Dyes and Pigments **15** (1991) 203–214

Fluorescent Dyes for Guest–Host Applications

K. Fiksiński, D. Bauman, A. Skibiński

Institute of Physics, Poznań Technical University, ul. Piotrowo 3, 60-965 Poznań, Poland

&

R. Stolarski

Institute of Dyes, Łódź Technical University, ul. Zwirki 36, 91–224 Łódź, Poland

(Received 12 April 1990; accepted 28 May 1990)

ABSTRACT

The spectral properties of some fluorescent dyes (bicarboxilic acid derivatives) in isotropic solvents and nematic liquid crystals have been studied and the temperature of the nematic–isotropic phase transition for dye–liquid-crystal mixtures has been determined. It was found that the dyes investigated emit green light, are aligned well in nematic liquid crystals, have quite high fluorescence efficiency and do not destabilize the nematic phase of the host. They can therefore be utilized in 'guest–host' liquid crystal display devices.

1 INTRODUCTION

Several electro-optic effects occur when certain types of dyes are mixed with liquid crystals. Since the concept of the 'guest–host' effect was introduced by Heilmeier, Castellano and Zanoni,[1,2] there has been considerable research and development interest in producing commercial liquid crystal display devices. In the last decade guest–host liquid crystal displays (G–H LCDs) have been widely utilized because of their many advantages, e.g., colour displaying information, wide viewing angle and high brightness. Moreover, one[1–3] or both[4,5] external polarizers can be eliminated. Stable high-contrast

Dyes and Pigments 0143-7208/91/$03·50

dyes are now available and guest–host displays have become a viable alternative to the standard twisted nematic displays.

Most G–H LCDs utilized the change in the light absorption by the pleochroic dye depending on the voltage applied.[6–10] In 1973 Larrabee[11] showed that the intensity of the fluorescence could be controlled in a similar way to the absorption. The pleochroism of the dye results in maximum fluorescence intensity occurring by an alignment of the molecules, where the absorption is most intense. By changing the orientation of the liquid crystal molecules using an electric field, it is possible to change the absorption of the light, and as a consequence the fluorescence intensity also. Some possibilities for the construction of G–H LCDs using fluorescent dyes have been reported.[12–14]

The good parameters of coloured LCDs depend upon the pleochroic properties of the dyes, the dye concentration and the applied voltage.[6–10,12,14] In the case of fluorescent displays, an excellent character for colour switching can be obtained if the quantum fluorescence yields of the dyes are high. Furthermore, the position of the fluorescence band is very important, it being preferably in the spectral region perceptible to the human eye. Therefore, in order to check the use of dyes in LCD devices, their basic spectral parameters in isotropic solvents and in the liquid crystal matric should be measured.

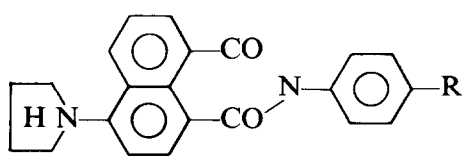
It has recently been shown[15–20] that addition of the guest dye to the liquid crystal results in a change in the nematic–isotropic transition temperature, T_{NI} (the clearing point) of the pure host, sometimes causing destabilization of the nematic phase. In selecting the dye for the G–H LCDs, it is therefore necessary also to determine the influence of the guest on the clearing temperature of the host used.

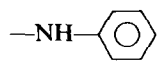
In this paper some new fluorescent dyes are prepared and the possibility of their application in G–H LCDs is discussed.

2 MATERIALS AND METHODS

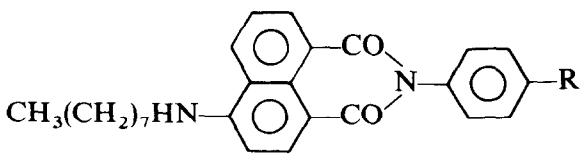
The following chromatographically purified naphthalene-1,8 dicarboxilic acid derivatives[21] were studied:

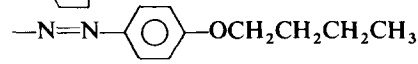
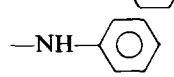
1.



