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Order Parameters of Dyes in a Biphenyl/Terphenyl Liquid Crystal Mixture†

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The order parameters of a number of azo- and anthraquinonoid dyes dissolved in a eutectic liquid crystal mixture composed of derivatives of 4-cyanobiphenyl- and 4-cyano-*p*-terphenyl (Type E7, B.D.H. Chemicals Ltd.) have been determined spectrometrically. Orientation was achieved using rubbed polyvinyl alcohol coated cells. A good correlation was found between order parameter and molecular structure, allowing order parameters to be predicted for other dyes based on the monazo-chromophore. Azo-dyes exhibited a marked red shift relative to the colour of the dye in slightly polar isotropic solvents, whereas anthraquinonoid dyes showed little change. The results are interpreted in terms of charge transfer perturbations arising from dipole-interactions between guest and host molecules.

INTRODUCTION

Recently, a number of dyes of different chemical classes containing various extended chromophore systems have been examined as solutions in liquid crystalline media with the purpose of effecting improvements in the contrast and viewing angle of optical display devices. Thus aryl-azo- and thiazole-azo-dyes,[1] azomethine dyes,[2] cholesteryl-substituted azo dyes[3] and 1,4-*bis*(alkylamino)anthraquinonoid dyes[4] have all been examined. The host in these studies has usually been a eutective mixture of Schiff's bases and relatively little work has been reported[5] on dye order parameters in

† Attention is drawn to a recent review by G. W. Gray presented at the Seventh International Colour Symposium, at Interlaken in September 1979. This was entitled Dyestuffs and Liquid Crystals. The review covered some of our work at Leeds, as well as that of other groups, and it is to be published in *Chimia*.

mixtures of cyano-biphenyl and terphenyl liquid crystals, although this type of liquid crystal, developed by Gray and co-workers[6] in 1973, is now much used in display systems.

This paper reports such a study using a wide range of dye structures. Although no dyes with exceptionally high order parameters were found, a good correlation between order parameters and structures of the dyes exists. Also, the relatively high dipole moment of the host medium causes changes in dye spectral characteristics which are shown to be independent of individual order parameters. With at least one dye possessing two visible absorption bands attributable to different structural features, the display cells exhibit a marked colour change on switching.

DETERMINATION OF ORDER PARAMETERS

The liquid crystal host was supplied as type E7 by BDH Chemicals Ltd. and consisted of a eutectic mixture of: 51% 4′-*n*-pentyl-4-cyanobiphenyl, 25% 4′-*n*-heptyl-4-cyanobiphenyl, 16% 4′-*n*-octyloxy-4-cyanobiphenyl and 8% 4″-*n*-pentyl-4-cyano-*p*-terphenyl, exhibiting a stable nematic phase over the range −10 to 60°C.

The dyes were obtained either as commercial samples or synthesised directly by conventional means. They were purified by aqueous extraction, repeatedly crystallised to constant m.p. using organic solvents, and assessed for purity by their giving single spots on thin layer chromatographic plates. All dyes were initially screened for their solubility in E7, and were dissolved in this medium at a concentration of 1% wt./vol.

The order parameter S was experimentally determined from spectrophotometric data by applying the following equation,

$$S = \frac{A_{\parallel} - A_{\perp}}{2A_{\perp} + A_{\parallel}}$$

where $A_{\parallel}$ is the optical density at λ_{max} for the dye in the host medium when the electric vector of the incident light is parallel to the director and $A_{\perp}$ is the corresponding optical density when the electric vector and alignment direction are perpendicular.

Cells were made from optically flat glass plates with a transparent coating of polyvinyl alcohol which has been rubbed in one direction. Cells, 12 μm thick, were filled with the dye solution and inserted in the light path of a Pye–Unicam SP6–200 spectrophotometer and behind a Polaroid HN42 neutral, linear polariser. An identical cell containing liquid crystal solvent alone was used for calibration. An optical density against wavelength scan was carried out to determine the wavelength of maximum absorption, and the polariser angle adjusted to ensure a maximum value for $A_{\parallel}$ at

λ_{max}. After realigning the polariser through 90°, a second absorption spectrum was obtained and the minimum value, $A_{\perp}$, determined from this curve at the same wavelength.

Monoazo-dyes

Figure 1 shows the spectra obtained for a 1% solution of dye No. XX (Table II) in both the parallel and perpendicular modes, using E7 as the host medium, and a cell thickness of 12 μm.

