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Litht-Stability of Guest-Host Cells

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Light-Stability of Guest-Host Cells

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Light-stability of liquid-crystal color display devices using the guest-host interactions were investigated. It was found theoretically as well as experimentally that a decrease of absorbance of the guest-host cell was almost proportional to the exposed light intensity and time while the decrease was not large. Therefore, the lifetime can be calculated by extrapolation from the initial decreasing rate of absorbance obtained from accelerated life test using an intense light.

Various azomethine-, disazo- and anthraquinone-dyes with large dichroic ratios were put to the test and some stable dyes were found.

1 INTRODUCTION

A liquid crystal display device using the guest-host interactions (abbreviated as GH-cell) makes use of dichroism of dichroic dye (guest) oriented by liquid crystal (host). This cell changes its color by applying a voltage. It has the characteristic of wide viewing angle compared with twisted nematic cell.[1] In 1968, Heilmeier and co-workers reported on the GH-cell,[2] but it was not put into practical use, because the dichroism of the dyes they used was not sufficient. But recently various dichroic dyes with a large dichroic ratio have been reported[3~9] and their practical application has been considered. According to it, the light-stability of the dyes has become of major interest. Therefore, the authors investigated basic light-degradation property of dichroic dyes and found some stable dichroic dyes. Here, the stability against visible light rather than ultraviolet light (UV-light) was considered because the actual cell is usually protected from UV-light by using UV-cut filter.

2 EXPERIMENT

In the experiments, a biphenyl mixture LIXON GR-41 of Chisso Corp. was used as a host, and azomethine-dyes, disazo-dyes, anthraquinone-dyes were

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used as guests. The GH-cells were constructed by using glass plates coated with transparent electrodes of In_2O_3. In these cells, the liquid crystal was aligned homogeneously by coating substrate surfaces with polyvinyl alcohol (PVA) followed by unidirectional rubbing. Thickness of the liquid crystal layer was 12 μm. Three different kinds of light sources were used for the light-stability test; fluorescent lamps, sunlight and incandescent lamp. As for the fluorescent lamps, fourteen tubes of FL30SW (30 watt) and six tubes of FL15SW (15 watt) of Tokyo Shibaura Electric Co. Ltd., were closely arranged and irradiated the GH-cells placed 12 cm away from them. The light intensity was 4.1×10^4 lx. The sunlight was 1.4×10^5 lx in intensity. The incandescent lamp was a photoreflector lamp of 500 watt made by Tokyo Shibaura Electric Co. Ltd. The light intensity in this case was controlled by adjusting the distance between the lamp and GH-cells. The lifetime was evaluated from the change of absorbance measured at 25°C with linearly polarized light at the maximum absorption wavelength, polarized in the direction which was parallel to the molecular orientational direction.

3 RESULT AND DISCUSSION

First, G165 was chosen as the guest, and wavelength dependences of absorbance of the GH-cell at initial and after irradiation of fluorescent light were measured. The results are shown in Figure 1 by the solid curve. The broken line in this figure shows the absorbance of the cell kept in the dark for comparison. It is seen that the dye was degraded by the fluorescent light and changed to another substance with different absorption property. Figure 2 shows wavelength dependences of the ratio A/A_0 in which A_0 is initial absorbance and A is the absorbance after exposure to the fluorescent light for 130 hours. The arrow in Figure 2 indicates the absorption maximum wavelength λ_m. It is seen that A/A_0 is constant at wavelengths longer than 530 nm, but it increases in the region of shorter wavelengths. It is considered to be due to the absorption by the degraded product. In general the degradation property is evaluated by measuring the absorbance at λ_m. Therefore, overlapping of absorption of the degraded product at λ_m causes an error in estimation of lifetime. Then, the overlapping of absorption was checked for dyes used in the experiment whose λ_m was close to the absorption peak of degraded product by the same method as shown in Figure 2. In the results, the overlapping did not occur for each dye.

