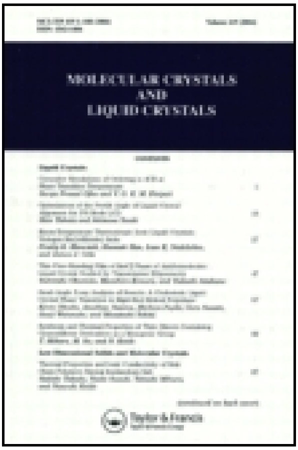

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The Use of Azo Dyes in Guest-Host Displays

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The Use of Azo Dyes in Guest-Host Displays†

J. COGNARD and T. HIEU PHAN

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Azo dye molecules are cylindrically shaped, and therefore, due to their resemblance to liquid crystal molecules, would seem to be suitable for use in guest-host mixtures. The dichroïc ratio of a dye in a given nematic host depends on the molecular length of the dye molecules, the order parameter of the liquid crystal host and its molecular dimensions. It is possible to obtain a guest-host mixture with an order parameter which is higher than that of the pure host. Lateral substitution of mono-azo dyes lowers the order parameter, whilst lateral substitution of the corresponding bis- and tris-azo molecules results in only a slight change in their order parameter.

The stability of these compounds to light is poor, and depends on the wavelength for maximum absorption, and on the host material. Whilst lateral substitution increases the fastness of azo compounds when used for textile dying, this is not the case when they are employed with liquid crystal mixtures. The kinetics of degradation are zero order in dye concentration.

It has been found that azo dyes are not in general suited to applications where prolonged exposure to sunlight may be encountered, e.g. watch applications.

1 INTRODUCTION

Liquid crystal displays (L.C.D.'s) are widely employed nowadays for the visual display of information. Displays for use in consumer products normally employ the effects arising from the deformation of twisted nematic layers caused by an applied electric field.[1]

An alternative technique, which avoids the use of polarizers, employs a solution of dyes in liquid crystals (L.C.'s). The contrast of such a "guest-host interaction" display, which was originally proposed by Heilmeier and Zannoni,[2] may be improved by the addition of a cholesteric to the mixture, as demonstrated by White and Taylor.[3]

Commercial interest in this type of display has been low, due to the negative contrast obtained, i.e. clear digits on a dark background. Recent investigations, however, have demonstrated the feasibility of realizing displays with good positive contrast.[4,5]

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†Presented at the Eighth International Liquid Crystal Conference, Kyoto, July 1980.

One of the major problems which remains in the industrialization of such a display is the lack of suitable guest dyes. To be of practical interest a dye should fulfil the six conditions outlined in Figure 1.

In the Color Index,[6] textile dyes are classified in ten categories on the basis of their molecular structure. Following a brief survey (Table I) of some of the dyes from each category, it appeared that azo compounds possessed most of the required characteristics, i.e.:

—their cylindrical shape is similar to that of L.C. molecules (some are, in fact, liquid crystals).[7]

—the charge transfer absorption band excitation, which gives rise to their color, is in the direction of the molecular axis.

—they possess high extinction coefficients.

—all shades are available.

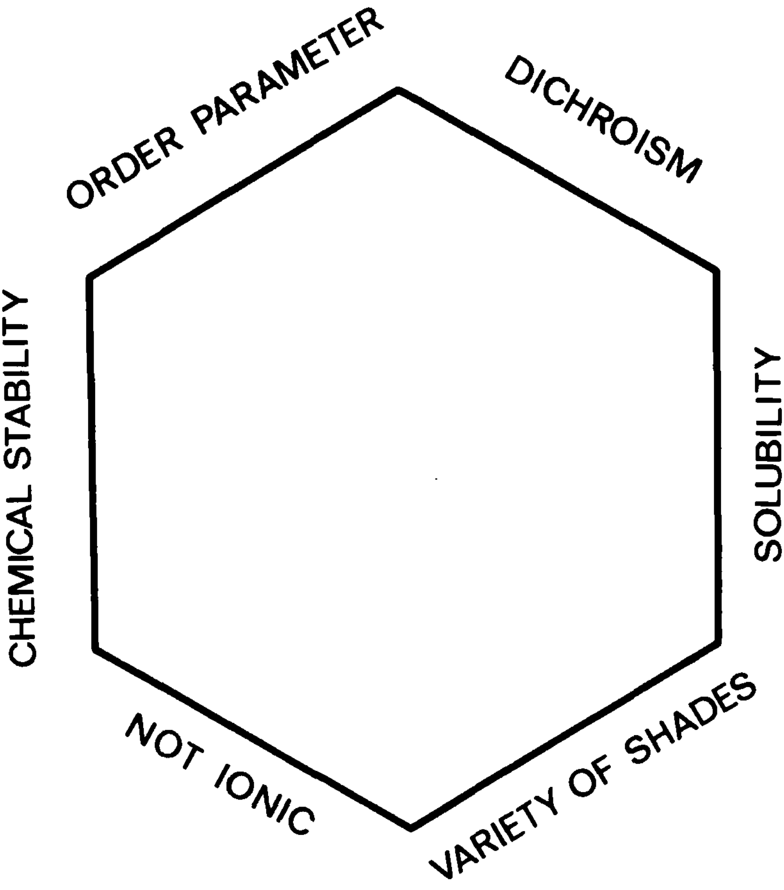


FIGURE 1 Constraints imposed on the properties of dyes used as guests.

TABLE I

Properties of the different classes of textile dyes

DYE PROPERTIES / DYE CLASS	NOT IONIC	SOLUBILITY (1)	DARK COLOR	DICHROISM	STABILITY (2)	ORDER
Azoics	+	+	+	+	=	+
Cyanines	+	−	±	+	=	+
Azo-methines	+	+	−	+	−	+
Triphenylmethane	−	−	+	?	=	−
Acridines	−	?	−	?	=	?
Azines	−	?	+	?	=	?
Quinones	+	=	+	+	+	+
Indigoids	+	−	+	?	=	−
Phtalocyanines	+	−	+	?	+	?
Nitro	+	−	±	?	=	−

Their suitability for guest-host applications was initially investigated using the results of earlier investigations (for a review see reference 8). It quickly became apparent that the highest order parameters were to be obtained with long polyazoic molecules[9, 10] in hosts possessing high nematic to isotropic transition temperatures (T_{NI}),[10] although the exact relationship was not entirely clear.[9, 11]

An evaluation of the properties of the dyes in solution indicated that they had poor stability to light.

These aspects will be more fully considered in the present paper, along with their implications for the fabrication of displays.

2 EXPERIMENTAL DETAILS

Dye evaluations, in general, employed mixtures of the dye with ROTN 103 and E7 L.C. eutectic mixtures. Evaluations of the influence of the host also considered ROTN 404, E8, and ZLi 1132. The compositions of these L.C. mixtures, determined by chromatographic analysis in this laboratory, are indicated in the Tables II(a) and (b).

Investigations of the effect of the host T_{NI} (Figure 3.3) on the order parameter of a dye employed, in addition to the above mentioned mixtures, ROTN 403, 405, and 430 from Roche, and ZLi 1132, 1237, 1252, 1253, and 1275 from Merck.

Dyes

The azo dyes employed in the evaluations were either synthesized in the laboratory by conventional diazotization reactions, or obtained from commercial sources. Purification by preparative liquid chromatography was carried out using a Jobin-Yvon "Chromatospac" on Merck H 60 silica columns eluted with a solvent mixture compatible with the individual dyes; a single spot on a thin layer chromatography plate (Merck Kieselgel 60F) was employed as a control criterion for each dye.

