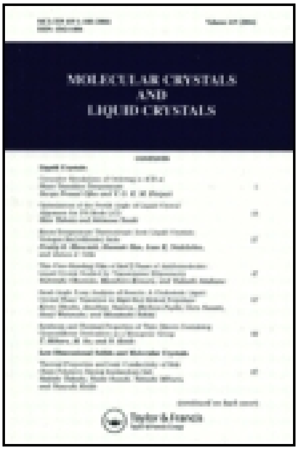

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

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Version of record first published: 20 Apr 2011.

To cite this article: Z. Salamon & A. Skibiński (1983): Fluorescence Emission of Guest Molecules as a Tool of Surface Alignment Study in Nematic Liquid Crystals, Molecular Crystals and Liquid Crystals, 90:3-4, 205-215

To link to this article: http://dx.doi.org/10.1080/00268948308072450

Mol. Cryst. Liq. Cryst., 1983, Vol. 90, pp. 205–215
0026-8941/83/9004–0205$18.50/0

Fluorescence Emission of Guest Molecules as a Tool of Surface Alignment Study in Nematic Liquid Crystals

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(*Received August 7, 1981; in final form June 10, 1982*)

A simple fluorescence method for surface alignment studies of nematic liquid crystals is presented. It is shown that, knowing the polarized fluorescence of a guest pleochroic dye, the surface order parameter can be calculated. For nematic liquid crystal matrixes with positive dielectric anisotropy and a pleochroic dye it is found that there is a remarkable difference between the degree of order at the surface and in the bulk, and that even in the isotropic temperature region the order parameter at the surface is not destroyed completely.

1. INTRODUCTION

Pleochroic dye liquid crystal displays are generally characterized by an order parameter S which depends on the nature of the liquid crystal and its interaction with the walls. Chemically[1] or mechanically[2,3] pretreated glass walls can give the liquid crystal molecules a strong preferred orientation.[4] Recent results[5,6] suggest that the order parameter is slightly larger at the wall than in the bulk. The wall orientation effects in nematic liquid crystals are, however, at present only poorly understood.

There are many ways to study the alignment of liquid crystal molecules[7,8] but a distinction between the alignment in the bulk and at the surface can not be made with those methods. Recently Mada and Kobayashi[5,9] have used an interferometric method for this purpose. In the present paper it is shown that the surface alignment can be calculated from the fluorescence of a guest pleochroic dye.

2. MATERIALS AND METHODS

The following liquid crystals with a positive dielectric anisotropy were used:

(1) RO-TN-570 (F. Hoffman–La Roche type),
(2) 4-cyano-4′-*n*-pentylbiphenyl (5CB),
(3) 4-cyano-4′-*n*-hexylbiphenyl (6CB).

As a fluorescent pleochroic dye we used one of the methine dyes 2[4(*N,N*-dimethyloamino)αstyrylo]benzothiazole.[10]

The spectral properties of this type of dye were recently investigated.[11,12]

The guest-host mixture was placed into a liquid crystal cell. The dye concentrations were 5×10^{-4} M for absorption and 3×10^{-3} M for fluorescence measurements. A sample thickness $d = 20$ μm was procured by a teflon spacer. In order to get a tilted homogeneous alignment of the liquid crystal molecules the glass was covered by evaporation with SiO_2 at angles of 7° and 30° to the surface.[13]

The absorption spectra were measured with an UV-VIS Zeiss Spectrophotometer equipped with two polaroid sheets to get the components of absorption polarized parallel and perpendicular (A_z and A_x) to the electric vector of the incident light (propagating along the Y axis Figure 1). The emission was excited through an interference filter

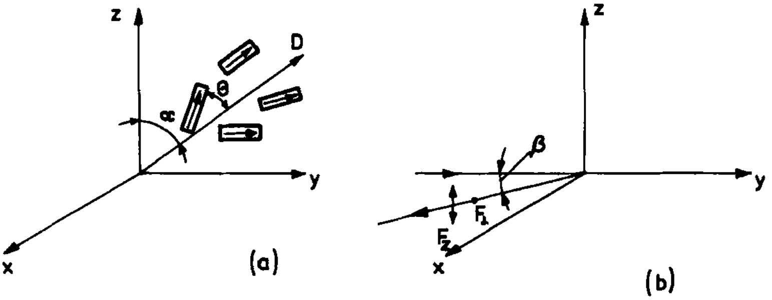

FIGURE 1 The glass plates are in the XZ plane and the director is in the YZ-plane (a) The arrangement of dye molecules around the director **D**. (b) Specification of excitation and fluorescence directions.

