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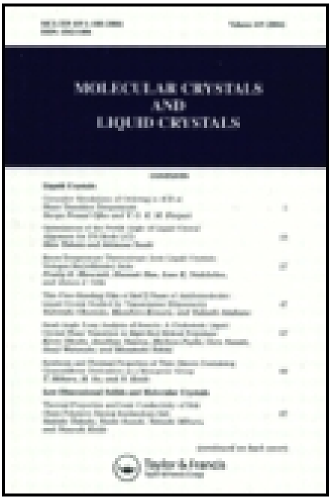

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N-Substituted 2,3-Dicarboximido-Anthraquinone Dichroic Dyes

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N-Substituted 2,3-Dicarboximido-Anthraquinone Dichroic Dyes

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(*Received June 25, 1981*)

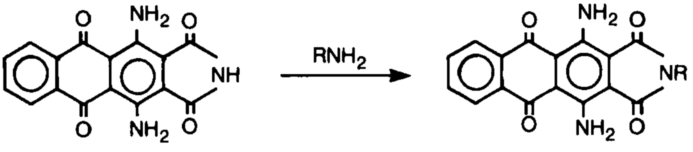
A series of *N*-substituted 1,4-diamino 2,3-dicarboximido-anthraquinone dyes has been synthesized. The location of the dicarboximido moiety in the 2,3-positions permits the elongation of the molecule in a direction collinear with the major axis of the anthraquinone nucleus by attaching substituents at the imido-*N*. The resulting dyes have improved order parameters, particularly when a phenyl group is directly bonded to the *N*.

INTRODUCTION

A variety of dichroic dyes for use in guest-host liquid crystal displays have been reported during the past five years, and these dyes have been recently reviewed.[1] Azo and anthraquinone dyes have received the most attention. The highest order parameters, up to 0.80, have been reported for azo dyes.[2] These dyes also have desirably high extinction coefficients and are relatively easy to synthesize. Since azo dyes tend to bleach gradually upon exposure to light, more recent efforts have been concentrated on anthraquinones which, as a class, tend to have better photostability. Simple anthraquinones of short molecular length have a low order parameter. To derive more elongated molecules, substituents have been placed in various positions of the anthraquinone nucleus such as in positions 1-, 1,5-, 2- and 2,6-, and dyes of higher order parameter have indeed been obtained.[3,4,5] In this paper we report the synthesis of anthraquinone derivatives elongated in a direction parallel to the major axis of the anthraquinone nucleus. Some of these dyes have a higher order parameter because the more lath-like shape of these molecules promotes a higher degree of order and/or a more favorable direction of the transition moment with respect to the alignment direction.

RESULTS AND DISCUSSION

The dyes, listed in Table I, are *N*-substituted derivatives of 1,4-diaminoanthraquinone-2,3-dicarboximide (I). With the exception of dyes 1, 8 and 11 of Table I, they were synthesized according to Scheme 1 by the reaction of 1,4-diaminoanthraquinone-2,3-dicarboximide with the appropriate aliphatic or aromatic amine in an autoclave.[6]



SCHEME 1

I

Dye 1 was obtained commercially under the trade name Genacron Brilliant Blue 8G, and dyes 8 and 11 were synthesized from 1,4-diaminoanthraquinone-2,3-dicarboxylic acid anhydride and the appropriate aniline derivative. Dye 6 was prepared by esterification of the product resulting from the reaction of the dicarboximide with ethanolamine. All the dyes, except dye 1, were purified by chromatography. Table 1 shows the order parameter and other pertinent properties.

The order parameter was measured in three liquid crystal hosts: E7 and E44 (manufactured by BDH Chemicals) and Licristal 1291 (manufactured by E. Merck). The clearing points were: E7, 60°; E44, 100°; 1291, 107°. The general trend of increasing order parameter with increasing clearing point was observed in going from E7 to one of the other two. Although 1291 has a higher clearing point than E44, the order parameter of dyes of high order parameter was actually lower in 1291.

