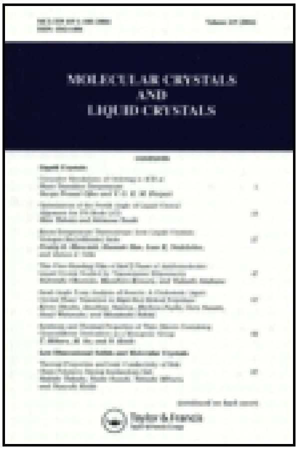

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Anthraquinone Dyes with Negative Dichroism

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Anthraquinone Dyes with Negative Dichroism

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A number of α-substituted anthraquinone dyes with negative dichroism have been prepared. Observed order parameters range from -0.05 to -0.34. The results of this study are discussed in terms of the effect of the dye structure on the order parameters. From a survey of the results it is found that an amide group attached to the α-position of the anthraquinone nucleus plays a dominant role in producing negative dichroism. In addition, the spectroscopic data on the dyes are reported.

1. INTRODUCTION

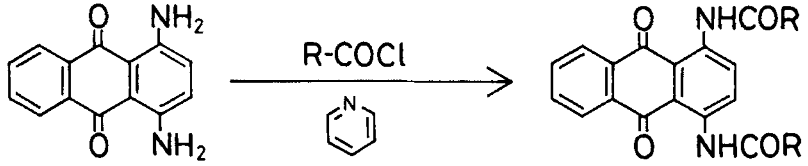
Dichroic dyes for guest-host application can be classified into two types—those with positive dichroism and those with negative dichroism. The majority of the dichroic dyes investigated so far are those with positive dichroism.[1–19] In contrast with this, there are only few reports[20–22] dealing with the dyes with negative dichroism.

Demus et al.[20] and Schadt[23] have demonstrated that it is possible to construct a color-switching display by employing guest-host systems containing two dichroic dyes with different signs of dichroism.

During the course of screening a large number of dichroic dyes, we have found that anthraquinone derivatives containing–NHCOR groups in the α-position give negative order parameters in nematic hosts. In order to further explore the anthraquinone dyes with negative dichroism, we have prepared a number of α-substituted anthraquinones. The effect of various substituents on the order parameters and spectroscopic properties of the dyes has been examined in detail.

2. EXPERIMENTAL

The preparation of the dyes is illustrated in Scheme 1. All dyes were purified by repeated column chromatography, recrystallization or sublimation. Molecular structures of the products were confirmed by IR, NMR and other spectroscopic analyses. The melting points of the dyes were determined with a Perkin-Elmer DSC 7 differential scanning calorimeter.



(R: Alkyl, 4'-Alkylcyclohexyl or Aryl group)

SCHEME 1

The nematic host used in the experiment is a cyanophenylcyclohexane mixture ZLI-1132 (produced by E. Merck), which has a positive dielectric anisotropy.

The cells used in the experiment consists of two glass plates, with an area of 4 × 4 cm, each having a transparent layer of indium oxide. The oxide layers were coated with a polymer layer followed by rubbing to obtain parallel alignment. Consistent with the solubilities of the dyes, three different cell gaps were employed: about 10, 50 and 100 μm.

The optical order parameter *S* of the dyes dissolved in the nematic liquid crystal was determined using plane-polarized light by the formula[1,3]:

$$S = \frac{A_{\parallel} - A_{\perp}}{2A_{\perp} + A_{\parallel}} \tag{1}$$

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. Baseline corrections were made using the cells containing only the nematic host liquid crystal. Optical absorption spectra were measured at 22°C using a Hitachi 340 spectrophotometer.

3. RESULTS AND DISCUSSION

3-1. *Order parameter*

Sixteen anthraquinone dyes have been prepared. These are summarized in Tables I and II. It can be seen that all the dyes listed here exhibit negative dichroism.

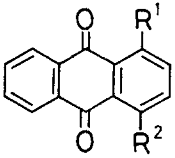
The optical order parameters for a series of 1,4-disubstituted anthraquinones in ZLI-1132 are shown in Table I. The results clearly indicate that an amide group –NHCOR plays a dominant role in producing negative dichroism. It is particularly noteworthy that Dyes 4,5 and 6 show order parameters ranging from –0.33 to –0.34 in ZLI-1132. It is obvious that the noticeable negative dichroism of these dyes can be attributed to the presence of an arylamide or 4′-alkylcyclohexylamide group in the 1- and 4-positions of the anthraquinone nucleus.

