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W. S. Park[a]; T. Uchida[a]
[a] Department of Electronic Engineering, Faculty of Engineering, Tohoku University, Sendai, Japan

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Effect of molecular structure of a dichroic dye and the ordering of a liquid crystal on the dichroism of the dye–liquid crystal binary mixtures

by W. S. PARK and T. UCHIDA
Department of Electronic Engineering, Faculty of Engineering,
Tohoku University, Sendai, 980 Japan

The orientational ordering of dyes doped into liquid crystals has been investigated. The experimental results show that the ordering of the dyes can be expressed as a function of the order parameter of the liquid crystal host and the molecular structure of the dye. In addition a theory of the ordering of molecules in a binary mixture system has been derived by extending Kimura's theory. The validity of the theory has been confirmed by comparison with the experimental results using various combination of azo dyes and liquid crystals.

1. Introduction

In a binary mixture such as a liquid crystal doped with a dichroic dye, the relationship between the orientational ordering of each molecule is interesting from the viewpoint of the intermolecular interactions as well as for device application. Some papers have already reported on such binary mixtures [1, 2], although they are not based on a molecular theory but rather present a phenomenological viewpoint. We have already investigated this problem experimentally and we have reported the definite relation between the order parameter of the dyes and their molecular structure [3]. However, the factors which affect the ordering of the dye are considered to be not only its structure, but also the intermolecular interaction between the liquid crystal and the dye. We have therefore investigated this problem experimentally and theoretically. Here, concerning to the molecular theory, there are several theories of liquid crystal ordering such as Onsager's excluded volume theory [4], the Maier–Saupe molecular field theory [5] and Kimura's theory [6] which combines the previous two theories. Among these theories, the authors have adopted Kimura's approach because of its validity [7], and have extended it to binary mixtures of a liquid crystal and a dye.

2. Experiment

The liquid crystals 4-*n*-pentyl-4′-cyanobiphenyl (5CB), 4-*n*-heptyl-4′-cyanobiphenyl (7CB) and a mixture of GR41 (Chisso Co.) were used. As for dyes, azo and anthraquinone dyes synthesized by Nippon Kankoh Shikiso Co. were used, and doped into the host to approximately 0·7 wt %. In these binary mixtures the dye molecules tend to align parallel to the average ordering direction of the liquid crystal (i.e. the director), because they have a rod-like structure analogous to the host liquid crystal. However, the long axis of each dye molecule deviates from the director, as shown in figure 1, because of its thermal fluctuation. Here it is convenient to introduce ordering parameter of the dyes, D_M, defined as

$$D_M = \frac{2S_M + 1}{1 - S_M}, \tag{1}$$

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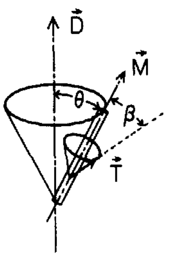


Figure 1. The orientation of the molecular axis **M** and the transition moment T of the dye in the liquid crystal; **D** denotes the director.

where S_M is the second rank orientational order parameter of the dye molecules. When the direction of the transition moment, T, deviates from the long axis of the dye by an angle of β, the order parameter, S_T, for the transition moment T is

$$S_T = \tfrac{1}{2} S_M (2 - 3 \sin^2 \beta). \tag{2}$$

Here, S_T can be expressed as a function of the dichroic ratio DR by

$$S_T = \frac{\mathrm{DR} - 1}{\mathrm{DR} + 2}. \tag{3}$$

Combination of equations (1) and (3) then gives

$$D_M = \frac{2\mathrm{DR} - \mathrm{DR} \sin^2 \beta - 2 \sin^2 \beta}{2 - \mathrm{DR} \sin^2 \beta - 2 \sin^2 \beta}. \tag{4}$$

The dichroic ratio of the dye, DR, is obtained from the ratio of absorbances for visible light polarized parallel and perpendicular to the director, and β is estimated from CPK molecular models. D_M can then be obtained by substituting D_T and β into equation (4). On the other hand, the ordering parameter of the liquid crystal, D_{LC}, can be determined in the same way but by using the dichroic ratio measured in the infrared spectral region [2]; this is directly related to the dipole moment along the cyano axis and along the *para* axis of benzene rings. The validity of this method was examined by comparing dichroic ratios measured in the infrared spectral region and in the visible spectral region for azo-liquid crystals because they have absorption in the visible as well as the infrared region. Both dichroic ratios are found to agree well, so this method is shown to be reliable.