Dyes	*R*	*Molecular weight*
DI	$-NH_2$	357
DII	$-N{=}N-C_6H_4-OCH_2CH_2CH_2CH_3$	518
DIII	$-NHCOCH_2CH_2CH_3$	427
DIV	$-NHCOCH_3$	399
DV		363
DVI		433

2.



Dyes	*R*	*Molecular weight*
DVII	$-NH_2$	415
DVIII	$NHCOCH_2CH_2CH_3$	485
DIX		469
DX		576
DXI		491

The structure and purity of the dyes was confirmed by TLC, ^{1}H-NMR (in $CDCl_3$) and mass spectroscopy.[21]

Toluene (non-polar) and ethanol (polar) as isotropic solvents and two nematic liquid crystals, viz. 6CB (*p*-hexylo-*p'*-cyanobiphenyl) and mixture W52 [both from POCh, Lublin, Poland] were used. The dye concentration in the isotropic solvents was 10^{-5}M for absorption measurements, 10^{-6}M for fluorescence measurements and 10^{-3}M in liquid crystals for both absorption and fluorescence measurements. The solubility of the dyes in the liquid crystals used was of the order of 10^{-2}M.

Solutions were prepared by dissolving powdered dyes immediately into the isotropic solvents and the nematic crystals host at room temperaure.

A 'sandwich' cell of 10 μm thickness was used to determine the optical parameters of the dye–liquid-crystal mixtures. Planar homogeneous alignment, using the rubbed polyimide technique was effected. After filling, the cells were heated to the isotropic phase and allowed to cool to room temperature before measurements.

Absorption spectra and their polarized components were recorded on a double beam spectrophotometer Spectord M40 (Carl Zeiss-Jena, Germany).

The dye extinction coefficients in the two solvents were calculated using the relationship:

$$\varepsilon = \frac{A}{c \times d} \tag{1}$$

where ε is the extinction coefficient, A the absorbance of the sample, c the concentration of the dye in moles and d the thickness of the layer in metres.

The order parameters of the dyes in the liquid crystal can be determined from the polarized components of the absorption spectra via the following formula:[22–24]

$$S_A = \frac{A_{\parallel} - A_{\perp}}{A_{\parallel} + 2A_{\perp}}(1 - \tfrac{3}{2}\sin^2\beta)^{-1} \tag{2}$$

where $A_{\parallel}$ and $A_{\perp}$ are the absorbances of light polarized parallel and perpendicular to the orientation axis of the liquid crystal, respectively, β is the angle between the direction of the absorption transition moment and the long molecular axis of the dye.

If $\beta = 0°$ then eqn (2) is reduced to the following:[25]

$$S'_A = \frac{A_{\parallel} - A_{\perp}}{A_{\parallel} + 2A_{\perp}} \tag{3}$$

However, for the fluorescent dyes investigated in this paper the β angles are unknown. Therefore eqn (3) was used to estimate the orientation of dyes dissolved in the liquid crystal matrices, although the symmetry group of these dyes is not high enough to fix β at 0°.

The fluorescence spectra were measured using equipment described elsewhere.[26] The wavelengths of the excitation light were chosen to correspond to the absorption maximum of the dyes.

The fluorescence quantum efficiency of the dyes in isotropic solvents was calculated using the approximate relationship[27]

$$Q_x = Q_r\left[\frac{A_r(\lambda)}{A_x(\lambda)}\right]\left[\frac{I_r(\lambda)}{I_x(\lambda)}\right]\left[\frac{n_r^2}{n_x^2}\right]\left[\frac{D_x}{D_r}\right] \tag{4}$$

where Q_r is the quantum fluorescence yield of a standard, $I(\lambda)$ is the relative

intensity of the exciting light at wavelength λ, n is the refractive index, D is the integrated area under the corrected emission spectrum, $A(\lambda)$ is the absorbance of the solution at the exciting wavelength λ and the subscripts x and r refer to the unknown and reference solutions, respectively. The validity of eqn (4) is for dye concentrations of the order 10^{-6}M. As a standard, fluorescein in 0·1M NaOH was used. The quantum fluorescence yield of fluorescein is 0·92 at room temperature.[28]

From the polarized components of the fluorescence spectra, the order parameters of the dyes in liquid crystals were calculated using the equation[25]

$$S_F = \frac{F_{\parallel} - F_{\perp}}{F_{\parallel} + 2F_{\perp}} \tag{5}$$

This equation is valid for excitation with unpolarized light. $F_{\parallel}$ and $F_{\perp}$ are the intensities of fluorescence light polarized parallel and perpendicular to the liquid crystal orientation axis, respectively.