In contrast with this, replacement of the arylamide or 4′-alkylcyclohexylamide group by the other substituents reduces negative dichroism (Dyes 7–10). This effect is particularly pronounced when R^2 is an arylamino group (Dye 8).

Table II shows the order parameters for 1,5-disubstituted, 1,8-disubstituted and 1,4,5,8-tetrasubstituted anthraquinones. These data give the information about the effect of the position of substitution on the order parameter.

Dyes 11, 12 and 13 have two –NHCOR groups in the 1,5- or 1,8-positions. A comparison of S values for these dyes with those for Dyes 4, 5 and 6 indicates that the 1,4-disubstituted derivatives surpass

Table I Experimental data on 1,4-disubstituted anthraquinones



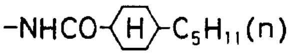
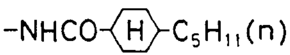
Dye No.	R^1	R^2	λ_{max}/nm (in ZLI-1132)	S (in ZLI-1132)	λ_{max}/nm (in chloroform)	m.p./°C
1.	$-NHCOC_5H_{11}(n)$	$-NHCOC_5H_{11}(n)$	471 $\underline{493}$ 530	-0.15	469 $\underline{486}$ 528	177.1
2.	$-NHCOC_9H_{19}(n)$	$-NHCOC_9H_{19}(n)$	471 $\underline{493}$ 530	-0.21	470 $\underline{486}$ 528	——
3.	$-NHCOC_{15}H_{31}(n)$	$-NHCOC_{15}H_{31}(n)$	$\underline{494}$ 530	-0.16	472 $\underline{486}$ 530	113.4
4.			472 $\underline{494}$ 536	-0.34	468 $\underline{489}$ 528	289.7

Table I Continued

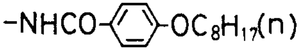
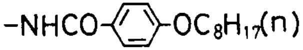
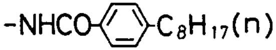
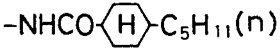
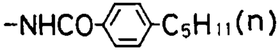
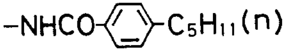
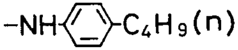
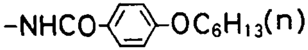
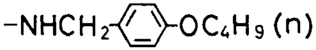
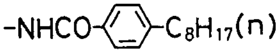
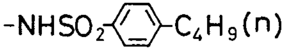
Dye No.	R^1	R^2	λ_{max}/nm (in ZLI-1132)	S (in ZLI-1132)	λ_{max}/nm (in chloroform)	m.p./°C
5.			480 508 548	-0.33	—	—
6.			472 499 542	-0.33	472 494 536	—
7.		$-NHC_8H_{17}(n)$	574 611	-0.23	503 572 608	174.1
8.			590	-0.05	522 570 604	149.6
9.			546 586	-0.16	500 533 572	210.9
10.			508 544 580	-0.15	501 533 570	212.7

Table II Experimental data on 1,5-disubstituted, 1,8-disubstituted and 1,4,5,8-tetrasubstituted anthraquinones

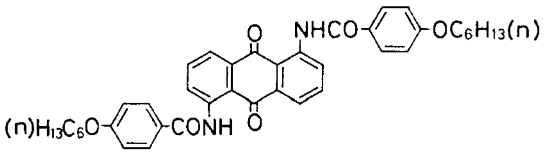
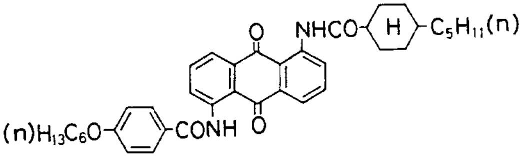
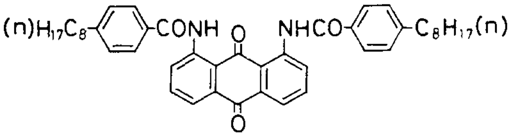
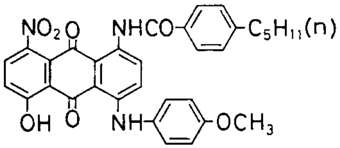
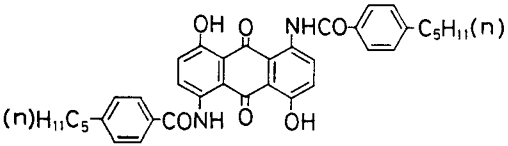
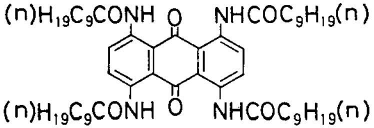
Dye No.	Molecular structure	λ_{max}/nm (in ZLI-1132)	S (in ZLI-1132)	λ_{max}/nm (in chloroform)	m.p./°C
11.		446	-0.11	445	277.6
12.		460	-0.08	450	296.2
13.		400 418 482	-0.13	399 420 471	179.5

