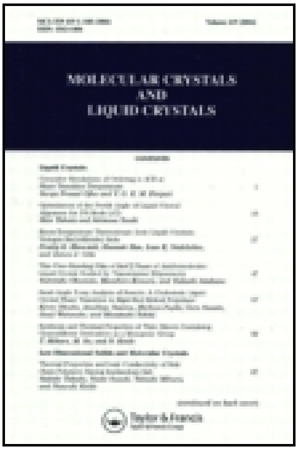

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# Anthraquinone Dyes Exhibiting the Negative Dichroism in Liquid Crystals III. Derivatives of Diaminodihydroxyanthraquinones

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# Anthraquinone Dyes Exhibiting the Negative Dichroism in Liquid Crystals III. Derivatives of Diaminodihydroxyanthraquinones†

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New 1, 5-diamino-4, 8-dihydroxy- and 1, 8-diamino-4, 5-dihydroxy-anthraquinones, pleochroic dyes exhibiting a high value of negative dichroism in liquid crystal media, have been synthesized and their spectral properties investigated.

## INTRODUCTION

Continuing our synthetic work and investigation of anthraquinone dyes exhibiting negative dichroism[1] in liquid crystal media, we have obtained derivatives of 1, 5-diamino-4, 8-dihydroxy-(I, II) and 1, 8-diamino-4, 5-dihydroxy-anthraquinones (III–XI) and studied their polarization spectra. The synthesis of the dichroic dyes I–XI is realized by acylating the corresponding diamino-dihydroxy-anthraquinones using acid chlorides.

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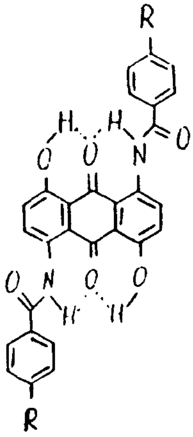
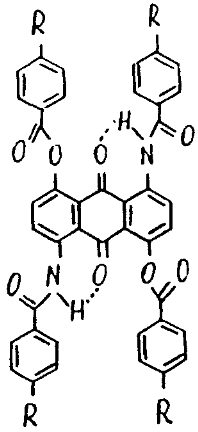
†Presented at the Tenth International Liquid Crystal Conference, York, July 15–21, 1984.



I



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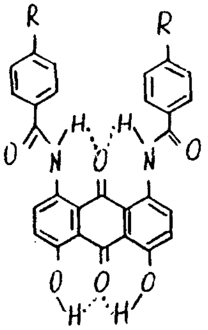
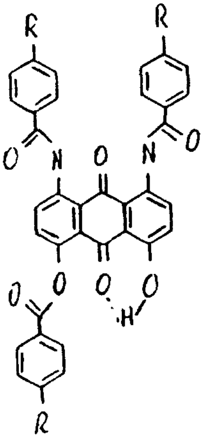
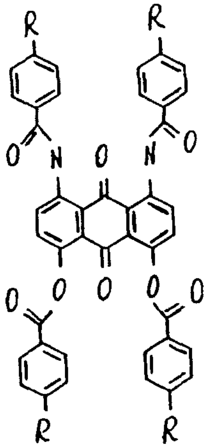


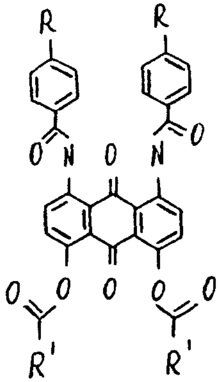
III – VI



VII, VIII

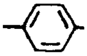


IX – X



XI

I, II, IV, VIII, X, XI: R = $C_7H_{15}$. III: R = $C_6H_{13}$.

V: *trans*  -$C_3H_7$. VI:  $C_8H_{17}$. VII, IX: t-$C_4H_9$.

XI: $R^1 = C_4H_9$.

