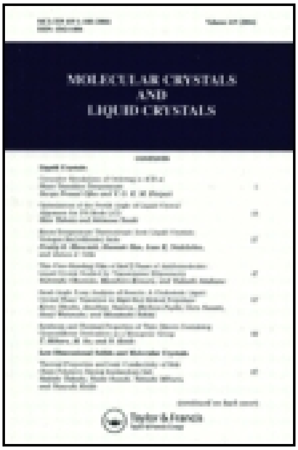

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Photodecomposition Rates of Some Dichroic Azo Dyes in Liquid Crystals

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Photodecomposition Rates of Some Dichroic Azo Dyes in Liquid Crystals

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Decomposition rates of ten dichroic trisazo and five monoazo dyes dissolved in liquid crystal hosts were derived by measuring the spectra periodically. The light source was a 1-kW Xenon lamp from which UV radiation had been filtered out. Depending on chemical structure, the rates spanned about two orders of magnitude.

1. INTRODUCTION

Dichroic azo dyes have many good attributes for use in displays such as high order parameter, satisfactory solubility, high absorption coefficient, and favorable spectral properties for saturated colors. However, azo dyes tend to decompose when exposed to light. The purpose of this work was to identify the most stable dyes from a selection of dyes with otherwise good display properties. Previously we reported on the stability of some anthraquinone dyes.[1] Other azo dyes[2-4] and anthraquinone dyes[5,6] have also been investigated.

2. RESULTS

Decomposition of the dyes was monitored by periodically measuring the spectra of dye solutions during exposure.

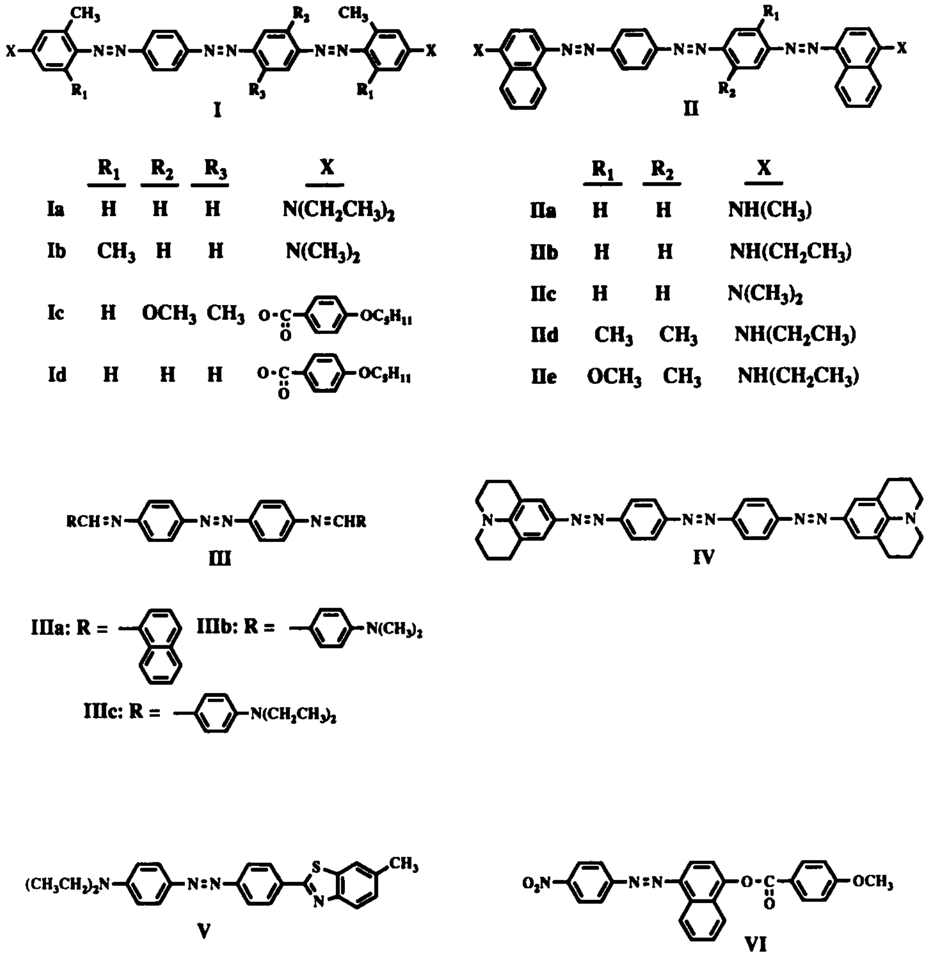
For isotropic solutions whose decomposition products do not absorb at the wavelength λ of interest, it was shown[7] that