These spectra are typical for all the monoazo-dyes and model compounds examined. There is no detectable shift in peak wavelength between the two modes, the only change being one of absorbance. The visual appearance of the cell when viewed through a polarising film set in the perpendicular position is almost colourless. It is also generally observed that λ_{max} for dyes dissolved in this liquid crystal medium undergoes a strong bathochromic shift in comparison with the same dyes dissolved in less polar, isotropic solvents (λ_{max}^{iso} in Tables).

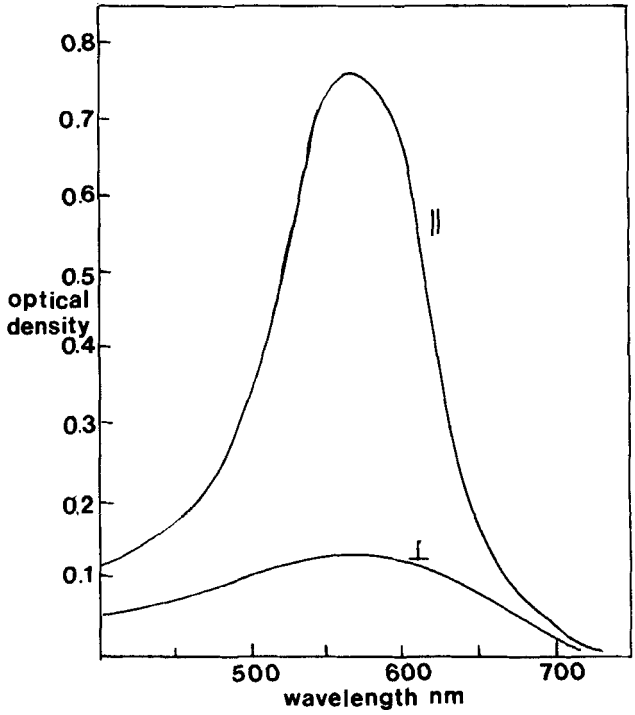
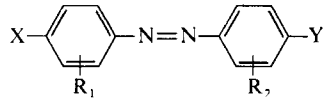


FIGURE 1 Absorption curves for dye No. XX in the parallel and perpendicular modes.

TABLE I

Order parameters of azobenzene and derivatives of azobenzene



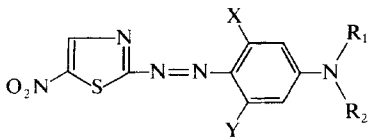
Dye number	X	Y	R_1	R_2	λ_{max} (nm)	λ_{max}^{iso} (nm)[a]	S	ΔS
I	H	H	H	H	450	318	0.37	0.00
II	NO_2	H	H	H	465	332	0.45	0.08
III	H	$N(CH_3)_2$	H	H	420	409	0.48	0.11
IV	NO_2	$N(CH_3)_2$	H	H	505	475	0.61	0.24
V	NO_2	$NH(CH_3)$	H	H	485	464	0.56	0.19
VI	NO_2	$N(C_2H_5)_2$	H	H	510	490	0.63	0.26
VII	NO_2	NHC_2H_5	H	H	475	468	0.43	0.06
VIII	NO_2	$N(C_2H_4OH)_2$	H	H	500	—	0.53	0.16
IX	NO_2	NH_2	H	H	455	—	0.57	0.20
X	NO_2	NH_2	H	2′-CH_3	465	—	0.53	0.16
XI	NO_2	$N(CH_3)_2$	H	3′-CH_3	470	422	0.43	0.06
XII	NO_2	$N(CH_3)_2$	H	2,′6′-CH_3	465	—	0.40	0.03
XIII	NO_2	$N(CH_3)_2$	2-Cl	H	530	—	0.56	0.19
XIV	NO_2	$N(CH_3)_2$	2,6-Cl	H	470	498	0.54	0.17
XV	NO_2	$NH(C_2H_5)$	3-Cl	H	415	—	0.25	−0.12

[a] Solvent:- Ethanol.

