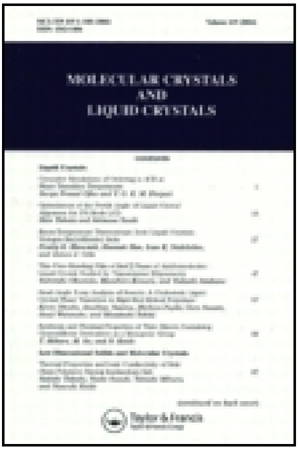


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Photostability of Dyes in Liquid Crystalline Media

F. Jones [a] & T. J. Reeve [a]
[a] Wolfson Organic Powders Research Unit, Department of Colour Chemistry, University of Leeds, Leeds, LS2 9JT, England

To cite this article: F. Jones & T. J. Reeve (1981): Photostability of Dyes in Liquid Crystalline Media, Molecular Crystals and Liquid Crystals, 78:1, 201-209

To link to this article: http://dx.doi.org/10.1080/00268948108082156

Mol. Cryst. Liq. Cryst., 1981, Vol. 78, pp. 201–209
0026-8941/81/7804-0201 $06.50/0

Printed in the United States of America

Photostability of Dyes in Liquid Crystalline Media

F. JONES and T. J. REEVE
Wolfson Organic Powders Research Unit, Department of Colour Chemistry, University of Leeds, Leeds LS2 9JT, England

(*Received June 30, 1981*)

A number of dyes of different types dissolved in a nematic medium have been exposed to ultraviolet and visible radiation under specific test conditions. The results are discussed and factors affecting the differences in photostability of the dyes are considered.

INTRODUCTION

The examination of the effect of dyes of widely differing structure, when present as guest material in liquid crystal display (LCD) systems, on legibility and contrast is a topic of current commercial interest. In a recent review, Cox[1] refers to work on at least eight chemically different classes of dyes applied for this purpose. The emphasis has naturally been on developing dyes which are compatible with the host material and which possess high order parameters. An equally important aspect, however, is that their application in viable display systems requires the achievement of high light stability. In this sense some aminoanthraquinonoid dyes have so far been found by Pellatt *et al.*[2] to be the most satisfactory, exposure to u.v. radiation in a liquid crystal host for 100 hours causing no detectable fading. In a recent paper[3] we have reported order parameters of a number of dyes based on the azobenzene-, 5-nitrothiazoleazo- and aminoanthraquinonoid chromophore systems in the same type of host (E7, BDH Chemicals Ltd.) as that used by Pellatt *et al.* for fading studies, namely a mixture of 4-cyano-4′-alkyl- and -alkoxy-biphenyls and a 4-cyano-4″-alkyl-*p*-terphenyl. At the same time, cells were examined by exposure to u.v. and visible radiation, and the present paper reports the results of these tests and considers some of the factors contributing to the differences in photostability of the dyes.

Determination of fading rates

Cells, prepared as previously,[3] were of 12 μm. thickness, coated with a transparent rubbed layer of polyvinyl alcohol, filled with a 1% wt./vol. solution of pure dye in E7, and hermetically sealed with epoxy resin, except where otherwise stated. The optical density of each cell at λ_{max} of the dye in the parallel mode was obtained using a Pye-Unicam SP6-200 fitted with a Polaroid HN42 neutral linear polariser. Irradiation of the cells was carried out with a 500 W Miscroscal MBTL fadeometer lamp at a distance of 15 cm from the lamp envelope. The total wattage at this distance was found to be 0.116 W cm^{-2} as determined by a Coherent Radiation 210 thermopile. The MBTL lamp (Microscal Ltd.) is a combined u.v.-tungsten filament lamp with a phosphor-coated envelope which converts some of the ultra-violet light to visible radiation, thus giving spectral characteristics approximating more closely to daylight than, e.g., a medium pressure Hg vapor lamp. Excellent correlation has been found[4] between conventional daylight fading trials and trials with this type of lamp in the field of dyed textiles, with the additional advantage of a more rapid fading rate.

