Determination of some Dye Parameters by Polarized Fluorescence Spectroscopy

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A method of determining the angles between the emission and absorption dipole moments and the molecular symmetry axis is described. The order parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$ of nematic-dye mixtures are also calculated. The method is applied in investigations of bicarboxylic acid derivatives dissolved in the nematic mixture E 18 (Merck).

I. Introduction

Many experimental methods, giving information about the molecular interactions in liquid crystalline mesophases, have been developed [1]. One of the most important ones is the polarized fluorescence experiment, which enables one to obtain the order parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$ of a dye probe dissolved in a liquid crystalline matrix ("guest-host" system) [2–9]. It was shown that under particular conditions, connected with the geometry of the dye and liquid crystal molecules, the order parameters for the "guest" are the same as for the "host" [10]. Such "guest-host" systems are also applied in constructing coloured liquid crystalline displays [11–13]. The $\langle P_2 \rangle$ and $\langle P_4 \rangle$ order parameters depend on the anisotropies of absorption and emission, the dynamic behaviour of the molecules, and the angles created by the dipole transition moments with the molecular symmetry axis. In [12, 13] the equations describing the emission anisotropies were derived for the case of dye molecules with the absorption and emission transition moments parallel to the molecular symmetry axis.

In this paper it is assumed that the transition dipole moments of absorption and fluorescence lie in one plane but not parallel to the molecular axis. The obtained equations are applied in investigations of bicarboxylic acid derivatives in the nematic mixture E 18. A short fluorescence decay time in comparison with the correlation times of rotation is assumed ($\tau_F \ll \tau_{mn}$). It is shown that when knowing the value of absorption anisotropy, S, and the angle between the absorption and the emission transition moments, δ, one can solve the equations and find the angles α and ε created by these transition moments and the molecule's symmetry axis (Figure 1). Additionally, the $\langle P_2 \rangle$ and $\langle P_4 \rangle$ order parameters of the nematic liquid crystal–dye system can be calculated. The δ angles were obtained from polarized fluorescence measurements of isotropic mixtures of bicarboxylic acid derivatives in a solid epoxy resin.
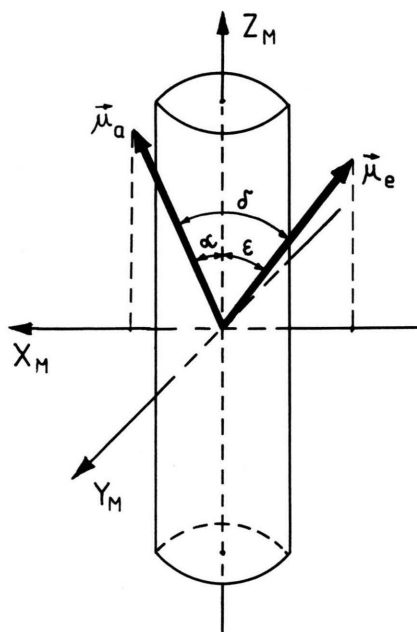

Fig. 1. Orientation of emission $\boldsymbol{\mu}_e$ and absorption $\boldsymbol{\mu}_a$ moments in the molecular frame. These moments are lying in the $X_M Z_M$-plane. The cylinder axis is parallel to the Z_M one.

II. Theoretical

Determination of the Angle δ in Isotropic Media

The excitation probability of a dye molecule under illumination with linearly polarized light depends on the angle between the absorption transition moment and the direction of the polarization of exciting light. For a sample composed of a huge number of fluorescent molecules this results in the photoselection process, characterized by the emission anisotropy [14]

$$r_{iso} = \frac{J_\| - J_\perp}{J_\| + 2 \cdot J_\perp}, \tag{1}$$

where $J_\|$ and $J_\perp$ denote intensities of the fluorescence light parallel and perpendicular to the polarization direction of the exciting beam.

Mixtures of the dyes in the epoxy resin, investigated here, can be treated as randomly oriented collections of immobile molecules. Then, the emission anisotropy depends on the intramolecular angle δ between the absorption and the emission dipole moments [4]:

$$r_{iso} = \tfrac{1}{5} (3 \cos^2 \delta - 1). \tag{2}$$

When knowing r_{iso} from experimental values of $J_\|$ and $J_\perp$ (1), one can calculate the intramolecular angle δ from (2).

