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DICHROIC DYES FOR GUEST-HOST INTERACTIONS IN LIQUID CRYSTALS

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A detailed study of electronic color switching of various dichroic dyes available in display devices by using the guest-host interactions, is presented. The dichroic properties of various dyes are quantitatively compared. Some of them can be used in display devices.

In the previous papers[1-3] the authors clarified in detail the basic properties of the guest-host type liquid crystal display devices and the effects of various parameters in these devices on the color display property. The results obtained showed that the optical densities parallel and perpendicular to the average direction of molecular orientation, $A_{\parallel}$ and $A_{\perp}$ respectively, are proportional to the dye concentration and the cell thickness. Then, in this paper, the properties of the electronic color switching are quantitatively compared in a number of dye cells.

The color switching property of the device itself is related to the difference between $A_{\parallel}$ and $A_{\perp}$. But this difference $(A_{\parallel} - A_{\perp})$ is not a useful parameter for comparing the dichroic property of dyes in guest-host interactions, because it depends on the dye concentration and the cell thickness. The dichroic ratio $A_{\parallel}/A_{\perp}$ is independent of the dye concentration and the cell thickness. The color density of each dye is normalized by considering the dichroic ratio. Then the dichroic ratio $A_{\parallel}/A_{\perp}$ seems to be available for quantitative comparison of dyes.

The mixed liquid crystal with positive dielectric anisotropy

p-methoxybenzylidene-p'-n-butylaniline	50wt%
p-ethoxybenzylidene-p'-n-butylaniline	35wt%
p-ethoxybenzylidene-p'-aminobenzonitrile	15wt%

is used as a host in the measurements. The surface of the glass plate of the cell is treated with N-methyl-3-amino-propyltrimethoxysilane (MAP)[4], followed by unidirectional rubbing to obtain homogeneous alignment. The measurements of $A_{\parallel}$ and $A_{\perp}$ are made by using linear polarized light with electric vectors which are parallel or perpendicular to the molecular orientation in the cell, and the measured values are corrected by subtracting absorption of the cell substrate and the liquid crystal.

Table 1 shows the methine-dyes with the molecular structure of

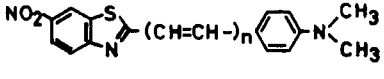
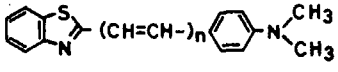
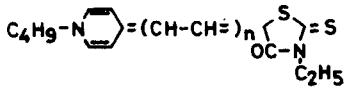
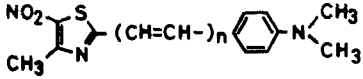
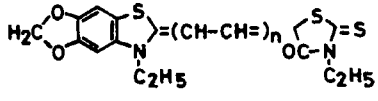
$$X = (CH - CH =)_n Y \quad \text{or} \quad X - (CH = CH -)_n Y$$

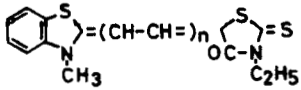
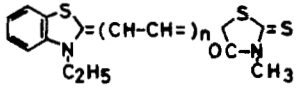
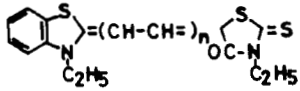
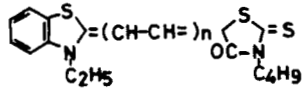
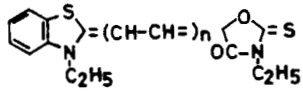
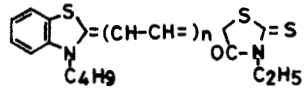
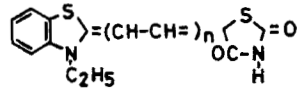
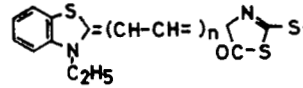
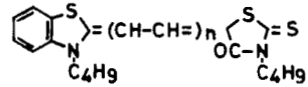
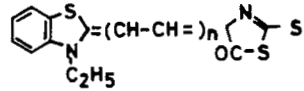
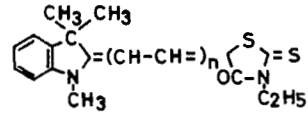
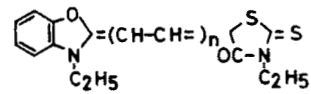
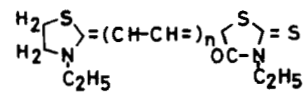
used in the measurements and the length of methine-chain n, the maximum absorption wavelength λ_m, the displayed color and the measured values of $A_{\parallel}/A_{\perp}$. Some researchers[5,6] used an order parameter S instead of $A_{\parallel}/A_{\perp}$. This order parameter is calculated from $A_{\parallel}/A_{\perp}$ by using the following relation on an assumption that no absorption was in the direction perpendicular to the long axis of the dye molecule:

