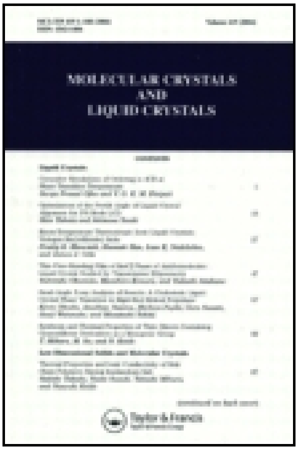

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Polarized Fluorescence of Dyes Oriented in Room Temperature Nematic Liquid Crystals†‡

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Abstract—Pleochroic absorption and polarized fluorescence of guest molecules oriented in nematic liquid crystals were observed in the nematic phase and at the nematic–isotropic phase transition. The order parameters calculated from fluorescence intensities were found to be smaller than those calculated from the absorption coefficients. For some guest–host combinations a change in the quantum yield of the fluorescence was observed at the nematic–isotropic transition point.

1. Introduction

Liquid crystals can be used as a matrix to orient pleochroic and fluorescent guest molecules.⁽¹⁻⁴⁾ The observed pleochroic absorption and polarized fluorescence emission is dependent upon the degree of order of these guest molecules.

Typical lifetimes of excited states of fluorescent molecules are of the order of 10^{-9} seconds which is long enough to allow interactions with the surroundings. These interactions may influence the quantum yield of the fluorescence emission.

In order to study these effects we introduced fluorescent molecules into room temperature liquid crystals and measured the quantum yield over the entire nematic temperature range including the nematic–isotropic transition point.

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‡ Presented at the Fourth International Liquid Crystal Conference, Kent State University, August 21–25, 1972.

2. Experimental

The guest molecules were chosen to have absorption and emission bands in a wavelength region where the liquid crystal is transparent. The electronic transition moments of our guest molecules were approximately either parallel or normal to the long molecular axis. The guest molecules used were dimethylamino-nitrostilbene (transition moment parallel to the long axis) and tetracene (transition moment perpendicular to the long axis). The liquid crystals were MBBA and a composition of disubstituted carbon esters from Merck called WI.(5)

The following systems were investigated:

I. DMAN-Stilbene in WI
II. DMAN-Stilbene in MBBA
III. Tetracene in WI
IV. Tetracene in MBBA

The molar concentrations of the solute molecules were less than 10^{-3} mol/liter. We made specimens of homogeneous (parallel oriented) textures with a thickness of 10, 20 and 50 μm. The area of the specimen penetrated by the light beam had a diameter of 10 mm. The absorption measurements were carried out with a Cary 14 spectrophotometer and the fluorescence measurements were made with a Baird-Atomic Fluorispec.

3. Determination of Order Parameters

The S-matrix for molecules having a more than 2-fold symmetry axis is reduced to one independent S-value which is given by

$$S = \tfrac{1}{2}\langle 3\cos^2\theta - 1\rangle \tag{1}$$

where θ is the angle between the long molecular axis and the optical axis of the liquid crystal. This is also true to a good approximation for all elongated molecules.

3.1. EVALUATION OF S-VALUES FROM ABSORPTION COEFFICIENTS

The oscillator strength f of an electronic absorption transition is proportional to the square of the transition moment M_a. If the snape of the absorption spectrum is unchanged during the experiment

f can be replaced by the maximum absorption coefficient μ

$$\mu \propto |M_a|^2$$

To get the S-value, we have to calculate the components of M_a in a laboratory coordinate system xyz. The z-axis coincides with the optical axis of the liquid crystal and the x-axis lies in the plane of the sample. The incident light propagates along the y-axis (normal to the plane of the sample). μ_z and μ_x are the absorption coefficients for light polarized parallel to the z- and x-directions, respectively.

