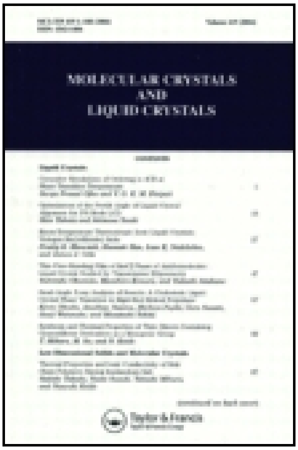

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Photodecomposition Rates of Some Anthraquinone Dyes in Liquid Crystals

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Photodecomposition rates of five anthraquinone dyes dissolved in liquid crystal hosts were measured by exposure to radiation at 300–800 nm. Depending on structure, the decomposition rates varied by almost 3 orders of magnitude.

INTRODUCTION

The application of dichroic dyes as guests in liquid crystal hosts for electronic displays[1,2] requires that the dye solutions be photochemically stable. In general, most dyes tend to bleach or change color when exposed to light in the visible or UV region of the spectrum. Some data on the relative stability of liquid crystal solutions of a number of anthraquinone dyes have already been reported.[3] The present work is a more detailed quantitative study of photodecomposition rates which allows one to estimate the potential photochemical life time of a display for applications where the exposure and the maximum tolerable color degradation are known.

RESULTS AND DISCUSSION

Photocomposition rates were determined from the change of absorbance of dye samples as function of exposure time at constant light intensity. For isotropic systems whose decomposition products do not absorb at the wavelength λ of interest, it can be shown[4] that

$$\log(10^{D} - 1) = -\phi I\epsilon L t + \log(10^{D_0} - 1) \qquad (1)$$

where D and D_0 are the values of absorbance at time t (hr) and $t = 0$, respectively, ϕ is the quantum yield, I is the light intensity (einstein/liter-hr), ϵ is the extinction coefficient to the base 10 (liter/mole-cm), and L is the light path (cm). Plotting $\log(10^{D} - 1)$ against time gives a straight line with slope $-\phi I\epsilon L$ and intercept $\log(10^{D_0} - 1)$. The basic parameter characterizing a photodecomposition reaction is the quantum yield which can be computed from the slope if I, ϵ and L are known. However, these quantities could not be readily determined with the required precision. For this reason, rate constant k was defined as $k = \phi I\epsilon L$ to give

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

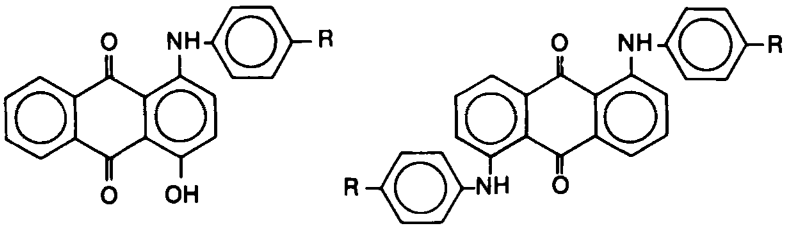
k is the decomposition rate constant with the unit hr^{-1} for light intensity I of the experiment. It is evident that k is independent of initial absorbance D_0.

The absorbance of the dyes in a cholesteric host is given by an equation of the form[5]

$$D = -\log\{\tfrac{1}{2}[\exp(-a_1\epsilon_0 cL) + \exp(-a_2\epsilon_0 cL)]\} \qquad (3)$$

where a_1 and a_2 are a measure of the ellipticity of polarized light in the host and depend on the pitch, order parameter and birefringence of the system, ϵ_0 is the extinction coefficient in an isotropic host and c is the concentration. For the systems under consideration, a_1 and a_2 are in the ratio of about 1:2. Consequently, the absorbance is not a linear function of dye concentration. Although Eq. (1) is predicated on the condition that absorbance is directly proportional to concentration, this equation was nevertheless applied in the treatment of the data because the departure from linearity over the small absorbance change studied (<25%) does not introduce an appreciable error.

The five anthraquinone dyes shown in Figure 1 were investigated. The dyes were dissolved in a cholesteric host prepared by adding 4-(2-methylbutyl)-4′-cyanobiphenyl (CB15) to a nematic mixture of biphenyls (E7) or phenylcyclohexanes (Licristal 1132). A cholesteric host was used because hosts of this type are used in practical applications. Furthermore, the light from the spectrophotometer employed in the initial work was substantially polarized, and the absorption of polarized light by a dichroic dye is highly dependent on the orientation of the dye



D16 $R = OC_9H_{19}$
D27 $R = N(CH_3)_2$

D35 $R = C_2H_5$
D43 $R = OC_5H_{11}$
D52 $R = N(CH_3)_2$

FIGURE 1 Structures of dyes.

with respect to the polarization plane, thus making it imperative to ensure perfect control of dye orientation in the cell and reproducible positioning of the cell in the spectrophotometer. More reliable and more easily interpretable results can be obtained in a cholesteric host because a change in sample orientation with respect to the polarization plane has a much smaller effect on absorbance when the host is a short-pitch cholesteric rather than a nematic material. The dye solutions were degassed before introduction into glass-frit sealed cells coated with indium tin oxide, and the fill aperture was sealed with solder.

