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Relations between the molecular structures and properties of anthraquinone-type dichroic dyes were studied. Newly developed asymmetric dyes with thiophenyl groups are highly soluble in fluorinated liquid crystals and the dichroic ratios of these dyes are high (about 10). However, ortho-position (thiophenyl)-substituted dyes have lower solubilities and dichroic ratios than other position-substituted dyes. The properties of anthraquinone dyes with anilino groups are much lower than those of dyes with thiophenyl groups. These results can be strongly related to the flexibility of substituents. We newly established a hypothesis concerning dyes in liquid crystal solvent. In liquid crystals, the dye has a suitable conformation to adjust to liquid crystal phase. In this conformation, the solubilities and dichroic ratios are increased because the interactions between the dye molecules and liquid crystal molecules are strengthened. Flexible substituents are considered to easily form a suitable conformation and realize excellent properties.

Keywords: dichroic dye; anthraquinone; solubility; dichroic ratio; flexibility; guest-host LCD

INTRODUCTION

Portable information systems require low power consumption to enlarge driving time, and reflective LCDs are suitable for this purpose. Guest-host-type liquid crystal displays (GH-LCDs) have been attracting a great deal of interest for reflective LCDs because of their excellent hues and high brightness levels. Three-layered reflective GH-LCDs, consisting of yellow, magenta and cyan guest-host layers, form a most desirable type [1-5]. To realize these advantages in reflective GH-LCDs, TFT–driving is indispensable and dyes must have excellent properties. However, TFT-driving LCD requires high electrical resistance of liquid crystal layer. This means that anthraquinone dyes as guests and fluorinated liquid crystals as hosts are indispensable for maintaining reliability.

Anthraquinone dyes have been the subject of intensive study due to their excellent photo-stability and good hues [6,7]. We concentrated on the anthraquinone dyes in our study and investigated molecular structures and properties. Previous results and theory have been reported concerning the molecular structures and solubilities of dyes. We found that dyes with specific molecular structures have high solubilities [8-11]. In this paper, the relation between molecular structures and properties of dyes is studied more precisely.

EXPERIMENTAL

Synthesis of Anthraquinone Dye

Yellow and magenta dichroic dyes **1**, **2**, **3**, **4**, **5**, **6**, **7**, **8**, **9** and **14** were

synthesized based on our previously reported work [8]. Magenta dichroic dyes **11**, **12** and **13** were synthesized using 1,5-dichloro-anthraquinone, by introduction of appropriate anilino groups. Magenta dye **10** was purchased from Nippon Photosensitive Pigment Research Co. Ltd. Cyan dichroic dyes **15**, **16** and **17** were synthesized using the processes shown in FIGURE 1. 1, 4-dihydro-5,8-dichloroanthraquinone was purchased from the Aldrich Chemical Co..

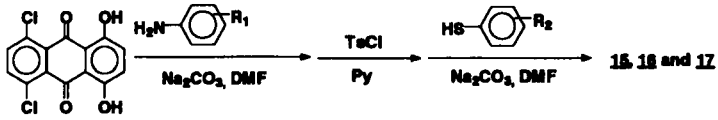

FIGURE 1. Synthesis process for cyan dyes **15**, **16** and **17**

Method for Measuring Solubilities in Liquid Crystals

The solubilities of the dyes in fluorinated liquid crystals (LIXON 5052XX, produced by Chisso Petrochemical Corp.) were measured spectroscopically. A saturated solution was obtained by adding an excess of dye to the liquid crystal host, shaking the mixture thoroughly, allowing it to stand for a month at 24°C or –6°C, and then passing it through a 0.2 μm filter. A known quantity of the solution was dissolved in a standard volume of cyclohexane, and its absorption was measured and compared with the absorption of a standard solution of the dye.

Measurement of Dichroic Ratios

Absorption spectra were measured with a Shimadzu UV-260 spectrophotometer. The maximum absorption of light horizontally and vertically polarized in the rubbing direction was measured and the ratios were calculated.

RESULTS AND DISCUSSION

The fundamental molecular structures of the dyes we studied are shown in FIGURE 2. As for dyes of type 1, yellow is realized when **X=S**, and magenta is realized when **X=NH**. In type 2, magenta is realized when **X=S**, and cyan is realized when **X=NH**. We investigated the relation between molecular structures and properties (solubilities in fluorinated liquid crystals and dichroic ratios) according to the **X**, $\mathbf{R_1}$ and $\mathbf{R_2}$ of the substituents.

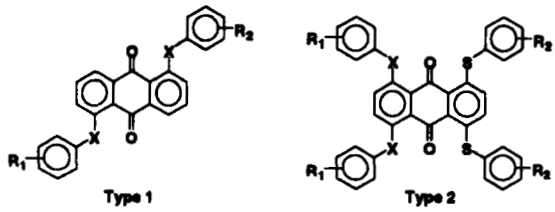

FIGURE 2. The fundamental molecular structures

Molecular Structures and Properties of Yellow Anthraquinone Dyes (type 1, X=S)

The relation between the molecular structures and properties of dichroic dyes (**type 1, X=S**) are shown in TABLE 1. We have already reported that only asymmetric dyes were highly soluble in fluorinated liquid crystals [8]. Dyes **2** and **5** provide the best comparison for clarifying the effect of asymmetry on solubilities. They have the same molecular quantity and structures except for the difference in the position of the t-butyl group. However, due to this difference, the solubilities are substantially different (dye **2**: 0.05 wt %, dye **5**: 1.8 wt % at r.t.).