The Dye Properties in an Anisotropic Medium

Let us assume that a macroscopically aligned uniaxial liquid crystal is doped with fluorescent dye molecules, which are characterized by cylindrical symmetry. In this situation the distribution function depends only on the polar angle ϑ between the molecular symmetry axis and the Z_L axis of the laboratory frame. Thus, it can be reproduced by a series expansion of the Legendre polynomials P_L [4, 15–17]:

$$f(\vartheta) = \sum_{L=0}^{\infty} \frac{2L+1}{2} \langle P_L(\cos \vartheta) \rangle \cdot P_L(\cos \vartheta), \tag{3}$$

where L are even numbers.

The statistical averages $\langle P_L(\cos \vartheta) \rangle$ are interpreted as the order parameters of L-rank. Only the $\langle P_2 \rangle$ and $\langle P_4 \rangle$ can be obtained from fluorescence experiment.

In the situation discussed here, the absorption and the emission dipole transition moments of the dye molecule are assumed to lie in the $X_M Z_M$ plane of the molecular frame. The unit vectors parallel to the absorption and emission moments define the polar

angles α and ε ($\varepsilon = \alpha - \delta$) with respect to the molecular symmetry axis Z_M. These angles should be taken into account in calculations of the order parameters from polarized fluorescence intensity components.

Under continuous illumination these components are defined as

$$J_{ij} = \int_0^\infty J_{ij}(t) \, dt, \tag{4}$$

where $J_{ij}(t)$ are the time dependent intensities observed after excitation with a pulse of light:

$$J_{ij}(t) = \langle [\mu_{a i}(0)]^2 [\mu_{e j}(t)]^2 \rangle F(t). \tag{5}$$

The average over the squares of projections of the unit absorption, μ_a, and emission, μ_e, vectors onto the i and j laboratory frame axes describes the molecular motions up to time t. The $F(t)$ factor is the fluorescence decay function

$$F(t) = \frac{1}{\tau_F} \exp\left(-\frac{t}{\tau_F}\right). \tag{6}$$

In a parallel geometry experiment, where the emitted light is observed in the direction of the exciting beam and the macroscopic axis of the mesophase symmetry is parallel to the Z_L axis of the laboratory frame, one can define the following emission anisotropies (Figure 2):

$$r = \frac{J_{zz} - J_{zy}}{J_{zz} + 2J_{zy}}, \tag{7}$$

$$h = \frac{J_{yz} - J_{yy}}{J_{yz} + 2J_{yy}}. \tag{8}$$

The formulae for $J_{ij}(t)$ were derived by Zannoni [6]. Thus, the appropriate combinations of the fluores-
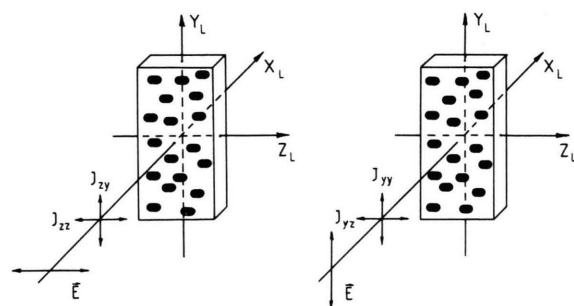

Fig. 2. Experimental geometries for measuring emission anisotropies h and r.

cence intensity components, given in (7), (8), are

$$
J_{zz} - J_{zy} = \int_0^\infty \left(\frac{1}{\sqrt{6}} \langle P_2 \rangle A_e^{20} \right. \\
\left. + \sum_n \Phi_{0n}(t) A_a^{2n} A_e^{2n*} \right) F(t)\, dt, \quad (9)
$$

$$
J_{zz} + 2 J_{zy} = \int_0^\infty \left(\frac{1}{3} + \sqrt{\frac{2}{3}} \langle P_2 \rangle A_a^{20} \right) F(t)\, dt, \quad (10)
$$

$$
J_{yz} - J_{yy} = \int_0^\infty \left(\frac{1}{\sqrt{6}} \langle P_2 \rangle A_e^{20} \right. \\
\left. - \frac{1}{2} \sum_n \{ \Phi_{0n}(t) + \Phi_{2n}(t) \} A_a^{2n} A_e^{2n*} \right) F(t)\, dt, \quad (11)
$$

$$
J_{yz} + 2 J_{yy} = \int_0^\infty \left(\frac{1}{3} - \frac{1}{\sqrt{6}} \langle P_2 \rangle A_a^{20} \right. \\
\left. + \sum_n \Phi_{2n}(t) A_a^{2n} A_e^{2n*} \right) F(t)\, dt, \quad (12)
$$

where A_a^{2n}, A_e^{2n} ($n = -2, -1, 0, 1, 2$) are the irreducible components of the tensors $A_a = \mu_a \otimes \mu_a$ and $A_e = \mu_e \otimes \mu_e$ [18], respectively, and they describe the directions of the dipole transition moments in the molecular frame.

