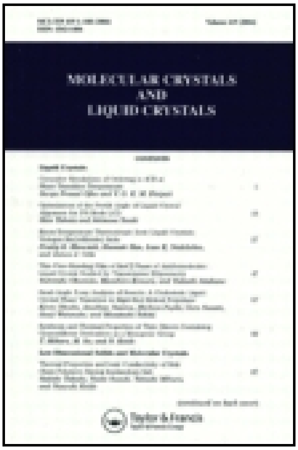

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Dichroic Dyes for Guest-Host Liquid-Crystal Cells

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Dichroic Dyes for Guest-Host Liquid-Crystal Cells

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To clarify the relation between molecular structure and an order parameter of dichroic dyes of the guest-host liquid-crystal cells, the ratio l/d of length l to diameter d of circumscribed cylinders of dichroic dyes is used as a parameter. Experimental results clarify that there exists an obvious correlation between l/d and order parameters of long axes of dye molecules; information is obtained on ordering states of dyes dissolved in a liquid crystal, especially the performance of flexible parts of dye molecules.

1. INTRODUCTION

Liquid crystal color display devices using the guest-host interactions[1,2] switch their colors by changing molecular orientation of dichroic dyes according to the voltage applied. The guest-host cells have many advantages, such as vivid color display, wide viewing angle and high brightness,[3,4] and attract attention not only for their color display devices but also for the light valve array of full color display devices.[5] Improvements of display properties of the guest-host cell, especially color contrast and brightness, however, are required. These properties depend mainly on dichroic ratios of dyes. Many researchers have investigated various kinds of dyes in order to improve dichroic ratio. Mainly, azo- and anthraquinone-dyes are investigated at present, because the azo-dyes have relatively high order parameters,[6-9] and the anthraquinone-dyes possess higher photochemical stability.[10,11] However, no systematic research on the relation between structure and dichroic ratio has yet been done, and moreover the order parameter of a molecular axis, S_M, and that of transition moment, S_T, are sometimes confused. The dichroic ratio directly relates to the order parameter S_T, while the molecular structure is considered to relate to the order parameter S_M. In general, these two order parameters, S_T and S_M, do not coincide unless the directions of transition moment and a molecular axis are parallel to each other. Therefore, in this paper, S_M is evaluated by S_T and the angle between a molecular axis and direction of transition moment, and then the relation between order parameters S_M and molecular structure of dichroic dyes is discussed.

2. ORDER PARAMETER OF DICHROIC DYE DISSOLVED IN LIQUID CRYSTAL

Dichroic dyes dissolved in a liquid crystal align averagely parallel to the director of liquid-crystal molecules. However, direction of each dye molecule deviates from the direction of the director **N** because of thermal fluctuation as shown in Figure 1, where **M** is the direction of a long axis of a dye molecule.

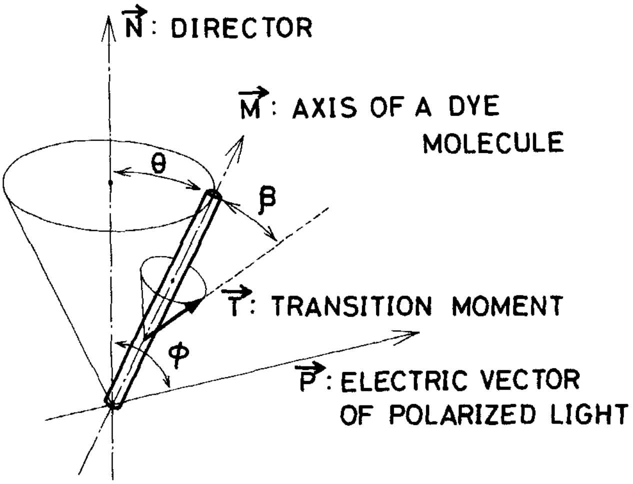


FIGURE 1 Thermal fluctuation of a dye dissolved in a liquid crystal.

