Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

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To cite this article: A. V. Ivashchenko , O. S. Petrova & V. V. Titov (1984): Heteroaromatic Azo Dyes Exhibiting Negative Dichroism in Liquid Crystals, Molecular Crystals and Liquid Crystals, 108:1-2, 51-60

To link to this article: http://dx.doi.org/10.1080/00268948408072097

Mol. Cryst. Liq. Cryst., 1984, Vol. 108, pp. 51–60
0026-8941/84/1082-0051/$18.50/0

Printed in the United States of America

Heteroaromatic Azo Dyes Exhibiting Negative Dichroism in Liquid Crystals

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(*Received December 21, 1983*)

Scientists working in the field of liquid crystals have become increasingly interested in the practical applications of dichroic dyes dissolved in liquid crystal matrices. This interest is due to a number of factors. Firstly an improved contrast of an image can be achieved in displays using this "guest-host" effect in comparison with displays solely using field effects or the "cholesteric-nematic" transition. Furthermore, utilization of dichroic dyes makes it possible to manufacture multi-coloured displays which do not require polarizers. This advance is a result of recent progress made in "quick-response" liquid crystalline materials and dichroic dyes with high order parameters in liquid crystal matrices.

INTRODUCTION

The principal criterion of dichroic dye effectiveness is the order parameter (S_{DD}) of the electron transition oscillator, responsible for the colour of a dichroic dye, with respect to the director of the liquid crystal in which the dye is dissolved. It must be taken into account that the order parameter (S_{DD}) can be different from the geometric ordering ($S_{\mathrm{DD}}^{\mathrm{G}}$) of dichroic dye molecules in a liquid crystalline matrix. This is the case when the electron transition oscillator and the longest geometrical axis of a dichroic dye molecule are at an angle β to each other (Figure 1).

Analogously to the liquid crystal order parameter (S_{LC}) determined[1] from equation (1), the order parameter (S_{DD}) can be calculated from equation (2) or determined experimentally using equa-

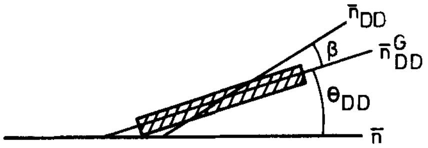


FIGURE 1 Deviation of dichroic dye geometric axis ($\bar{n}^{G}_{DD}$) and oscillator of electron transition ($\bar{n}_{DD}$) from liquid crystal director ($\bar{n}$).

tion (3)[2,3]:

$$S_{LC} = \tfrac{1}{2}\left(3\,\overline{\cos^2\theta_{LC}} - 1\right) \tag{1}$$

$$S_{DD} = \tfrac{1}{2}\left(3\,\overline{\cos^2\theta_{DD}} - 1\right) \tag{2}$$

$$S_{DD} = \frac{D_{\parallel} - D_{\perp}}{D_{\parallel} + 2D_{\perp}} \tag{3}$$

where $D_{\parallel}$ and $D_{\perp}$ are the optical densities of a dichroic dye dissolved in a liquid crystal matrix measured parallel and perpendicular to the liquid crystal director.

Equation (2) only holds for dichroic dyes where $\beta = 0°$ or $\beta = 90°$. The dependence of the order parameter (S_{DD}) on an angle θ_{DD} is presented in Figures 2a and 2b. This dependence of the order parameter (S_{DD}) on the angle β, where $\theta_{DD} = 0°$ is shown in Figure 2c. This can be seen to be identical with the dependence of the order parameter (S_{DD}) on the angle θ_{DD} when $\beta = 0°$ (Figure 2a). As Figure 2c shows, the order parameter S_{DD} decreases with increasing β, and the order parameter S_{DD} is greater than zero if the following conditions are fulfilled:

$$0° \leq \beta < 54°44'8''$$

These types of dye are classified as positive dichroic dyes. Dichroic

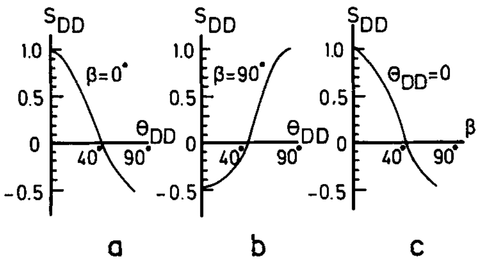


FIGURE 2 Dependences of dichroic dye order parameter on angles θ_{DD} and β.