No attempt was made to cool cells during exposure. Within a short time, equilibrium fading temperatures of 38–40°C were attained in the fadeometer. Control cells containing only liquid crystal host were also exposed for use as blanks in the spectrophotometric determinations. All cells were cooled to ambient temperature (20°C) prior to measurement.

Assuming a first order or pseudo-first order degradation of the photoactivated dye molecule the equation,

$$\log_e \frac{[D]_o}{[D]_t} = Kt \tag{1}$$

where $[D]_o$ and $[D]_t$ represent dye concentrations at times $t = o$ and $t = t$ respectively, may be applied. Since the generalized Beer-Lambert law states that absorbance or optical density is proportional to solute concentration for a monomolecularly dispersed species, the above Eq. 1 can be expressed in the form

$$\log_e \frac{[O\cdot D]_o}{[O\cdot D]_t} = Kt \tag{2}$$

where $[O\cdot D]$ is optical density at the wavelength of maximum absorption of the dye. K is the reaction rate constant and can be determined from the gradient of the curve when $\log_e [O\cdot D]_o/[O\cdot D]_t$ is plotted against time t. Alternatively, the directly related time of half-fading, $t_{1/2}$, may be used. This is the time required for the dye concentration to fall to half its initial value. From (2) it follows that

$$\log_e \frac{[O\cdot D]_o}{[O\cdot D]_t} = \log_e 2 = Kt_{1/2} = 0.693. \tag{3}$$

Where fading is rapid, $t_{1/2}$ may be determined experimentally, or, for a first order reaction where the fading rate is concentration dependent, and the rate of fading is low, the time of half-fading may be obtained by extrapolation using the above mentioned plot. Both K and $t_{1/2}$ values may thus be used to compare the fading properties of dyes of different structure in the same medium.

Figure 1 shows typical rate curves for three azo dyes (I, VI, and VIII) of widely differing photostability. The rates were found to be linear in all cases. Values of K, determined by least mean squares, for all the dyes examined in this manner, varied over the range 6.3×10^{-4} to 4.0×10^{-8} s.$^{-1}$ and are shown in Tables I-III. Times of half-fading shown in these Tables were either directly determined from rate curves or by extrapolation of initial linear fading rates. Corresponding times of half-fading ranged from 0.5 to > 3000 h.

The dyes listed in Tables I and II were chosen from the previously mentioned series,[3] but limiting the choice to those of higher order parameter.

In the azo dye series, only the dyes I and II may be considered to approach an adequate photostability and in comparison with the data for dyes given in Table III may be regarded as less than adequate. Although the presence of electrophilic nitro- or cyano- groups or the inclusion of an electrophilic thiazole ring system (dyes VII and VIII) increases the red shift with respect to color, the same groups drastically decrease the photostability. Since the guest-host interactions do not vary significantly, as reflected in the narrow order

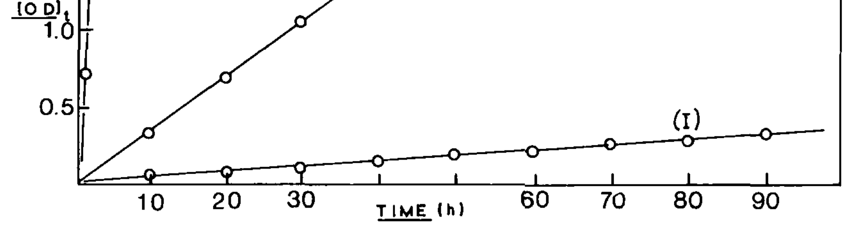
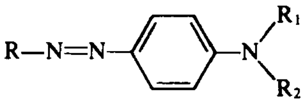


FIGURE 1 Fading rates of three azo dyes (I, VI and VIII-Table I).

TABLE I

Fading Rate Constants of Some Mono-azo Dyes.