If θ denotes the angle between **N** and **M**, the order parameter S_M of **M** is expressed as,[3]

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

where, $\langle\cos^2\theta\rangle$ is the average of $\cos^2\theta$ for whole dye molecules. Assuming the direction of transition moment **T** deviates from the direction of molecular axis **M** at an angle β, the absorbance A for the incident polarized light, whose electric vector **P** deviates from the director **N** at an angle φ, is expressed as,[12,13]

$$A(\beta,\varphi) = kcd[(S_M/2)\sin^2\beta + (1 - S_M)/3 + (S_M/2)(2 - 3\sin^2\beta)\cos^2\varphi], \tag{2}$$

where k denotes the magnitude of transition moment **T** and c and d respectively denote the concentration of dyes and the thickness of liquid-crystal layer. Therefore, the dichroic ratio D is expressed as the ratio of the absorbances for $\varphi = 0°$ and $\varphi = 90°$ as follows,

$$D = \frac{A(\beta,\varphi = 0°)}{A(\beta,\varphi = 90°)} = \frac{2 + 4S_M - 6S_M\sin^2\beta}{2 - 2S_M + 3S_M\sin^2\beta}. \tag{3}$$

On the other hand, the order parameter S_T of transition moment **T** is expressed as,

$$S_T = \frac{D - 1}{D + 2}. \tag{4}$$

Therefore, we obtain the following equation from Eqs. (3) and (4),

$$S_T = \frac{S_M(2 - 3\sin^2\beta)}{2}. \tag{5}$$

Figure 2 shows the relation between S_T/S_M and β according to Eq. (5). It is seen from this figure that S_T/S_M decreases remarkably as β increases and hence β should be decreased as much as possible to increase dichroic ratio.

Next, in order to discuss the relation between dichroic ratios and molecular structure of dyes quantitatively, we introduce a parameter

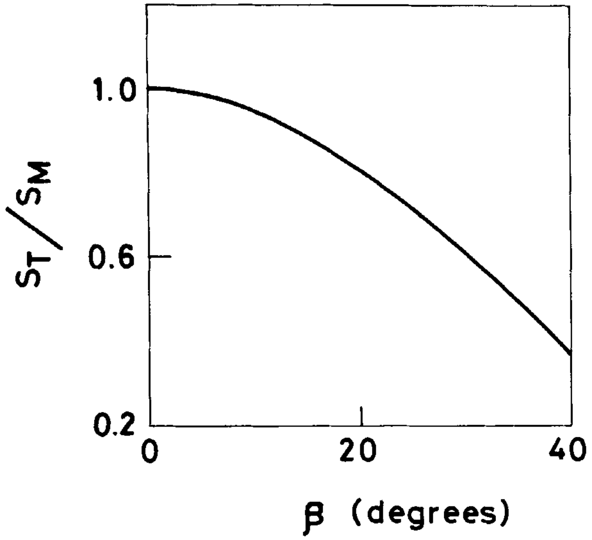


FIGURE 2 β dependence of S_T/S_M.

to evaluate orientability of the molecular structure. That is, the ratio l/d of length l to diameter d of a circumscribed cylinder of a dye molecule as shown in Figure 3 is defined as a parameter of the molecular structure. Here, most dyes have several conformation isomers. Therefore, all the corresponding circumscribed cylinders are considered by using the three dimensional molecular model with van der Waals' radius. Among them, the circumscribed cylinder with the largest l/d, is taken as the inherent circumscribed cylinder in a given dye. Then, a molecular axis **M** of a dye is defined as the long axis of the circumscribed cylinder.