## EXPERIMENTAL

The purity of the compounds synthesized was checked by TLC on Silufol UV-254. The electronic spectra of 1% solutions of the compounds in an oriented liquid crystal matrix were measured[2] using a Hitachi spectrophotometer. A mixture of 4-alkyl- and 4-alkoxy-4′-cyanobiphenyls with a temperature range 0–60°C was used as the liquid crystal matrix.

1, 5-*Bis*-(4-*n*-*heptylbenzoylamino*)-4, 8-*dihydroxy*- (I), 1, 8-*bis*-*aroylamino*-4, 5-*dihydroxy*- (III–VI) *and* 4-*aroyloxy*-1, 8-*bis*-*aroylamino*-5-*hydroxyanthraquinones* (VII, VIII). 2 mmol of the corresponding diaminodihydroxyanthraquinone and 3 mmol of the aromatic acid chloride are boiled in 30 ml of chlorobenzene for one h. The reaction mixture is diluted with ethanol at 60°C, cooled to ambient temperature, and the residue is filtered, washed with ethanol in chloroform and checked for purity by chromatography on silica gel with chloroform as solvent. The crimson and violet fractions are collected.

Dyes VII, VIII (crimson fraction) and I, III–VI (violet fraction) are obtained after distillation of the solvent.

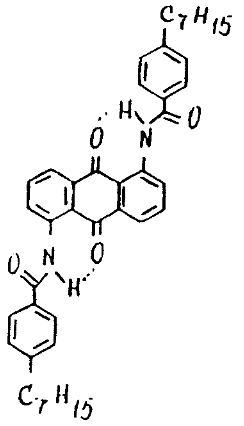
1, 5-*Bis*-(4-*n*-*heptylbenzoylamino*)-4, 8-*bis*-(4-*n*-*heptylbenzoyloxy*)-(II) *and* 1, 8-*bis-aroylamino*-4, 5-*bis-aroyloxy-anthraquinones* (IX, X). 2 mmol of the corresponding diaminodihydroxyanthraquinone and 6 mmol of 4-t-butyl- or 4-n-heptyl-benzoyl chloride are boiled in 30 ml of pyridine for 30 min. The reaction mixture is diluted with ethanol at 60°C, cooled to ambient temperature, and the residue is filtered, washed with ethanol, dissolved in chloroform and checked for purity by chromatography on silica with chloroform. The yellow dye is obtained after distillation of the solvent.

1, 8-*Bis*-(4-*heptylbenzoylamino*)-4, 8-*bis*-(*valeryloxy*)*anthraquinone* (XI). 2 mmol of 1, 8-diamino-4, 5-dihydroxyanthraquinone and 2.5 mmol of 4-n-heptylbenzoyl chloride are boiled in 30 ml of chlorobenzene for one h. The reaction mixture is diluted with ethanol at 60°C, cooled to ambient temperature, and the residue is filtered, washed with ethanol and dried. The product and 2.5 mmol of valeroyl chloride are boiled in 30 ml of pyridine. The reaction mixture is diluted with ethanol at 60°C, cooled to ambient temperature, and the residue is filtered, washed with ethanol, dissolved in chloroform and checked for purity by chromatography on silica gel with chloroform as solvent. The yellow dye is obtained after distillation of the solvent.

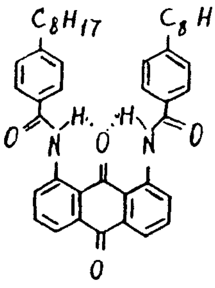
1, 5-*Bis*-(4-*heptylbenzoylamino*)*anthraquinone* (XII). 2 mmol of 1, 5-diaminoanthraquinone and 2.5 mmol of 4-n-heptylbenzoyl chloride are boiled in 30 ml of chlorobenzene for one h. The reaction mixture is diluted with ethanol at 60°C, cooled to ambient temperature, and the residue is filtered, washed with ethanol, dissolved in chloroform and checked for purity by chromatography on silica gel with chloroform as solvent. The yellow dye is obtained after distillation of the solvent.

