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Anthraquinone Dyes Exhibiting Negative Dichroism in Liquid Crystals II. Derivatives of 1, 4-Diamino- and 1-Amino-4-Hydroxy-Anthraquinones

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Anthraquinone Dyes Exhibiting Negative Dichroism in Liquid Crystals II. Derivatives of 1, 4-Diamino- and 1-Amino-4-Hydroxy-Anthraquinones†

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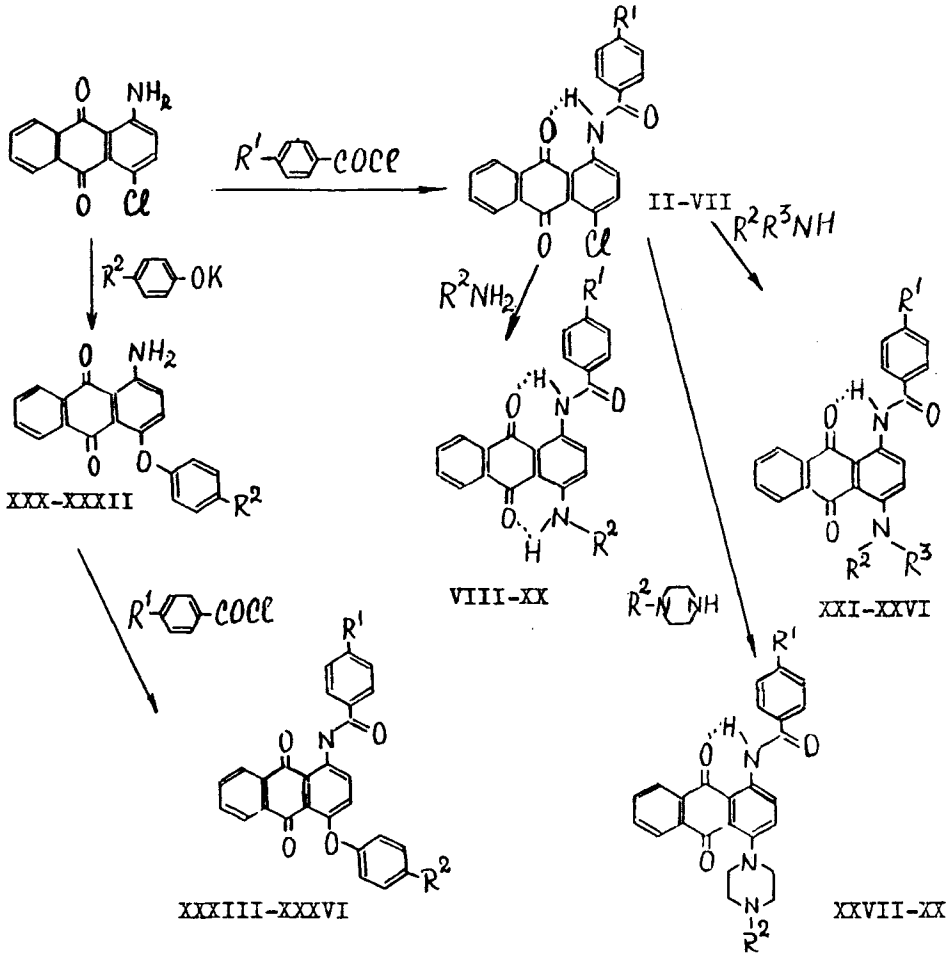
1-Alkylamino-, 1-dialkylamino-, 1-(4-alkylaryl)-amino-, 1-aralkylamino-, 1-alkyl(aryl) piperazinyl- and 1-aryloxy-4-aroylaminoanthraquinones with negative dichroism ($S = -0.13 \div -0.35$, $\lambda_{max} = 445 \div 612$ nm) in liquid crystal solvents have been obtained and the influence of the substituents on the dichroism and the position of the long wave absorption band of the dyes is considered.

INTRODUCTION

On continuing the synthesis of dichroic dyes for liquid crystal displays,[1-3] the derivatives of 1,4-diamino- (VIII–XXIX) and 1-amino-4-hydroxyanthraquinones (XXXIII–XXXYI) were obtained starting from 1-amino-4-chloroanthraquinone (I); for compounds (VIII–XXIX) and (XXXIII–XXXYI), with regard to the dependence on structure, the order parameter of the oscillator for the long wave electronic absorption is equal to -0.13 to -0.35, the absorption being 445–612 nm (Table I).

†Presented at the Tenth International Liquid Crystal Conference, York, July 15–21, 1984.



