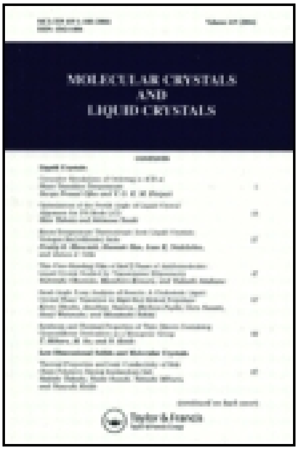

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Anthraquinone Dyes Exhibiting Negative Dichroism in Liquid Crystals I. Derivatives of 1-amino-and 1, 4-Diaminoanthraquinones

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Anthraquinone Dyes Exhibiting Negative Dichroism in Liquid Crystals I. Derivatives of 1-amino- and 1,4-Diaminoanthraquinones†

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Anthraquinone dyes with negative dichroism in liquid crystals have been synthesized; value of the negative dichroism are of practical interest. The structural influence for the dichroic dyes on their dichroism in liquid crystals is discussed.

INTRODUCTION

In recent years, anthraquinone dyes with positive dichroism have been widely used in liquid crystal displays with the "guest-host" effect, due to the synthesis of a number of anthraquinone derivatives with a high ordering in liquid crystals[1–3] and with high-electro- and photo-stability of their solutions in liquid crystals.[4–6]

As a rule, electronic spectra of anthraquinone dyes have 5–6 absorption bands.[15] Two are due to electronic transitions with polarization along the X axis; two others are along the Y axis.[7–9] The position of the long wave absorption bands or bands of charge transfer of anthraquinone dyes is determined by the nature, position, and number of donor substituents. For symmetrically substituted anthraquinones, for example in 1,4- or in 2,3-diaminoanthraquinones (I) this electronic transition is strictly polarized along

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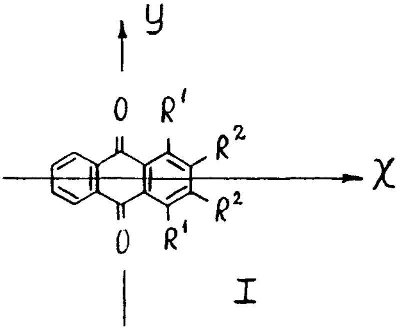
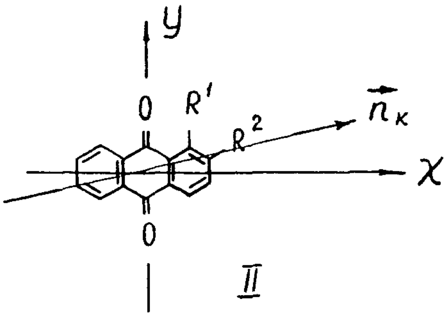
the X or Y axis. In this case the order parameter of the oscillator for the long wave electronic transition (S), which was determined on the base of polarization spectra, is equal to the geometrical order parameter of the dye molecules (S_G). If donor substituents are situated asymmetrically in anthraquinone dyes, for example in 1-amino- or 2-amino-anthraquinones (II), then the electronic transition is polarized at some angle β to the X axis.[8,9] So $S \neq S_G$.[10]



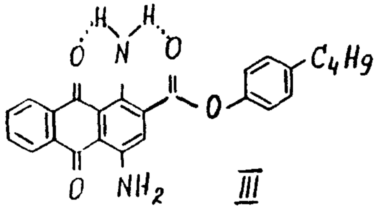
I



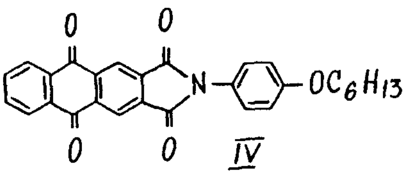
II

I, II: $R^1 = NH_2$, $R^2 = H$; $R^1 = H$, $R^2 = NH_2$.

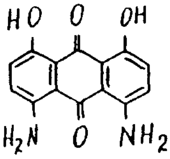
The efforts of most specialists in the field of structural modification of anthraquinone dyes for application in liquid crystal displays were directed first to a lengthening of the molecule along the X axis to achieve a maximum geometrical anisotropy of the dichoric dyes, and to obtain the maximum value of the positive dichroism. As a result of these efforts, for example, dichroic anthraquinones III-V with order parameter $S = 0.74$ were obtained.[11-13]



III



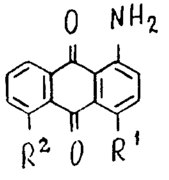
IV



V

Based on the approach proposed by us to the design of dichroic dyes,[14] we studied the possibility of structurally modifying anthraquinones in order to obtain dyes with negative dichroism.