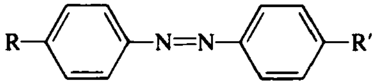
Dye Number	R	R_1	R_2	$t_{1/2}$ (h)	K (s^{-1})	S
I	4'-nitrophenyl-	$—CH_3$	$—CH_3$	236	8.2×10^{-7}	0.61
II	4'-nitrophenyl-	$—C_2H_5$	$—C_2H_5$	234	6.5×10^{-7}	0.63
III	4'-nitrophenyl-	$3—CH_2CH_2CH_2—$ (julolidine)	$5—CH_2CH_2CH_2—$	37	4.0×10^{-6}	0.59
IV	4'-cyanophenyl-	$—C_2H_5$	$—C_2H_5$	128	1.2×10^{-6}	0.61
V	2',3'-dicyanophenyl-	$—C_2H_5$	$—C_2H_5$	78	1.7×10^{-6}	0.46
VI	2',4',6'-tricyanophenyl-	$—C_2H_5$	$—C_2H_5$	2	6.9×10^{-5}	0.53
VII	5'-nitrothiazole-2-	H	H	3	5.5×10^{-5}	0.57
VIII	5'-nitrothiazole-2-	$—CH_3$	$—CH_3$	26	5.6×10^{-6}	0.62

parameter (S) range (0.5–0.6), it may be assumed that decreases in photostability could arise from the presence of excited-state dye molecules of relatively low, but higher energy level than that of the ground state. The photostability of bis- and tris-azo dyes is still further reduced as shown in Table II. Whereas these dyes possess high order parameters in the E7 medium, the times of half fading are such that they render such dyes inoperable in nematic phase change displays.

We have been able at the same time to confirm the data given by Pellat *et al.*[2] on the photostability of 1,4- and 1,5-disubstituted-anthraquinone dyes (B.D.H. Chemicals Ltd.) and the results are given in Table III.

TABLE II

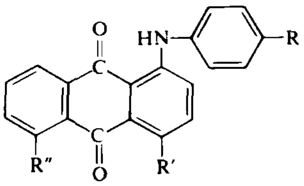
Fading Rate Constants of Some Bis- and Tris-azo Dyes.



Dye Number	R	R^1	$t_{1/2}$ (h)	K (s^{-1})	S
IX	H	phenylazo-	2	7.8×10^{-5}	0.62
X	H	-*p*-(*N*-dimethylamino)-phenylazo-	8	1.4×10^{-5}	0.66
XI	phenylazo	phenylazo-	5	3.7×10^{-5}	0.64
XII	2-hydroxy-1-naphthylazo-	2-hydroxy-1-naphthylazo-	0.5	6.3×10^{-4}	0.66

TABLE III

Photostability of Amino-anthraquinonoid Dyes in Two Liquid Crystalline Media.



Dye Number	Code	R	R′	R″	RO-TN-103		E7		S (in E7) Ref. No. 2
					$t_{1/2}$ (h)	K (s^{-1})	$t_{1/2}$ (h)	K (s^{-1})	
XIII	(D27)	—$N(CH_3)_2$	—OH	H	552	1.8×10^{-7}	537	2.6×10^{-7}	0.63
XIV	(D16)	—OC_9H_{19}	—OH	H	2912	5.0×10^{-8}	656	2.2×10^{-7}	0.65
XV	(D35)	—C_2H_5	H	-*p*-ethylphenylamino-	816	1.7×10^{-7}	3072	4.0×10^{-8}	0.67
XVI	(D52)	—$N(CH_3)_2$	H	-*p*-dimethylamino-phenylamino-	572	2.5×10^{-7}	400	3.7×10^{-7}	0.65
XVII	(D43)	—OC_5H_{11}	H	-*p*-pentyloxyphenyl-amino-	185	8.7×10^{-7}	270	5.6×10^{-7}	0.62