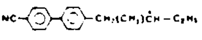
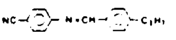
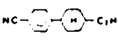
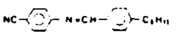
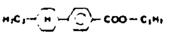
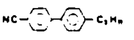
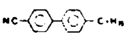
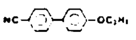
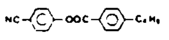
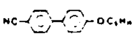
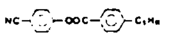
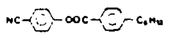
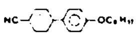
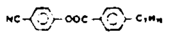
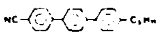
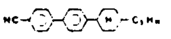
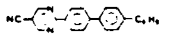
TABLE II(a)

Composition of L.C. mixtures from our chromatographic analysis

Code	Composition	T_{NI} °C	Source
Zli 1132	0.15 BCH-5 ; 0.24 PCH-3 ; 0.36 PCH-5 0.25 PCH-7	70	Merck
E 3	0.55 K15; 0.14 M 15; 0.13 M 21; 0.18 M 24	54.3	BDH
E 7	0.51 K15 ; 0.25 K 21 ; 0.16 M 24 ; 0.08 T 15	59.8	BDH
E 8	0.45 K15 ; 0.16 M9 ; 0.12 M 15 ; 0.16 M 24 0.11 T 15	70.5	BDH
ROTN 103	0.05 PEPN 4 ; 0.24 PEPN5 ; 0.13 PEPN 6 0.18 PEPN 7 ; 0.12 P_3 5 ; 0.08 P_3 7 ; 0.20 T P_3 4	81.4	Roche
ROTN 200	0.33 S3 ; 0.67 S 6	65.2	Roche
ROTN 404	0.31 M 15 ; 0.14 M 24 ; 0.14 T 15 ; 0.09 P_3 5 0.18 P_3 7 ; 0.14 T P_3 4	105	Roche

TABLE II(b)

L.C. code

C B 15		PCH-5	
S 3		PCH-7	
S 6		HPE-33	
K-15		HPEH-23	
K-21		HPEH-43	
M-9		PEPN 4	
M-15		PEPN 5	
M-21		PEPN 6	
M-24		PEPN 7	
T-15		$P_3$5	
BCH-5		$P_3$7	
PCH-3		T$P_3$4	

Preparation of L.C.-dye solutions

Dyes were dissolved in the relevant L.C. mixture, with the aid of ultrasonic agitation (Sonicator, Ultrasonic Ltd.), giving saturated solutions, which were subsequently filtered. The maximum solubility was determined from measurements of the optical density of a small quantity of the L.C.-dye solution diluted with chloroform, for which the molar extinction coefficient had been measured.[12]

Most evaluations employed wherever possible a 0.5% solution by weight as, at this concentration, the dye had little effect on the properties of the L.C.

Order Parameter (O.P.)

Optical densities of L.C.-dye solutions were measured with a Perkin Elmer 555 Spectrophotometer, at the wavelength of maximum absorption. For these measurements, the solutions were contained in reusable, glass frit-sealed cells.[13] The cell thickness employed was either 15μ or 30μ. A matching cell, filled with the pure L.C., was positioned in the reference beam, the polarization of both beams being defined using two HN32 polarizers (Polaroid Corp.).

Homogeneous alignment of the L.C. mixtures was assured by the use of a 1000 Å thick S_iO_x layer evaporated at an angle of 30° onto a sputtered S_iO_x layer, also 1000 Å thick, on each substrate. The homogeneity of the alignment was controlled with the aid of crossed polarizers. The polarization of the spectrophotometer beams was arranged so as to be parallel with the alignment directions of the cells, by examining the position of the absorption maximum.

The optical densities (D) of a solution were measured with the light beam polarized either parallel ($D_{\parallel}$) or perpendicular ($D_{\perp}$) to the L.C. alignment direction by means of a 90° rotation of the cells.

The dye order parameter, S_D, was calculated from the dichroic ratio, r, using the following relationships:

$$r = \frac{D_{\parallel}}{D_{\perp}}$$

and,

$$S_D = \frac{r-1}{r+2}$$

No correction was made for the anisotropy of the L.C. polarization field ($r_{\text{corrected}} = g.r.$, where $g = n_{\parallel}/n_{\perp}$),[9] the reproducibility of the measurements being such as to not warrant it. Even when great care is paid to the experimental conditions, variations in the value of S_D of 0.05 units are common. The higher values measured are normally quoted, as the lower values are normally caused by imperfect experimental conditions, e.g. L.C. misalignment, cell birefringence, etc.

Cells which included conducting electrodes and employed field orientation of the L.C. gave similar values of S_D. The construction of such cells, however, was more complicated. Measurements of this nature, employing the first type of cell, offered some advantages over the method consisting in measuring the optical density of a mixture in both the homeotropic and isotropic states—which necessitates corrections to be made to the results to counter the effect of temperature variations.[14, 15]

Stability to Sun Light

The photodegradation of L.C.-dye solutions is activated by the presence of oxygen. The cells employed for O.P. measurements were not therefore suitable for use in evaluations of the stability of dyes to sun light. For this evaluation, glass frit assembled cells, similar to those described above, were employed, but with two holes drilled in opposite corners of the upper plate, to facilitate filling. After filling, these holes were plugged with teflon cones. Both plates of each cell included an In_2O_3 coating beneath an aligning layer of 30° evaporated S_iO_x, or rubbed polyimide. During the evaluations, the filled cells were placed on a black background in a Leybold-Heraeus "Sun Test Apparatus". The cell tray was maintained at 30° C, although the cell temperature was, in fact, higher. The optical density and cell current (under 6V, 32Hz excitation) were measured after appropriate periods of exposure.

3 THE ORDER PARAMETER OF AZO DYES

The absorption of visible light by azo dyes results from a $\pi \rightarrow \pi^*$ charge transfer transition, the direction of which is parallel to the molecular plane.[16] It is generally accepted that the transition moment **M**, for such a reaction, is directed along the molecular axis, D_z, and has only one component, M_z.[9, 14, 17] Although this may be the case for mono-azo dyes, the complex shape of poly-azo dyes prohibits the definition of a molecular axis. A second component, M_x, could therefore exist, giving rise to two distinct, planar, orthogonal absorption coefficients.

The interpretation of the U.V.-visible spectrum of even a simple molecule, such as azobenzene in solution, is unclear, and the situation for poly-azoic molecules is much more complex. As a result, very little is known concerning the origins of their absorption spectra. Cis-trans-isomerization, and vibrational state mixing result in broad absorption bands (breadth at half height $L_{1/2} \simeq 120$ nm.), from which it is impossible to assign energy levels precisely.

Shifts in the wavelength, λ_{max}, at which maximum absorption occurred, were observed for solutions of a dye in different hosts, and attributed to the effects of the solvent reaction field. For dyes dissolved in solvents of differing polarities and permittivities, but identical internal reaction fields,[19] such as chloroform, methanol, and acetone, no shift in λ_{max} was observed. In nitrobenzene, however, the value of λ_{max} was the same as that for L.C. mixtures of high positive dielectric anisotropy ($\Delta\epsilon \gg 0$), e.g. E8 and ROTN 404. As all L.C.'s have similar refractive indices, n, ($n_{L.C.} \simeq 1.5$), the shift in λ_{max} can be roughly correlated with the isotropic permittivity (Figure 2).

It was frequently observed that the value of λ_{max} depended on the direction of polarization of the incident illumination ($(\lambda_{max})_{\parallel}$ and $(\lambda_{max})_{\perp}$). This phenomenon suggested the existence of two absorption coefficients. The values of λ_{max} for perpendicularly polarized illumination and for the isotropic phase were in general, found to be identical. The existence of this shift in λ_{max} leads to different values of S, determined from O.D. measurements, depending on whether one compares $D\|$ and $D\perp$ at (λ_{max}) or at both $(\lambda_{max})_{\parallel}$ and $(\lambda_{max})_{\perp}$.

