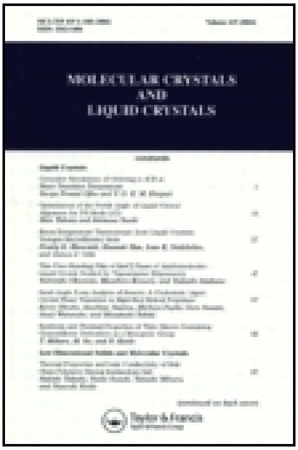

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# Naphthoquinone Colouring Matters. Part 7.[1] Order Parameters of Pleochroic 2-Aryl-1,4-Naphthoquinone Dyes in a Nematic Liquid Crystal System

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# Naphthoquinone Colouring Matters. Part 7.[1] Order Parameters of Pleochroic 2-Aryl-1,4-Naphthoquinone Dyes in a Nematic Liquid Crystal System

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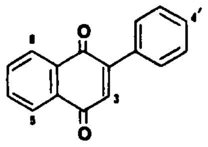
The order parameters of a number of novel 2-aryl-1,4-naphthoquinone dyes dissolved in a mixed cyanobiphenyl-terphenyl nematic liquid crystal system (Type E43, B.D.H. Chemicals Ltd.) have been determined. Observed values range from 0.80 to 0.09, and can be interpreted qualitatively by consideration of the $\pi$-dipole moment and transition moment directions of the dyes calculated by the PPP-SCF-CI MO method.

## INTRODUCTION

Anthraquinone dyes are particularly useful in guest-host liquid crystal display systems, because of their potentially high order parameters,[2-5] and their superior light fastness properties.[6-8] Exploration of other quinonoid chromogens, *e.g.* 1,4-naphthoquinones, would therefore seem worthwhile in view of possible improvements in solubility and colour range that might accrue. We have examined a number of 2-(4-aminoaryl)-1,4-naphthoquinone dyes, members of a recently-described new chromogenic class,[1,9] and order parameters have been determined in a Type E43 (B.D.H. Chemicals Ltd.) nematic liquid crystal system. Pariser-Parr-Pople MO calculations have been used to calculate the directions of the ground state $\pi$-dipole moment and the first absorption band transition moment for each dye. The relative magnitudes of the order parameters have been discussed qualitatively in terms of the calculated data.

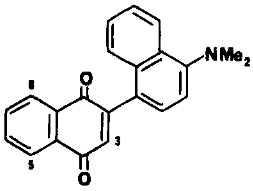
## 2-ARYL- AND RELATED 1,4-NAPHTHOQUINONE DYES

It has been demonstrated recently that 2-aryl-1,4-naphthoquinones with an amino-group in the 4-position of the aryl ring, *e.g.* (I) and (II), are more bathochromic and more intensely coloured than corresponding 2-amino-1,4-naphthoquinones, *e.g.* (III).[1,9] The elongated structures of the former chromogens suggested that such compounds might show useful pleochroic properties in liquid crystal media. Representative compounds (I) and (II) were chosen for study, giving a range of colours from red [*e.g.* (Ia)] to blue-green [*e.g.* (Id)]. For comparison purposes, order parameters of (III), (IV) and the mixed azo-quinone bichromophoric dye (V) were also determined. Spectroscopic properties of the dyes in isotropic solution (cyclohexane) and in E43 are summarised in Table I. Dyes were purified by preparative thin layer chromatography and/or recrystallisation. Details of their preparation and characterisation have been described elsewhere.[9]



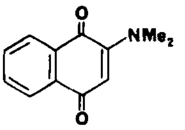
(I)

a; $4'\text{-NH}_2$
b; $4'\text{-NMe}_2$
c; $4'\text{-NEt}_2$
d; $4'\text{-NEt}_2\text{-3-CN}$
e; $4'\text{-NEt}_2\text{-3-NHMe}$
f; $4'\text{-NEt}_2\text{-5-NO}_2$
g; $4'\text{-NEt}_2\text{-8-NO}_2$
h; $4'\text{-NEt}_2\text{-5-NH}_2$
i; $4'\text{-NEt}_2\text{-8-NH}_2$

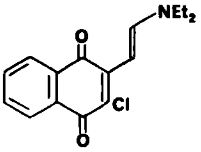


(II)

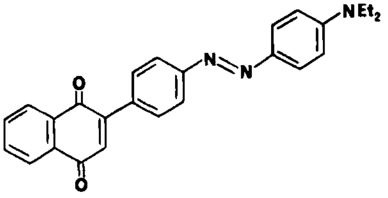
a; unsubstituted
b; $5\text{-NH}_2$
c; $8\text{-NH}_2$
d; $3\text{-Cl-8-NH}_2$



(III)



(IV)



