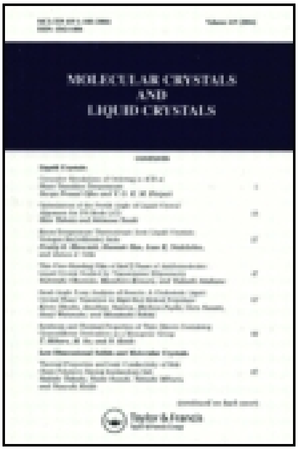

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Order Parameters of β-Substituted Anthraquinone Dyes II: 1,4-Diaminoanthraquinone Derivatives

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Order Parameters of β-Substituted Anthraquinone Dyes II: 1,4-Diaminoanthraquinone Derivatives

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A study is presented of the optical order parameters and spectroscopic properties of 1,4-diaminoanthraquinone derivatives containing various substituents in the 2-position in a nematic liquid crystalline mixture composed of cyanophenylcyclohexane derivatives. The results are discussed in terms of the effects of the dye structure on the order parameters. By introducing a *trans*-4′-alkylcyclohexyloxycarbonyl or aryloxycarbonyl group into the 2-position, blue dyes have been obtained which show high order parameters and solubilities.

I. INTRODUCTION

In recent years guest–host systems consisting of dichroic dyes and liquid crystals have found sophisticated applications such as to automotive dashboards,[1] multicolor liquid-crystal displays[2,3] and liquid-crystal shutters for electrophotographic printers.[4]

Anthraquinone dyes[5–10] have been the subject of intense study because of their excellent photostability and wide range of colors. However, more extensive experimental work is required in order to obtain information leading to the control of the order parameter, spectroscopic properties and solubility in a predicable manner by structural variation.

In the preceding paper,[11] we reported the optical order parameters and spectroscopic properties of 1-amino-4-hydroxyanthraquinone derivatives containing various substituents in the 2-position. In the present work, we have extended our studies to 1,4-diaminoanthraquinone derivatives. The effect of various substituents on the order parameter has been examined in detail, particularly that of a branched alkyl chain, a *trans*-4′-alkylcyclohexyl ring[11] and a bridging group such as —COO—, —COS—, —CONH— and —CON(CH_3)—. Sufficient attention has not as yet been paid to the effect of these substituents on the order parameter.

II. EXPERIMENTAL

The simplified structure of 1,4-diaminoanthraquinone derivatives examined in this study is shown in Figure 1. A typical reaction pathway used in the preparation of the dyes is illustrated in Scheme 1. Molecular structures of the products were confirmed by IR, NMR and other spectroscopic analyses. The melting points of the dyes were determined on a Perkin-Elmer DSC 7 differential scanning calorimeter. Unless mentioned otherwise, the nematic host used was a cyanophenylcyclohexane mixture ZLI-1132 (produced by E. Merck), which has a positive dielectric anisotropy. The cells used in the experiment consisted of two glass plates, with an inner 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, 25 and 50 μm.

The optical order parameter S of the dyes dissolved in the nematic liquid crystal was determined using plane-polarized light by the formula[12,13]:

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

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

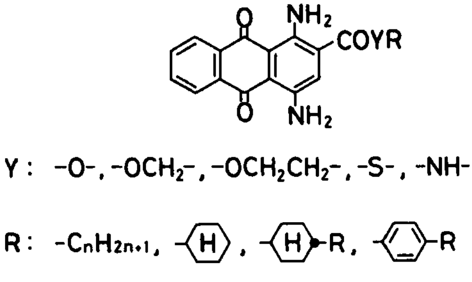
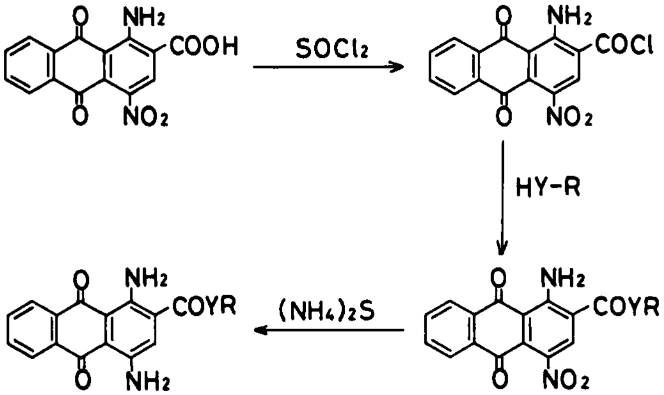


FIGURE 1 Simplified chemical structure of the 1,4-diaminoanthraquinone derivatives containing various substituents in the 2-position.



