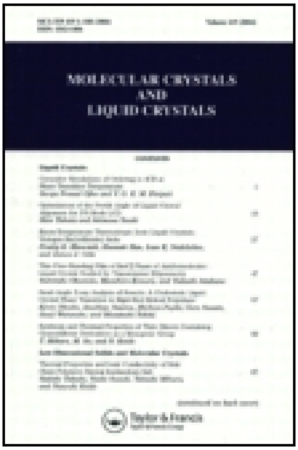

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Photostable Anthraquinone Pleochroic Dyes

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Photostable Anthraquinone Pleochroic Dyes

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Pleochroic anthraquinone dyes have been prepared with order parameters of up to 0.70 when dissolved in liquid crystals. Over 100 dyes have been synthesised, in which a variety of substituents have been incorporated into the 1,4, and 5 positions on the anthraquinone nucleus, affording red, purple, blue and green dyes.

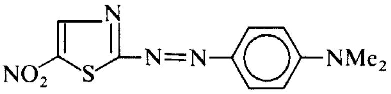
Several dyes showed significantly higher stability than most other high order parameter azo-dyes. Some dyes showed solubility and order parameter sufficiently high to allow their employment in liquid crystal displays.

1 INTRODUCTION

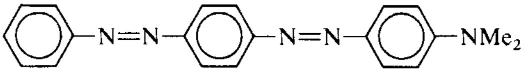
The use of pleochroic dyes as additives in liquid crystals was first suggested by Heilmeier, *et al.*,[1] but the contrast ratio of their display device was poor. A major advance in the application of pleochroic dyes came when White and Taylor[2] discovered that the cholesteric-nematic phase-change effect produced a good display with dye additives. They also pointed out that the key to a high contrast was a high order parameter for the dye in the liquid crystal.

Most of Heilmeier's work was carried out by using Indophenol Blue as the pleochroic dye. Vorlander[3] prepared some liquid crystal azo-dyes many years earlier, but despite their high order parameters (up to 0.77), these were thought unsuitable by White and Taylor because of the wavelength of their absorption maxima (~415 nm). White and Taylor synthesised several dyes of various colours with quite high order parameters, but they encountered problems with dye stability to U.V. light and applied electric fields. Difficulties with dye stability have also been encountered with azo, azomethine and methine dyes.[4]

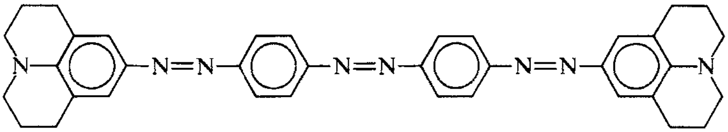
The structural requirements for high order parameter in azo-dyes have been investigated in considerable detail,[5] and a general trend towards higher values was noted as the length of the molecules was increased by incorporation of more azo groups. The authors were the first to note the dependence of order parameters on the nature of the liquid crystalline host, the figure generally increasing with the N → I transition temperature of the nematic. The best dyes they synthesised (I, II, III—see below) had high order parameters, but the U.V. stability of the thiazole dye (I) and the julolidine dye (III) was poor.



I



II



III

The primary objective of our work has been to discover a dye system that would be stable indefinitely to light, since without this characteristic the dyestuffs are not useable. Obviously, the dyes must not contain any ionic or ionisable groups, and must be sufficiently soluble in liquid crystal phases to give a display of the required intensity. Suitable dyes must have a high order parameter in order that a high contrast display may be obtained, but in the first instance order parameter was of secondary consideration, since we believed that sufficient was known about the relationship of this to molecular geometry to enable the desirable properties to be introduced by chemical manipulation of the basic structure. These considerations led us to a study of the anthraquinone dyes, some of which are noted for their high stability.

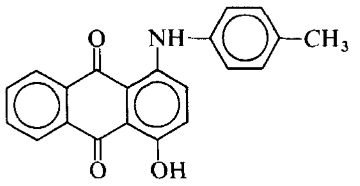
2 RESULTS AND DISCUSSIONS

2.1 1,4-Anthraquinone dyes

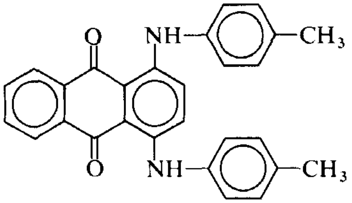
Our study of anthraquinone dyes commenced with an examination of readily available compounds, and the first promise of attractive properties was found in the blue dye (IV).

This was found to be soluble readily in the cyanobiphenyl/cyanoterphenyl mixture E7[6] to a blue solution with λ max at 595 nm, and to show an order parameter of 0.615. The hydrogen atoms of the hydroxyl- and imino-groupings in the molecule are firmly hydrogen-bonded to the adjacent carbonyl groups and thus are not ionisable or otherwise likely to be the source of chemical instability through susceptibility to oxidation or other means of decomposition.