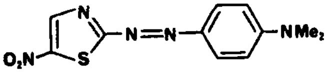
(V)

TABLE I

Visible absorption spectroscopic data for dyes (I)–(V)

| Dye | $\lambda_{max}(C_6H_{12})$ /nm | $\lambda_{max}$(calc.) /nm | $\lambda_{max}$(E43) /nm | $\epsilon_{max}(C_6H_{12})$ $l\ mol^{-1}\ cm^{-1}$ |
|---|---|---|---|---|
| Ia | 453, 439[a] | 458 | 500 | 5 800[b] |
| Ib | 498 | 498 | 549 | 8 450 |
| Ic | 516 | 516 | 566 | 10 700 |
| Id | 593 | 542 | 650 | 14 900 |
| Ie | 521 | 598 | 560 | 1 800 |
| If | 559 | 532 | 615 | 5 150 |
| Ig | 550 | 542 | 598 | 9 450 |
| Ih | 527 | 527,448 | 570 | 7 100 |
| Ii | 494 | 495,460 | 526 | 11 250 |
| IIa | 483 | 553 | 509 | 1 950 |
| IIb | 493 | 553,451 | 529 | 4 200 |
| IIc | 480 | 523,459 | 508 | 6 300 |
| IId | 486 | 514,461 | 520 | 6 050 |
| III | 444 | 444 | 463 | 3 400 |
| IV | 547 | 530 | 587 | 13 000 |
| V | 479,406[c] | 473,381 | 512,438 | 21 300<br>24 400 |

[a] Vibronic components of a single absorption band.
[b] In toluene.
[c] Two separate electronic transitions.



(VI)

## DETERMINATION OF ORDER PARAMETERS

The liquid crystal host (Type E43, B.D.H. Chemicals Ltd.) was selected because it has been reported to provide optimum order parameters for anthraquinone dyes.[10] Cells were constructed in the manner described by Jones and Reeve,[3] using microscope slides coated with oriented polyvinyl alcohol and with a cell gap of 12 μ thickness. Dyes were dissolved in the host at temperatures above the nematic–isotropic transition point (83 °C) and the concentration was adjusted to give optical density readings in the cell between 0.2 and 1.5, corresponding approximately to 1% solutions of the dye. Order parameters were determined by the method described elsewhere,[3] using a Perkin–Elmer SP-800 spectrophotometer. Each batch of cells was checked for uniformity using the reference dye (VI), which gave a value of $S = 0.62$ (literature value in E7, $S = 0.62$).[3]

The order parameters were calculated from the equation

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

and the results are summarised in Table II for dyes (I)–(V).

## MOLECULAR ORBITAL CALCULATIONS.

A standard PPP-MO procedure was used, in which two-centre electron repulsion integrals were calculated by the Nishimoto-Mataga method. For the purposes of the calculations all dye molecules were assumed to be planar, with bond angles of 120°. It should be noted, however, that in some cases [*e.g.* (Ie), (II), and (IV)] considerable deviations from planarity are known to occur,[1] and no attempt was made to take this into account in the calculations. Bond lengths, ionisation potentials, resonance-and one-centre-repulsion integrals were those described previously.[1] Calculated transition wavelengths and transition moments

TABLE II

Order parameters and calculated dipole moment data for dyes (I)–(V)

| Dye | $S^a$ | $\theta_m{}^b$ /° | $\theta_\mu{}^c$ /° | $\mu^d$ /D | $\Delta\theta^e$ /° |
|---|---|---|---|---|---|
| Ia | 0.44 | 19 | 17 | 3.7 | 36 |
| Ib | 0.47 | 17 | 14 | 4.9 | 31 |
| Ic | 0.49 | 17 | 13 | 5.4 | 30 |
| Id | 0.39 | 20 | 33 | 7.0 | 53 |
| Ie | 0.09 | 38 | −24 | 4.3 | 62 |
| If | 0.54 | 19 | 26 | 8.2 | 45 |
| Ig | 0.31 | 50 | −22 | 4.8 | 72 |
| Ih | 0.72 | 3 | −9 | 2.8 | 12 |
| Ii | 0.43 | 10 | 37 | 6.5 | 47 |
| IIa | 0.40 | 12 | 13 | 6.0 | 25 |
| IIb | 0.80 | 4 | −7 | 3.2 | 11 |
| IIc | 0.45 | 9 | 36 | 7.1 | 45 |
| IId | 0.51 | 5 | 36 | 7.8 | 41 |
| III | 0.19 | 38 | 40 | 2.9 | 78 |
| IV | 0.21 | 56 | −33 | 7.2 | 89 |
| V | $0.73^f$ | $3^f$ | 3 | 6.7 | $6^f$ |
|  | 0.73 | −25 |  |  | 28 |

[a] Order parameter.
[b] Calculated transition moment direction relative to MAA (Figure 2).
[c] Calculated $\pi$-dipole moment direction relative to MAA.
[d] Calculated $\pi$-dipole moment.
[e] $|\theta_m| + |\theta_\mu|$.
[f] Data for longer wavelength band quoted first.

were obtained after a limited configuration interaction (CI) treatment involving the nine lowest singly excited singlet states.

