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Naphthoquinone Dyes in Liquid Crystalline Media

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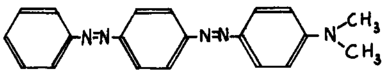
A number of dyes based on the 1,4-naphthoquinone structure have been synthesised. By ring closure across positions 2- and 3-, naphthimidazoles have been obtained which show improved order parameters and also photo-stabilities comparable with commercial anthraquinonoid dyes. The results are discussed on the basis of comparison with ground state dipole and transition moments as calculated by PPP-MO methods. Solubilities of the dyes in E44 (BDH Chemicals Ltd.) liquid crystal host have also been determined, but little correlation between saturation concentration and solubility parameter has been found.

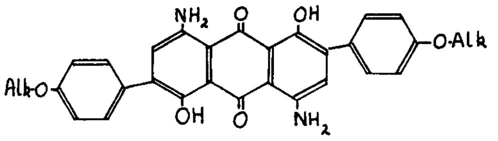
INTRODUCTION

The limitations imposed on the use of dyes in LCD's, namely, a high dichroic ratio, good solubility, high photostability and electrical resistivity, and a low viscosity, have meant that the number of useful commercially available dyes is still relatively small. The dyes used are non-ionic, organic soluble compounds and are azo and more particularly anthraquinonoid derivatives. Some typical examples are shown in Figure 1.

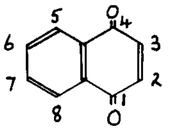
Whilst the azo derivatives have a high order parameter in oriented liquid crystalline media, they suffer from low solubility and poor light stability. On the other hand, anthraquinone derivatives[1] exhibit a much better light stability, but generally have a somewhat lower order parameter. Improvements in order parameter can be achieved by introducing substituents in positions 2- and 6- of the anthraquinone



Dis-azo- Dye - Orange S~0.74(E7)



Anthraquinonoid Dye - Blue S~0.65(E7)



1,4-Naphthoquinonoid Deriv. S~0.5-0.6(E43)

FIGURE 1 Dye Structures used in LCD's.

nucleus, e.g., alkyl, alkoxy, phenoxy or thioether groups as shown in Figure 1. Auxochromic groups in positions 1-, 4-, 5, and 8- are necessary to impart colour.

Further, the molar absorptivity of anthraquinone derivatives is considerably less (1-2 $\times 10^4$) than azo compounds 2-3 $\times 10^4$). Consequently higher concentrations of anthraquinone dye per unit cell are required to achieve high colour intensity and good contrast and can lead to problems of dye crystallisation at sub-ambient temperatures.

During the course of screening a large number of dyes, we have found[2] that 1,4-naphthoquinone (Figure 1) derivatives containing simple donor groups in the 5- and 8-positions give order parameters in the range 0.5–0.6. Their similarity with the partial, chromophoric structure of the anthraquinone derivatives can be seen in Figure 1, and the possibility of enhanced solubility in liquid crystalline hosts acted as an inducement to synthesise and examine a range of 1,4-naphthoquinones for this purpose.

EXPERIMENTAL

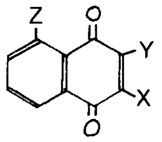
Details of synthesis of the dyes are to be given elsewhere. Each compound was verified by elemental analysis and i.r. spectra after purification to single spot standard using T.L.C. The 1,2-dialkylnaphthoquinone-imidazole intermediates were each nitrated to give a mixture of the corresponding 5- and 8-nitro-dialkylnaphthimidazoles. By direct nucleophilic replacement of the nitro-groups, a mixture of the two amines could be obtained and readily separated by T.L.C. These are shown in Table II. Their visible absorption spectra were used to characterise the 5- and 8-isomers; the 5-amino derivatives consistently showed λ_{max} values higher than the corresponding 8-amino-derivative[3]. Liquid crystal hosts included E7, E43 and E44 and were obtained from BDH Chemicals Ltd, Poole, Dorset, U.K. Order parameters were determined from optical densities at λ_{max} in parallel and perpendicular modes using glass cells coated with rubbed poly-vinylalcohol layers. Cell thickness was 17 μm and dye concentration 1% w/v. At least two and usually three cells were used to determine each order parameter.

RESULTS

Table I gives order parameters (S) and λ_{max} wavelengths for a series of relatively simple substituted 1,4-naphthoquinones containing an

TABLE I

Order Parameters (S) of 1,4-Naphthoquinone in E43 (BDH Chemicals Ltd.)