Next, the degradation property is theoretically analyzed. It is considered that the GH-cell is exposed to a light of intensity $I(\lambda)$ per unit area as shown in Figure 3. $I(\lambda)$ is given as a function of wavelength λ. And d is the whole thickness of liquid crystal layer. Let c denote the dye concentration, then the

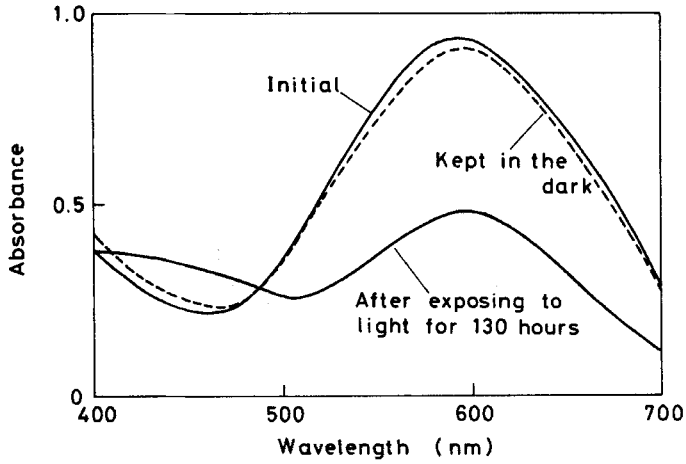


FIGURE 1 Wavelength dependence of absorbance of the GH-cell exposed to the fluorescent light (G165: 0.5 wt%).

amount of dye contained in the shaded part in Figure 3 is $c\Delta x$. If $P(\lambda)$ denotes the degradation probability of the dye of unit concentration when it absorbs unit intensity of light of wavelength λ, then the degradation rate in the shaded part in Figure 3 is expressed as

$$-\frac{dc}{dt}\Delta x = \Delta x \int_0^\infty P(\lambda)\left\{-\frac{1}{c}\frac{dI(\lambda, x)}{dx}\right\} c\, d\lambda, \tag{1}$$

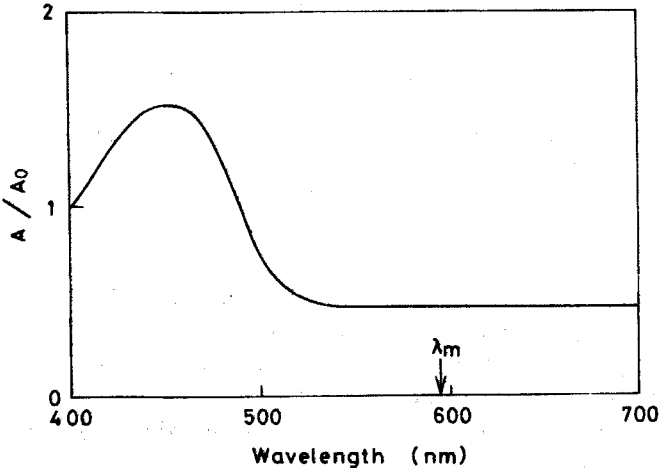


FIGURE 2 Wavelength dependence of ratio A/A_0 in which A_0 is the initial absorbance and A is the absorbance after exposing to the fluorescent light for 130 hours.

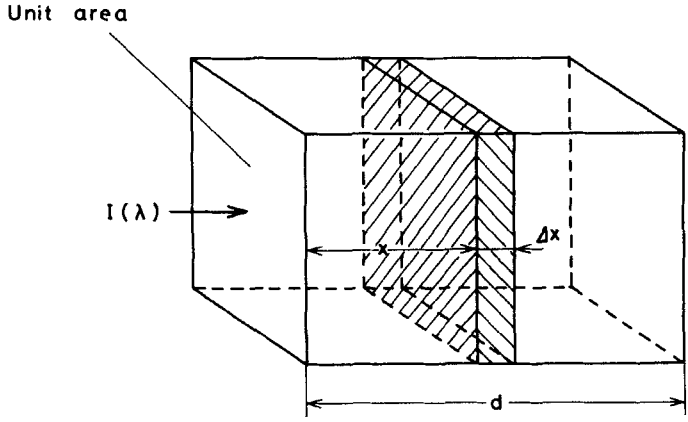


FIGURE 3 Schematic representation of the degraded GH-cell.

where $\{-(1/c)(\mathrm{d}I(\lambda, x)/\mathrm{d}x)\}$ indicates the amount of absorbed light of wavelength λ per unit concentration at depth x. $I(\lambda, x)$ can be written as

$$I(\lambda, x) = I(\lambda)10^{-k(\lambda)cx}, \tag{2}$$

where $I(\lambda)$ and $k(\lambda)$ are respectively incident light intensity at $x = 0$ and absorption coefficient as a function of λ. By substituting Eq. (2) for Eq. (1), the following equation is obtained.

$$-\frac{\mathrm{d}c}{\mathrm{d}t} = \frac{1}{\log e}\int_0^\infty k(\lambda)P(\lambda)I(\lambda)c10^{-k(\lambda)cx}\,\mathrm{d}\lambda. \tag{3}$$