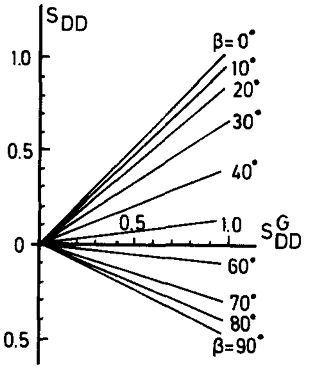


FIGURE 3 Dependence of dichroic dye geometric ordering (S^G_{DD}) in liquid crystals on order parameter of electron transition oscillator (S_{DD}) of the dye at different angles β.

dyes are said to have a negative dichroism when the order parameter (S_{DD}) is less than zero:

$$54°44'8'' < \beta \leq 90°$$

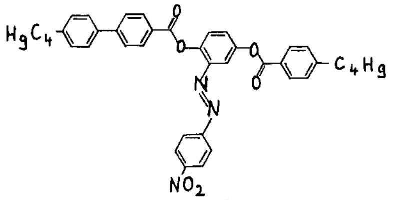
Moreover, there are also dyes having an order parameter (S_{DD}) equal to zero ($\beta = 54°44'8''$ at $\theta = 0°$; $\theta = 54°44'8''$ at $\beta = 0°$ or $\beta = 90°$). These dyes are called background dyes, i.e., they behave isotropically ($D_\parallel$ and $D_\perp$ are equal).

A more accurate determination of the geometrical order parameter of a dichroic dye can be calculated using[4,5] equation (4):

$$S^G_{DD} = \frac{D_\parallel - D_\perp}{D_\parallel + 2D_\perp} * \frac{1}{1 - \frac{3}{2}\sin^2\beta} = \frac{S_{DD}}{1 - \frac{3}{2}\sin^2\beta}$$

The ratio of S_{DD} to S^G_{DD} as a function of the angle β is presented in Figure 3. If $\beta = 0°$, the order parameter (S_{DD}) is equal to the geometrical order parameter (S^G_{DD}); at $\beta = 90°$ the order parameter (S_{DD}) is equal to $-1/2(S^G_{DD})$. The greatest difference between the order parameters (S_{DD}) and (S^G_{DD}) is observed near the "magic angle" ($\beta = 54°44'8''$).

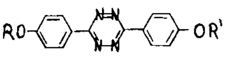
In this region the geometrical order parameter (S^G_{DD}) is greater than the order parameter (S_{DD}). This fact may be demonstrated using the example of compound (I) for which we have found[6,7] the order parameter (S_{DD}) to be equal to -0.11.



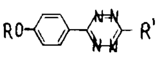
I

By using the bond lengths and valency angles for compound (I), the angle β calculated is 60°. Using equation (4), it is now easy to calculate the geometrical order parameter ($S^{\mathrm{G}}_{\mathrm{DD}}$) which equals 0.88. Supposing however that the angle β is not equal to 60° in compound (I), but that it is 59.5°, 61° or even 62°; then the geometrical order parameter ($S^{\mathrm{G}}_{\mathrm{DD}}$) is respectively 0.965, 0.748 or 0.6151.

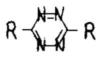
Tetrazines (II–IV) have been reported[8] as the first dyes possessing a negative dichroism ($S_{\mathrm{DD}} < 0$; $D_{\mathrm{a}} = D_{\parallel} - D_{\perp} < 0$). Of specific interest is the absorption band at 550 nm caused by a n–π^* transition with $\beta = 90°$.



II



III



IV

(with R, R′ = n-alkyl)

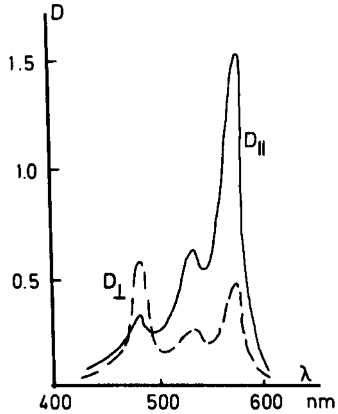
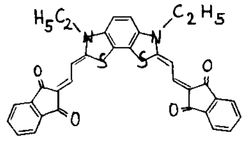


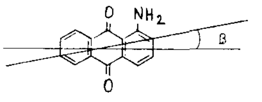
FIGURE 4 Polarization of bismerocyanine (V) absorption bands in MBBA.