We examined (as examples) 1-amino- (VI), 1-amino-4-chloro- (VII), 1-amino-4-bromo- (VIII), 1-amino-4-hydroxy- (IX), 1,4-diamino- (X) and 1,4-diamino-5-nitro-anthraquinones (XI).



	R^1	R^2
VI	H	H
VII	Cl	H
VIII	B	H
IX	OH	H
X	NH_2	H
XI	NH_2	NO_2

Using the above structures, we synthesized the corresponding 1-aroylaminoanthraquinones (XII–XVII), 1,4-*bis*-(aroylamino)-(XVIII-XXVI), 1,4-*bis*-(4-alkyl-*trans*-cyclohexylcarbonylamino)-(XXVII, XXVIII), 1,4-*bis*-(alkanoylamino)- (XXIX) and 1,4-*bis*-alkenoylamino)-anthraquinones (XXX) with negative dichroism.

EXPERIMENTAL

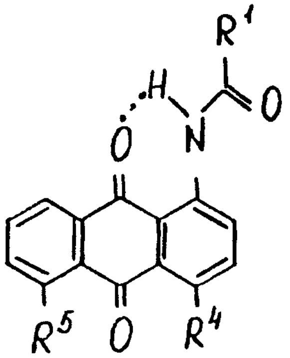
The purity of the compounds synthesized was checked by TLC on Silufol UV-254. Electronic spectra of 1% solutions in an oriented liquid crystal matrix were measured by using a Hitachi spectrophotometer.[15] A mixture of 4-alkyl- and 4-alkoxy-4'-cyanobiphenyls with a nematic temperature range 0-60°C was used as the liquid crystal matrix.

2 mmols of VI–XI and 2.5 mmols (4.5 mmols of X–XI) of the corresponding aromatic or cyclohexanecarboxylic acid chloride were boiled in chlorobenzene for 30 min. The reaction mixture was diluted with propan-1-ol at 60°C, cooled to ambient temperature, filtered, and the residue washed with propan-2-ol. The residue was dissolved in benzene and purified by chromatography in benzene on silica gel. The compounds XII–XXX were obtained after distillation of the solvent.

Spectral and orientational characteristics of the dichroic dyes are shown in Table I and their physical constants and yields are given in Table II. A typical spectrum of compound XXIX is shown in Fig. 1.

TABLE I

Spectral and orientational characteristics of dichroic dyes



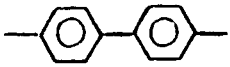
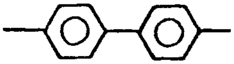
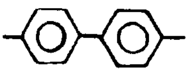
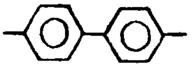
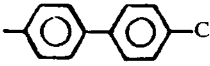
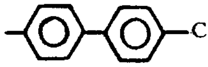
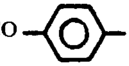
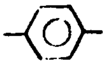
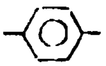
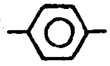
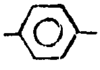
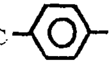
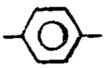
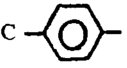
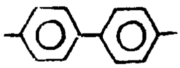
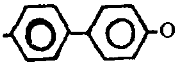
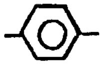
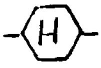
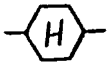
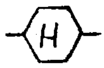
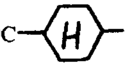
No. of compound	R¹	R⁴	R⁵	λ max nm	
XII	 C_4H_9	H	H	430	–
XIII	 C_7H_{15}	Cl	H	434	–
XIV	 C_8H_{17}	Cl	H	436	–
XV	 C_8H_{17}	—Br	—H	440	–
XVI	 C_8H_{17}	—OH	—H	500	–
XVII	 C_8H_{17}	—OCO  C_8H_7	—H	422 433	–
XVIII	 C_4H_9	—NHOC  C_4H_9	—H	508	–
XIX	 C_6H_{13}	—NHOC  C_6H_{13}	—H	512	–
XX	 C_7H_{15}	—NHCO  C_7H_{15}	—H	510	–
XXI	 C_9H_{19}	—NHOC  C_9H_{19}	—H	510	–
XXII	 C_4H_9-tert.	—NHOC  C_4H-tert.	—H	510	–