The transition moment vector of dye molecule is determined as follows. The structures of the dis- and tris-azo dyes (a) to (o) in Table I are fairly rod-like, so that the transition moment vector of these dyes is considered to be parallel to the connecting direction of azo linkage. For the anthraquinone dyes from (p) to (t), the direction of transition moment vector is approximated to be parallel to the bisector of the basic anthraquinone structure of the molecule. This definition is considered to be reasonable for the dyes (s) and (t) because of the molecular symmetry. As for the α-substituted anthraquinone dye (r), deviation of the transition moment differs from the indicated direction is supposed to be few degrees according to the result obtained by M. A. Osmman et al.[14] In this case, the deviation

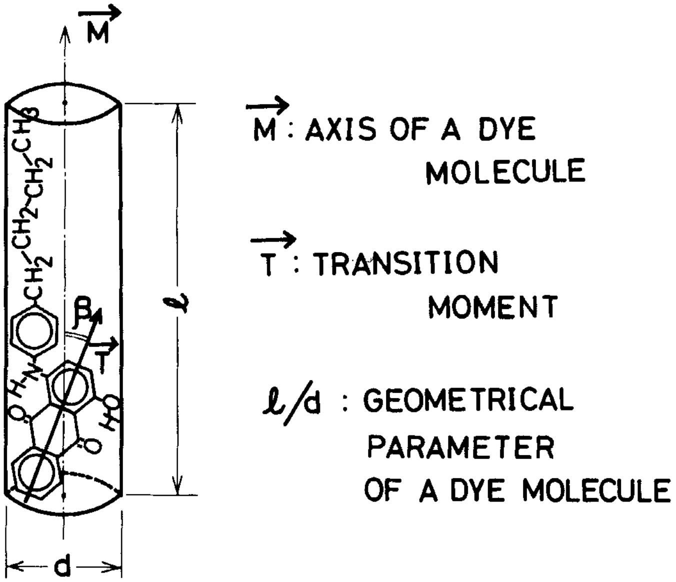


FIGURE 3 Circumscribed cylinder of a dye molecule.

of S_M is less than few percent. But in the case of the dyes (p) and (q) with both α- and β-substitution, the deviation of the transition moment is considered to be around fifteen degrees which corresponds to 10% increase in S_M value. However, the exact direction of the transition moment of these anthraquinone dyes have not yet been clarified at present. Therefore, further investigation must be done about the transition moment for the dyes like (p) and (q) for more detailed discussion than that in this paper.

In any way, according to the approximation for the circumscribed cylinder as mentioned above, the angle β is determined diagrammatically. Then, the order parameter S_M of the molecular axis is calculated from the measured value of dichroic ratio D and β by using Eqs. (4) and (5). In the following sections, the relation between the molecular structure and S_M obtained by the method mentioned above is discussed.

3. EXPERIMENT

Liquid-crystal host LIXON GR-41 produced by Chisso Co., Ltd. and dichroic dyes produced by Nippon Kankoh Shikiso Kenkyusho Co., Ltd. were used in the experiment. Zero point five weight percent of dyes was dissolved in the liquid crystal. Dichroic ratios D were obtained by using homogeneously aligned guest-host cells; that is, the absorbances parallel and perpendicular to the direction of the molecular alignment, $A_{\|}$ and $A_{\perp}$, respectively, were measured and the dichroic ratios were calculated as ratios $A_{\|}/A_{\perp}$. The homogeneous alignment of the guest-host cell was obtained by surface treatment of polyvinyl alcohol (PVA) and rubbing process. The thickness of the liquid-crystal layer was 12 μm and temperature of the cell was controlled at 25°C while the measurement was made.

4. RESULTS AND DISCUSSION

Absorption of various dyes was measured and their S_M and l/d are obtained as mentioned in the section 2. The results are shown in Table I. Figure 4 shows the relation between order parameters S_M of these dyes and l/d. It is seen from this figure that there is a weak correlation, though it is not evident correlation.