Dyes of this type were prepared by reacting 1,4-dihydroxyanthraquinone and 1,4,9,10-tetrahydroxyanthracene with a substituted arylamine in the presence of boric acid. The reaction of *p*-toluidine, for example, afforded a mixture of the 1-*p*-methylphenylamino-4-hydroxy-compound (IV) and the corresponding 1,4-bis-*p*-methylphenylamino-compound (V), which could be separated easily, and the desired product was purified by conventional chemical methods. The 1,4-disubstituted compounds, which afforded green solutions, showed much lower order parameters and were not studied in detail.

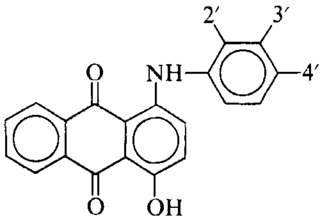


IV



V

The first permutations of the anthraquinone dye (IV) to be investigated in the search for higher order parameters were those in which the 1-*p*-methylphenylamino-grouping was replaced by an aliphatic group. The resulting dyes (Table I) all showed lower values, as evidently the rigidity of the aromatic ring is necessary to create an optic axis in the molecule sufficiently long for good alignment in the nematic phase. Attempts were therefore made to extend this axis by introducing longer substituents into the phenylamino ring, and in Table II are listed some derivatives of the parent compound, 1-phenylamino-4-hydroxyanthraquinone (VI).



VI

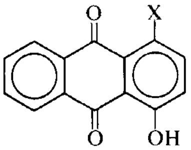
The results show, first of all, that the nature of the substituent affects the wavelength of the absorption maximum as expected, electron releasing auxochromic groups producing a bathochromic shift to longer wavelengths, and electron attracting groups a hypsochromic shift. The effect of the position of the substituent on order parameter is consistent in the order 4′ > 3′ > 2′. This effect seems to be independent of the electronic nature of the substituent, and is presumably steric, the 4′-substituent lengthening the optic axis and raising the order parameter. The next logical step in the search for higher order parameters was therefore to increase the length and size of the 4′-substituent, and some of these derivatives are listed in Table III.

In the 4′-*n*-alkyl series (D1–D6), order parameters decline from the single carbon substituent (D2), but in the 4′-*n*-alkoxy series (D7–D17) the values rise gradually with the length of the chain. Increasing the bulk of the substituent to 4′-(4-biphenylyloxy) (D26) has a similar beneficial effect, but diminishes the solubility adversely.

Incorporation of the less bulky 4′-phenyloxy group (D57) decreases the order parameter, but the solubility is significantly increased. The order

TABLE I

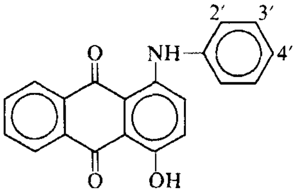
Experimental data on 1-substituted 4-hydroxyanthraquinones



Dye No.	1-Substituent X	λ max nm	Order parameter	m.pt. °C
D2	1-*p*-methylphenylamino	596(E7)	0.615(E7)	183
D18	1-*n*-butylamino	570(E3)	0.43(E3)	117.5–119
D19	1-*n*-dodecylamino	615(E3)	0.39(E3)	79–81
D20	1-benzylamino	602(E3)	0.45(E3)	174–175

TABLE II

Experimental data on derivatives of 1-phenylamino-4-hydroxyanthraquinone (VI)



Dye No.	Substituent in 1-phenylamino ring	λ max in E7 (nm)	Order parameter in E7	m.pt. °C
D1	none	587	0.59(E8)	161–162
D2	4′-methyl	596	0.615	183
D21	3′-methyl	590	0.56	144–145.5
D22	2′-methyl	592	0.50	170–171
D3	4′-ethyl	595	0.54	133.5–135
D60	3′-ethyl	592	0.48	154–156
D7	4′-hydroxy	598	0.615(E8)	260–262
D8	4′-methoxy	597	0.59	188.5–190
D23	3′-methoxy	592	0.52	149–150
D24	2′-ethoxy	598	0.51	170–172
D30	4′-chloro	572	0.57	245–246.5
D31	3′-chloro	493	0.50	141–142.5
D27	4′-dimethylamino	612	0.63	233–235
D28	4′-diethylamino	616	0.59	160–161.5
D29	4′-*N*-morpholino	604	0.60	266–269
D64	4′-*N*-ethyl-*N*-hydroxyethyl	614	0.60	175–177.5
D61	4′-*iso*propyl	595	0.57	143.5–145
D65	4′-(2-hydroxyethyl)	595	0.60	200–202
D62	4′-benzyloxy	595	0.61	184.5–187
D32	4′-ethoxycarbonyl	566	0.61	211–212.5

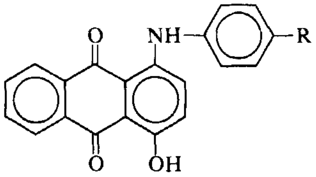
parameter and solubility of D58, which contains the 4′-phenylamino group, are higher but this dye is rather unstable. The highest order parameter found in the 1-substituted phenylamino-4-hydroxyanthraquinone dyes was 0.65 in the 4′-*n*-nonoxy-compound (D16).

