and $J_\perp$ are the intensities of emission polarized in parallel and perpendicularly to the orientation axis, respectively, measured in the parallel geometry.[1,2]

If all assumptions mentioned above are satisfied and if we assume additionally 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 the rotational motion on the fluorescence depolarization can be neglected, then R_1 and R_2 are related with the order parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$ as follows[10]:

$$R_1 = \frac{\left[\frac{2}{5} + \frac{11}{7}\langle P_2 \rangle + \frac{36}{35}\langle P_4 \rangle\right] P_2(\cos\delta)}{1 + 2\langle P_2 \rangle}, \tag{3}$$

$$R_2 = \frac{\left[\langle P_2 \rangle - \frac{2}{5} - \frac{21}{35}\langle P_4 \rangle\right] P_2(\cos\delta)}{1 - \frac{1}{3}\langle P_2 \rangle + 2\left[\frac{1}{5} - \frac{2}{7}\langle P_2 \rangle + \frac{3}{35}\langle P_4 \rangle\right] P_2(\cos\delta)}, \tag{4}$$

where δ is the angle between the absorption and emission oscillators. Knowing δ, the order parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$ can be calculated from Equations (3) and (4).

The second-rank order parameter $\langle P_2 \rangle$ can also be evaluated on the basis of the polarized absorption spectra from:

$$\langle P_2 \rangle = \frac{A_{\parallel} - A_{\perp}}{A_{\parallel} + 2A_{\perp}}, \tag{5}$$

where $A_{\parallel}$ and $A_{\perp}$ are absorbance components polarized, respectively, in parallel and perpendicularly to the orientation axis of the sample.

Equations (3)–(5) are valid when the angle between the direction of the absorption transition moment and the long axis of the dye molecule is 0°. For the dye probe DANS the absorption transition in the longest wavelength range is polarized parallel to the long axis of the molecule.[11]

4. RESULTS AND DISCUSSION

Phase Transitions

The temperatures of the crystal-nematic (T_{CN}) and nematic-isotropic (T_{NI}) phase transitions for the pure liquid crystals and the dye-liquid crystal mixtures are gathered in Table II. T_{CN} and T_{NI} for the pure nematics are in substantial agreement with the data given in literature.[12–14] It is worth noting, that the liquid crystals containing the bicyclo(2,2,2) octane ring exhibit much higher temperature of the melting point than the similar compounds with the benzene or cyclohexane ring. However, the range of the mesophase is very wide, what makes these liquid crystals very useful as the components of the liquid crystal mixtures.[15]

TABLE II

Phase transitions temperatures

Liquid crystal	T_{CN}[K]	T_{NI}[K]	
		liquid crystal	liquid crystal + DANS
I	287.7	302.0	302.5
II	304.6	323.1	323.3
III	285.5	315.6	315.7
IV	323.7	362.9	363.1
V	324.7	378.9	379.1
VI	334.2	380.9	381.3
VII	315.5	369.1	369.1

