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A. Ivashchenko^a, V. Lazareva^a, E. Prudnikova^a, V.

Rumyantsev^a & V. Titov^a

^a Organic Intermediates & Dyes Institute, Moscow, 103787, USSR

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High Soluble Anthraquinone *T*-Type Dichroic Dyes

A. IVASHCHENKO, V. LAZAREVA, E. PRUDNIKOVA, V. RUMYANTSEV and V. TITOV

Organic Intermediates & Dyes Institute, Moscow 103787, USSR

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Dichroic dyes of negative dichroism of the anthraquinone series have been developed. The dyes possess increased solubility in liquid crystalline matrices and are applicable in guest host displays. The high solubility of the dyes is ensured by presence of alkyl groups in β -positions of anthraquinone and depends both on the substituents in anthraquinone positions 1,4,5,8 and on the LC matrix type.

Keywords: dichroic dyes, anthraquinone, high solubility

INTRODUCTION

To obtain liquid crystal displays (LCD) with a good contrast of the coloured image using guest host effect, it is essential to have dichroic dyes (DD) with high solubility in liquid crystals (LC). We have found that solubility of anthraquinone dyes exhibiting negative dichroism in LC (*T*-type, $S < 0$) increases drastically with introduction of lateral alkyl substituents in the anthraquinone fragment.

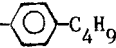

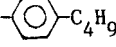
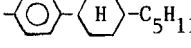
Starting from 2-alkyl-(1a) and 2,7-dialkyl-4,5-diamino-1,8-dihydroxy-anthraquinones (1b) and acyl chlorides, we have synthesized anthraquinone DD of *T*-type II–XIV (1) exhibiting good negative dichroism ($S = -0.30$ to -0.39) and a higher solubility in LC.

Tables I–III contain long-wave absorption maxima (λ , nm), values of negative dichroism (S) and maximal solubility at the ambient temperature (C , %) of some obtained DD in the liquid crystalline mixture ZK-807 comprising alkyl- and alkoxy-cyanobiphenyls and Hoffman-La Roche mixture 3010.

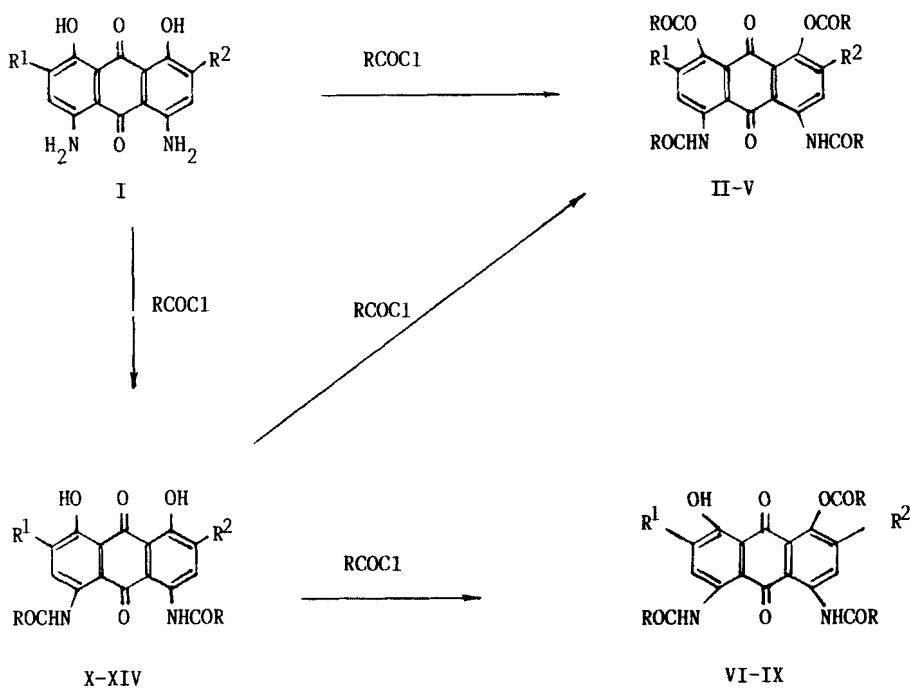
RESULTS AND DISCUSSION

The total acylation of anthraquinones I leads to II–V (Table I) with $\lambda_{\max} = 465$ to 470 nm, a high value of negative dichroism (S is equal to -0.39) and a high solubility at the ambient temperature (C is equal up to 11%). As can be seen from Table I, the solubility of DD depends to a great extent on the nature of the LC