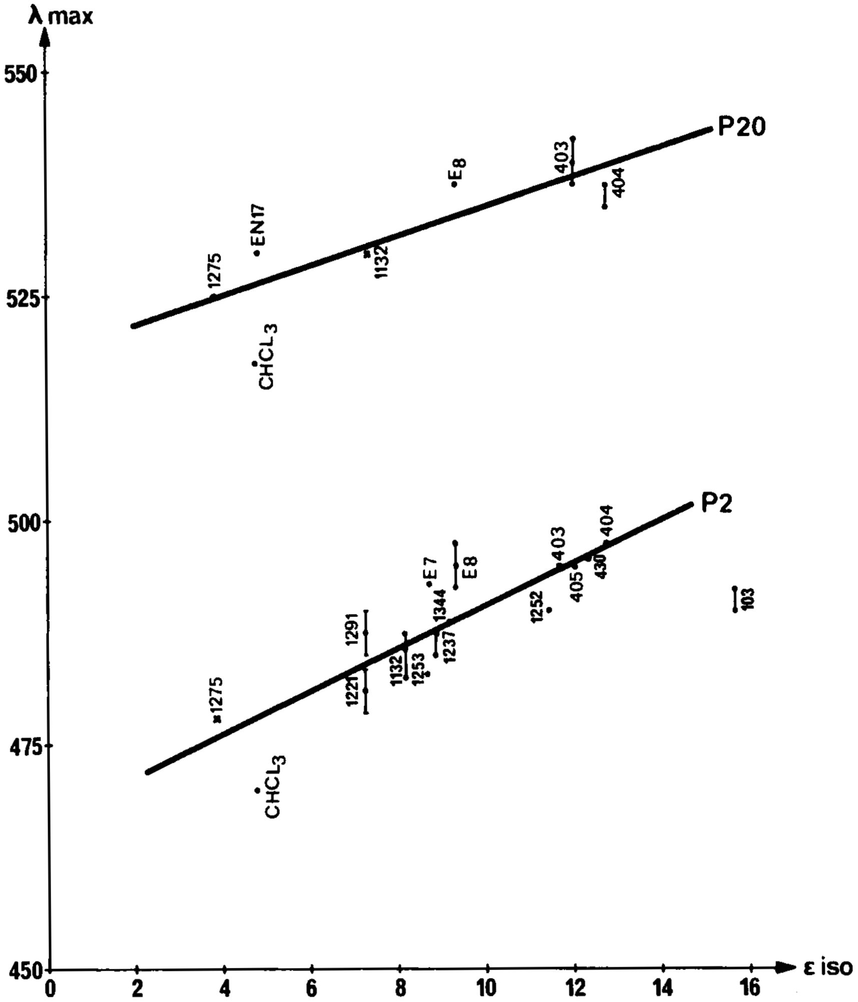


FIGURE 2 Wave-length maxima of azo dyes (P2 and P20) undergo a bathochromic shift as the L.C. permittivity increases.

The values of S_D quoted in the present work were obtained using the second technique, which may explain why they are lower than some of the published results.

The orientation of the molecules of a dye by a L.C. host should result in an order parameter, S_D, equal to that of the L.C., $S_{L.C.}$. The theory of Maier and Saupe (M.S.)[20] enables this value to be calculated. The continuum approximation does not take into account the differences in the chemical structure of L.C. molecules; eutectic mixtures must, therefore, be treated as a single L.C.

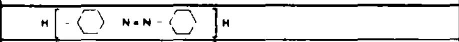
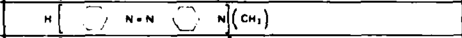
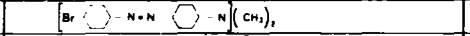
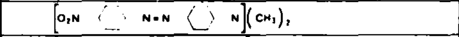
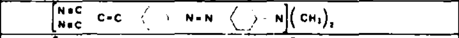
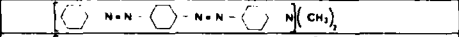
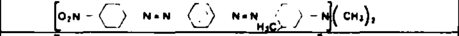
for which the order parameter depends on the nematic to isotropic transition temperature, T_{NI}, alone.

Numerical values computed from M.S.'s theory have been tabulated,[21] permitting the calculation of the M.S. equilibrium order parameter at 25° C. For: E7, $T_{NI} = 60°$ C and $S_{E7} = 0.63$; E8, $T_{NI} = 70.5°$ C, $S_{E8} = 0.66$; *TN* 404, $T_{NI} = 105°$ C, $S_{404} = 0.73$. From studies of mixtures containing different 4,4′-substituted azo dyes dissolved in E7, one observes that S_D varies with the molecular dimensions. The molecular cross-section of these molecules is nearly constant, and hence the effect of the substitution must be to increase their length. If the azo dyes are assumed to be planar with an angle of 120° between the —C—N and N=N bonds,[18] the molecular length may be calculated from the known bond lengths.[21] *Para*-substitution by an alkyl chain does not affect the O.P. (e.g. dye no. 2, Table III.1); hence only the delocalized electron cloud (aromatic ring and heteroatoms) needs to be considered. The dependence of the order parameter, S_D, on the length of the projection of the molecular length on the *para*-axis, L_D, has been considered (Figure 3.1). Figure 3.2 was obtained from the results shown in Table III.1.

The L.C. order parameters, calculated as described above, are also shown in Figure 3.2. These values led to an apparent molecular length, *L*, for each mixture: i.e. E7, *L* = 14 Å; E8, *L* = 14.75 Å; *TN* 404, *L* = 16 Å.

For the case where the dye molecule was shorter than the L.C. molecule, e.g. monoazo dyes, S_D was found to be lower than the value of the L.C. order pa-

TABLE III.1
Lengths and order parameters for selected azo dyes

CODE	DYE	C-X	C-Y	l Å	$S_{in E7}$	$S_{in E8}$	$S_{in 404}$
P5				11,05	0,50		
P6				11,05	0,51		
P1			1,47	12,52	0,56 0,57	0,57	0,57
P7		1,93	1,47	14,45	0,62		
P3		2,08	1,47	14,60	0,62	0,62	0,64
P8		2,11	1,47	14,65	0,62		
P9		2,66	1,47	15,18	0,64		
P11		4,68	1,47	17,20	0,70		
P2		7,25	1,47	19,79	0,73	0,74	0,79
P4		8,95	1,47	21,47	0,69		
P10		9,33	1,47	21,85	0,69		
P12		8,72	1,47	21,26	0,73		
P13		15,97	1,47	28,50	0,72	0,76	0,80
P20		15,97	1,47	28,50	0,72	0,76	0,80

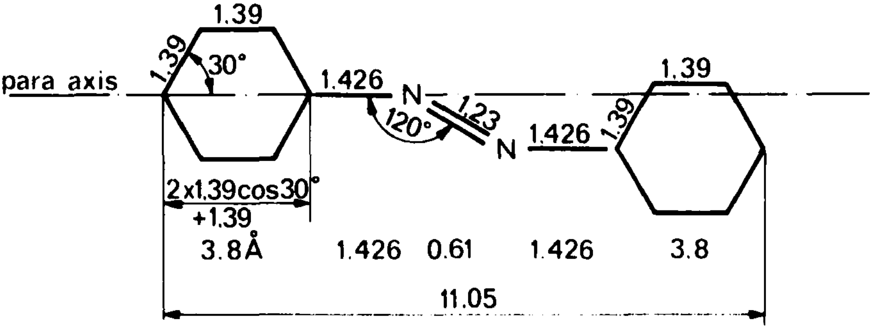


FIGURE 3.1 Molecular dimensions of an azo dye. Only the π-electron cloud is considered. Dye length is measured in projection on the *para*-axis.

