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DYES AND LIQUID CRYSTALS

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SUMMARY

This short article represents an updating of a previously published review of the same title, and draws attention to advances in the area of anthraquinone dyes that may be used in commercially viable liquid crystal display devices.

1. INTRODUCTION

The subject of dyes and liquid crystals was reviewed by the author in 1979 in a paper presented at the 7th Internationales Farbensymposium held in Interlaken and later published in *Chimia.*[1]

The basic principles underlying the design of the best types of liquid crystal material *and* of the display devices in which they may be used were fully covered in this review, as were the advantages/disadvantages connected with the more conventional and commercially successful Twisted Nematic electro-optical display and the Dyed Cholesteric–Nematic Phase Change electro-optical display for the presentation of information (in watches, calculators, instrument panels, etc). Although this material was presented again at the York meeting of the Royal Society of Chemistry, at the invitation of the organisers, it is not judged to be necessary to repeat these facts in print here.

However, although the displays in which liquid crystals are used are passive in nature, the state of knowledge in this area is not, and since the Interlaken meeting, there have been certain important advances in relation to the synthesis and availability of suitable dyes for use in Cholesteric–Nematic Phase Change displays. For the purpose of these proceedings of the York meeting, this article therefore simply sets out to summarise the situation at the time of the Interlaken meeting and to present the new results reported at York.

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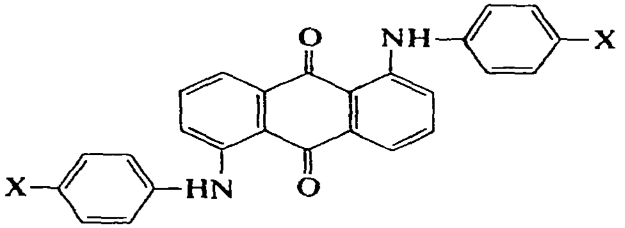
The situation when the *Chimia* article[1] was written was the following:

(i) Much basic work[2-4] on azo-(mono-, bis-, tris-) dyes had been carried out and it had been clearly established that dichroic dyes whose elongated molecules align well with the elongated (but often shorter) molecules of the nematic host could be obtained. Such dyes may be described as high order parameter dyes: the order parameter S would have a value of zero for a disordered isotropic liquid, but for a perfectly aligned nematic host or for a dye perfectly aligned in a nematic host, S would have a value of 1. Most nematic hosts have S values of about 0·6, but dye order parameters as high as 0·8 were achieved. This simply reflects the fact that the longer dye molecules can be better aligned than the host itself. Satisfactory as these results were in defining order conditions that would ensure good colour contrast between the 'off' and 'on' states of the display, the dyes themselves presented problems. Most serious amongst these was the photochemical instability of the azo-dyes, and this was at its worst for the blue or violet-blue range of azo-dyes.

Examples of some azo-dyes and their order parameters in a nematic host are given in Table 1.

(ii) As a direct result, work[5] was initiated in the area of anthraquinone (AQ) dyes, which have a reputation for good photochemical stability. The dyes eventually produced were 1,5-disubstituted anthraquinones of structure (**I**), and some results for the order parameters of these dyes in a nematic host are given in Table 2.



(**I**)

Although the photochemical stabilities of these dyes† were quite excellent, their somewhat lower S values, coupled with their only moderate solubilities in many cases, gave a performance in Cholesteric–Nematic Phase Change displays which, whilst acceptable, was poorer in both contrast and colour intensity than would have been desired.

Moreover, although a coloured display is attractive, the commonest and most acceptable form of display requires a black/white contrast. To achieve this, three dyes are needed—yellow, red, and blue. The AQ dyes under discussion could meet the demand for the blue-violet situation, but azo- or other dyes of lower stability had to be employed to cover the yellow and red regions of the visible spectrum. A combination of the best high order parameter azo- and AQ dyes could therefore give

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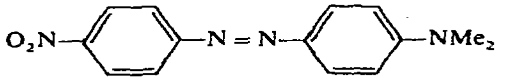
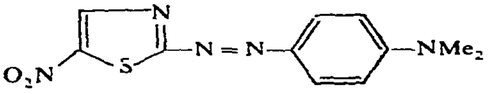
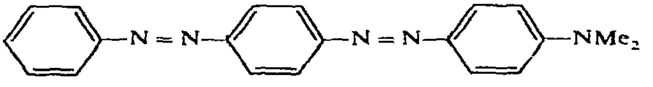
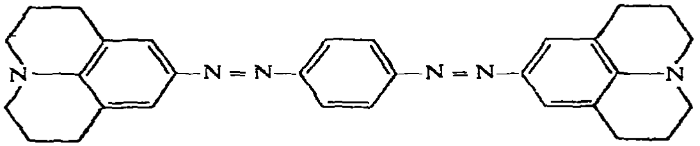
† Available from BDH Chemicals Limited, Broom Road, Poole, Dorset, Great Britain.