## DISCUSSION

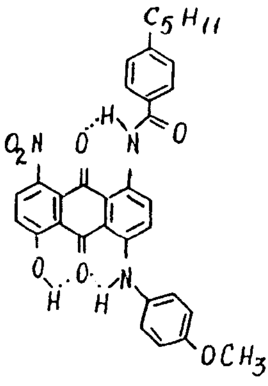
1,5-*Bis*-(4-heptylbenzoylamino)-4,8-dihydroxy- (I) and 1,5-*bis*-(4-heptylbenzoylamino)-4,8-bis(4-heptylbenzoyloxy)anthraquinones (II) have comparatively low order parameters (Table I) and absorb at 562–600 nm and 468 nm respectively (Fig. 1). This may probably be explained by the existence of an angle slightly less than 90° between the charge transfer band oscillator and the long geometrical axis due to electronic asymmetry. 1.5-*Bis*-(4-heptylbenzoylamino)anthraquinone (XII: $S = -0.13$ at $\lambda_{max} = 458$ nm), 1, 8-*bis*-(4-octylbenzoylamino)anthraquinone (XIII: $S = -0.13$ at $\lambda_{max} = 482$ nm), and 1-(4-pentylbenzoylamino)-4-(4-methoxyanilino)-8-nitro-5-hydroxyanthraquinone (XIV: $S = -0.05$ at $\lambda_{max} = 642$ nm) (the two latter compounds were obtained by Japanese scientists) have still lower order parameters in liquid crystal media for the same reasons.



XII



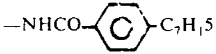
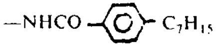
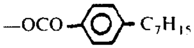
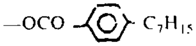
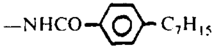
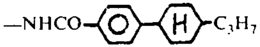
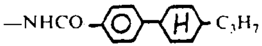
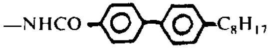
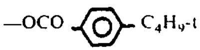
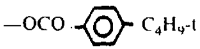
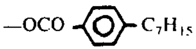
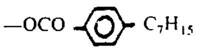
XIII



XIV

Derivatives of 1,8-diamino-4,5-dihydroxyanthraquinone (III–XI) give absorption bands (Fig. 2), which depend on the degree of acylation, at 560–600 nm (III–VI), 535–540 nm (VII, VIII) or 467–

TABLE I

| Compound | 1-Substituent | 4-Substituent | 5-Substituent | 8-Substituent | λmax, nm | *S* |
|---|---|---|---|---|---|---|
| I |  | —OH |  | —OH | 562; 600 | − 0.18; − 0.18 |
| II |  |  |  |  | 468 | − 0.27 |
| III |  | —OH | —OH |  | 560; 600 | − 0.32; − 0.32 |
| IV |  | —OH | —OH |  | 562; 600 | − 0.34; − 0.35 |
| V |  | —OH | —OH |  | 560; 600 | − 0.34; − 0.34 |
| VI |  | —OH | —OH |  | 560; 600 | − 0.34; − 0.34 |
| VII |  |  | —OH |  | 540 | − 0.3 |
| VIII |  |  | —OH |  | 535 | − 0.35 |
| IX |  |  |  |  | 467 | − 0.33 |
| X |  |  |  |  | 470 | − 0.36 |
| XI |  | —OCO—$C_4H_9$ | —OCO—$C_4H_9$ |  | 471 | − 0.33 |
| XII |  | —H |  | —H | 458 | − 0.13 |

