Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

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Version of record first published: 28 Mar 2007.

Mol. Cryst. Liq. Cryst., 1979, Vol. 54, 161-174
0026-8941/79/5403-0161$04.50/0

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(*Received December 5, 1978; in final form March 22, 1979*)

The liquid crystal display device using guest-host interactions has attracted interest recently because of displaying color and wide viewing angle. This paper describes dyes with high dichroic ratio, and proposes two new types of the guest-host cell being more useful than usual one. One of them is the cell with twisted molecular alignment and has sharper threshold voltage than the usual cell with homogeneous alignment. The other one with small pretilt from homeotropic alignment is made of a host nematic with negative dielectric anisotropy and is the positive type display device with high color contrast. The optimal pretilt angle of this cell is also clarified.

1 INTRODUCTION

Twisted nematic liquid crystal cells have been widely used as display devices in portable equipment such as watches or electronic calculators. But as fields of the application have expanded, their narrow viewing angle has become a serious problem.

On the other hand, the guest-host type display device, which is made of host liquid crystal containing a small amount of guest dichroic dye, has a wide viewing angle. Because of this feature as well as a wide variety of color, the guest-host cell has attracted special interest recently as a promising display device.

The authors have investigated the dichroic dyes used in this cell[1] and clarified the effects of various parameters on the display characteristics of the cell.[2] In this paper, we report some new dyes with pronounced dichroism and propose two new types of guest-host cells, in which molecular alignment of a host nematic liquid crystal is different from those of the usual homogeneously-aligned guest-host cell[3] using a host nematic with positive dielectric anisotropy (N_p liquid crystal). Characteristics of the two new types of cells are also clarified.

The first type cell is a twist-aligned cell using an N_p liquid crystal. This cell has a sharper voltage-threshold than the usual cell with homogeneous alignment.

The second type cell with small pretilt from homeotropic alignment is made of a host nematic with negative dielectric anisotropy (N_n liquid crystal). This cell displays positive patterns, that is, colored patterns on colorless background, contrary to the usual cell. This positive pattern display seems to be more useful than the usual negative one in practical uses.

2 LIQUID CRYSTALS AND DICHROIC DYES

The N_p liquid crystal used in the experiments is a mixture of

p-methoxybenzylidene-*p*′-*n*-butylaniline (MBBA)	50 wt %,
p-ethoxybenzylidene-*p*′-*n*-butylaniline (EBBA)	35 wt %,

and

p-ethoxybenzylidene-*p*′-aminobenzonitrile (EBAB) 15 wt %.

The N_n liquid crystal is a mixture of MBBA 50 wt % and EBBA 50 wt %.

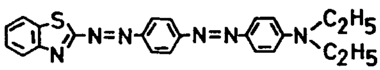
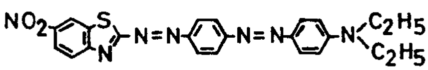
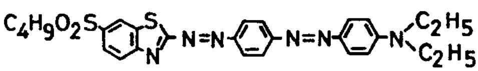
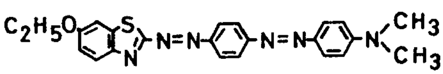
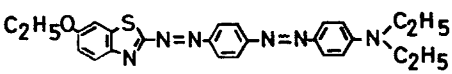
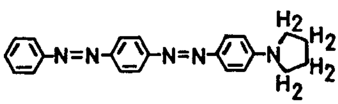
The authors have already reported methine-, azo- and azo-methine-dyes with pronounced dichroism, but some better dichroic dyes have been found in recent experiments. These are disazo-dyes shown in Table I, where $A_{\parallel}/A_{\perp}$ is the dichroic ratio; $A_{\parallel}$ and $A_{\perp}$ are the absorbance of light polarized parallel and perpendicular to the nematic director, respectively, and S is the order parameter of the dye given by

$$S = \left(\frac{A_{\parallel}}{A_{\perp}} - 1\right) \Bigg/ \left(\frac{A_{\parallel}}{A_{\perp}} + 2\right).$$

Table II shows the properties of azo-dyes compared with disazo-dyes in Table I, where end groups of the dyes 1, 2, 4 resemble those of 1′, 2′, 4′ respectively. From these tables, it is clear that the disazo-dyes have a high dichroic ratio. However, the methine-dye shown in Figure 1 is used in the following experiments so as to compare the results with those of previous experiments[2] in which the same dyes were used.

