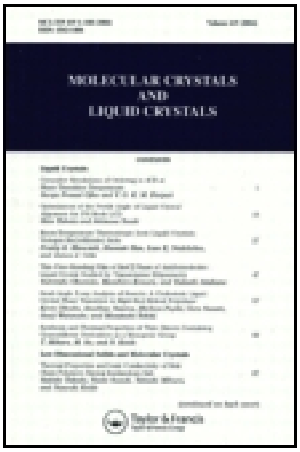

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Order Parameters of α-Substituted Anthraquinone Dyes in a Nematic Liquid Crystalline Host

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Order Parameters of α-Substituted Anthraquinone Dyes in a Nematic Liquid Crystalline Host

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A study is presented of the optical order parameters and spectroscopic properties of α-substituted anthraquinone dyes in a nematic liquid crystalline mixture composed of cyanophenylcyclohexane derivatives. Then, the results of this study are discussed in terms of the effects of the dye structure on the order parameters. From the systematic variation in structure, the order parameters are found to be improved when a biphenylamino group is introduced into the α-position of the anthraquinone nucleus. In addition, preliminary data on the solubility and photostability of the dyes are reported.

Keywords: guest-host, dichroic dye, liquid crystal, anthraquinone, order parameter

1. INTRODUCTION

The use of dichroic dyes in liquid crystal displays is a subject of continuing scientific and commercial interest. More recent efforts have been concentrated on anthraquinone dyes which are noted for their excellent photostability. Much research has been concerned with this chemical class of dyes,[1–6] so some with exceptionally high order parameters have already been discovered.[3,5,6,7] However, much basic research still remains on the relationship between the molecular structures and properties of dichroic anthraquinone dyes.

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This paper reports on the order parameters and spectroscopic properties for a number of α-substituted anthraquinone dyes. The effect of various substituents on the dye order parameters is examined in detail, especially that of a biphenyl ring and a very long flexible chain, such as an *n*-octadecyl group. This work is part of a systematic investigation aimed at obtaining a detailed picture of dichroic dye behavior in nematic liquid crystalline hosts.

2. EXPERIMENTAL

Simplified chemical structures of the investigated α-substituted anthraquinone dyes are given in Figure 1. These dyes include 1-arylamino-4-hydroxyanthraquinone (Type I dyes), 1,5-bisarylaminoanthraquinone (Type II dyes), and 1,4-bisarylaminoanthraquinone (Type III dyes). The dyes were obtained either commercially or were synthesized by slightly modifying standard methods. The syntheses and characterization of the dyes are not described in detail here. Each dye was ultimately purified until it was made 'single-spot' pure by thin-layer chromatography. On the other hand, the commercial samples were purchased from BDH Chemicals Ltd. and not further purified. The nematic host used is the cyanophenylcyclohexane mixture ZLI-1132 (produced by E. Merck), which has a positive dielectric anisotropy.

The cells used during experimentation consisted of two glass plates, 4 × 4 cm in area, each having a transparent layer of indium oxide. These oxide layers were coated with a rubbed polymer layer to obtain parallel alignment. The cell gaps were about 10, 50, and 100 μm.

The optical order parameter S of the dyes dissolved in the nematic liquid crystal was obtained using plane-polarized light by the formula:[8,9]

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

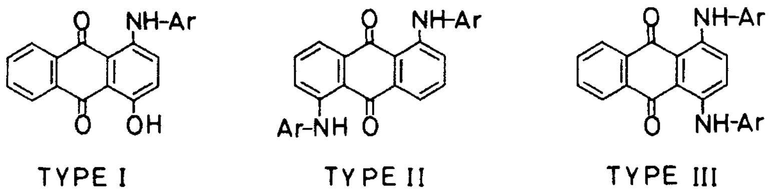


FIGURE 1 Simplified chemical structures of the α-substituted anthraquinone dyes investigated. Ar indicates a aryl group.

where $A_{\parallel}$ is the absorbance of the dye at its maximum absorption wavelength (λ_{max}) when the polarization is parallel to the alignment direction and $A_{\perp}$ is the absorbance at λ_{max} when the polarization is perpendicular to the alignment direction. Optical absorption spectra were measured at 22°C using a Hitachi 340 spectrophotometer.