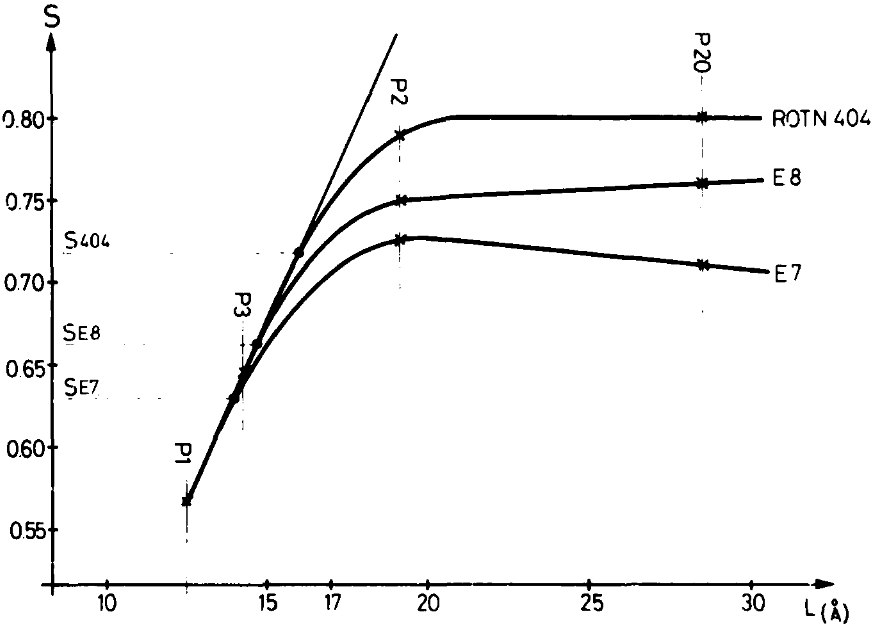


FIGURE 3.2 Variation of the dye order parameter S_D with the azo dye length. A linear variation is observed until $S_D = S_{GL}$.

rameter predicted by the M.S. theory.[23] S_D increased linearly with L_D, and was found to be independent of the L.C.'s T_{NI}. For $L_D \sim L_{L.C.}$ the order parameter of the dye at room temperature was equal to the M.S. order parameter. (dye P_3.). For cases where $L_D < L_{L.C.}$, the order parameter, S_D, continued to increase above $S_{L.C.}$ as L_D increased. These results confirmed both the results obtained with mono-azo dyes in E7[14] and the observed dependence of S_D on molecular length.[9]

Depending on the number of azo chromophores present, we obtained the

TABLE III.2

Range of the order parameters for azo dyes in E_7

AZO DYES	ORDER PARAMETER
MONO AZO	0,45 – 0,60
DI AZO	0,60 – 0,72
TRI AZO	0,70 – 0,80

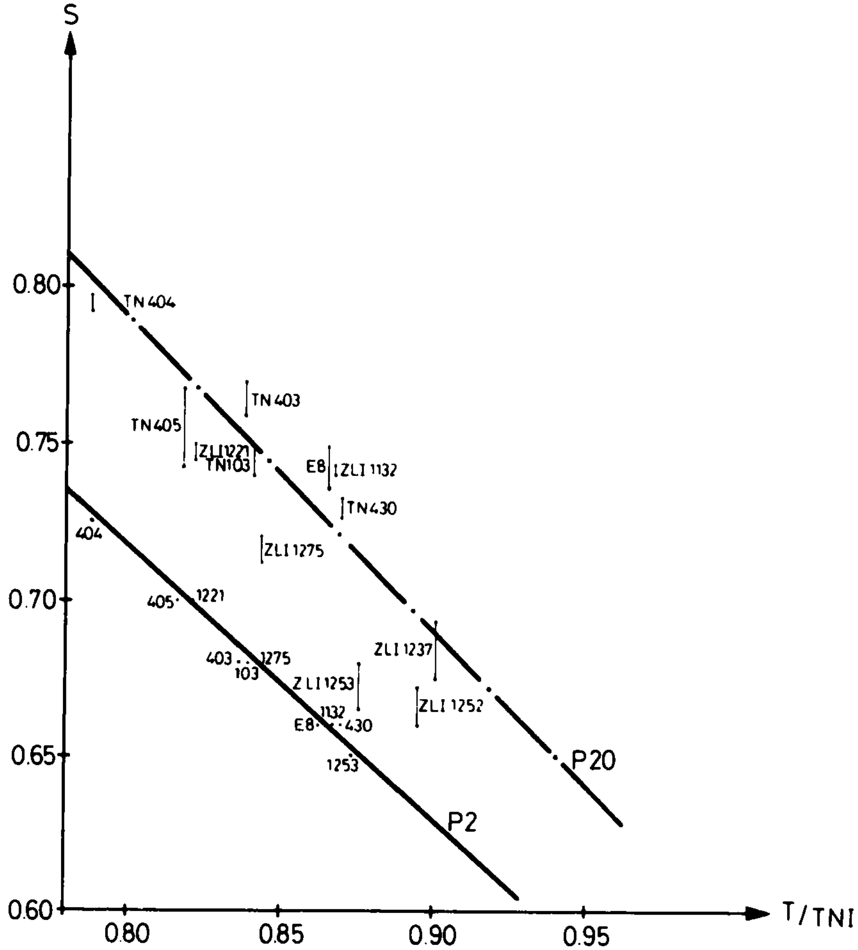


FIGURE 3.3 The dye order parameter S_D increases with the host critical temperature T_{NI}.

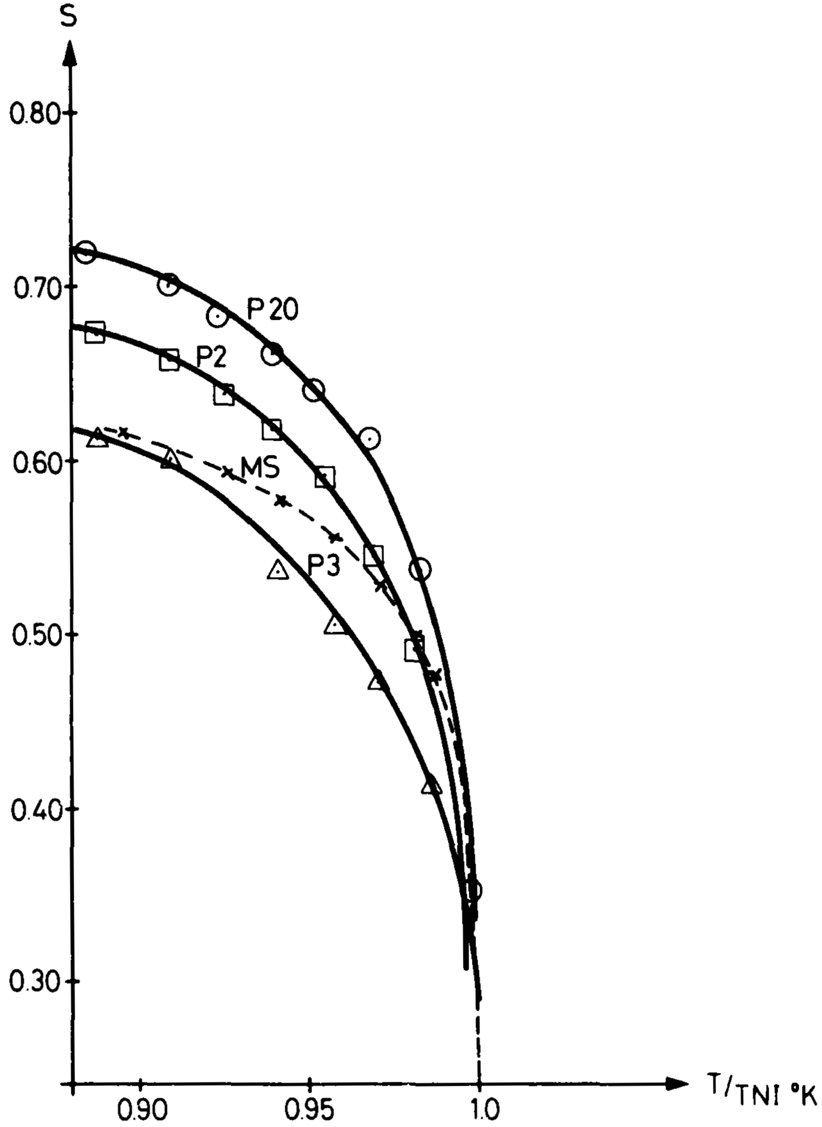


FIGURE 3.4 The dye order parameter, S_D, decreases faster than expected from M.S. theory, as the temperature increases.

values of S_D in E7 shown in Table III.2. Azo dyes having molecules longer than the L.C. molecules, e.g. bis- and tris-azo dyes, had order parameters which increased with the L.C.'s T_{NI}.