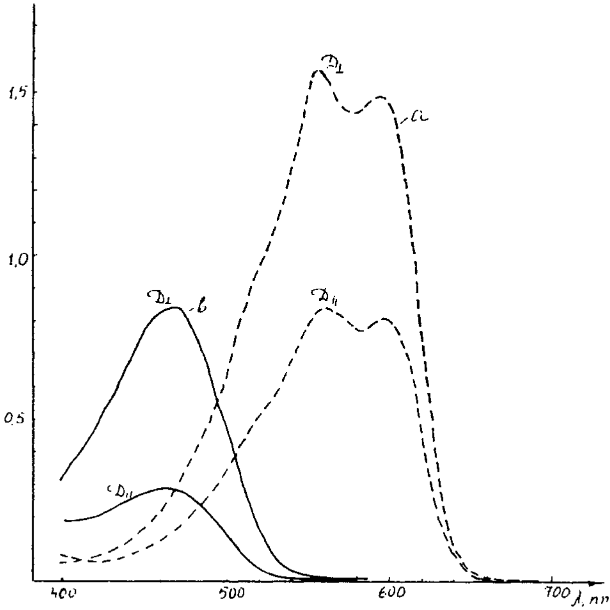


FIGURE 1 Polarization spectra obtained using solutions of derivatives of 1,5-diamino-4,8-dihydroxyanthraquinone in ZK-807: *a*—I *B*—II

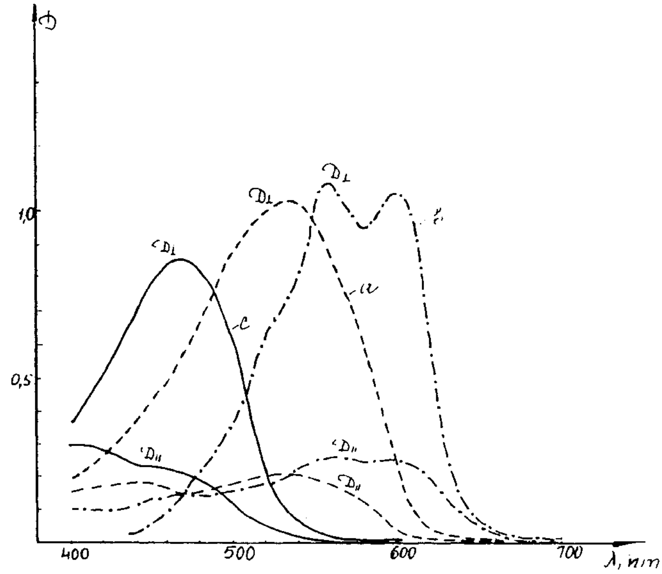
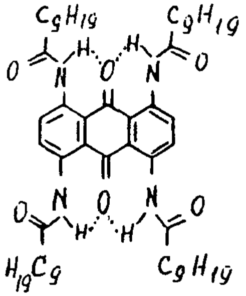


FIGURE 2 Polarization spectra obtained using solutions of derivatives of 1,8-diamino-4,5-dihydroxyanthraquinones in ZK-807: *a*—IV *b*—VIII *c*—X

471 nm (IX–XI); like 1,4,5,8-tetra(decanoylamino)anthraquinone (XV: $S = -0.33$ at $\lambda_{max} = 543$ nm),[3] they have higher order parameters ($S = -0.30$ to $-0.36$).



XV

In conclusion it should be noted that the value of the order parameter for the range of dichroic dyes III–XI and XV changes insignificantly despite the range of different acyl fragments: 4-alkylbenzoyl (III, IV, VII–X), 4-(*trans*-4-alkylcyclohexyl)benzoyl (V), 4-(4-alkylphenyl)benzoyl (VI) and finally alkanoyl (XV) or 4-alkylbenzoyl and alkanoyl (XI).

## References

1. A. V. Ivashchenko, V. T. Lazareva, E. K. Prudnikova, V. G. Rumyantsev, and V. V. Titov, *Mol. Cryst. Liq. Cryst.*, these proceedings.
2. L. M. Blinov, V. A. Kizel, V. G. Rumyantsev, and V. V. Titov, *J. Phys. (Paris)* **36**, 69 (1975).
3. Japanese Patent 006329 (1982).