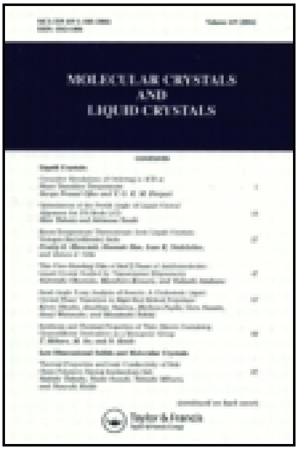

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

The Effect of Dye Structure on Order Parameter in a Nematic Liquid Crystalline Host[1]

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To cite this article: Allen Bloom & P. L. K. Hung (1977): The Effect of Dye Structure on Order Parameter in a Nematic Liquid Crystalline Host[1] , Molecular Crystals and Liquid Crystals, 40:1, 213-221

To link to this article: http://dx.doi.org/10.1080/15421407708084484

Mol. Cryst. Liq. Cryst., 1977, Vol. 40, pp. 213–221

Printed in Holland

The Effect of Dye Structure on Order Parameter in a Nematic Liquid Crystalline Host[1]

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(*Received October 14, 1976*)

The order parameters (S) of a number of substituted azobenzenes and phenylazothiazole, -benzothiazole and -heterocyclic compounds dissolved in a nematic liquid crystalline host have been determined. The measured order parameters for a class of azo compounds bear a strong relationship to the structure of the dye. For azobenzenes, there is an additivity of substituent effects which leads to good agreement between empirically-derived and observed S values. Disazo dyes give higher S values than the corresponding monoazo dyes. For heterocyclic phenylazo dyes, the end group substituents on the phenyl ring play a significant role in influencing S, whereas the nature of the heterocyclic system, as well as the end group substituents on the heterocyclic ring, are only of minor importance. The presence of an N—H moiety as part of a heterocyclic ring, or the fusion of a benzene ring onto a heterocyclic ring, can lead to significant changes in the order parameter.

INTRODUCTION

The phenomena associated with the addition of pleochroic dyes to liquid crystalline hosts have been the focus of several studies[2–5] since the report of Heilmeier and Zanoni.[6] The order parameter, S, is used as a measure of how well a dye molecule is aligned with the orientation direction of the liquid crystalline host. If dye molecules are chosen such that their geometric long axis corresponds to the direction of absorption polarization and the contribution to the absorption caused by molecular polarization in the perpendicular direction are small, then the order parameter can be obtained using plane polarized light by means of the formula[3]

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

where $A_{\parallel}$ is the optical density of the dye at its absorption maximum ($\lambda^{\max}$) when the polarizer direction is parallel to the alignment direction, and $A_{\perp}$ is the optical density at $\lambda^{\max}$ when the polarizer direction is perpendicular to the alignment direction.

In this paper we present the results of a study of the influence on order parameter of dye structure and substitution.

A number of azobenzenes, disazobenzenes, and heterocyclic phenylazo compounds were used, and a consistent pattern of correlations between structure and order parameter emerged. The host used was a Schiff base mixture having a positive dielectric anisotropy with a nematic range of −9 to 63°C.[7] This host allowed us to see small changes in dye structure reflected in the order parameter. We found that dyes of high purity, as determined by combustion analysis, were necessary for accurate, reproducible results.

EXPERIMENTAL

A Measurements

The cell used consisted of two glass plates, 2.5 × 2.5 cm in area. each having a transparent, conductive layer of indium-doped tin oxide onto which a SiO_x layer was evaporated at an angle of 30° to the horizontal to give parallel alignment.[8,9] The top plate had two diagonally placed holes (1 mm diameter) to allow flow filling. The plates were separated by 12 μm spacers and epoxy-sealed together. The cells were flushed with acetone, methanol, and nitrogen prior to filling. The dye concentration was *ca.* 0.3 wt %.

The optical density was measured on a Cary 14 spectrophotometer equipped with a Glan-Foucoult calcite polarizer using a modified sample holder which has been previously described.[2] Corrections were made for host and cell absorption, reflection, and scattering.

B Dye Preparation

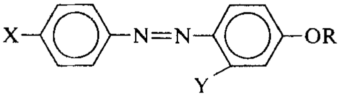
The dyes were synthesized by variations of standard methods[10–13] which will be described elsewhere. All compounds were made analytically pure by column chromatography using 60–200 mesh silica gel (MCB), and by repeated recrystallization until silica gel tlc (Eastman) showed only one component. The dyes were characterized by ir and nmr spectroscopy, and elemental analysis.