Here let us assume that the degradation of the dye is induced by the light of wavelength region of $\lambda_0 \pm \Delta\lambda/2$, and in this region $k(\lambda)$, $P(\lambda)$ and $I(\lambda)$ are constant with respect to λ, so that $k(\lambda) = k(\lambda_0)$, $P(\lambda) = P(\lambda_0)$, $I(\lambda) = I(\lambda_0)$. Then Eq. (3) can be written as

$$-\frac{\mathrm{d}c}{\mathrm{d}t} = \frac{1}{\log e}\Delta\lambda k(\lambda_0)P(\lambda_0)I(\lambda_0)c10^{-k(\lambda_0)cx}. \tag{4}$$

This equation indicates that the degradation induces a slope of dye concentration in the direction perpendicular to the surface, while the slope is decreased by diffusion of dye. In general, the effect of diffusion is considered to be dominant, so that the concentration can be assumed to be independent of depth x and the degradation rate of dye in the whole layer per unit area can be written as

$$-\frac{\mathrm{d}(cd)}{\mathrm{d}t} = -\int_0^d \frac{\mathrm{d}c}{\mathrm{d}t}\,\mathrm{d}x. \tag{5}$$

Substituting Eq. (4) into Eq. (5), we can obtain

$$-d\frac{dc}{dt} = \frac{1}{\log e}\int_0^d \Delta\lambda k(\lambda_0)P(\lambda_0)I(\lambda_0)c10^{-k(\lambda_0)cx}\,dx. \tag{6}$$

By practicing the integrals of Eq. (6), the following equation is obtained

$$k(\lambda)(c - c_0)d + \log\left\{\frac{1 - 10^{-k(\lambda_0)cd}}{1 - 10^{-k(\lambda_0)c_0d}}\right\} = -\Delta\lambda k(\lambda_0)P(\lambda_0)I(\lambda_0)t, \tag{7}$$

where c_0 is the initial dye concentration. If A_0 and A denote absorbances at the maximum absorption wavelength λ_m of initial and after irradiation time t respectively, then A_0 and A are given as follows.

$$A_0 = k(\lambda_m)c_0d. \tag{8}$$

$$A = k(\lambda_m)cd. \tag{9}$$

By using Eqs. (8) and (9), Eq. (7) can be rewritten as follows.

$$\log\{10^{Ak(\lambda_0)/k(\lambda_m)} - 1\} = \log\{10^{A_0k(\lambda_0)/k(\lambda_m)} - 1\} - \Delta\lambda k(\lambda_0)P(\lambda_0)I(\lambda_0)t. \tag{10}$$

Let α denote $\Delta\lambda k(\lambda_0)P(\lambda_0)I(\lambda_0)$ and suppose $A_0 = 0.2$, 5.0, the relationship between A and αt obtained by numerical analysis are shown in Figure 4. From this figure, it is found that absorbance A decreases almost linearly with time t in the range of $A = A_0 \sim 0.8A_0$ for any values of A_0 and $k(\lambda_0)/k(\lambda_m)$. Life properties of the cell irradiated by several kinds of light sources are shown in Figure 5 by the solid curve. The broken lines in the figures

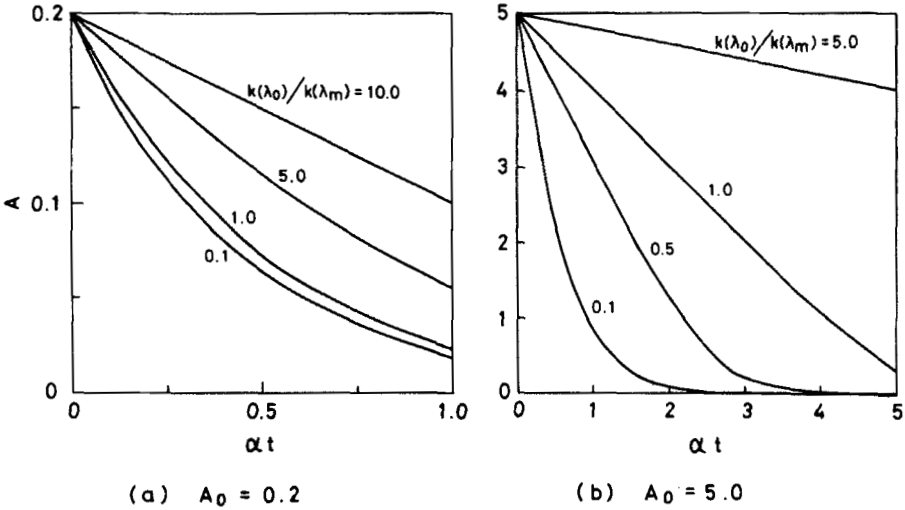


FIGURE 4 Relationship between A and αt obtained by theoretical calculation for $A_0 = 0.2$, 5.0.