Since

$$\mu_z \propto \langle |M_{az}|^2 \rangle$$
$$\mu_x \propto \langle |M_{ax}|^2 \rangle$$

and

$$\frac{\mu_z}{\mu_x} = \frac{\langle |M_{az}|^2 \rangle}{\langle |M_{ax}|^2 \rangle} = F \tag{2}$$

we get from (1)

$$S = \frac{F-1}{F+2} \qquad \text{for } \beta = 0$$

$$S = \frac{2(1-F)}{F+2} \quad \text{for } \beta = \frac{\pi}{2} \tag{3}$$

β is the angle between the long molecular axis and the direction of the transition moment.

3.2. Evaluation of S-Values from Fluorescent Emission

The evaluation of S-values from fluorescence measurements is more complicated because the emission is preceded by an absorption process. For the following calculations we assume

$$\tau_{\text{relaxation}} < \tau_{\text{life}}$$

$\tau_{\text{relaxation}}$ is the time required for the excited molecules to relax to the equilibrium state. τ_{life} is the lifetime of the excited state of the guest molecules.

J_{ik} are the emitted fluorescence intensities. i and k (i, $k = u, x, z$) indicate the polarization of the excitation and emission respectively (u = unpolarized; x, z = linear polarized in x resp. z direction).

3.2.1. *Unpolarized excitation*

The fluorescence intensities polarized parallel and perpendicular to the optical axis (z) are given by

$$J_{uz} = \frac{1}{\gamma_u} J_0 \langle |M_{ax}|^2 + |M_{az}|^2 \rangle \langle |M_{ez}|^2 \rangle$$

$$J_{ux} = \frac{1}{\gamma_u} J_0 \langle |M_{ax}|^2 + |M_{az}|^2 \rangle \langle |M_{ex}|^2 \rangle \tag{4}$$

M_e = emission transition moment
J_0 = excitation intensity
γ = corrects the intensities for thick layers.

The ratio of the fluorescence intensities

$$\frac{J_{uz}}{J_{ux}} = \frac{\langle |M_{ez}|^2 \rangle}{\langle |M_{ex}|^2 \rangle} = F \tag{5}$$

is equal to the squares of the components of the emission moment on the axes of the laboratory coordinate system. From a comparison of (2) and (5) we get the same expression (3) for the fluorescence intensities as we did for the absorption case.

3.2.2. *Polarized excitation*

The fluorescence intensities polarized parallel and perpendicular to the z-axis are given by

$$J_{zz} \propto \frac{1}{\gamma_z} J_0 \langle |M_{az}|^2 \rangle \langle |M_{ez}|^2 \rangle$$

$$J_{xx} \propto \frac{1}{\gamma_x} J_0 \langle |M_{ax}|^2 \rangle \langle |M_{ex}|^2 \rangle \tag{6}$$

for excitation light polarized parallel to the polarization of the observed emission. γ_x and γ_z correct the intensities for thick layers. The ratio of these intensities corrected for thick layers

$$\frac{J_{zz}\gamma_z}{J_{xx}\gamma_x} = \frac{\langle |M_{az}|^2 \rangle \langle |M_{ez}|^2 \rangle}{\langle |M_{ax}|^2 \rangle \langle |M_{ex}|^2 \rangle} = F \tag{7}$$

contains products of averages of squares of emission and absorption transition moments.

In this case we get from the definition of S given in (1)

$$S = \frac{(F+2) - 3\sqrt{F}}{F-4} \qquad \beta = 0$$

$$S = \frac{-(2F+4) + 6\sqrt{F}}{F-4} \qquad \beta = \frac{\pi}{2} \tag{8}$$

4. Results and Discussion

The experimental results of the absorption measurements are shown in Fig. 1. The absorption coefficients show the expected