The temperatures of the nematic–isotropic phase transitions for pure nematics and doped with the dye were determined by means of a polarizing microscope (PZO Warszawa, Poland) with an accuracy of $\pm 0{\cdot}05$ K.

3 RESULTS AND DISCUSSION

3.1 Isotropic solvents

Tables 1 and 2 show the optical parameters of the dyes as obtained from absorption and fluorescence measurements in both of the solvents used.

TABLE 1
Spectral Properties of the Dyes in Toluene

Dye	λ_A^{max} (*nm*)	ε (1/*M cm*)	δ (*nm*)	λ_F^{max} (*nm*)	δ (*nm*)	Q_x	$\bar{\nu}_A - \bar{\nu}_F$ (cm^{-1})
DII	351	28 233[a]	70	480	60	0·09	7 557
	435		77				2 155
DV	431	16 000	70	485	54	0·42	2 583
DVI	435	10 450	69	485	50	0·61	2 370
DVII	420	17 659	66	480	53	0·27	2 976
DIX	420	14 480	69	480	53	0·35	2 976
DX	350	22 434[a]	72	485	55	0·17	7 551
	430		64				3 078
DXI	421	17 867	66	480	55	0·24	2 919

[a] Extinction coefficient calculated for long-wavelength maximum.
Dyes **DI**, **DIII**, **DIV** and **DVIII** were not soluble in toluene.

TABLE 2
Spectral Properties of the Dyes in Ethanol

Dye	λ_A^{max} (*nm*)	ε ($1/M\,cm$)	δ (*nm*)	λ_F^{max} (*nm*)	δ (*nm*)	Q_x	$\bar{\nu}_A - \bar{\nu}_F$ (cm^{-1})
DI	452	20694	71	515	62	0·21	2706
				535			3432
DII	346	17756[a]	85	513	62	0·13	2729
	450			533			3461
DIV	450	26174	72	518	58	0·38	2917
				540			3704
DV	450	11129	74	515	61	0·41	2706
				538			3635
DVI	450	14617	70	518	71	0·39	2917
				536			3566
DVII	445	24457	76	520	71	0·07	3241
				540			3953
DVIII	446	24975	70	513	59	0·74	2928
				538			3834
DIX	445	26610	74	515	75	0·27	3054
				536			3815
DX	346	29913[a]	74	520	71	0·08	3141
	447			533			3610
DXI	447	22282	73	513	66	0·32	2878
				536			3715

[a] Extinction coefficient calculated for long-wavelength maximum.
Dye **DIII** was not soluble in ethanol.

Figure 1 shows the absorption spectra of dyes **DVI** and **DX** in toluene and ethanol, and Fig. 2 the fluorescence spectra of dye **DIX** in both isotropic media.

As can be seen from the data presented in Tables 1 and 2 and in Figs 1 and 2, the polarity of the solvent significantly influences the spectral properties of the dyes. With increase in the solvent polarity, both the absorption and the emission maxima are shifted towards longer wavelenths. The absorption half-bandwidths of the dyes are independent of solvent polarity and are similar to each another. However, there is a distinct change in the fluorescence spectra when the polarity of the solvent increases. The fluorescence spectra in ethanol are broadened with respect to the spectra in toluene and this can be explained in terms of solute–solvent interactions.[29,30] Also, a second long-wavelength maximum appears in ethanol. On the basis of these observations, it is suggested that two fluorescence maxima are observed in polar solvents 'see below) in contrast to only one band in

