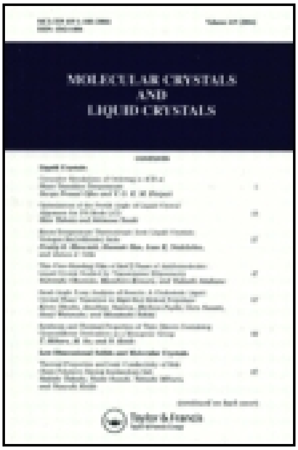

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Anthraquinone-Based Dichroic Dyes for Achromatic Black Guest-host Liquid Crystal Display

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Anthraquinone-Based Dichroic Dyes for Achromatic Black Guest-host Liquid Crystal Display†

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The properties of three different classes of 2, 3-substituted 1, 4-diaminoanthraquinone dichroic greenish blue dyes with a maximum absorption peak in the long wavelength region from 660 nm up to 760 nm, which are useful as a guest dye in an achromatic black guest-host liquid crystal display, have been investigated.

1, 4-Diaminoanthraquinone-(N-substituted-3-imino)-2, 3-dicarboximidines (I) and 1, 4-diaminoanthraquinone-(N-substituted-3-thioxo)-2, 3-dicarboximidines (II) exhibit higher dichroic ratios and higher solubilities and moreover the latter class (II) shows a maximum absorption peak at a much longer wavelength, compared to 1, 4-diaminoanthraquinone-(N-substituted)-2, 3-dicarboximides (III).

The order of various properties in the three classes of dyes are as follows: II > I > III for dichroic ratio, II > I > III for solubility, and II > III > I for maximum absorption wavelength, respectively.

1. INTRODUCTION

Recently a great interest is taken in an achromatic black guest-host liquid crystal display (LCD), since it is very useful as a light valve for use in multicolor and full-color LCDs with color filters and also is expected as an attractive candidate to overcome the serious problems inherent in a conventional twisted nematic LCD, such as a dull appearance and a narrow viewing-angle.

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To the practically applicable realization of such an achromatic black guest-host LCD, the plural number of variously colored dichroic dyes are essentially prerequisite, which can absorb as a whole substantially all of the visible light in the wavelength range from 380 nm to 780 nm and moreover have the high dichroic ratio and solubility in a liquid crystal, together with the reasonable stability.

A variety of dichroic dyes for use in guest-host LCDs have been reported during the past years.[1-5] Nevertheless, almost no greenish blue dyes are available, which can effectively absorb the light in the long wavelength region over ca. 660 nm and at the same time fulfill the other requirements mentioned above. The absorption of a dichroic dye in such a long wavelength range is essential to prevent a reddish hue and realize an achromatic black guest-host LCD.

In this paper, the development of three difference classes of 2,3-substituted 1,4-diaminoanthraquinone dichroic dyes having an absorption peak in the long wavelength region from 660 nm up to 760 nm is described and their various properties as a guest dye in a liquid crystal are studied.

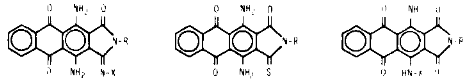
2. EXPERIMENTAL

The greenish blue dichroic dyes investigated[6] were three different classes of 2,3-substituted 1,4-diaminoanthraquinones and the classes had the general chemical formulas shown in Figure 1. The class (I) included 1,4-diaminoanthraquinone-(N-substituted-3-imino)-2,3-dicarboximidine dyes, wherein X was a hydrogen or alkoxyalkyl radical† and R was either of an alkyl or alkoxyalkyl substituent. The class (II) comprised 1,4-diaminoanthraquinone-(N-substituted-3-thioxo)-2,3-dicarboximidine dyes, having an alkoxyalkyl radical as the substituent R. The class (III) contained N-substituted dyes of 1,4-diaminoanthraquinone-2,3-dicarboximide, wherein X was a hydrogen or methyl radical‡ and the substituent R was selected from the group consisting of alkyl, straight or branched-chain alkoxyalkyl, dialkylaminoalkyl radicals and alkyl radicals with heterocyclic rings.

All dyes were recrystallized and column-chromatographed on silica gel using xylene and/or ethylacetate as an eluent. As for some dyes used to examine a purification-grade effect on electrical resistivity in

†Hereinafter, the dyes of class (I) with X = alkoxyalkyl are often called as the class (IV).