Under the above assumptions, the components of A_a can be calculated (for A_e the angle α should be changed with the ε one):

$$
A_a^{00} = \tfrac{1}{3}, \quad (13)
$$

$$
A_a^{20} = \sqrt{\tfrac{2}{3}} P_2(\cos \alpha), \quad (14)
$$

$$
A_a^{21} = -A_a^{2-1} = -\sin \alpha \cdot \cos \alpha, \quad (15)
$$

$$
A_a^{22} = A_a^{2-2} = \tfrac{1}{2} \sin^2 \alpha. \quad (16)
$$

The reorientational correlation functions $\Phi_{mn}(t) = \langle D_{mn}^2(0) \cdot D_{mn}^2(t) \rangle$ contain information about molecular dynamics. D_{mn}^2 are components of the Wigner matrix, depending on the Euler angles which connect the laboratory frame with the molecular one [19].

An approximate form of Φ_{mn} should be assumed for further calculations [6]:

$$(17)$$

$$
\Phi_{mn}(t) = \{ \Phi_{mn}(0) - \Phi_{mn}(\infty) \} \exp\left(-\frac{t}{\tau_{mn}} \right) + \Phi_{mn}(\infty).
$$

The $\Phi_{mn}(0)$ values are described by the $\langle P_2 \rangle$ and $\langle P_4 \rangle$ order parameters. Moreover, in the infinity limit

one can obtain $\Phi_{mn}(\infty) = \langle P_2 \rangle^2 \delta_{m0} \delta_{n0}$ (δ_{ij} are the Kronecker symbols). The τ_{mn} are correlation times of rotational diffusion.

In the case when the rotational diffusion is highly hindered ($\tau_F \ll \tau_{mn}$), (7), (8) take the form

$$
r = \frac{\frac{1}{3} \langle P_2 \rangle P_2(\cos \varepsilon) + A + B \langle P_2 \rangle + 6 C \langle P_4 \rangle}{\frac{1}{3} + \frac{2}{3} \langle P_2 \rangle P_2(\cos \alpha)}, \quad (18)
$$

$$
h = \frac{\frac{1}{3} \langle P_2 \rangle P_2(\cos \varepsilon) - \frac{1}{2} (2 A + 7 C \langle P_4 \rangle)}{\frac{1}{3} - \frac{1}{3} \langle P_2 \rangle P_2(\cos \alpha) + A - B \langle P_2 \rangle + C \langle P_2 \rangle}, \quad (19)
$$

where

$$
A = \frac{1}{10} \sin^2 \alpha \cdot \sin^2 \varepsilon + \frac{2}{5} \sin \alpha \cdot \cos \alpha \cdot \sin \varepsilon \cdot \cos \varepsilon \\
+ \frac{2}{15} P_2(\cos \alpha) P_2(\cos \varepsilon), \quad (20)
$$

$$
B = -\frac{1}{7} \sin^2 \alpha \cdot \sin^2 \varepsilon + \frac{2}{7} \sin \alpha \cdot \cos \alpha \cdot \sin \varepsilon \cdot \cos \varepsilon \\
+ \frac{4}{21} P_2(\cos \alpha) P_2(\cos \varepsilon), \quad (21)
$$

$$
C = \frac{1}{140} \sin^2 \alpha \cdot \cos^2 \varepsilon - \frac{4}{35} \sin \alpha \cdot \cos \alpha \cdot \sin \varepsilon \cdot \cos \varepsilon \\
+ \frac{2}{35} P_2(\cos \alpha) P_2(\cos \varepsilon). \quad (22)
$$

The equations (18), (19) contain four unknowns: α, δ ($\delta = \alpha - \varepsilon$), $\langle P_2 \rangle$ and $\langle P_4 \rangle$ (the emission anisotropies r and h are given from measurements of the fluorescence intensity components). Independent investigations of the dye molecules, for example in an isotropic medium, as it was described in the previous subsection, enable one to extract the value of the intramolecular angle δ.