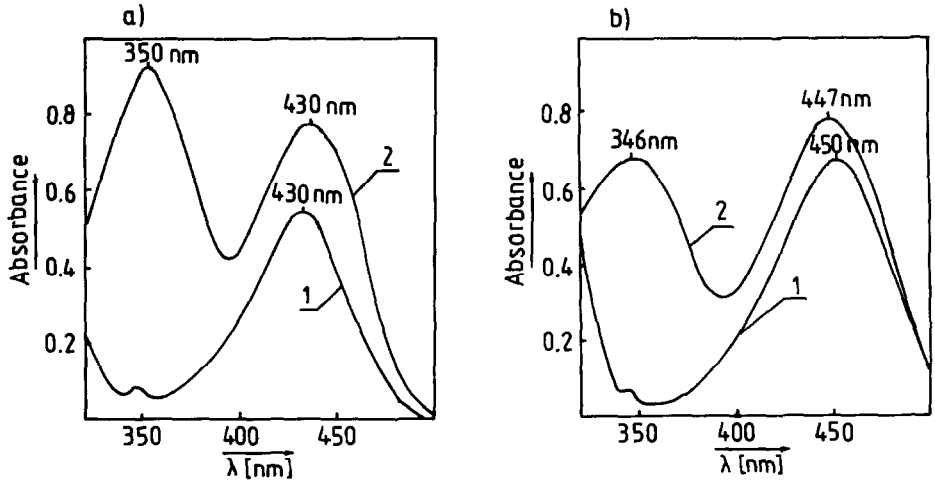


Fig. 1. Absorption spectra of dyes **DVI** (1) and **DX** (2) in (a) toluene and (b) ethanol.

non-polar solvents. The origin of this double peak is being investigated further.

There is no relationship between the polarity of the solvent and the quantum fluorescence yield of the dyes. The Q_x value appears to be affected by the individual molecular interactions between the dye and the solvent molecules.

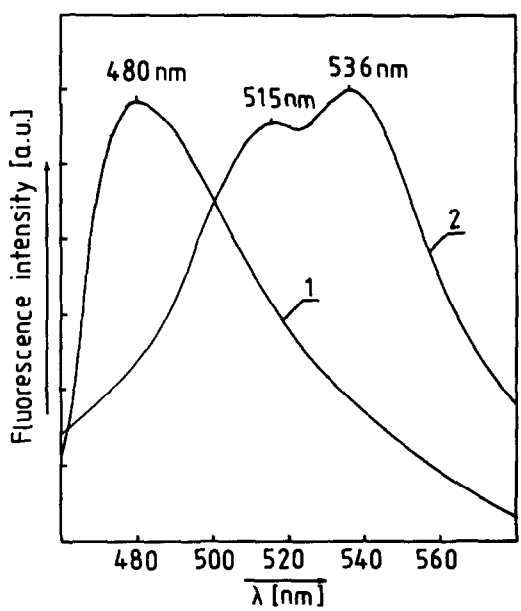


Fig. 2. Fluorescence spectra of dye **DIX** in (1) toluene and (2) ethanol.

TABLE 3
Optical Parameters of the Dyes in 6CB

Dye	λ_A^{max} (*nm*)	S_A'	λ^{max} (*nm*)		S_F	$\bar{\nu}_A - \bar{\nu}_{F\parallel}$ (cm^{-1})	$\bar{\nu}_A - \bar{\nu}_{F\perp}$ (cm^{-1})
			$F_\parallel$	$F_\perp$			
DI	443	0·61	509	506	0·40	2927	2811
			536	535		3917	3882
DII	448	0·52	507	505	0·33	2598	2519
			538	537		3734	3699
DIII	445	0·35	508	505	0·25	2787	2670
			537	535		3850	3780
DIV	441	0·51	508	507	0·35	2991	2952
			536	535		4019	3984
DV	445	0·51	510	508	0·34	2864	2787
			536	535		3815	3780
DVI	444	0·52	509	507	0·35	2826	2797
			539	539		3970	3970
DVII	446	0·56	503	500	0·40	2541	2422
			536	536		3765	3765
DVIII	446	0·55	504	503	0·38	2580	2541
			535	535		3730	3730
DIX	439	0·51	505	504	0·47	2977	2938
			538	537		4192	4157
DX	443	0·57	—	—	—	—	—
DXI	439	0·50	502	499	0·37	2859	2739
			538	537		4192	4157

Dye **DX** does not fluoresce in 6CB.