TABLE I

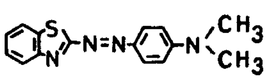
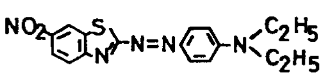
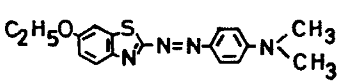
Dichroic disazo-dyes.

No.	Molecular structure	λ_m (nm)	Displayed color	$\frac{A_\parallel}{A_\perp}$	S
1		566	Violet	9.6	0.74
2		600	Blue	9.4	0.74
3		590	Bluish violet	9.3	0.73
4		553	Violet	9.2	0.73
5		566	Violet	9.1	0.73
6		509	Yellowish red	8.6	0.72

λ_m: Maximum absorption wavelength.

TABLE II

Dichroic azo-dyes.

No.	Molecular structure	λ_m (nm)	Displayed color	$\frac{A_\parallel}{A_\perp}$	S
1′		512	Pink	6.2	0.63
2′		555	Reddish violet	6.2	0.63
4′		514	Pink	6.4	0.64

λ_m: Maximum absorption wavelength.

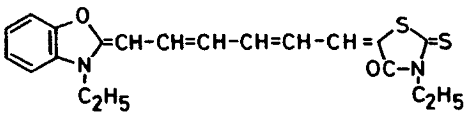


FIGURE 1 The guest dye NK2233 used in the measurements.

3 THE GUEST-HOST CELL WITH TWISTED ALIGNMENT

In this section, the properties of the twist-aligned guest-host cell are compared with those of the usual homogeneously aligned cell (abbreviated as twisted cell and homogeneous cell, respectively), and the feature of the twisted cell is explained.

Molecular alignments of these cells were controlled by treatment with N-β(aminoethyl)γ-aminopropyltrimethoxysilane[4] followed by rubbing. The N_p liquid crystal was used in these cells, however, a small amount (0.04 wt %) of cholesteryl nonanoate was added to it in the twisted cell to prevent reverse twisting, which was previously confirmed not to affect the essential property. The liquid crystal layer was 13 μm in thickness.

Figure 2 shows the schematic arrangements of polarizers and liquid crystal cells used in the measurements. On the surface of the light-incident side, polarizing directions parallel and perpendicular to the nematic director are denoted by $P_{\parallel}$ and $P_{\perp}$, respectively. Figures 3 and 4 show the voltage

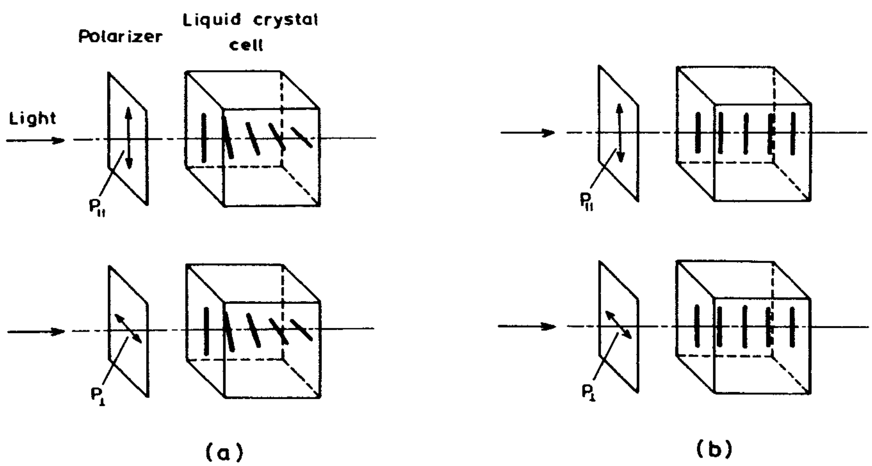


FIGURE 2 The direction of the electric vector of the polarized light transmitted through the polarizer and the direction of the orientation of liquid crystal molecules in (a) the twisted cell, and (b) the homogeneous cell.

