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ASYMMETRIC ORIENTATIONAL DISTRIBUTION OF AN ANTHRAQUINONE DYE IN NEMATIC LIQUID CRYSTAL HOSTS

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ABSTRACT

By studying an anthranquinone dye with two orthogonal transition moments in the visible, asymmetry of the molecular orientational distribution function in nematic hosts E43 and 1132 has been demonstrated experimentally and estimates obtained for the order parameter $<\frac{1}{2}\sqrt{3}\sin^2\theta\cos2\Psi>$ of the dye.

INTRODUCTION AND THEORY

Consider a particular molecule in a fluid. Cartesian "molecular axes" (x' y' z') fixed relative to the molecular framework are related to externally-fixed "laboratory axes" (x y z) by the Euler angles[1] (ϕ θ Ψ), see Figure 1. The statistical distribution of molecular orientations relative to the laboratory axes is described by the orientational distribution function $f(\phi, \theta, \Psi)$. We take as part of the definition of a nematic that the macroscopic phase has axial symmetry, and thus $f = f(\theta, \Psi)$ where Oz is taken parallel to the symmetry axis (the "director"), and also that

$$f(\theta, \Psi) = f(\pi-\theta, \Psi) = f(\theta, -\Psi) = f(\pi-\theta, -\Psi), \qquad (1)$$

corresponding to a non-ferroelectric phase. In developing the molecular theory of nematics it is often assumed that f is also independent of Ψ. In this paper we give evidence for strong Ψ-dependent asymmetry of the orientational distribution function of an anthranquinone dye molecule dissolved in nematic liquid crystal. This confirms a hypothesis made previously on the basis of more tenuous evidence.[2]

Taking the principal axes of the molecular rotational diffusion tensor as the molecular axes (x' y' z') with Oz' parallel to the axis about which rotational diffusion is most rapid (the "long axis" of the nematogen[3]) the optical order parameter S_{op} is given by[2]

$$S_{op} = (A_{//} - A_{\perp})/(A_{//} + 2A_{\perp}) \qquad (2)$$

$$= \tfrac{1}{2}(3\cos^2\beta - 1)S_G + \tfrac{1}{2}\sqrt{3}\,\sin^2\beta\cos 2\gamma D_G \qquad (3)$$

where $A_{//}$, $A_{\perp}$ are the absorbances of a particular transition for light polarized parallel and perpendicular to the nematic director, (β γ) are the angular polar coordinates of the corresponding transition moment $\underset{\sim}{\mu}$ in the molecular frame (Fig 1), and the order parameters S and D are given by

$$S = \langle\tfrac{1}{2}(3\cos^2\theta - 1)\rangle \qquad (4)$$

$$D = \langle\tfrac{1}{2}\sqrt{3}\sin^2\theta\cos 2\Psi\rangle \qquad (5)$$

the subscript G denoting that the statistical averages are taken over the "guest" anthraquinone molecules. Note that $D \equiv 0$ if f is independent of Ψ.

Consider the ratio of optical order parameters for two distinct transitions with $\beta_1 \neq \beta_2$:

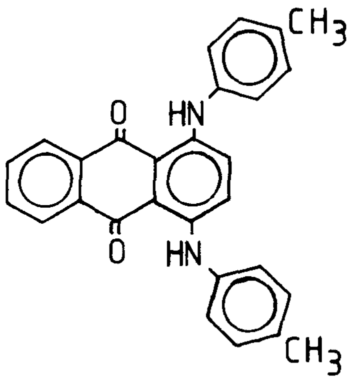
$$\frac{S^2_{op}}{S^1_{op}} = \frac{\frac{1}{2}(3\cos^2\beta_2 - 1)S_G + \frac{1}{2}\sqrt{3}\sin^2\beta_2\cos2\gamma_2 D_G}{\frac{1}{2}(3\cos^2\beta_1 - 1)S_G + \frac{1}{2}\sqrt{3}\sin^2\beta_1\cos2\gamma_1 D_G} . \tag{6}$$

Since $(\beta_1\ \gamma_1)$ and $(\beta_2\ \gamma_2)$ will be virtually independent of temperature, whereas S and D are quite strongly temperature dependent, the ratio S^2_{op}/S^1_{op} will be temperature dependent only if $D_G \neq 0$.