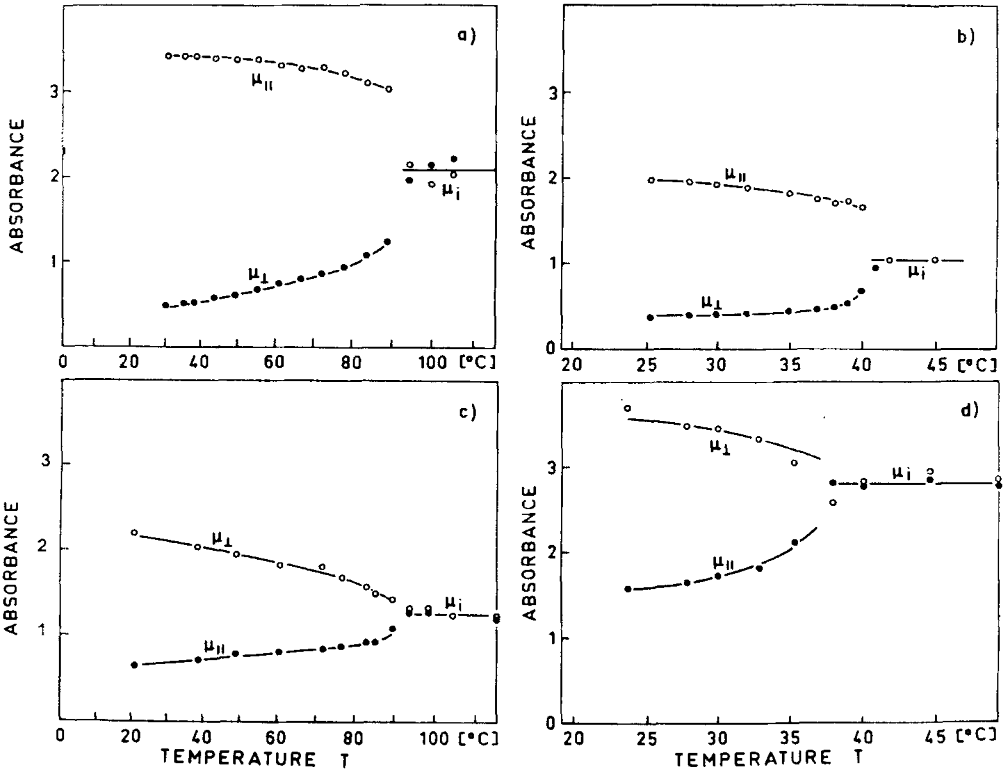


Figure 1. Absorbance μ_K of DMAN-stilbene ($\lambda = 445$ nm) in (a) WI (system I), (b) MBBA (system II); and of tetracene ($\lambda = 480$ nm) in (c) WI (system III), (d) MBBA (system IV).
$K = \parallel, \perp, i$ indicating polarizations parallel and perpendicular to the optical axis and in the isotropic phase.

behavior at the nematic–isotropic phase transition: $\mu_\parallel$ decreases and $\mu_\perp$ increases with increasing temperature for systems I and II, whereas $\mu_\parallel$ increases and $\mu_\perp$ decreases for systems III and IV.

The polarized fluorescence emission was stimulated by polarized and unpolarized light which was normally incident to the homogeneous (parallel oriented) liquid crystal layer. Figure 2 shows the fluorescence emission $J_\parallel$ and $J_\perp$ of systems I and II for the case of unpolarized excitation. For dimethylamino-nitrostilbene in WI we found good agreement between the temperature dependence of the emission intensities and of the absorption coefficients at the nematic–isotropic transition point. The corresponding measurements for the systems III and IV are shown in Fig. 3. Here the fluorescence intensities $J_\perp$ are always greater than $J_\parallel$ since the 0-0-transition of the emission of tetracene is polarized perpendicular to the long molecular axis. In the case