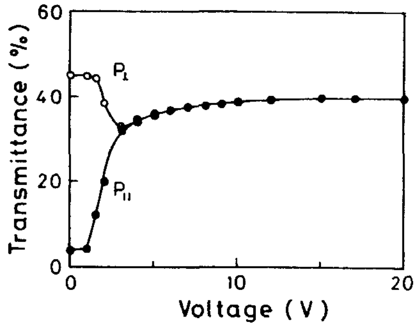


FIGURE 3 The voltage dependence of transmittances of $P_{\parallel}$ and $P_{\perp}$ in the twisted cell (square voltage of 50 Hz).

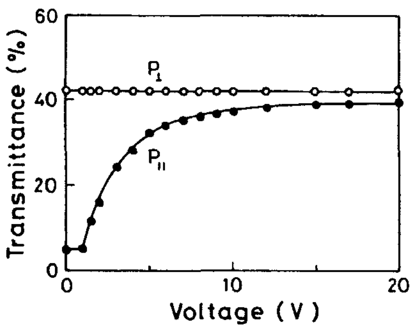


FIGURE 4 The voltage dependence of transmittances of $P_{\parallel}$ and $P_{\perp}$ in the homogeneous cell (square voltage of 50 Hz).

dependences of transmittance of twisted and homogeneous cells at the maximum absorption wavelength (624 nm). These $P_{\parallel}$ characteristics of both cells are compared in Figure 5. In these figures, the following differences are seen between two cells.

1) Transmittance of $P_{\perp}$ in the homogeneous cell is independent of applied voltage, while that of the twisted cell decreases at the threshold voltage.

2) Transmittance of $P_{\parallel}$ in the twisted cell increases more sharply and saturates at a lower voltage than that in the homogeneous cell.

Reasons for the differences between the characteristics of twisted and homogeneous cells are explained as follows. First, the transmittance of $P_{\parallel}$ in the homogeneous cell increases relatively gradually when the voltage increases above threshold. This is because surface layers SL_1 and SL_2 at both sides of the liquid crystal layer as shown in Figure 6 become thin. The fact that the transmittance of $P_{\perp}$ in the same cell is independent of voltage indicates that molecules are always perpendicular to the polarization plane

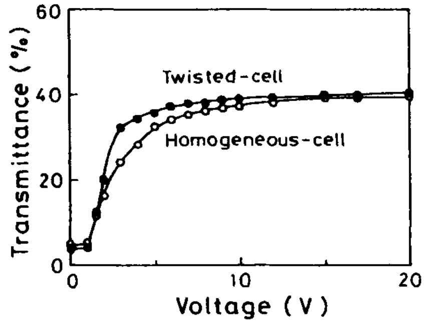


FIGURE 5 The voltage dependence of transmittances of $P_{\parallel}$ in the twisted and the homogeneous cells (square voltage of 50 Hz).

of the incident light. On the other hand, the transmittances of $P_{\parallel}$ and $P_{\perp}$ in the twisted cell at lower voltage than the threshold voltage are similar to those in the homogeneous cell respectively, because the polarization plane of the incident light rotates along the twisted structure of liquid crystal molecules. But when applied voltage is increased higher than the threshold voltage, the twisted structure is deformed and then the rotation of the polarization plane disappears (Figure 7). Then, the incident light $P_{\parallel}$ becomes not absorbed in the surface layer SL_2 and the transmittance sharply increases. Contrarily, at this state the incident light $P_{\perp}$ is absorbed in SL_2, and then the transmittance dcreases. As applied voltage is increased above 3V, the transmittances of $P_{\parallel}$ and $P_{\perp}$ in the twisted cell increase in a similar manner. This is because SL_1 and SL_2 decrease similarly with increase of the voltage.