The values of S_D measured for twelve different L.C.'s of positive dielectric anisotropy confirmed previously published results,[10] which showed a definite increase in S_D with increasing T_{NI}. Some mixtures, however, gave a lower

TABLE III.3

Influence of the length of the azo dye on solubility and optical properties

Dye	l (A°)	Sol °/o	λ max	$\epsilon \times 10^{-4}$
P_3	15,2	> 5	475	6
P_2	19,8	2,2	492	9
P_{20}	28,5	0,6	527	16

value than expected from their transition temperature, presumably due to molecular volume differences between the L.C. and the dye (Figure 3.3).

It has been suggested that dye molecules could be used as "probes" of the L.C. order parameter.[9,14] The temperature dependence of S_D for the dye P_3 was considered. For P_3 in E7, $S_D = S_{L.C.}$ at 25° C. Comparison of experimental and calculated values showed larger (Figure 3.4) discrepancies than those previously reported. Some variations were observed with longer dyes, such as P2 and P20. Even though the dye mixtures were very dilute ($\sim 10^{-2} \mathrm{M\,l}^{-1}$), specific L.C. dye interactions could have occurred, as reflected by the small, but reproducible variations in the values of T_{NI} of different dye-L.C. mixtures. Solutions of the dyes P_3, P_2, and P_{20} in E7, ($T_{NI} = 59.5°C$) had T_{NI}'s of 59.5°C, 60.1° C, 60.6° C, respectively. It should be noted that these variations were much too small to account for the increase in S_D found with the dyes P_2 and P_{20}. The M.S. theory predicts that such variations would require a T_{NI} of 89° C.

The significance of experimental values obtained using dyes as L.C. probes should therefore be considered with caution.

As the length of a dye increases, its solubility, *s*, in a L.C. decreases. Due to their high extinction coefficients (Table III.3), tris-azo dyes may still be usable in displays, but tetrakis azo dyes are insoluble.

4 THE KINETICS OF DEGRADATION DUE TO SUN LIGHT

The decrease of the optical density of a L.C.-azo dye solution, due to illumination by sun light, is initially linear with time, provided that the L.C. orientation does not vary with time, and that degradation products do not absorb light at the same wavelength, or modify the degradation path. Frequently, the initially homogeneous alignment of the solution becomes homeotropic after a period of illumination, due to the formation of surface active products from the degradation of either the L.C. or the dye. If this occurs, then the rate of change of O.D. with time, decreases, leading to an apparently longer lifetime. The linear variation of the O.D. corresponds to zero order kinetics of degradation. The variation of the dye concentration, C_D(M.l^{-1}), with time, may therefore be expressed as:

$$-\frac{dC_D}{dt} = J_A\phi. \tag{1}$$

where ϕ is the quantum yield, and J_A is the number of absorbed photons, in (moles Einstein l^{-1}s^{-1}). As J_A is related to the indicent photon flux, J_0, by the expression

$$J_A = J_0\,[1 - \exp\,(-\,a\ C_D l)] \tag{2}$$

where ϵ is the extinction coefficient ($\alpha = 2,3\epsilon$) and l is the cell thickness, Eq. (1) can be written as:

$$\frac{-\,dC_D}{dt} = J_0\,[1 - \exp\,(-\,aCl)]\phi \tag{3}$$

If C_D^0 is the initial dye concentration giving an O.D. of D_0, and if the familiar expression for the optical density is assumed,

$$D = \log\frac{I_0}{I} = \epsilon Cl,$$

where ϵ is the molar extinction coefficient, then integration of Eq. (3), gives,

$$D_{(t)} = 0.43\ \ln\,[1 + (e^{2.3D_0} - 1)e^{-\beta t}] \tag{4}$$

where, β is a measure of the dye stability,

$$\beta = 2.3\epsilon J_0\phi \tag{5}$$

For time, $t < \beta^{-1}$

$$e^{-\beta t} \sim 1 - \beta t,$$

and hence the variation of O.D. is linear with time,

$$D \sim D_0 - [0.43\,(1 - 10^{D_0})]\beta t.$$

It is usual to define the lifetime of a dye, $T_{1/2}$ as the time taken for the O.D. to half its initial value, giving,

$$T_{1/2} = \frac{1}{\beta}\ln\left[\frac{10^D - 1}{10^{D_0}/2 - 1}\right]$$

$T_{1/2}$ is therefore a function of the initial O.D., and β^{-1} is the lifetime of a cell for which $D_0 = 0.4$. Due to the variation of $T_{1/2}$ with D_0, it is usual to employ

$D_0 = 1$ for comparative measurements of lifetimes, $T^{d}_{1/2}$, in which case

$$T^{d}_{1/2} = 1.42\,\beta^{-1} \tag{6}$$

If the transmission, T, of a cell is measured, instead of its optical density, β may be calculated from the linear relation,

$$\ln\left(\frac{1}{T} - 1\right) = \ln\left(\frac{1}{T_0} - 1\right) - \beta t \tag{7}$$

This approach permits the techniques of linear regression to be employed, allowing β to be determined with greater precision. Figures 4.1 and 4.2 compare experimental results with values obtained from Eqs. (4) and (7), respectively.

Equation 7 indicates that β is proportional to the molar extinction coefficient, ϵ. This relationship was verified experimentally by comparing the change in O.D. with time for cells with homeotropic, homogeneous and isotropic mixture orientations. The cells contained 5% of an optically active L.C., 4-cyano-4′-(2-methyl)butyl biphenyl, and had extinction coefficients with the dye P10, of $\epsilon_{\parallel}(E_8) = 5.0.10^4$; $\epsilon_{\perp}(E_8) = 0.1\,\epsilon_{\parallel} = 5.10^3$; $\epsilon_{iso} = \frac{1}{3}(\epsilon + 2\epsilon_{\perp}) =$

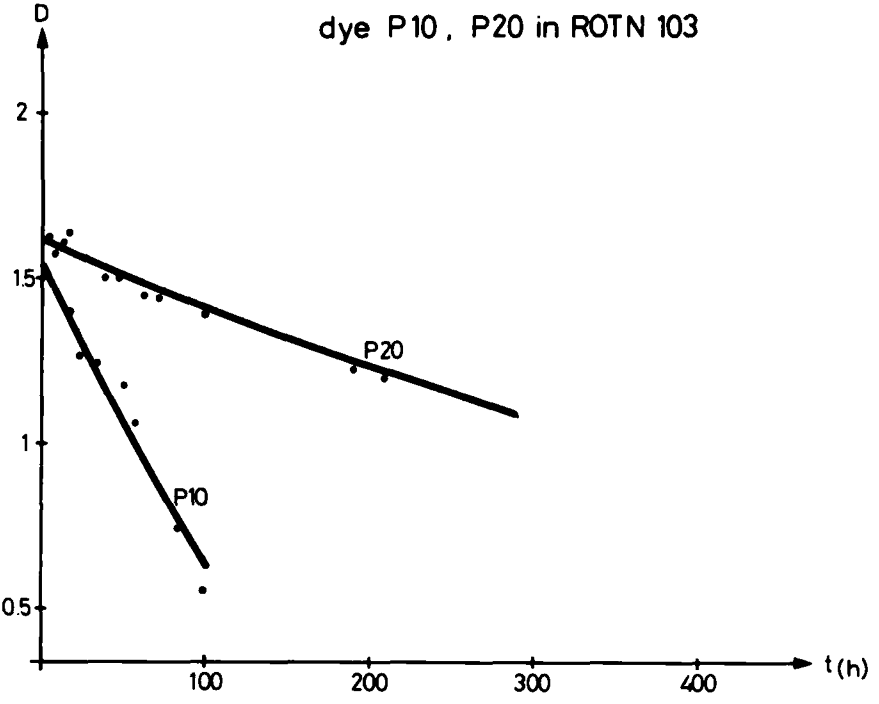


FIGURE 4.1 Decrease of optical density of cells filled with dyes P_{20} and P_{10} under Sun Test exposure. Comparison of experimental results and calculation from Eq. 4.