‡Hereinafter, the dyes of class (III) with X = methyl are often called as the class (V).



(I) (II) (III)

FIGURE 1 Anthraquinone-based greenish blue dichroic dyes with a long-wavelength maximum absorption.

dyed liquid crystals, the foregoing chromatographic purification was repeated by one or two more times.

The properties of a guest dye such as maximum absorption wavelength λ_m, dichroic ratio $D = A_{\parallel}/A_{\perp}$ (order parameter $\bar{S}$†), solubility S and absorbance $A_{\parallel}$ were measured in a host liquid crystal of a phenylcyclohexane class ZLI UP-1565 supplied by E. Merck. ZLI UP-1565 was the LC mixture ultrapurified so as to show the higher resistivity compared with conventional ZLI-1565; the value of resistivity was 1.6×10^{11} Ω cm, and the clearing temperature and dielectric anisotropy were 85°C and +6.0, respectively.

The concentration of a guest dye in the host liquid crystal was 0.2% wt., if otherwise stated and the nominal thickness of a dyed liquid crystal layer used in the measurements was 9 μm. The notation $A_{\parallel}$ and $A_{\perp}$ in the above denote the absorbance measured, respectively, parallel and perpendicular to the director of a homogeneously-aligned dyed liquid crystal layer at 25°C, by using a polarized light. Practically, the values of $A_{\parallel}$ and $A_{\perp}$ were measured so as not to involve the absorption of liquid crystal itself.

The solubility was determined by observing a vial filled with a 0.2% wt. dyed liquid crystal after keeping it at −10°C for 24 hrs. The influence of dye addition on the resistivity of a host liquid crystal was examined by measuring the current density of a 0.2% wt. dyed liquid crystal layer at an applied voltage of 5 V.

3. RESULTS AND DISCUSSION

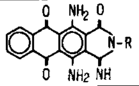
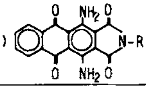
3.1. 1,4-Diaminoanthraquinone-(N-substituted-3-imino)-2,3-dicarboximidine and 1,4-diaminoanthraquinone-(N-substituted)-2,3-dicarboximide dyes

Table I gives the properties of 1,4-diaminoanthraquinone-(N-substituted-3-imino)-2,3-dicarboximidines (hereinafter, abbreviated as

†$\bar{S} = (D - 1)/(D + 2)$, wherein the absorbing transition moment is assumed to be parallel to the long axis of a dye molecule.

TABLE I

Properties comparison of the antraquinone-based dichroic dye classes of iminodicarboximidine (I) and dicarboximide (III)

Dye series	(I) 					(III) 				
Substituent R	λ_m (nm)	D ($\bar{S}$)	$A_{\parallel}$ (0.2%wt)	S (-10°C)	m.p. (°C)	λ_m (nm)	D ($\bar{S}$)	$A_{\parallel}$ (0.2%wt)	S (-10°C)	m.p. (°C)
$-C_4H_9$	670 (667)	6.1 (0.63)	0.10	0.2%wt	225~227	680 (675)	5.6 (0.61)	0.10	~0.2%wt	203~208
$-C_2H_4OC_4H_9$	669 (666)	5.2 (0.58)	0.14	0.2%wt	144~147	682 (677)	5.1 (0.58)	0.14	~0.2%wt	169~170
$-C_2H_4OC_6H_{13}$	674 (666)	5.4 (0.60)	0.15	0.2%wt	130~131	682 (674)	4.7 (0.55)	0.14	0.2%wt	162~164
$-C_3H_6OC_8H_{17}$	670 (667)	6.1 (0.63)	0.13	0.2%wt	103~108	680 (676)	5.4 (0.60)	0.12	0.2%wt	117~118
$-C_3H_6OC_9H_{19}$	670 (666)	6.1 (0.63)	0.12	0.2%wt	114~117	682 (676)	4.6 (0.55)	0.11	0.2%wt	134~135
$-(C_2H_4O)_3C_2H_5$	671 (665)	6.1 (0.63)	0.15	0.2%wt	85~87	682 (677)	4.2 (0.52)	0.14	<0.2%wt	125~127

