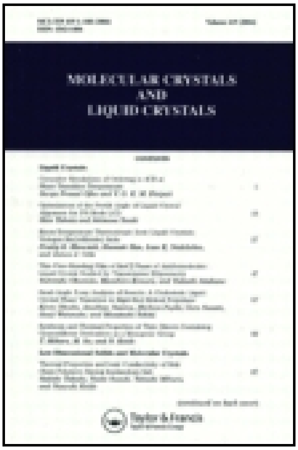

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

A Study of Orientational Characteristics of Nematics by Means of Polarized Fluorescence

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Version of record first published: 19 Oct 2010.

To cite this article: H. Yoshida , S. Kobinata & S. Maeda (1985): A Study of Orientational Characteristics of Nematics by Means of Polarized Fluorescence, Molecular Crystals and Liquid Crystals, 131:3-4, 209-216

To link to this article: http://dx.doi.org/10.1080/00268948508085043

Mol. Cryst. Liq. Cryst., 1985, Vol. 131, pp. 209–216
0026-8941/85/1314–0209/$15.00/0

A Study of Orientational Characteristics of Nematics by Means of Polarized Fluorescence

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(*Received February 14, 1985; in final form June 7, 1985*)

Depolarization ratios in polarized fluorescence have been measured for 4-amino-4′-nitrobiphenyl dissolved in 5CB as a fluorescent probe. The temperature dependence of orientational order parameters $\overline{P}_2$ and $\overline{P}_4$ and anisotropic rotational correlation times have been investigated.

1. INTRODUCTION

Experimental determination of order parameters is the subject of primary importance in the fundamental research of liquid crystals. The second ($\overline{P}_2$) and fourth ($\overline{P}_4$) orientational order parameters have been obtained from the polarization characteristics of Raman scattering,[1-4] fluorescence,[5,6] ESR,[7] X-ray[8] etc. Among those, fluorescence method has an advantage over others in that it provides not only the averaged quantities $\overline{P}_2$ and $\overline{P}_4$ but also, in principle, dynamical information such as the orientational relaxation time. There has been considerable effort to obtain such information from the polarization characteristics of fluorescence, but no satisfactory method has been established so far.[5,6,9-11]

In this work, the fluorescence depolarization ratio of 4-amino-4′-nitrobiphenyl (ANB) dissolved in nematic 4-pentyl-4′-cyanobiphenyl (5CB) has been measured to probe the molecular orientational behavior of the liquid crystal. The result has been used to derive $\overline{P}_2$ and $\overline{P}_4$ and the anisotropic orientational relaxation time near the nematic-isotropic phase transition temperature.

2. EXPERIMENTAL

ANB was synthesized by the reported method,[12] and was purified by recrystallization from ethanol before use. It was dissolved in 5CB at a concentration of 0.08wt%, and the fluorescence measurement was carried out on the isotropic and nematic phase in a sandwich-type glass cell. The experimental set-up was essentially the same as in the previous resonance Raman studies.[4] 457.9nm line of Ar^+ laser was used for excitation of fluorescence. The depolarization ratio of the fluorescence was determined by averaging the measured values at seven points within the broad band ranging over 550–770nm, as shown in Figure 1.

For homogeneously aligned samples, the exciting light polarized either in Z (optical axis) or Y axis was irradiated along the X-axis, and the depolarization ratios $R_1 = I_{YZ}/I_{ZZ}$ and $R_2 = I_{ZY}/I_{YY}$ were measured in the X-direction. I_{YZ} denotes the intensity of Y-polarized component of fluorescence excited by Z-polarized laser light.

Another ratio $R_3 = I_{XY}/I_{YY}$ was measured in a homeotropic sample, in which the exciting light was irradiated along the optical Z-axis.