Table II Continued

Dye No.	Molecular structure	λ_{max}/nm (in ZLI-1132)	S (in ZLI-1132)	λ_{max}/nm (in chloroform)	m.p./°C
14.		556 600 642	-0.05	544 598 632	——
15.		519 556 592	-0.18	512 552 588	273.3
16.		514 548 590	-0.33	510 541 577	206.3

the 1,5- and 1,8- disubstituted ones with regard to the negative dichroism.

It appears that smaller negative dichroism of Dye 14 is due to the presence of the arylamino group in the 4-position, similar to the case of Dye 8.

It must be emphasized here that Dye 16 shows considerably large negative dichroism ($S = -0.33$). A comparison of Dyes 2 and 16 definitely demonstrates that the introduction of two more alkylamide groups into the 5- and 8-positions leads to the enhancement of negative dichroism.

3-2. *Absorption spectra*

The maximum absorption wavelengths (λ_{max}) for the anthraquinones investigated here are shown in Tables I and II. It is generally observed that λ_{max} for the dyes dissolved in ZLI-1132 undergoes an appreciable bathochromic shift in comparison with that for the same dyes in chloroform. This bathochromic shift is attributable to the difference in solvent polarity: absorption bands due to electronic transitions which cause an increase in the dipole moment of the molecule are shifted to longer wavelengths with increasing polarity of the solvent.[24]

Typical dichroic absorption spectra for the dyes with negative dichroism are illustrated in Figure 1.

Among the 1,4-disubstituted derivatives shown in Table I, Dyes 1–6 give a range of colors from orange to red-orange. When the electron-donating power of the substituent attached to the 4-position is stronger than that of $-$NHCOR, violet to blue-violet colors are produced (Dyes 7–10).

Dyes 11–13, in which the two $-$NHCOR groups are in the 1,5- or 1,8- positions, range in color from yellow to orange. Closer inspection reveals that when the anthraquinone nucleus is substituted by two $-$NHCOR groups (Dyes 1–6 and Dyes 11–13), the order of increasing λ_{max} is the following: 1,5-disubstituted $<$ 1,8-disubstituted $<$ 1,4-disubstituted. This relationship between λ_{max} and the position of substitution is similar to that in the case of the diaminoanthraquinones.[25]

Of the 1,4,5,8-tetrasubstituted derivatives (Dyes 14–16), the maximum bathochromic shift is found in Dye 14, which yields a green-blue color. This pronounced bathochromic shift may be due to the presence of the arylamino group in the 4-position: the electron-donating power of this group is stronger than that of $-$OH or $-$NHCOR. When three substituents or more are attached to anthraquinone nu-