3. Experimental results

The ordering parameter of dyes is dominated by two factors: the molecular structure of the dye and the intermolecular interaction between the dye and the liquid crystal. As for the former effect, we [3] have reported that there exists a definite relation between the ordering parameter of the dyes and an effective structural parameter $(l/d)^*$. This is defined as a modified value of the ratio of the length, l, to the diameter, d, of a circumscribed cylinder of the dye, as shown in figure 2, allowing for their flexible structures. The relation is shown in figure 3. In this investigation, however, the host liquid crystal was kept constant, so that the influence of the host liquid crystal on the ordering parameter of the dyes could not be studied. We have therefore measured precisely the ordering parameters of some liquid crystals, D_{LC}, to investigate the relationship between D_{LC} and the ordering parameters of the dyes, D_M. The

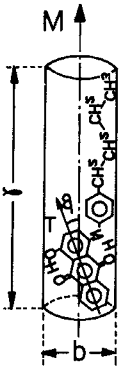


Figure 2. The circumscribed cylinder of a dye molecule. **M** is the molecular axis of the dye, T is the transition moment, l is the molecular length and d the width.

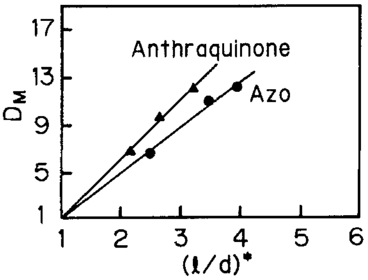


Figure 3. Relation between the ordering parameter and structural parameter of the dye.

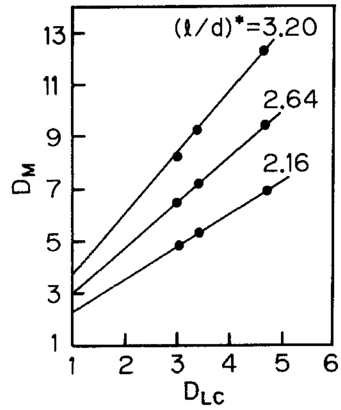


Figure 4. Relation between the ordering parameter of the dye and that of the liquid crystal for various values of $(l/d)^*$.

results are shown in figure 4, and from these results the properties can be expressed by

$$D_M - 1 = a(D_{LC} - 1) + b, \qquad (5)$$

where a and b are the slope and intercept of the straight line, respectively. Now, coefficients a and b of equation (5) must be a function of the structural parameter of the dyes $(l/d)^*$ because the ordering parameter of the dyes, D_M, is also expressed as a

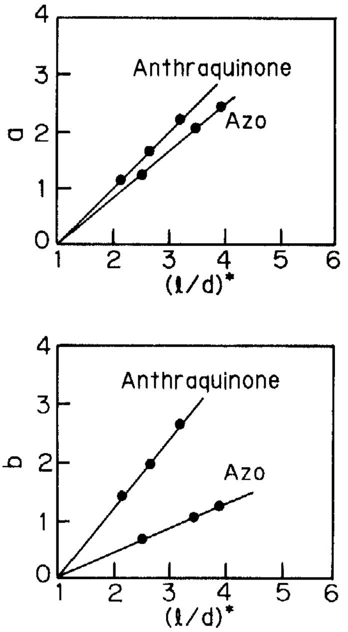


Figure 5. The relation between the slope a and the intercept b of figure 4 as a function of $(l/d)^*$.