TABLE 4
Optical Parameters of the Dyes in W52

Dye	λ_A^{max} (*nm*)	S_A'	λ^{max} (*nm*)		S_F	$\bar{\nu}_A - \bar{\nu}_{F\parallel}$ (cm^{-1})	$\bar{\nu}_A - \bar{\nu}_{F\perp}$ (cm^{-1})
			$F_\parallel$	$F_\perp$			
DIV	439	0·61	499	498	0·52	2739	2699
			539	538		4226	4192
DVII	443	0·62	499	498	0·56	2533	2493
			541	541		4089	4089
DVIII	440	0·62	496	493	0·51	2566	2443
			543	541		4311	4243
DIX	447	0·67	499	498	0·54	2331	2291
			540	539		3353	3818
DX	440	0·44	—	—	—	—	—
DXI	438	0·55	499	498	0·54	2739	2699
			539	538		4226	4192

Dye **DX** does not fluoresce in W52.

3.2 Liquid crystals

Tables 3 and 4 present the values of the absorption and fluorescence maxima (λ^{max}), the Stokes shifts ($\bar{\nu}_A - \bar{\nu}_{F_\parallel}$), ($\bar{\nu}_A - \bar{\nu}_{F_\perp}$) and order parameters S'_A and S_F of the dyes in nematic liquid crystals 6CB and W52, and Fig. 3 shows the polarized components of the fluorescence spectra for dye **DIX** in 6CB.

From Tables 3 and 4 and Fig. 3, it is apparent that the positions of the maxima and values of the Stokes shifts for both polarized components of fluorescence are different. This is related to the anisotropy of the dielectric constant and the refractive index, both of which influence $\Delta\nu$ and maxima positions.[31]

For practical guest–host applications it is important to choose dyes with a high ability of orientation in the liquid crystal matrix and this is significantly dependent on dye structure,[32] dye concentration[9,16,17] and molecular interactions between the nematic host and the guest molecules.[17]

The order parameters of the dyes were different in both of the liquid crystals studied and were higher in W52 than in 6CB. Such differences in the dye order parameters in various liquid crystals indicate that molecular interactions in binary mixtures are specific to each guest–host system, as has been previously observed.[19,33] The values of S obtain in this present study

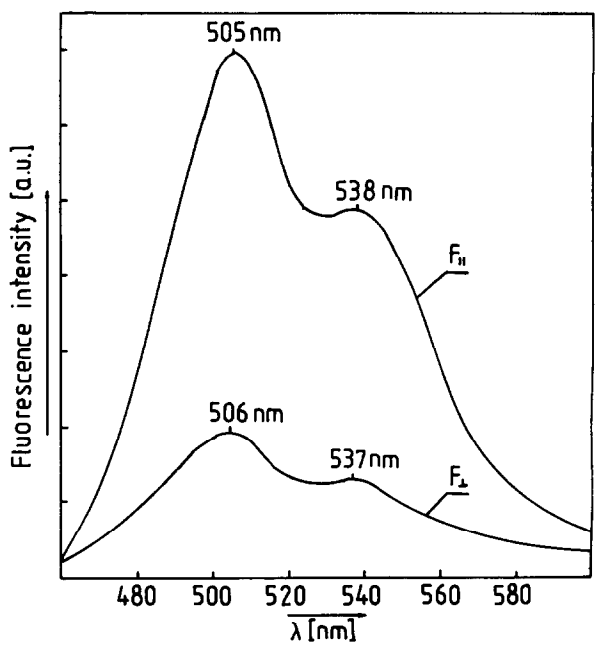


Fig. 3. Polarized components of the fluorescence spectra of dye **DIX** in 6CB.

TABLE 5
Temperature Data for Dye–6CB Mixtures

Substance	T_{NI} [K]	ΔT_{NI} [K]
pure 6CB	302·9	—
6CB + **DI**	303·0	+0·1
6CB + **DII**	303·1	+0·2
6CB + **DIII**	303·1	+0·2
6CB + **DIV**	303·0	+0·1
6CB + **DV**	303·0	+0·1
6CB + **DVI**	302·9	+0·0
6CB + **DVII**	303·0	+0·1
6CB + **DVIII**	303·1	+0·2
6CB + **DIX**	303·1	+0·2
6CB + **DX**	303·2	+0·3
6CB + **DXI**	302·8	−0·1

are higher than those for other fluorescent dyes previously investigated[12] and are acceptable for fluorescence display application.