Next, the rise and recovery times of homogeneous and twisted cells were measured. The results are shown in Figure 8. The rise and recovery times are defined by a 90% change of transmittance at the maximum absorption

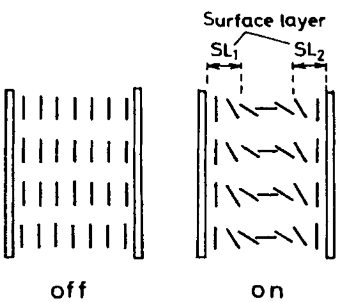


FIGURE 6 The molecular orientation in the homogeneous cell with and without applied voltage.

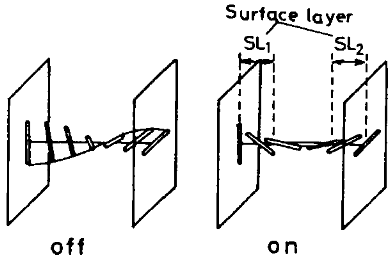


FIGURE 7 The molecular orientation in the twisted-cell with and without applied voltage.

wavelength. In Figure 8, the twisted cell is seen to have almost the same property as the homogeneous cell has.

4 THE GUEST-HOST CELL WITH TILTED ALIGNMENT

A guest-host cell displaying a positive pattern can be simply made by aligning a N_n liquid crystal homeotropically. But its color contrast is poor because the molecular alignment in the cell became non-uniform as the voltage was applied, as shown in Figure 9.[5] Then, the authors designed a cell with small pretilt from the homeotropic alignment (abbreviated as a tilted cell) to obtain the homogeneous alignment under application of a voltage as shown in Figure 10. The pretilt alignment was obtained by oblique evaporation of SiO followed by treatment with *N*,*N*-dimethyl-*N*-octadecyl-3-aminopropyltrimethoxysilyl chloride (DMOAP), which was known as a surface coupling agent for the homeotropic alignment.[6]

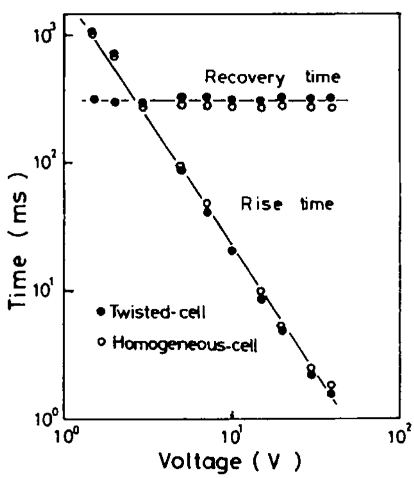


FIGURE 8 The voltage dependences of the rise time and the recovery time in the twisted and the homogeneous cells (square voltage of 50 Hz).

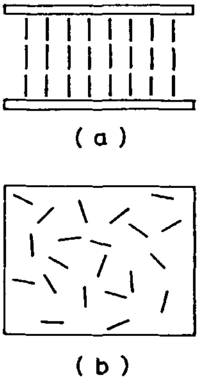


FIGURE 9 Molecular alignments of (a) off-state (vertical sectional view) and (b) on-state (top view) in the homeotropically aligned cell.

First, the fundamental characteristics of the tilted cell are clarified by using a cell with pretilt angle of about 2.5° from the normal of the substrate. The alignment was controlled by the above-mentioned method, in which the oblique evaporation angle was 60° and the evaporated film was about 150 nm in thickness.

The transmittance of the cell is shown in Figure 11 as a function of wavelength of the vertically incident light whose polarization plane is parallel to the tilted direction of the liquid crystal molecules. The solid line and the broken line show the characteristics without and with the applied voltage of 20 V of 1 kHz, respectively. For comparison, Figure 12 shows the characteristics of the usual homogeneous cell with the N_p liquid crystal. It is clear that the color switching property shown in Figure 11 is contrary to that shown in Figure 12.

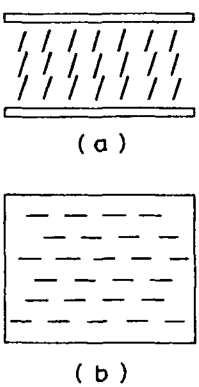


FIGURE 10 Molecular alignments of (a) off-state (vertical sectional view) and (b) on-state (top view) in the tilted cell.

