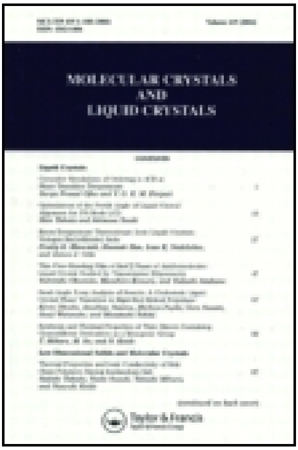

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Guest-Host Interaction of Pleochroic Dyes in Liquid Crystal Mixtures E $_8$ and PCH-1132

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The ordering of a large number of pleochroic azo and anthraquinone dyes, has been investigated in two technologically important mesogenic mixtures E_8 and PCH-1132 at various temperatures. The effect of molecular geometry (i.e. length and breadth) of the dyes and the nature of the host on the order parameter of these dyes are examined.

INTRODUCTION

Liquid crystal, black and white displays based on twisted nematic and dynamic scattering modes have been put to practical use for electronic watches, calculators, digital instruments etc. Low power consumption, low voltage operation, ease in fabrication etc. are the distinctive features which makes these displays preferable to other displays like gas discharge, L.E.D. etc. However, compared to light emitting diodes where displays are available in almost every desired color, LCD's, presently available in the market have the distinct disadvantage of eye appeal being only black on a colorless background. Attempts are being made throughout the world to overcome this lacuna of LCD's by developing colored liquid crystal displays.[1–4] Liquid crystal colored displays based on guest-host interaction in conjunction with the cholesteric-nematic phase transition seem to have considerable potentiality.[1,2] The performance characteristics of displays of this type are strongly dependent on various physical parameters of the dye like its compatibility with the host, its order parameter, dichroic ratio etc. In this paper we are reporting physical parameters of a large number of dyes with different stereochemistry in two technologically important mixtures E_8 and PCH-1132. Some of the dyes reported in this study are presently being exploited for display fabrication. Very little work has been done to study the temperature variation of the order parameter of the dyes in the liquid crystal matrix,[5] which is not only important from basic physics point of view but also to evaluate the satisfactory performance of the display over a wide temperature range. The temperature variation of the order parameter of some of these dyes are also reported here.

EXPERIMENTAL

(a) Material

Dyes were procured in purest available form from M/s BDH (England) and Riedel de Haen (Germany) and were used as such. In Table I are given the structure of the various dyes used in the present investigations. Dyes Nos. 1 to 8 are azo dyes and Nos. 9 to 11 are anthraquinone dyes. The host liquid crystals for these investigations were E_8 and PCH-1132, obtained from M/s BDH (England) and M/s E. Merck (Germany) respectively. E_8 is the eutectic mixture of three cyanobiphenyls and one cyanoterphenyl while PCH-1132 is the eutectic mixture of three cyanophenylhexanes and one cyanobiphenylhexane.[6] The transition temperatures of these materials are

E_8: Solid $\xrightleftharpoons{-12°C}$ Nematic $\xrightleftharpoons{70°C}$ Isotropic

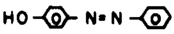
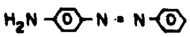
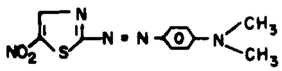
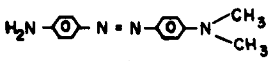
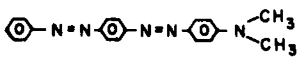
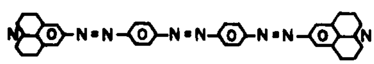
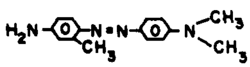
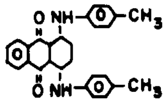
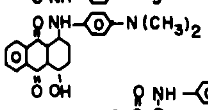
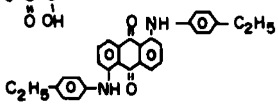
PCH-1132: Solid $\xrightleftharpoons{-6°C}$ Nematic $\xrightleftharpoons{70°C}$ Isotropic