Table I gives the order parameters (S) of azobenzene and some of its derivatives, together with their λ_{max} values. If azobenzene (I) is considered as the parent compound, all order parameters except one show a positive incremental value dependent on the nature, position and number of the substituent groups. The presence of an individual substituent in a terminal position (dye II or III) increases the order parameter, and when both terminal positions are occupied by nucleophilic and electrophilic groups (e.g., dye IV), S is increased to a value which makes use of the dye in a liquid crystal display feasible. Two important factors emerge from a comparison of structure and order parameter. Firstly, the nature of the amino group in the 4′-position strongly influences the value of the order parameter. For a symmetrically substituted primary (dye IX) or tertiary (dyes IV, VI or VIII) nitrogen atom the value of S is relatively high, whereas a secondary, non-symmetrically substituted nitrogen (dyes V, VII, or XV) gives a much lower value of S. In the last example (dye XV), the order parameter falls below that of the parent compound due to the combined effect of a non-symmetrical substituted amino group and a nitro group in the 4-position sterically hindered by an adjacent substituent. This type of steric hindrance is also observed when dye (XI) is compared with (IV). Secondly, the efficiency of

TABLE II

Order parameters of 5-nitrothiazole-azo-dyes



Dye number	X	Y	R_1	R_2	λ_{max} (nm)	λ_{max}^{iso} (nm)[a]	S	ΔS
XVI	H	H	H	H	550	538	0.57	0.00
XVII	H	H	H	$-C_2H_5$	580	561	0.56	−0.01
XVIII	H	H	$-CH_3$	$-CH_3$	590	580	0.62	0.05
XIX	H	H	$-C_2H_5$	$-C_2H_5$	595	588	0.62	0.05
XX	H	H	$-C_2H_5$	$-C_2H_4CN$	565	518	0.52	−0.05
XXI[b]	H	H	3′-$CH_2CH_2-CH_2$- (julolidine)	5′-$CH_2CH_2-CH_2$-	580	569	0.59	0.02
XXII	H	H	$-CH_3$ (kairoline)	3′-$CH_2CH_2-CH_2$-	610	—	0.57	0.00
XXIII	$-CH_3$	H	$-CH_3$	$-CH_3$	605	—	0.56	−0.01
XXIV	$-CF_3$	H	$-CH_3$	$-CH_3$	575	—	0.52	−0.05
XXV	$-Si(CH_3)_3$	H	$-CH_3$	$-CH_3$	615	—	0.51	−0.06
XXVI	$-CH_3$	$-CH_3$	$-CH_3$	$-CH_3$	565	543	0.45	−0.12
XXVII	$-CH_3$	H	H	H	565	547	0.51	−0.06
XXVIII	H	H	3′-$(CO)CH_2CH_2$- (keto-julolidine)	5′-$CH_2CH_2CH_2$-	525	—	0.47	−0.10

[a] Solvent:- Ethanol.

[b] See, e.g. structure XXXIII, Table III.

orientation of the dye molecule in the mesomorphic environment is always reduced when lateral substituent groups (R_1 and R_2 in Table I) are present. This effect is observed not only with dyes (X–XV) in Table I but also with dyes (XXIII–XXVII) in Table II, and is also cumulative depending on the number of lateral groups. Both lack of symmetry in structure and the presence of lateral groups will reduce guest-host van der Waals interaction by preventing close alignment with the host molecules which determine the director.

Data in Table II refer to 4′-amino-substituted azo-dyes based on the 2-amino-5-nitrothiazole-structure. The same conclusions relating structure and order parameter particularly with reference to lateral substitution and the nature of the terminal amino-group also apply to this sub-class. It is noticeable that the presence of the 5-nitrothiazole residue causes a marked red shift in λ_{max} of up to 104 nm, in comparison with the corresponding λ_{max} for the analogous dyes related to azobenzene. The dyes are therefore much more blue, and although electronic excitation of the polarisation band is more easily achieved, there is no attendant increase in order parameter.

The consistency of the quantitative effects of substituent groups on the order parameters of the parent compounds (i.e., dyes I and XVI) is reflected in the incremental ΔS values given in Tables I and II. By allocating specific determined values to ΔS for each substituent[1] and by taking account of the number and position of the substituents in their summation, it is possible to calculate an order parameter S_{cal} which can be compared with that experimentally determined. A linear equation of the form

$$S_{cal} = S_0 + \Sigma \Delta S$$

where S_0 is the order parameter of the parent compound, can be applied, values of ΔS being obtained from Tables I and II. Figure 2 relates the calculated and observed order parameters for dyes from both series.