Scheme 1

at λ_{max} when the polarization is perpendicular to the alignment direction. The baseline was determined using cells containing only the nematic host liquid crystal. Optical absorption spectra were measured at 22°C using a Hitachi 340 spectrophotometer.

III. RESULTS AND DISCUSSION

3-1. Order parameter

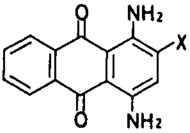
The optical order parameters for forty 1,4-diaminoanthraquinone derivatives in ZLI-1132 are summarized in Table I. Of the dyes shown in this table, dyes 19 and 39 have previously been reported by Basturk et al.[8]

Dyes 2–5 have an *n*-alkoxycarbonyl group in the 2-position of the anthraquinone nucleus. With the exception of dye 4, these dyes show somewhat higher order parameters compared with the parent compound, dye 1. The effect of the *n*-alkoxycarbonyl group on the order parameter is much more pronounced when the dyes are dissolved in a nematic host with negative dielectric anisotropy (*Nn* host). For instance, dye 3 exhibits an *S* value of 0.61 in EN-18, which is a typical commercially available *Nn* host (produced by Chisso Corp.). In contrast, dye 1, containing no substituents in the 2-position, has a much lower *S* (0.48) in the same host. This difference in *S* between dye 1 and dye 3 suggests that the introduction of an *n*-alkoxycarbonyl group into the 2-position gives a substantial increase in *S*.

In the series of dyes 2–5, the order parameter is almost independent of the length of the alkyl chain. Such insensitivity of *S* to the length of the terminal alkyl chain is also seen in three other series of the dyes, namely, dyes 9–12, dyes 14–20 and dyes 24–26. These results are consistent with experimental findings reported by Seki et al.[14] They examined the relation between the carbon number *n* of the terminal alkoxy or alkyl chain and *S* for some azo dyes. In these dyes, the saturation of the order parameter was observed in the region of $n \geq 2$ or 3.

TABLE I

Experimental data on 1,4-diaminoanthraquinone derivatives containing various substituents in the 2-position.



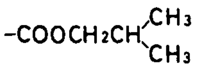
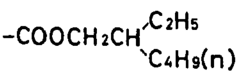
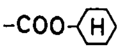
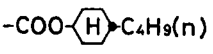
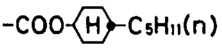
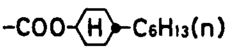
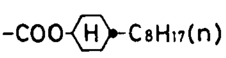
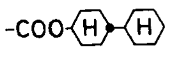
Dye no.	*X*	λ_{max}/nm (in ZLI-1132)	*S* (in ZLI-1132)	m.p./°C
1.	$-H$	518 $\underline{553}$ 595	0.68	———
2.	$-COOCH_3$	550 598 $\underline{638}$	0.71	234.3
3.	$-COOC_4H_9(n)$	550 598 $\underline{638}$	0.71	135.8
4.	$-COOC_8H_{17}(n)$	550 597 $\underline{638}$	0.68	113.9
5.	$-COOC_{18}H_{37}(n)$	550 598 $\underline{639}$	0.72	110.9
6.	 $-COOCH_2CH\begin{smallmatrix}CH_3\\CH_3\end{smallmatrix}$	550 598 $\underline{639}$	0.70	154.1
7.	 $-COOCH_2CH\begin{smallmatrix}C_2H_5\\C_4H_9(n)\end{smallmatrix}$	550 598 $\underline{639}$	0.67	103.1
8.		550 597 $\underline{637}$	0.71	162.2
9.		552 596 $\underline{638}$	0.76	146.6
10.		552 598 $\underline{638}$	0.77	151.4
11.		552 597 $\underline{638}$	0.76	137.2
12.		548 598 $\underline{638}$	0.78	137.6
13.		550 597 $\underline{637}$	0.76	———