(b) Absorption measurements

The dyes were dissolved in liquid crystal host in very small quantity (~0.5%) so that the dye molecules have liquid crystal molecules as near and near near neighbors and supposedly experience only the influence of the liquid crystal molecules. In order to know the effect of concentration of the dye molecules in liquid crystalline host, two dyes D_3 and D_4 were mixed in E_8 and PCH-1132 in various concentrations (upto solubility limit of 1–2%). Hermetically sealed cells treated for unidirectional homogeneous alignment through PVA, silane or SiO with a spacing of ~12 μm were filled with dye liquid crystal mixture.

The wavelength of maximum absorption (λ_{max}) was recorded by placing the cell in Karl Zeiss spectrophotometer. The cell (A) filled with dye in liquid crystal host along with the compensatory cell (B) identically fabricated but filled with liquid crystal host alone were mounted vertically in a heating assembly which is placed in between a monochromator (M) and photomultiplier detector P_{21}. A polarizer which can be rotated along a horizontal axis with respect to cell is placed in front of the cell to polarize the monochromatic light in the desired direction i.e. parallel or perpendicular to the optic axis of the cell. Transmission of the light polarized parallel to optic axis ($T_{\parallel}$) and that polarized perpendicular to the optic axis ($T_{\perp}$) were measured. Temperature of the

TABLE – I

S. NO.	STRUCTURE		WAVELENGTH OF MAXIMUM ABSORPTION IN nm λ_{max}	ORDER PARAMETER IN			
				E_8		PCH–1132	
				$S_{obs.}$	$S_{cor.}$	$S_{obs.}$	$S_{cor.}$
1.			430	.46	.51	.50	.53
2			450	.60	.64	.61	.64
3			455	.62	.66	.64	.67
4		(D_1)	594	.68	.71	.69	.71
5			450	.71	.74	.71	.73
6		(D_2)	505	.75	.78	.76	.78
7		(D_3)	568	.79	.82	.79	.81
8			450	.55	.59	.57	.60
9		(D4)	660	.46	.51	.50	.53
10		(D_{27})	554	.64	.68	.66	.68
11		(D_{35})	612	.66	.70	.67	.69

REMARK : D_1 , D_2 , etc. ARE THE NAMES GIVEN TO DYES BY BDH (ENGLAND)

cell was controlled with an accuracy of $\pm 0.1°$ by circulating water in the heating jacket from the thermostat model U 10. Temperature of the cell was monitored by a copper constantan thermocouple. $T_{\parallel}$ and $T_{\perp}$ are measured at λ_{max}. Experimental arrangement is shown in Figure 1.

RESULTS AND DISCUSSION

If a dye, having an attenuation constant α_0 in an isotropic host, is dissolved in a liquid crystalline host, the transmission of the light polarized parallel, $T_{\parallel}$,

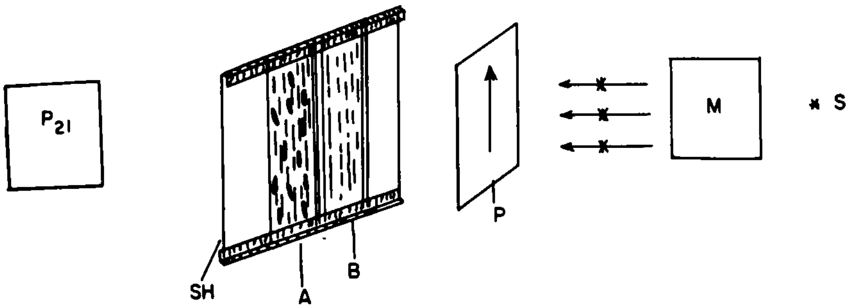


FIGURE 1 Experimental set up for the measurement of order parameter of dye.