2.2 1,5-Anthraquinone dyes

The length of the optic axis in anthraquinone dyes can be increased further by introducing an appropriate substituent into the 5-position, such as in the parent compound, 1,5-bisphenylaminoanthraquinone (VII). These compounds are accessible readily by reaction of 1,5-dichloroanthaquinone with arylamines. The parent compound (VII) proved readily soluble in E7 to a purple-red coloured solution and showed a reasonably high order parameter of 0.58. The position of the absorption maximum at 544 nm

TABLE III

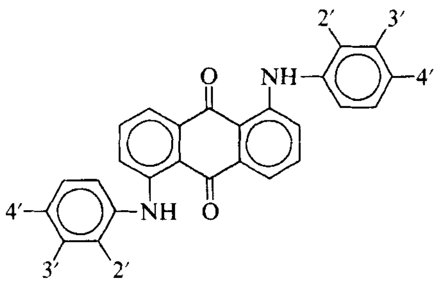
Experimental data on 1-4′-substituted phenylamino-4-hydroxyanthraquinones



Dye No.	4′-Substituent R	λ max in E7 (nm)	Order parameter in E7	m.pt. °C
D1	none	587	0.59(E8)	161–162
D2	4′-methyl	596	0.615	183
D3	4′-ethyl	595	0.54	133.5–135
D4	4′-*n*-propyl	593	0.56	120–122
D5	4′-*n*-butyl	594	0.60(E8)	122.5–124
D6	4′-*n*-pentyl	594	0.57	81–83
D7	4′-hydroxy	598	0.615(E8)	260–262
D8	4′-methoxy	597	0.59	188.5–190
D9	4′-ethoxy	598	0.63	172–173
D10	4′-*n*-propoxy	598	0.59	149–150
D11	4′-*n*-butoxy	600	0.595	114.5–116
D12	4′-*n*-pentoxy	598	0.62	99–100
D13	4′-*n*-hexoxy	599	0.59	97.5–99
D14	4′-*n*-heptoxy	596	0.62	99–101
D15	4′-*n*-octoxy	596	0.59	103.5–105
D16	4′-*n*-nonoxy	596	0.65	102.5–103
D17	4′-*n*-decoxy	597	0.63	101.5–103
D26	4′-(4-biphenylyloxy)	596	0.64	180–181.5
D57	4′-phenyloxy	592	0.60	160–163.5
D58	4′-phenylamino	604	0.63	163–164.5
D61	4′-*iso*propyl	595	0.57	143.5–145
D62	4′-benzyloxy	595	0.61	184.5–187
D65	4′-(2-hydroxyethyl)	595	0.60	200–202
D64	4′-*N*-ethyl-*N*-2-hydroxyethyl	614	0.60	175–177.5

coincided with the wavelength which Bloom and Priestley[7] found to be optimum to maximise the descriptor, "perceived contrast ratio," they introduced to characterize pleochroic dyes that takes into account the relative spectral luminous efficiency for photo-optic vision of the human eye.

Once again, an arylamino-grouping was necessary at positions 1 and 5 of this structure for high order parameter (see Table IV). Longer substituents were introduced into the phenylamino ring in the three possible positions (Table V) and the same bathochromic and hypsochromic effects were observed. The effect of the position of the substituent on order parameter



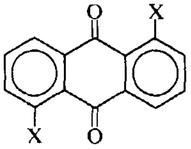
VII

was again consistent in the order 4′ > 3′ > 2′, and appeared to be independent of the nature of the substituent.

Furthermore, 4′-alkyl-substituted compounds absorbed at higher wavelengths than 3′- or 2′-, whilst 4′- and 2′-alkoxy compounds absorbed at similar wavelengths and approximately 5 nm higher than their 3′-substituted analogues. The order parameter of the 1,5-bis-arylaminoanthraquinone dyes was improved by incorporating a 4′-substituent (Table VI) and the order parameters observed for the 4′-alkyl series were slightly lower than the best members of the 4′-alkoxy series. Order parameters of about 0.69 were achieved which produced devices with eminently satisfactory contrast. The 4′-dimethylamino compound (D52) was also attractive because of its broad absorption band.