The equations (18), (19) can be rewritten in the form of two linear equations, in which $\langle P_2 \rangle$ and $\langle P_4 \rangle$ are treated as unknown parameters:

$$
(2 r P_2(\cos \alpha) - P_2(\cos \varepsilon) - 3 B) \langle P_2 \rangle - 18 C \langle P_4 \rangle \\
= 3 A - r, \quad (23)
$$

$$
(h P_2(\cos \alpha) + P_2(\cos \varepsilon) + 3 B h) \langle P_2 \rangle - C \left(\tfrac{21}{2} + h \right) \langle P_4 \rangle \\
= 3 A (1 + h) + h. \quad (24)
$$

The order parameters calculated from this equation system depend on the angle α as a variable parameter. If an unequivocal solution of (23), (24) is needed, then

one should introduce an additional equation, for example

$$S = \langle P_2 \rangle \, P_2(\cos \alpha) \,, \tag{25}$$

where S is the absorption anisotropy [20] obtained from the polarized absorbance components of the sample. Then $\langle P_2 \rangle$, $\langle P_4 \rangle$ and α can be found.

If one assumes $\tau_F \gg \tau_{mn}$, contrary to the above considerations, the emission anisotropies (7), (8) are equal. It can be shown that in the case of a uniformly oriented sample

$$r = h = \langle P_2 \rangle \, P_2(\cos \varepsilon) \,, \tag{26}$$

and determination of $\langle P_4 \rangle$ is impossible. For isotropic mixtures $r = h = 0$ in this case [4].

The condition $r = h$ can be found very useful in checking if the correlation times of diffusion are much greater than the fluorescence lifetime of a dye molecule dissolved in nematic liquid crystal.

III. Experimental

Materials and Methods

The set of the investigated dyes consists of seven derivatives of bicarboxylic acid. Their chemical structure is given in Table 1.
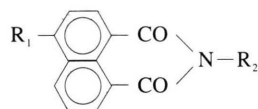
For the estimation of the angle between the absorption and the emission dipole transition moments, these compounds were dissolved in the epoxy resin at a concentration of about 10^{-5} M. The mixtures were put into small cubic glass test-tubes and left for about 24 hours to obtain solid isotropic samples. They were

transparent, without defects. The stability of the dyes in the epoxy resin was checked by observation of the intensity and shape of the fluorescence emission spectra just after dissolving the dye and one day later, in the solid state. No significant changes of the fluorescence spectra were recorded, which ensured that the dye molecules in the epoxy resin were not chemically destroyed.

Next, the dyes were dissolved in E 18 (Merck) nematic liquid crystal at a concentration of about $1.5 \cdot 10^{-2}$ M. Polarized fluorescence intensity components for these anisotropic mixtures were obtained using oriented "sandwich" cells. The glass surfaces of the cells were coated with a polyimide layer, rubbed in one direction and separated using teflon spacers. The sample thickness was checked for empty cells by the interference and the electric capacity methods. It was 20 ± 2 µm. Next, they were filled with the nematic-dye mixture. Uniform planar orientation of the liquid crystalline layers was examined for accuracy by a microscope with polarizers.

The polarized fluorescence intensity components were measured using a home-made photon-counting fluorimeter controlled by a computer. Appropriate corrections, connected with the apparatus and geometry of the sample were made [21]. In all cases the 436 nm line of a mercury lamp was used for excitation of fluorescence. For isotropic mixtures of the dyes in the epoxy resin measurements were carried out in perpendicular geometry, whereas the parallel geometry was used for the nematic layers. To minimize light scattering effects, the excitation of the dye molecules in "sandwich" cells and observations of the emitted light were carried out on the same side of the sample. The liquid crystalline samples were stored at room temperature, which corresponded to the reduced temperature $T^* = T/T_{NI} = 0.889$ for the E 18 (T_{NI} is the temperature of nematic-isotropic phase transition).

Results and Discussion

Table 2 presents the absorption anisotropies S obtained from [13], the emission anisotropies r_{iso}, r, h, calculated from the polarized fluorescence intensity components by solving (1), (7), (8), and the intramolecular angles δ obtained for the dyes investigated here. Additionally r/h ratios are given. Experimental errors of the emission anisotropies are not greater than ± 0.035. Thus the accuracy of the angle δ determination is about $\pm 4.0°$.

Table 1. Molecular structure of investigated dyes.