TABLE 1
ORDER PARAMETERS OF SOME AZO-DYES IN E7[a]

Dye	*Colour*	*Order parameter (S)*
	orange-red	0·70
	blue	0·70
	orange	0·74
	purple	0·78

[a] E7 is a commercially available room-temperature nematic liquid crystal mixture consisting mainly of cyano-biphenyls (BDH Chemicals Limited, Broom Road, Poole, Dorset, Great Britain).

a perfectly acceptable white on black display, but only by forfeiting the photochemical stability of the AQ dye through the employment of yellow and red azo-dyes. (iii) From what has been said, it will be appreciated that the Dyed Phase Change display as commonly understood is a negative contrast display—giving white information on a coloured or black background. To achieve the reverse situation is more difficult,[1,6] requiring a host cholesteric of (a) carefully defined pitch relative to the thickness of the display, and (b) strongly negative dielectric anisotropy. Experimental devices of this kind have been made, but a chiral nematic (cholesteric) host of suitable quality does not yet exist. Moreover, when it is found, it must not be assumed that existing dyes which operate well in negative contrast displays of the

TABLE 2
ORDER PARAMETERS FOR SOME DYES OF STRUCTURE I IN E7[a]

X in I	*λ_{max} in E7 (nm)*	*Order parameter (S) in E7*
$C_5H_{11}O$	557	0·68
$C_7H_{15}O$	557	0·69
$C_9H_{19}O$	556	0·68
$C_{10}H_{21}O$	556	0·67
Me_2N	546	0·65

[a] See footnote to Table 1.

type discussed in section (ii) above will necessarily be ideal for the strongly negative $\Delta\varepsilon$ hosts.

Points (i), (ii) and (iii) summarise the situation as it stood at th.› time of writing of the *Chimia* review.[1]

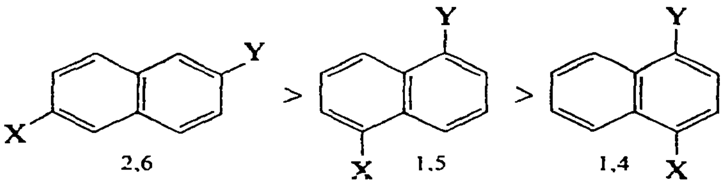
With regard to (i) and (ii), little has changed. Azo-dyes[7] are still too unstable to ensure long life-time displays, and no progress has been made over a good host nematic for positive contrast Phase Change displays.

However, there have been significant advances in the area of AQ dyes and these are summarised in the following section.

2. NEW ANTHRAQUINONE DYES

If one allows the assumption (or presumption) that the more elongated the structure of a dye molecule is, the higher its order parameter in the chiral nematic host will be, then 1,5-disubstituted AQ dyes appear less suitable than 2,6- or perhaps even 2,7-disubstituted AQ dyes.

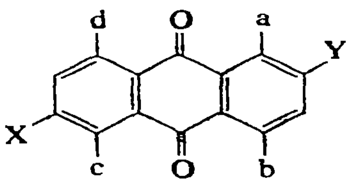
Again on the premise that a high $T_{N\text{-}I}$ value (nematic–isotropic transition temperature) reflects a high degree of liquid crystal order in the system, this idea is supported by the established fact that for a number of comparable systems derived from naphthalene, $T_{N\text{-}I}$ does fall[8] in the order



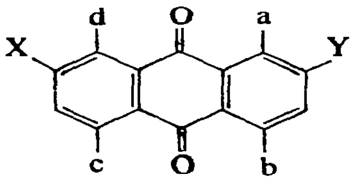
where X and Y represent suitable substituents that extend the axis of the molecule along the direction of the particular ring—X bond. Indeed, 1,4-disubstituted AQ dyes do have[5] somewhat lower S values than their 1,5-disubstituted analogues.

However, if at least one of the 1-, 4-, 5-, or 8-positions in the AQ system is not occupied by a group carrying a readily exchangeable hydrogen atom linked to the ring system, e.g. —NH_2, —OH, —NHR, etc., then the chromophore system of the dye is not complete.

A number of different workers independently combined these underlying principles and arrived at model AQ dye structures of the type

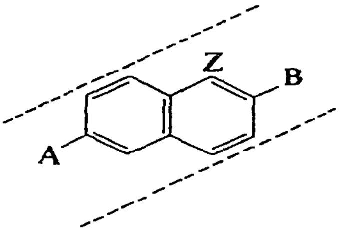


and



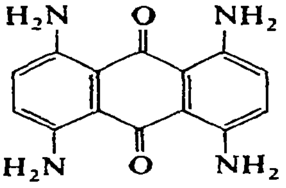
where at least one of the substituents a, b, c, or d at the 1-, 4-, 5-, 8-positions would be a small group carrying a suitable exchangeable hydrogen. The group would preferably be small, so that the length/width (*L*/*W*) ratio of the 2,6- or 2,7-disubstituted AQ system was not reduced and *S* diminished as a consequence.