$$\log(10^{D} - 1) = -\phi\varepsilon ItL + \log(10^{D_0} - 1) \qquad (1)$$

where D_0 is the initial absorbance, D is the absorbance after exposure $E = It$ where I is light intensity (einstein/liter-hr) and t is time (hr), ϕ is the quantum yield, ε is the extinction coefficient to base 10 (liter/mole-cm) and L is the light path (cm). Plotting $\log(10^{D_0} - 1)$ against exposure gives a straight line with slope $-\phi\varepsilon L$ and intercept $\log(10^{D_0} - 1)$. Although the quantum yield is a primary measure of stability, we did not have the precise extinction coefficients and path length to compute the yield. Instead, we defined $R = \phi\varepsilon L(\mathrm{cm}^2/\mathrm{w\text{-}hr})$ to give

$$\log(10^{D} - 1) = -RIt + \log(10^{D_0} - 1) \qquad (2)$$

The absorption of a dichroic dye solution depends not only on the concentration and extinction coefficients but also on the orientation of the dye with respect to the light beam of the spectrophotometer. To ensure that orientation effects would be minimal or negligible, cholesteric liquid crystal hosts were used. Further, since the intended practical application utilized cholesteric hosts, the tests were more relevant in this type of host. The absorption depends on the pitch of the host.[8] The pitch was about 3 μm.



	R_1	R_2	R_3	X
Ia	H	H	H	$N(CH_2CH_3)_2$
Ib	CH_3	H	H	$N(CH_3)_2$
Ic	H	OCH_3	CH_3	$O\text{-}C(=O)\text{-}C_6H_4\text{-}OC_5H_{11}$
Id	H	H	H	$O\text{-}C(=O)\text{-}C_6H_4\text{-}OC_5H_{11}$

	R_1	R_2	X
IIa	H	H	$NH(CH_3)$
IIb	H	H	$NH(CH_2CH_3)$
IIc	H	H	$N(CH_3)_2$
IId	CH_3	CH_3	$NH(CH_2CH_3)$
IIe	OCH_3	CH_3	$NH(CH_2CH_3)$

FIGURE 1 Structures of dyes.

Structures of the dyes are shown in Figure 1. The hosts were liquid crystal formulations E7 or ZLI-1291 (biphenyl and phenylcyclohexane derivatives, respectively) to which 5% CB15 (4-(2-methylbutyl)-4′-cyanobiphenyl) was added to obtain a cholesteric texture. The solutions were degassed and introduced into glass frit sealed cells which were plugged with solder to ensure hermeticity and inertness. The samples were exposed to a 1-kW Xenon lamp whose output was filtered through IR and UV filters (Figure 2).

The distribution of power incident on the samples is shown in Table I. Incident light intensity at 350 to 800 nm and total exposure are listed in Table II. Figure 3 shows an example of spectra before and after exposure; the dye in this figure was IIIa. Figures 4 to 7 show absorbance D vs. exposure. The absorbance is for the wavelength of maximum absorption λ_{max} in Table II. The initial absorbance at λ_{max} was different for each dye as shown in Table II.

Data analysis according to Equation (2) gave the rate constants R shown in Table II. These values are related, but not equivalent, to the slopes of the lines in Figures 4 to 7 because the latter correspond to D (not $\log(10^D - 1)$) plots. For a

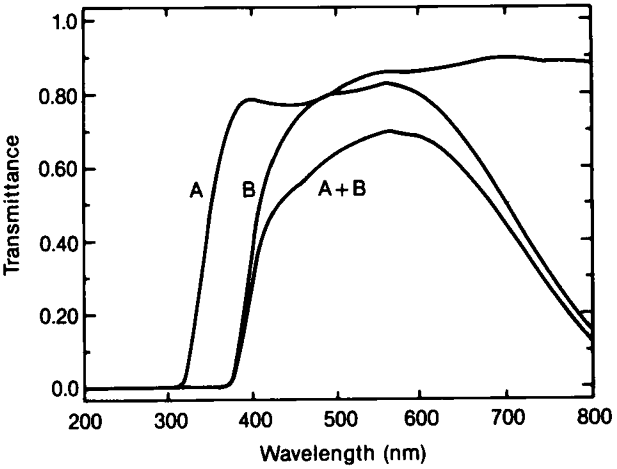


FIGURE 2 Spectra of IR and UV filters (A-IR filter, B-UV filter).