and that polarized perpendicular, $T_\perp$, to the optic axis of the mixture will be given by

$$T_\parallel = \exp[-(2S + 1)\alpha_0 D] \qquad \text{or } \alpha_\parallel = (2S + 1)\alpha_0$$

$$T_\perp = \exp[-(1 - S)\alpha_0 D] \qquad \text{or } \alpha_\perp = (1 - S)\alpha_0$$

where D is the thickness of the sample. When $S = 1$, $T_\perp = 1$ and $T_\parallel = \exp(-3\alpha_0 D)$ and when $S = 0$, $T_\parallel = T_\perp = \exp(-\alpha_0 D)$ i.e. similar to an isotropic medium. It is easy to see that if $T_\parallel$ and $T_\perp$ of a particular liquid crystal + dye system are known, one can compute the order parameter of the dye S from the relation

$$S_{\text{obs}} = \frac{\text{Log } T_\parallel - \log T_\perp}{\log T_\parallel + 2 \log T_\perp}$$

The losses due to scattering, reflection and transmission from the cell walls and the host molecules can be compensated by taking the transmission from a similar cell, filled with liquid crystal host only, as the reference.

In the above relation the effect of the internal fields are not considered. The correction to $T_\parallel$ and $T_\perp$ for the local field yields slightly different value of the order parameter.[5,7] The corrected order parameter was evaluated from the relation.

$$S_{cor} = \frac{n_e \log T_{\parallel} - n_o \log T_{\perp}}{n_e \log T_{\parallel} + 2n_o \log T_{\perp}} = \frac{\dfrac{n_e}{n_o} \log T_{\parallel} - \log T_{\perp}}{\dfrac{n_e}{n_o} \log T_{\parallel} + 2 \log T_{\perp}}$$

Here n_o and n_e are the ordinary and extraordinary refractive indices of liquid crystal at λ_{max}. Taking the measured values of n_e and n_o at $\lambda = 5893$ Å (which is slightly different from λ_{max}) and assuming that n_e/n_o is essentially unaffected by small change in λ, we have calculated S_{cor} from the above relation.†

The order parameter (S_{obs} and S_{cor}) of the various dyes in the two liquid crystalline hosts E_8 and PCH-1132 are given in Table I. These measurements were carried out at 20°C (room temperature). In one of the columns of this table, the wavelength of maximum absorption of the dye in liquid crystal E_8 is also given. D_1, D_2 etc. are the names given to the dyes by M/s BDH Chemicals. To avoid the writing of long names we will designate them in Table I as dye 1, dye 2 etc. in serial order. From the data of order parameter given in Table I, the following observations can be made:

Effect of length on the order parameter of dye

It may be noted that the length of the dye increases as one moves from dye 1 to dye 7. Interestingly, both in E_8 and PCH-1132, the order parameter of the dye increases as we move from dye 1 to dye 7. From the table we also observe that the order parameter of the dye with single azo-linkage (dye 5) is less than that of the dye with two azo-linkage (dye 6) which is again less than the order parameter of dye with three azo-linkages (dye 7). This general trend of the increase in the order parameter with increase in length of the dye molecule is in agreement with the work reported by Blinov *et al.*,[5] and by Constant *et al.*[10] Similarly in anthraquinone dyes, the order parameter of dye 11, (the length of which is more than that of dye 10), is more than the order parameter of dye 10 in the same host. In general, the order parameter of the dye is less than that of the host [~0.7 for E_8 and PCH-1132 at room temperature[11] (Figure 2)], the difference being more for dyes with smaller lengths. However, in few cases like that in dye 6 and dye 7, we find that the order parameter of the dye is more

† The correction factor (n_e/n_o) for E_8 is nearly equal to that of E_7, a composition similar to E_8. In the case for E_7 the data for n_e and n_o in the entire temperature range and at various wavelengths is available.[8,9] To see the effect of using the values of correction factor n_e/n_o at wavelength different from λ_{max} on the order parameter, we used for E_8, the corresponding values of n_e/n_o for E_7 at various wavelengths ($\lambda = 436$ nm, 509 nm, 577 nm and 644 nm) and found that the order parameter of the various dyes in E_8 does not deviate by more than 2% at any temperature.