iminodicarboximidines) and their corresponding 1,4-diamino-anthraquinone-(N-substituted)-2,3-dicarboximides having the same substituents *R* (hereinafter, abbreviated as dicarboximides), as a guest dye, using the host liquid crystal ZLI UP-1565. The values of λ_m in parentheses are those measured in xylene. The both classes of dyes show the maximum absorption in the long wavelength region above 660 nm; this is very useful and substantially needed to realize an achromatic black guest-host liquid crystal mixture. The wavelength of maximum absorption λ_m is approximately constant at 670 nm for the imidodicarboximidines and at 680 nm for the dicarboximides, being almost independently of their substituents.

As for the dichroic ratio *D* (consequently, order parameters $\bar{S}$), there seems also no distinct substituent dependence in the both classes of dyes but the values of $D(\bar{S})$ for the iminodicarboximidines are apparently higher ($D = 6.1 \sim 5.2$), compared with those for the dicarboximides ($D = 5.6 \sim 4.2$). The absorbance $A_{\parallel}$ measured in a 0.2% wt. dyed liquid crystal layer with the 9 μm thickness is nearly the same for each pair of the corresponding both classes of dyes having the same substituents.

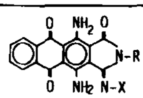
The big difference in the properties of the both classes of dyes may be their solubility in a host liquid crystal and furthermore the great substituent dependence is found in their solubility. The dicarboximides generally have the considerably poor solubility; this is one of the reasons, from a practical viewpoint, which compelled us to develop such other classes of dyes as the iminodicarboximidines in this section and thioxodicarboximidines in the next section. The solubility of the dicarboximides, except those incorporating a long chain alkoxyalkyl substituent *R*, is lower or much lower than 0.2% wt. in the phenylcyclohexane host liquid crystal ZLI UP-1565 at $-10°C$, whereas the iminodicarboximidines except only the one with a substituted butyl radical exhibit the solubility higher or much higher than 0.2% wt. in the same host at the same temperature.

The above results indicate that the incorporation of a (3-imino)-2, 3-dicarboximidino moiety, instead of a 2, 3-dicarboximido moiety, as a 2, 3-substituent of 1, 4-diaminoanthraquinone increases effectively the solubility as well as the dichroic ratio. The increased solubility of the iminodicarboximidine dyes may be explained by a structural asymmetry of a (3-imino)-2, 3-dicarboximidino moiety, since the asymmetric moiety possibly hinders a crystallization of the dyes from a host liquid crystal. However, it is presently not clear how the asymmetric moiety improves the dichroic ratio. The difference of a substituent *R*, attached to the nitrogen in the both classes of dyes, has no definite effect on all of their properties but their solubility. The solubility can be apparently improved by incorporating an alkoxyalkyl radical as the substituent and moreover by elongating an alkyl chain length of the substituent.

TABLE II

Properties comparison of the anthraquinone-based dichroic dye classes of iminodicarboximidines with *X* = hydrogen (I) and alkoxyalkyl (IV)

Dye series: (IV) & (I)



Substituent X	Substituent R	λm (nm)	D ($\bar{S}$)	$A_{\parallel}$ (0.2%wt)	S (-10°C)	m.p. (°C)
$-C_3H_6OC_6H_{13}$	$-C_2H_4OC_6H_{13}$	672 (666)	6.1 (0.63)	0.12	>0.2%wt	85 ~ 86
-H		674 (666)	5.4 (0.60)	0.15	>0.2%wt	130 ~ 131
$-C_3H_6OC_8H_{17}$	$-C_3H_6OC_8H_{17}$	671 (666)	5.6 (0.61)	0.12	>0.2%wt	54 ~ 59
-H		670 (667)	6.1 (0.63)	0.13	>0.2%wt	103 ~ 108
$-C_3H_6OC_8H_{17}$	$-C_3H_6OC_9H_{19}$	671 (667)	6.0 (0.63)	0.11	>0.2%wt	75 ~ 77
-H		670 (666)	6.1 (0.63)	0.12	>0.2%wt	114 ~ 117

These summarized tendencies are almost true for a host liquid crystal of a biphenyl class E-8 (BDH chemicals), although the dichroic ratio and solubility in E-8 are generally higher than in ZLI UP-1565.