R^1 = C_6H_{13} (II, VIII, XVIII, XXI), C_7H_{15} (III, IX, XIX, XXII), -C$_6$H$_4$-C_4H_9 (IV, X, XXIII), -C$_6$H$_4$-C_5H_{11} (V, XI, XXIV), -C$_6$H$_4$-C_6H_{13} (VI, XII, XXV, XXXIII), -C$_6$H$_4$-C_8H_{17} (VII, XIII-XVII, XX, XXVI-XXIX, XXXIV-XXXVI); R^2 = C_4H_9 (XIII, XXX, XXXIII, XXXIV), C_7H_{15} (XXXII, XXXVI), C_8H_{17} (VIII, X-XIII, XIV, XXVII), $C_{18}H_{37}$ (IX), t-C_4H_9 (XXXI, XXXV), —CH(C_2H_5)C_4H_9 (XV), —CH(CH_3)-C$_6$H$_4$-C_4H_9-t (XVI), -C$_6$H$_4$-C_4H_9 (XVII, XXVII), 2,6-(CH_3)$_2$-C$_6$H$_3$-CH_3 (XXIX), C$_6$H$_5$-OC_4H_9 (XVIII), C$_6$H$_5$-OC_8H_{17} (XX), — C$_6$H$_5$-O$C_{18}H_{37}$ (XIX)

EXPERIMENTAL

The purity of the compounds synthesized was checked by TLC on Silufol UV-254. The polarization spectra of 1% dye solutions in an orientated liquid crystal matrix (a mixture of 4-alkyl- and 4-alkoxy-4′-cyanobiphenyls with temperature range 0–60°C) were measured by using a Hitachi spectrophotometer EPS-3T.[4]

1-Aroylamino-4-chloroanthraquinones (II–VII)

20 mmol of 1-amino-4-chloroanthraquinone (I) and 30 mmol of the corresponding aroyl chloride are boiled in 40 ml of chlorobenzene for 30 min. The reaction mixture is cooled to 60°C, 80 ml of propan-2-ol is added, the mixture is cooled to ambient temperature, the mixture is filtered, and the residue is washed with propan-2-ol and dried. The yield of compound (VII) is 89%, m.p. 180–181°. Yields for II–VI are 65–85%

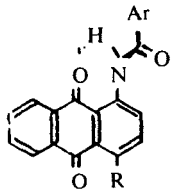
Derivatives of 1,4-diaminoanthraquinone (VIII–XXIX)

10 mmol of II–VII, 100 mmol of the corresponding amine and 15 mmol of sodium acetate are boiled (for aromatic amines and piperazines it is necessary to keep the temperature at 160–165°C) with stirring in the presence of copper powder or a copper salt for 4 hours. The mixture is cooled to ambient temperature, 70 ml of 10% hydrochloric acid is added, the residue is filtered off and washed by water. After drying, it is dissolved in chloroform and checked for purity by chromatography on silica gel with chloroform as solvent. The dichroic dyes VIII–XXIX are obtained after evaporation of the corresponding eluate fractions. Spectral characteristics and analysis results are given in the Tables I and II.

1-Aryloxy-4-aroylaminoanthraquinones (XXXIII–XXXVI)

10 mmol of potassium hydroxide and 10 mmol of compound I are added to 100 mmol of the corresponding phenol. The mixture is heated to 190–200°C with water removal and stirred at this temperature for 4 hours. The reaction mixture is cooled to 100°C, 50 ml of 70% aqueous propan-2-ol are added and the mixture is stored at ambient temperature for 2–6 hours. The residue is filtered off, washed with 50% aqueous propan-2-ol, dried, dissolved in chloroform and checked for purity by chromatography on silica gel with chloroform as solvent. Compounds XXX–XXXII are obtained after eluent evapo-