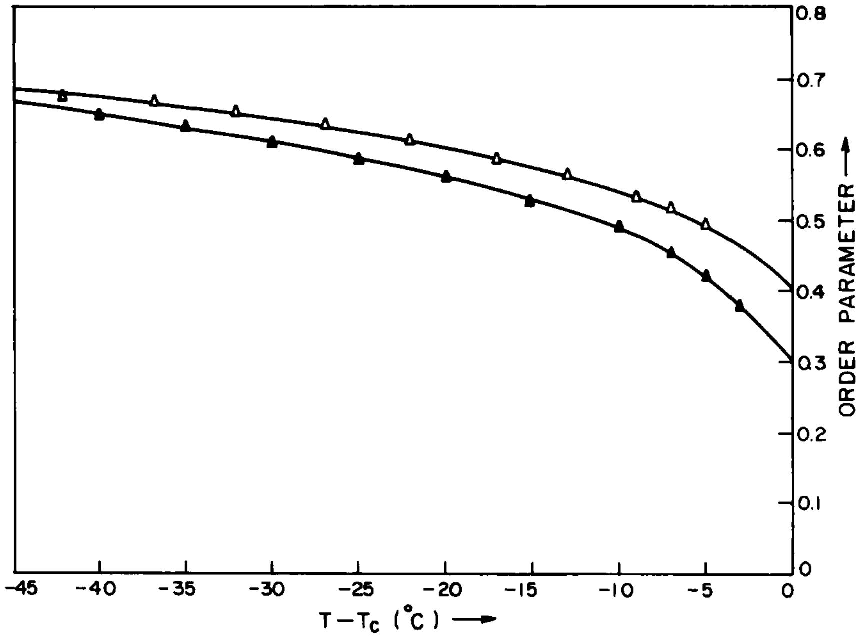
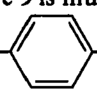


FIGURE 2 Temperature variation of order parameter of E_8 (—▲—▲—) and PCH-1132 (—Δ—Δ—) obtained using Vuks approach.

than that of the liquid crystalline host. In these cases it seems that the dye molecules, because of their long lengths, are able to overcome the thermal fluctuations to some extent.

Effect of breadth on the order parameter of dye

The molecular length of dye 8 is nearly equal to that of dye 5 and is more than that of dye 2. However, the order parameter of dye 8 is less than that of both dye 2 and dye 5. The reason for this is the increase in the breadth of dye 8 because of the CH_3 substituent at the ortho position of the ring. Similarly, although the lengths of dye 9 and dye 10 are nearly equal, the order parameter of dye 9 is much less than that of dye 10 because of the presence of additional NH—  —CH_3 side group in dye 9 which makes it more spherical in structure. From these results it seems that the order parameter of the dye decreases with increasing breadth. This order parameter behavior may be due to the transition moment of the dye becoming non-parallel to the director in the host and rotating about the director at an angle to it rather than to an increase in the angular thermal fluctuations of the dye or to a decrease in the dichroic ratio (ratio of the optical densities $A_{\parallel}/A_{\perp}$) of the dye. This may happen in two ways: (a) the transition moment of the dye becomes non-parallel to the geometrical long axis of the dye (b) the dye transition moment remains parallel to the long axis of the dye but the molecular structure of the dye is altered so that its long axis lies at an angle to the director in the host and rotates precessionally about the director. This explanation is highly speculative and more experimentation is needed to ascertain the exact mechanism. Constant *et al.*[4] believe that both these effects may occur together to give the observed reduction in the measured order parameter associated with such side substituents.