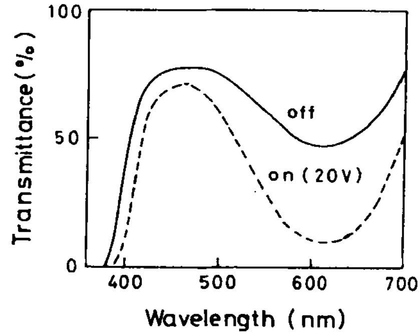


FIGURE 11 Color switching characteristics of the tilted cell; square voltage of 1 kHz is applied.

Figure 13 shows the voltage dependences of the transmittance of polarized lights, whose polarization planes are parallel and perpendicular to the tilted direction of the molecules. These polarization conditions are denoted by $P'_{\parallel}$ and $P'_{\perp}$, respectively. The wavelength of the polarized light is 609 nm, which is the maximum absorption wavelength of this cell. This wavelength is different from that of the homogeneous or the twisted cell because the absorption bands of dyes generally shift according to the host material. Voltage independence of transmittance of $P'_{\perp}$ in Figure 13 indicates that the director of the liquid crystal molecules is always perpendicular to the polarization plane of the incident light. From this fact molecular alignment is confirmed to be uniform under application of the voltage. Figure 14 shows the characteristics of the homeotropically aligned cell treated with DMOAP (without oblique evaporation of SiO) for comparison. P_1 and P_2 in this figure denote the conditions of the vertically incident lights whose polarization planes are parallel and perpendicular to an arbitrary direction, respectively. As shown in Figure 14, the transmittance of the homeotropically

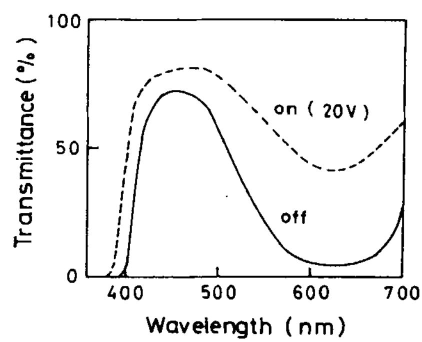


FIGURE 12 Color switching characteristics of the usual homogeneous cell with the N_p liquid crystals; square voltage of 50 Hz is applied.

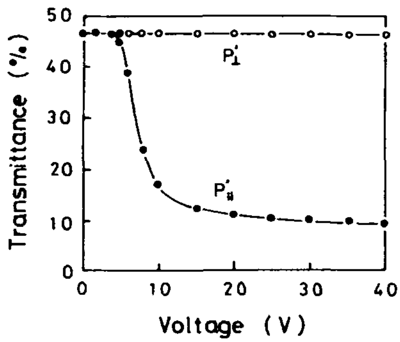


FIGURE 13 Voltage dependences of transmittance of the tilted cell (square voltage of 1 kHz).

aligned cell does not change so much when the direction of the polarization plane is changed, because the director of the liquid crystal molecules under application of the voltage is parallel to substrates but random in azimuth. It is seen from Figures 13 and 14 that the condition of $P'_{\parallel}$ of the tilted cell is desirable in view of color switching.

Figure 15 shows the transmittance of $P'_{\parallel}$ in the tilted cell as a function of voltage with various frequencies. When the voltage of a low frequency was applied, the transmittance rose at the portions indicated by downward arrows in Figure 15. This is because the molecular alignment is disturbed by occurrence of the electrohydrodynamic instability. Then, if it is necessary to apply a high voltage to the cell, its frequency must be high enough.