The accelerated photodegradation tests of the dyes in the liquid crystalline medium were carried out with an Atlas Sunshine Weather O'meter, Type 65/XW-WR (Atlas Electric Co.). A carbon arc lamp was used as the light source for exposing samples, and the total light intensity at the cells was about 1×10^2 mW · cm^{-2}. During exposure, the cells were put on an aluminium plate. A UV filter was not employed. The accelerated tests were performed at temperatures of about 50°C in a dry atmosphere. The photostability of the dyes was examined by monitoring the absorbance changes of the dyes in the parallel mode during the tests. The cells containing only the host liquid crystal were also exposed for use as reference in the spectroscopic measurement.

3. RESULTS AND DISCUSSION

3.1. 1-arylamino-4-hydroxyanthraquinone (Type I dyes)

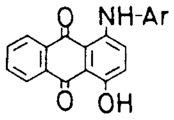
The order parameters and maximum absorption wavelengths (λ_{max}) for 1-arylamino-4-hydroxyanthraquinones (Type I dyes) are shown in Table I. This type of α-substituted anthraquinone dyes gives a range of colors from violet to blue.

Dyes 1–12 contain a phenyl ring. The 4'-alkylphenylamino and 4'-alkoxylphenylamino derivatives have previously been reported in detail by Pellatt et al.[1] The order parameter values of the phenylamino derivatives shown in Table I can be roughly classified into three categories: (A) dyes with order parameters ranging from 0.60 to 0.62 (Dyes 1, 2, 4, 5, 9, and 10), (B) ones with S-values ranging from 0.66 to 0.67 (Dyes 3, 11, and 12) and (C) those ranging from 0.51 to 0.54 (Dyes 6, 7, and 8). A comparison of Dyes 1 and 7 shows that the introduction of a fluorine atom into 2'-position of the phenyl ring considerably decreases the order parameter. A similar effect of the substituent position on the order parameter has been reported by Pellatt et al.[1]

Next, Dyes 13–22 contain a biphenyl ring. The effect of this ring on the order parameter is demonstrated by comparing S for Dye 2 with that for Dye 14. It can be seen that the replacement of the phenyl

TABLE I

Experimental data on 1-arylamino-4-hydroxyanthraquinone dyes (Type I dyes)



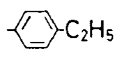
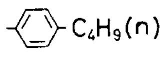
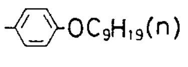
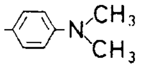
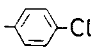
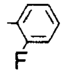
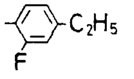
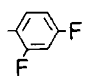
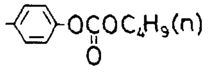
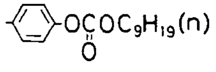
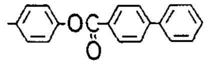
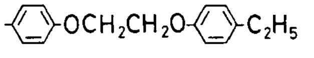
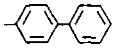
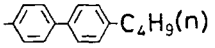
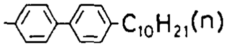
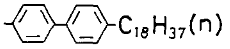
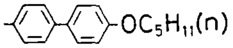
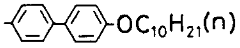
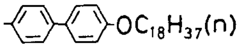
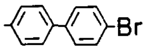
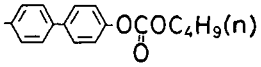
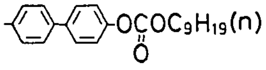
Dye No.	Ar	λ_{max}/nm (in ZLI-1132)	S	λ_{max}/nm (in chloroform)
1.		560 586	0.60	556 586
2.		564 587	0.61	559 586
3.		553 590	0.66	—
4.		554 598	0.62	—
5.		562 588	0.60	—
6.		550 574	0.53	545 573
7.		556 570	0.51	549 575
8.		542 572	0.54	540 572
9.		562 584	0.61	556 580
10.		562 584	0.61	556 580
11.		561 592	0.66	556 580