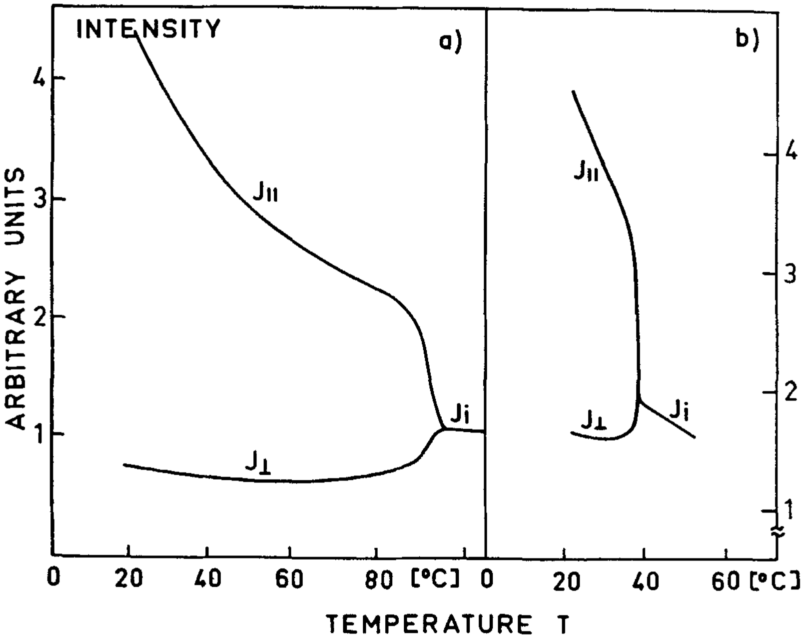


Figure 2. Polarized fluorescence emission J_K of DMAN-stilbene in (a) WI (system I, $\lambda = 615$ nm), (b) MBBA (system II, $\lambda = 645$ nm).
$K = \parallel, \perp, i$ indicating polarizations parallel and perpendicular to the optical axis and in the isotropic phase.

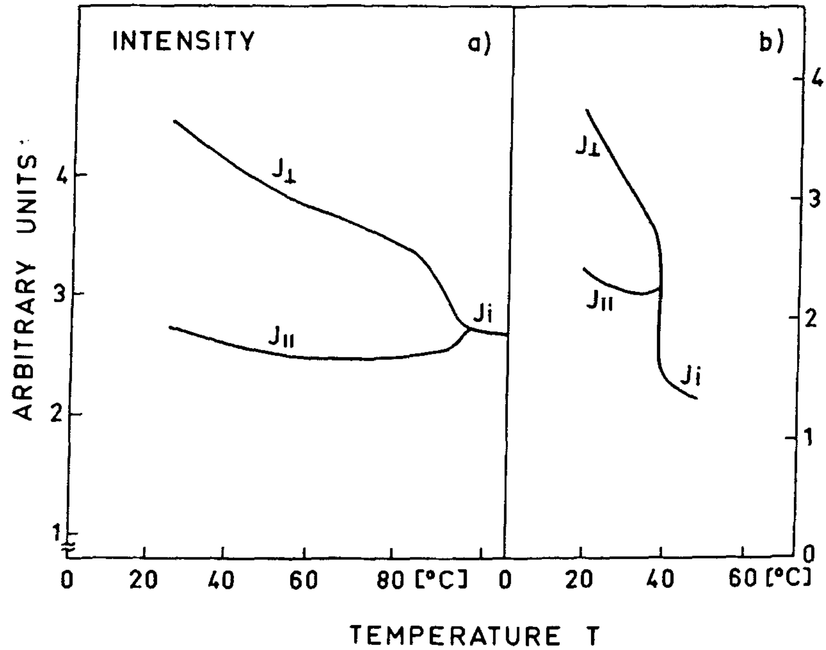


Figure 3. Polarized fluorescence emission J_K of tetracene in (a) WI (system III, $\lambda = 484$ nm), (b) MBBA (system IV, $\lambda = 486$ nm).
$K = \parallel$, $\perp$, i indicating polarizations parallel and perpendicular to the optical axis and in the isotropic phase.

of system IV we found at the nematic–isotropic phase transition a strong decrease of the fluorescence for both $J_\perp$ and $J_\parallel$. One should expect an increase of $J_\parallel$ because of the decreasing order parameter. This unexpected decrease of both fluorescence intensities $J_\parallel$ and $J_\perp$ is interpreted as a change of the quenching rate at the nematic–isotropic phase transition.

Figures 4 and 5 show order parameters computed from absorption coefficients as well as from fluorescence intensities excited by polarized and unpolarized light for systems I and IV. In all cases the order parameters calculated from the fluorescence intensities are smaller than those calculated from the absorption coefficients.