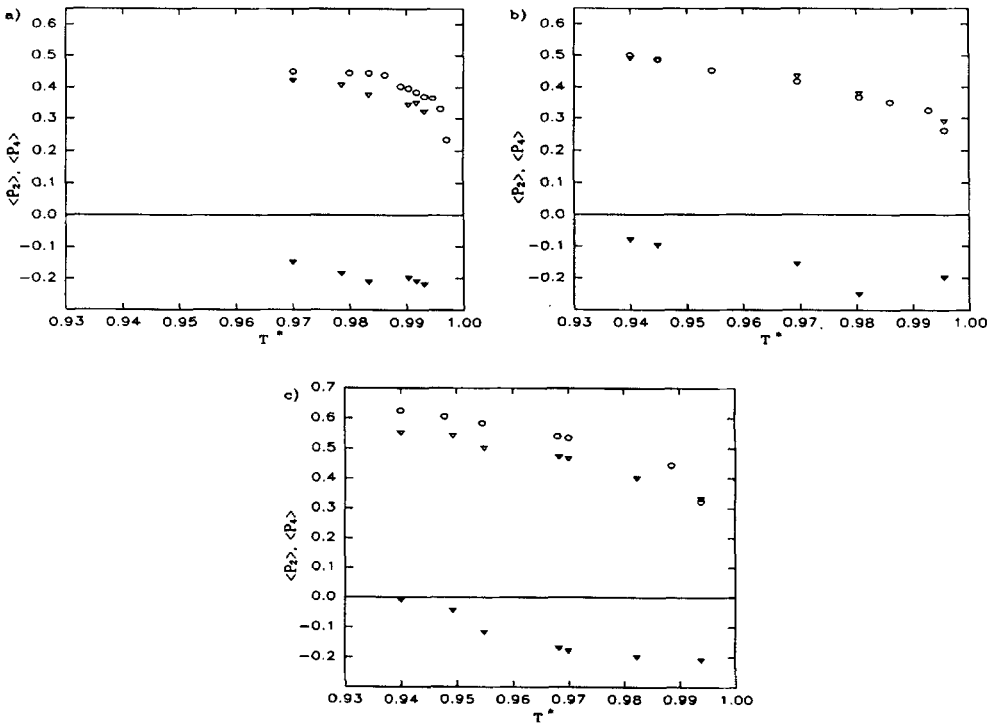


FIGURE 1 Order parameters $\langle P_2\rangle_A$ (circles), $\langle P_2\rangle_F$ (open triangles) and $\langle P_4\rangle_F$ (filled triangles) *versus* reduced temperature for liquid crystals I (a), II (b) and III (c) doped with DANS. $\Delta\langle P_2\rangle_A = \pm 0.01$, $\Delta\langle P_2\rangle_F = \pm 0.03$, $\Delta\langle P_4\rangle_F = \pm 0.06$.

The DANS added to the liquid crystals under investigation as the guest probe up to concentration of 5×10^{-3} M does not influence the temperature of the melting point of the pure nematic within experimental uncertainties. The temperature of the nematic-isotropic phase transition, however, increases somewhat in the presence of the dye. Similar influence of DANS on the clearing point of the liquid crystal 5CB was observed previously.[16]

Orientational Order

Figures 1 and 2 present the dependence of the order parameters determined from Equation (5) and Equations (3) and (4) on the basis of the absorption ($\langle P_2\rangle_A$-circles) and fluorescence ($\langle P_2\rangle_F$-open triangles, $\langle P_4\rangle_F$-filled triangles) measurements *versus* the reduced temperature $T^* = T/T_{NI}$ for the liquid crystals doped with DANS. For calculations the values of the absorbance and the fluorescence intensity were taken at the wavelengths corresponding to the maxima of the absorption (λ_A^{max}) and emission (λ_F^{max}), respectively. These wavelengths as well as the Stokes shifts ($\bar{\nu}_A - \bar{\nu}_F$) are listed in Table III.

It is seen from Table III that both the position of the absorption and fluorescence maxima as well as the values of the Stokes shifts for DANS in various liquid crystals are different. They increase in the series:

$$\text{VII} < \text{VI} < \text{IV} < \text{V} < \text{III} < \text{II} < \text{I}$$