TABLE I (*continued*)

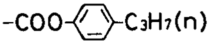
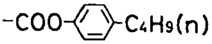
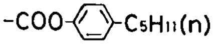
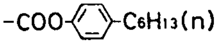
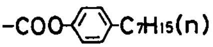
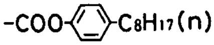
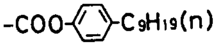
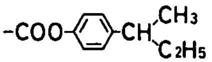
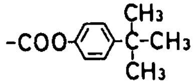
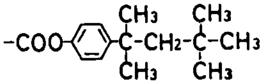
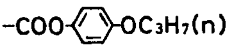
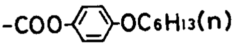
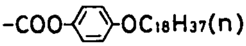
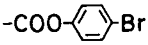
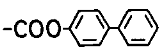
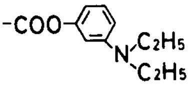
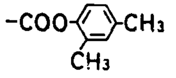
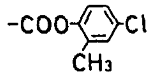
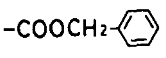
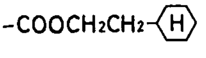
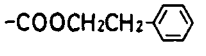
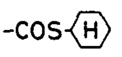
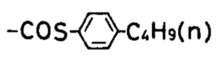
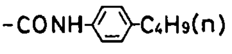
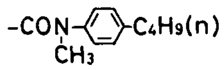
Dye no.	*X*	λ_{max}/nm (in ZLI-1132)	*S* (in ZLI-1132)	m.p./°C
14.		556 604 643	0.76	172.5
15.		556 605 643	0.77	115.1
16.		556 604 642	0.78	178.2
17.		556 604 642	0.77	158.8
18.		556 604 642	0.77	——
19.		556 606 643	0.77	102.5
20.		552 604 642	0.76	200.9
21.		556 606 643	0.77	197.7
22.		554 606 642	0.77	240.6
23.		554 602 642	0.74	260.7
24.		556 605 643	0.78	210.9
25.		556 605 643	0.78	176.8
26.		554 604 642	0.77	150.1
27.		556 608 644	0.76	241.0
28.		556 606 643	0.78	248.4
29.		556 602 642	0.77	163.1

TABLE I (*continued*)

Dye no.	X	λ_{max}/nm (in ZLI-1132)	S (in ZLI-1132)	m.p./°C
30.		556 604 642	0.76	188.8
31.		556 608 644	0.77	———
32.		550 600 641	0.67	172.2
33.		550 599 639	0.72	———
34.		550 599 639	0.72	193.6
35.	$-COSC_8H_{17}(n)$	554 610 645	0.74	148.6
36.	$-COSC_{18}H_{37}(n)$	556 614 646	0.74	119.3
37.		556 614 644	0.76	202.5
38.		560 614 644	0.71	186.5
39.		586 611	0.72	205.7
40.		520 564 600	0.57	162.0

So far there have only been a few reports[11,15] about the effect of branching in the terminal alkyl chain on *S*. A comparison of the results for dyes 3, 6, and dyes 4, 7 shows that the chain branching brings about little variation in *S*. Similar results are observed for dyes 21–23, in which a branched alkyl group is attached to the phenylene ring.

A very interesting substituent effect is observed for dyes 9–13. Although these dyes have no rigid aromatic substituents in the 2-position, they exhibit high order parameters (0.76–0.78) comparable to those of their aromatic analogues (dyes 14–20). The remarkable ordering of dyes 9–13 can be attributed to the presence of a *trans*-4′-alkylcyclohexyl group. It must be emphasized here that there are distinct differences in *S* between these dyes and dye 8: replacement of a *trans*-4′-alkylcyclohexyl group by an unsubstituted cyclohexyl one causes a significant decrease in *S*.