The rise time of the cell with pretilt angle of 2.5° was measured. The results obtained showed that it varied inversely as the square of voltage up to about 15 V, but increased abruptly above the voltage of about 15 V. This did not result from the electrohydrodynamic instability, because the frequency of the applied voltage was 1 kHz. It was found by the microscopic observation that

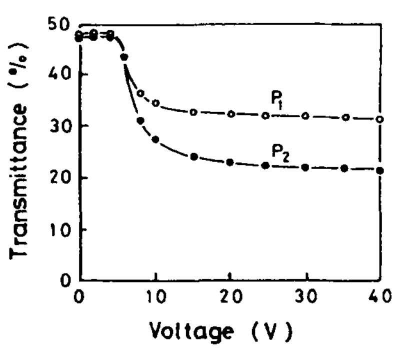


FIGURE 14 Voltage dependences of the homeotropically aligned cell (square voltage of 1 kHz).

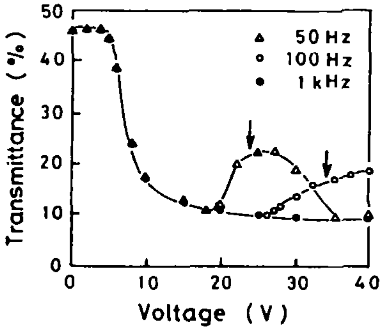


FIGURE 15 Transmittance of the tilted cell vs. the applied square voltage of 50 Hz, 100 Hz or 1 kHz.

the molecular alignment became parallel to the surface but random in azimuth just after application of a voltage higher than 15 V, and then gradually changed to be homogeneous. This phenomenon seemed to be due to the too small pretilt angle. Then, the cells with various pretilt angles were investigated. The pretilt angle θ can be controlled by changing the thickness of the 85°-obliquely evaporated film. The detailed relationship between the evaporation condition and the molecular alignment of liquid crystals will be reported by another journal. Figure 16 shows the voltage dependence of the rise time for the cells with various values of θ, in which "$\theta = 3.4°/24.9°$" means the cell composed of two substrates with different pretilt angles of 3.4° and 24.9°. Figure 17 shows the θ dependence of the rise time at various applied voltages. It is found from these figures that an abnormal increase of transmittance occurs when a higher voltage than about

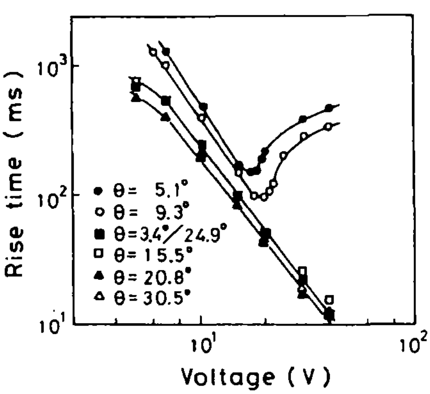


FIGURE 16 Voltage dependences of the rise time for the cells with various pretilt angles, θ (square voltage of 1 kHz).

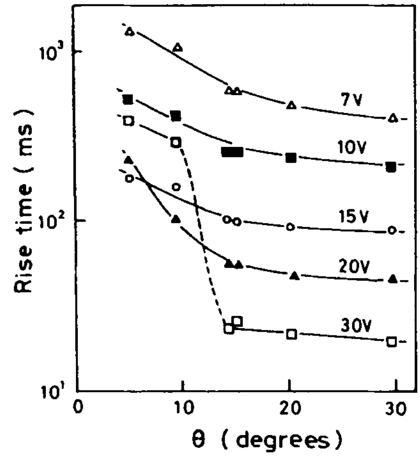


FIGURE 17 Rise time vs. pretilt angle θ as a parameter of voltage (square voltage of 1 kHz).

15 V is applied to the cell with θ less than about 15°. Then, when it is necessary to apply higher voltage than 15 V, θ must be larger than 15°.

The effect of θ on display characteristics was also investigated. Figure 18 shows the voltage dependence of absorption A of the cell at the wavelength of 609 nm. The results obtained can be summarized as follows.

1) As θ increases, the absorption of the cell with no voltage (abbreviated as A_0) increases, which indicates coloration of the background.

2) The threshold voltage decreases and becomes indistinct according to increase of θ.