1,4-Naphthoquinones in E43

X	Y	Z	S order parameter	$\lambda_{max.}$ nm
$-NHCH_3$	$-OCH_3$	-H	0.48	535
$-NHCH_3$	$-OCH_3$	$-NH_2$	0.45	530
$-NHCH_3$	-CN	$-NH_2$	0.53	525
$-NHC_6H_5$	-Cl	$-NH_2$	0.64(E7)	545
$-NHC_{10}H_7$ (1-naphthyl)	-H	$-NH_2$	0.60	530
$-OCH_3$	$-NHCH_3$	$-NH_2$	0.25	465

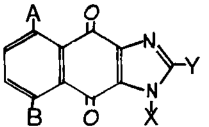
amino group (*Z*) in the 5-position. The presence of this electron donor group is necessary to improve the colour intensity, but has little effect on the order parameter.

Variation in the type and size of donor groups (*X*), particularly when present in position 2-, increases the order parameter so that phenyl- and naphthyl-amino groups give values greater than 0.6.

The major disadvantage of these naphthoquinones is that the proximity of carbonyl oxygen atoms to substituents *X* and *Y* in positions 2- and 3- causes such groups to be labile or chemically unstable. By ring closure across positions 2- and 3- the naphthoquinones can be made generally more stable and the order parameter increased. This is

TABLE II

Order Parameters (S), λ_{max} and ϵ values of Naphthoquinone-imidazoles in E44 (BDH Chemicals Ltd.)



Naphthoquinone - imidazoles

A	B	S E44	$\lambda_{max.}$ nm	ϵ ($CHCl_3$)
X=CH_3; Y=n-butyl-				
$C_6H_{11}NH$-	H-	0.62	537	5930
p-$C_4H_9C_6H_4NH$-	H-	0.71	542	5150
C_6H_5NH-	H-	0.58	534	4970
H-	$C_6H_{11}NH$-	0.45	534	5040
H-	p-$C_4H_9C_6H_4NH$-	0.61	536	5070
H-	C_6H_5NH-	0.33	530	4970
X=n-butyl- ; Y=CH_3				
$C_6H_{11}NH$-	H-	0.57	536	5820
p-$C_4H_9C_6H_4NH$-	H-	0.67	543	5190
C_6H_5NH-	H-	0.65	536	5050
H-	$C_6H_{11}NH$-	0.19	532	5000
H-	p-$C_4H_9C_6H_4NH$-	0.43	536	5060
H-	C_6H_5NH-	0.37	530	4950
X=CH_3;Y=cyclohexylamino-				
H-	H-	-0.36	490	2020

achieved by synthesising an imidazole ring structure between these positions as shown by the general structure given in Table II.

From the systematic variation in structure, we can observe that order parameters are improved when relatively large cyclic aromatic or cycloalkyl-amino groups (A) are introduced in the 5-position of an imidazole containing a linear butyl group in the 2-position. On the other hand, when identical groups (B) are shifted to position -8, there is an average reduction in order parameter of 0.14. Similarly in the second series, where groups X and Y are interchanged, there is an average lowering of order parameter of 0.30. The effect in this second series is probably enhanced by the presence of the longer alkyl chain substituted in the lateral 1-position. In the last example in this Table is shown a dye which exhibits a negative order parameter which cannot be explained in the above terms. It is however possible to gain further information by the application of the Pariser Parr, Popple[4] molecular orbital (PPP-MO) method. The method allows one to predict not only the wavelength of max. absorption of the dye, but also the intensity, the direction of the ground state dipole moment and, more important in this context, the orientation of the π-electron transition dipole moment.

(The method requires data concerning i) a core charge value of each atom; ii) the valence state ionisation potential of each atom; iii) the resonance integral energy between each pair of bonded atoms; iv) the electron repulsion energy when two electrons reside on the one atom; v) the total geometry - bond lengths and angles.)

A low optical order parameter can arise either from incomplete alignment of dye and director molecules or, when complete alignment occurs, from a transition dipole moment which is no longer parallel with the geometric axis of the dye. The transition dipole moment, as the name implies, occurs momentarily between the ground and excited states of the dye on interaction between the electric vector of the radiation and the π-electron system. It is only when the electric vector and the transition dipole moment are parallel that maximum colour is achieved.