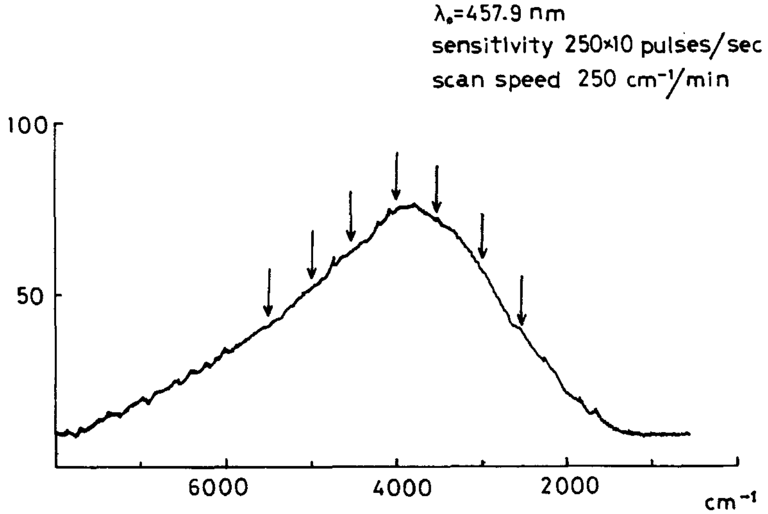

FIGURE 1 The fluorescence spectrum of ANB excited Ar^+ laser. Abscissa indicates the Stokes shift from 457.9nm. Arrows are the sampling points of fluorescence depolarization ratio.

3. RESULT AND DISCUSSION

In Figure 2, experimental depolarization ratios are plotted against the reduced temperature $T^* = T/T_{NI}$, where T_{NI} denotes the nematic-isotropic phase transition temperature. The measurement was carried out at two different thicknesses of the sample, resulting no appreciable difference in the R-values within the accuracy of measurement;

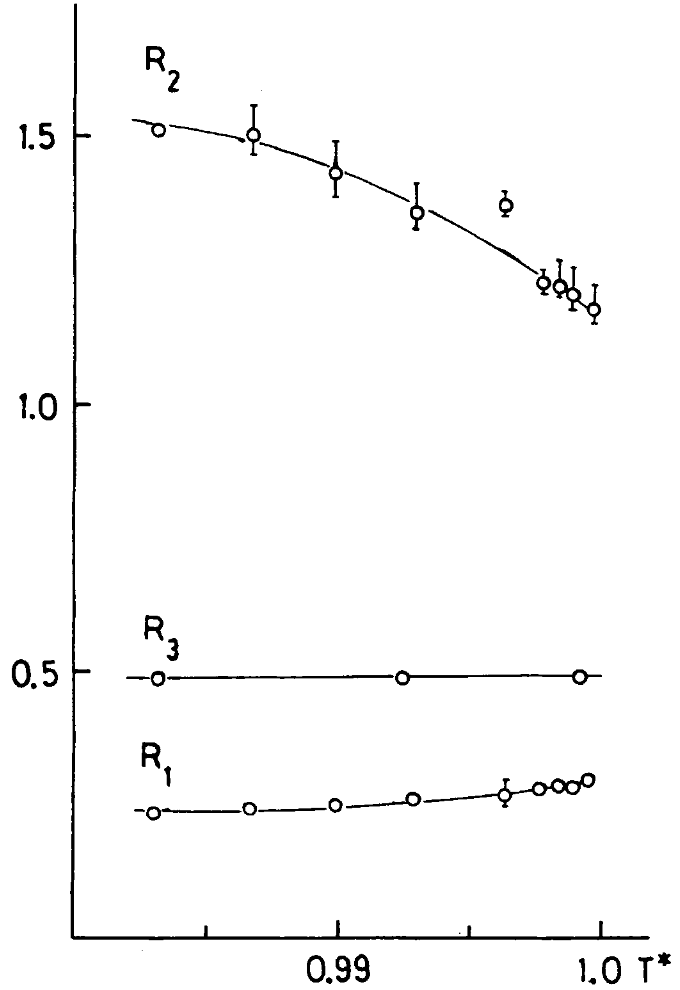

FIGURE 2 The variation of depolarization ratios of fluorescence R_1, R_2 and R_3 against the reduced temperature $T^* = T/T_{NI}$ (cell thickness 25 μ).