TABLE I

Approximate Power Distribution Incident on Cells

Range (nm)	Power (%)
< 350	0.004
350–400	1.6
400–500	30.5
500–600	34.7
600–700	23.5
700–800	9.7

TABLE II

Experimental Data and Results for Dye Solutions

Dye	Color	Purity	LC Host	I (w/cm^2)	Total Exp ($w\text{-}hr/cm^2$)	λ_{max} (nm)	D_0 at λ_{max}	10^3R ($cm^2/w\text{-}hr$)	ΔE ($W\text{-}hr/cm^2$)
IC	Yellow	1	1291	0.112	36.3	416	0.389	1.19	94.9
ID	Yellow	1	E7	0.176	75.3	405	0.766	1.20	93.5
IIIA	Yellow	1*	1291	0.112	37.6	406	0.675	2.31	48.7
IA	Purple	2*	E7	0.173	54.1	565	0.821	2.51	44.9
IB	Violet	1*	E7	0.176	56.5	555	0.206	3.77	29.9
IID	Blue	3*	1291	0.112	16.1	582	0.295[a]	3.88	29.1
IIB	Blue	2*	E7	0.162	44.3	595	0.564	4.03	28.0
IIE	Blue	3*	1291	0.112	37.6	596	0.489[a]	6.06	18.6
VI	Yellow	3	E7	0.171	40.9	412	0.584	8.19	13.8
IIA	Blue	1	E7	0.162	25.1	590	0.319	10.9	10.3
IIC	Violet	1*	E7	0.094	15.2	550	0.635	11.1	10.1
V	Orange	3	E7	0.186	16.9	480	0.628	16.6	6.81
IIIC	Yellow	1	E7	0.162	25.1	455	0.709	22.9	4.92
IV	Purple	5*	E7	0.106	2.9	564	1.268	55.0	2.05
IIIB	Yellow	3	E7	0.162	3.2	440	0.160	121.0	0.93

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*Single spot in thin-layer chromatography
(a)Absorbance measured at 624 nm

Purity:
1. Recrystallized
2. Gel-permeation chromatographed
3. Chromatographed on alumina

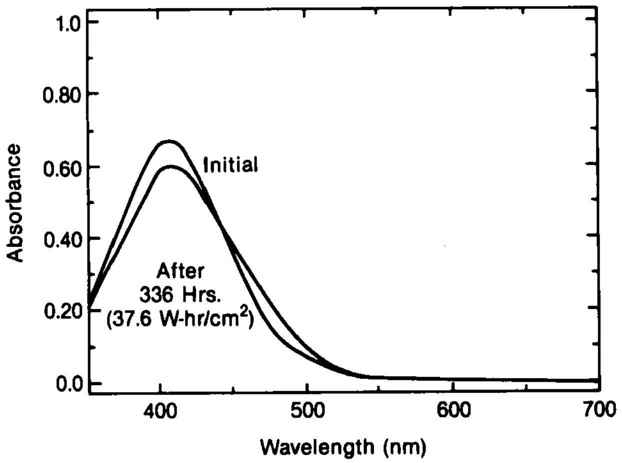

FIGURE 3 Spectra of dye IIIA.

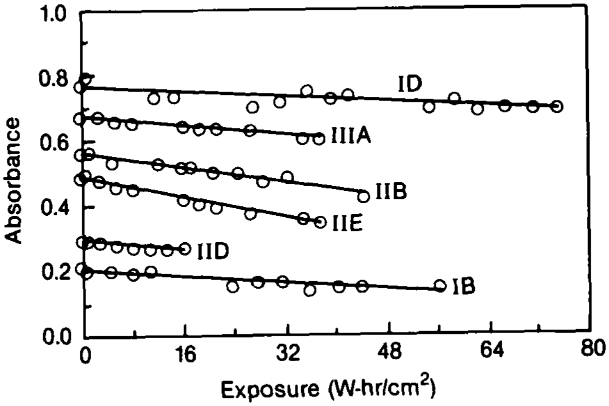

FIGURE 4 Absorbance at λ_{max} vs. exposure (absorbance at 624 nm for IID and IIE).