Certain dyes, e.g. bismerocyanine (V), have two absorption bands (Figure 4) caused by electron transitions with a perpendicular arrangement of the oscillators.[9]

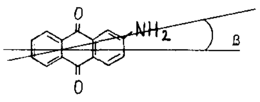


V

If a dichroic dye structure has a structure similar to a liquid crystal and $\beta = 0°$, the order parameter of the dye is equal to that of the liquid crystal, i.e. the order parameter (S_{DD}) is equal to the order parameter (S_{LC}).[10] Typical examples are 1-aminoanthraquinone (VI) and 2-aminoanthraquinone (VII).[11,12]

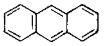


VI

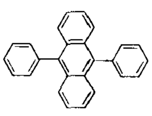


VII

These observations lead us to the conclusion that not only the order parameter (S_{DD}), but also its sign can be changed by altering the structure of a dye without considerable modification of its conjugated system. This can be shown by the following examples. It is known that the long-wave absorption band of anthracene (VIII) has an order parameter (S_{DD}) equal to 0.51. The same band in 9,10-diphenylanthracene (IX), however, has an order parameter (S_{DD}) of -0.17.[13]



VIII



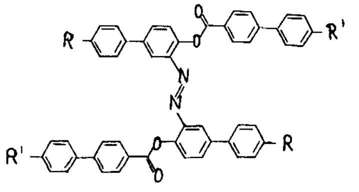
IX

The same effect is observed in the case of azobenzenes which usually exhibit a positive dichroism.[14] We have however synthesized azobenzenes[6,7] with a negative dichroism, e.g., compound (I).

A review of the above data has allowed us to realise a new approach to the design of dichroic dyes. The essence of such an approach consists in the concept that a dichroic dye may include one or several blocks with separate chromophore systems whose oscillators have strictly defined directions. These dyes ought to have a structure which allows them to orient themselves to a high degree in a liquid crystal matrix.

This approach is very effective in the search for dyes with a negative dichroism and having absorption bands of opposite dichroism. It is our own opinion that, before the synthesis of a new dichroic dye is carried out, it is necessary to analyse the structure of the dye, taking into account the linkage lengths, the valency angles and the direction of the oscillator of the long-wave electron transition, in order to evaluate the maximum theoretical order parameter (S_{DD}) where $\theta_{DD} = 0°$.

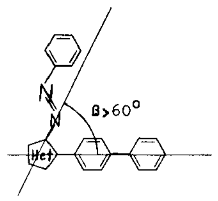
As a result, the dye can be either synthesized or the design rejected. Should the dye design be rejected, a further design is necessary with a higher theoretical order parameter (S_{DD}). One example is compound (X) ($\beta = 60°$, $S_{DD} = -0.11$). The calculation results in a low theoretical order parameter (S_{DD}) in spite of its possibly high geometric order parameter (S^{G}_{DD}).



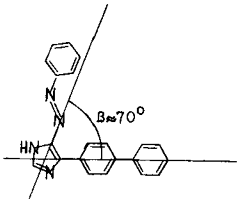
(R, R′ = *n*-Alkyl)

X

By applying the valency angles and linkage lengths for substituted azo compounds containing a five membered heterocycle, e.g. compound (XI), we found the prospect of their having a negative dichroism to be very likely, the angle β being about 60°. In the case of the 5-arylazoimidazole (XII), the angle $\beta \approx 70°$ corresponding to an order parameter (S_{DD}) of -0.325, where the geometric order parameter S^{G}_{DD} is equal to 1.

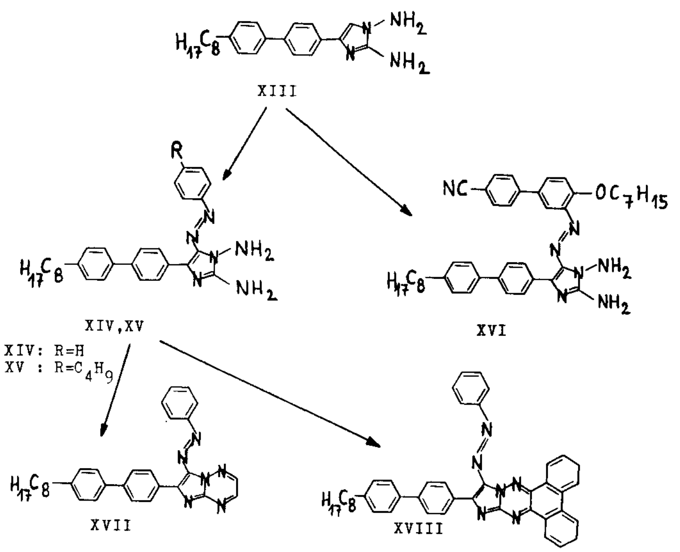


XI



XII

To confirm the validity of such an approach we synthesized the azo dyes (XIV–XVIII, XX and XXI) (Tables I, II) using the following schemes:



XIII

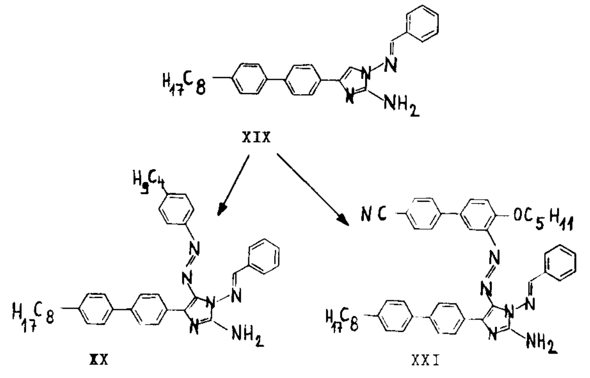
XIV,XV

XIV: R=H
XV : R=C_4H_9

XVI

XVII

XVIII



XIX

XX

XXI

TABLE I

Elemental analysis and melting points of synthesized compounds

Compounds	Found [%] C	H	N	Formula	Calculated [%] C	H	N	Mp. [degr. C]
XIV	74.9	7.1	18.0	$C_{29}H_{34}N_6$	74.7	7.3	18.0	224–226
XV	78.0	8.1	15.9	$C_{33}H_{42}N_6$	75.9	8.0	16.1	140–142
XVI	76.0	7.7	14.3	$C_{43}H_{51}N_7O$	75.8	7.5	14.4	177–180
XVII	76.3	6.4	17.3	$C_{31}H_{32}N_6$	76.2	6.6	17.2	180–182
XVIII	81.0	6.2	12.8	$C_{43}H_{38}N_6$	80.9	6.0	13.1	222–223
XX	78.7	7.3	14.0	$C_{40}H_{46}N_6$	78.7	7.5	13.8	147–148
XXI	77.9	6.8	13.3	$C_{48}H_{51}N_7O$	77.7	6.6	13.2	207–210

TABLE II

Order parameter of dichroic dyes

Compound	XIV	XV	XVI	XVII	XVIII	XX	XXI
S	−0.18	−0.19	−0.30	0	−0.05	−0.20	−0.30
nm	476	482	500	413	414	476	496

EXPERIMENTAL

1,2-Diamino (XIII) and 2-amino-1-benzylideneamino-4-(4′-octyl-biphenylyl-4)-imidazole (XIX) were produced as described by A. V. Ivashchenko *et al.*[16] The azo dyes (XIV–XVI, XX, XXI) were synthesized by coupling the compounds (XIII) and (XIX) with the corresponding diazonium chlorides.[17] The phenylazotriazines (XVII and XVIII) were obtained by condensation of the azo compound (XIV, R = H) with glyoxal and phenanthraquinone respectively.[16]

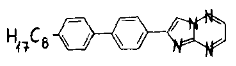
Polarized spectra of the dichroic dyes under investigation were determined using a method described by L. M. Blinov *et al.*[18] The host was a liquid crystalline mixture of 4-alkoxy- and 4-alkyl-4′-cyano-biphenyls having a clearing point of 60 °C.

DISCUSSION

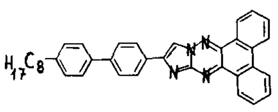
The arylazoimidazoles (XIV, XV and XX) have absorption bands at 476–482 nm and order parameters of −0.18 to −0.2 (Table II). These order parameters considerably surpass the order parameter determined for the azo compound (I). This appears to be due to the greater angle

β of the compounds in comparison with the angle β for compound (I). By assuming the angle β to be 70° for the compounds (XIV, XV and XX), it is possible to calculate, using equation (4), a geometric order parameter (S^{G}_{DD}) of 0.60 for these compounds. The azo dyes (XVI and XXI) exhibit an even greater degree of geometric ordering ($S_{DD} = -0.3$, $S^{G}_{DD} = 0.92$, where $\beta = 70°$).

Unexpected results have been obtained in experiments with the phenylazoimidazolazines (XVII and XVIII). We supposed that a higher geometric anisotropy of these compounds in comparison with the compound (XIV) would elicit an increase in the negative dichroism. It appeared however, that the order parameter (S_{DD}) of the compound (XVII) was equal to 0 at $\lambda = 413$ nm and the order parameter (S_{DD}) of the compound (XVIII) was -0.05 at $\lambda = 414$ nm and $+0.50$ at $\lambda = 513$ nm. Taking into account that the imidazotriazine (XXII) has an order parameter of 0.78 at $\lambda = 410$ nm and that the imidazotriazine (XXIII) has an order parameter (S_{DD}) of 0.49 at $\lambda = 475$ nm and 0.50 at $\lambda = 500$ nm,[16] a low negative dichroism of the compounds (XVII) and (XVIII) may be explained by the presence of the absorption bands caused by the azo group and the imidazotriazine fragment exhibiting the opposite dichroism.



XXII



XXIII

Thus we have demonstrated that it is necessary to consider the valency angles and linkage lengths when designing dichroic dyes. Furthermore we have shown that an arylazoimidazole fragment is useful for dyes with a negative dichroism.

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