A second factor influencing orientation of the dye molecule is the orientation of the π-ground state dipole moment, the angle of which can be calculated by PPP-MO methods. Both the ground state (μ) and transition moment (M) angles are related to a base line arbitrarily considered to be the major or geometric axis of the dye molecule. Some examples of these calculated angles are shown in Figures 2 and 3. In these figures, the π-electron distribution in the ground state is given qualitatively as conventional positive $(+)$ and negative $(-)$

charge density. In practice, the PPP-MO method gives a quantitative charge distribution for each atom of the structure. In Figure 2a, for a symmetrically substituted anthraquinone the ground state dipole moment μ is 0 and guest-host interaction is assumed to be caused by relatively weak induced dipole and dispersion forces. The transition dipole moment lies at an angle of 20° to the geometric axis and the order parameter is low. In Figure 2b the chosen geometric axis lies between carbon atoms 2,3- and 6,7-, with a transition moment angle of 35.7°. It is noticeable that the ground state dipole moment is orthogonal to the geometric axis and the order parameter (0.64) could be better explained if a less arbitrary geometric axis were chosen.

With the 5-cyclohexylamino-naphthimidazole derivative shown in Figure 3a there is a much closer correlation between transition and ground state dipole moments, the angular values depending on the arbitrarily chosen geometric axis. In the case of the 2-cyclohexy-

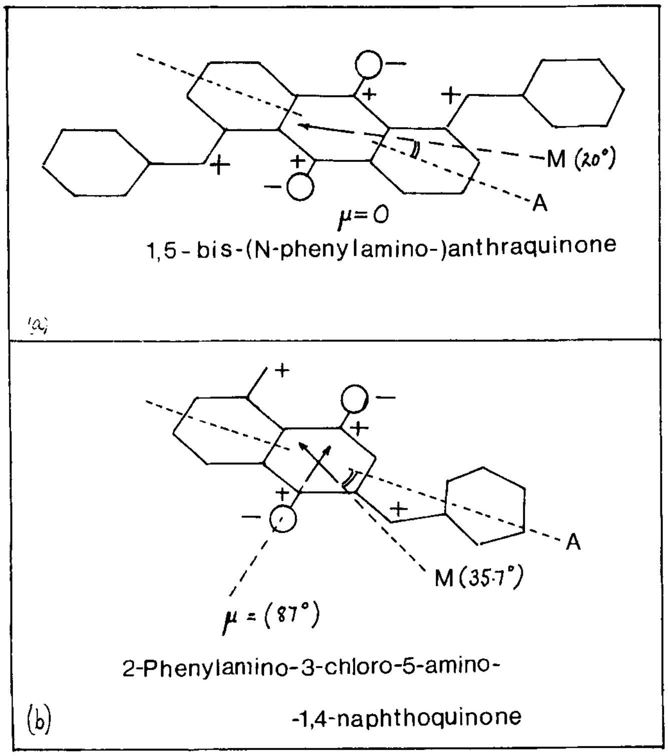


FIGURE 2 Transition Dipole Moment (*M*) angles for (*a*) an anthraquinonoid dye (*b*) a naphthoquinonoid dye.

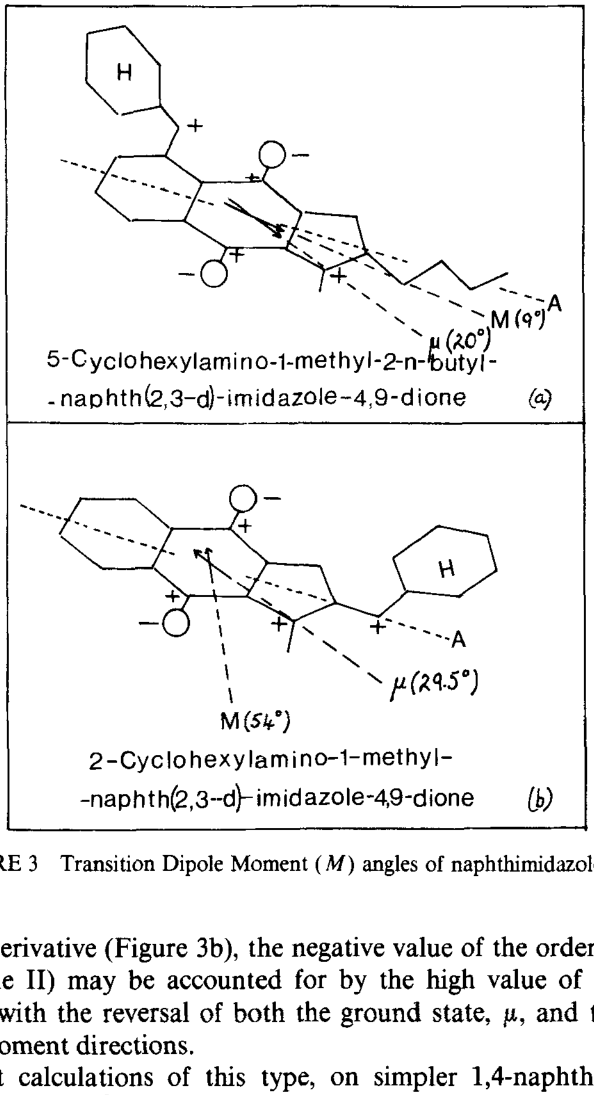


FIGURE 3 Transition Dipole Moment (*M*) angles of naphthimidazole dyes.

lamino-derivative (Figure 3b), the negative value of the order parameter (Table II) may be accounted for by the high value of *M* (54°) coupled with the reversal of both the ground state, μ, and transition dipole moment directions.