±0.01 for R_1 and R_3 and ±0.03 for R_2. In the isotropic phase ($\overline{P}_2 = \overline{P}_4 = 0$, $C_0 = C_2$), all the depolarization ratios degenerated into $R_{\mathrm{iso}} = 0.49 \pm 0.02$.

Both the absorption and resulting emission under consideration are most probably assigned to an identical intramolecular charge-transfer transition. The absorption transition moment is parallel to the C_2 axis of ANB. Since ANB molecule most probably retains the C_2 symmetry in the excited state, the emission transition moment is concluded to be parallel to the C_2 axis from the nature of the transition. Thus, the transition moments of absorption and emission are taken to be parallel each other, lying in the molecular long axis. This fact brings a considerable simplification in the interpretation of the experimental results, allowing one to consider only the effect of rotational Brownian motion of ANB molecules on the depolarization of fluorescence.

According to the theory of rotational diffusion of effectively cylindrical molecule in a uniaxial anisotropic media, the intensity of fluorescence is given, when both of the absorption and emission moments are in the molecular axis as present case, as[11]

$$
\begin{aligned}
I_{ZZ} &= 1/9 + (4/9)\overline{P}_2 + (4/9)R_{00} \\
I_{YZ} = I_{ZY} &= 1/9 + (1/9)\overline{P}_2 - (2/9)R_{00} \\
I_{YX} = I_{XY} &= 1/9 - (2/9)\overline{P}_2 + (1/9)R_{00} - (1/3)R_{20} \\
I_{XX} = I_{YY} &= 1/9 - (2/9)\overline{P}_2 + (1/9)R_{00} + (1/3)R_{20}
\end{aligned}
\tag{1}
$$

where

$$
\begin{aligned}
R_{00} &= (1.0/\tau_F) \int_0^{\infty} \phi_{00}\,(t)\exp(-t/\tau_F)\,dt \\
R_{20} &= (1.0/\tau_F) \int_0^{\infty} \phi_{20}\,(t)\exp(-t/\tau_F)\,dt
\end{aligned}
\tag{2}
$$

for the steady state experiment. R_{00} and R_{20} represent the effect of rotational Brownian motion on fluorescence intensities. τ_F is the fluorescence life time. ϕ_{00} and ϕ_{20} are the correlation function of Wigner rotation matrix $D^{(k)}_{m,n}\,(\Omega)$ defined as

$$
\begin{aligned}
\phi_{00}\,(t) &= \overline{D^{(2)}_{0,0}\,(\Omega(0))D^{(2)}_{0,0}\,(\Omega(t))}, \\
\phi_{20}(t) &= \overline{D^{(2)}_{2,0}\,(\Omega(0))D^{(2)}_{2,0}\,(\Omega(t))}
\end{aligned}
\tag{3}
$$

where $\Omega(t) = (\alpha(t), \beta(t), \gamma(t))$ represents a set of Eulerian angles of molecular-fixed coordinates with respect to laboratory-fixed coordinates at time t, and the bar implies an ensemble average. It can be easily shown from Eq. 1 that $\overline{P}_2$ is represented analytically by R_1, R_2 and R_3, independent of details of relaxation, as[10]

$$\overline{P}_2 = (R_2(1+R_1) - R_1(1+R_3))/(R_2(1+4R_1) + 2R_1(1+R_3)) \tag{4}$$

Assuming an exponential decay for $\phi_{00}(t)$ and $\phi_{20}(t)$,

$$\phi_{mn}(t) = (\phi_{mn}(0) - \phi_{mn}(\infty))\exp(-t/\tau_{mn}) + \phi_{mn}(\infty), \tag{5}$$