Calculated wavelength values correspond most closely to experimental values measured using non-polar solvents, *e.g.* cyclohexane, and such a comparison is made in Table I. In the host liquid crystal medium, substantial bathochromic shifts of the visible absorption band are observed (Table I). Calculated transition moment directions (after CI) and ground state $\pi$-electron dipole moment properties are summarised in Table II.

## DISCUSSION

The 2-(4-aminoaryl)-1,4-naphthoquinones show a wide variation in order parameters, ranging from very high, [*e.g.* (IIb), $S = 0.80$] to low [*e.g.* (Ie), $S = 0.09$]. Comparison of dyes (Ib) and (III) ($S = 0.47$ and

0.19 respectively) shows that interposing a *para*-phenylene bridge between the amino-group and quinonoid ring of a 2-amino-1,4-naphthoquinone dye does produce a marked increase in the order parameter. It is noteworthy that a corresponding 1,4-naphthylene bridge, as in (II), is equally effective, although spectroscopic studies have shown conclusively that such compounds are twisted out of plane due to steric crowding.[1] In contrast, a vinylene bridge, as in (IV), has little effect, and (III) and (IV) show comparable order parameters, although they differ markedly in their spectroscopic properties.

The 2-aryl systems (I) and (II) show a pronounced dependence of the order parameter on the presence of substituents in the 5- and 8-positions of the naphthoquinone residue, and it appears that 5-substituents induce the higher value. For example, a 5-amino group in (II) gives an order parameter of 0.80, whereas the corresponding 8-amino dye shows a value of 0.45. It seems unlikely that such relatively minor structural changes could cause large differences in the abilities of the dyes to align with the host molecule, and thus the reasons for the widely differing order parameters must be sought elsewhere, *e.g.* differences in transition moment directions.

Several factors contribute to the observed order parameter of a dye, and these have been elaborated by Osman *et al.*[4] For a series of closely related dyes with a similar molecular alignment axis (MAA), a particularly important variable is the angle, $\theta_m$, between the transition moment for the visible band of the dye and the MAA. The larger is $\theta_m$, the smaller will be the order parameter. Osman and co-workers have calculated the transition moments of various anthraquinone dyes by the PPP-MO method, and were able to derive useful predictions for substituted anthraquinones with optimum order parameters.[4]

Another factor worthy of consideration is the permanent ground state dipole moment of the dye ($\mu$). If the dipole moment is in the same direction as the MAA then strong interaction between the dye and host molecules will be favoured, and high degree of alignment should result. A large angle ($\theta_\mu$) between the two axes will be unfavourable for alignment. The $\pi$-electron component of the dipole moment of a dye can be calculated by the PPP method, and although the absolute magnitude of the calculated moment is generally inaccurate, predicted moment directions are useful quantities. The generally minor contribution from the $\sigma$-framework of the molecule can be ignored for the present purposes.

The most uncertain factor in discussing the orientation properties of dyes is the MAA. This will be dependent on the topology of the dye molecule, where maximization of overlap between the dye and host

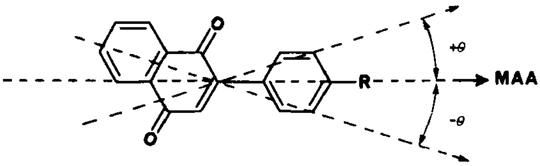


FIGURE 1 The assumed molecular alignment axis (MAA) for dyes (I)–(V).

molecules needs consideration, and also the magnitude and direction of the dipole moment of the dye, and the presence of substituents exhibiting specific interaction with the host molecule (*e.g.* hydrogen bonding). For convenience the MAA of the dyes (I)–(V) is assumed to lie parallel to the bond linking the aryl group to the naphthoquinone ring (Figure 1). This corresponds approximately to the maximum elongation axis of the molecule and is also oriented more closely to the $\pi$-dipole moment of parent compounds (Ia)–(Ic) than is the alternative MAA perpendicular to the line joining the quinone carbonyl groups. In practice any axis between the two limits leads to the same general conclusions in the following discussion, provided the major assumption is made that the dyes all have approximately the same MAA.

Calculated angles between the chosen MAA and the $\pi$-dipole moment ($\theta_\mu$) and between the MAA and the transition moment ($\theta_m$) are listed in Table II. The implications of the algebraic signs given to these values are made clear in Figure 1.