The order parameter values fall roughly into two categories. Dyes with aliphatic groups attached to the imido nitrogen have values of 0.66–0.70 in E7 whereas those with a substituted phenyl ring attached directly to the nitrogen have values of 0.73–0.75 in the same host. A direct comparison may be made for dyes 7 and 11 which have the same molecular length. Dye 7, whose aliphatic group is bonded to nitrogen, has an order parameter of 0.69 in E7, whereas dye 11, with the phenyl ring bonded to nitrogen, has an order parameter of 0.74. This is not surprising since dyes of the latter type have greater rigidity. Dye 11 has been previously reported[7] as having an order parameter of 0.74 in host GR-41. Dye 12, bearing a dodecyl substituent, has a particularly low order parameter of 0.68. This is perhaps not unusual, as a decrease of order parameter with increasing chain length beyond an optimum length has been found in the 1-alkoxyphenyl-4-hydroxyanthraquinone series.[3]

The wavelength of maximum absorption (λ_{max}) is approximately constant

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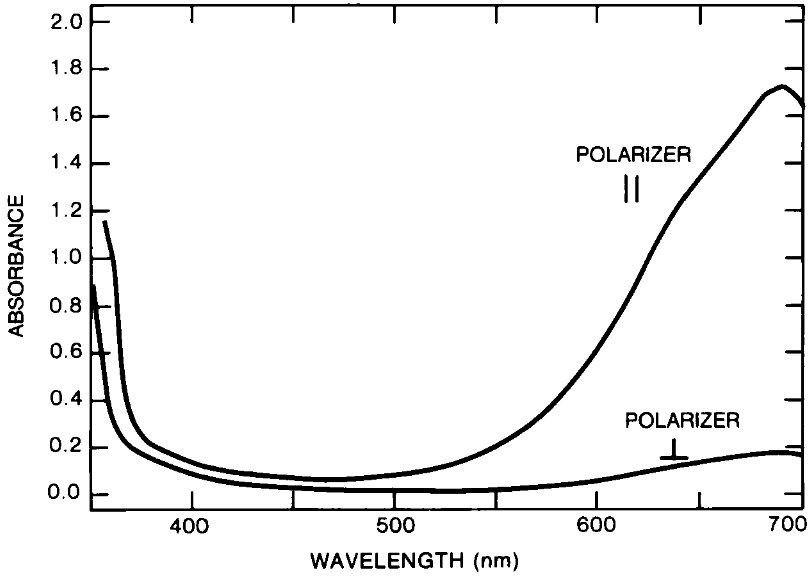

FIGURE 1 Absorption Spectra of Dye 8 in Host E7 with Polarizer Parallel and Perpendicular to the Nematic Director.

at 680 nm for all the dyes in the three hosts. Figure 1 shows polarized spectra of dye 8 which are typical of all the other dyes. λ_{max} in chloroform is about 680 nm. The extinction coefficients in chloroform are shown in Table I.

The solubility of the dyes is generally low but it is much higher in E44 than in 1291. Dyes 1–4 with purely aliphatic substituents on the nitrogen have lower solubility in E44 than dyes incorporating a phenyl ring at that position. Dye 6 incorporating an ester linkage has a relatively high solubility but it is not clear whether this is due to the ester linkage or some other structural feature.

In summary, it has been shown that the order parameter of dichroic anthraquinone dyes can be increased by elongating the molecule in a direction parallel to the major axis of the anthraquinone nucleus.

EXPERIMENTAL

Synthesis

All the dyes, except dyes 1, 8 and 11, were synthesized by the method adapted from Laucius and Speck[4] illustrated here for dye 8. A 300-mL stainless steel autoclave was charged with 15 g (0.05 mole) 1,4-diaminoanthraquinone-2,3-dicarboximide, 7.5 g (0.05 mole) 4-phenylbutylamine, and 85 mL each of methanol and o-dichlorobenzene. The mixture was heated with agitation to 182° over a 1-hr period during which the pressure increased to 320 psig, and these conditions were kept for about 48 hrs. After cooling to room temperature, the