Effect of the host on the order parameter of the dye

In order to study the effect of the host on the order parameter of the dye, the order parameter of all the dyes were determined in two liquid crystalline mixtures E_8 and PCH-1132. The molecular structure of E_8 and PCH-1132 are quite different. E_8 consists of cyanobiphenyl and cyanoterphenyl components whereas PCH-1132 consists of cyanophenylhexane and cyanobiphenylhexane components. We find from the order parameter curves of E_8 and PCH-1132 (Figure 2)[11] that the order parameter of E_8 and PCH-1132 at room temperature are very close (~0.7). From Table I we find that the values of the order parameter of all the dyes are nearly equal in the two hosts. It appears that the order parameter of the dye is governed more by the order parameter of the host rather than by the structure of the host.

Temperature variation of the order parameter of dyes

It is of interest to see how the ordering of the dye molecules dissolved in a particular liquid crystalline matrix changes with the change in the ordering of the liquid crystal molecules as the temperatures of the mixture is varied. For this purpose the order parameter of the liquid crystal obtained from the birefringence measurements is compared with the order parameter of the dye obtained from the absorption measurements. The order parameter of the liquid crystal + dye mixture obtained from refractive indices measurements is found to be same as that of the pure liquid crystal. (The refractive indices n_o, n_e are found to be same and the density is not expected to change appreciably by the addition of 0.5% of dye.) The order parameters of liquid crystals E_8 and PCH-1132 in the nematic liquid crystalline range at various temperatures is given in Figure 2. The order parameter of six dyes (D_1, D_3, D_4, dye 3, D_{27}, D_{35}) dissolved in E_8 in the same temperature range are shown in Figures 3 to 8. The order parameter of the same six dyes in PCH-1132 are also shown in Figures 3 to 8. The dyes chosen for the purpose consist of four azo dyes and two anthraquinone dyes with minimum as well as maximum order parameter.

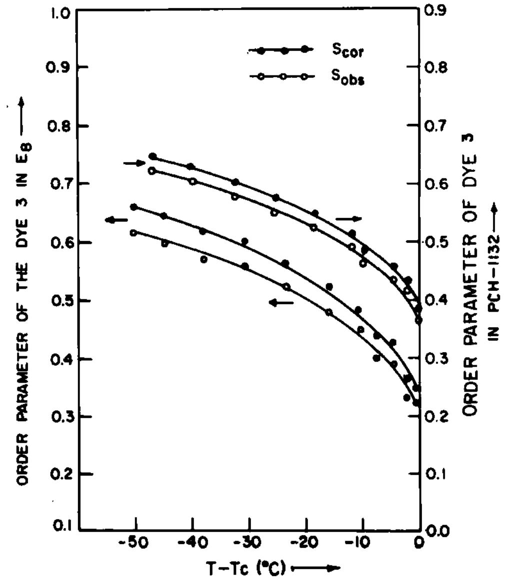


FIGURE 3 Temperature variation of the order parameter of dye 3 in the liquid crystal E_8 and PCH-1132.

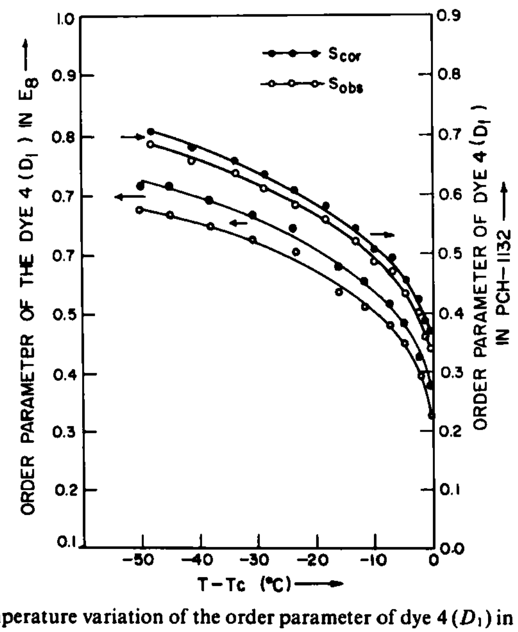


FIGURE 4 Temperature variation of the order parameter of dye 4 (D_1) in the liquid crystal E_8 and PCH-1132.