The introduction of an aryloxycarbonyl group into the 2-position again results in high order parameters (dyes 14–31). It is obvious that the high *S* values of these dyes are due to the elongation of the rigid portion of the dye molecules by interposing a phenylene ring. In general, the 2-aryloxycarbonyl derivatives show little sensitivity to the nature and the position of substituents on the phenoxycarbonyl moiety. A particularly noteworthy result is found in dye 28. In view of its molecular structure, this dye would be expected to give a much higher *S* value than the other dyes of the 2-aryloxycarbonyl series. But, as can be seen from Table I, the differences in *S* between dye 28 and the other members of this series are quite small. This finding is in contrast to the behavior of α-substituted anthraquinones.[10]

Next, we consider the manner in which *S* is influenced by variation of the bridging groups.

The comparative effects of —$COOCH_2$— and —$COOCH_2CH_2$— bridging groups on *S* can be judged from the data for dyes 32–34. The results show that a considerable lowering of *S* occurs as a result of using the —$COOCH_2$— group (dye 32). On the other hand, dyes 33 and 34, containing the —$COOCH_2CH_2$— group, exhibit moderately high *S* values.

Dyes 35–37 have an alkylthiocarbonyl group. A comparison of the *S* values for the thioesters (dyes 35–37) with those for the corresponding oxy-esters (dyes 4, 5 and 8) suggests that the —COS— group is more effective in increasing the order parameter than the —COO— group. A similar effect of a thioester linkage has already been found for perylene dyes.[15] A comparison between dyes 35–37 and dye 38, however, shows the surprising result that dye 38 has a lower *S* value than dyes 35–37. This situation is contrary to what is generally expected and to what is experimentally observed in the cases of the bridging groups such as —O—[11] and —COO—.[15] At present, we cannot offer any satisfactory explanation for this unexpected result.

When a —CONH— group is used as a bridging group (dye 39), the order parameter is appreciably lower than that of the corresponding —COO— analogue, dye 15. This result is consistent with that reported by Basturk et al.[8] Replacement of —CONH— by —$CON(CH_3)$— results in a drastic decrease in *S* (dye 40). This lowering in *S* may be attributed to the reduction of planarity of the dye skeleton due to the twisting of the —$N(CH_3)$— group induced by the steric repulsion between the —$N(CH_3)$— group and the neighboring bulky residues.

3-2. Colors and the absorption spectra

The maximum absorption wavelengths (λ_{max}) for the 1,4-diaminoanthraquinone derivatives in ZLI-1132 are shown in Table I. In general, the λ_{max} values in ZLI-1132 are displaced to longer wavelengths by 10–15 nm relative to those in less polar chloroform.

From a survey of the results, it is obvious that the bathochromic effect of 2-substituents increases in the order —$CON(CH_3)$—<—CONH—< —COO—<—COS—. This fact suggests that the λ_{max} of 1,4-diaminoanthraquinone