The order parameter (S'_A) in all the cases was greater than S_F, and this is probably related to the large angle between the absorption and emission transition moments, especially in 6CB.

The nematic–isotropic temperatures T_{NI} were measured both for pure nematic and for dye-nematic mixtures. Values of T_{NI} for the dyes in 6CB are listed in Table 5, together with values of the shift in clearing point with respect to the pure liquid crystal (ΔT_{NI}).

Table 6 collates the results of temperature investigations of some dyes dissolved in W52. In the region of the clearing point, a two-phase region is observed in the case of W52. In this region both nematic and isotropic phases coexist. Therefore, in Table 6, T_N is the temperature at which the first drop of isotropic liquid appears, T_I is the temperature at which the last drop

TABLE 6
Temperature Data for Dye–W52 Mixtures

Substance	T_N [K]	T_I [K]	$T_I - T_N$	ΔT_N	ΔT_I	$\bar{T}_{NI}$	$\Delta \bar{T}_{NI}$
W52	334·3	335·4	1·1	—	—	334·85	—
W52 + **DIV**	334·6	336·0	1·4	+0·3	+0·6	335·30	+0·45
W52 + **DVII**	334·6	335·8	1·2	+0·3	+0·4	335·20	+0·35
W52 + **DVIII**	333·7	335·7	2·0	−0·6	+0·3	334·70	−0·15
W52 + **DIX**	335·3	336·4	1·1	+1·0	+1·0	335·85	+1·00
W52 + **DX**	333·5	335·2	1·7	−0·8	−0·2	334·35	−0·50
W52 + **DXI**	333·5	335·6	2·1	−0·8	+0·2	334·55	−0·30

of the nematic disappears when heated; $(T_I - T_N)$ is the range of the two-phase region and ΔT_N and ΔT_I are the shifts of T_N and T_I in relation to such temperatures for pure liquid crystals, respectively. In Table 6, the values of the average clearing temperature $\bar{T}_{NI}$ for the mixtures studied, and the average shifts $\Delta\bar{T}_{NI}$, are also listed.

Data from Tables 5 and 6 indicate that the dyes, with the exception of, dye **DXI**, do not destabilize the nematic phase of 6CB. For W52 there are some dyes which increase, and some which decrease, the transition temperature $\bar{T}_{NI}$, but this effect is rather small (less than 0·5 K). In most cases, extension of the two-phase region was observed after addition of the guest molecules. Such an effect has been predicted theoretically for nematic–non-mesogenic solute mixtures.[17,34] Comparing the results from Tables 5 and 6 with those from Tables 3 and 4, it can be concluded that some correlation between the order parameter S'_A and the transition temperature $\bar{T}_{NI}$ of the dye–liquid-crystal mixture occurs. Dyes which have quite high order parameters are more effective in stabilizing the nematic phase, causing an increase in the clearing temperature. However, dyes with low order parameter decrease the temperature of the nematic–isotropic phase transition. For example, dye **DX** ($S'_A = 0{\cdot}57$) increases $\bar{T}_{NI}$ of 6CB, whereas in W52 (where $S_A = 0{\cdot}44$), the clearing temperature after addition of dye is lowered. Similar effects have been previously observed for some azo dyes.[17,19,20,32]

The results obtained show that some of the dyes investigated can be used as guest species in fluorescent liquid crystal displays. They have an advantageous spectral region for the human eye, high or satisfactionary high quantum fluorescence yield and good pleochroic properties. Furthermore, they do not destabilize the nematic phase of the liquid crystal.

ACKNOWLEDGEMENT

This work was supported by project RP.II.13 coordinated by A. Mickiewicz University, Poznań, Poland.