The slope of the line drawn in the graph is unity and it passes through the origin, indicating good agreement between the calculated and observed order parameters and that the equation can be used to predict S values for other dyes based on the azobenzene or 5-nitrothiazole-azo-structures when they are used in the liquid crystal medium under study.

Bis- and tris-azo-dyes

As already described, terminal substitution in the azobenzene series can give a positive increase in the order parameter. The effect is further enhanced on introducing a second and third phenyl-azo-group in the terminal positions. This is shown in Table III which gives the maximum order parameters found for a series of *bis*- and *tris*-azo-dyes. With one exception no

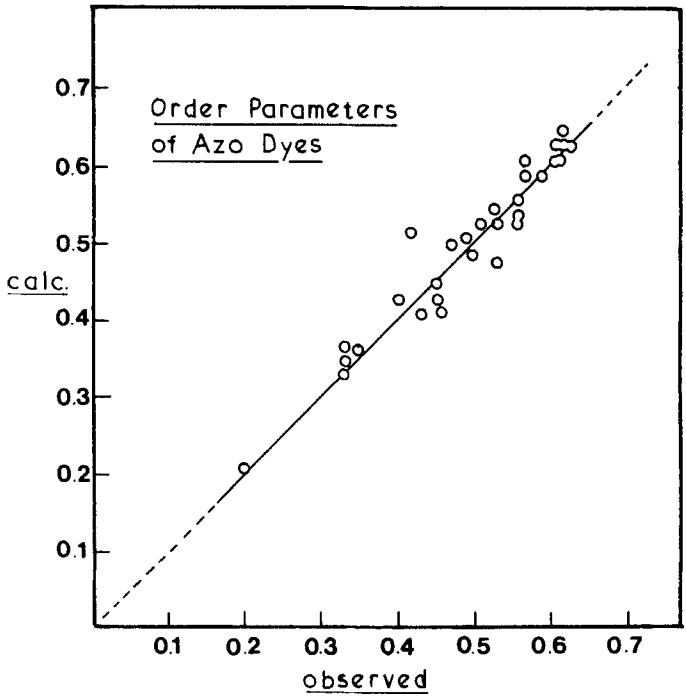


FIGURE 2 Calculated and observed values of order parameter.

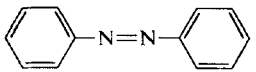
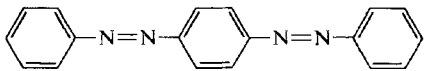
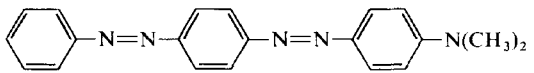
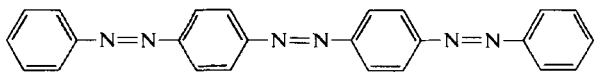
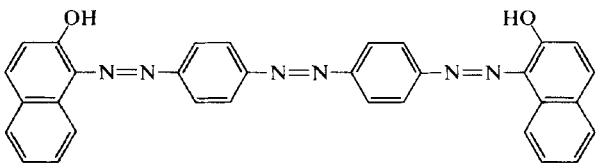
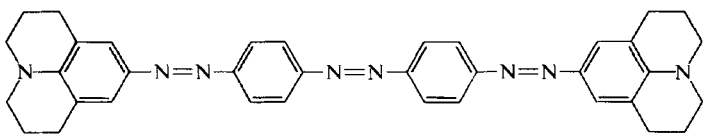
lateral substituent groups are present. The addition of a third azo-group does not have such a marked effect on ΔS as the second. It is possible that such extended systems have reduced co-planarity leading to a converging series of order parameters. Additional evidence for this is to be found in the λ_{max} values in the all-phenyl systems which do not undergo any marked red shift which might be anticipated solely on the basis of an extended conjugated system. Although the dyes exhibit order parameters which are adequate for optical display systems, they do not in general meet requirements concerning contrast whereby dyes (blue-green) absorbing in the low energy region of the visible spectrum are preferable.

Amino-anthraquinonoid dyes

On the basis of colour the choice of blue dyes soluble in cyano-biphenyl and -terphenyl liquid crystals is to be found with the 1,4- and 1,5-di-amino-anthraquinones. In view of their molecular structure, such compounds would not be expected to give high order parameters, but, as can be seen

TABLE III

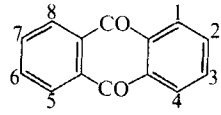
Order parameters of bis- and tris-azo-dyes

Dye Number	Structure	λ_{max} (nm)	λ_{max}^{iso} (nm)[a]	S	ΔS
I		450	318	0.37	0.00
XXIX		359	<400	0.62	0.25
XXX		500	481	0.66	0.29
XXXI		400	<400	0.64	0.27
XXXII		575	572	0.66	0.29
XXXIII		560	560	0.71	0.34

[a] Solvent:- ethanol.