TABLE IV

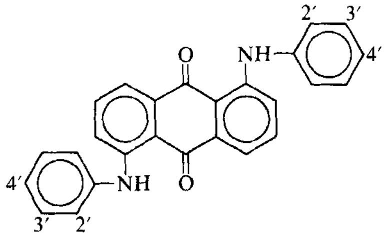
Experimental data on 1,5-disubstituted anthraquinones



Dye No.	1,5-Disubstituents X	λ max in E7 (nm)	Order parameter in E7	m.pt. °C
D33	phenylamino	544	0.58	215.5–217
D49	dimethylamino	515	0.44	156.5–158
D50	diethylamino	522	0.43	167–169
D51	di-*n*-butylamino	526,554	0.30	152.5–155
D56	benzylamino	519,540	0.28	229.5–231
D68	cyclohexyl	560	0.41	245.5–247.5

TABLE V

Experimental data on derivatives of 1,5-bisphenylaminoanthraquinone (VII)



Dye No.	Substituent in phenylamino ring	λ max in E7 (nm)	Order parameter in E7	m.pt. °C
D34	4′-methyl	555	0.65	301.5–303
D70	3′-methyl	552	0.58	194–196
D72	2′-methyl	545	0.52	228–230
D39	4′-methoxy	555	0.67	248–250
D69	3′-methoxy	550	0.57	178–180
D71	2′-methoxy	556	0.53	188–190
D40	4′-ethoxy	555	0.65	157–158.5
D73	2′-ethoxy	561	0.60	204.5–206.5
D35	4′-ethyl	554	0.67	217–220.5
D75	3′-ethyl	554	0.56	176–178
D74	2′-ethyl	544	0.53	183.5–185.5

2.3 Solubility of anthraquinone dyes

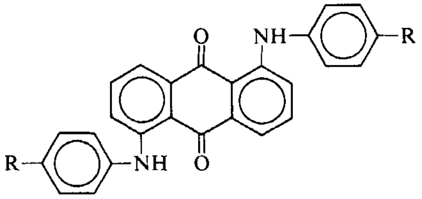
The solubility of the anthraquinone dyes varied considerably. In general, alkoxy-substituted arylaminoanthraquinones were less soluble than their alkyl analogues, whilst 4′-substituted compounds tended to be less soluble than isomeric 3′- and 2′-substituted dyes. The solubility of the dye was required to be sufficient to give an absorbance of at least 1.0 in a 12 μm cell; anthraquinone dyes with solubilities of 1.5% or greater satisfied this requirement. The best 1-4′-substituted arylamino-4-hydroxyanthraquinones are listed in Table VII, whilst Table VIII lists the best 1,5-disubstituted anthraquinone dyes.

2.4 Stability of anthraquinone dyes

Several representative members of both anthraquinone series were subjected to rigorous testing in order to determine their stability to U.V. light. Some comparative measurements were also made on the azo-dyes I, II and III.[5] Cells containing an unstable dye "guest" would be expected to show evidence of decomposition of the dye contents after exposure to U.V. light, apparent

TABLE VI

Experimental data on 1,5-4′-substituted bisphenylaminoanthraquinones



Dye No.	4′-Substituent R	λ max in E7 (nm)	Order parameter in E7	m.pt. °C
D33	none	544	0.58	215.5–217
D34	methyl	555	0.65	301.5–303
D35	ethyl	554	0.67	217–220.5
D36	*n*-propyl	556	0.65	176–177.5
D37	*n*-butyl	556	0.66	157.5–159
D38	*n*-pentyl	555	0.63	154–156
D67	hydroxy	524	0.59	222.5–224
D39	methoxy	555	0.67	248–250
D40	ethoxy	555	0.65	157–158.5
D41	*n*-propoxy	555	0.625	224.5–227
D42	*n*-butoxy	556	0.66	197–198.5
D43	*n*-pentoxy	557	0.68	195–196.5
D44	*n*-hexoxy	556	0.69	192–193.5
D45	*n*-heptoxy	557	0.69	180–181
D46	*n*-octoxy	556	0.69	165.5–167
D47	*n*-nonoxy	556	0.68	156–158
D48	*n*-decoxy	556	0.67	146–148
D52	dimethylamino	546	0.65	234–236
D53	*n*-morpholino	542	0.65	252–254
D54	phenylazo	524	0.71	179–182
D66	phenyloxy	554	0.67	224–225.5
D76	*N*-ethyl-*N*-2-hydroxyethyl	551	0.62	159.5–161.5
D77	*iso*propyl	558	0.68	203.5–206

from a decrease in measured resistivity accompanied by visible fading of the cell colour and change in order parameter. The resistivity of the cells was therefore monitored throughout the experiments, and the fading was determined by measuring the change in absorbance of the cell contents. The order parameter was also monitored throughout the tests.