(425 ± 5.5 nm). The directions of the excitation and fluorescence observation were both on the same side of the cell in the XY plane (Figure 1b). The angle between these directions was β. The excitation was performed with unpolarized light. Two components of the fluorescence (F_z and $F_\perp$), referring to an electric vector of the emitted light parallel and perpendicular to the Z axis (Figure 1b), were measured. The temperature dependence of the polarized absorption and fluorescence components were measured in a range of 293 K–343 K.

The clearing temperature (T_c) was measured with MPI-5 polarization-interference microscope equipped with an electric heater, supplied from a thermoregulator permitting temperature stabilization with an accuracy of ±0.03 deg. Temperature inhomogeneities in the field of vision did not exceed 0.01 deg.[14] The tilt angle α has been measured with a capacitive method.[8]

3. RESULTS AND DISCUSSION

The degree of orientation of the dye molecules can be described by an order parameter S defined as:[15]

$$S = \left\langle \frac{3}{2} \cos^2 \theta - \frac{1}{3} \right\rangle, \tag{1}$$

where θ is the angle between the molecular long axis and the director **D** (Figure 1a). The dye's order parameter is a function of the specific guest-host interaction. It may be assumed that the dye's order parameter reflects the order parameter of the host. Therefore, we use the optical properties of dye as the indicators of the liquid crystal order parameter.

The fluorescence method of the surface alignment study is based on the following assumptions: (a) the order parameter of the liquid crystal matrix may be calculated from the fluorescence emission of the guest dye, (b) the fluorescence is emitted mainly from the surface of the cell.

In order to meet the first of the above requirements, the dye molecule must be long and liquid crystalline-like, and its transition moment should be parallel to its long molecular axis.

Moreover, the fluorescent lifetime should be longer than the vibrational relaxation time and should be much shorter than the correlation time of the dye. We assumed that the vibrational relaxation time fulfills this requirement.[12] In order to check experimentally the relation between the lifetime of fluorescence and the correlation time we compare the order parameters calculated from absorption and emission in the bulk liquid crystal. Because we have found the same values for both order parameters,[16] we assume that condition stated above concerning those times is true.

The second condition can be fulfilled taking a sufficiently high concentration. As the excitation intensity decreases exponentially with the entrance depth, the fluorescence intensity emitted from different depths diminishes in the same way, if one can neglect the fluorescence reabsorption.[11] In this case, the ratio of the surface fluorescence F_s, emitted from a layer $0 < y < \xi$, to the bulk fluorescence from the layer $\xi < y < d$ is given by

$$\frac{F_s}{F_B} = \frac{\int_0^{\xi} e^{-A\frac{y}{d}}dy}{\int_{\xi}^{d} e^{-A\frac{y}{d}}dy} = \frac{e^{-A\frac{\xi}{d}} - 1}{e^{-A} - e^{-A\frac{\xi}{d}}}. \tag{2}$$

The absorbance A for the thickness d of the cuvette is proportional to the concentration of the fluorescence molecules. If the realtive thickness of the surface layer ξ/d is chosen, the concentration necessary to obtain a preferable surface fluorescence, $F_s/F_B > 1$, can be determined from the above relation. To measure the surface fluorescence the absorbance A should be high; but the value of ξ/d should usually be very low, thus $e^{-A} - e^{-A}\xi/d \approx -e^{-A}\xi/d$, and we get in very good approximation for the critical limit

$$\frac{F_s}{F_B} = 1 = \frac{e^{-A\frac{\xi}{d}} - 1}{-e^{-A\frac{\xi}{d}}}, \quad \text{or} \quad e^{-A\frac{\xi}{d}} = \frac{1}{2},$$

$$\text{and} \quad A\frac{\xi}{d} = 0.7. \tag{2a}$$

When the order parameter or the tilt angle in the surface and bulk layers are different, we should measure different anisotropy values of the fluorescence/and absorption/for the surface and bulk layer at corresponding different concentrations.