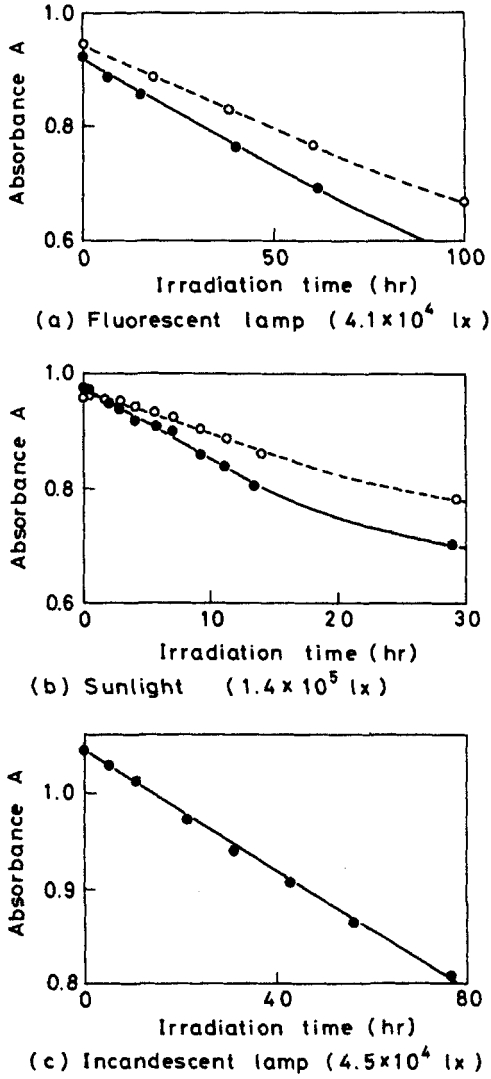


FIGURE 5 Irradiation time dependence of absorbance of the GH-cell with the guest of G165 (0.5 wt %) irradiated by fluorescent lamps, sunlight and incandescent lamp. – – – ○ – – – with a UV-cut filter; —— ● —— no UV-cut filter.

shows the property of the cell with a UV-cut filter whose transmission property is shown in Figure 6. In each case, the linear relationship can be obtained in the region of $A = A_0 \sim 0.8A_0$. Here the lifetime is defined as the time required for the absorbance to change from A_0 to $0.8A_0$. Therefore

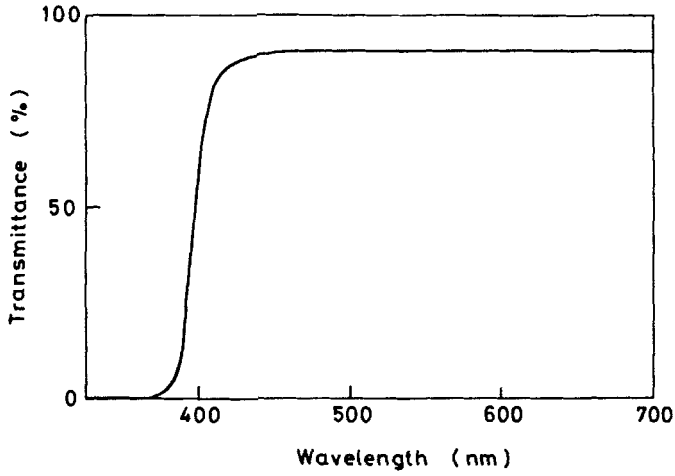


FIGURE 6 Wavelength dependence of transmittance of the UV-cut filter.

the lifetime can be calculated by extrapolating the gradient of initial property. In this case the lifetime t can be obtained from Eq. (10) as follows.

$$t = -\frac{1}{\Delta\lambda k(\lambda_0)P(\lambda_0)I(\lambda_0)} \log\left\{\frac{10^{0.8A_0k(\lambda_0)/k(\lambda_m)} - 1}{10^{A_0k(\lambda_0)/k(\lambda_m)} - 1}\right\}. \tag{11}$$

On the other hand, the lifetime t' calculated by extrapolating the gradient of the initial property is expressed as follows.