Generally, dichroic dyes are composed of a relatively rigid central group and flexible terminal groups. So that, the effect of flexibility of terminal groups on the order parameter S_M is examined. First, the

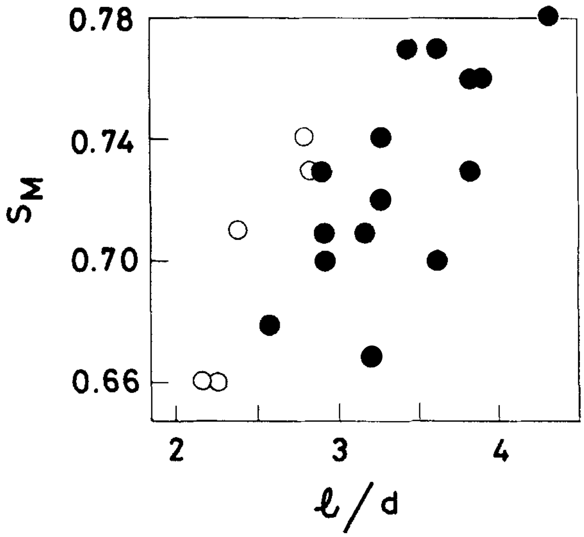


FIGURE 4 Relation between S_M and l/d for various azo-dyes (●) and anthraquinone-dyes (○).

TABLE I

Dyes used in the experiment

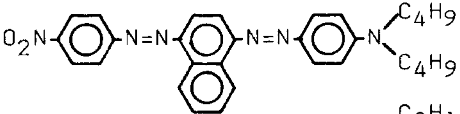
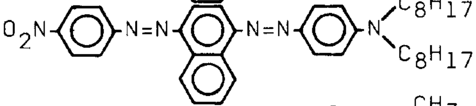
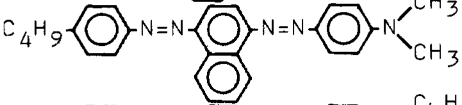
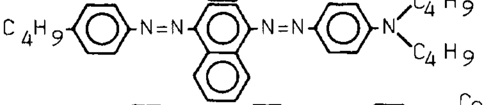
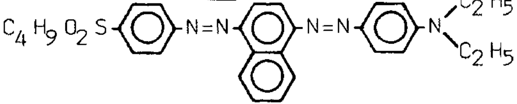
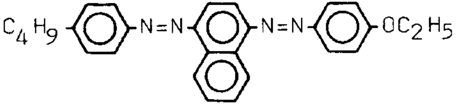
No.	Molecular Structure	λ_m (nm)	S_T	1/d	1/d*	S_M
a		591	0.66	2.57	2.55	0.68
b		590	0.65	3.20	2.55	0.67
c		533	0.73	2.88	2.86	0.73
d		546	0.68	2.88	2.69	0.70
e		573	0.70	2.88	2.82	0.71
f		446	0.71	3.16	2.98	0.71

TABLE I *continued*

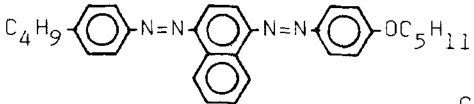
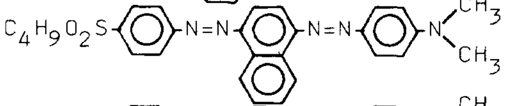
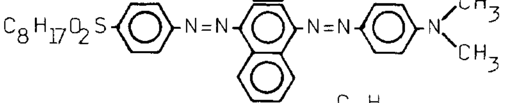
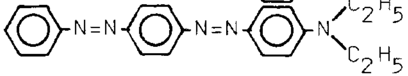
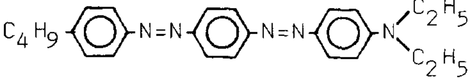
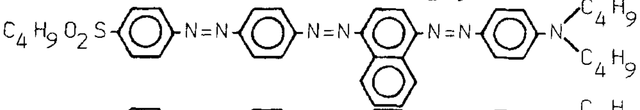
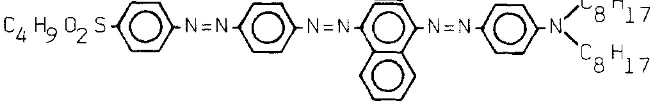
No.	Molecular Structure	λ_m (nm)	S_T	1/d	1/d*	S_M
g		445	0.70	3.60	2.98	0.70
h		560	0.72	3.25	2.99	0.72
i		560	0.73	3.83	2.99	0.73
j		506	0.73	3.26	3.26	0.74
k		508	0.76	3.85	3.69	0.76
l		589	0.76	3.40	3.35	0.77
m		588	0.75	3.87	3.35	0.76