Dye no.	R_1	R_2
I	$-N(CH_3)_2$	$-CH_2-CH_2-CH_2-CH_3$
II	$-N(CH_2)_2$	$p-C_6H_4-CH_3$
III	$-NHCH_2-CH_2-O-CH_3$	$-CH_2-CH_3$
IV	$-NHCH_2-CH_3$	$-CH_2-CH_3$
V	$-NHCH_2-CH_2-CH_2-CH_3$	$-CH_2-CH_3$
VI	$-N(C_8H_{17})_2$	$-C_6H_4-O-C_6H_4-CH_3$
VII	$-N(C_8H_{17})_2$	$-C_6H_4-CSN-C_6H_3CH_3$

Table 2. Absorption S and emission r, h anisotropies of dyes in E18 nematic liquid crystal and in epoxy resin, r_{iso}. Intramolecular angle δ.

Dye no.	S [a]	r	h	r/h	r_{iso}	δ
I	0.40	0.453	0.317	1.429	0.222	33.0°
II	0.44	0.470	0.371	1.267	0.266	28.2°
III	0.35	0.356	0.228	1.561	0.143	40.9°
IV	0.37	0.355	0.244	1.455	0.239	31.2°
V	0.42	0.347	0.234	1.483	0.225	32.7°
VI	0.53	0.456	0.176	2.591	0.259	29.0°
VII	0.63	0.546	0.180	3.033	0.267	28.1°

[a] from [13].

As it can be seen from Table 2, the r_{iso} anisotropies of the dye-epoxy resin isotropic mixtures do not exceed the theoretically predicted limit of 0.4 (2). The angles δ, except the dye III, are similar and about 30°.

Information about the correlation times of diffusion τ_{mn} and the fluorescence decay time τ_F of the dyes in an oriented nematic is given through the r/h ratios. Taking (26) into account, one finds that the relation $\tau_F \gg \tau_{mn}$ is not satisfied for the investigated systems.

Figure 3 presents plots of the order parameter $\langle P_2 \rangle$ versus the angle α on the assumption that $\tau_F \ll \tau_{mn}$ for the dye II in E18. Curve 1 gives the $\langle P_2 \rangle$ values calculated from the fluorescence data, by solving (23), (24), while curve 2 is obtained from the absorption anisotropy S (25). The dashed lines show the error limits (the accuracy of S was taken to be ± 0.02). The curves intersect at $\alpha = 14.2°$, $\langle P_2 \rangle = 0.48$. These values, with the next calculated $\langle P_4 \rangle = -0.01$, present the solution of (23)–(25). The experimental uncertainty of the angle δ and of the absorption and emission anisotropies leads to displacements of the intersection point in the plot. These shifts are limited by the $ABCD$ curve. Thus, the experimental errors of α and $\langle P_2 \rangle$ can be estimated: $\Delta\alpha = \pm 6.0°$ and $\Delta\langle P_2 \rangle = \pm 0.04$.

The angles α, ε, and the order parameters of the dyes in the E18 nematic liquid crystal, calculated from (23)–(25), are stored in Table 3.

It is seen that for the dyes I, II, and III the absorption and the emission transition moments deviate almost symmetrically with respect to the axis of the cylinder, described on the dye molecule. However, the other dyes have their absorption moments nearly parallel to their cylinder axes.

Values of the angles α and ε of the dyes VI and VII, calculated here, are not equal to those obtained in a
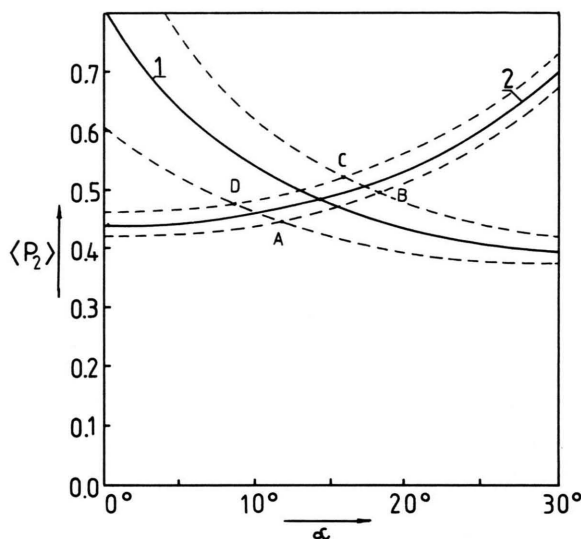

Fig. 3. Order parameter $\langle P_2 \rangle$ versus α angle. Curve 1 is obtained from fluorescence, and curve 2 from absorption measurements. Dashed lines describe the error limits.