TABLE I *Continued*

Dye No.	Ar	λ_{max}/nm (in ZLI-1132)	S	λ_{max}/nm (in chloroform)
12.		558 589	0.67	556 584
13.		586	0.64	582
14.		588	0.67	584
15.		588	0.66	584
16.		590	0.67	586
17.		590	0.67	586
18.		590	0.69	586
19.		590	0.71	584
20.		584	0.68	576
21.		585	0.69	578
22.		585	0.67	580

ring by a biphenyl one acts to increase the order parameter by 0.06. Furthermore, from a survey of the results shown in Table I, a general trend can be observed; that is, the dyes containing a biphenyl ring have a higher order parameter than those containing a phenyl ring.

When the terminal substituent of the biphenyl ring is an *n*-alkyl group (Dyes 14, 15, and 16), the order parameters of the dyes do not seem to depend on the chain length. This result is somewhat surprising, where a very long chain, such as an *n*-octadecyl group, does not appreciably effect the order parameter. For the dyes containing an alkoxy group (Dyes 17, 18, and 19), on the other hand, the order parameter increases with the length of the alkoxy chain, i.e. *S*(Dye 19) > *S*(Dye 18) > *S*(Dye 17).

Typical absorption spectra for Type I dyes in chloroform are shown in Figure 2. The spectra in the liquid crystalline medium are similar to those in chloroform, where the band shape is maintained and a wavelength shift of only a few nanometers is observed.

The visible absorption band of the dyes containing the phenyl ring (Dyes 1–12) has double-headed characteristics. When the phenyl ring has an alkyl or alkoxy group at its 4′-position (Dyes 1, 2, and 3), the shorter wavelength peak is observed as a shoulder of the main absorption peak. On the other hand, in dyes with Cl, F, or —OCOO— group in the 2′- or 4′-position of the phenyl ring (Dyes 5, 6, 8, 9, 10, and 11), the shorter wavelength peak is more intense than the longer one, and it makes the major contribution to the observed absorption band. Because of the greater influence of the shorter wavelength peak, Dyes 6 and 8 are violet in color. When Ar is the biphenyl ring, the double-headed characteristics in the band shape are hardly discernible (Dyes 13–22).

3.2. 1,5-bisarylaminoanthraquinone (Type II dyes)

The order parameters and maximum absorption wavelengths for 1,5-bisarylaminoanthraquinones (Type II dyes) are shown in Table II.