TABLE I *continued*

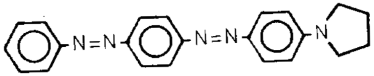
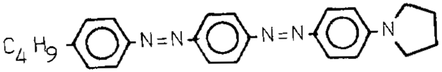
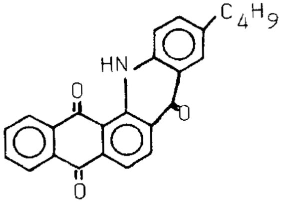
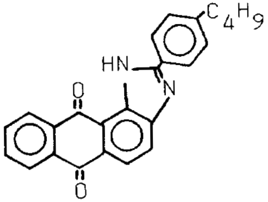
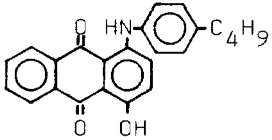
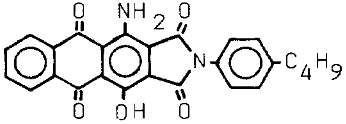
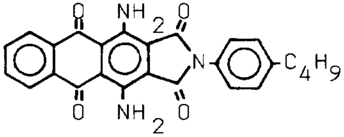
No.	Molecular Structure	λ_m (nm)	S_T	l/d	l/d*	S_M
n		509	0.77	3.60	3.60	0.77
o		509	0.78	4.28	4.04	0.78
p		532	0.41	2.18	2.11	0.66
q		417	0.45	2.42	2.30	0.71

TABLE I *continued*

No.	Molecular Structure	λ_m (nm)	S_T	1/d	1/d*	S_M
r		590	0.59	2.26	2.13	0.66
s		611	0.73	2.84	2.68	0.73
t		687	0.74	2.81	2.65	0.74

* Revised values considered the flexibility of molecules.

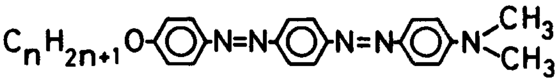


FIGURE 5 Molecular structure of the Type I-dye.

Type I-dye as shown in Figure 5 with normal alkoxy chain as a terminal group is examined to clarify the effect of the terminal group on the dichroism. Figure 6 shows the relation between carbon number *n* of the alkoxy chain and absorption maximum λ_m of the dyes. It is seen from this figure that the length of alkoxy chain does not affect on the absorption maximum λ_m and hence the absorption occurs only in the central part of dye molecules. Therefore, the terminal groups do not affect on the transition moment **T** and will affect only on the order parameter S_M. Figure 7 shows the relation between their carbon number *n* and S_M. It can be seen that S_M increases as *n* increases up to 2, and saturates for $n \geqq 2$. This behavior is considered to be due to a certain flexibility of an alkoxy chain caused by rotation of its single bond, and the flexibility increases according to the alkoxy chain length. It is also assumed from Figure 7 that the carbon chain of $n \geqq 3$ in the alkoxy chain does not contribute to the increment of effective length of a dye molecule because of its flexible structure, that is, the effectively rigid length of the alkyl chain is $n = 2$ as shown in Figure 8.