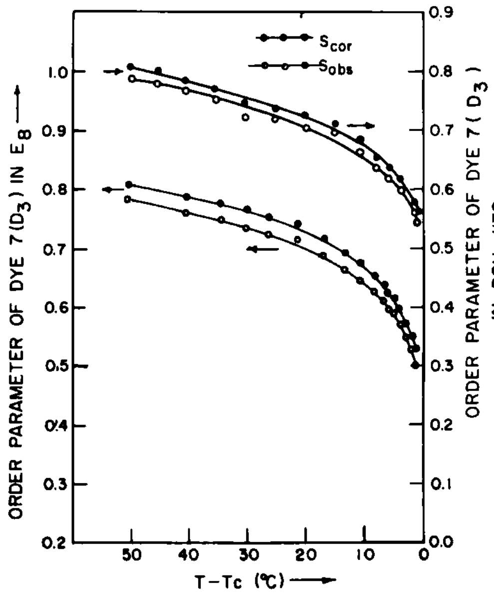


FIGURE 5 Temperature variation of the order parameter of Dye 7 (D_3) in the liquid crystal E_8 and PCH-1132.

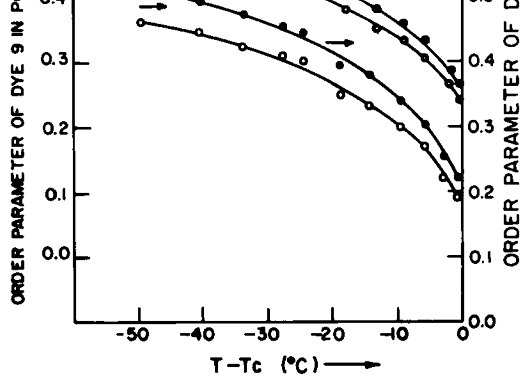


FIGURE 6 Temperature variation of the order parameter of dye 9 (D_4) in the liquid crystal E_8 and PCH-1132.

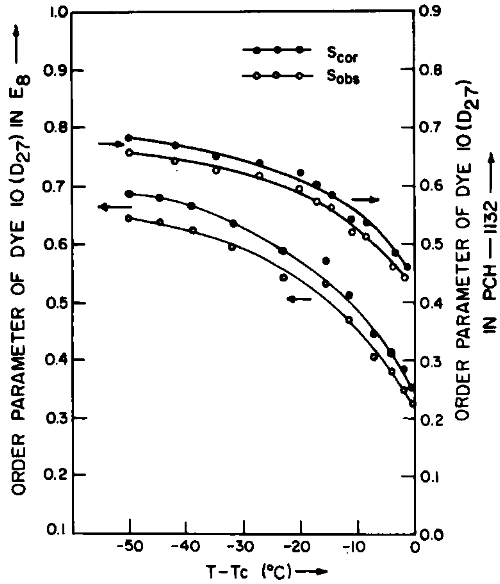


FIGURE 7 Temperature variation of the order parameter of dye 10 (D_{27}) in the liquid crystal E_8 and PCH-1132.

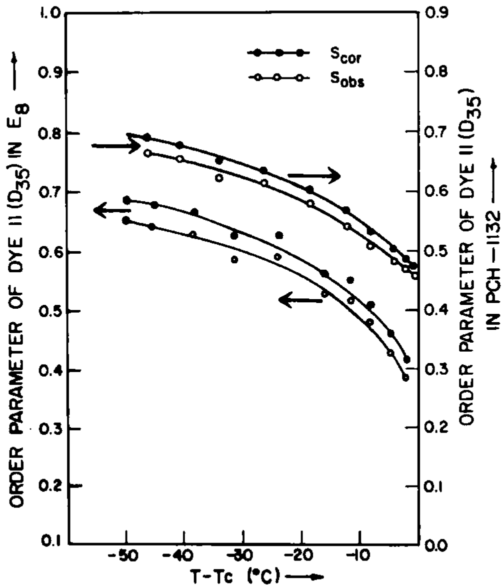


FIGURE 8 Temperature variation of the order parameter of Dye 11 (D_{35}) in the liquid crystal E_8 and PCH-1132.

