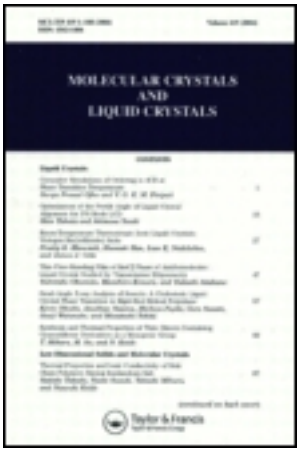

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THE EFFECT OF HOST ON PLEOCHROIC DYE ORDER PARAMETER

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Abstract The order parameters of three dyes in seven nematic liquid crystalline hosts have been measured. A correlation between a dye's length and its order parameter could be seen. Variations of as much as 50% in a dye's order parameter occurred on changing host.

A number of investigations have been concerned with the properties of pleochroic dyes in nematic liquid crystalline hosts.[1-6] We have previously shown that the order parameter, S, of a dye in a nematic host is greatly affected by the structure of the dye.[6] Here we report on the effect of host on dye order parameter. Indeed, variations of S of 50% or more can be observed by changing host.

The order parameter is given by the formula

$$S_{obs} = \frac{A_{\parallel} - A_{\perp}}{2A_{\perp} + A_{\parallel}} \qquad (1)$$

where $A_{\parallel}$ is the optical density of the dye at its absorption maximum when aligned parallel to the liquid crystal host as measured with plane-polarized light oriented parallel to the liquid crystal director, and $A_{\perp}$ is the optical density of the dye at its absorption maximum as measured by plane-polarized light oriented perpendicular to the liquid crystal director. The measuring techniques have been previously described.[6] A number of workers have suggested that it is appropriate to correct the dye order parameter for the refractive index anisotropies of the host:[3,5]

$$S_{cor} = \frac{A_{\parallel} n_{\parallel} - A_{\perp} n_{\perp}}{2A_{\perp} n_{\perp} + A_{\parallel} n_{\parallel}} \qquad (2)$$

where $n_{\parallel}$ is the refractive index of the host in the alignment direction and $n_{\perp}$ is the refractive index of the host perpendicular to the alignment direction.

The hosts we have used in this study, as well as some of their relevant physical properties, are listed in Tables I and II, respectively. These nematic hosts have been used by many workers and most are commercially available. The dyes were carefully purified by repeated column chromatography and recrystallized until the material showed one tlc spot in several solvents and had satisfactory elemental analysis. S_{obs} for three dyes in the seven hosts we investigated are shown in Table III along with the absorption maximum for the dye in the liquid crystalline host. The order parameters, S_{obs} and S_{cor}, were calculated using (1) and (2), respectively. The refractive index values at 546 nm were used for these calculations.[7] The small deviations of the absorption maxima of the dyes from 546 nm does not introduce an error of more than a few percent.[3,5] In all cases, the S_{cor} value was 0.03 to 0.05 higher than the corresponding S_{obs} value.

TABLE I Nematic Hosts

Designation	Host
I.	4-Methoxybenzylidene-4'-butylaniline (MBBA).
II.	A 1:1 molar mixture of 4-ethoxybenzylidene-4'-butylaniline (EBBA) and MBBA.
III.	A mixture containing 85 wt% of a 70:30 molar mixture of MBBA-EBBA and 15 wt% of 4-ethoxybenzylidene-4'-aminobenzonitrile.[a]
IV.	Hoffmann-LaRoche RO-TN-101, an ester mixture.
V.	Hoffmann-LaRoche RO-TN-200, a Schiff base mixture.
VI.	BDH E-7, a mixture of biphenyls and terphenyls.
VII.	A 1:1:1 molar mixture of 4-butoxybenzylidene-4'-aminobenzonitrile, 4-hexoxybenzylidene-4'-aminobenzonitrile, and 4-octanoyloxybenzylidene-4'-aminobenzonitrile.[b]

[a] H.A.Tarry, S.E.R.L.Tech.J. 23, 5.1(1973).

[b] M.Schadt and W.Helfrich, Appl.Phys.Lett. 18, 127(1971).

TABLE II Physical Properties of Nematic Hosts

Host	T_{CN}(°C)	T_{NL}(°C)	$T_{NL}-T_{23}$(°C)	$\varepsilon_{\parallel}^{a}$	$\varepsilon_{\perp}^{a}$
I.	22	48	25	4.6	5.2
II.	0	60	37	4.6	5.1
III.	-9	40	63	8.8	5.7
IV.	0	71	48	24.9[b]	7.2[b]
V.	-15	41	64	26.8	7.7
VI.	-10	37	60	18.5	5.3
VII.	20	94	71	26[c]	8[c]

[a] See Ref.7.

[b] Hoffmann-LaRoche product bulletin.

[c] M.Schadt, J.Chem.Phys. 56, 1494(1972).

TABLE III Order Parameters of Dyes in Liquid Crystal Hosts

Host \ Dye	O_2N-⟨⟩-N=N-⟨⟩-$N(C_2H_5)_2$			O_2N-⟨⟩-N=N-⟨⟩-N=N-⟨⟩-$N(C_2H_5)_2$			O_2N-⟨S,N⟩-N=N-⟨⟩-$N_2(C_2H_5)_2$		
	S_{OBS}	A	$\lambda^{max}_{(nm)}$	S_{OBS}	B	$\lambda^{max}_{(nm)}$	S_{OBS}	C	$\lambda^{max}_{(nm)}$
I.	0.42		505	0.54		540	0.38		595
II.	0.51		505	0.70		542	0.48		593
III.	0.55		506	0.65		538	0.46		595
IV.	0.50		510	0.66		545	0.48		595
V.	0.50		513	0.66		550	0.52		603
VI.	0.60		513	0.73		545	0.59		600
VII.	0.62		514	0.72		550	0.60		603

There appears to be a general correlation between the length of the dye molecule and its order parameter. We have previously shown that dye structure is an important factor in influencing dye alignment,[6] but since the three dyes described here do have the same end groups, some comparisons can be made. B, the longest dye molecule has a higher order parameter than A or C in all hosts. Dyes A and C are of about the same length and, in most hosts, A and C do have similar order parameters. However, as A and C in Host III demonstrate, the solute-solvent interactions

are host dependent and can cause changes in the relationship dye order parameters have with each other. It is, therefore, hazardous to infer the order parameter of the host from that of the dye. A ranking of each dye's order parameter in the different nematic hosts allows us to speculate that the order parameters of the nematic liquid crystalline hosts increase as follows: I < II-V < VI, VII.

No ready correlation exists between the physical properties of the hosts listed in Table II and the order parameter of the dye guest. A more detailed understanding of the interactions on a molecular level between guest and host will have to be developed before firm structure-property correlations can be made.

In conclusion, we have measured the order parameters for three pleochroic dyes in seven liquid crystalline hosts, and found the dye order parameter to be host-dependent. We demonstrate the difficulties involved in determining a host's order parameter from a guest dye's order parameter.

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