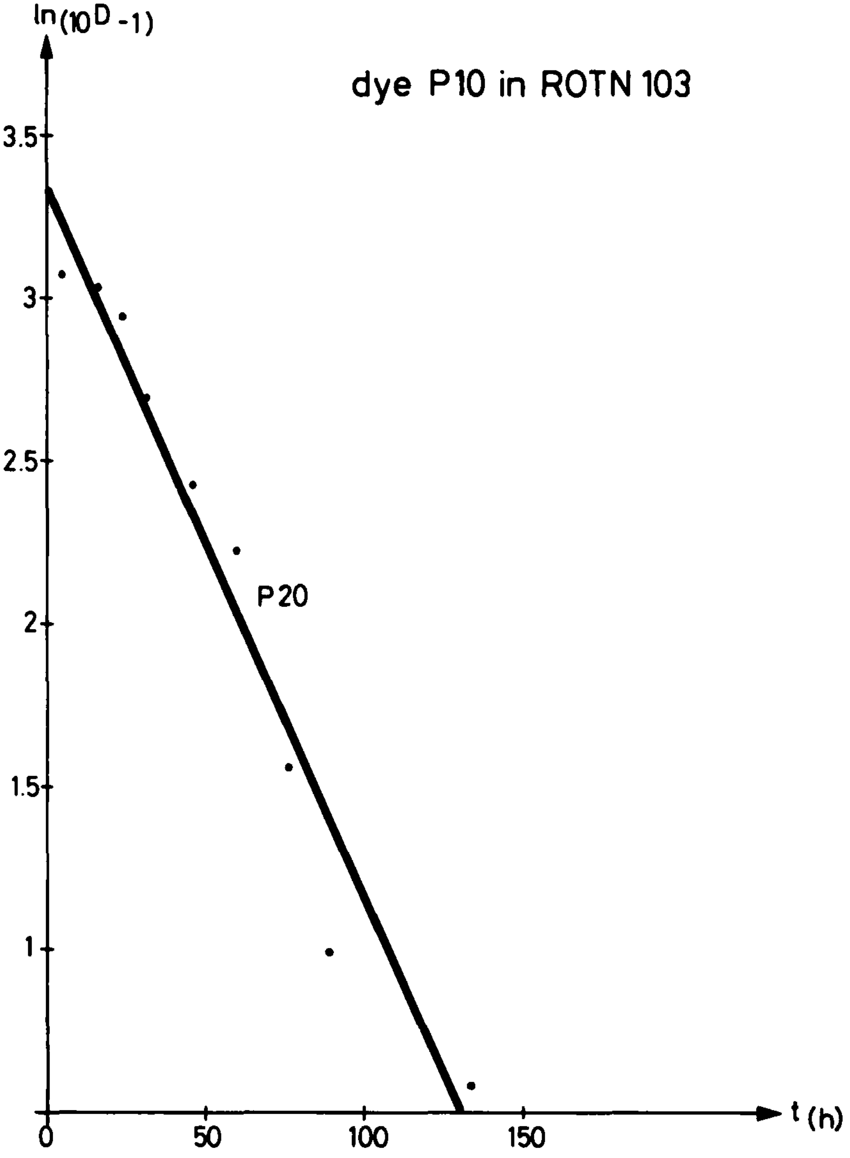


FIGURE 4.2 Decrease in optical density of cells filled with dye P_{10} under Sun Test exposure. Comparison of experimental results and calculation from Eq. 7.

2.10^4 (exp $2.5.10^4$). The excellent agreement between theoretical and experimental values is shown in Figure 4.3.

The proportionality of β to the incident flux, I_0, was verified using neutral filters of varying transmissions. The results are summarized in Figure 4.4.

The exposure of cells to illumination during either two hour or two day pe-

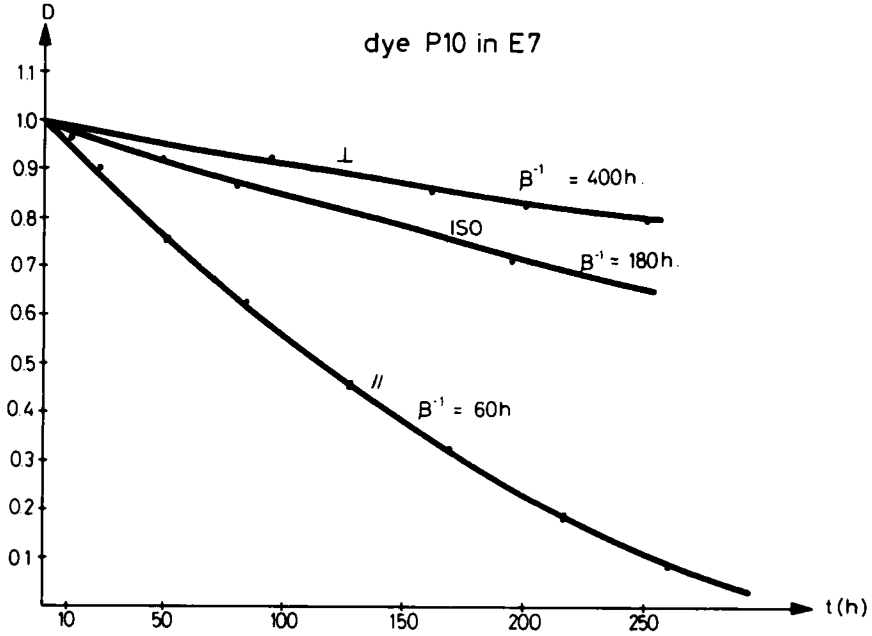


FIGURE 4.3 The decrease in O.D. depends upon the dye orientation (experimental curves normalized to $D = 1$).

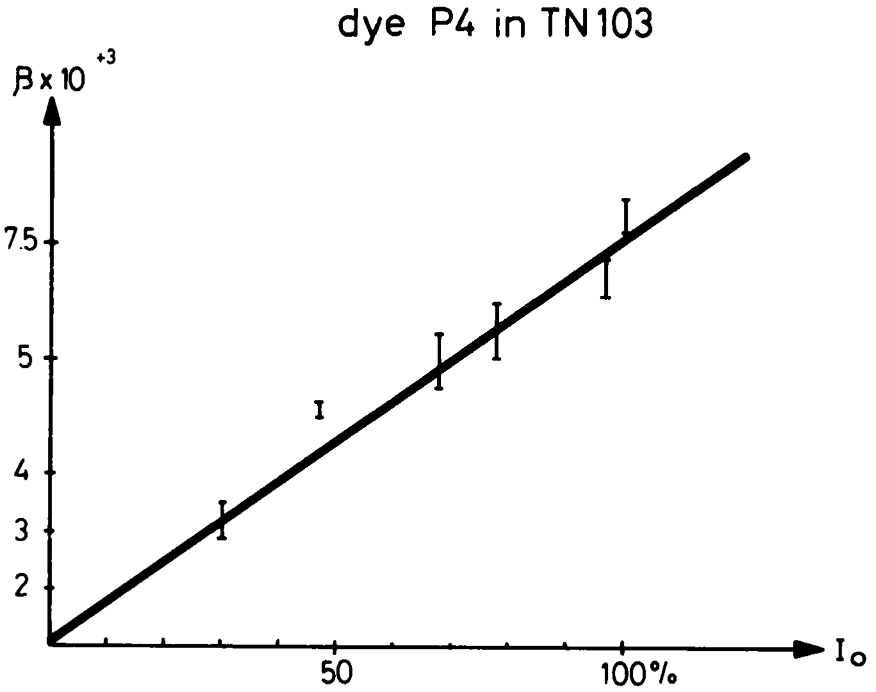


FIGURE 4.4 The decrease in O.D. varies linearly with the intensity of the incident light.

riods resulted in the same values of β relative to the total effective time of irradiation.