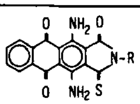
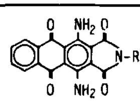
Table II compares the properties of some of the iminodicarboximidine dyes and their corresponding dyes incorporating a substituted alkoxyalkyl radical in place of the imino hydrogen. The incorporation of a significantly bulky alkoxyalkyl pendant radical replacing a hydrogen shows virtually almost no effect on the properties of the parent iminodicarboximidines. In view of the difference in molecular shape, this is rather surprising but it is not clear what this is due to.

3.2. 1,4-Diaminoanthraquinone-(N-substituted-3-thioxo)-2,3-dicarboximidine and 1,4-diaminoanthraquinone-(N-substituted)-2,3-dicarboximide dyes

Table III compares the properties of 1,4-diaminoanthraquinone -(N-substituted-3-thioxo)-2,3-dicarboximidines (hereinafter, abbreviated as thioxodicarboximidines) and their corresponding 1,4-diaminoanthraquinone-(*N*-substituted)-2,3-dicarboximides (hereinafter abbreviated as dicarboximides) with the same substituents *R*, as a guest dye, using the host liquid crystal ZLI UP-1565. The maximum absorption wavelength λ_m is approximately at 760 nm for the thioxodicarboximidines. When compared with the values λ_m of ca. 680 nm in the dicarboximides, these λ_m values are found to be shifted towards the significantly longer wavelength region.

TABLE III

Properties comparison of the anthraquinone-based dichroic dye classes of thioxodicarboximidine (II) and dicarboximide (III)

Dye series	(II) 					(III) 				
Substituent R	λ_m (nm)	D ($\bar{S}$)	$A_\parallel$ (0.2%wt)	S (-10°C)	m.p. (°C)	λ_m (nm)	D ($\bar{S}$)	$A_\parallel$ (0.2%wt)	S (-10°C)	m.p. (°C)
$-C_2H_4OC_6H_{13}$	763 (761)	8.0 (0.70)	0.18	~0.2%wt	126–127	682 (674)	4.7 (0.55)	0.14	0.2%wt	162–164
$-C_3H_6OC_8H_{17}$	762 (759)	8.1 (0.70)	0.15	~0.2%wt	99–100	680 (676)	5.4 (0.60)	0.12	0.2%wt	117–118
$-C_3H_6OC_9H_{19}$	761 (758)	7.1 (0.67)	0.13	~0.2%wt	110–111	682 (676)	4.6 (0.55)	0.11	0.2%wt	134–135

As for the dichroic ratio D (consequently, oder parameter $\bar{S}$) as well as the solubility S, the thioxodicarboximidine dyes show highly improved properties, compared with not only the dicarboximide but also iminodicarboximidine dyes (see Table I). In comparison with the dicarboximides, the D values and also absorption $A_{\parallel}$ in the thioxodicarboximidines are improved by 50–60% and 20–30%, respectively. Their solubilities in the host liquid crystal are extremely in excess of 0.2% wt. at $-10°C$. These improvements do not seem to be greatly influenced by the difference of the alkoxyalkyl substituents R.

The above-mentioned behaviors are qualitatively observed also in case of the biphenyl host liquid crystal E-8.

From these comparative studies, it may be concluded that the replacement of one of two oxygens in the dicarboximido moiety of 1,4-diaminoanthraquinone-(N-alkoxyalkyl)-2,3-dicarboximides by a sulfur results in the significantly improved and practically favorable properties of the corresponding thioxodicarboximidines. In this case also, like the case of iminodicarboximidines described in the section 3.1, the presence of a structural asymmetry of a (3-thioxo)-2,3-dicarboximidino moiety may induce the highly improved solubility.

3.3. Various *N*-substituted dyes of 1,4-diaminoanthraquinone-2, 3-dicarboximide

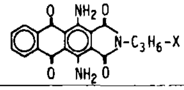
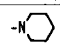
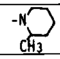
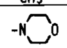
Table IV presents the properties of 1,4-diaminoanthraquinone-2,3-dicarboximides (hereinafter, abbreviated as dicarboximides) with various propyl substituents ($-C_3H_6-X$) bonded to the imido nitrogen, as a guest dye, using the host liquid crystal ZLI UP-1565, and illustrates the effects of different X radicals attached to the 3-position of the propyl substituents. The wavelength of maximum absorption λ_m is approximately constant at 680 nm for all the dyes, almost independently of the X radicals.