Next, the Type II-dyes, which have alkyl chains elongated to the direction deviating from the molecular long axis as shown in Figure

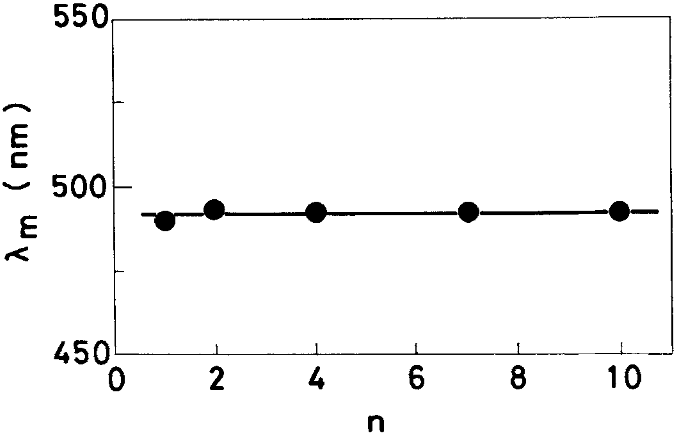


FIGURE 6 Dependency of the alkoxy chain length *n* on the maximum absorption wavelength λ_m for the Type I-dye.

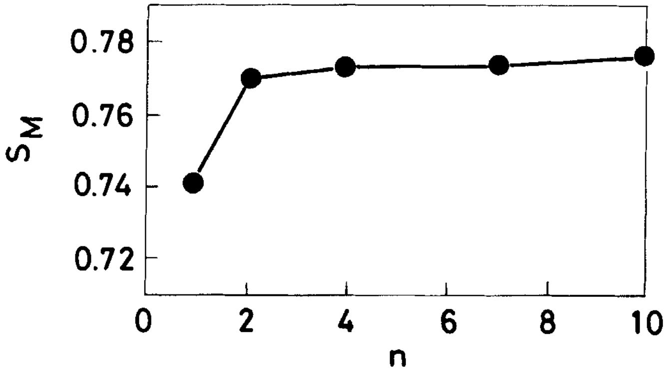


FIGURE 7 Dependency of the alkyl chain length n on order parameter S_M for the Type I-dye.

9, are also investigated. The relation between their carbon number n and S_M is shown in Figure 10. In this figure, S_M decreases as n increases up to 3. Therefore, also the carbon chain of $n > 3$ in the alkyl chain does not contribute to the increment of width and length of a dye molecule. This effectively rigid length of $n = 3$ agrees with the effective length of the alkoxy chain of the Type-I dye if its oxygen atom is taken into account.

From the results mentioned above, the carbon number of alkoxy and alkyl chains is effectively regarded to be 2 for the Type I-dye and 3 for the Type II-dye if $n \geqq 2$ and $n \geqq 3$, respectively. According to the revised definition of l/d mentioned above, the correlation between l/d and S_M is investigated for the same dyes as shown in Figure 4. The result is shown in Figure 11. It can be seen from this figure that an obvious correlation exists between S_M and l/d, and S_M increases as l/d increases. Therefore, the result indicates that the dichroic ratios of dyes can be predicted from their molecular structure

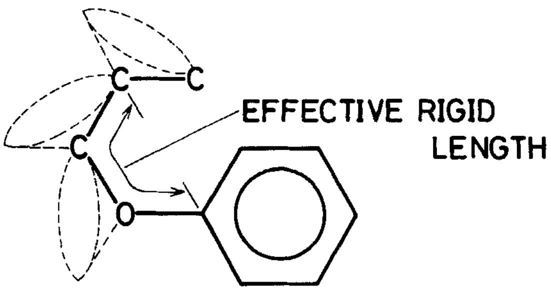


FIGURE 8 Effectively rigid length of a terminal group of a dye molecule.

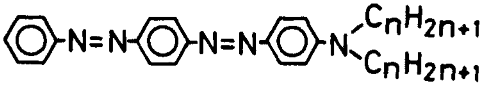


FIGURE 9 Molecular structure of the Type II-dye.

by considering the flexibility of terminal groups. By the way, there is slight deviation of the above mentioned relation between azo-dyes and anthraquinone-dyes. The reason is not clarified at present.