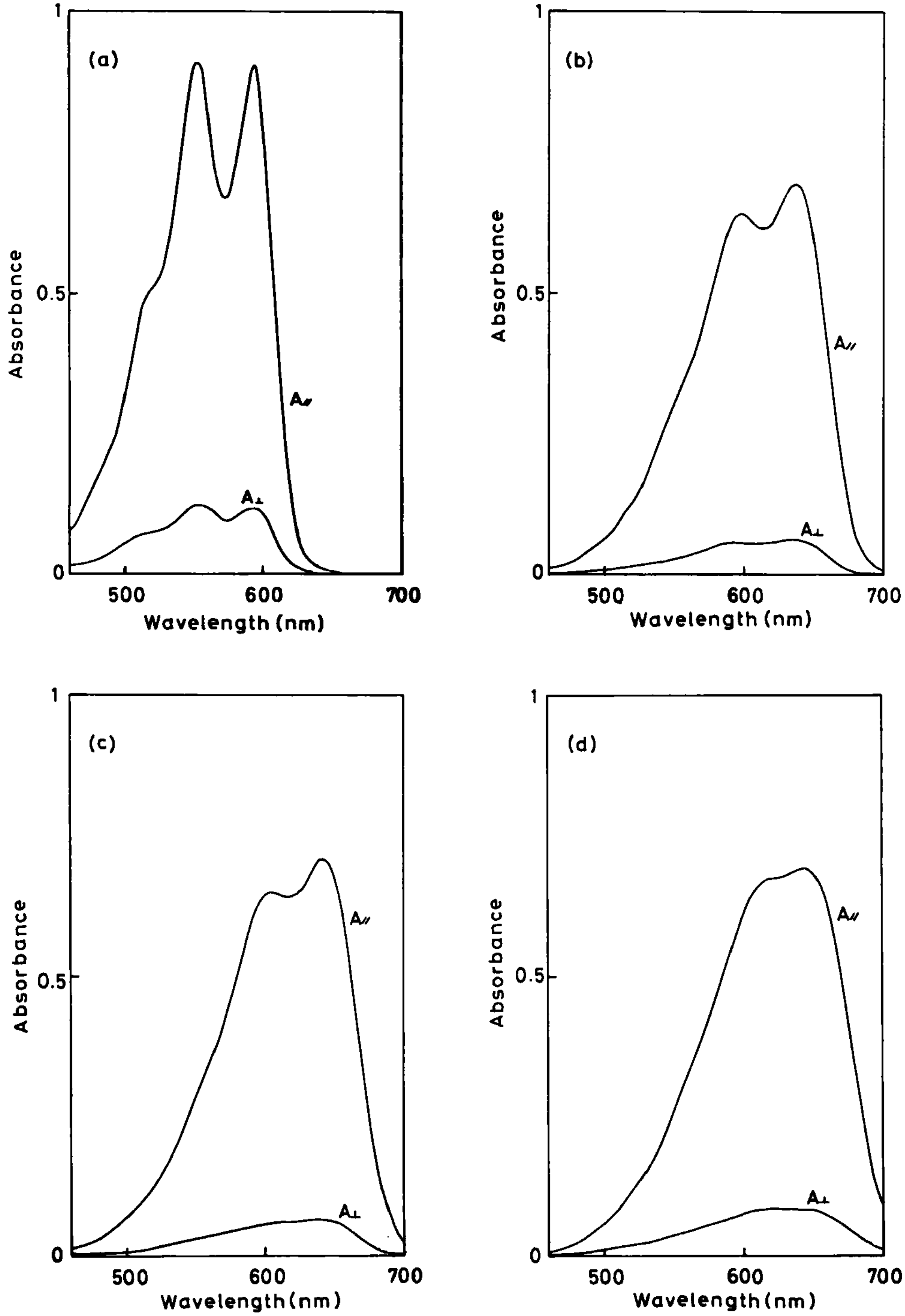


FIGURE 2 Typical dichroic spectra for the dyes in ZLI-1132. (a) Dye 1, (b) Dye 10, (c) Dye 18, (d) Dye 38, (e) Dye 39 and (f) Dye 40.