Recent calculations of this type, on simpler 1,4-naphthoquinone dyes, by Griffiths[5] show that there is an approximately linear correlation between the sum of the angles of *M* and μ and the optical order parameter.

Solubilities of Naphthoquinonoid Dyes

Saturation solubilities of some of the naphthoquinonoid dyes have been obtained over a range of temperatures using E44 (BDH Chemicals Ltd.) as solvent by filtration and spectrophotometric estimation of filtrates. From the data shown in Figure 4, of the dyes examined, the anthraquinone derivative shows the highest temperature coefficient corresponding to an enthalpy of solution of 5.2 kcal.mol^{-1}, whereas the enthalpy values of the naphthoquinonoids are somewhat less, in the range 3.3–4.8 kcal.mol^{-1}.

The inference is that, assuming a reasonable solubility at room temperature, the tendency of the naphthoquinonoids to recrystallise at sub-ambient temperatures will be less than that of the anthraquinone dyes.

As stated earlier, high colour intensity and good contrast are achieved when a high order parameter is coupled with a high saturation solubility and molar absorptivity. Values of the latter for an

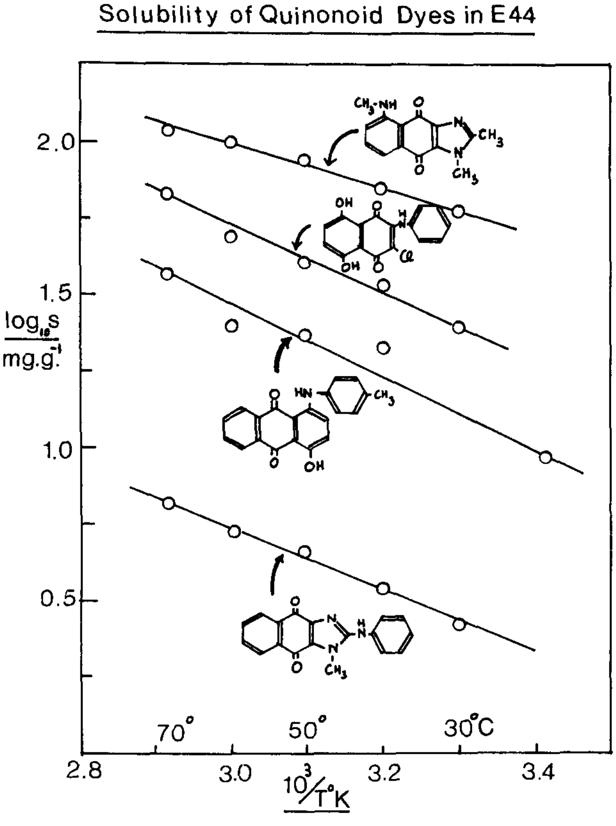


FIGURE 4 Solubility (mg.g.$^{-1}$) of Quinonoid Dyes in E44 (BDH Chemicals Ltd.).

isotropic solvent (chloroform) are given for the naphthoquinone-imidazoles in Table II. The saturation solubilities at 25 °C for the first three members of each of the two series shown in Table II were found to be between 4.10 and 5.98% wt./wt. and therefore some 4–5 times greater than quoted values[6] for commercial dyes (temperature unspecified) and comparable with the solubility of 2,6-dialkoxy-1,5-diamino-4,8-dihydroxyanthraquinones described by Cognard and Phan[7]. More recently anthraquinonoid dyes containing 2,7-di-alkyl or 1,5-dithio-phenyl groups in addition to auxochromic groups have been reported[8] with solubilities higher than 10% wt./wt.

Further, we suggest that predictions concerning the solubility of dyes in liquid crystal media can be made on the basis of the solubility parameter concept developed by Hildebrand and Scott[9]. The solubility parameter of the dye and of the liquid crystal host can be calculated from atomic and group contributions to vaporisation energies and molar volumes. Such data have been tabulated by Small[10], Beerbower[11] and Fedors,[12] and the efficiency of mixing is related to the difference between solute and solvent solubility parameters. The solubility data at 25 °C for dyes reported in this paper have been compared with the calculated parameters, but the correlation is found to be only approximate. The method assumes compatible (ideal) behaviour between solute and solvent and the discrepancies may possibly be due to dye aggregation in saturated solution in the liquid crystal host.