$$S = \frac{A_{\parallel}/A_{\perp} - 1}{A_{\parallel}/A_{\perp} + 2}$$

The values of S are shown in Table 1. But the abovementioned assumption is not always adequate. Figure 1 shows the

TABLE 1 Properties of methine-dyes.

Dye No.	Molecular structure	n	λ_m	Displayed color	$A_{\parallel}/A_{\perp}$	S
1-1		1	457	Yellowish-orange	8.0	0.70
1-2		1	413	Yellow	5.4	0.59
1-3		1	582	Violet	5.4	0.59
1-4		1	510	Red	4.9	0.57
1-5		1	551	Reddish-violet	4.9	0.57

1- 6		1	529	Light-red	4.5	0.54
1- 7		1	529	Light-red	4.2	0.52
1- 8		1 2 3	532 610 640	Red Blue Bluish-green	4.0 4.7 6.3	0.50 0.55 0.64
1- 9		1	530	Light-red	4.0	0.50
1-10		1 2 3	505 578 613	Orange Violet Blue	3.6 4.1 5.3	0.46 0.51 0.59
1-11		3	640	Blue	5.0	0.57
1-12		1	474	Yellowish-orange	3.1	0.41
1-13		1	534	Light-red	3.1	0.41
1-14		1 2 3	531 611 637	Light-red Bluish-violet Blue	2.9 3.5 4.8	0.39 0.45 0.56
1-15		1	535	Light-red	2.9	0.39
1-16		3	608	Blue	4.7	0.55
1-17		1 2 3	497 577 624	Yellowish-orange Reddish-violet Greenish-blue	2.7 3.2 4.5	0.36 0.42 0.54
1-18		1 2 3	487 563 603	Yellow Violet Blue	1.9 2.7 3.8	0.23 0.36 0.48

relation between $A_{\parallel}/A_{\perp}$ of dyes Nos. 1-8, 1-10, 1-14, 1-17, 1-18 and n. Table 2 shows azo- and azomethine-dyes with the molecular structure of

$$X - N = N - Y \quad \text{or} \quad X - N = CH - Y ,$$

λ_m, the displayed color, $A_{\parallel}/A_{\perp}$ and S.

The results are summarized as follows :

(1) The dichroic ratio $A_{\parallel}/A_{\perp}$ of the dyes in each homologous series increases with n as shown in Figure 1.

(2) The $A_{\parallel}/A_{\perp}$ versus n curves shift nearly parallel for various dyes as shown in Figure 1. Then the dichroic ratios of various dyes can be compared with the dyes with the same value of n. By using this method, dyes in Table 1 are numbered in the order of $A_{\parallel}/A_{\perp}$ values.

(3) Dyes shown in Table 2 are also numbered in the order of $A_{\parallel}/A_{\perp}$ values. By comparing these dyes with those of n=1 in Table 1, it can be seen that the values of $A_{\parallel}/A_{\perp}$ of azo- and azomethine-dyes are larger than those of methine-dyes. In particular, this relationship can clearly be seen among the dyes in the group of Nos. 1-2, 2-5, 2-9 and in the group of Nos. 1-4, 2-10 in which each group has a common structure except the central group. Although $A_{\parallel}/A_{\perp}$ of methine-dye is exceptionally large in Nos. 1-1 and 2-4, it cannot be seen what is responsible for it.

(4) Among the dyes which have alkyl side chain or such alkyl chains as $-S-C_nH_{2n+1}$ or $-N(C_nH_{2n+1})_2$ at one end of the molecule, $A_{\parallel}/A_{\perp}$ is larger as the alkyl chain is shorter. But the longer alkyl chain makes the dye more soluble, so that the length of the chain should be adequately controlled. Further work is under way to solve this problem.