The situation had already been demonstrated many years earlier[8] in the context of 2,6-disubstituted naphthalene derivatives. Indeed, 5-substituted 6-alkoxy-2-naphthoic acids (e.g. **II**) have higher $T_{N\text{-}I}$ values than the parent acids where the 5-position is occupied only by a hydrogen atom, provided that the 5-substituent Z is not too large. Thus Z = Cl and Br enhance $T_{N\text{-}I}$, but Z = I slightly lowers $T_{N\text{-}I}$. The relatively small 5-substituents are shielded or exist within the cylindrical rotational envelope (dashed lines) of the parent acid, and do not affect the *L*/*W* ratio of the molecule.



(II)

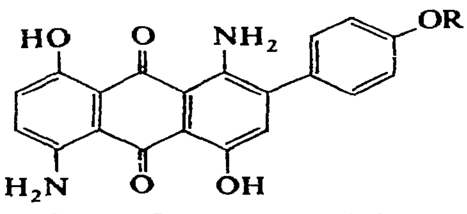
A = alkoxy; B = CO_2H



(III)

S in E43† = 0·65

Realisation of these points and the fact that the simple dye **III**—without 2,6- or 2,7-substituents to elongate the molecule—has itself a good order parameter,[3] stimulated the study of AQ dyes such as **IV**[9,10] and **V**[10]



(IV)

when R = C_7H_{15} *S* = 0·73–0·74

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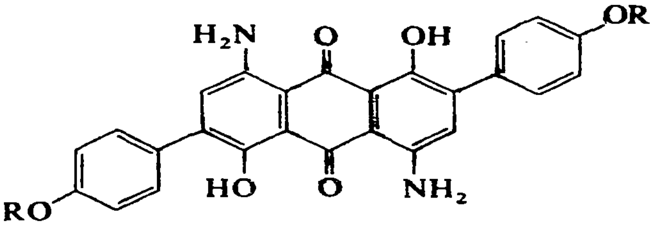
† A further commercial cyanobiphenyl mixture—see footnote to Table 1.



(V)

Such studies were initiated more or less concurrently at a number of centres, and the following references acknowledge and direct the reader's attention to the work in this area: M. Schadt and P. Gerber[9] (Hoffman–La Roche, Basle, Switzerland); J. Cognard and T. Hieu Phan[10] (Asulab, Neuchatel, Switzerland); A. Möller and G. Scherowsky[11] (Technischen Universität, Berlin, Germany); D. Thompson and N. Corby[12] (ICI Organics Division, Blackley, Manchester, Great Britain) in collaboration with F. Saunders, E. P. Raynes, and K. J. Harrison[13] (Royal Signals and Radar Establishment, Great Malvern, Worcestershire, Great Britain).

The as-yet unpublished work of Thompson and Corby[12] is worthy of particular note. Whilst others have produced blue dyes of the type mentioned above, they have succeeded in producing companion materials that are yellow and red. High order parameter AQ dyes of all three colours have been made available. Their order parameters are higher than those of the earlier 1,5-disubstituted AQ dyes (in some cases $>0{\cdot}8$), as are their solubilities in nematic hosts of strongly positive $\Delta\varepsilon$. By combining these dyes, in suitable concentration, it is therefore possible to obtain a highly acceptable black dye system which is the basis of very good white on black contrast, dyed, Cholesteric–Nematic Phase Change displays. Since these dyes have the excellent stability characteristics of the 1,5-disubstituted AQ dyes, no life-time problems should exist for commercial displays based upon them. Unfortunately, because of commercial and patent restrictions, it is not yet possible to divulge the structures of these successful dye systems, samples of mixtures of which can however be obtained from Dr B. Sturgeon, BDH Chemicals Limited, Broom Road, Poole, Dorset, Great Britain, or from E. Merck, Darmstadt, West Germany.

It is not implied that no work remains to be done in this area. The new dyes are difficult to synthesise and their production has to be made cost effective. Also, one is perhaps not satisfied that the highest extinction coefficients for the dyes have yet been achieved (a matter of possible importance to those aiming to use the dyes in a Twisted Nematic shutter device). There is no doubt however that knowledge and the state of the art have advanced in the last year or so, and it is hoped that this short updating article and the references contained in it serve a useful purpose in drawing attention to this progress.

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