function of $(l/d)^*$. Therefore, we have sought a relation between coefficients a, b and $(l/d)^*$, and found that shown in figure 5. These properties may be expressed as

$$a = k_1 [(l/d)^* - 1], \tag{6}$$

$$b = k_2 [(l/d)^* - 1], \tag{7}$$

where k_1 and k_2 are coefficients depending on the combination of liquid crystal and dye. From equations (5)–(7), the ordering parameter of dyes can be written as a function of the ordering parameter of the liquid crystal and the structural parameter of the dye as

$$D_M - 1 = [k_1 (D_{LC} - 1) + k_2][l/d)^* - 1]. \tag{8}$$

4. Theory of orientational ordering in binary mixtures

In §3 we clarified experimentally the relation between the ordering parameter of the dye, that of the liquid crystal and the structural parameter of the dye. In this section we investigate the relationship theoretically and compare experiment with theory. As for the theory of the ordering of liquid crystals themselves, there are Onsager's excluded volume theory, the Maier–Saupe molecular field theory and Kimura's theory, which combines both theories. Among these theories, Kimura's theory is considered to be most valid as it can explain various properties of liquid crystals [7]. We have therefore adopted Kimura's theory and extended it to binary liquid crystal mixtures to introduce the orientational order of the dye.

The equilibrium state of a system is generally determined by minimizing its free energy. In the original version of Kimura's theory the free energy is obtained by introducing the intermolecular potential ϕ_{ij}:

$$\phi_{ij} = \begin{cases} +\infty, & \text{if molecules } i \text{ and } j \text{ intercept,} \\ -A(r_{ij})P_2(\cos\theta_{ij}), & \text{otherwise.} \end{cases} \tag{9}$$

where the first law represents rigid body repulsive forces due to the excluded volume between the molecules, and the second law is the anisotropic part of the dispersion forces. On the other hand, in a binary mixture the intermolecular potential between the liquid crystal and the dye molecules as well as that between liquid crystal molecules should be included to obtain the free energy. Therefore, the partition function can be expressed as

$$Z(\eta_1, \eta_2) = \iiiint d\Omega^{N_1}\, d\Omega^{N_2}\, dr^{N_1}\, dr^{N_2} \exp\left[\eta_1 \sum_{i=1}^{N_1} P_2(\cos\theta_i) - (1/kT)\sum_{i>j}\phi_{ij} + \eta_2 \sum_{k=1}^{N_2} P(\cos\theta_k) - (1/kT)\sum_{k>l}\phi_{kl}\right]. \tag{10}$$

The first and second terms in the brackets represent the interaction between the liquid crystal molecules themselves. The third and fourth terms, which are new, represent the interaction between liquid crystal and dye molecules. i, j and l denote arbitrary liquid crystal molecules, and the subscript k denotes an arbitrary dye molecule. N_1 and N_2 are the numbers of liquid crystal and dye molecules, respectively. η_1 and η_2 are the strengths of the imaginary symmetry-breaking potentials of liquid crystals and dyes, respectively. The other symbols are defined in Kimura's paper [6]. If the partition function $Z(\eta_1, \eta_2)$ is known, the order parameters of liquid crystal and dye, S_1 and S_2 are obtained from equation (10) as

$$S_1 = (1/N_1)\,\partial \ln Z(\eta_1, \eta_2)/\partial\eta_1, \tag{11}$$

$$S_2 = (1/N_2)\,\partial \ln Z(\eta_1, \eta_2)/\partial\eta_2, \tag{12}$$

Expanding equation (10) by using Mayer's f factors and Kimura's model and substituting it into equations (11) and (12), the order parameters, S_1 and S_2, are obtained as

$$S_1 = \frac{\int_0^{\pi/2} P_2(\cos\theta)\exp[\Gamma_{11}S_1 P_2(\cos\theta)]\sin\theta\, d\theta}{\int_0^{\pi/2}\exp[\Gamma_{11}S_1P_2(\cos\theta)]\sin\theta\, d\theta} \tag{13}$$