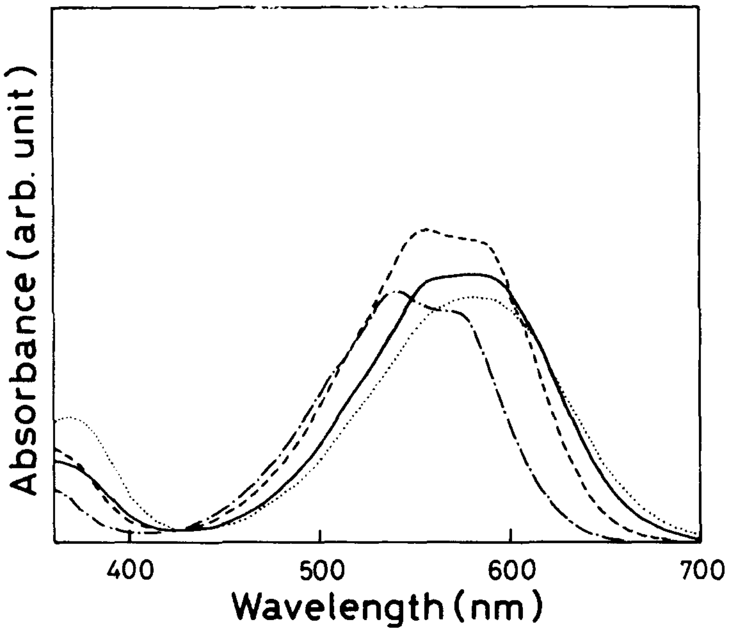
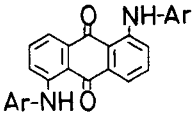
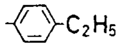
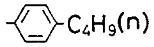
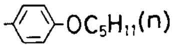
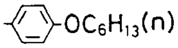
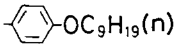
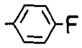
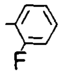
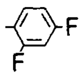
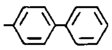
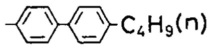
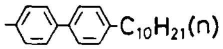
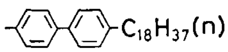


FIGURE 2 Typical absorption spectra for Type I dyes in chloroform: ———, Dye 1; —·—, Dye 8; – – –, Dye 9; · · · · ·, Dye 15.

TABLE II

Experimental data on 1,5-bisarylaminoanthraquinone dyes (Type II dyes)



Dye No.	Ar	λ_{max}/nm (in ZLI-1132)	S	λ_{max}/nm (in chloroform)
23.		548	0.67	540
24.		548	0.66	541
25.		548	0.67	—
26.		548	0.69	542
27.		546	0.66	542
28.		530	0.64	530
29.		516 540	0.60	518
30.		513	0.59	510
31.		550	0.72	544
32.		553	0.73	544
33.		552	0.73	546
34.		548	0.72	544

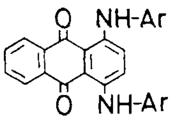
This type of α-substituted anthraquinone dyes ranges in color from red to violet.

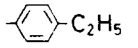
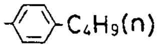
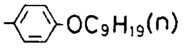
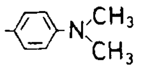
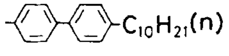
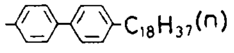
Dyes 23–30 contain phenyl rings. These dyes have order parameters ranging from 0.59 to 0.69 in ZLI-1132. The replacement of hydrogen in the 2′-position of the phenyl ring by fluorine (Dyes 29 and 30) results in lower *S* values, similar to the case of Type I dyes.

Dyes 31–34 contain biphenyl rings. These dyes exhibit *S* values over 0.70. A comparison of the order parameter between Dyes 24

TABLE III

Experimental data on 1,4-bisarylaminoanthraquinone dyes (Type III dyes)



Dye No.	Ar	λ_{max}/nm (in ZLI-1132)	S	λ_{max}/nm (in chloroform)
35.		410	−0.09	410
		610		608
		649	0.49	645
36.		412	−0.12	411
		610		606
		650	0.50	646
37.		430	−0.13	418
		606		608
		644	0.58	642
38.		658	0.43	652
39.		420	−0.18	415
		616		610
		654	0.58	650
40.		420	−0.20	414
		616		610
		655	0.58	650

and 32 definitely shows that a biphenyl ring induces higher *S* values. This is a similar behavior to that of Type I dyes.

The order parameters of the 1,5-bisarylamino series do not seem to strongly depend on the length of the terminal flexible chain. Even a very long chain, such as an *n*-octadecyl group, does not play a significant role in increasing the order parameter.

3.3. 1,4-bisarylaminoanthraquinone (Type III dyes)

The order parameters and maximum absorption wavelengths for 1,4-bisarylaminoanthraquinones (Type III dyes) are shown in Table III. This type of α-substituted anthraquinone dyes gives a blue-green color.