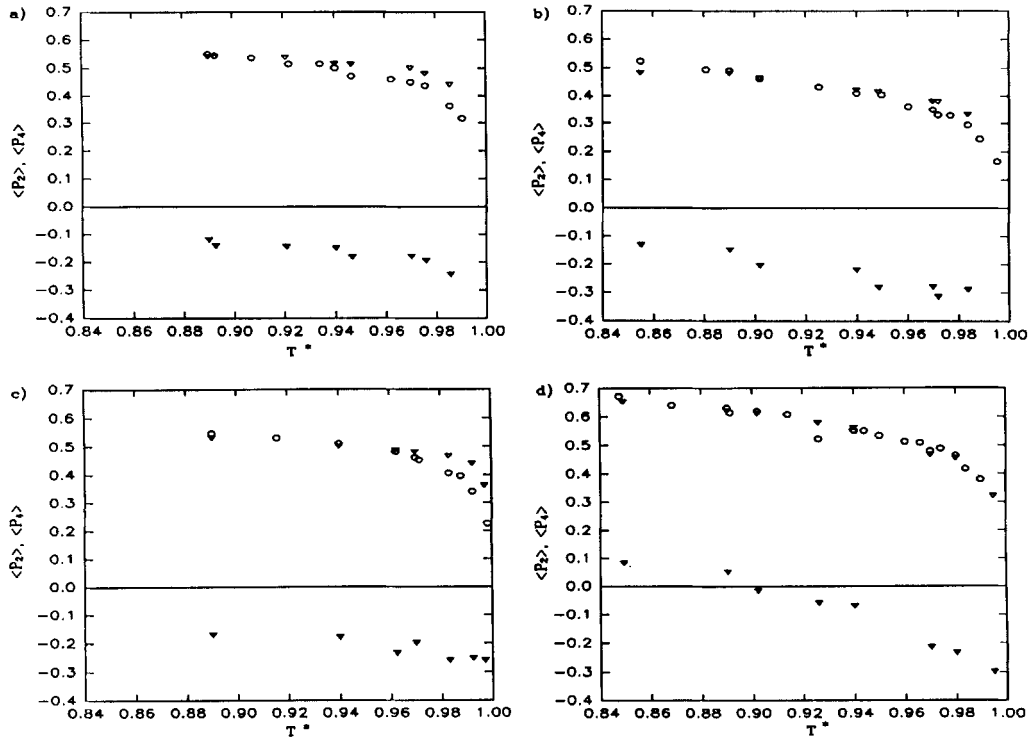


FIGURE 2 Order parameters $\langle P_2\rangle_A$ (circles), $\langle P_2\rangle_F$ (open triangles) and $\langle P_4\rangle_F$ (filled triangles) *versus* reduced temperature for liquid crystals IV (a), V (b), VI (c) and VII (d) doped with DANS. $\Delta\langle P_2\rangle_A = \pm 0.01$, $\Delta\langle P_2\rangle_F = \pm 0.03$, $\Delta\langle P_4\rangle_F = \pm 0.06$.

TABLE III

Wavelengths of absorption and emission maxima and Stokes shifts for DANS-liquid crystal mixtures

Liquid crystal	λ_A^{max}[nm]	λ_F^{max}[nm]	$\bar{\nu}_A$-$\bar{\nu}_F$[cm^{-1}]
I	447.8	613.0	6018.5
II	443.2	603.8	6000.2
III	442.6	601.5	5968.1
IV	440.8	573.0	5234.0
V	442.3	590.9	5685.8
VI	438.9	570.0	5190.3
VII	429.2	541.9	4845.3

As the dipole moment of the end —CN group is somewhat higher than that of —CNS group and they both are much higher than the dipole moment of $—OC_2H_5$ group, it follows that the positions of the absorption and emission maxima shift towards longer wavelength and the values of the Stokes shifts increase when the polarity of the liquid crystal rises.

TABLE IV

Order parameter $\langle P_2 \rangle_A$ for nematics doped with DANS

Liquid crystal	T*=0.89	T*=0.94	T*=0.97
I	_	_	0.45
II	_	0.48	0.42
III	_	0.61	0.53
IV	0.55	0.50	0.45
V	0.49	0.41	0.35
VI	0.55	0.51	0.46
VII	0.63	0.55	0.46

The angle δ between the absorption and emission oscillators of DANS molecule, which is needed to evaluate the order parameters from Equations (3) and (4) was taken from Reference 17. It had been calculated on the basis of the polarized absorption and fluorescence measurements for DANS dissolved in the oriented acrylate liquid crystalline polymer in the glassy state. The value of δ was obtained to be equal to 9°.

From Figures 1 and 2 it is seen that the values of the order parameter $\langle P_2 \rangle$ estimated from the absorption measurements are within the experimental error the same as those obtained from the fluorescence studies. The character of the changes of $\langle P_2 \rangle$ with the rise of temperature is similar for all the liquid crystals investigated. It is characteristic for the nematics and is in agreement with the mean-field theories.[18,19]

For the comparison of the order parameter for various liquid crystals used in our studies, in Table IV the values of $\langle P_2 \rangle_A$ at three different reduced temperatures are gathered.

From results presented in Figures 1 and 2 and in Table IV it follows, that the molecular structure of the liquid crystal significantly influences the orientational order in the guest-host mixture. The following indications can be seen:

The liquid crystals with the terminal —NCS group exhibit much higher order parameter than analogous compounds with —CN group (compare the values of $\langle P_2 \rangle$ for the liquid crystals II and III), but the results for the liquid crystals VI and VII shows, that the group $-OC_2H_5$ could further improve the degree of the orientational order.

Comparison of the results for liquid crystals I and II as well as III and IV shows that the order parameter decreases as the ring at the alkyl group is changed from benzene through cyclohexane to bicyclooctane.

The bridging group influences strongly the order parameter: if the group $-CH_2CH_2$ is replaced by —COO group the $\langle P_2 \rangle$ value decreases rapidly (liquid crystals V and VI).

From Figures 1 and 2 it is seen that $\langle P_4 \rangle$ values obtained for the liquid crystals under investigations are very low and in the most cases they are negative. These results are in disagreement with theoretical calculations: neither Maier-Saupe the-

ory of nematics[18] nor that of Humphries *et al.*[19] predict the negative value of $\langle P_4 \rangle$ parameter. However, the non-typical behaviour of $\langle P_4 \rangle$ for some nematic liquid crystals had been observed by many authors studying the orientational order in nematics using Raman scattering[20–25] and fluorescence depolarization[1,2,5] methods. In order to explain the observed phenomenon many attempts were undertaken,[22–24,26,27] but up till now the reason of the deviation of the experimentally obtained $\langle P_4 \rangle$ values from the theories has not been found.

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