$$t' = -\frac{0.2A_0}{\left\{\frac{dA}{dt}\right\}_{A=A_0}} = \frac{0.2A_0 10^{A_0k(\lambda_0)/k(\lambda_m)}}{\Delta\lambda k(\lambda_m)P(\lambda_0)I(\lambda_0)\{10^{A_0k(\lambda_0)/k(\lambda_m)} - 1\}}. \tag{12}$$

Then the error of the extrapolating method is given as follows.

$$\frac{t' - t}{t} = \frac{0.2A_0\{k(\lambda_0)/k(\lambda_m)\}10^{A_0k(\lambda_0)/k(\lambda_m)}}{\{10^{A_0k(\lambda_0)/k(\lambda_m)} - 1\}\log\left\{\frac{10^{A_0k(\lambda_0)/k(\lambda_m)} - 1}{10^{0.8A_0k(\lambda_0)/k(\lambda_m)} - 1}\right\}} - 1. \tag{13}$$

From this equation, an error is estimated within 10% for various values of $k(\lambda_0)/k(\lambda_m)$. By the way, Eq. (10) indicates that the lifetime is inversely proportional to the light intensity, or the gradient of the initial property (denoted by β) is directly proportional to the light intensity, unless the spectrum distribution of the light source changes. Figure 7 shows the light intensity dependence of β measured by using the incandescent light. Here the light intensity is

defined by illumination intensity I (lx). This figure indicates that the following proportional expression is established.

$$\beta = -7.8 \times 10^{-8} I\,(\mathrm{hr}^{-1}). \tag{14}$$

From the results, the linear relationship between A and t, and between β and I are confirmed experimentally, and the propriety of Eq. (10) is established. Therefore, the practical lifetime of the dye can be easily obtained by accelerated life test by using intense light.

Table I shows the lifetime of various dyes. Here, the accelerated lifetime indicates the experimental value obtained by the method mentioned above by using 4.1×10^4 lx light of fluorescent lamps. The calculated lifetime of the transmissive cell indicates the value calculated by using the accelerated lifetime and the linear relationship between β and I, assuming that the cell is irradiated by a 6 watt-fluorescent lamp through a diffuser, a polarizer and the UV-cut filter. The light intensity of this condition was evaluated to be 800 lx. The calculated lifetime of the reflective cell was estimated by assuming that the cell was exposed to 400 lx light of fluorescent lamp through the UV-cut filter. As shown in Table I, the lifetime of the GH-cell using UV-cut filter becomes $1.3 \sim 5.3$ times as long as the GH-cell without a UV-cut filter. The conventional anthraquinone-dyes Nos. 1 and 2^{10} have a long lifetime but the dichroic ratios are not sufficiently large. On the other hand, the disazo-dyes of Nos. 3, 4 with thiazole base have large dichroic

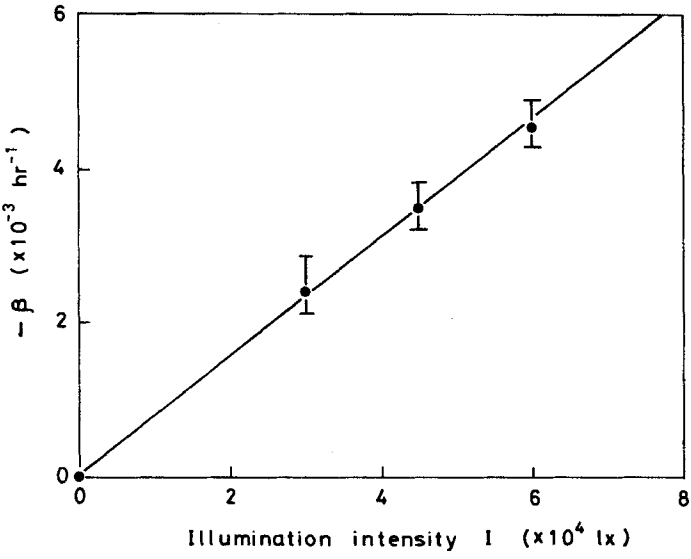
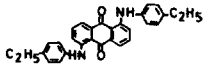
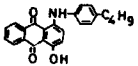
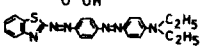
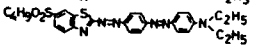
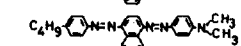
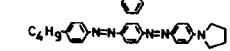
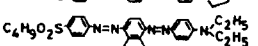
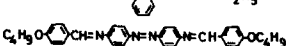
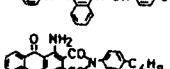


FIGURE 7 Light intensity dependence of degradation rate β.