EXPERIMENTAL AND RESULTS

Experiments were performed on the anthraquinone dye I, which has two absorption bands within the range of our apparatus. Figure 2 shows polarized absorption spectra for I in the nematic host E43 (a BDH Chemicals proprietary eutectic mixture of cyanobiphenyl compounds with high clearing point additive). Optical order parameters of both bands were carefully measured as functions of temperature by a previously described technique.[2] The absorbance $A^2_{/\!/}$ was corrected for overlap with band 1 by continuing the latter smoothly to shorter wavelengths as shown by dot-dash lines in Fig 2. Note that whereas S^1_{op} is positive S^2_{op} is negative; this has been observed previously[4] in the tertiary butyl homologue of I.

Values of S_{op} were calculated directly from experimental absorbances using eqn (2) without any local field corrections. Although local field corrections may in principle influence S_{op} the effect is certainly small, and the form of the correction is unclear.[5]



I

Each data point quoted is normally the mean of independent determinations using two different cells. All error bars quoted are ± 2 (standard error), where the standard error of S_{op} is calculated by multiplying the difference between the two determinations by[6] $0.8862/\sqrt{2}$, and the other standard errors are then obtained from the standard errors of S^1_{op} and S^2_{op} by use of the usual formulae. The error bounds for S^1_{op} obtained by this procedure agree well with our extensive experience that we can measure this order parameter to within 0.005.

Figure 3 shows S^1_{op}, S^2_{op} and their ratio plotted as functions of reduced temperature T/T_c for E43 host. The ratio shows significant temperature dependence, confirming that $D_G \neq 0$.

The directions of the transition moments $\underset{\sim}{\mu}_1$ and $\underset{\sim}{\mu}_2$ are essentially molecular properties which are unlikely to be much perturbed by the solvating nematic molecules, particularly since PPP/CI molecular orbital calculations[7] suggest that in I these transitions are largely localized

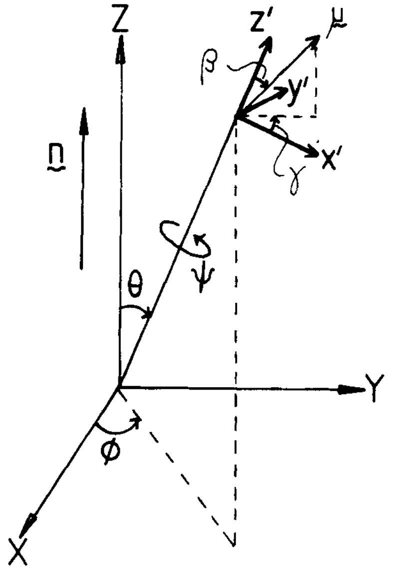


FIGURE 1. Definitions of axes and angles used in the text.

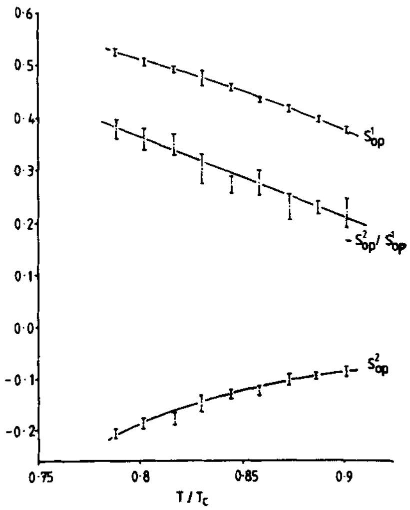


FIGURE 3. Temperature dependence of S^1_{op}, S^2_{op}, and S^2_{op}/S^1_{op} for dye I in E43.