Photostability

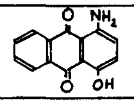
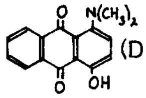
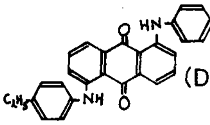
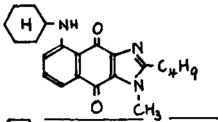
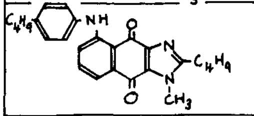
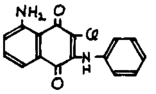
We have previously reported[13] fading rate constants for a number of commercial anthraquinone dyes (B.D.H. Chemicals Ltd.) which agree reasonably with the data given by Aftergut and Cole,[14] when one takes into account the different intensities of the light sources used.

Table III compares the first order fading rate constant, k, and times of half fading, $t_{1/2}$, of two imidazole and one 1,4-naphthoquinone dye with the commercial dyes D27 and D35. The fading rates of the imidazoles are equally as good as the anthraquinones. The lower light stability of the 1,4-naphthoquinone is reflected in the comparatively high rate constant and the lower half-life value. Unfortunately, fading rates are dependent not only on dye structure, but also on the liquid crystal host used and until more detailed information on the fading mechanisms involved is available it is not possible to make predictions in this direction.

TABLE III

Fading Rate Constants (k) and Times of Half-fading ($t_{1/2}$) of Quinonoid Dyes

Fading Rate Constants (k) and Times of Half-Fading ($t_{1/2}$) of Quinonoid Dyes

Dye	Host	k h^{-1} $\times 10^4$	$t_{1/2}$ h.
	E44	10.98	631
 (D27)	E7	9.360	537
 (D35)	E7	1.440	3072
	E44	2.780	2489
	E44	2.258	3070
	E7	43.20	387

CONCLUSIONS

By specifically 'tailoring' aminoaphthimidazole dyes to maximize order parameters, it is possible to obtain dyes which are comparable in application properties to many commercially available anthraquinones, but with enhanced solubility in liquid crystal media. The dyes obtained so far are however restricted in colour.

The predictions of ground state and transition moment dipole orientation by PPP-MO methods apply not only to the dyes described but also to any other new, but not yet synthesised, dye systems. Further headway could be made if a correlation between dye transition moment and the ground state dipole moment of the liquid crystal director, probably *via* the ground state dipole moment of the dye, could be found.

This prediction coupled with the application of the solubility parameter concept could lead to the development of new dye systems without the prolonged process of dye synthesis and trial and error testing.

Acknowledgments

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References

1. J. Cognard and T. H. Phan, *Mol. Cryst. and Liq. Cryst.*, **70**, 1279 (1981).
2. T. J. Reeve, *Ph.D. Thesis*, University of Leeds, 1979.
3. G. Green-Buckley and J. Griffiths, *J. Chem. Soc., Perkin I*, 704 (1979).
4. R. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 466, 767 (1953).
   J. A. Pople, *Trans. Faraday Soc.*, **49**, 1375 (1953).
5. C. Blackburn and J. Griffiths, *Mol. Cryst. and Liq. Cryst.*, (in press).
6. B.D.H. Chemicals Ltd., '*Static Drive and Host Eutectics*' - Appendix 8a, p. 24.
7. J. Cognard and T. Hieu Phan, *Mol. Cryst. and Liq. Cryst.*, **70**, 1 (1981).
8. F. C. Saunders, K. J. Harrison, E. P. Raynes, and D. J. Thompson, *I.E.E.E. Trans. Electron Devices*, **ED-30**, 499 (1983).
9. J. H. Hildebrand and R. L. Scott, "*The Solubility of Non-electrolytes*," Reinhold, New York, 1950, p. 129.
10. P. A. Small, *J. Appl. Chem.*, **3**, 71 (1953).
11. C. M. Hanson and A. Beerbower, "*Kirk-Othmer Encyclopedia of Chem. Technology*," Suppl. Vol., J. Wiley and Sons, New York, p. 889, 1971.
12. R. F. Fedors, *Polym. Eng. and Sci.*, **14**, 152 (1974).
13. F. Jones and T. J. Reeve, *Mol. Cryst. and Liq. Cryst.*, **78**, 201 (1981).
14. S. Aftergut and H. S. Cole, *Mol. Cryst. and Liq. Cryst.*, **89**, 37 (1982).