and

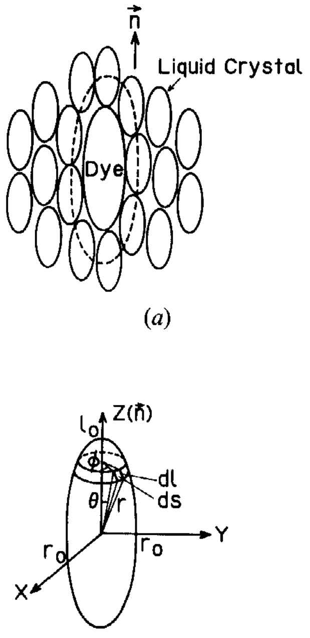
$$S_2 = \frac{\int_0^{\pi/2} P_2(\cos\theta)\exp[\Gamma_{12}S_1 P_2(\cos\theta)]\sin\theta\, d\theta}{\int_0^{\pi/2}\exp[\Gamma_{12}S_1P_2(\cos\theta)]\sin\theta\, d\theta} \tag{14}$$

where

$$\Gamma_{11} = A_{T1}/kT + (5\pi/32)\Delta V_{11}n_1, \tag{15}$$

$$\Gamma_{12} = A_{T2}/kT + (5\pi/32)\Delta V_{12}n_1. \tag{16}$$

In equation (16), Γ_{12} is a function of the total intermolecular interaction between a dye molecule and the surrounding liquid crystal molecules, the parameter A_{T2} is related to the excluded volume, ΔV_{12}, and the concentration of the liquid crystal molecules, n_1. Here S_1 and n_1 can be measured directly and ΔV_{12} can be obtained from the molecular structures of the liquid crystal and dye molecules. On the other hand, A_{T2} cannot be



(*a*)

(*b*)

Figure 6. Distribution model of liquid crystal–dye binary mixtures. (*a*) Distribution of the nearest neighbour liquid crystal molecules around a dye molecule. (*b*) A coordinate system representing the centres of the nearest neighbour liquid crystal molecules.

measured and so we have tried to evaluate it by assuming that dispersion forces are dominant and that they are effective only between a dye molecule and its nearest neighbour liquid crystal molecules. The centres of the liquid crystal molecules surrounding a dye molecule are considered to be located on the surface of an ellipsoid as shown by the broken line in figure 6 (*a*), in which the volumes of the dye and liquid crystals are estimated by considering the thermal, orientational fluctuations [8]. Here we introduce spherical coordinates whose origin is on the centre of a dye molecule and the z axis is parallel to the director, **n**. Defining dp to be the probability of liquid crystal molecules existing in an elemental area ds, the total intermolecular interaction A_{T2} is given by

$$\begin{aligned} A_{T2} &= \int (A_{12}/r^6)\,dp \\ &= (4\pi A_{12}/r_0^4 l_0^4) \int_0^{\pi/2} (l_0^2 \sin^2\theta + r_0^2 \cos^2\theta)\,(r_0^4 \cos^2\theta + l_0^4 \sin^2\theta)^{1/2} \\ &\quad \times \sin\theta\, p_\perp (p_\perp \cos\theta + p_\parallel \sin\theta)\, d\theta, \end{aligned} \tag{17}$$

where A_{12} is the intermolecular interaction parameter between liquid crystal and dye molecules. $p_\perp$ and $p_\parallel$ denote the probabilities of a liquid crystal molecule existing in a unit length along the x or y axes and the z axis, respectively; these probabilities can be estimated from the density of the liquid crystal.

5. Comparison between theory and experiment

In §4 we have shown that the order parameter of a dye is represented theoretically by equation (14). In this equation every parameter except A_{12} can be determined from experiment and the molecular structures. However, the intermolecular interaction parameter A_{12} between the liquid crystal and the dye molecules cannot be determined directly. We have therefore used various values of A_{12} to calculate the relation between the ordering parameter and the structural parameter of the dyes. The results obtained by using the relating parameters corresponding to a mixture of cyanobiphenyl liquid crystals and mono-azo dyes are shown in figure 7 as the full lines. For comparison the experimental result is also shown on the same figure as the broken line. These results reveal that the value of A_{12} is roughly of the order of $10^{-64}\,\mathrm{J\,cm^6}$. This value agrees with the intermolecular interaction parameter of liquid crystals, $3{\cdot}6 \times 10^{-64}\,\mathrm{J\,cm^6}$, which is calculated from the material parameters given by Wulf [9]. It is considered that the intermolecular interactions between liquid crystal and dye and between liquid crystals themselves are of the same order, so that this agreement indicates the validity of the derived theory to some extent.