5. THEORY OF THE EXCLUDED VOLUME

In this section, the relation between order parameters S_M and l/d is examined theoretically. It is considered that the excluded volume model is effective for treating geometrical effects of dye molecules on their order parameters. If the excluded volumes are denoted $V_\parallel$ and $V_\perp$ for the typical cases that two molecules align parallel and perpendicular to each other, respectively, the order parameter S for one component system can be obtained from the next equation,[15]

$$\log[(1 + 2S)/(1 - S)] = \rho(V_\perp - V_\parallel)S \,, \tag{6}$$

where ρ is the density. Let us expand this model to a binary mixture of dye and liquid-crystal molecules. By maximizing the entropy of

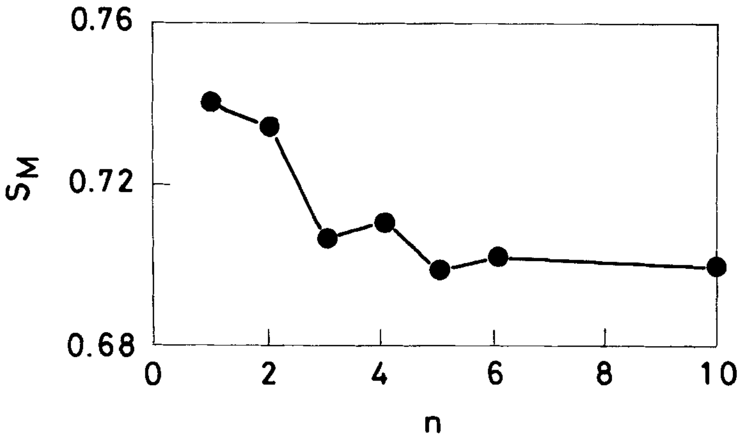


FIGURE 10 Dependency of the alkyl chain length n on order parameter S_M for the Type II-dye.

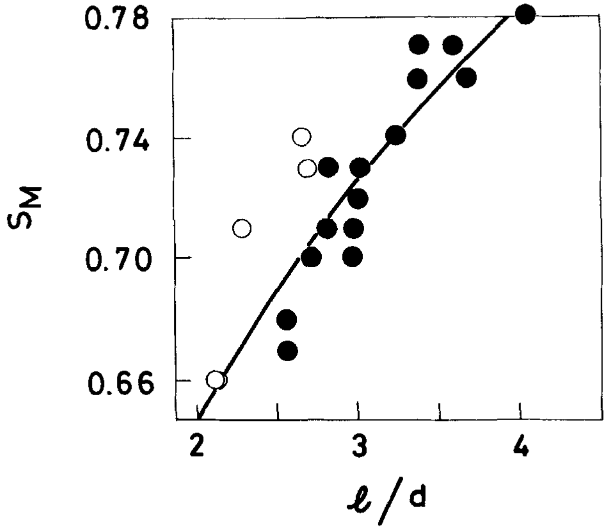


FIGURE 11 Relation between S_M and revised l/d for various azo-dyes (●) and anthraquinone-dyes (○).

this system, the relation between order parameters S_M of dye molecules and S_L of liquid crystal molecules are expressed as follows,

$$\log\left[\frac{1 + 2S_M}{1 - S_M}\right] = \rho[cS_L(V_\perp^{DD} - V_\parallel^{DD}) + (1 - c)\,S_L(V_\perp^{DL} - V_\parallel^{DL})]\,, \tag{7}$$

$$\log\left[\frac{1 + 2S_L}{1 - S_L}\right] = \rho[cS_M(V_\perp^{DL} - V_\parallel^{DL}) + (1 - c)\,S_M(V_\perp^{LL} - V_\parallel^{LL})]\,. \tag{8}$$