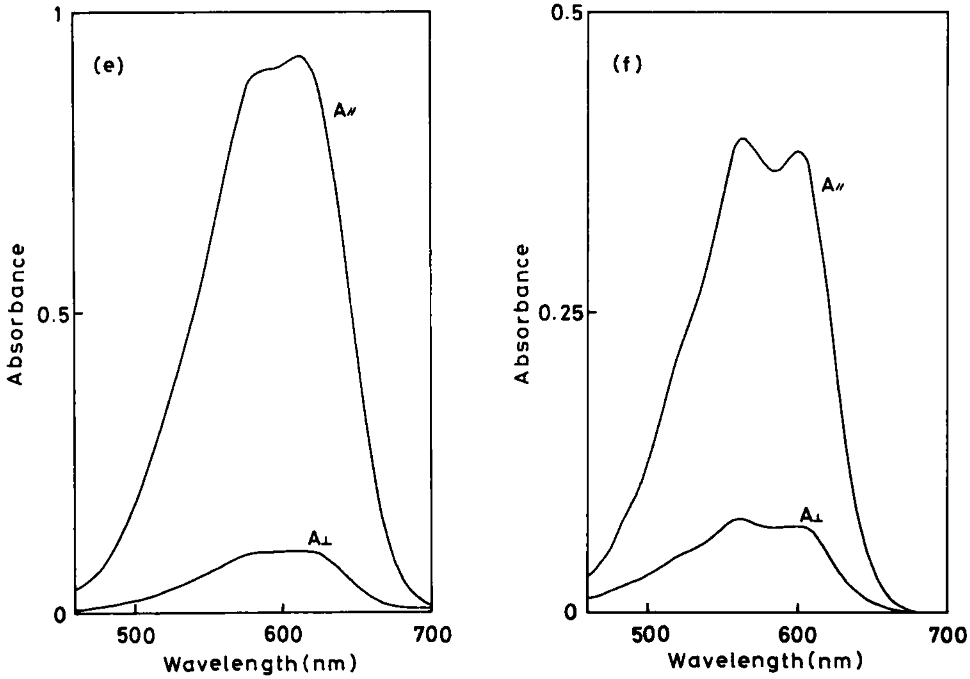


FIGURE 2 *continued*

derivatives increases as the electron-withdrawing ability of the 2-substituents increases.

When the —COO— or —COS— is attached to the 2-position, the dyes give deep-blue solutions in ZLI-1132. In contrast, dyes 39 and 40 are violet-blue and violet in color, respectively.

Typical dichroic spectra for the dyes in ZLI-1132 are shown in Figure 2(a)–(f). The visible absorption band for the anthraquinone derivatives reported here shows a vibronic structure consisting of two main peaks and a weak shoulder. The vibronic structures observed in dyes 10, 18, 38, 39 and 40 are less clear than that of the parent compound, dye 1. This fact suggests that the introduction of the electron-withdrawing group into the 2-position of 1,4-diaminoanthraquinone causes blurring of the vibronic structures.

3-3. Solubility

A sufficient solubility of dichroic dyes is indispensable for their practical applications to liquid-crystal devices.[16,17] Many of the dyes reported here give notable solubility in ZLI-1132. For instance, dyes 3, 4, 6–12, 14, 15, 17–21, 33 and 38 exhibit a solubility over 3 wt% at room temperature. In particular, the values for dyes 12, 14, 15, 17 and 20 exceed 5 wt%.

The solubility is affected by the terminal group of dye molecules. In general, *n*-alkylphenoxycarbonyl derivatives (dyes 14–20) are more soluble than their *n*-alkoxy analogues (dyes 24–26). Further, it has been found that branching in the alkyl group on the phenoxycarbonyl moiety causes a marked change in the solubility: the solubilities for dyes 21, 22 and 23 are considerably lower than those for the corresponding *n*-alkyl derivatives (dyes 15 and 19).

IV. CONCLUSION

The effects of molecular structure on the order parameter, spectroscopic properties and solubility have been examined for a number of 1,4-diaminoanthraquinone derivatives containing various substituents in the 2-position. The main conclusions to be drawn from the results are as follows. First, the introduction of a *trans*-4'-alkylcyclohexyl group into the dye system can lead to a significant increase in the order parameter. Second, the dye order parameter shows little sensitivity to the length of the terminal alkyl chain. Third, branching in the terminal alkyl chain brings about little variation in the order parameter, while it causes a marked change in the solubility. Fourth, the 1,4-diaminoanthraquinone exhibits bathochromic displacement in absorption when the hydrogen in the 2-position is replaced by the electron-withdrawing groups such as —COOR, —COSR, —CONHR and —CON(CH_3)R.

The 1,4-diaminoanthraquinone derivatives with the —COOR or —COSR group in the 2-position give deep-blue solutions in a nematic host. Some of these dyes have been found to have high order parameters and solubility to allow their practical use[18] in the various fields of liquid-crystal devices.

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