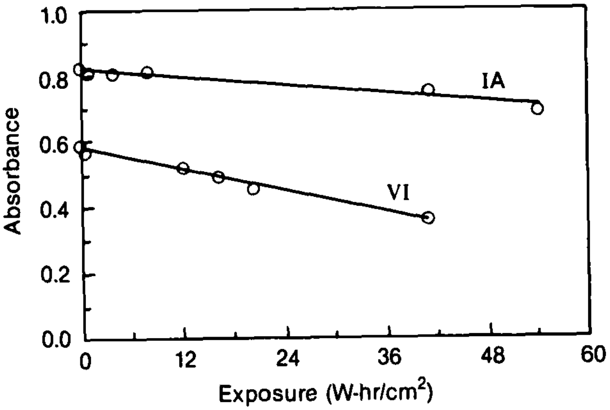

FIGURE 5 Absorbance at λ_{max} vs. exposure.

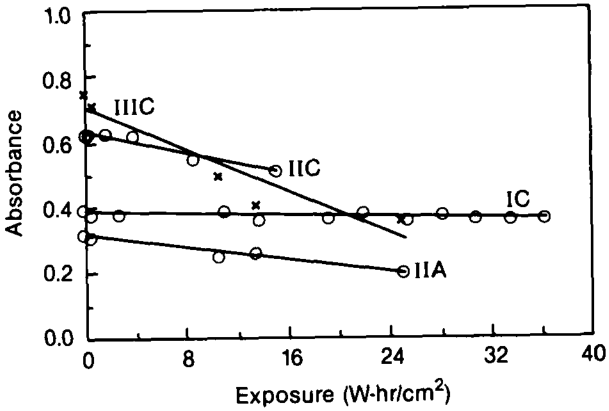

FIGURE 6 Absorbance at λ_{max} vs. exposure.

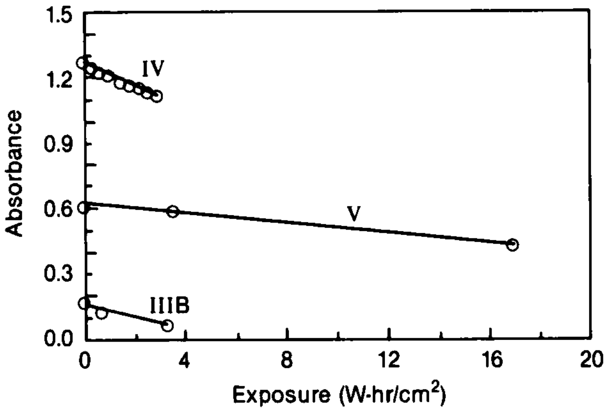

FIGURE 7 Absorbance at λ_{max} vs. exposure.

comparison of practical dye stability, Equation (2) was used to compute the exposure required for a 10% decrease in absorbance from an initial value of $D_0 = 1$. The results are shown in the last column of Table II under ΔE.

3. DISCUSSION

The rate of absorbance changes for the investigated dyes varied by about two orders of magnitude. For the hypothetical case of dyes of identical extinction coefficients at λ_{max}, the computed exposure ΔE would be inversely proportional to the quantum yield of dye decomposition. Although the extinction coefficients were not identical, we estimate that they did not vary by more than a factor of 2 or 3. It may, therefore, be concluded that the order of the dyes in Table II approximately represents the sequence of increasing quantum yield for dye decomposition. Dyes IC and ID are the most stable; they also are, incidentally, the largest molecules with the highest molecular weight. Schiff bases IIIB and IIIC are among the least stable as expected, but the naphthyl-substituted Schiff base IIIA is relatively stable. When the UV filter was omitted, the degradation proceeded at a much faster rate.

4. EXPERIMENTAL

The equipment and measurement technique were the same as reported earlier.[1] Dyes I and II[9] were synthesized by diazotization of the appropriate azodianiline derivative and coupling with the proper amine, except for dyes IC and ID, which were first coupled with m-toluol and then esterified with p-(n-pentoxy)benzoyl chloride. Schiff bases III were prepared from azodianiline and the appropriate aldehyde. Dye IV was obtained as dye D3 from BDH. Dyes V and VI were synthesized by diazotization/coupling and esterification reactions, respectively. The dyes were purified as indicated in Table II.

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