TABLE 1. Effect of asymmetry and position of substituent on the properties of dyes (type 1 X=S)

		Dye		Solubility (wt %)		DR
		R_1	R_2	r.t.	-6 °C	
Sym.	1	H	H	0.07	0.01>	
	2	t-Bu (para)	t-Bu (para)	0.05	0.01>	
	3	CF_3 (meta)	CF_3 (meta)	0	0	
Asym.	4	t-Bu (para)	H	4.0	1.7	10
	5	t-Bu (para)	t-Bu (ortho)	1.8	1.6	7.9
	6	t-Bu (para)	CF_3 (meta)	5.4	3.5	10
	7	t-Bu (ortho)	CF_3 (meta)	1.0	0.5	7.2
	8	t-Bu (para)	F (para)	3.1	2.1	11
	9	t-Bu (ortho)	F (para)	1.4	1.3	7.8

Among asymmetric dyes, both the solubilities and dichroic ratios of the ortho-substituted dyes 7 and 9 are lower than those of dyes 6 and 8 respectively, having the same molecular structures except for the positions of the t-buthyl groups. This is considered to be due to the lower flexibility of the substituents. The flexibility of ortho-substituted thiophenyl group is restricted by the steric repulsion with the anthraquinone skeleton. The substantial reduction of dichroic ratios of dye 5, 7 and 9 cannot be fully explained by the smaller molecular length.

Molecular Structures and Properties of Magenta Anthraquinone Dyes (type 1, X=NH)

The results of the dichroic dyes (type 1, X=NH) are shown in TABLE 2. Dye 10 with flexible substituents (n-butyl groups) is highly soluble at room temperature. However, its solubility severely decreases at low temperatures [8]. We newly prepared dye 11 with the same molecular structures except that the substituents of the anilino groups were t-buthyl groups. The effect of flexible groups on increase in the

solubilities of dyes at room temperature is clarified from the comparison of dyes **10** and **11**.

TABLE 2. Effect of asymmetry on the properties of dyes (type 1, X=NH)

	Dye		Solubility (wt %)		DR
	R_1	R_2	r.t.	-6 ℃	
10	n-Bu (para)	n-Bu (para)	2.3	0.11	6.7
11	t-Bu (para)	t-Bu (para)	0.23	0.04	6.7
12	t-Bu (para)	H	1.6	0.6	6.7
13	t-Bu (para)	CF_3 (meta)	0.35	0.03	5.5

The asymmetric dye **12** is highly soluble at room temperature, and the solubility did not decrease much even at low temperatures. The asymmetric dye **13** was found to have a relatively lower solubility. The dichroic ratios of dyes shown in Table 2 are much lower than those of dyes shown in Table 1, even if the substituents R_1 and R_2 are the same. This is apparently due to the difference in the connection part X. Flexibility of anilino groups is considered to be inferior to that of thiophenyl groups because of the following reasons. The bond length of C-N bond is smaller than that of C-S bond. We also calculated bond orders of type 1 dyes by the PPP-CI quantum chemical calculation method (TABLE 3).

TABLE 3. The calculated bond orders of C-N and C-S bonds

	bond order	
X	Ph (C)-X	AQ (C)-X
S	0.32	0.39
NH	0.44	0.54

The bond orders of C-N bonds were found to be larger than those of C-S bonds. Stronger double bonding property of C-N bond is considered to restrict the flexibility of anilino groups. Inner molecular hydrogen bond also restricts the flexibility of anilino groups.

Molecular Structures and Properties of Magenta and Cyan Anthraquinone Dyes (type 2)

The results of the dichroic dyes (type 2) are shown in TABLE 4. Magenta dye **14** has high solubility and dichroic ratio [8]. On the other hand, these properties of cyan dyes **15**, **16** and **17** were much lower. This marked difference is considered to be due to the effects of the connection part, **X=S** or **NH**. This phenomenon is the same as in the case of the results for type 1 dyes.

TABLE 4. Effects of connection part (X) on the properties of dyes (type 2)

Dye				Solubility (wt %)		DR
	X	R_1	R_2	r.t.	-6 ℃	
14	S	t-Bu (para)	CF_3 (meta)	1.7	1.5	10
15	NH	t-Bu (para)	H	0.06	0.04	5.1
16	NH	t-Bu (para)	t-Bu (para)	0.09	0.06	5.7
17	NH	t-Bu (para)	SMe (para)	0	0	-

THE HYPOTHESIS OF THE SUITABLE CONFORMATION OF DYES IN LIQUID CRYSTALS

The solubilities and dichroic ratios of dyes are strongly related to the flexibility of substituents. From these results, we established the hypothesis described below. A dichroic dye in liquid crystals forms a suitable conformation to adjust to the liquid crystal phase, and this is different from the conformation in usual solvents. In this conformation,

the solubilities and dichroic ratios are increased because the interactions between the dye molecules and liquid crystal molecules are strengthened. The dyes with the limited flexibility make it hard to form a suitable conformation and have inferior properties.

CONCLUSIONS

Asymmetric dyes with thiophenyl groups have high solubilities in fluorinated liquid crystals and high dichroic ratios (about 10). Among these dyes, ortho-position-substituted-dyes have properties that are inferior to those of other position-substituted-dyes. The properties of anthraquinone dyes with anilino groups were greatly inferior. These results are strongly related to the flexibility of substituents. We hypothesized the existence of a suitable conformation of dyes in liquid crystals.

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