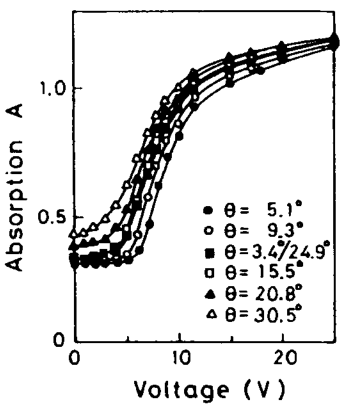


FIGURE 18 Voltage dependences of absorption of the tilted cell at the wavelength of 609 nm (square voltage of 1 kHz).

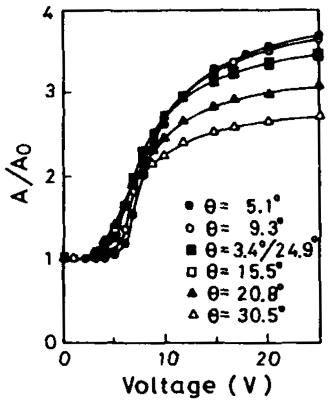


FIGURE 19 Voltage dependences of the effective dichroic ratio, A/A_0.

Figure 19 shows the effective dichroic ratios, which is obtained by normalizing absorption A shown in Figure 18 with A_0 for each cell. From this figure, the effective dichroic ratio at a sufficiently high voltage is found to decrease as θ increases. Figure 20 shows θ-dependences of absorption at off-state, A_0, absorption at 15 V, A_{15}, and effective dichroic ratio at 15 V, A_{15}/A_0. It is found from this figure that A_{15}/A_0 decreases a little as θ increases up to 15°, but the A_{15}/A_0 decreases acceleratedly above 15°. It is also found that the cell denoted by $\theta = 3.4°/24.9°$ can be assumed to have pretilt angle of about $(3.4° + 24.9°)/2 = 14.15°$ as shown in Figure 20 with open circles.

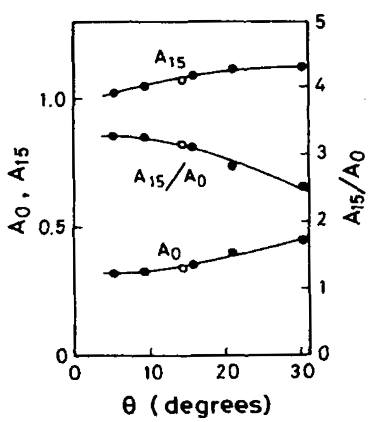


FIGURE 20 The θ-dependences of absorption at off-state, A_0, absorption at 15 V, A_{15}, and the effective dichroic ratio at 15 V, A_{15}/A_0. Open circles are the characteristics of the cell denoted by $\theta = 3.4°/24.9°$.

From the experimental results mentioned above, the change in display properties of the tilted cell as the increase of θ is summarized as follows.

1) The threshold voltage decreases and becomes unclear.

2) Effective dichroic ratio decreases.

3) Homogeneous alignment can be obtained even if a voltage higher than 15 V is applied.

Considering these facts, it is clarified that the suitable value of θ is about 5° for a lower driving voltage than 15 V and is about 15° for the higher voltage than that.

5 CONCLUSION

Some of the disazo-dyes with high dichroic ratio were reported, and two new types of the guest-host cells which were different in molecular alignment from the usual cell were proposed. The cells are,

1) the twist-aligned cell using the N_p liquid crystal: twisted cell,

2) the pretilt-aligned cell using the N_n liquid crystal: tilted cell.

It was found from experimental results that the twisted cell had a sharp voltage threshold and was more available for matrix-driving than the usual cell. And it was also found that the tilted cell displayed good positive patterns. The effect of the pretilt angle θ of the tilted cell on its display characteristics was also investigated and the suitable value of θ was found to be about 5° for driving a lower voltage than 15 V and about 15° for a higher voltage than that.

Acknowledgement

We are indebted to Dr. K. Banno and Mr. S. Yasui of Nippon Kanko–Shikiso Kenkyusho for the cooperation in dye synthesis and to Mr. M. Ogawara in our laboratory for the cooperation in SiO evaporation.

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