TABLE I

Lifetimes of various dyes

No.	Dye	Molecular structure	Maximum absorption wavelength (nm)	Displayd color	Dichroic ratio	Accelerated lifetime(hr) No UV-cut filter	Accelerated lifetime(hr) With a UV-cut filter	Calculated lifetime(hr) Transmissive type	Calculated lifetime(hr) Reflective type
1	D35		553	Violet	6.5	——[a]	——[a]	——	——
2	D5		590	Blue	5.3	1.7×10^3	5.9×10^3	3.1×10^5	6.2×10^5
3	G168		574	Bluish-violet	10.6	3.3×10	3.8×10	1.9×10^3	3.8×10^3
4	G165		595	Blue	10.3	4.2×10	7.0×10	3.6×10^3	7.2×10^3
5	G224		574	Bluish-violet	9.7	2.3×10^2	5.3×10^2	2.7×10^4	5.4×10^4
6	G239		533	Reddish-violet	9.0	5.1×10^2	2.3×10^3	1.2×10^5	2.4×10^5
7	G205		507	Red	11.4	5.8×10^2	2.3×10^3	1.2×10^5	2.4×10^5
8	G214		573	Bluish-violet	8.0	6.3×10^2	3.2×10^3	1.7×10^5	3.4×10^5
9	G232		450	Yellow	12.1	1.2×10^3	3.8×10^3	2.0×10^5	4.0×10^5
10	G209		687	Blue	9.5	3.7×10^3	——[a]	——	——

[a] Almost no change was observed. No. 1, 2: Producted by BDH Chem. Ltd. No. 3 ~ 10: Produced by Nippon-Kankoh-Shikiso Laboratory Co., Ltd.

ratios but relatively short lifetimes. Though only two examples of the dye with thiazole base are shown in the table, the authors have confirmed that the other dye of this kind has a relatively short lifetime. The disazo- and azomethine-dyes of Nos. 5~9 without thiazole base have large dichroic ratios and considerably long lifetimes. Dye No. 10 is a new anthraquinone-dye and has a large dichroic ratio compared with Nos. 1, 2. Therefore, those types of dyes Nos. 5~10 are considered to be feasible practically at present as long as they are used indoors.

4 CONCLUSION

Light-stability of dichroic dyes were investigated. From the results, it was found that the decrease of absorbance of the guest-host cell was almost proportional to the exposed light intensity and time. Therefore, the lifetime can be obtained by accelerated life-test using an intense light. Various dyes were put to the accelerated life test, and it is found that the disazo- and azomethine-dyes without thiazole base have lifetimes longer than 3×10^4 hours. These kinds of dyes have large dichroic ratios in various colors, so that they can be put into practical use at present. Nevertheless, more suitable dyes in terms of stability as well as in dichroic ratio are expected to be developed henceforth.

Acknowledgements

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References

1. M. Schadt and W. Helfrich, *Appl. Phys. Lett.*, **18**, 127 (1971).
2. G. H. Heilmeier and L. A. Zanoni, *Appl. Phys. Lett.*, **13**, 91 (1968).
3. D. L. White and G. N. Taylor, *J. Appl. Phys.*, **45**, 4718 (1974).
4. L. M. Blinov, V. A. Kizel, V. G. Rumyantsev, and V. V. Titov, *J. de Phys., Coll. C1*, **36**, C1-69 (1975).
5. J. Constant, J. Kirton, E. P. Raynes, I. A. Shanks, D. Coates, G. W. Gray, and D. G. McDonnell, *J. Phys. D: Appl. Phys.*, **11**, 479 (1978).
6. T. Uchida, C. Shishido, H. Seki, and M. Wada, *Mol. Cryst. Liq. Cryst. Lett.*, **34**, 153 (1977).
7. T. Uchida, C. Shishido, H. Seki, and M. Wada, *Mol. Cryst. Liq. Cryst.*, **39**, 39 (1977).
8. A. Bloom and P. L. K. Hung, *Mol. Cryst. Liq. Cryst.*, **40**, 213 (1977).
9. A. Bloom, P. L. K. Hung, and D. Meyerhofer, *Mol. Cryst. Liq. Cryst. Lett.*, **41**, 1 (1977).
10. J. Constant, M. G. Pellat, and I. H. C. Roe, The 7th International Liquid Crystal Conference, Bordeaux, DP33 (1978).