Table 3. Angles between the molecular symmetry axis and the absorption transition moment (α), and the emission (ε) one. Order parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$ of the dyes in E18 nematic liquid crystals.

Dye no.	α	ε	$\langle P_2 \rangle$	$\langle P_4 \rangle$
I	18.1°	14.9°	0.47	-0.01
II	14.2°	14.0°	0.48	-0.01
III	18.9°	22.0	0.42	0.06
IV	8.5°	22.7°	0.38	-0.22
V	6.4°	26.3°	0.43	-0.16
VI	6.5°	22.5°	0.54	0.14
VII	9.7°	18.4°	0.65	0.41

smectic phase of liquid crystal 8CB [22]. This disagreement may be due to different viscosities and consequently unlike rotational correlation times of molecules in nematic E18 and smectic 8CB liquid crystals.

Neglect of the molecular dynamics in (23), (24) also results in inaccuracy of the $\langle P_2 \rangle$ and $\langle P_4 \rangle$ estimations, but these errors do not explain significant differences between the order parameters describing the orientation of the investigated dyes. It was shown in [10] that the order parameters of dyes in a nematic matrix depend on the length to width ratio of the dyes. The molecules VI and VII are the longest of the ones given

in Table 1. Thus the great order parameters of these two dyes seem to be justifiable.

It seems to be appropriate to examine more viscous mixtures of these dyes with liquid crystalline polymers, for example. Such experiments were described for stilbene dye in liquid crystalline side chain polymer [23, 24].

[1] G. R. Luckhurst and G. W. Gray (eds.), The Molecular Physics of Liquid Crystals, Academic Press, London 1979.
[2] E. Sackman, Chem. Phys. Lett. 3, 253 (1969).
[3] E. Sackman and D. Rehm, Chem. Phys. Lett. **4,** 537 (1970).
[4] L. L. Chapoy and D. B. DuPre, J. Chem. Phys. **69,** 519 (1978).
[5] A. Szabo, J. Chem. Phys. **72,** 4620 (1980).
[6] C. Zannoni, Mol. Phys. **38,** 1813 (1979).
[7] I. N. Dozov and I. I. Penchev, J. Luminescence **22,** 69 (1980).
[8] A. Arcioni, F. Bertinelli, R. Tarroni, and C. Zannoni, Mol. Phys. **61,** 1161 (1987).
[9] E. Wolarz and D. Bauman, Mol. Cryst. Liq. Cryst. **197,** 1 (1991).
[10] L. M. Blinov, V. A. Kizel, V. G. Rumyantsev, and V. V. Titov, Kristallografiya **20,** 1245 (1975).
[11] D. Bauman, A. Skibinski, and R. Stolarski, Mol. Cryst. Liq. Cryst. **138,** 367 (1986).
[12] K. Fiksiński, D. Bauman, A. Skibiński, and R. Stolarski, Dyes and Pigments **15,** 203 (1991).
[13] E. Wolarz, H. Moryson, and D. Bauman, Displays, submitted to publication.
[14] A. Jabłoński, Bul. Acad. Polon. Sci., Ser. Sci. Math. Astron. Phys. **8,** 259 (1960).
[15] G. R. Desper and I. Kimura, J. Chem. Phys. **38,** 4225 (1967).
[16] S. Nomura, H. Kawai, I. Kimura, and M. Kagiyama, J. Pol. Sci. A-2 **8,** 383 (1970).
[17] L. L. Chapoy, D. B. DuPre, and E. T. Samulski, in: Liquid Crystals and Ordered Fluids (J. F. Johnson and R. S. Porter, eds.), Plenum Press, New York 1978.
[18] J. A. R. Coope, R. F. Snider, and F. R. McCourt, J. Chem. Phys. **43,** 2269 (1965).
[19] M. E. Rose, Elementary Theory of Angular Momentum, Wiley, New York 1967.
[20] A. Saupe, Z. Naturforsch. **19a,** 161 (1964).
[21] E. Wolarz and T. Martynski, Mol. Cryst. Liq. Cryst. **193,** 25 (1990).
[22] M. Moryson, D. Bauman, and E. Wolarz, Acta Physica Polon., submitted to publication.
[23] D. Bauman and E. Wolarz, Mol. Cryst. Liq. Cryst. Lett. **7,** 161 (1990).
[24] E. Wolarz and D. Bauman, J. Polym. Sci., submitted to publication.