The light source was a 1 KW Xenon lamp. To remove excessive heat, the radiation was filtered through an IR filter whose transmission is shown in Figure 2. The curve for the IR filter includes the effect of that of a piece of glass which was used to clamp the sample to the water-cooled holder. The spectral distribution of the light (arbitrary units) incident on the filter is shown in Figure 2. Table I shows the fraction of light at different wavelength intervals incident on the samples after passing through the filter. The temperature of the samples was 22 ± 1°.

Figure 3 shows the spectra of dye D27 (dissolved in E7/3.5% CB15) before exposure and after exposure for 170 hrs. at a light intensity of 0.124 w/cm^2 at 350–700 nm. The absorbance at λ_{max} of 606 nm decreased from 0.23 to 0.18 during this period. Figure 4 shows that a plot of log $(10^D - 1)$ at 606 nm vs. time has a good fit to Eq. 2. From the slope of the straight line derived by the least-squares method, k for this exposure is 6.99×10^{-4} hr^{-1}.

Spectra for the other dyes before exposure are shown in Figure 5, and experimental data for these dyes are shown in Figure 6 in a plot of log $(10^D - 1)$ at λ_{max} vs. exposure expressed as w-hr /cm^2. The product of light intensity and time was chosen for this presentation because the

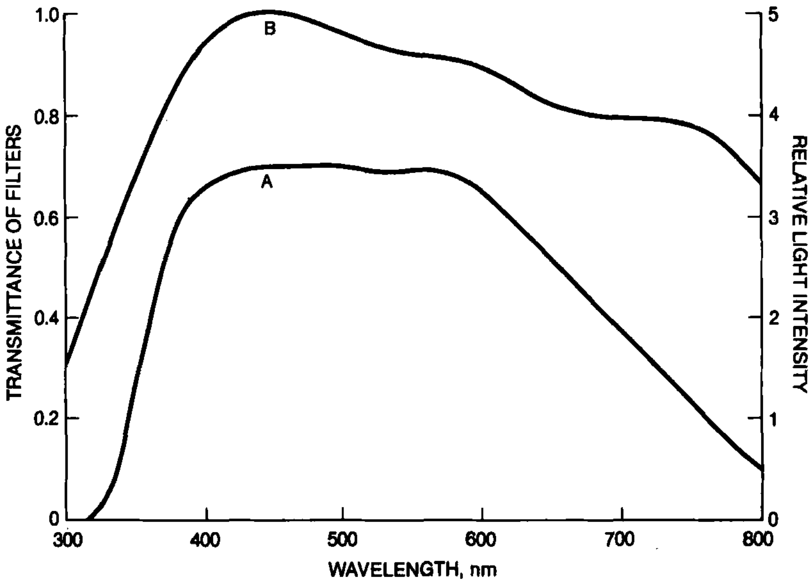


FIGURE 2 Transmittance of filter (A) and spectral distribution of radiation (B).

TABLE I

Spectral distribution of power incident on cells

λ_2 (nm)	Fraction of power between λ_2 and $\lambda_1 = 300$ nm
320	4×10^{-5}
350	0.008
370	0.036
400	0.111
450	0.269
500	0.430
550	0.580
600	0.725
650	0.841
700	0.921
750	0.975
800	1.000