Figure 1 illustrates the mean resistivity of the contents of three cells which were measured at intervals for a period of up to 1500 hours of exposure to a low power U.V. lamp. Resistivity measurements taken during the first few hours of testing were regarded as unreliable because of the possibility of trace amounts of ionic material being deposited onto the surface of the cells. The order parameter of the contents of cells was measured

TABLE VII

Experimental data on D5, D16 and D27

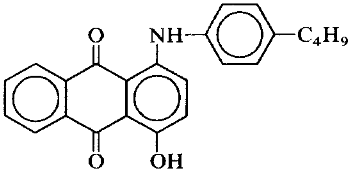
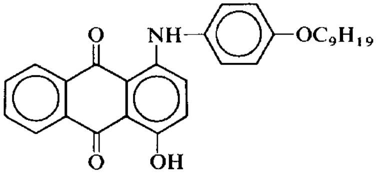
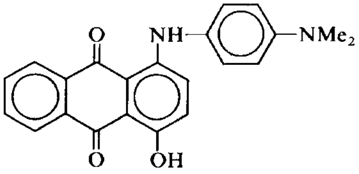
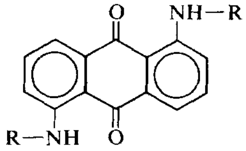
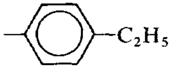
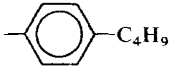
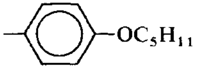
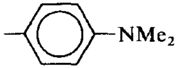
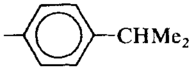
Dye No.	Structure	λ max in E7 (nm)	O.P. in E7	λ max ($CHCl_3$) nm	$\varepsilon \times 10^4$ ($CHCl_3$)	m.pt. °C	Solubility in E7 (25°)
D5		594	0.60	586	1.20	122–124	>5% wt
D16		596	0.65	586	1.20	102.5–103	2.2% wt
D27		612	0.63	594	1.10	233–235	0.8% wt

TABLE VIII

Experimental data on D35, D37, D43, D52 and D77



Dye No.	R	λ max in E7 (nm)	O.P. in E7	λ max ($CHCl_3$) nm	$\varepsilon \times 10^4$ ($CHCl_3$)	m.pt. °C	Solubility in E7 (25°)
D35	 $-C_2H_5$	554	0.67	540	1.53	217–220.5	1.7% wt
D37	 $-C_4H_9$	556	0.66	545	1.53	157.5–159	>5% wt
D43	 $-OC_5H_{11}$	557	0.68	542	1.49	195–196.5	0.4% wt
D52	 $-NMe_2$	546	0.65	527	0.84	234–236	0.8% wt
D77	 $-CHMe_2$	558	0.68	545	1.35	203.5–206	1.6% wt