As for the dichroic ratio D (consequently, order parameter $\bar{S}$) and also the solubility S, the X radical dependence is distinctly observed, although both of the properties in most of the dyes are not excellent. The dyes with X = branched and heterocyclic radicals have the lower D values of 3.1–4.8, compared with the dyes having X = straight alkyl and alkoxyalkyl radical showing the D values of 5.4–6.4.

The solubility of the dicarboximides in the host liquid crystal is considerably low in general, as explained in the section 3.1. Especially, the dyes with X = alkyl and heterocyclic (except a pipecolino) radicals show an extremely poor solubility. However, the results suggest that the solubility may be somewhat effectively improved by

TABLE IV

Properties of the anthraquinone-based dichroic dye class of dicarboximide (III) with various *X* substituent

Dye series	(III) 				
Substituent X	λ_m (nm)	D ($\bar{S}$)	$A_\parallel$ (0.2%wt)	S (-10°C)	m.p. (°C)
$-CH_3$	680 (675)	5.6 (0.61)	0.10	~0.2%wt	203 ~ 208
$-OC_8H_{17}$	680 (676)	5.4 (0.60)	0.12	~0.2%wt	117 ~ 118
$-OCH_2CH<(CH_3)_2$	680 (676)	3.9 (0.49)	0.12	~0.2%wt	191 ~ 192
$-OC_2H_4OC_4H_9$	682 (676)	6.4 (0.64)	0.13	~0.2%wt	157 ~ 160
$-N<(C_4H_9)_2$	682 (677)	3.7 (0.47)	0.12	~0.2%wt	108 ~ 109
	680 (676)	4.8 (0.56)	0.10	~0.2%wt	223 ~ 226
	682 (676)	4.7 (0.55)	0.15	~0.2%wt	196 ~ 200
	680 (676)	3.1 (0.41)	0.05	~0.2%wt	235 ~ 238

incorporating some alkylamino and alkoxyalkyl groups as an *X* radical.

The absorption $A_\parallel$ observed in a 0.2% wt. dyed liquid crystal layer seems too low for the dyes with *X* = alkyl and heterocyclic (except a pipecolino) radicals, compared with the $A_\parallel$ values for the other dyes of the same class. This may be due to their poor solubilities, lower than 0.2% wt., even at 25°C.

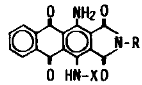
Table V shows the effect of a methyl radical replacing one of the aminohydrogens in an anthraquinone nucleus of the dicarboximide dyes. The presence of the methyl radical somewhat red-shifts the maximum absorption peak λ_m, and definitely increases the width of the absorption peak, i.e., $\lambda_{1/2}$, by more than 30% (see Figure 1), compared with the parent dicarboximide dyes. The latter phenomenon has never been observed in both cases of the imido- and thioxodicarboximidines themselves described in the sections 3.1 and 3.2.

The dichroic ratio *D* as well as the solubility *S* is also favorably influenced by incorporating the methyl radical, whereas the absorption $A_\parallel$ does not seem to be definitely influenced by it.

The above-mentioned behaviors concerning the various dicarboximide dyes are qualitatively true also in case of the biphenyl host liquid crystal E-8.

TABLE V

Properties comparison of the anthraquinone-based dichroic dye classes of dicarboximides with X = hydrogen (III) and methyl (V)

Dye series	(V) & (III) 					
Substituent X	Substituent R	λ_m (nm)	D ($\bar{S}$)	A_u (0.2%wt)	S (-10°C)	m.p. (°C)
$-CH_3$	$-C_3H_6OC_9H_{19}$	686 (682)	5.5 (0.60)	0.10	0.2%wt	93 94
-H		682 (676)	4.6 (0.55)	0.11	0.2%wt	134 135
$-CH_3$	$-C_3H_6OC_{12\ 13}H_{25\ 27}$	686 (682)	5.2 (0.58)	0.09	0.2%wt	77 93
-H		682 (677)	4.3 (0.52)	0.10	0.2%wt	153 155

Applying some of the above-described 2,3-substituted 4-diaminoanthraquinone dichroic dyes of class (I) and class (II), an achromatic black guest-host liquid crystal mixture has been successfully formulated. Figure 2 shows a multicolor liquid crystal display car dashboard[7] employing the achromatic black liquid crystal mixture.