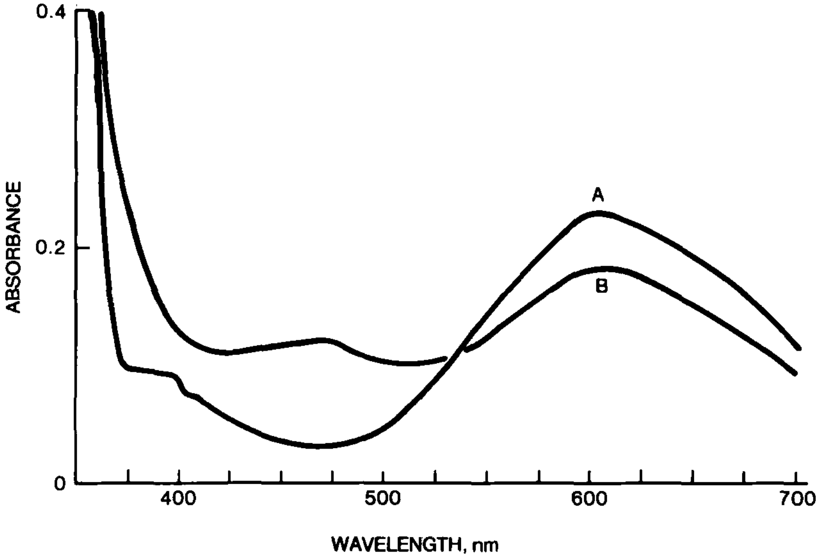


FIGURE 3 Specra of dye D27 before exposure (A) and after exposure for 170 hrs. to 0.124 w/cm^2 at 350–700 nm (B).

light intensity ranged between 0.117 and 0.201 w/cm^2 for different tests. Table II summarizes the results obtained on all the dyes. To eliminate the varying light intensity as a factor in comparing decomposition rates, the last column of Table II shows the normalized decomposition rate ($k/I = k_I$), normalized to an exposure of 1 w/cm^2.

In experiments designed to test the influence of the host, it was found that the difference of response between the biphenyl- and phenylcyclohexane-based hosts at λ_{max} of the dyes was within the limits of experimental error. Thus, we expect that dye D35, which was investigated only in host Licristal 1132, would behave similarly in the E7 host.

Although no quantitative quantum yield data are available for a fundamental and precise assessment of stability, several observations are noteworthy. The extinction coefficients at λ_{max} for the different dye samples varied by much less than an order of magnitude and the light intensity varied by less than a factor of 2. However, the decomposition rates varied by almost 3 orders of magnitude. It may, therefore, be concluded that to a first approximation the quantum yields are roughly proportional to the decomposition rates, and that large differences in stability due to chemical structure factors exist within the class of anthraquinones. The least stable anthraquinones D16 and D27 have a

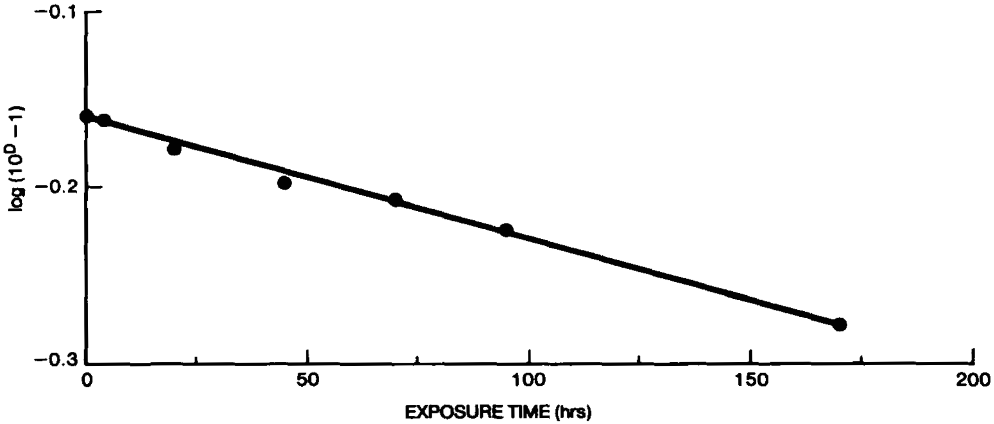


FIGURE 4 Plot of log $(10^D - 1)$ vs. exposure time for dye D27 at 606 nm.

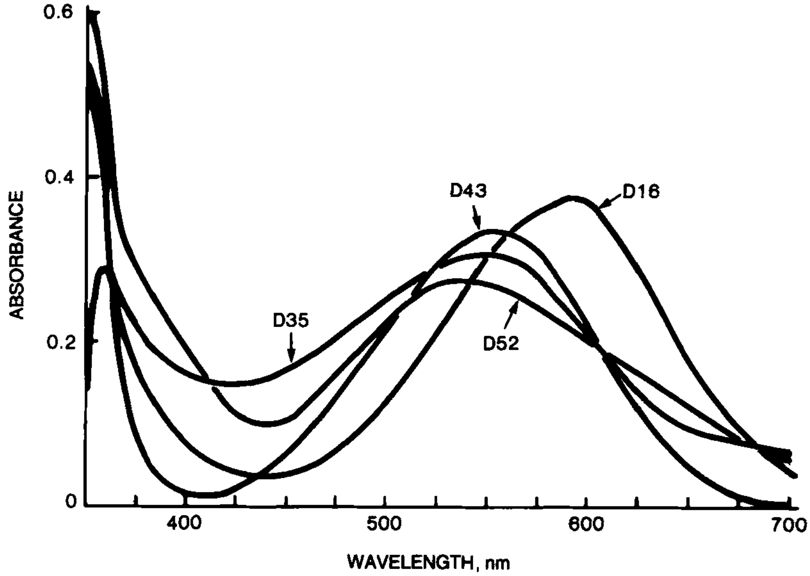


FIGURE 5 Spectra of dyes before exposure.