TABLE I



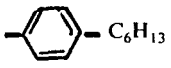
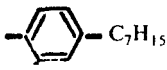
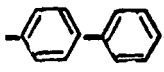
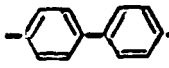
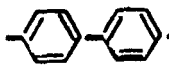
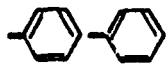
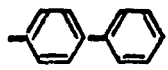
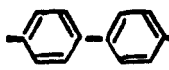
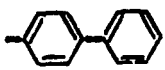
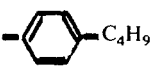
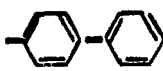
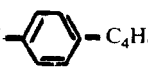
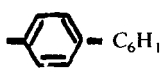
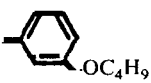
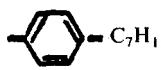
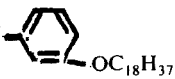
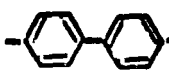
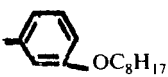
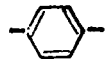
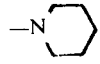
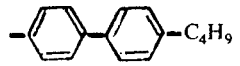
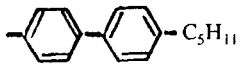
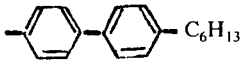
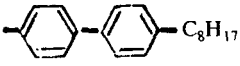
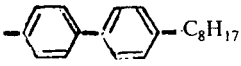
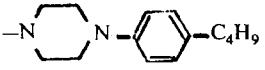
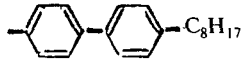
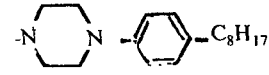
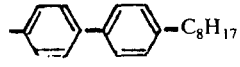
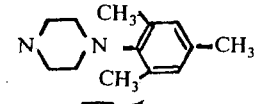
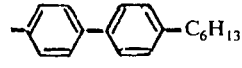
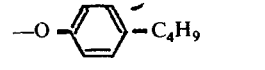
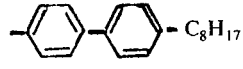
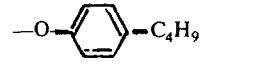
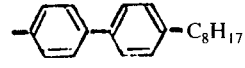
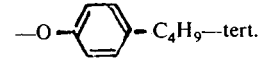
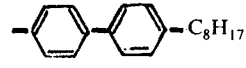
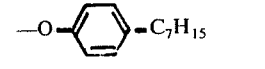
Compound	Ar	R	λ_{max}	S
VIII		$-HNC_8H_{17}$	578	− 0, 23
IX		$-HNC_{18}H_{37}$	582, 616	− 0, 24; − 0, 24
X		$-HNC_8H_{17}$	578; 616	− 0, 31; − 0, 31
XI		$-HNC_8H_{17}$	580; 618	− 0.32; − 0, 31
XII		$-HNC_8H_{17}$	578; 617	− 0, 31; − 0, 31
XIII		$-HNC_4H_9$	580	− 0, 29
XIV		$-HNC_8H_{17}$	580	− 0, 35
XV		$-HNCH(C_2H_5)(C_4H_9)$	581; 621	− 0, 30; − 0, 31
XVI		$-HNCH(CH_3)$- 	589	− 0, 35
XVII		-HN- 	605	− 0, 22
XVIII		—HN- 	590	− 0, 13
XIX		—HN- 	595	− 0, 21
XX		—HN- 	590	− 0, 22

TABLE I

(Continued)

Compound	Ar	R	λ_{max}	S
XXI		$-N(C_4H_9)_2$	580	− 0, 20
XXII			585	− 0, 20
XXIII		$-N(C_4H_9)_2$	578; 616	− 0, 30; − 0, 3
XXIV		$-N(C_4H_9)_2$	579; 614	− 0, 32; − 0, 33
XXV		$-N(C_4H_9)_2$	580; 618	− 0, 32; − 0, 32
XXVI		$-N(C_4H_9)_2$	580; 617	− 0, 35; − 0, 32
XXVII			578; 612	− 0, 34; − 0, 34
XXVIII			580; 620	− 0, 34; − 0, 34
XXIX			563; 598	− 0, 21; − 0, 23
XXXIII			445	− 0, 24
XXXIV			464	− 0, 25
XXXV			446	− 0, 22
XXXVI			460	− 0, 21

corresponding aroyl chloride is stored in 5 ml of nitrobenzene at 160–165° for 1,5 h. The reaction mixture is cooled to ambient temperature, 20 ml of ethanol is added, and the residue is filtered off. This is washed with ethanol, dissolved in chloroform and checked for