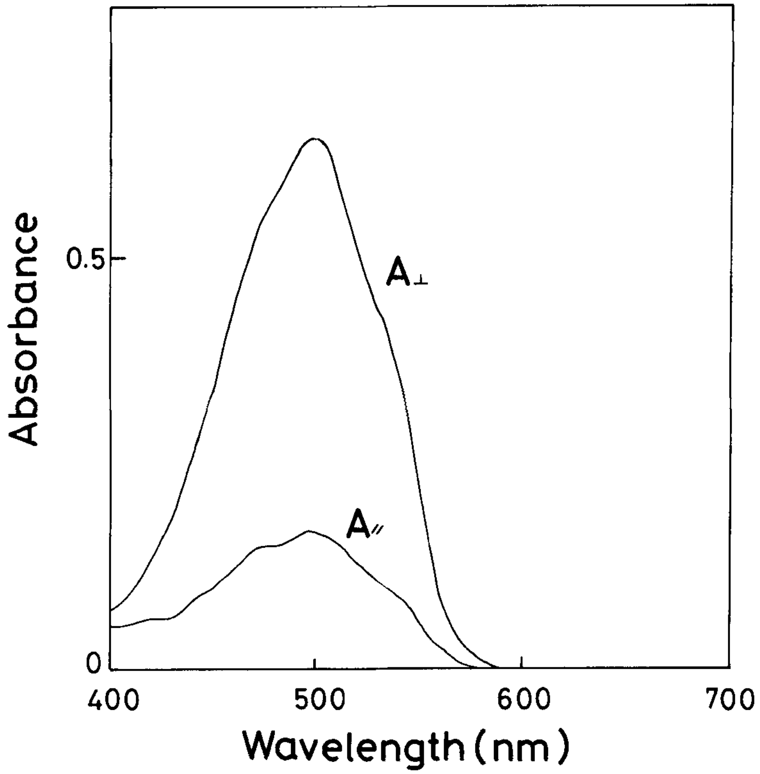


FIGURE 1 Dichroic absorption spectra for Dye 6 in ZLI-1132.

cleus, the relationship between λ_{max} and the dye structure is really complicated. It appears to be extremely difficult to find a simple rule regarding prediction of λ_{max}.

Some of the absorption spectra for the dyes in chloroform are shown in Figure 2. As can be seen from this figure, the band shape of the dyes reported here considerably varies with the dye structure. The visible absorption bands for Dyes 7 and 15 are characterized by a well-defined vibronic structure. In contrast, Dyes 3, 12 and 13 show rather structureless bands. The band shapes in ZLI-1132 resemble those in chloroform.

3-3. *Solubility*

The solubility of anthraquinone dyes containing an –NHCOR group is generally low. Some of the dyes examined here, however, have

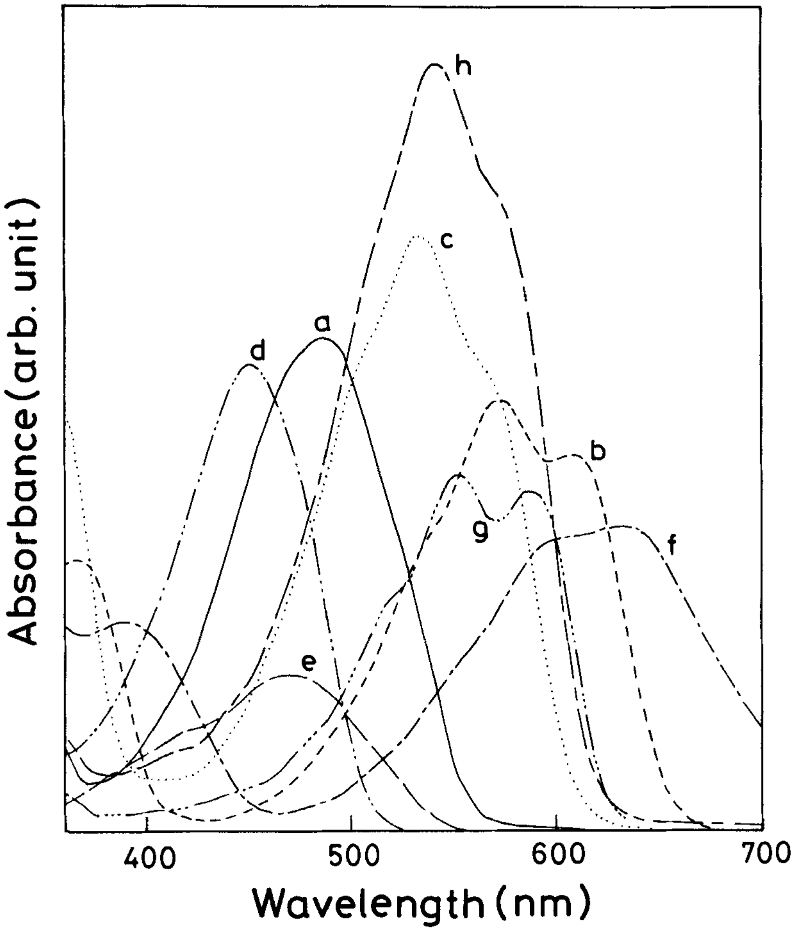


FIGURE 2 Absorption spectra in chloroform solutions. a: Dye 3, b: Dye 7, c: Dye 10, d: Dye 12, e: Dye 13, f: Dye 14, g: Dye 15, h: Dye 16.

been found to give relatively high solubility in ZLI-1132. In particular, the value for Dye 8 is greater than 2 wt%.

Further improvement in the solubility is required for practical application. We believe that this problem can be overcome by appropriate structural modification.