Although the order parameters found were slightly lower than those previously reported, the times of half-fading and calculated reaction rate constants indicated a much higher degree of photostability than for the azo dyes quoted in Tables I and II. Pellatt *et al.* reported little or no fading when these aminoanthraquinonoid dyes were exposed, with cooling, for a period of 100 h. to radiation from a Hanovia u.v.-visible lamp of total wattage 0.009 Wcm^{-2}. This radiation energy is much less than that used in the present work (0.116 Wcm^{-2}). Times of half-fading show that these dyes do eventually fade on prolonged exposure. The dye of greatest photostability is dye XV (B.D.H. Chemicals, D35) in E7 with a rate constant of $4.0 \times 10^{-8} s^{-1}$. Dyes of acceptable photostability would require a rate constant approaching this value. Although changing the dye structure may be one method of achieving this, Table III shows that the nature and type of liquid crystal host must also be taken into account. When the same procedure is carried out using the RO—TN-103 liquid crystal eutectic mixture of Hoffmann-La Roche, dye XVI (D16) shows enhanced photostability and XV only a moderate stability. Other dyes also exhibit different photostability in these two media, and it becomes of importance to specify both the dye and the liquid crystal host in defining light stability. In comparing the results for the two host media, no consistency can be seen relating the stability to the molecular properties of the hosts.

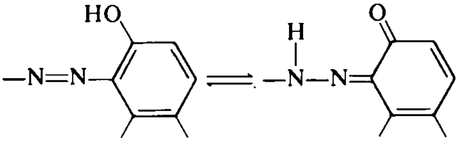
DISCUSSION

Firstly it must be pointed out that the fading of dyes by the action of light depends, amongst other factors, on the intensity of radiation to which the dye is exposed. Direct comparisons between sets of results can only be made when the results have been obtained by the use of standardized light sources, all other conditions remaining constant. Within these restrictions it is, however, possible to relate fundamental dye structures to their photochemical activity in a specific host system.

PHOTOREDUCTION

Apart from the observations of Pellatt *et al.*,[2] mainly on anthraquinonoid dyes, no data are currently available on dye fading in liquid crystalline media. On the other hand, the behavior of dyes in isotropic aqueous and organic solvents and in polymeric and textile substrates is well documented.[5a,5b] Fading mechanisms are influenced by many factors including the chemical structure of both polymer and dye, concentration of the latter, temperature, and the presence of otherwise of moisture and oxygen, factors which make the overall fading process more complex. In an hermetically sealed optical display device, these factors may be minimized by considering the system as a solution of dye in a mainly hydrocarbon solvent from which oxygen and moisture have been excluded.

Under these conditions, it has been found[6] that azobenzene and 4′-nitro-4-aminoazobenzene in *iso*-octane and phenylazo-2-naphthols in polypropylene film[7] undergo, in the absence of oxygen, reductive fading by hydrogen abstraction from the solvent environment. With the latter class of dye, the fading effect is accelerated by the presence of electrophilic groups in the phenyl ring; confirmatory evidence[8] suggests that a π, π^* excited state of the dye molecule is involved and that the site of hydrogen attack is the electron deficient nitrogen of the azo group. The gradual increase in fading rate constant with the number of electrophilic groups conjugated with the azo linkage, as seen in Tables I and II, confirms a reductive fading process. An additional feature for dye XII is the existence of azo-hydrazone tautomeric forms, exemplified by



azo form hydrazone form.

The presence of conjugated electron-withdrawing groups shifts the equilibrium in the direction of the hydrazone form. When faded on polypropylene in the absence of oxygen, those dyes possessing a higher hydrazone to azo ratio fade more rapidly, since the hydrazones are already in a partially reduced form.[8]

The comparatively low fading rates of the aminoanthraquinonoid dyes shown in Table III may also be explained in terms of reductive fading. On irradiation of amino- or hydroxy-anthraquinones, the lowest excited state is considered[5b] to be a π, π^* state having strong charge transfer character. Such states which give rise to the color originate from electron transfer from substituents in α- (1,4,5 or 8-) positions of the anthraquinone nucleus to the carbonyl oxygen atoms. They are sensitive to the polarity of the environment, as previously discussed,[3] and intermolecular dipolar interactions cause a lowering of the energy of the excited state compared with the ground state. The electron displacement to the carbonyl oxygen atoms from the amino nitrogen atoms situated in α-positions will therefore reduce their capacity to act as electron or hydrogen acceptors and improve the resistance of the dye to reductive fading processes.