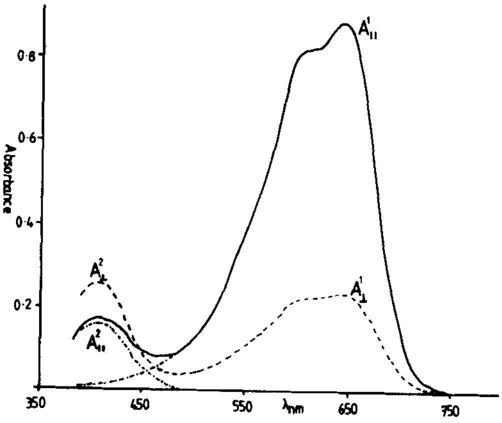


FIGURE 2. Polarized absorption spectra of dye I in nematic E43 at 20°C.

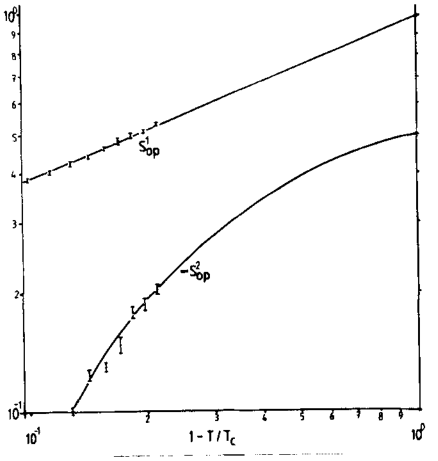


FIGURE 4. Extrapolations of S^1_{op} and $-S^2_{op}$ to T = 0 for dye I in E43.

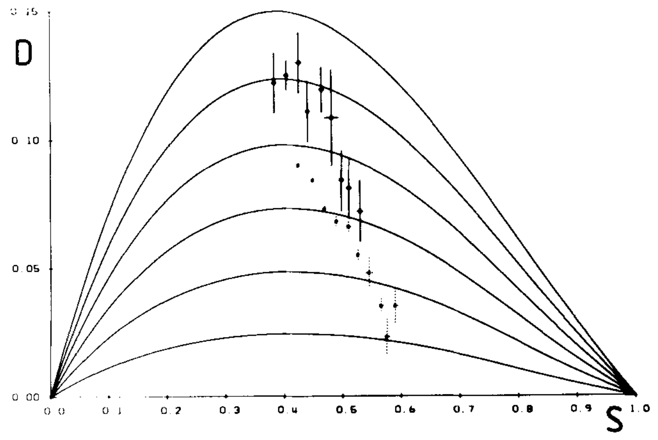


FIGURE 5. Plots of D_G against S_G for dye I in E43 (large solid error bars) and in 1132 (small or negligible dotted error bars). Values have been derived assuming that the long axis lies in the molecular plane. Theoretical curves are for the pseudopotential eqn (8) with $\lambda = 0.1$ to 0.6 in steps of 0.1.

on the anthraquinone nucleus. Thus, by symmetry, $\underset{\sim}{\mu}_2$ is perpendicular to $\underset{\sim}{\mu}_1$. Since the direction of the long axis is a property of the solvated molecule, we cannot assume a priori that $\beta_1 = 0$, but extrapolation of S^1_{op} to absolute zero[2] (Figure 4) yields $S^1_{op}(T=0) = 1$ in E43, implying $\beta_1 = 0$ and thus $\beta_2 = \pi/2$. Note also from Fig 4 that a similar plot of $-S^2_{op}$ is curved, but can be continued smoothly back to the value $S^2_{op}(0) = -\frac{1}{2}$ consistently with $\beta_2 = \pi/2$. The shape of this curve lends support to our previous suggestion[2] that difficulties experienced when attempting to extrapolate S_{op} data for other dye-host systems to absolute zero may be caused by $\beta \neq 0$ combined with $D_G \neq 0$.