3-4. *Negative dichroism and molecular structure*

At the present stage, it is beyond the scope of this study to give a general account of the mechanism of negative dichroism in the anthraquinone dyes. However, only when the discussion is limited to the case of 1,4-bisarylamideanthraquinone, may it be possible to give a tentative explanation in a qualitative way as follows.

Assuming that the long axis of the dye molecule is uniformly oriented with an angle of θ around the director of the host liquid crystal and that the optical transition moment is uniformly oriented with an angle of α around the long axis of the dye molecule, the optical order parameter S can be expressed by the following equation:[16,26]

$$S = \frac{1}{2}(3\cos^2\alpha - 1) \cdot \frac{1}{2}(3\overline{\cos^2\theta} - 1) \tag{2}$$

where $\overline{\cos^2\theta}$ denotes the average value of $\cos^2\theta$. This equation is based on the assumption that the dye molecule is cylindrical. According to Equation (2), it follows that when α is over 54°44′, S takes negative values.

Unfortunately, the direction of the transition moment in the 1,4-bisarylamideanthraquinone is not known. Nevertheless, from a consideration of the molecular symmetry and the data on the 1,4-diaminoanthraquinone,[27] it is reasonable to assume that the transition moment is perpendicular to the C=O bond axis.

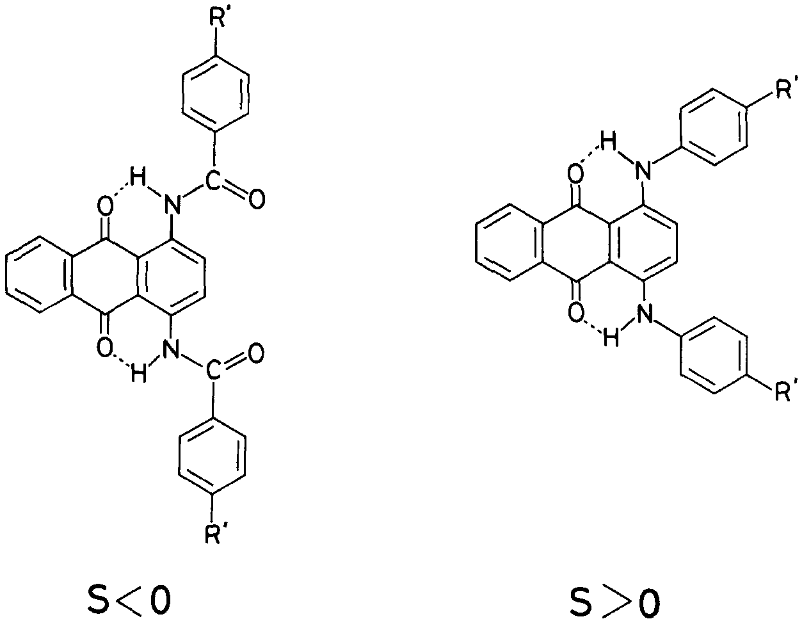
On the other hand, the 1,4-bisarylamideanthraquinone molecule is expected to exist in configuration as shown in Figure 3(a), owing to its intramolecular hydrogen bonding[25] and the planarity of the amide group.[28] The configuration of 1,4-bisarylaminoanthraquinone[17] is also shown in Figure 3(b) for the sake of comparison. Figure 3(a) suggests that the long axis of the 1,4-bisarylamideanthraquinone molecule prefers the direction parallel to the C=O bond axis.

Thus, the optical order parameter for 1,4-bisarylamideanthraquinone takes negative values, the α between the transition moment and the long axis of the molecule being 90°.

It is to be emphasized here that the above-mentioned discussion can be applied only to the case of 1,4-bisarylamideanthraquinone. It is questionable whether the above discussion is applicable to the remaining cases. Real dye molecules are not cylindrical but rather planar.[29] In order to further elucidate the exact mechanism of negative dichroism in the anthraquinone dyes, it may be necessary to consider the shape biaxiality of dye molecule.[30,31]

4. CONCLUSION

A number of α-substituted anthraquinones with negative dichroism have been prepared. From the systematic variation in structure, it



(a) 1,4-bisarylamideanthraquinone (b) 1,4-bisarylaminoanthraquinone

FIGURE 3 Molecular structures of 1,4-bisarylamideanthraquinone and 1,4-bisarylaminoanthraquinone. *R'* denotes a flexible terminal group.

has been found that an amide group −NHCOR plays a dominant role in producing negative dichroism. Further, the negative dichroism has been discussed in terms of the relation between the transition moment and the long axis of the molecule.

Acknowledgment

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