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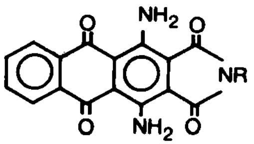
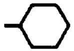
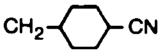
TABLE I

Properties of *N*-substituted 1,4-Diaminoanthraquinone-2,3-dicarboximides (I)



No.	R	Melting Point (°C)	Order Parameter in E7	Order Parameter in E44	Order Parameter in 1291	λ_{max} in E7 (nm)	10^{-4} ϵ in $CHCl_3$ at 680 nm	Solubility (%) in E44	Solubility (%) in 1291
1	$CH_2CH_2CH_2OCH_3$	195	0.68	0.70	0.71	680	1.57	0.15	0.07
2	C_6H_{13}	212	0.66			680	1.60	~0.25	0.15
3		>300	0.69	0.72	0.73	680	1.52	~0.25	0.10
4		>300	0.63	0.70		682	1.42	0.20	0.05

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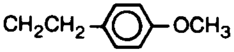
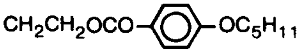
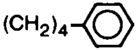
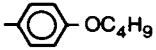
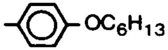
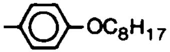
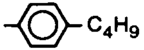
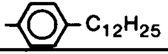
5		248	0.70	0.74		682	1.48	0.35	0.09
6		176	0.67	0.74		684	1.29	0.63	
7		195	0.69	0.74	0.73	680	1.46	0.45	0.28
8		279	0.75	0.77	0.74	680	1.52	0.58	
9		250	0.74	0.77	0.74	686	1.50	0.51	0.10
10			0.73	0.78	0.77	686			
11			0.74		0.78	686			
12			0.68			686			

TABLE II

Elemental Analysis of Dyes

		% Carbon		% Hydrogen		% Nitrogen	
Dye	Formula	Calcd.	Found	Calcd.	Found	Calcd.	Found
2	$C_{22}H_{21}N_3O_4$	67.50	67.12	5.41	5.59	10.74	10.92
3	$C_{22}H_{19}N_3O_4$	67.85	68.21	4.92	5.19	10.79	10.63
4	$C_{24}H_{20}N_4O_4$	67.28	67.22	4.71	5.07	13.08	12.50
5	$C_{25}H_{19}N_3O_5$	68.02	67.37	4.34	4.51	9.52	9.69
6	$C_{30}H_{27}N_3O_7$	66.53	67.66	5.03	5.56	7.76	7.42
7	$C_{26}H_{21}N_3O_4$	71.06	70.49	4.82	4.95	9.56	9.76
8	$C_{26}H_{21}N_3O_5$	68.56	69.66	4.65	5.32	9.23	8.34
9	$C_{28}H_{25}N_3O_5$	69.55	68.04	5.21	5.54	8.69	8.18

precipitate was collected, washed with methanol and chromatographed on alumina using chloroform or 9:1 chloroform/acetonitrile as eluent. The dyes gave a single spot in thin layer chromatography. For dye 6, the amine was ethanolamine, and the product was esterified with *p*-pentyloxybenzoyl chloride.

Dyes 8 and 11 were synthesized as follows: A mixture of 1 g 1,4-diaminoanthraquinone-2,3-dicarboxylic acid anhydride and 25 mL of the appropriate aniline derivative was heated at 125° for 5 hrs, the mixture was cooled and diluted with isopropyl alcohol, and the precipitate was collected, washed and chromatographed.

Elemental analysis data are given in Table II.

Solubility Measurement

The solubility of the dyes at room temperature (about 25°) was determined as follows: A vial filled with a mixture containing excess dye in the liquid crystal host was placed in an ultrasonically agitated bath for 15 min., removed from the bath for about 1 hr and this procedure was repeated. Excess dye was filtered off through a membrane of 0.22 μm pores. An aliquot of the filtrate was added to a large volume of chloroform, and the dye concentration was determined from the absorbance of the chloroform solution.

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