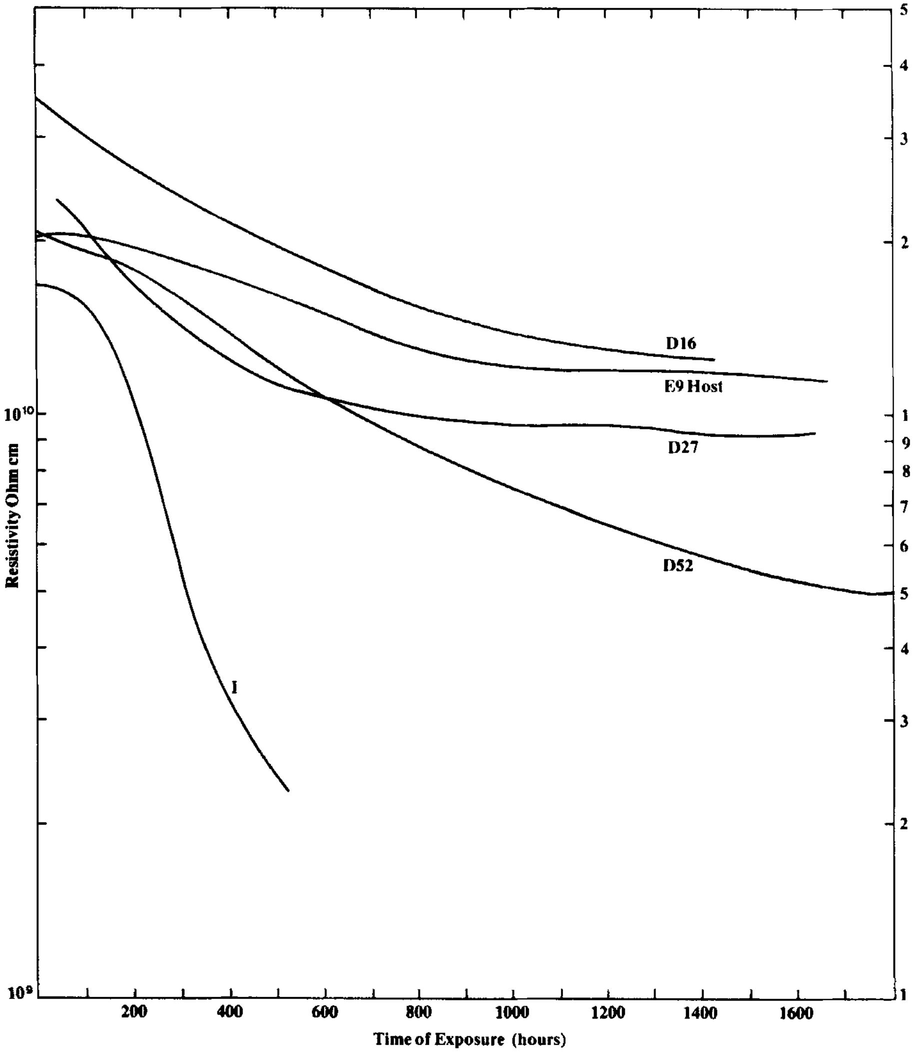


FIGURE 1 Change in resistivity on exposure to G. E. Black Fluorescent Lamp

in a similar experiment after exposure to the low power U.V. lamp for up to 1500 hours, and the results are depicted in Figure 2. The results show that the resistivity and order parameter of cells containing the anthraquinone dyes remain largely unchanged after long exposure, whilst the azo dyes I, II and III were degraded under the test conditions. D54 contained an azo-grouping and turned yellow and faded after 24 hours of test, whilst the

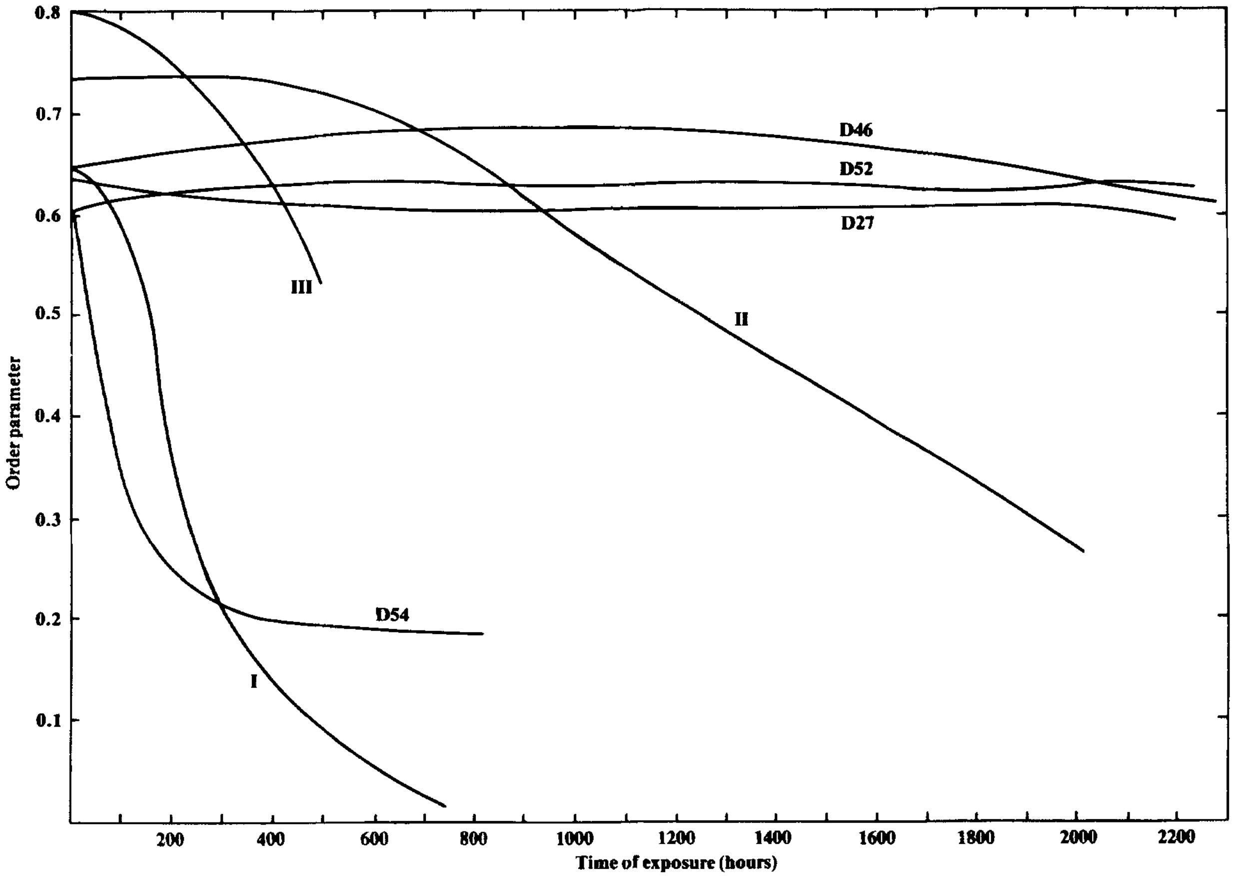


FIGURE 2 Change in order parameter on exposure to G. E. Black Fluorescent Lamp (in E7)