We have measured the two polarized components of absorption and fluorescence parallel (A_z, F_z) and perpendicular (A_x and $F_\perp$) to the Z axis (Figure 1) and have calculated the absorption and fluorescence anisotropies, R^A and R^F_β, of absorbed excitation light propagating along the Y direction:

$$R^A = \frac{A_z - A_x}{A_z + 2A_x}, \tag{3}$$

$$R^F_\beta = \frac{F_z - F_\perp}{F_z + 2F_\perp}, \tag{4}$$

Having such experimental values we have evaluated a correlation between the order parameter S, defined by Eq. (1), and the two anisotropies R^A and R^F_β (see Appendix):

$$R^A = \frac{S_A \cos^2_\alpha}{1 + S_A(\cos^2_\alpha - 1)}, \tag{5}$$

$$R^F_\beta = \frac{\frac{2}{15}(1 - S_F)\sin^2_\beta + S_F\cos^4_\alpha - S_F\cos^2_\alpha\sin^2_\alpha\sin^2_\beta}{\frac{4}{15}(1 - S_F)(1 + \sin^2_\beta) + \frac{8}{15}(1 - S_F)\cos^2_\beta + S_F\cos^4_\alpha + 2S_F\cos^2_\alpha\sin^2_\alpha\sin^2_\beta} \tag{6}$$

Figure 2 and 3 show these correlations for typical values of α and β.

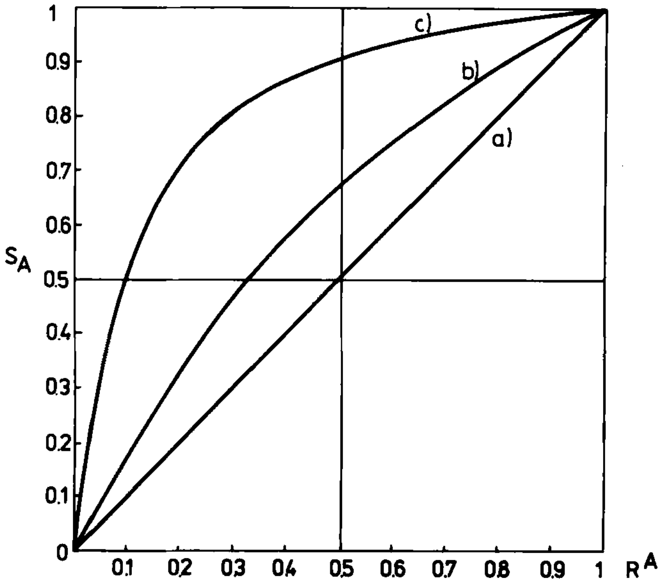

FIGURE 2 Plots of the order parameter S_A vs. the anisotropy R^A for given tilt angles α (a) $\alpha = 0°$ (b) $\alpha = 45°$ (c) $\alpha = 71.5°$.

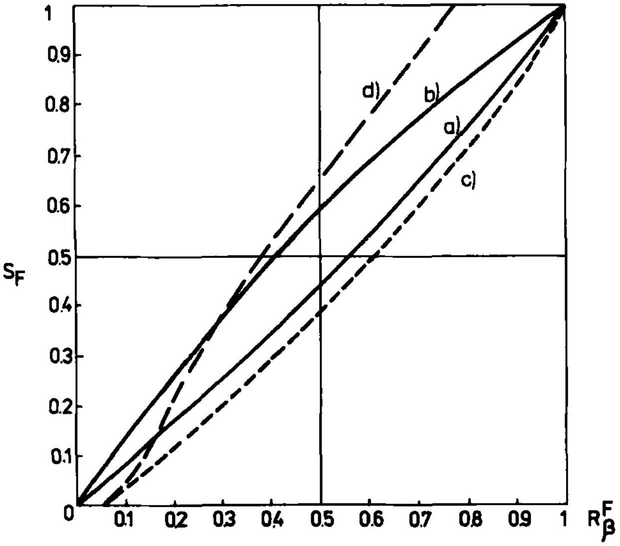

FIGURE 3 Plots of the order parameter S_F vs. the fluorescence anisotropy R^F_β for given values of α and β (a) $\alpha = 0$, $\beta = 0$ (b) $\alpha = 30°$, $\beta = 0$ (c) $\alpha = 0$, $\beta = 32°$ (d) $\alpha = 30°$, $\beta = 32°$.