TABLE I

(*continued*)

No. of compound	R^1	R^4	R^5	λ max nm	*S*
XXIII	 OC$_5$H$_{11}$	—NHOC  OC$_5$H$_{11}$	—H	520	− 0.29
XXIV	 OC$_{18}$H$_{37}$	—NHOC  OC$_5$H$_{11}$	—H	520	− 0.30
XXV	 C$_8$H$_{17}$	—NHOC  OC$_8$H$_{17}$	—H	512	− 0.36
XXVI	 C$_6$H$_{13}$	—NHOC  C$_6$H$_{13}$	—NO$_2$	520	− 0.12
XXVII	 C$_4$H$_9$	—NHOC  C$_4$H$_9$	—H	502	− 0.30
XXVIII	 C$_6$H$_{13}$	—NHOC  C$_6$H$_{13}$	—H	502	− 0.33
XXIX	—C$_8$H$_{17}$	—NHOC—C$_8$H$_{17}$	—H	497	− 0.19
XXX	—C$_{17}$H$_{33}$	—NHOC—C$_{17}$H$_{33}$	—H	500	− 0.13

DISCUSSION

Analysis of the dichroism values of the 1-aroylaminoanthraquinones (XII–XVII) with different substituents in position 4 (Table I) demonstrates that the low value of the negative dichroism is first of all due to the deviation of the oscillator for the long wave electronic transition from the *X* axis. The order parameters of 4-chloro- (XIV) and 4-aroyloxy-1-aroylaminoanthraquinone (XVII) are −0.12 and −0.17 respectively. A higher value *S* for compound XVII, in comparison with those for compounds XIV and XV, is explained by its higher geometrical anisotropy. The geometrical anisotropy of the 4-hydroxy-derivate (XVI) and the 4-chloro- (XIV) and 4-bromo-derivatives (XV) are approximately equal. Nevertheless, the order parameter of oscillator absorption for compound (XVI) is considerably higher than those for compounds XIV and XV. This may be explained by the additional intermolecular hydrogen bond in compound (XVI); this bond is formed by carbonyl- and hydroxy-groups and leads to a lowering of the molecular electronic asymmetry and consequently to a diminution of the oscillator deviation of the long wave electronic transition from the *X* axis in comparison with the deviation of these oscillators for

TABLE II

Characteristics of the compounds XII–XXX

Compound	M.P., °C	Found, % C	H	N	Molecular formula	C	H	Calculated, % N	Yield, %
XII	259–260	81.15	5.32	2.97	$C_{31}H_{25}NO_3$	81.04	5.48	3.05	49.5
XIII	140–141	73.02	5.91	2.98	$C_{28}H_{26}ClNO_3$[x]	73.11	5.70	3.04	89.07
XIV	180–181	76.34	5.88	2.76	$C_{35}H_{32}ClNO_3$[xx]	76.42	5.86	2.55	89.00
XV	—	70.88	5.31	2.58	$C_{35}H_{32}BrNO_3$[xxx]	70.70	5.42	2.35	65.86
XVI	185–186	78.00	5.13	2.72	$C_{31}H_{25}NO_4$	78.3	5.3	2.90	62.34
XVII	255–257	81.42	6.88	1.98	$C_{56}H_{57}NO_5$	81.62	6.97	1.70	48.31
XVIII	217–219	77.62	5.83	5.17	$C_{36}H_{32}N_2O_4$	77.39	6.13	5.01	54.7
XIX	198–200	78.13	6.95	4.67	$C_{40}H_{42}N_2O_4$	78.21	6.88	4.55	67.28
XX	207–210	78.60	7.35	4.28	$C_{42}H_{46}N_2O_4$	78.47	7.21	4.36	71.85
XXI	198–195.5	79.21	7.63	4.25	$C_{46}H_{54}N_2O_4$	79.05	7.79	4.01	48.21
XXII	above 300	77.12	6.14	4.93	$C_{36}H_{34}N_2O_4$	77.40	6.13	5.01	52.89
XXIII	229–231	73.59	6.08	4.67	$C_{38}H_{38}N_2O_6$	73.77	6.19	4.53	63.61
XXIV	177–178	80.94	9.61	2.75	$C_{64}H_{90}N_2O_4$	80.79	9.53	2.94	64.73
XXV	274–276	81.95	7.21	3.15	$C_{56}H_{58}N_2O_4$	81.72	7.10	3.40	70.98
XXVI	—	65.98	6.32	8.15	$C_{28}H_{33}N_3O_6$	66.24	6.55	8.28	38.95
XXVII	above 250	75.88	8.02	4.76	$C_{36}H_{46}N_2O_4$	75.76	8.12	4.91	48.23
XXVIII	269–270	76.48	8.91	4.39	$C_{40}H_{54}N_2O_4$	76.64	8.68	4.47	52.39
XXIX	141–143	74.32	8.24	5.61	$C_{32}H_{42}N_2O_4$	74.10	8.16	5.40	28.13
XXX	113–115	78.11	9.54	3.78	$C_{50}H_{74}N_2O_4$	78.28	9.72	3.65	36.04