Strictly, the slopes of the experimental results and calculated results given in figure 7 deviate from each other, which reveals that the parameter A_{12} changes along with the structural parameter of the dyes $(l/d)^*$. Figure 8 shows A_{12} as a function of $(l/d)^*$, obtained from figure 7. The properties for the dis-azo dyes or anthraquinone dyes are also plotted in figure 8. These results can be summarized as follows.

(*a*) The interaction parameter A_{12} increases monotonically with increase in the structural parameter $(l/d)^*$.

(*b*) For anthraquinone dyes, it should be noted that especially strong intermolecular interactions exist.

Here the value of the interaction parameter A_{11} between liquid crystal molecules themselves is predicted to coincide with A_{12} when the structural parameter of the dye is equal to that of the liquid crystal. Therefore, the value of A_{11} for the liquid crystal 5CB used in the experiment was evaluated by two methods based on Kimura's theory. One method is to measure the order parameter of the liquid crystal, S_1, followed by substituting it into equations (13), (15) and (17). The other method is to measure the nematic–isotropic transition temperature and the density at the transition, and to

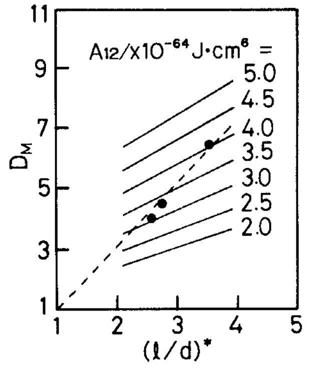


Figure 7. Relation between the ordering parameter and the structural parameter of the dye for various values of A_{12}. The broken line indicates the experimental result.

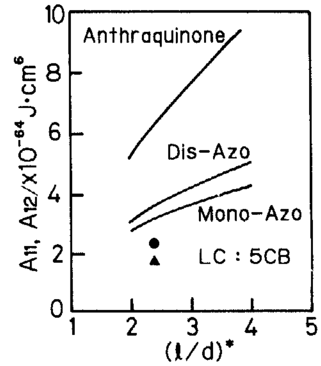


Figure 8. Dependence of the intermolecular interaction parameter, A_{12}, on $(l/d)^*$. (●) and (▲) indicate the calculated intermolecular interaction parameter, A_{11}, between liquid crystal molecules themselves.

substitute them along with $\Gamma_{11} = 4{\cdot}54$ into equation (15), in which the value of Γ_{11} is a theoretical result necessary to obtain a phase transition [6]. The values of A_{11} obtained by these two methods are plotted in figure 8, considering its structural parameter $(l/d)^*$. These values almost agree with A_{12} for the azo-dye which has the same value of $(l/d)^*$ as 5CB. This fact confirms again the validity of the theory derived for binary nematogenic mixtures.

6. Summary

The results obtained may be summarized as follows.

(*a*) From the experimental results, the ordering parameter D_M for a dye is represented by both the ordering parameter D_{LC} of the liquid crystal host and the structural parameter for the dye $(l/d)^*$:

$$D_M - 1 = [k_1(D_{LC} - 1) + k_2][(l/d)^* - 1],$$

where k_1 and k_2 are coefficients.

(*b*) The order theory of dye–liquid crystal binary mixtures was derived on the basis of Kimura's theory.

(*c*) The proposed theory agrees reasonably well with the experimental results.

Finally, the proposed theory is expected to be applicable to the optimal design of dye molecules and the choice of liquid crystal to obtain a high dichroic ratio in guest–host liquid crystal display devices.

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