5 THE INFLUENCE OF LATERAL SUBSTITUENTS

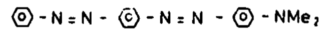
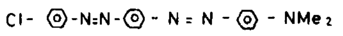
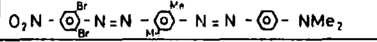
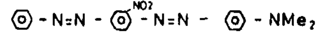
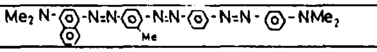
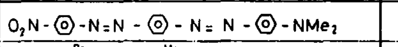
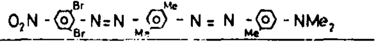
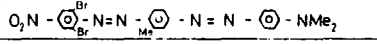
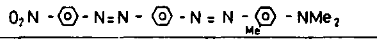
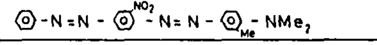
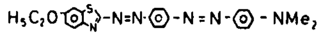
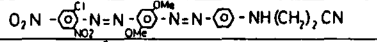
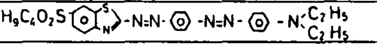
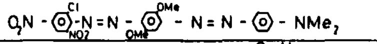
The textile industry has succeeded in obtaining azo dyes of high fastness by means of substitution of the phenyl rings of the dye.[25,27] In the case of light fastness increases for different substituents R, according to the sequence,[26]

$$NO_2 < OM_e < M_e < H < Cl < CN,$$

electron attracting groups being found to be more efficient. Lateral substitution decreases the order parameter of mono-azo dyes from an initial value by approximately 0.15 units (NO_2, Br). If this decrease in order parameter were the same for longer molecules, it would be unacceptable, but the decrease for

TABLE IV

Photochemical stabilities of some substituted bis-azo dyes

N°	FORMULA	λmax.in $CHCl_3$	COLOUR	O.P	$^1/_\beta$	T^1
P2		474	ORANGE	0.71	120	160
G156		486	RED	0.74	200	284
P14		488	RED	0.69	133	188
P26		500	RED	0.68	40	56.8
P15		500	RED	0.65	100	140
P50		501	RED	0.72	$45^{\pm 10}$ *	63.9
P9		504	RED	0.67 0.70	$30^{\pm 10}$ *	42.6
P27		510	RED	0.65	60	84
P11		516	RED	0.62	$25^{\pm 5}$ *	35.5
P10		520	RED	0.69	$60^{\pm 20}$ *	85.2
P16		520	RED	0.60	$180^{\pm 50}$ *	255.6
G162		530	VIOLET	0.77	40	56.8
P42/2		540	VIOLET	0.50	35	49.7
G165		576	BLUE	0.76	65	92.3
P41		578	BLUE	0.70	23	32
G170		588	BLUE	0.76	< 20	< 28.4

* average values an 10 cells.

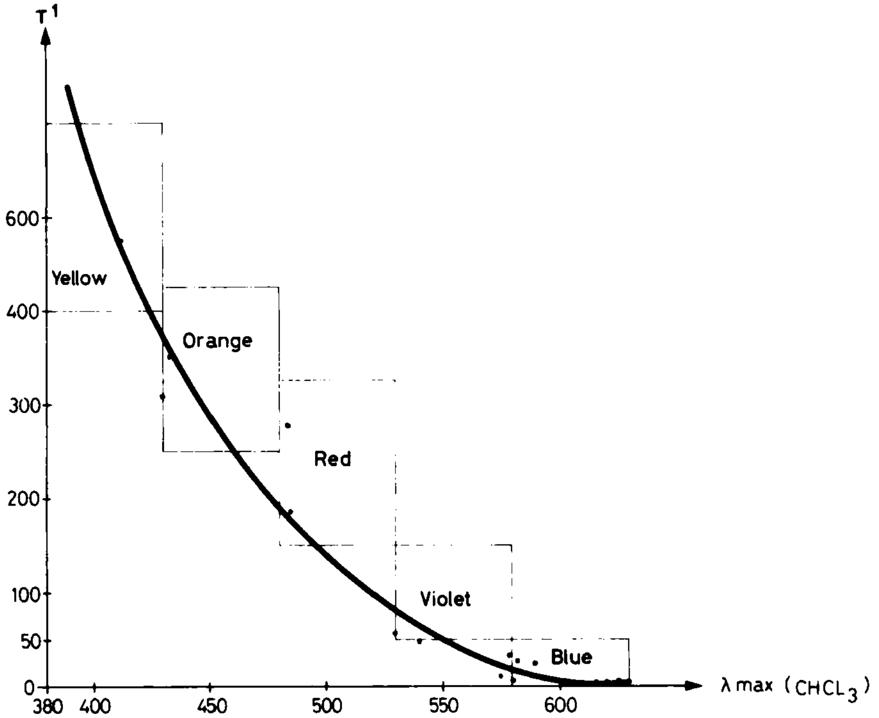


FIGURE 5 The light stability depends on the color of the dye.

bis- or tris-azo dyes is smaller. In the case of polysubstitution, the decrease in order parameter is equal to that obtained with the most perturbing substituent alone. Strongly substituted poly-azo dyes may therefore have good order parameters in E7 (Table IV), which indicates that the O.P. is related to the length-to-breadth ratio.

In view of the considerations outlined above, bis-azo dyes substituted with attracting groups were synthesized in the laboratory, and their stability to sun light was evaluated by the method described above. The summary of results presented in Table IV indicates that the substituents did not influence the light stability of the dye. The results do suggest, however, that lifetime is related to dye color. Blue azo dyes have very low β^{-1}'s (or $T^1_{1/2}$), and even Resolin BBLS the most stable dye of textile chemistry (fastness 6) has a lifetime, $T^1_{1/2}$, of only 27 hours in E7. Violet dyes have values of $T^1_{1/2}$ ranging from 50–100 hours, and yellow dyes appear to be the most stable. The graph in Figure 5 was obtained from a study of more than 60 substituted azo dyes, and shows the huge decrease in the light stability of azo dye-L.C. solutions as the wavelength of maximum absorption increases.

6 THE STABILITY OF AZO DYES DISSOLVED IN L.C.'s TO U.V. ILLUMINATION

Practical L.C. cells are made from glass plates which absorb the majority of the U.V. spectrum. Above the glass cut-off ($D = 1$ at $\lambda = 303$ nm), azo dyes exhibit, with the exception of their absorption band, a low U.V. absorption. Exposure of dichroïc cells to U.V. lamps leads, therefore, to apparently longer lifetimes than would be expected. Care should be taken to ensure that the stability of a dye to illumination is evaluated in a wavelength range which encompasses its absorption band.

The lifetime of L.C.-dye solutions also depends on the particular host employed. In general, L.C.'s have an absorption edge lying above the glass cut-off (Figure 6.1), which, in the absence of a dye, results in its photodecomposition. This effect is not observed in twisted nematic displays, where the L.C. is protected by the U.V. absorbing polarizer, but must be taken into account for dichroic cells.

A dye dissolved in a L.C. may be photosensitized as a result of the L.C. being excited (Figure 6.2). The effect of this process is to inhibit the degradation of the L.C. and to accelerate the decomposition of the dye. Solutions of dyes in L.C. mixtures exhibiting low absorption above the glass cut-off exhibit longer lifetimes. (Table V.1).

The photosensitization of a dye can be greatly reduced by the addition of a U.V. filter, such as a plastic layer containing U.V. absorbing particles, to the upper glass plate of a cell (Table V.2). This technique, together with a suitable choice for the host material can considerably increase the lifetimes of yellow through to red azo dyes, but has little effect for blue azo dyes.

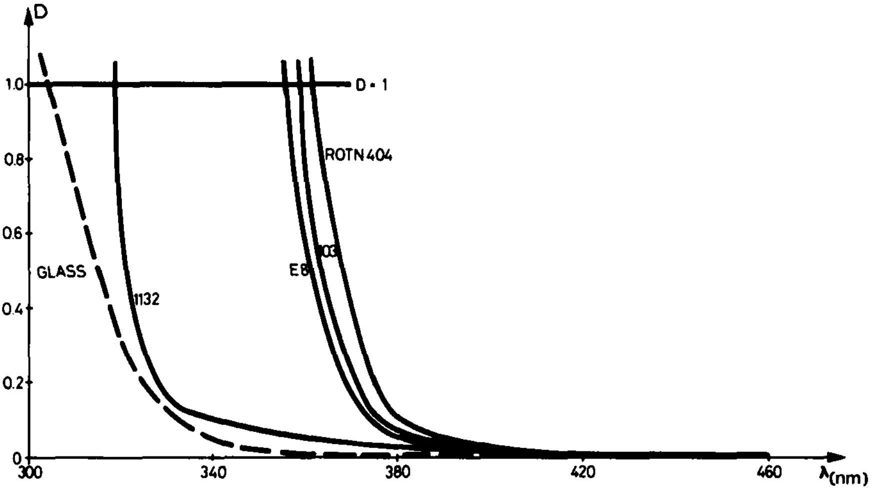


FIGURE 6.1 Absorption of light by L.C.'s above the glass cut-off.