TABLE IV

Order parameters of amino-anthraquinones



Dye number	Anthraquinone derivative	λ_{max} (nm)	λ_{max}^{iso} (nm)	S
XXXIV	1-NH_2	560	475[a]	0.54
XXXV	1,4-di-NH_2	575	550[c]	0.56
XXXVI	1,5-di-NH_2	490	492[b]	0.58
XXXVII	1,4,5-tri-NH_2	565	564[b]	0.61
XXXVIII	1,4,5,8-tetra-NH_2	615	607[b]	0.62
XXXIX	1-NH_2,4-$NHCH_3$	590	588[d]	0.53
XL	1,4-di-$NHCH_3$	600	623[b]	0.38
XLI	1-NH_2,4-NHC_6H_5	600	601[c]	0.38
XLII	1,4-di-NHC_6H_5	610	630[c]	0.33
XLIII	1,4-di-NHC_6H_4-$C(CH_3)_3$-*p*	635	—	0.45
		415	—	−0.08

[a] Solvent:- methanol.
[b] Ethanol.
[c] Dimethylformamide.
[d] Acetone.

from Table IV, the order parameters, provided there are no bulky N-substutuents present such as in dyes XL–XLIII, are as high as those in the mono-azo series. Similar compounds with amino-groups present in the 2- or 6-positions of the anthraquinone nucleus are not sufficiently soluble in the liquid crystalline medium, due to the high probability of intermolecular H-bonding between dye molecules. In addition the molar absorptivity is lower than that of the corresponding 1- or α-substituted derivatives. The order parameter of the sparingly soluble 2-aminoanthraquinone can, however, be determined, and has been found to be as low as 0.13.

The absorption maxima given in Table IV represent the wavelengths of absorption of the more intense of the double peaks observed in the long wavelength region. The 1,4-*N*, *N*-diarylamino-anthraquinones, as represented by dye XLII, are greener in colour than the corresponding dialkylaminoanthraquinones[7] due to the presence of a small additional peak in the blue region of the spectrum. It is of interest to note that this band, which is more pronounced in 1,4-di-(*p*-tert-butyl)anilino-anthraquinone, XLIII (Figure 3), shows a negative anisotropy which gives rise not only to a change in intensity but also to a change in colour from blue-green to yellow-green when the cell is observed in the parallel and perpendicular modes respectively. This effect could be of significance in future developments in the field of optical displays.

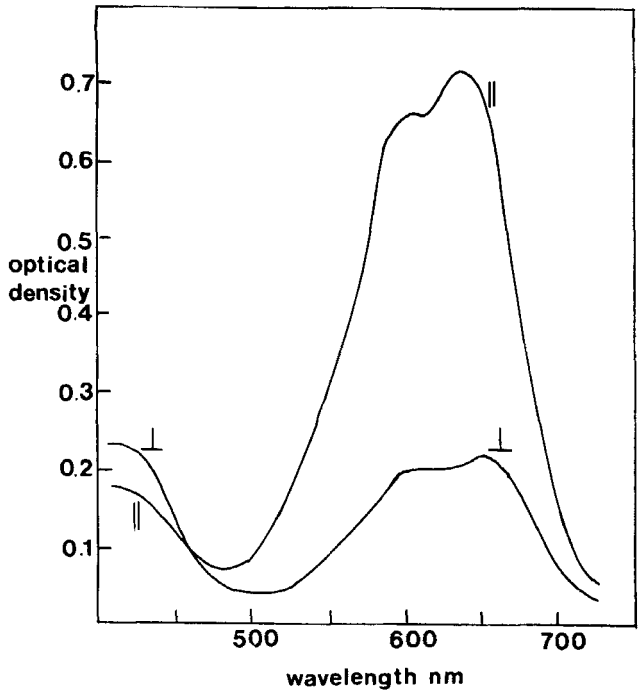


FIGURE 3 Absorption curves for 1,4-(p-tert-butyl)anilinoanthraquinone in parallel and perpendicular modes.