R_{00} and R_{20} can be written as

$$\begin{aligned} R_{00} &= \overline{P}_2^2\tau_{00}/(\tau_F+\tau_{00}) + (\overline{P}_2)^2, \\ R_{20} &= (1/5 - (2/7)\overline{P}_2 + (3/35)\overline{P}_4)\tau_{20}/(\tau_{20} + \tau_F), \end{aligned} \tag{6}$$

where τ_{mn} represents the reorientational correlation time. Then, depolarization ratios are given, from Eqs. 1 and 6, as

$$\begin{aligned} R_1 &= \frac{1/15 + (1/21)\overline{P}_2 - (4/35)\overline{P}_4 + (2/9)C_0A_0}{1/5 + (4/7)\overline{P}_2 + (8/35)\overline{P}_4 - (4/9)C_0A_0} \\ R_2 &= \frac{1/15 + (1/21)\overline{P}_2 - (4/35)\overline{P}_4 + (2/9)C_0A_0}{1/5 - (2/7)\overline{P}_2 + (3/35)\overline{P}_4 - (1/9)C_0A_0 - C_2A_2} \\ R_3 &= \frac{1/15 - (2/21)\overline{P}_2 + (1/35)\overline{P}_4 - (1/9)C_0A_0 + C_2A_2}{1/5 - (2/7)\overline{P}_2 + (3/35)\overline{P}_4 - (1/9)C_0A_0 - C_2A_2} \end{aligned} \tag{7}$$

where

$$C_0 = \tau_F/(\tau_F + \tau_{00}),\ C_2 = \tau_F/(\tau_F + \tau_{20}) \tag{8}$$

and

$$\begin{aligned} A_0 &= 1/5 + (2/7)\overline{P}_2 + (18/35)\overline{P}_4 - (\overline{P}_2)^2 = \overline{(P_2 - \overline{P}_2)^2} \\ A_2 &= 1/15 - (2/21)\overline{P}_2 + (1/35)\overline{P}_4 \end{aligned} \tag{9}$$

Note that these expressions for R_1, R_2 and R_3 of fluorescence depolarization reduce to those of resonance Raman scattering, if τ_F

is set equal to zero, i.e. $C_0 = C_2 = 0$.[4] In the isotropic phase, $\overline{P}_2 = 0$, $\overline{P}_4 = 0$ and $C_0 = C_2 = C_{iso}$ hold, and three expressions of Eq. 7 naturally degenerate to single expression, $R_{iso} = (1 + (2/3)C_{iso})/(3 - (4/3)C_{iso})$. Of the four unknown quantities in Eq. 7, $\overline{P}_2$, $\overline{P}_4$, C_0 and C_2, $\overline{P}_2$ is easily evaluated by Eq. 4, but it should be noted that the unique determination of $\overline{P}_4$, C_0 and C_2 is not allowed in Eq. 7, because only two quantities, for example $-(4/35)\overline{P}_4 + (2/9)C_0A_0$ and $(3/35)\overline{P}_4 - (1/9)C_0A_0 - C_2A_2$, are independent unknowns in Eq. 7 besides $\overline{P}_2$. This can be seen more clearly in Eq. 1. In order to be determined all the four quantities $\overline{P}_2$, $\overline{P}_4$, C_0 and C_2, a relation is required to be known between these. This reminds us of the observation that the variance of the second order parameter $\overline{(P_2 - \overline{P}_2)^2}$ changes continuously from the nematic to isotropic phase.[13] This fact was shown to be valid in a number of systems studied previously and is likely to hold in general. When the continuous change of variance is assumed, one obtains the following equation at T_{NI},

$$\overline{P_4^{NI}} = (5/18)\overline{P_2^{NI}}\,(7\overline{P_2^{NI}} - 2) \qquad (10)$$

The depolarization ratios at T_{NI} are obtained by extrapolation in Fig. 2 to give $R_1^{NI} = 0.30 \pm 0.01$, $R_2^{NI} = 1.10 \pm 0.02$ and $R_3^{NI} = 0.49 \pm 0.02$. Then, we have

$$\overline{P_2^{NI}} = 0.30 \pm 0.01,\ \overline{P_4^{NI}} = 0.01 \pm 0.01,$$

$$C_0^{NI} = 0.44 \pm 0.04,\ C_2^{NI} = 0.38 \pm 0.03.$$

Since the local environment of a molecule changes rather slowly with temperature in a liquid crystalline state, C_2 may be assumed to be approximately constant in the temperature range near T_{NI} in the nematic phase, i.e. $C_2 = C_2^{NI} = 0.38 \pm 0.03$. In the isotropic phase near T_{NI}, depolarization ratios reduce to $R_1 = R_2 = R_3 = 0.49 \pm 0.02$. Then we obtain $C_2 = C_0 = 0.36 \pm 0.02$ in the isotropic phase. Thus we found that C_2 remains nearly constant even for the nematic-isotropic phase transition. This fact is an encouraging guarantee of accuracy of the assumption made above. Then, we can determine $\overline{P}_2$, $\overline{P}_4$ and C_0 and C_2 from Eq. 7 so as to reproduce the observed R_1, R_2 and R_3. $\overline{P}_2$ thus obtained are shown in Figure 3.