We have measured the value of α using a capacitive method and, knowing the R^A value from absorption measurements, we have calculated the order parameter S_A from Eq. (5). The obtained values of S_A and α (Table I) describe the average alignment of the liquid crystal molecules in the bulk. In order to get information about the alignment of molecules at the surface of the cell from the experimentally obtained fluorescence anisotropy (R^F_β) we should assume that: (a) either the tilt angle is constant throughout the cell, indicating a difference between the sur-

TABLE I

Values of the order parameter S_A and S_F obtained using Eqs. (5) and (6) with given data of α, β and R^A, R^F_β.

Angle of Evaporation	Liquid Crystal	α	R^A	S_A	β	R^F_β	S_F
30°	5CB	10°	0.38	0.39	32°	0.60	0.53
	6CB	9°	0.37	0.38	32°	0.59	0.51
	RO-TN-570	14°	0.39	0.40	32°	0.56	0.51
7°	5CB	20°	0.39	0.41	32°	0.63	0.65
	6CB	19°	0.40	0.43	32°	0.63	0.64
	RO-TN-570	26°	0.41	0.44	32°	0.61	0.72

face and bulk order parameters, or (b) the order parameter has the same value at the surface and in the bulk, but we have a difference in the tilt angle α. Unfortunately, on the basis of our experimental data it is impossible to distinguish between the above two cases. However, we can easily show how large a difference in alignment between the surface and bulk layers might exist. Taking into consideration the case (a) with the values of α, given in Table I we have calculated the S_F values using Eq. (6) with experimental data of the angle β and R_β^F. The results are shown in Table I (last column). The results in Table I show the differences between the surface (S_F) and the bulk (S_A) order parameters.

Because the fluorescence and absorption data were taken at different dye concentrations such results of S might be understood as the effect of transition temperature change (T_c) of the liquid crystal and dye molecules mixture. Our results with different types of molecule dyes have shown that methines dissolved in the liquid crystals used change neither the transition temperature of mixture in the dye concentration range between 3×10^{-3} M $-$ 10^{-5} M nor a value of S calculated using the absorption data.[16,17]

It should be noticed that fluorescence reabsorption which can reduce the measured value of S_F might be, in our case, neglected because an absorption coefficient for the fluorescence light is very low.[12]

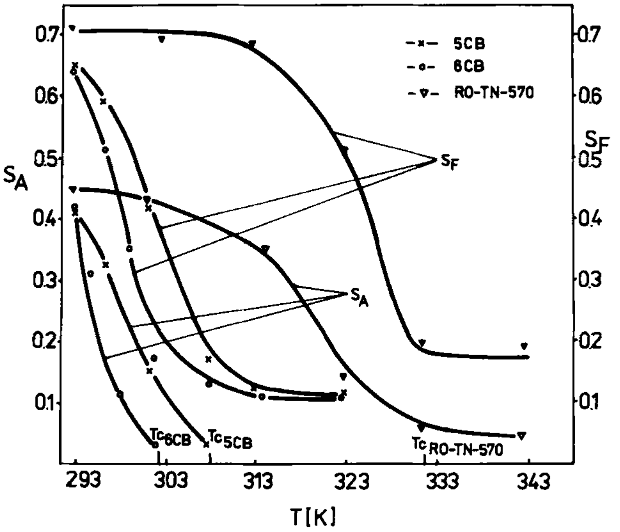

FIGURE 4 Dependence of the order parameters (S_A and S_F) on the temperature of the sample with 5CB, 6CB and RO-TN-570 liquid crystal matrix.

Recently, similar differences of the order parameters between the bulk and the surface have been observed.[5]

The nematic order is influenced by temperature. S should be zero in the isotropic temperature region.[5] Results plotted in Figure 4 show that the ordered state at the surface is not destroyed completely even in the isotropic temperature region. S_F does not become zero at the clearing point T_c in Figure 4 whereas S_A practically does. This temperature effect indicates that in our liquid crystal cell the order parameter has different values in the bulk and at the surfaces of the cell, which agrees with our recent data.[6]

We believe that our results confirm the suggestion that the fluorescence of guest molecules might be used as a convenient method for surface alignment measurements. This kind of study should complete the usual absorption measurements on liquid crystal cell.

Acknowledgment

The authors are greatly indebted to Professor A. Schmillen for valuable discussions.