Dye-liquid crystal interaction

The comparatively high values of order parameter and the extent of the red shifts observed, particularly for azo-compounds, indicate strong molecular interaction with the liquid crystal host. Such shifts observed with azo compounds[8] and amino-anthraquinones[9] dissolved in isotropic solvent media have been interpreted in terms of localised intramolecular charge transfer configurations in which both ground state and excited state energy levels are perturbed by solvent polarity. For both types of dye, the charge transfer lies along a direction approximately parallel to the main geometric axis of the dye. Thus, possible dipole-induced dipole interaction between the dye and the liquid crystal polarised along its major axis can be depicted as in Figure 4. The charge transfer configurations of 1-amino- and 1,4-diamino-anthraquinone shown in this Figure are those postulated by Moran and Stonehill.[10] Although we are not aware of the dipole moment of the E7 eutectic mixture, its fundamental composition would indicate a polarity in a non-oriented mode, similar to that of benzonitrile ($\mu = 4.05$D)[11] or

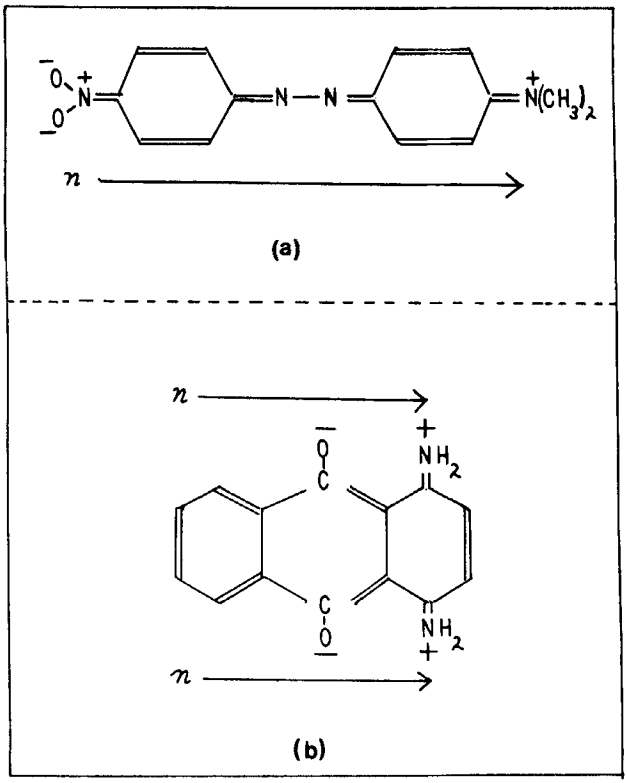


FIGURE 4 Interaction between director, n, and polarization bands in a) Azo- and b) amino-anthraquinonoid derivatives

4-cyanobiphenyl (μ = 4.33D), and higher than that of dimethylformamide (μ = 3.82D) where red shifts are also observed. The corresponding values for the dipole moments of mono-azo-dyes lie within the range 3.6 to 7.2D[11] depending on the separation and the type of the terminally situated electron donor and acceptor groups. Dipole and induced dipole interactions would therefore give rise to a qualitatively greater increase in perturbation effects with these dyes than in the case of amino-anthraquinone dyes which possess[12] dipole moments in the range 1.5 to 5.4D attributable to shorter charge transfer separations (Figure 4b). Additionally, the strong intermolecular attraction and close proximity between dye and liquid crystal molecules could possibly give rise to inter-, in addition to intra-molecular charge transfer, with an extension of the π-electron system between neighbouring molecules, so leading to an extended dipole. Such a model has been proposed by Kuhn to account for red shifts observed with dye aggregates,[13]

although in the present work the extent of the spectral shifts can be adequately accounted for on the basis of solute-solvent interaction alone.

Finally, the colour change from blue-green to yellow-green observed with dye (XLIII) indicates that the shorter wavelength peak can be attributed to an independent chromophore since it possesses negative anisotropic properties. By comparing changes in the absorbance maximum of this peak with the relative angle of orientation of the plane of polarisation of the incident light in spectrophotometric measurements, we can conclude that the two chromophore systems in this dye are approximately mutually perpendicular. This method could therefore be used as an additional tool for peak assignment studies of other dyes, provided they are compatible with the orienting medium in which they are present.

Acknowledgement

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