FIGURE 2 Multicolor liquid crystal display car dashboard.

The liquid crystal car dashboard is based on a combination of a Heilmeier guest-host mode and color filters with a back illumination. It displays four different colors (blue, green, red, yellow), depending on the function of each meter and each signal clustered in it. Its display performances are such as a contrast ratio of more than 20:1, a viewing cone of 75°, response times of 15 msec (on) and 30 msec (off) at 25°C and an operating temperature range of −30°C to +85°C.

4. CONCLUSIONS

The three different classes of 2,3-substituted 1,4-diamino-anthraquinone dichroic greenish blue dyes have been developed and their properties as a guest dye in a host liquid crystal have been studied.

1,4-Diaminoanthraquinone-(*N*-substituted-3-imino)-2,3-dicarboximidines (I) and 1,4-diaminoanthraquinone-(*N*-substituted-3-thioxo)-2,3-dicarboximidines (II) exhibit definitely or significantly higher dichroic ratios (consequently, higher order parameters) and

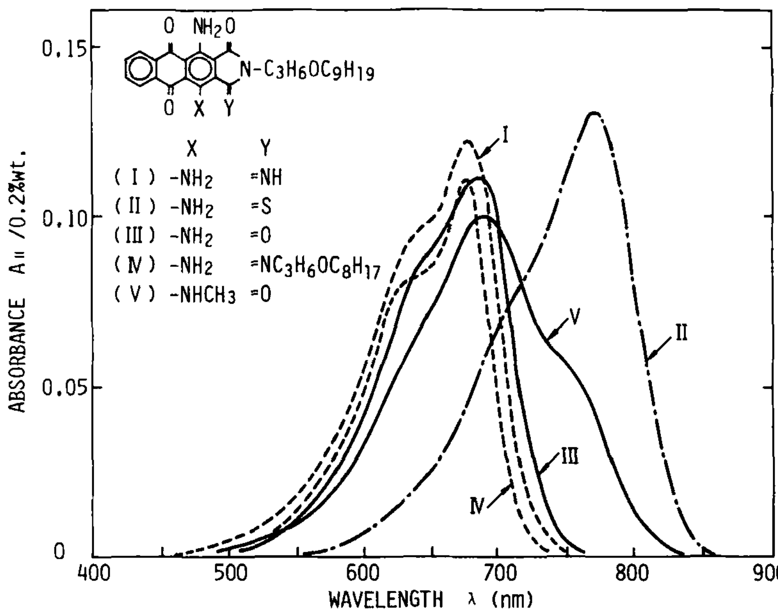


FIGURE 3 Absorption spectra $A_{\parallel}$ of the various anthraquinone-based dichroic dye classes in the host LC for light polarized parallel to the director.

higher solubilities, compared with 1,4-diaminoanthraquinone-(*N*-substituted)-2,3-dicarboximides (III). The high solubilities in dye classes (I) and (II) may be explained by the presence of a structurally asymmetric dicarboximidino moiety incorporated in the 2,3-position of the antraquinone nucleus, whereas it is not clear how the asymmetric moiety induces the high dichroic ratios.

The representative parallelly-poralized absorption spectra $A_{\parallel}$ of the various dye classes in the host liquid crystal (ZLI UP-1565), are summarized in Figure 3, where the classes (IV) and (V) are the modified ones corresponding to the classes (I) and (III), respectively. The maximum absorption peaks of all the dye classes exist in the long wavelength region from 660 nm up to 760 nm. This long wavelength absorption is very useful and has been eagerly sought after to realize an achromatic black guest-host liquid crystal mixture.

In summary, the order of various properties observed in the three classes of dyes are as follows: II > I > III for dichroic ratio, II > I > III for solubility and II > III > I for maximum absorption wavelength, respectively.

Acknowledgements

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