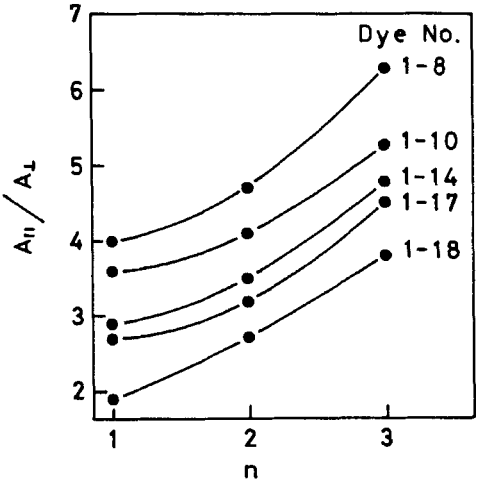
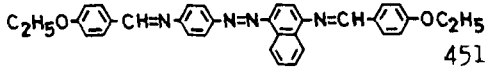
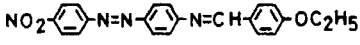
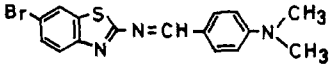
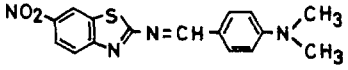
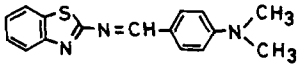
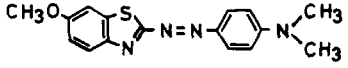
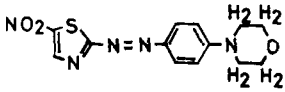
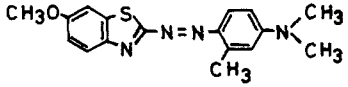
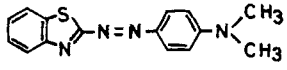
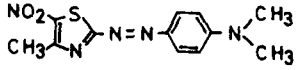
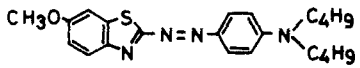
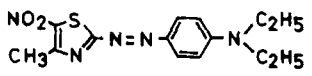
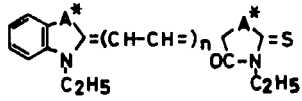


FIGURE 1 The relationship between the dichroic-ratio $A_{\parallel}/A_{\perp}$ and the length of methine-chain n.

TABLE 2 Properties of azo- and azomethine-dyes.

Dye No.	Molecular structure	λ_m	Displayed color	$A_{\parallel}/A_{\perp}$	S
2- 1		451	Yellow	11.3	0.77
2- 2		413	Yellow	8.8	0.72
2- 3		437	Yellow	7.9	0.70
2- 4		446	Yellow	7.7	0.69
2- 5		430	Yellow	7.4	0.68
2- 6		512	Light-red	6.9	0.66
2- 7		570	Bluish-violet	6.9	0.66
2- 8		523	Light-red	6.2	0.63
2- 9		512	Light-red	6.2	0.63
2-10		585	Bluish-violet	5.5	0.60
2-11		517	Light-red	4.8	0.56
2-12		588	Blue	4.4	0.53

(5) Among the dyes of Nos. 1-8, 1-10, 1-17 with the molecular structure of



(A^* : S or O)

$A_{\parallel}/A_{\perp}$ of the dye with S as A^* is superior to that of the dye with O.

(6) The dyes of Nos. 2-1, 2-2, which have the long molecular structure and the end group similar to those of the host liquid crystals, show an extremely large value of $A_{\parallel}/A_{\perp}$.

When the guest-host cell is observed macroscopically the dye with $A_{\parallel}/A_{\perp}$ above four gives sufficient color switching. About two-thirds of the dyes reported in this paper are available for the color display devices.

The relationship between molecular structures of dyes and the dichroic ratio $A_{\parallel}/A_{\perp}$ was discussed, but the detailed physicochemical mechanism has not yet been clarified. Further experiments with a larger number of dyes are performed, then the effect of the molecular structure of dyes on the guest-host interactions will be clarified.

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