The *S* values for Type III dyes range from 0.49 to 0.58 in ZLI-1132. In addition, the biphenyl ring tends to increase the order parameter in this series, too.

Typical polarized spectra for Type III dyes are illustrated in Figure 3.

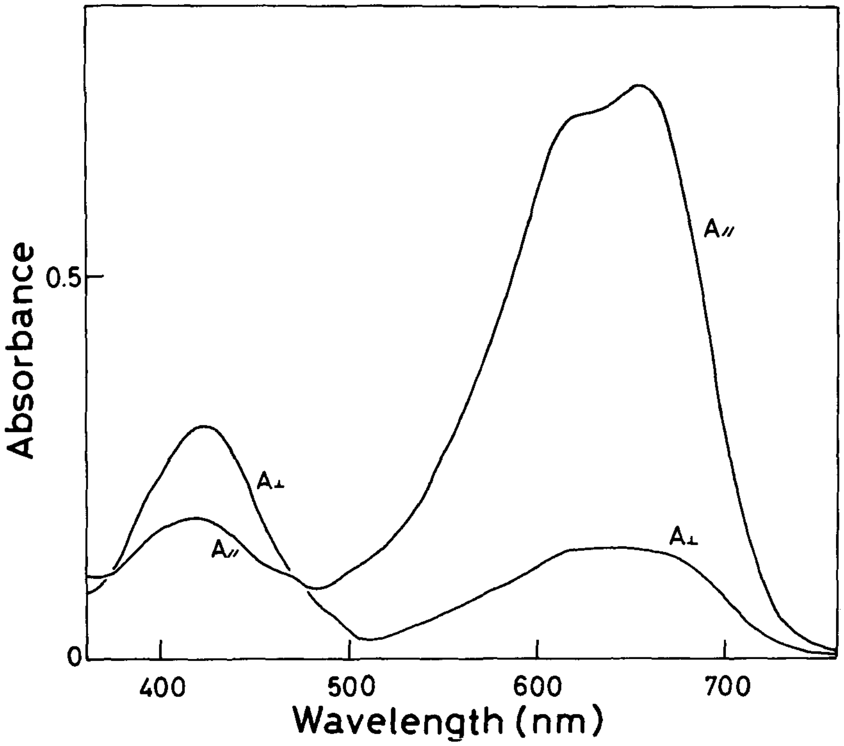
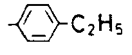
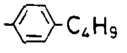
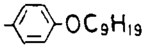
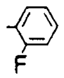
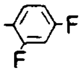
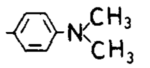
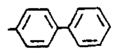
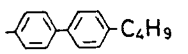
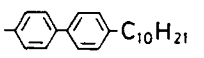
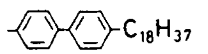


FIGURE 3 Polarized absorption spectra for Dye 39.

TABLE IV

Comparison of some selected *S* values for the α-substituted anthraquinone dyes

Aryl group	1,5-bis-arylamino derivative	1-arylamino-4-hydroxy derivative	1,4-bis-arylamino derivative
	0.67	0.60	0.49
	0.66	0.61	0.50
	0.66	0.66	0.58
	0.60	0.53	—
	0.59	0.54	—
	—	0.62	0.43
	0.72	0.64	—
	0.73	0.67	—
	0.73	0.66	0.58
	0.72	0.67	0.58

The visible absorption spectra for these dyes have a weak band in the short wavelength region in addition to the double-headed one in the long wavelength region. As shown in the figure, this short wavelength band has a negative anisotropy which gives negative order parameter values. Similar observations have previously been reported by Jones et al.[2] and Clark et al.[10]

3.4. Additional results

Some selected data for the order parameters of the dyes investigated here are shown in Table IV. The table shows that the order parameters decrease in the order 1,5-bisarylamino (Type II) > 1-arylamino-4-hydroxy (Type I) > 1,4-bisarylamino (Type III). This clearly shows that the rigid portion in the dye molecules is a primary factor in determining the order parameter.