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Appendix

Let us assume that an ensemble of anisotropically absorbing molecules can be divided into two groups. A first group absorbing isotropically

(A^i) and a second one absorbing as linear oscillators oriented perfectly along the director (A^a). The absorbances of light polarized parallel to a given axis of the system (XYZ) Figure 1 are.[19]

$$A_z = A^i_z + A^a_z, \tag{1}$$

$$A_y = A^i_y + A^a_z, \tag{2}$$

$$A_x = A^i_x, \quad \text{(the director in the } ZY \text{ plane).} \tag{3}$$

The isotropically absorbing ensemble yields the absorbances

$$A^i_x = \frac{1}{3} A(1 - S), \tag{4}$$

$$A^i_y = \frac{1}{3} A(1 - S), \tag{5}$$

$$A^i_z = \frac{1}{3} A(1 - S), \tag{6}$$

whereas the anisotropic ensemble under our conditions director without an x component absorbs with

$$A^a_x = 0, \tag{7}$$

$$A^a_y = AS \sin^2_\alpha, \tag{8}$$

$$A^a_z = AS \cos^2_\alpha, \tag{9}$$

The absorbance A is proportional to $|\boldsymbol{\mu}|^2$, where $\boldsymbol{\mu}$ is a transition moment of absorption (Figure 1a).

Applying (4–9) in Eqs. (1–3) one obtains the following results:

$$A_z = \frac{1}{3} A(1 - S) + AS \cos^2_\alpha, \tag{10}$$

$$A_y = \frac{1}{3} A(1 - S) + AS \sin^2_\alpha, \tag{11}$$

$$A_x = \frac{1}{3} A(1 - S). \tag{12}$$

The **k** vector of excitation being in the y direction, we define an absorption anisotropy

$$R^A = \frac{A_z - A_x}{A_z + 2A_x}. \tag{13}$$

Using Eqs. (10), (11), (12) and taking $S = S_A$, the absorption anisotropy is given by,

$$R^A = \frac{S_A \cos^2_\alpha}{1 + S_A(\cos^2_\alpha - 1)}. \tag{14}$$

A similar correlation between S and polarized fluorescence can be obtained starting from the fluorescence anisotropy R^F_β about the Z axis for a given value defined as:

$$R^F_\beta = \frac{F_z - F_\perp}{F_z + 2F_\perp}, \tag{15}$$

where $F = F_x \cos^2_\beta + F_y \sin^2_\beta$, and lies in the XY plane (Figure 1b).

In order to find the polarized fluorescence components F_z and $F_\perp$ one can substitute an ensemble of statistically oriented oscillators, excited by linear polarized light by three vertical oriented oscillators emitting with three polarized components in the intensity ratio:[20]

$$F_z : F_\perp : F_\perp = \frac{3}{5} : \frac{1}{5} : \frac{1}{5}.$$

Therefore, in our case, the polarized fluorescence components, having an unpolarized excitation light propagating along the Y direction with two equal intensities $(I_0/2)$ are given by,

$$F_x = \frac{I_0}{2}\left(\frac{3}{5} A^i_x + \frac{1}{5} A^i_z\right), \tag{16}$$

$$F_y = \frac{I_0}{2}\left(\frac{1}{5} A^i_x + \frac{1}{5} A^i_z + A^a_z \sin^2_\alpha\right), \tag{17}$$

$$F_z = \frac{I_0}{2}\left(\frac{1}{5} A^i_x + \frac{3}{5} A^i_z + A^a_z \cos^2_\alpha\right). \tag{18}$$

Using Eqs. (16, 17, 18) and (4–9) one obtains:

$$F_\perp = \frac{I_0}{2}\left[\frac{4}{15}(1 - S)A \cos^2_\beta + \left[\frac{2}{15}(1 - S)A + AS \cos^2_\alpha \sin^2_\alpha\right] \sin^2_\beta\right] \tag{19}$$

$$F_z = \frac{I_0}{15}\left[2(1 - S)A + \frac{15}{2} AS \cos^4_\alpha\right] \tag{20}$$

Substituting F_z and $F_\perp$ in Eq. (15) by (19, 20) and taking $S = S_F$ one obtains the final formula:

$$R_\beta^F = \frac{\frac{2}{15}(1 - S_F)\sin^2_\beta + S_F\cos^4_\alpha - S_F\cos^2_\alpha\sin^2_\alpha\sin^2_\beta}{\frac{4}{15}(1 - S_F)(1 + \sin^2_\beta) + \frac{8}{15}(1 - S_F)\cos^2_\beta + S_F\cos^4_\alpha + 2S_F\cos^2_\alpha\sin^2_\alpha\sin^2_\beta}.$$