TABLE II

Compound	M.p. °C	Found, % C	H	N	Formula	Calculated, % C	H	N	Yield, %
I	173,5–175	78,23	7,98	5,37	$C_{35}H_{42}N_2O_3$	78,03	7,86	5,20	30,1
II	—	79,86	9,41	3,96	$C_{46}H_{64}N_2O_3$	79,72	9,31	4,04	28,7
III	200–201	80,03	7,34	4,65	$C_{39}H_{42}N_2O_3$	79,86	7,17	4,78	77,2
IV	—	79,68	7,24	4,53	$C_{40}H_{44}N_2O_3$	79,96	7,38	4,66	52,3
V	198–200	80,37	7,34	4,63	$C_{41}H_{47}N_2O_3$	80,18	7,49	4,56	33,4
VI	202,5–204,5	80,13	7,31	4,63	$C_{39}H_{42}N_2O_3$	79,86	7,17	4,78	28,3
VII	189–190,5	80,05	7,80	4,15	$C_{43}H_{51}N_2O_3$	80,34	7,84	4,36	38,6
VII	179–180	79,98	7,72	4,28	$C_{42}H_{48}N_2O_3$	80,22	7,69	4,45	32,2
IX	225–227	81,33	7,59	4,28	$C_{47}H_{50}N_2O_3$	81,64	7,29	4,14	28,4
X	176,4–179	81,33	7,21	4,35	$C_{45}H_{46}N_2O_3$	81,54	6,98	4,22	41,3
XI	126–127	77,56	6,54	4,78	$C_{37}H_{39}N_2O_4$	77,20	6,80	4,90	21,9
XII	79–80	79,76	8,65	3,47	$C_{52}H_{68}N_2O_4$	79,55	8,73	3,57	20,4
XIII	—	80,19	7,24	3,67	$C_{49}H_{54}N_2O_4$	80,08	7,41	3,81	25,7
XIV	202–203	77,81	7,93	5,15	$C_{35}H_{42}N_2O_3$	78,03	7,86	5,20	42,3
XV	140	77,72	7,35	5,61	$C_{33}H_{36}N_2O_3$	77,92	7,13	5,50	48,4
XVI	—	79,54	7,18	4,56	$C_{39}H_{42}N_2O_3$	79,83	7,21	4,77	37,5
XVII	—	79,87	7,25	4,42	$C_{40}H_{44}N_2O_3$	79,97	7,38	4,66	34,9
XVIII	219–220	80,25	7,89	4,48	$C_{41}H_{46}N_2O_3$	80,09	7,54	4,56	35,8
XIX	199,5–202	80,02	7,98	4,22	$C_{43}H_{50}N_2O_3$	80,02	7,98	4,22	34,3
XX	250	80,64	7,67	5,51	$C_{49}H_{53}N_2O_3$	80,42	7,24	5,74	22,8
XXI	250	79,00	8,12	6,20	$C_{47}H_{57}N_3O_3$	79,30	8,05	5,90	20,3
XXII	250	81,47	6,82	4,31	$C_{44}H_{44}N_2O_3$	81,13	7,03	4,72	24,1
XXIII	246–248	81,29	6,71	2,36	$C_{43}H_{41}NO_4$	81,26	6,45	2,20	65,9
XXIV	180–182	81,58	6,59	2,03	$C_{45}H_{45}NO_4$	81,42	6,83	2,11	62,4
XXV	—	81,27	6,75	2,13	$C_{45}H_{45}NO_4$	81,42	6,83	2,11	58,7
XXVI	—	81,75	7,33	2,11	$C_{48}H_{51}NO_4$	81,67	7,28	1,98	58,4

ration. The solution of 4 mmol of XXX–XXXII and 10 mmol of the purity by chromatography on silica gel with the benzene-acetone (10:1) mixture as solvent. The compounds XXXIII–XXXVI are obtained after eluent evaporation.

DISCUSSION

In contrast to the 1,4-*bis*(aroylamino)anthraquinones[1] with absorption bands at 508–520 nm, the new derivatives of 1,4-diaminoanthraquinone (VIII–XXIX) have absorption bands at 560–620 nm (Fig. 1,2, Table I); in liquid crystal solvents, the order parameter of the oscillator for this electronic transition depends greatly both on aroylamine and amine fragments.

The absolute value of S is increased by 0.08 to 0.12 (by 30–50%) when passing from benzoyl to biphenylcarbonyl derivatives with the

same amine fragment. For example, $S = -0.23$ for 1-(4-hexylbenzoylamino)-4-octylaminoanthraquinone (VIII) and $S = -0.31$ for the biphenylcarbonyl analog (XII). The same dependence is observed when comparing dyes XXI and XXV where the values S are equal to -0.20 and -0.32 respectively. The value S is insignificantly

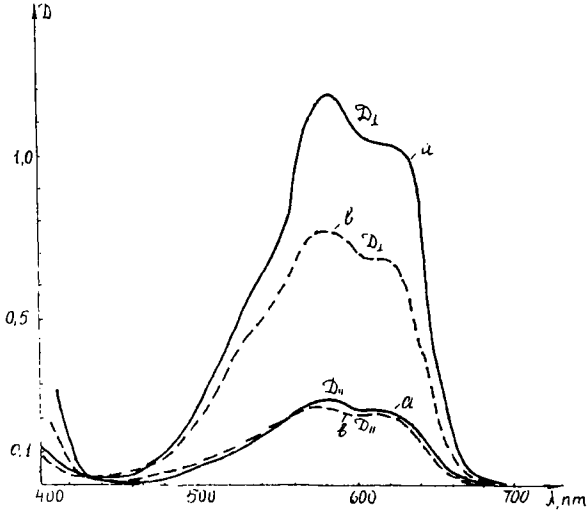


FIGURE 1 The polarization solution spectra of the derivatives of 1-amino-4-aroylaminoanthraquinones in ZK-807: *a*—XIY, *b*—XXYI.