We have also measured absorption dichroic ratio $R = A_{\parallel}A_{\perp}$ of probe molecule, where $A_{\parallel}$ and $A_{\perp}$ are the absorbance for parallel and perpendicular polarization of the incident light. Then $\overline{P}_2$ was evaluated by

$$\overline{P}_2 = \frac{(n_e/n_o)R - 1}{(n_e/n_o)R + 2} \tag{11}$$

Here n_e and n_o are refractive indices of the sample for extraordinary and ordinary light. In Figure 3, we can see that $\overline{P}_2$ from fluorescence is in good agreement with that from absorption dichroic ratio over the measured temperature range. The agreement of both results is quite encouraging as a measure of accuracy of the present results.

We found C_0 is substantially independent on temperature over the measured temperature range, that is

$$C_0 = 0.40 \pm 0.05$$

The approximate constancy of C_0 is in accord with the assumption of unchangeable molecular local environment used in the calculation. From the values of C_0 and C_2 thus estimated, we obtain $\tau_{00}/\tau_F = 1.6 \pm 0.3$ and $\tau_{20}/\tau_F = 1.5 \pm 0.3$. The result clearly shows that reorientational correlation times are of same order of magnitude with fluorescence life time, hence they are of essential importance to the

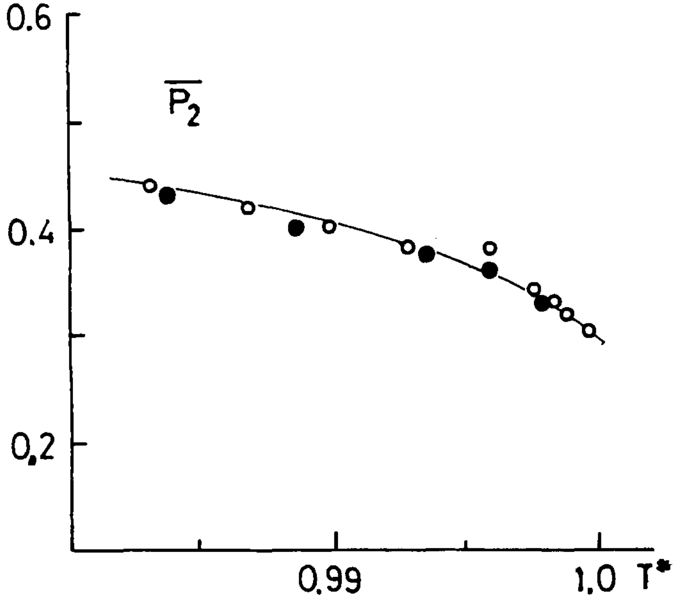

FIGURE 3 —o—o—o—; $\overline{P}_2$ of the present method. —•—•—•—; $\overline{P}_2$ evaluated from absorption dichroic ratio of ANB.

fluorescence depolarization in a liquid crystalline state. The conclusion agrees with that of Dozov and Penchev.[10] The two correlation times τ_{00} and τ_{20} were estimated to be equal within the range of errors. In the isotropic phase there is no difference between τ_{00} and τ_{20}. Then, the approximate equality of τ_{00} and τ_{20} in the nematic phase, and a rather small difference of correlation time in nematic and isotropic phase will imply a close similarity of local environment of a molecule in both phases.

As regard to $\overline{P}_4$, we evaluated a rather small value $\overline{P}_4 = 0.02 \pm 0.06$ without observing definite systematic change in the temperature range of measurement. Probably, a more accurate measurement of depolarization ratios would be needed to detect a slight change of $\overline{P}_4$ with the change of temperature.

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