The order parameter computed from the absorption coefficients is assumed to be representative of the true alignment of the excited guest molecules in the liquid crystal matrix. The S-parameters calculated from the fluorescence emission can differ from this value

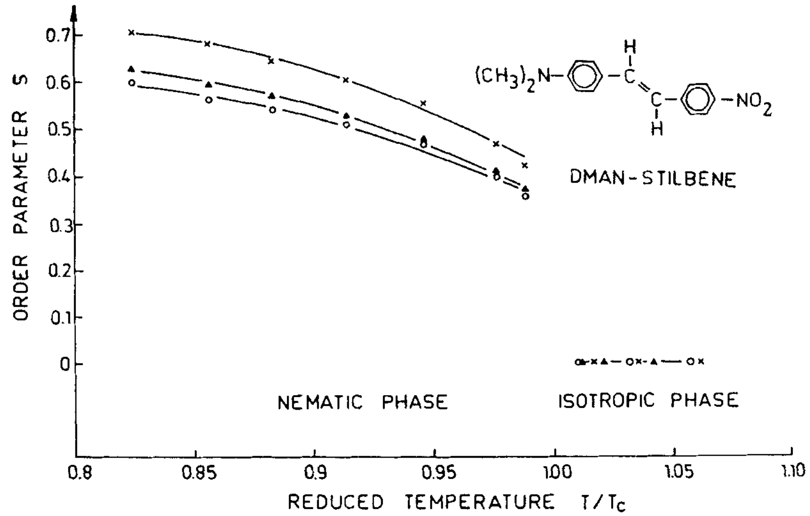
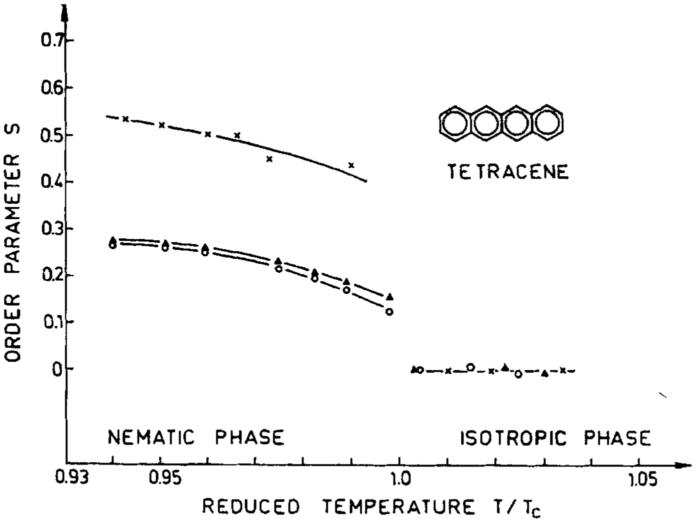


Figure 4. Order parameter S of DMAN-stilbene in WI (system I) computed from: × absorption coefficients; ○ fluorescence intensities (unpolarized excitation); ▲ fluorescence intensities (polarized excitation).



igure 5. Order parameter S of tetracene in MBBA (system IV) computed from: × absorption coefficients; ○ fluorescence intensities (unpolarized excitation); ▲ fluorescence intensities (polarized excitation).

because of an interaction of the dye molecules in their excited state with their anisotropic surroundings. First this interaction can result in a change of the order parameter caused by the different polarizability of the excited molecules as one can expect from the Maier–Saupe theory.(6) Secondly the lifetime of the excited molecules can be orientation-dependent because of the anisotropic dielectric constant (refractive index) or an anisotropic quenching of the quantum yield.

The unexpected decrease of both fluorescence intensities $J_\perp$ and $J_\parallel$ in the case of system IV is interpreted as a dramatic change of the quenching rate at the nematic–isotropic phase transition. It is also this system that shows the largest difference in S-values computed from the absorption coefficients and those computed from the fluorescence intensities. Because of this coincidence we interpret this discrepancy as being due to an orientation-dependent lifetime in the nematic phase rather than to a possible change of the polarizability and consequently of the order of the excited guest molecules.

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