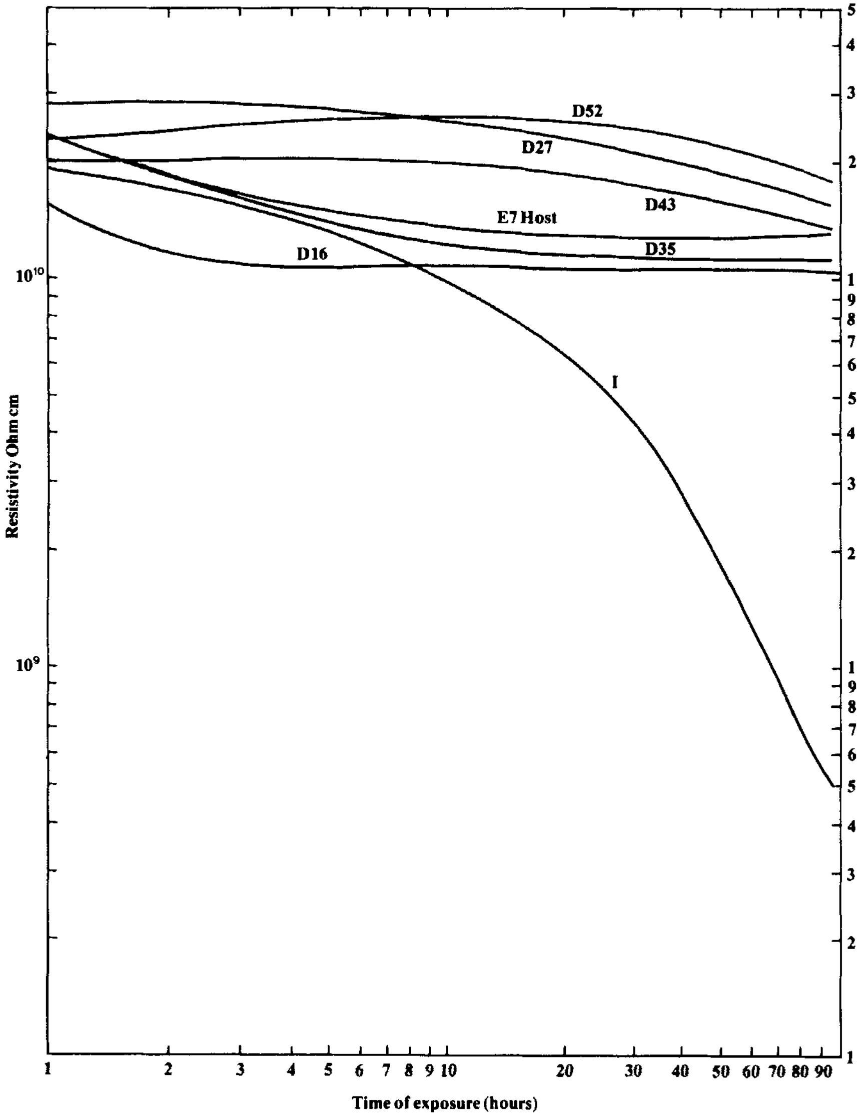


FIGURE 3 Change in resistivity on exposure to Hanovia Arc Tube (in E7-mean of 5 cells).

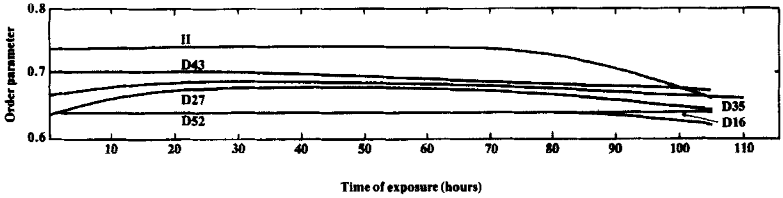


FIGURE 4 Change in order parameter on exposure to Hanovia Arc Tube.

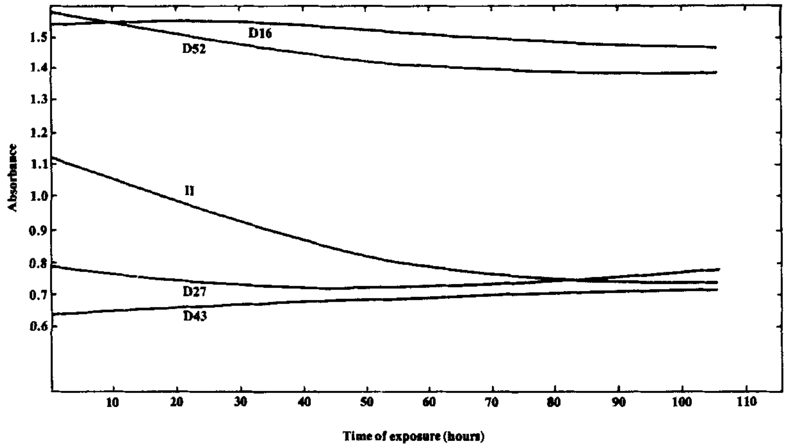


FIGURE 5 Change in absorbance on exposure to Hanovia Arc Tube.

azo-dye III turned red during the first 100 hours of test. Changes in resistivity and order parameter of the contents of cells after exposure to the 500 watt Hanovia U.V. lamp are given in Figures 3 and 4 respectively. Similar results were obtained, again illustrating the comparatively high stability of the anthraquinone dyes. No fading of the cells containing anthraquinone dyes was observed during the tests, and this is confirmed by measurement of the absorbance (Figure 5), which was largely unchanged after exposure to the Hanovia lamp for up to 100 hours.