[x] I: Found, 7.79%; Calculated, 7.70%.

[xx] I Found, 6.54%; Calculated 6.44%.

[xxx] I Found, 13.52%; Calculated 13.44%.

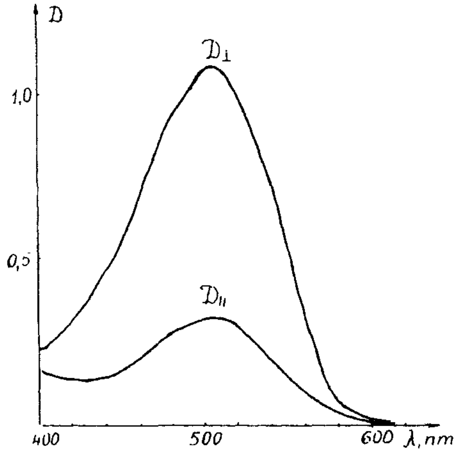


FIGURE 1 Polarization spectra for the dichroic dye XIX (in solution in ZK-807).

compounds XIV and XV, i.e., $\beta(\mathrm{XVI}) < \beta(\mathrm{XIV, XV})$. Moreover, although the geometrical anisotropy of compound XVII is considerably higher than that of compound XVI, its order parameter is somewhat lower than that of compound XVI. This also may be explained by $\beta(\mathrm{XVI}) < \beta(\mathrm{XVII})$ and demonstrates the strong influence of angle value on the observed dichroism.

The maximum value of the negative dichroism (as may be expected) is when $\beta = 0$, as in the case of 1,4-*bis*(aroylamino) anthraquinones (XVIII–XXV). For example, 1,4-*bis*(aroylamino) anthraquinone (XXV) has an order parameter $S = -0.36$, whereas the order parameter of XVII ($\beta \neq 0$ and the geometrical anisotropy is approximately equal to that of compound XXV) has a value of only −0.17. Introduction of a nitro group in the 5-position of 1,4-*bis*(aroylamino)anthraquinone (XXVI) causes an oscillator deviation of the long wave electronic transition to an angle and also leads to a lowering of the value of S to −0.12 (Table I).

Depending on the aryl substituent, the order parameter of 1,4-*bis*(aroylamino)anthraquinones (XVIII–XXV) is changed from −0.29 to −0.36 (Table I). Dichroic dyes based upon 4-alkoxybenzoic acids have lower order parameters (−0.29 to −0.30) in comparison with the dyes (XVIII–XXII) based upon 4-alkylbenzoic acids (−0.31 to −0.36). It should be noted that the order parameters of the latter are slightly different from the order parameter (−0.36) of dye XXV obtained on the basis of 4′-n-octylbiphenyl-4-carboxylic acid. Replacement of the 4-n-alkylbenzoyl group by the 4-t-butylbenzoyl or the *trans*-4-n-alkyl-cyclohexylcarbonylamedo group also leads to some lowering of the order parameter of the dichroic dyes (compare the S values for compounds XVIII, XXII and XXVII). The greatest lowering of the order parameters is observed for 1,4-*bis*(alkanoylamino)anthraquinones, for example XXIX, XXX (−0.19 and −0.13, respectively); their geometrical anisotropy is slightly different from that of the dichroic dyes (XVIII–XXVIII).

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