TABLE I
Properties of anthraquinone dichroic dyes II-V

| Comp. N° | R | R ¹ | R ² | $\lambda_{\max}, \text{nm}$ | S | C _{max} , % | LC |
|-------------|---|--------------------------------|--------------------------------|-----------------------------|-------|----------------------|--------|
| II |  | -CH ₃ | -H | 465 | -0.34 | 5 | ZK-807 |
| | | | | | | 1.04 | 3010 |
| III |  | -CH ₃ | -H | 468 | -0.36 | 5.7 | ZK-807 |
| | | | | | | 0.76 | 3010 |
| IV |  | -C ₄ H ₉ | -C ₄ H ₉ | 468 | -0.32 | 9.0 | ZK-807 |
| | | | | | | 0.76 | 3010 |
| V |  | -C ₄ H ₉ | -C ₄ H ₉ | 466 | -0.38 | 11 | ZK-807 |
| | | | | | -0.39 | 5.0 | 3010 |

in which the DD is dissolved. Thus, for example DD II in ZK-807 is 5 times more soluble than in 3010 mixture, while DD IV and V are twice more soluble.



I-XIV: R' = C_nH_{2n+1}, n=1-8; R²=H or R'.


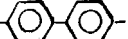

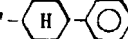
II-XIV: R=R', R'-, R'-, R'-, R'-.

TABLE II
Properties of anthraquinone dichroic dyes VI–IX

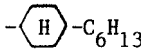

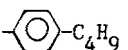
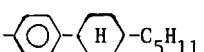
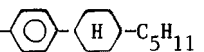
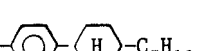
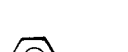
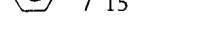
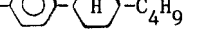
| Comp. No | R | R ¹ | R ² | λ_{\max} nm | S | C _{max} , % | LC |
|-------------|---|--------------------------------|--------------------------------|---------------------|----------------|----------------------|----------------|
| VI |  -C ₆ H ₁₃ | -CH ₃ | -H | 530 536 | -0.33 -0.32 | 1.5 0.7 | ZK-807 3010 |
| VII |  -C ₅ H ₁₁ | -CH ₃ | -H | 540 | -0.38 | 1.9 1.16 | ZK-807 3010 |
| VIII |  -C ₄ H ₉ | -C ₄ H ₉ | -C ₄ H ₉ | 534 | -0.31 | 2.7 0.7 | ZK-807 3010 |
| IX |  -C ₅ H ₁₁ | -C ₄ H ₉ | -C ₄ H ₉ | 540 | -0.38 | 5.8 4.8 | ZK-807 3010 |

TABLE III
Properties of anthraquinone dichroic dyes X–XIV

| Comp. | R | R ¹ | R ² | λ_{\max} nm | S | C _{max} , % | LC |
|-------|---|--------------------------------|--------------------------------|---------------------|----------------|----------------------|----------------|
| X |  -C ₅ H ₁₁ | -CH ₃ | -H | 562 603 | -0.33 -0.33 | 0.5 1.0 | ZK-807 3010 |
| XI |  -C ₅ H ₁₁ | -C ₄ H ₉ | -H | 562 604 | -0.33 -0.33 | 0.7 | 3010 |
| XII |  -C ₇ H ₁₅ | -C ₄ H ₉ | -C ₄ H ₉ | 562 604 | -0.24 -0.24 | 0.2 | ZK-807 |
| XIII |  -C ₄ H ₉ | -C ₄ H ₉ | -C ₄ H ₉ | 566 608 | -0.34 -0.34 | 0.7 0.7 | ZK-807 3010 |
| XIV |  -C ₅ H ₁₁ | -C ₄ H ₉ | -C ₄ H ₉ | 560 604 | -0.32 -0.34 | 0.5 0.21 | ZK-807 3010 |

Introduction of three aryl fragments in the anthraquinone I molecule leads to DD VI–IX (Table II) with λ_{\max} = 530 to 540 nm and S = -0.31 to -0.38. The maximum solubility of this series of DD is somewhat lower than that of DD II–V.

DD X–XIV (Table III) with two free hydroxy groups have λ_{\max} = 560 to 608 nm and S = -0.32 to -0.34. The maximum solubility does not exceed 1% but in any case it is considerably higher than that of the analogues containing no lateral alkyl substituents (C 0.03%).

CONCLUSION

Due to a great value of negative dichroism and a good solubility in liquid crystals, the synthesized dichroic dyes allow to compose liquid crystalline materials for LCD using the guest host effect.

References

1. A. V. Ivashchenko, V. T. Lazareva, E. K. Prudnikova and V. G. Rumyantsev, PCT WO 88/03158 (1988).