In these equations, c is the concentration of dye molecules. V^{DD}, V^{DL} and V^{LL} are the excluded volumes for combinations of dye—dye, dye—liquid crystal, liquid crystal—liquid crystal, respectively, and they are expressed as follows,

$$V_\perp^{DD} - V_\parallel^{DD} = 2(l/d + d/l - 2)d^2l\,, \tag{9}$$

$$V_\perp^{DL} - V_\parallel^{DL} = (1 + d/d')(l/d' + d/l' - l/l' - d/d')d'^2l'\,, \tag{10}$$

$$V_\perp^{LL} - V_\parallel^{LL} = 2(l'/d' + d'/l' - 2)d'^2l'\,, \tag{11}$$

where l and d are respectively the length and the diameter of a dye molecule, and l' and d' are those of a liquid crystal molecule. In the case of infinite dilute solution ($c \approx 0$), S_M can be deduced from Eq. (6) as,

$$S_M = \frac{\exp[S_L(V_\perp^{DL} - V_\parallel^{DL})] - 1}{\exp[S_L(V_\perp^{DL} - V_\parallel^{DL})] + 2}. \tag{12}$$

The solid line in Figure 12 shows relation between S_M and l/d, assuming the following equation and values ($d = d'$, $S_L = 0.654$, $d'^2l' = 1.97$). The value of S_L is for 25°C and is calculated from the phase change temperature of the GR-41 ($T_{NI} = 70$°C) by using Maire-Saupe theory.[16] The value of d'^2l' for the liquid crystal is obtained by substituting $c = 0$ and l'/d' to Eq. (8), where the value of l'/d' is obtained from Figure 11 on the assumption that l'/d' of the liquid crystal is equal to l/d of the dye in the case of which S_L is equal to S_M. The circles in Figure 12 are same as that in Figure 11. This theoretical curve agrees with the experimental data qualitatively, but not quantitatively. For the further discussions, critical definition of parame-

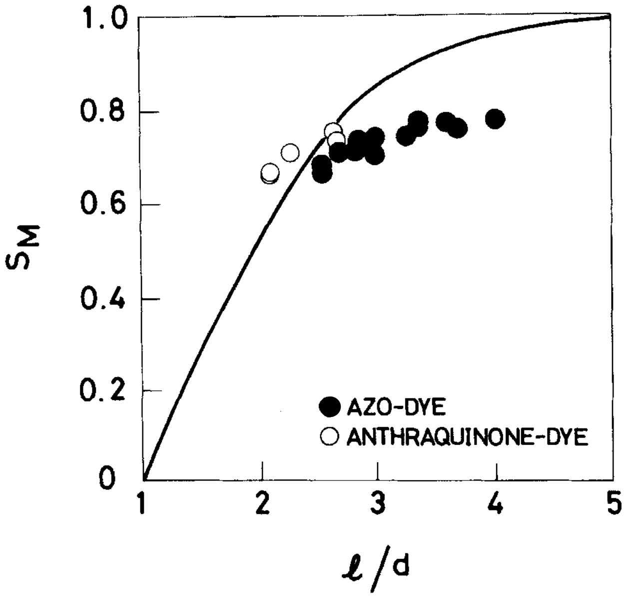


FIGURE 12 Comparison between calculated curve and experimental results with respect to the relation between S_M and l/d.

ters, such as concentration of dye, the effect of flexibility of central groups of molecular structure, approximation of inter-molecular potential and so on, will be necessary.

6. RESULTS

From the above discussions on dichroic dyes dissolved in a liquid crystal, the following results are obtained.

(1) The order parameter S_M of molecular long axis of dyes must be considered separately from the order parameter S_T of transition moment, and S_M must be used for discussing the relation between order parameter and geometrical structure of dyes.

(2) There exists an evident correlation between S_M and a parameter l/d of molecular structure, which is the ratio of length l to diameter d of circumscribed cylinders of dye molecules.

(3) Terminal alkoxy or alkyl groups up to 2 or 3 carbon atoms, respectively, contribute to the rigid molecular structure and further part of carbon chains should be ignored because of its flexibility.

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