Considering the transition moment angles in isolation, it is possible to explain most of the trends in the order parameters for the dyes (I)–(IV), and in general the larger the value of $\theta_m$, the lower the order parameter. Trends are not uniform, however, and as noted by Osman *et al.* for the anthraquinones, a small $\theta_m$ value is not necessarily indicative of a high order parameter [*e.g.* (Ii), $\theta_m = 10°$, $S = 0.43$]. Differences between 5- and 8-substituted isomeric structures can be accounted for in this way however, *e.g.* (If), (Ig); (Ih), (Ii); (IIb), (IIc). The 5- and 8-amino-derivatives (Ih), (Ii), (IIb), (IIc) and (IId) show a single absorption band which in fact consists of two overlapping transitions (Table I). The longer wavelength component is considerably more intense than the shorter wavelength band and makes the major contribution to the observed $\lambda_{max}$ value.[1] The calculated data of Table II refer to the former electronic transition only.

As discussed previously, two separate factors can be considered to contribute to the order parameter of a dye: (*a*) the deviation of the transition moment direction from the MAA, defined by $\theta_m$; (*b*) the deviation of the ground state dipole moment from the MAA, defined by $\theta_\mu$. The first effect is essentially optical in origin. The second effect relates to the lowered orientation ability of a dye as $\theta_\mu$ increases. It would seem reasonable therefore that some combination of the parameters $\theta_\mu$ and $\theta_m$ might give a better indication of order parameter than $\theta_m$ alone. To test this a simple summation of $\theta_\mu$ and $\theta_m$ (ignoring algebraic signs) was carried out, affording a quantity termed for convenience $\Delta\theta$. The correlation was poorer if algebraic signs were taken into account. The need to neglect sign suggests that the effects of the permanent dipole, $\mu$, and the transition moment, $M$, are mutually independent, and their relative orientation in the molecule is unimportant. This implies that $\mu$ exerts no specific orientational effect on the dye, but that any conflict between $\mu$ and the MAA causes a general reduction in the degree of alignment of the MAA with the host alignment axis. The resultant values of $\Delta\theta$ for dyes (I)–(V) are summarised in Table II, and the correlation between $\Delta\theta$ and order parameter $S$ is depicted in Figure 2. As might be expected, no mathematical relationship pertains, but a better qualitative correlation is observed between $S$ and $\Delta\theta$ than between $S$ and $\theta_m$ alone. Dyes with order parameters below *ca.* 0.3 have $\Delta\theta$ values exceeding 60 °, whereas those with intermediate values of $S$ (*ca.* 0.3 – 0.6) have $\Delta\theta$ values in the approximate range 20 °–60 °. High order parameter dyes ($S$ > 0.6) have $\Delta\theta$ values below *ca.* 20 °.

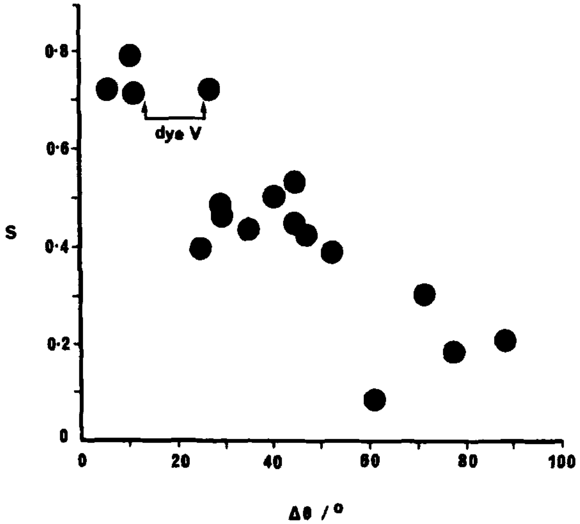


FIGURE 2 Relationship between order parameter ($S$) and $\Delta\theta$ for dyes (I)–(V).

The mixed azo-quinone bichromophoric dye (V) is interesting in that in E43 it exhibits two distinct absorption bands ($\lambda_{max}$ 512 and 438 nm) and both have the same high order parameter (0.73). Polychromophoric dyes are of potential value as sources of single-component blacks, but have been little investigated. The 1,4-bis-arylaminoanthraquinones also show two visible bands, but these are polarised perpendicularly to each other and thus switching LCD's containing such compounds causes a hue change rather than a uniform decrease in colour intensity.[3-5] In the case of (V) the two transitions are polarised in similar directions and thus no hue change occurs on rotating the plane of polarisation of the incident light through 90°. MO calculations show the two transitions to be polarised in similar directions, with an angle of 28° between the two transition moments. The high order parameters for the two transitions may be attributed to their low $\Delta\theta$ values (6° and 28° for the longer and shorter wavelength transitions respectively) and to the elongated structure of the molecule.

## Acknowledgment

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