RESULTS AND DISCUSSION

The first group of dyes, shown in Table I, are 4-nitro-4′-alkoxy derivatives of azobenzene. Since they have absorption maxima in the UV region, their

TABLE I

Effect of structure on order parameter for alkoxy-azobenzenes



Dye	X	Y	R	S	λ (nm)[a]
I	NO_2	H	CH_3	0.69	430
II	NO_2	OH	C_2H_5	0.59	450
III	NO_2	OH	n-C_9H_{19}	0.57	440

[a] Wavelength at which order parameter was obtained.

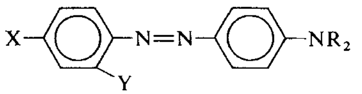
order parameters were obtained from their visible-region absorption tails. The lower optical density as well as the various phenomena which contribute to the absorption tail make these S values less reliable than those obtained using absorption maxima.

Change of the alkoxy substituent from ethyl (II) to nonyl (III) causes a modest decrease in the order parameter value. However, a more drastic decrease in S is observed in replacing a hydrogen in the 2′-position, as in (I), by a hydroxy group, as in (II) or (III). The 2′-hydroxy group forms an intramolecular hydrogen bond with an azo nitrogen[14] which tends to decrease the hydroxyl group's length in the lateral direction. Nonetheless, we expect any substitution by a group bulkier than hydrogen in a lateral position to lower the order parameter by preventing the long-axis absorption direction from aligning as well with the host direction. Introduction of an auxochrome in the lateral position of an azobenzene may lead to a change in the absorption polarization direction which can also result in a non-correspondence of the absorption axis to the alignment direction of the host. The results show that the length of the alkoxy group plays only a minor role in determining the order parameter, and we attribute the large change in S from (I) to (II) to the lateral interaction of the 2′-OH group with the nematic host. We have not determined if chain lengths, intermediate between C_2 and C_9, may indeed have higher order parameters.

The order parameters for a number of dialkylaminoazobenzenes are shown in Table II. In the 4-nitro-4′-dialkylaminoazobenzene series (IV–XIV), the order parameter decreases with increasing length of the N,N-dialkyl group $S(\mathrm{IV}) > S(\mathrm{V}) > S(\mathrm{IX}) > S(\mathrm{XII})$. As the N-alkyl chains lengthen, it tends to occupy a greater effective volume than the simple N,N-dimethylamino group, thus preventing the long axis absorption direction from aligning as well with the host director, resulting in a lower order parameter.

TABLE II

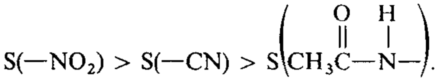
Effect of structure on order parameter for dialkylamino-azobenzenes



Dye	X	Y	R	S	max λ (nm)[a]
IV	NO_2	H	CH_3	0.62	500
V	NO_2	H	C_2H_5	0.55	506
VI	NO_2	CH_3	C_2H_5	0.46	506
VII	NO_2	OCH_3	C_2H_5	0.43	514
VIII	NO_2	H	$(CH_2)_2$ [pyrrolidine]	0.62	515
IX	NO_2	H	n-C_4H_9	0.51	508
X	NO_2	CH_3	n-C_4H_9	0.40	506
XI	NO_2	OCH_3	n-C_4H_9	0.34	516
XII	NO_2	H	n-C_6H_{13}	0.48	507
XIII	NO_2	CH_3	n-C_6H_{13}	0.42	509
XIV	NO_2	OCH_3	n-C_6H_{13}	0.31	519
XV	CN	H	CH_3	0.60	464
XVI	CN	H	C_2H_5	0.52	474
XVII	$CH_3\overset{\overset{O}{\|}}{C}\overset{\overset{H}{\vert}}{N}$	H	C_2H_5	0.50	425

[a] Absorption maximum in the nematic host.

When the ethyl ends are linked together to form a pyrrolidine ring which minimizes off-axis contributions, the order parameter S(VIII) is found to be higher than that for *N,N*-diethyl analog S(V). In fact, it is the same as that for the *N,N*-dimethyl analog S(IV). Replacement of a hydrogen in the 2-position of the 4-nitro-4′-*N,N*-dialkylaminobenzenes by a methyl group or a methoxy group in the series V, VI, VII; IX, X, XI; and XII, XIII, XIV results in dramatic decrease in the order parameter values. The results in Table II show that, if all other structural factors are the same, S varies with different end group substituents in the 4-position. The following order is observed:

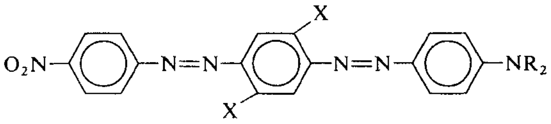


$$S(\text{—}NO_2) > S(\text{—}CN) > S\left(CH_3\overset{\overset{O}{\|}}{C}\text{—}\overset{\overset{H}{|}}{N}\text{—}\right).$$