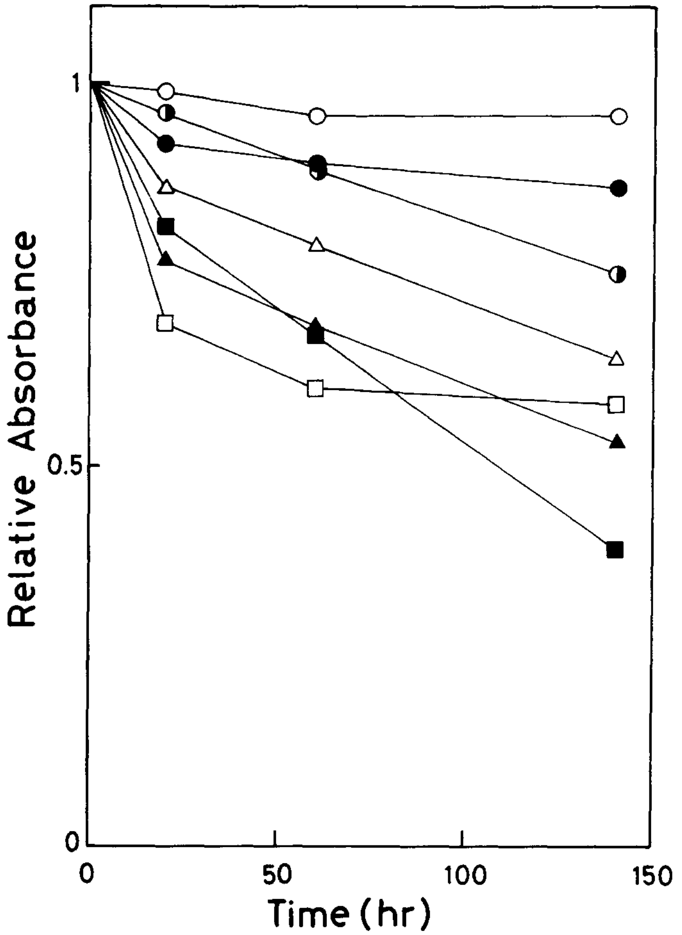


FIGURE 4 Time dependence of the absorbance for the various anthraquinone dyes during the accelerated photodegradation tests: ○, Dye 12 (589 nm); ●, Dye 26 (548 nm); ◑, Dye 16 (586 nm); △, Dye 28 (530 nm); ▲, Dye 30 (513 nm); □, Dye 11 (561 nm); ■, $H_9C_4OOC{-}\phi{-}N{=}N{-}\phi{-}N(CH_3)_2$ (reference dye).

Although the solubility of the dyes has not yet been precisely examined, some of them have been found to give excellent solubility in ZLI-1132. For example, Dyes 1, 2, 3, 10, 15, and 24 provide a solubility over 3 wt% at room temperature. In particular, the value for Dye 10 is greater than 10 wt%. On the other hand, the solubility of dyes containing a fluorine atom or biphenyl ring is generally low.

Some selected results from the accelerated photodegradation tests are shown in Figure 4. For comparison, a well known dye has been subjected to the same test. From Figure 3, it can be seen that the less stable dyes have —F or —OCO—. These figures indicate that the effects of the terminal group on photostability cannot be ignored.

4. CONCLUSION

The effects of molecular structure on the order parameters and spectroscopic properties have been examined for a number of α-substituted anthraquinone dyes. From the systematic variation in structure, it has been found that the order parameters can be improved when a biphenylamino group is introduced into the α-position of the anthraquinone nucleus. However, the behavior of the dyes containing a very long flexible chain, such as the *n*-octadecyl group, illustrates the complicated nature of guest-host interactions.

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