Visible fading of cells containing an azo-dye II was observed, and the absorbance measured dropped accordingly, but the order parameter remained constant, which suggests that the products of degradation of this dye do not absorb at the wavelength at which the order parameter measurements were carried out.

A slight decrease in absorbance of the anthraquinone dye D52 was also measured, whilst the order parameter remained constant.

3 CONCLUSION

The results illustrate the high stability of some anthraquinone dyes, notably 1-phenylamino-4-hydroxy and 1,5-bisphenylaminoanthraquinones incorporating 4′-alkyl or 4′-alkoxy substrates. Such dyes show significantly higher stability than most other high order parameter dyes containing azo-linkages, and some have sufficiently high order parameter and solubility in a liquid crystal host to allow their successful employment in liquid crystal displays.

4 EXPERIMENTAL

4.1 Physical measurements

The order parameters of the dyes dissolved in the nematic liquid crystal were deduced from the absorbance $A = -\log_{10}$ (transmission) of light polarised parallel ($A_{\parallel}$) and perpendicular ($A_{\perp}$) to the director of parallel homogeneously aligned layers, using the expression

$$S = \frac{A_{\parallel} - A_{\perp}}{A_{\parallel} + 2A_{\perp}}$$

The absorbances were measured by a Perkin Elmer 137 double beam spectrophotometer, with the baseline ($A = 0$) being determined from a control nematic layer with no dissolved dye. The nematic layers were generally 12 μm or 25 μm thick and were aligned with a small tilt angle of 2° by using a rubbed polyvinyl alcohol coating on the glass substrates. The dye concentrations were typically 0.5 % or 1 % by weight, but occasionally either the dye concentration or layer thickness was altered to keep $A_{\parallel}$ within the range $1.0 < A_{\parallel} < 2.0$ and $A_{\perp} > 0.10$ in order to ensure an accurate determination of the order parameter. A high grade Polaroid (HN32) was used to minimise errors arising from the poor extinction of the poorer grades at short wavelengths. Order parameter measurements were made in E7 (BDH Chemicals Ltd) in order to obtain a direct comparison of the dyes. Some additional measurements were also made in E8 and E9; such mixtures have higher N → I transition temperatures and dyes dissolved in them, as expected, gave slightly higher order parameters.[5]

Solubilities were determined spectroscopically. A sample of the dye was dissolved in a liquid crystal host and a saturated solution was allowed to equilibrate in a water bath at 25°. Excess solid was removed by filtration, and a small aliquot of the solution obtained was dissolved in chloroform. Its absorbance was measured and compared with the absorbance of a standard solution of the dye.

In order to determine dye stabilities, samples of each dye were dissolved in a liquid crystal host, commonly E7 or E9, and cells containing the solution were exposed to low level U.V. light from a low power lamp (A General Electric F20T12 BLB Black Light Fluorescent lamp) or strong U.V. light from a medium power lamp (Hanovia U.V.S. 500 Arc Tube Type 509/10 with quartz tube, total output 500 watts). Control cells containing only the liquid crystal host were used throughout, and cells were placed on a heat sink plate 15 cm from the G.E. Black Lamp, or 20 cm from the Hanovia lamp. The Hanovia lamp gave the following major lines: wavelength, nm; (intensity, 20 cm from centre of lamp, microwatts cm^{-2}) 254 nm (619 microwatts cm^{-2}); 265 (450); 297 (315); 303 (647); 313 (1350); 365/7 (1970); 405 (844); 436 (1294); 546 (1378).

Resistivity tests were carried out in SiO—aligned frit-sealed cells, 10–12 μm thick, with the filling holes sealed by epoxy resin. Capacitance and dissipation factor were measured in the unenergised state at 0.5 V r.m.s., 1 kHz (sine-wave) using a Marconi TF1313A universal bridge.[6]

4.2 Preparation of materials

Dyes of the 1,4-substituted type (VI) were prepared[8] from the reaction of 1,4-dihydroxyanthraquinone and 1,4,9,10-tetrahydroxyanthracene in boiling ethanol with a substituted arylamine in the presence of boric acid. The crude product was recovered by filtration and purified by column chromatography and recrystallisation.

Dyes of the 1,5-substituted type (VII) were prepared[9] from the reaction of 1,5-dichloroanthraquinone in boiling 2-butoxyethanol with a substituted arylamine in the presence of cupric acetate. The crude product was recovered by filtration and purified by column chromatography and recrystallisation. The purities of all the dyes synthesised were checked by tlc, and satisfactory elemental analysis results were obtained for all the materials.

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