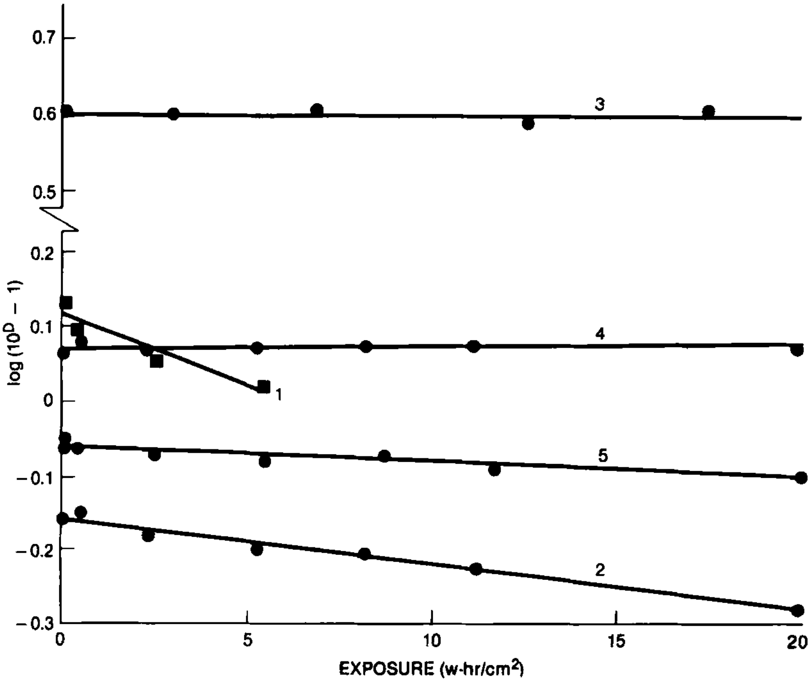


FIGURE 6 Plots of log ($10^D - 1$) vs. exposure. Key to plots in Table II.

TABLE II

Decomposition rate constants of dyes

Plot	Dye	Host	λ_{max} (nm)	I (w/cm^2) at 350–700 nm	10^4 k (hr^{-1})	10^3 k/I (cm^2 w^{-1} hr^{-1})
1	D16	A	594	0.124	22.5	18.1
2	D27	A	606	0.117	6.99	5.97
3	D35	B	545	0.201	0.465	0.231
4	D43	A	556	0.117	−0.023	−0.0194
5	D52	A	536	0.124	3.21	2.58

A: E7/3.5% CB15.
B: 1132/5% CB15.

hydroxy group in the 4-position. This group is absent in the most stable anthraquinones D35 and D43 and these two dyes also do not have a tertiary amino group. These observations might form the basis for future mechanistic studies.

EXPERIMENTAL

The light source for exposing the samples was a 1 KW ozone-free, high-pressure Xenon lamp (Canrad Hanovia, type L5179-000). Light intensity was measure with a pyroelectric radiometer (Laser Precision Corporation, Model RkP-345 Probe and Model Rk-3440 Power Meter). The radiation was filtered through an infrared filter (Oriel G776-7100). During exposure, the cells were held down on a water-cooled platform by a piece of glass. The reflectance of the platform surface was estimated at about 50%. The platform surface was at a distance of 5 in. from the collimating lens.

The tests were made in cells coated with layers of indium tin oxide and silica. The cells were hermetically sealed with glass frit and plugged with solder. The region around the solder plug had been metallized by sputtered coatings to promote adhesion of the solder. The gap in the cells, defining the length of the light path, was about 25–30 μm. To fill the cells, they were placed in a beaker in a vacuum chamber. After pumping down the system, the liquid crystal formulation was introduced into the beaker, and the vacuum was released to permit the fluid to be sucked into the cells. Since the formulations were in the vacuum chamber for several minutes during pumpdown, they must have been substantially degassed. It cannot be assumed, however, that all the air was removed from the formulations. The filled cells were plugged with solder in air after removal from the liquid crystal-containing beaker.

The anthraquinones were obtained from BDH Chemicals. Hosts E7 and Licristal 1132 and the optically active CB15 were obtained from EM Chemicals.

The spectra were measured with a Cary 14 or Hewlett Packard Model 8450A spectrophotometer, and the results were corrected for reflection and other losses with the aid of spectra taken on cells containing the host without dyes.

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