As the temperature is increased from room temperature, the order parameter of the dye starts decreasing and near the nematic-isotropic phase transition, the order parameter decreases sharply and goes to zero as the material turns completely isotropic, a behavior similar to that exhibited by pure liquid crystals. The ratio of the order parameter of dye (S_{cor}) obtained from absorption measurements and the order parameter of liquid crystal (S_v) determined through birefringence technique (Vuks approach) is given in Table II for the entire temperature range. From Table II and Figures 3 to 14, it can be seen that the nature of the order parameter curve of all the dyes follows approximately that of the host. From the observation, it follows that the order parameter of liquid crystals can be estimated using a suitable dye and employing the transmission technique. Another conclusion that can be drawn is that since the order parameter of the dye follows a variation similar to that of a liquid crystal, the choice of the dye-liquid crystal mixture for use in colored displays will depend upon the choice of the liquid crystal whose order parame-

TABLE II

Ratio of the order parameter of dye (S_d) and the order parameter of liquid crystal calculated by using Vuks approach (S_V)

Dyes dissolved in E_8

Temperature T-T_c (°C)	S_{d3}/S_V	S_{d4}/S_V	S_{d7}/S_V	S_{d9}/S_V	S_{d10}/S_V	S_{d11}/S_V
5	1.00	1.14	1.45	0.70	1.01	1.10
10	0.96	1.09	1.36	0.70	1.00	1.06
15	0.95	1.08	1.33	0.72	1.00	1.04
20	0.96	1.08	1.30	0.74	1.01	1.04
25	0.96	1.07	1.27	0.74	1.02	1.03
30	0.97	1.07	1.25	0.75	1.02	1.03
35	0.97	1.07	1.23	0.75	1.03	1.03
40	0.97	1.06	1.21	0.75	1.02	1.07

Dyes dissolved in PCH-1132

Temperature T-T_c (°C)	S_{d3}/S_V	S_{d4}/S_V	S_{d7}/S_V	S_{d9}/S_V	S_{d10}/S_V	S_{d11}/S_V
5	0.93	0.93	1.28	0.66	1.02	1.04
10	0.92	0.95	1.24	0.67	1.02	1.01
15	0.91	0.96	1.22	0.68	1.02	1.01
20	0.92	0.97	1.19	0.69	1.01	1.01
25	0.92	0.98	1.18	0.70	1.01	1.01
30	0.92	0.99	1.17	0.71	1.00	1.00
35	0.92	1.00	1.16	0.72	0.99	1.00
40	0.93	1.00	1.16	0.73	0.99	1.00

Note: S_{d1}, S_{d2}, . . . etc. are the order parameter of the dye 1, dye 2 . . . etc.

ter is high and also does not appreciably change with temperature in the temperature range of interest.

A close examination of Table II reveals that dyes having order parameter more than the host in entire temperature region exhibit different thermal behavior than those having order parameter less than the host. Dyes having S_d/S_v appreciably higher than 1 show that S_d/S_v increases with increasing temperature whereas the reverse is observed for dyes have $S_d/S_v < 1$. This means that the dyes appreciably longer than the liquid crystal host are more resistant to thermal fluctuations while the dyes shorter than the liquid crystal host are less resistant to thermal fluctuations compared to the host liquid crystals. This also indicates that elongated dyes will have an additional advantage for colored liquid crystal displays.

Effect of concentration on the order parameter of dye

Since the dyes used are soluble in liquid crystals upto only a very small percentage (~1–2%), the measurements were taken separately for 0.2, 0.5 and 1.0 per cent of dyes D_3 and D_4 dissolved in liquid crystal E_8 in entire temperature range. Within the solubility limit it was found that the concentration of the dye has no effect on the order parameter of dye.

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