Disazo compounds, having a longer molecular axis, can be better aligned with the host director and are expected to have a higher order parameter than the corresponding monoazo analog. The results in Table III show that the order parameter for disazo dyes XVIII, and XIX are considerably higher than their monoazo analogs V and IX, respectively. When lateral

TABLE III

Effect of structure on order parameter for disazobenzenes



Dye	X	R	S	max λ (nm)
XVIII	H	C_2H_5	0.65	538
XIX	H	n-C_4H_9	0.61	544
XX	OCH_3	CH_3	0.59	579
XXI	OCH_3	C_2H_5	0.52	585

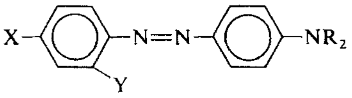
methoxy group substituents are present in the central benzene ring of the disazo compound, a marked decrease in the order parameter is observed as in XXI compared to XVIII.

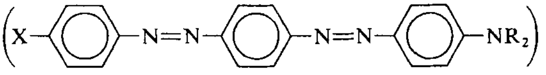
The effect of end group and phenyl-ring substitution on lateral interactions and thereby on S are cumulative. Using IV as the parent compound with an $S = 0.62$, the effect of selected structural features on incremental changes in the order parameter (ΔS) were empirically-derived and compiled in Table IV. S(calc) was obtained by using the formula

$$S(\mathrm{calc}) = 0.62 + \sum \Delta S. \tag{2}$$

TABLE IV

Parameters for calculating S



Structural feature	ΔS
$X=NO_2$	0
$X=CN$	−0.02
$X=CH_3CN$	−0.05
$Y=H$	0
$Y=CH_3$	−0.09
$Y=OCH_3$	−0.15
$R=CH_3, (CH_2)_2$	0
$R=C_{(2+n)}H_{(5+2n)}$ (n = 0, 1, 2, . . .)	$(-0.07 - 0.02n)$
Disazo 	+0.10

(A. Bloom and P. L. K. Hung, Mol. Cryst. Liq. Cryst., 40, 213-221, 1977.)

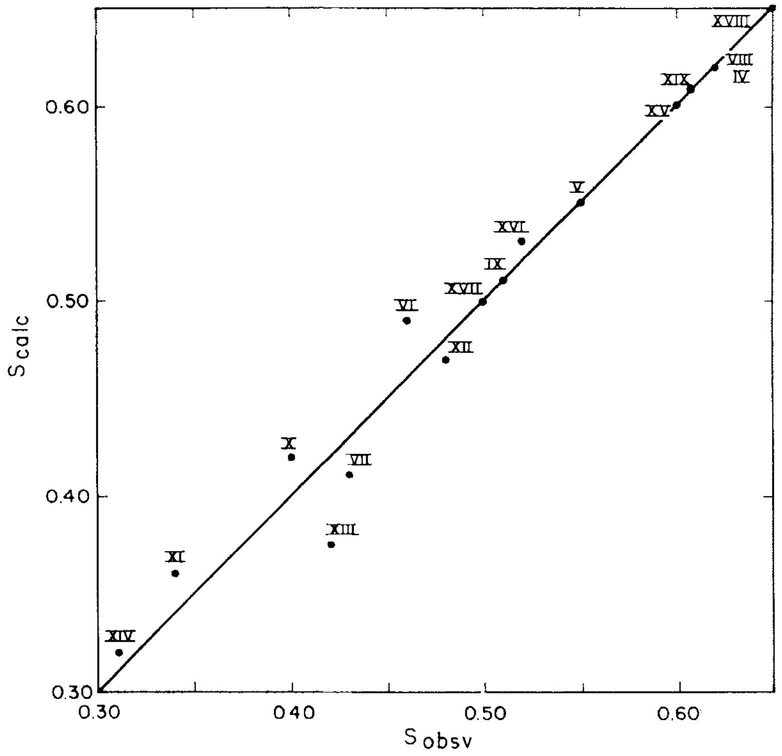


FIGURE 1 Calculated and observed order parameters for mono- and disazobenzenes. (A. Bloom and P. L. K. Hung, Mol. Cryst. Liq. Cryst., 40, 213-221, 1977.)

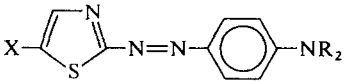
To show the additivity of structural components, a plot of calculated *vs* observed order parameters for IV–XIX is given in Figure 1. A line of slope = 1 which passes through the origin demonstrates that agreement between observed and calculated values is good.

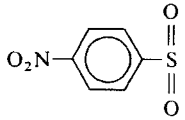
The ΔS values shown in Table III carry over to other related molecules. For example, in the case of XX and XXI, the substitution of $R = C_2H_5$ for $R = CH_3$ leads to a calculated ΔS of 0.07 which is in fact observed.