It also follows, in both cases of azo and aminoanthraquinonoid dyes that reductive fading will depend on the existence of excited states in, and the ease of hydrogen abstraction from the host material. Both E7 and RO-TN-103 liquid crystal eutectics used in the present work contain components possessing alkyl and alkoxy groups[9] from which hydrogen abstraction is possible, particularly on irradiation to give excited states. The strong fluorescence observed in these mixtures would indicate a high population of singlet excited states from which hydrogen transfer would be more easily achieved.

The model proposed for reductive fading in a liquid crystal substrate would thereby be consistent with that generally encountered for non-ionic dyes in an organic solvent or polymer[5a] in which the singlet excited dye molecule firstly undergoes a non-radiative transition to the triplet (^{3}D) state. The latter can abstract a hydrogen to form a semi-reduced dye species according to Eq. 5, together with an oxidized liquid crystal

$$D \xrightarrow{hs} {}^1D^* \rightsquigarrow {}^3D \qquad (4)$$

$$^3D + RH \rightarrow DH\cdot + R\cdot \qquad (5)$$

radical ($R\cdot$). In the absence of oxygen the radical $R\cdot$ can decay by reaction with a dye molecule to produce a second semi-reduced dye radical which can disproportionate to give the fully reduced form (Eqs. 6 and 7).

$$R\cdot + D \rightarrow DH\cdot + \text{product} \qquad (6)$$

$$DH\cdot + DH\cdot \rightarrow DH_2 + D \qquad (7)$$

The fully reduced azo dyes would be colorless but anthraquinone derivatives would undergo a blue shift (i.e., become yellower) relative to the fully oxidized state of the dye. We have observed that irradiation of cells which remain unsealed leads to color changes which differ from the above in that the initial reductive process occurring in the center of each cell is superceded by a diffusion controlled oxidative process which is more rapid than the reduction process. Current investigations on oxidative fading and the effects of adding a singlet oxygen quencher on fading rates will be published shortly.

Acknowledgments

Acknowledgements are made to the Science and Engineering Research Council for a CASE award (T.J.R.) and to Rank Research Laboratories Ltd., the co-operating body, with which the above research was carried out.

References

1. R. J. Cox, *Mol. Cryst. Liq. Cryst.*, **55**, 1 (1979).
2. M. G. Pellatt, I. H. C. Roe and J. Constant, *Mol. Cryst. Liq. Cryst.*, **59**, 299 (1980): "B.D.H. Liquid Crystals", Information Booklet, B.D.H. Chemicals Ltd., Broom Road, Poole, Dorset, BH12 4NN, England.
3. F. Jones and T. J. Reeve, *Mol. Cryst. Liq. Cryst.*, **60**, 99 (1980).
4. J. Park, *J. Soc. Dyers Col.*, **95**, 304 (1979).

5. (a) *Photochemistry of Dyed and Pigmented Polymers* (Eds. N. S. Allen and J. F. McKellar), App. Sci. Pubn., London (1980); (b) H. Meier, *Chemistry of Synthetic Dyes* (Ed. K. Venkataraman), Vol. 4, Academic Press, New York, 389 (1971).
6. B. E. Blaisdell, *J. Soc. Dyers Col.*, **65,** 618 (1949).
7. M. Ahmed and V. N. Mallet, *J. Soc. Dyers Col.*, **84,** 313 (1968).
8. V. N. Mallett and B. T. Newbold, *J. Soc. Dyers Col.*, **90,** 4 (1974).
9. M. Schadt and F. Muller, *I.E.E.E. Trans. Electron. Devices, Ed-25,* 1125 (1978).