With $\beta_1 = 0$ and $\beta_2 = \pi/2$, eqn (6) becomes

$$S^2_{op} = -\tfrac{1}{2}S^1_{op} + \tfrac{1}{2}\sqrt{3}\cos 2\gamma_2 D_G \, . \tag{7}$$

We further assume that solvation of the dye is not sufficiently asymmetric to perturb the long axis out of the molecular plane; thus $\gamma_2 = 0$. Values of D_G derived on this basis are shown plotted against S_G in Figure 5; larger values of D_G would be derived if $\gamma_2 \neq 0$. It is convenient to present experimental data as a D against S plot since the corresponding theoretical curves are easily calculated given the pseudopotential experienced by the guest molecule. The solid lines in Fig 5 show theoretical curves for the pseudopotential[8]

$$U/k_BT = A(T)[\tfrac{1}{2}(3\cos^2\theta - 1) + \tfrac{1}{2}\sqrt{6}\lambda\sin^2\theta\cos 2\Psi] \tag{8}$$

The quantitative agreement of theory with experiment is rather poorer than was found for the (smaller) nematic D parameter of 4,4'-dimethoxyazoxybenzene (PAA),[8] and may reflect inadequacies of the pseudopotential eqn (8). Note that our D parameter is $\sqrt{2}$ times the parameter $\langle d^2_{0,2}\cos 2\gamma\rangle$ used by Luckhurst[8] although our λ is identical to his δ; the normalization $\frac{3}{2}\langle\sin^2\beta\cos 2\gamma\rangle = \sqrt{3}D$ is also used in the literature.[9]

An identical set of experiments were performed for I in the nematic host 1132 (an E Merck proprietary mixture of three cyanophenylcyclohexanes and one biphenylcyclohexane). Very similar temperature dependence of S^2_{op}/S^1_{op} was found (Figure 6), with noticeably smaller error bars due to the greater solubility of I in 1132. The extrapolation of S^1_{op} to absolute zero was highly linear, yielding $S^1_{op}(0) = 0.897$ with a correlation coefficient of 0.996. Thus, despite reservations based on our previous experiences[2] we have analysed our data for D_G using the value $\beta_1 = 15^\circ$ implied by this result. The values obtained (Fig 5) also depend on the assumption that both γ_1 and γ_2 are zero, which may be more suspect in this case than for E43. The temperature dependence of S^2_{op} is consistent with a curved extrapolation to the value $S^2_{op}(0) = -0.4$ predicted from $S^1_{op}(0) = 0.9$.

CONCLUSIONS

The work reported clearly demonstrates asymmetry of the molecular orientational distribution function for dye I in nematic hosts. From Fig 5, values of the order parameter D_G, derived assuming that the long axis lies in the molecular plane ($\gamma = 0$), clearly show stronger temperature dependence than would be predicted from the pseudopotential eqn (8), asymmetry decreasing more rapidly with decreasing temperature. Possible factors in this include flexibility of I or precrystallizational nucleation of dye molecules. Emphasizing our view that the long axis is determined by local fluid structure,[2,3] extrapolation to absolute zero indicates that the transition moment is parallel to the long axis for I in E43, but makes an angle of 15° with the long axis in 1132, suggesting that the dye is asymmetrically solvated in the latter host. This host sensitivity can be associated with the N—H--O hydrogen bonding in dye I.[2] The curve of $\log(-S_{op}^2)$ against $\log(1 - T/T_c)$ supports the explanation previously given of observed anomalies in extrapolations of S_{op} to absolute zero.[2]

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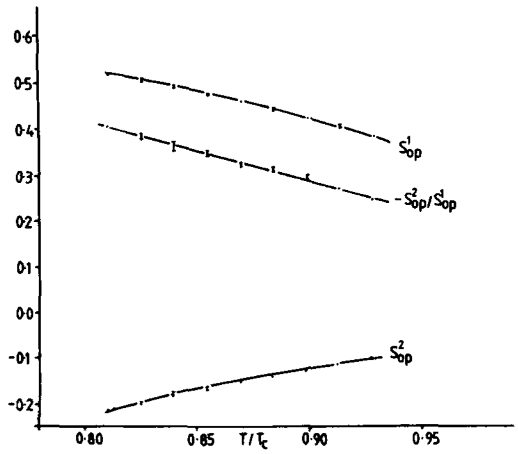

FIGURE 6. Temperature dependence of S^1_{op}, S^2_{op}, and S^2_{op}/S^1_{op} for dye I in 1132.