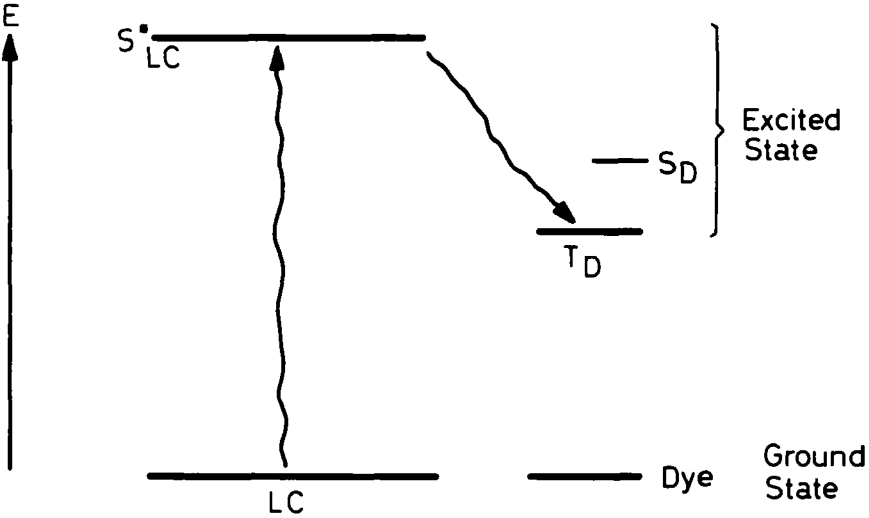


FIGURE 6.2 Photosensitization of dyes by the excited state of the L.C.

Guest-host displays must be stable to light, if they are to gain commercial acceptance. The filtered radiation of a Sun Test Xenon lamp produces an incident light energy of 585 $JM^{-2}s^{-1}$. This represents an acceleration factor of 5 for outdoor exposure in Europe (average sun light energy = $10^7.J.M^{-2}y^{-1}$).[25] In considering the dye stability required, the particular display application should be carefully considered, e.g. for what proportion of its life will a display be used indoors? A watch dial receives an average power of $7.J.M^{-2}s^{-1}$, as deter-

TABLE V.1

Lifetimes of solutions of azo dyes in L.C.'s of different residual absorption

L. C.	Glass	1132	E 8	103	404
λ Cut. off for D = 1 +	303	317	352	359	362
T^1 (h)		630	325	355	250

+ 30 μ thick quartz cells.

TABLE V.2

Lifetimes of dye P10 in ZLi 1132 and ROTN103 with and without U.V. absorbing layer

L. C.	1132	1132 + UVp*	103	103 + UVp*
T^1 (h)	630	1500	355	950

* UVp : UV protection

mined from measurements of the current output of solar cells.[29] The sun test acceleration factor for a watch display, is therefore 85, a 500 hour lifetime ($T\frac{1}{2}$) corresponding to 5 years' use. Commercial requirements, however, cannot be satisfied by currently available blue or black azo dyes.

CONCLUSION

The properties of azo dyes in solution in L.C.'s are much more complex than was originally believed. The relationship between the order parameters of a dye and a L.C. are incompletely understood, involving both the length of the dye's π-electron cloud, and the T_{NI} of the L.C.. In practice, solutions with good order parameters may be obtained by combining long dyes with hosts having high T_{NI} values.

The kinetics of degradation are zero order, and lifetimes may be calculated from considerations of incident photon flux and the molar extinction coefficient of the dye.

The lifetime of a dye is not affected by lateral substitution, but does depend on the dye's color.

High quality displays may be fabricated by employing a mixture of high initial optical density, and a host with a low absorption coefficient. This approach is preferable to the use of a U.V. protection layer, which suffers, although to a lesser extent, from the same drawbacks as polarizer layers.

The lifetimes of most azo dye solutions are suitable for the majority of applications that do not call for continuous outdoor exposure to sunlight; the exceptions are blue and violet dyes, which can be employed only in displays which will not be exposed to sun light.

Acknowledgments

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References

1. L. A. Goodman in *Introduction to Liquid Crystals*, (Eds: E. B. Priestley, P. J. Wojtowicz and P. Cheng) Plenum Press (1974), Chap. XIV.
2. G. H. Heilmeier and L. A. Zannoni, *Appl. Phys. Lett.*, **19**, 91 (1968).
3. D. L. White and G. N. Taylor, *J. Appl. Phys.*, **45**, 4718 (1974).
4. G. Gharadgedaghi, Y. Ruedin and E. Saurer, *E.D. Meet.*, **23-4**, 536 (1979).
5. F. Gharadgedaghi, *Mol Cryst. Liq. Cryst.*, Kyoto Proceedings, in press.
6. Color Index, Soc. Dyers and Col., 3^{d} Ed., **4**, (1971).
7. D. Demus, *Flüssige Kristalle in Tabellen*, VEB Deutscher Verlag für Grundstoffind., Leipzig (1974).
8. R. J. Cox, *Mol. Cryst. Liq. Cryst.*, **55**, 1 (1979).

9. L. M. Blinov, V. A. Kizel, V. G. Rumyantser and V. V. Titov, *J. Phys.*, (Paris), **36**, 69 (1975).
10. J. Constant, J. Kirton, E. P. Raynes, I. A. Shanks, D. Coates, G. W. Gray and D. G. McDonnell, *Electron Lett.*, **12**, 514 (1976).
11. A. Bloom, P. L. K. Hung and D. Meyerhofer, *Mol. Cryst. Liq. Cryst. Lett.*, **41**, 1 (1979).
12. This method was suggested to us by T. J. Scheffer.
13. T. J. Scheffer and J. Nehring, *J. Appl. Phys.*, **48**, 1783 (1977).
14. G. Pezl, D. Vetters and D. Demus, *Krist. und Technik*, **14**, 427 (1979).
15. H. S. Cole and S. Aftergut, *J. Chem. Phys.*, **68**, 896 (1978).
16. H. Meier in *Chemical Synthesis of Dyes*, Ed: (Venkataraman) Acad. Press (1971), **IV**, Chap. VII.
17. T. Watanabe, M. Sukigara, K. Honda, K. Toda and S. Nagaura, *Mol. Cryst. Liq. Cryst.*, **31**, 285 (1975).
18. P. Jacques, Thesis, Mulhouse (1977).
19. C. J. F. Böttcher, *Theory of Electric Polarization*, Elsevier (1973), 2nd Ed., **1**, Chap. IV.
20. W. Maier and A. Saupe, *Z. Naturforsch*, **14a**, 882, (1959).
21. P. J. Wojtowicz, Chap. III in Ref. 1.
22. *Handbook of Chem. and Phys.*, 60th Ed., CRC (1979).
23. E. Sackman and H. Möhwald, *Chem. Phys. Lett.*, **12**, 467 (1972).
24. F. Jones and T. J. Reeves, *J.S.D.C.*, 351 (1979).
25. M. C. Clark and J. D. Hildreth, *Rep. Progr. Chem.*, III (1972).
26. V. N. Ufimstev and L. V. Arinich, *Zh. Vses Khim. Obst.*, **19**, 50 (1974).
27. F. I. Abdel Hay, S. H. Etaiw, M. Anwar and M. El-Morsi, *Indian J. Text. Res.*, **2**, 92 (1977).
28. J. Cognard and T. Hieu Phan presented at the Eighth International Liquid Crystal Conference, Kyoto, July 1980. Abstract 123 to be published in *Mol. Cryst. Liq. Cryst.*
29. J. F. Tricaud, *Atlas Energètique du Rayonnement Solaire*, Pyc (1978).
30. F. Callias, *Energie Solaire Recuperee au Poignet*, C.E.H. Technical Report, No. 188.