REFERENCES

1. Heilmeier, G. & Zanoni, L. A., *Appl. Phys. Lett.*, **13** (1968) 91.
2. Heilmeier, G., Castellano, J. & Zanoni, L. A., *Mol. Cryst. Liq. Cryst.*, **8** (1969) 293.
3. Morita, M., Imamura, S. & Yatabe, K., *Jpn. J. Appl. Phys.*, **14** (1975) 315.
4. White, D. L. & Taylor, G. N., *J. Appl. Phys.*, **45** (1974) 4718.
5. Kawarada, H., Tatsumichi, T. & Otsuka, T., Paper presented at International Electron Devices Meeting, **301**, December 1981.

6. Uchida, T., Seki, H. & Shishido, C., *Proc. SID*, **22** (1981) 41.
7. Uchida, T., Shishido, C., Seki, H. & Wada, M., *Mol. Cryst. Liq. Cryst.*, **39** (1977) 39.
8. Cognard, J. & Phau, T. H., *Mol. Cryst. Liq. Cryst.*, **68** (1981) 207.
9. Salamon, Z. & Bauman, D., *Mol. Cryst. Liq. Cryst. Lett.*, **82** (1982) 115.
10. Bauman, D. & Salamon, Z., *Opt. Comm.*, **48** (1984) 306.
11. Larrabee, R., *RCA Review*, **34** (1973) 329.
12. Bauman, D., Skibiński, A. & Stolarski, R., *Mol. Cryst. Liq. Cryst.*, **138** (1986) 367.
13. Van Ewyk, R. L., O'Connor, I., Mosley, A., Cuddy, A., Hilsum, C., Blackburn, C., Griffiths, J. & Jones, F., *Displays*, **10** (1986) 155.
14. Fiksinski, K. J. & Stolarski, R., *Proc. XII International Liquid Crystal Conference*, **376**, Freiburg (1988).
15. Diot, P., Foitzik, J. K. & Haase, W., *Rev. Phys. Appl.*, **20** (1985) 121.
16. Haase, W., Trinquet, O., Quotschalla, U. & Foitzik, J. K., *Mol. Cryst. Liq. Cryst.*, **148** (1987) 15.
17. Bauman, D., *Mol. Cryst. Liq. Cryst.*, **159** (1988) 197.
18. Bauman, D., *Mol. Cryst. Liq. Cryst. Lett.*, **5** (1988) 123.
19. Bauman, D., *Mol. Cryst. Liq. Cryst.*, **172** (1989) 41.
20. Bauman, D., Jadżyn, J. & Czechowski, Z., *Acta Phys. Polon.*, **A75** (1989) 697.
21. Stolarski, R. & Jankowski, Z., Polish Patent Appl. 264991/87.
22. Cehelnik, E. D., Cundall, R. B., Timmons, C. J. & Bowley, R. M., *Proc. Roy. Soc. London Ser.*, **A335** (1973) 387.
23. Filas, R. W. & Labes, M. M., *J. Appl. Phys.*, **52** (1981) 3949.
24. Ivashchenko, A. V., Petrova, O. S. & Titov, V. V., *Mol. Cryst. Liq. Cryst.*, **108** (1984) 51.
25. Baur, G., *Local Properties at Phase Transitions.* Editrice Compositori, Bologna (Italy) LIX Corso, 1975.
26. Frackowiak, D., Erokhina, L. G., Balter, A., Lorrain, L., Szurkowski, J. & Szych, B., *BBA*, **85** (1986) 173.
27. Demas, J. N. & Crosby, G. A., *J. Phys. Chem.*, **75** (1971) 991.
28. Boardman, N. K. & Thorne, S. W., *Biochim. Biophys. Acta*, **153** (1968) 448.
29. Liptay, W., *Z. Naturforsch.*, **20a** (1965) 1441.
30. Kawski, A. & Pasztor, B., *Acta Phys. Polon.*, **31** (1967) 357.
31. Kawski, A., *Acta Phys. Polon.*, **25** (1964) 285.
32. Bloom, A. & Hung, P. L. K., *Mol. Cryst. Liq. Cryst.*, **40** (1977) 213.
33. Bauman, D., *Mol. Cryst. Liq. Cryst.*, **172** (1989) 41.
34. Martire, D. In *The Molecular Physics of Liquid Crystals*, ed. G. R. Luckhurst and G. W. Gray. Academic Press, 1979, Ch. 10.