The order parameter for a number of phenylazo-thiazole compounds are listed in Table V. As with the azobenzenes, an increase in S is observed in the 5-substituted-4′-*N*,*N*-dialkylaminophenylazothiazoles on changing the *N*,*N*-dialkylamine group from *N*,*N*-diethylamine to pyrrolidine. The difference in S is larger for the 5-chlorothiazole derivative ($\Delta S = 0.12$) than for the 5-nitro analog where $\Delta S = 0.08$. Both values are greater than that found for azobenzene ($\Delta S = 0.07$). The nature of the 5-substituent does not appear to affect appreciably the order parameter in changing from NO_2

TABLE V

Effect of structure on order parameter for phenylazo-thiazole dyes



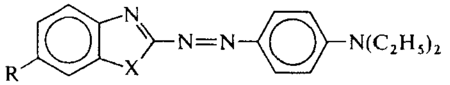
Dye	X	R	S	max λ (nm)
XXII	NO_2	C_2H_5	0.46	595
XXIII	NO_2	$(CH_2)_2$ [pyrrolidine]	0.54	607
XXIV	Cl	C_2H_5	0.46	520
XXV	Cl	$(CH_2)_2$	0.58	526
XXVI	Br	C_2H_5	0.45	522
XXVII		C_2H_5	0.27	566

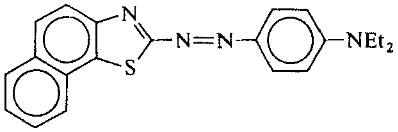
(XXII) to Cl (XXIV) to Br (XXII) unless a much bulkier group such as that found in XXVII is employed.

The effect of a benzene ring fusion onto a phenylazo-thiazole compound is demonstrated by an increase of 0.12 in order parameter found when comparing S for XXII with that for XXVIII in Table VI. The addition of a benzene ring lengthens the molecular axis thereby improving the alignment of the dye with the host. However, when the benzene ring is not added along

TABLE VI

Effect of structure on order parameter for phenylazo-benzothiazole dyes

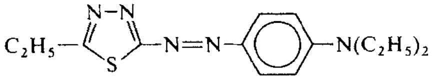
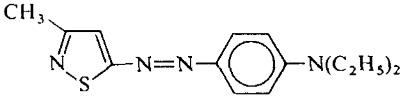
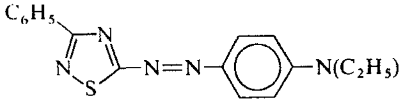
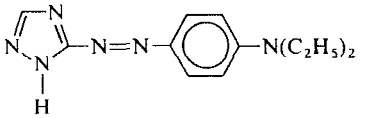


Dye	X	R	S	max λ (nm)
XXVIII	S	NO_2	0.58	551
XXIX	S	C_2H_5O	0.57	522
XXX			0.54	539
XXXI	NH	Cl	0.46	507

the molecular axis of the dye molecule as in XXX, a lower order parameter is observed. The phenylazo-benzothiazole compounds show little sensitivity to changes of substituents from nitro to ethoxy on the heterocyclic moiety. A significant change in *S* value is observed ongoing from benzothiazole as in XXVIII to benzimidazole in XXXI. The lower *S* value can be attributed to disorientation of the dye molecule caused by hydrogen bonding, with the host and to decreased alignment with the host due to changes in geometry caused by tautomerization of the N—H bond.

TABLE VII

Effect of structure on order parameter for miscellaneous phenylazo-heterocyclic dyes

Dye	Structure	*S*	max λ (nm)
XXXII		0.48	502
XXXIII		0.47	491
XXXIV		0.45	528
XXXV		0.16	456

The order parameters for a number of arylazo heterocyclic compounds are listed in Table VII. Only modest changes in *S* are observed for a number of structural changes on the heterocyclic moiety. For 5-membered rings, substituents on the carbon atoms β and γ to the C-azo linkage are both about the same radial distance from the molecular axis which may account for the observed insensitivity of *S* to hetero-ring substituents found for all the heterocyclic systems we examined. Similar arguments can be made for the benzene-ring fused heterocycles. For XXXV, a triazene containing an N—H group the order parameter is extremely low for the same reasons given for XXXI.

CONCLUSIONS

We have investigated correlations between the order parameter and the molecular structure for a number of azo compounds in a liquid crystalline host by varying the structural characteristics of the dye molecule. We found for azobenzenes an additivity of substituent effects which leads to good agreement between empirically-derived and observed *S* values. For heterocyclic phenylazo dyes, the end group substituents on the phenyl ring play a significant role in influencing *S*, whereas the nature of the heterocyclic systems, as well as the end group substituents on the heterocyclic ring, are only of minor importance. Benzene ring fusion onto a heterocyclic ring, as well as the presence of an N—H moiety in such a system, can lead to significant changes in the order parameter.

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