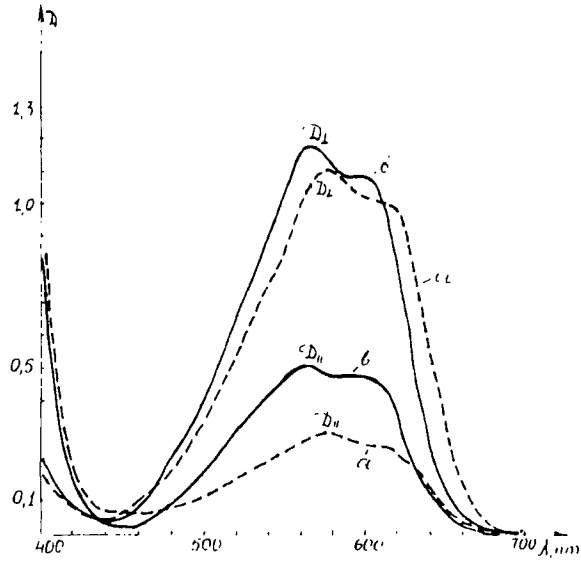


FIGURE 2 The polarization spectra of the derivatives of 1-aroylamino-4-(piperazin-1-yl)anthraquinones in ZK-807: *a*—XXVII, *b*—XXIX.

changed when passing from 1-alkylamino- (X–XVI) and 1-dialkylamino-4-aroylaminoanthraquinones (XXIII–XXVI) to the corresponding dyes with a piperazine fragment (XXVII, XXVIII). It is noted that the values S for the dyes with 4-alkylpiperazinyl (XXVIII) and 4-(4-alkylphenyl)piperazinyl fragments (XXVII) are the same and equal to -0.34. In the case of the dye XXIX with a 4-mesitylpiperazinyl fragment, not only is a lowering of S to -0.21 observed, but also a hypsochromic shift of the long wave absorption band (Fig. 2).

The significant lowering of S is also observed in the case of 1-arylamino-4-aroylaminoanthraquinones (XVII-XX); the absorption band at 590–605 nm (Fig. 3) is typical for these compounds and $S = (-0.13 \div -0.22)$. 1-Aryloxy-4-aroylaminoanthraquinones (XXXIII–XXXVI) have the same value $S = -0.20$ to -0.25, but the absorption band is at 445 nm (Fig. 3, Table I). Besides this, the solution spectra of the compounds (XXXIII–XXXVI) in liquid crystal solvents are changed when storing for 24 hours (Fig. 3)—two additional absorption bands with negative dichroism are appeared at 540–590 nm.

The lengths of the alkyl substituents both in the amino- and aroylamino-fragments influence noticeably the value S (Table I). For example, replacement of the butyl group by the octyl group in dyes X and XIV leads to an increase in the absolute value of S from -0.31 to -0.35 and in the dyes XIII and XIV—from -0.29 to -0.35.

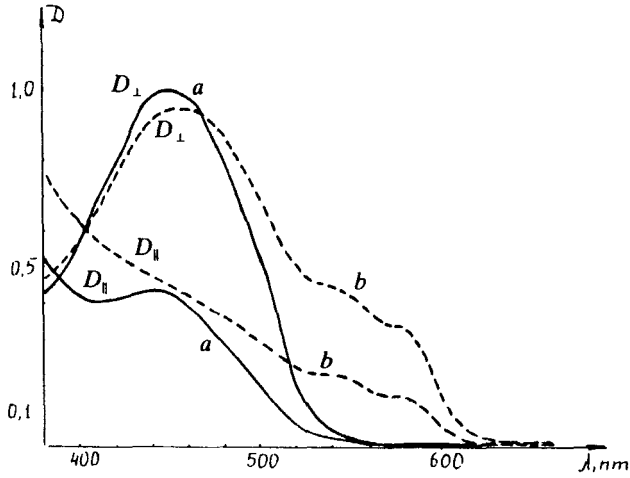


FIGURE 3 The polarization spectra of the dichroic dye XXXIV in solution in ZK-807: *a*—freshly-prepared solution; *b*—the solution after 18 h.

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