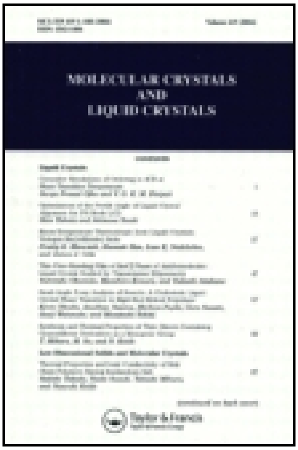

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Influence of the Molecular Structure on the Photoanisotropic Properties of Azodyes

Elena K. Prudnikova [a], Galina N. Dorozhkina [a], Nikolai V. Novoseletskii [a], Sofia I. Torgova [a] & Boris A. Umanskii [a]

[a] SSC RF "NIOPIK" (Organic Intermediates & Dyes Institute), B. Sadovaya 1/4, Moscow, 103787, Russia

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Influence of the Molecular Structure on the Photoanisotropic Properties of Azodyes

ELENA K. PRUDNIKOVA, GALINA N. DOROZHKINA,
NIKOLAI V. NOVOSELETSKII, SOFIA I. TORGOVA
and BORIS A. UMANSKII

SSC RF "NIOPIK" (Organic Intermediates & Dyes Institute), B.Sadovaya 1/4, Moscow 103787, Russia

The influence of azo-dye molecular structure, especially of the terminal substituents on the photo-induced anisotropic properties of their films was investigated. In order to avoid the solubility of azo-dyes in liquid crystals (LC), their sodium salts were synthesised. The photoinduced anisotropic properties were studied both as individual substances and as mixtures with polyamide acid (PAA). The pretilt angles of nematic liquid crystals oriented by photoanisotropic films of azo-dye with PAA were measured.

Keywords: azo-dyes; molecular structure; liquid crystals; photoanisotropy

INTRODUCTION

The photoanisotropic properties of dichroic dyes (DD) used for aligning nematic liquid crystals are under intensive study during several years[1-3]. For the study of photooptical processes mostly different dichroic dyes are used: the derivatives of azobenzene, spiropyrane, stilbene[4]. The most popular are azodyes. It is well known, that their illumination by UV light leads to cis-trans isomerisation. This isomerisation is one of the possible explanation of photoinduced anisotropy effect[5]. The application of DD as orienting layers for LC requires some special conditions:

1. The presence of photoinduced anisotropy.
2. The insolubility of DD in LC.

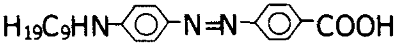
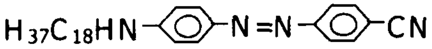
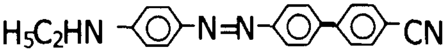
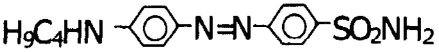
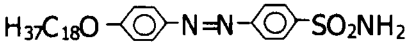
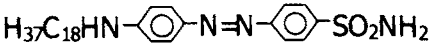
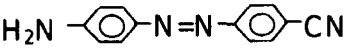
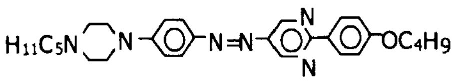
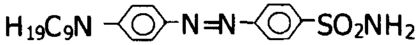
We would like to underline, that the presence of terminal alkyl substituents in the molecule of DD is necessary for providing the optimal pretilt angle[2-7].

The aim of the present study is the investigation of the dependence of the azo-dyes photoanisotropic properties and orienting ability on their molecular structure.

EXPERIMENT

We have synthesised some azo-dyes with different terminal substituents (Table 1), using common methods[8].

TABLE 1 Structure and photoanisotropic properties of azo-dyes

NN	Structure formula	λ_{max}* nm	S' (DD)
I		450	0.1
II		445	0.2
III		439	0.01
IV		440	0.30
V		430	-
VI		440	0.05
VII		455	0.01
VIII		450	0.05
IX**		430	0.5

* λ_{max} - Maximum absorption wavelength of dye molecules.
** The order parameter S' (degree of orientation) of this DD was measured by authors[2].

Thin (100 - 150 nm) films of single azodye or polymer - azodye compositions were prepared by spin -coating technique; the glass plates were covered by ITO. We used the well known method of "double illumination"[9] for the photooriented films preparation: thin layers were exposed by polarised (first stage) and nonpolarised (second stage) light. In order to orient the layers the empty cell was exposed to 250 W high-pressure mercury lamp radiation.

The commercially available (produced by SSC RF NIOPIK) nematic liquid crystals ZhKM-1630 and ZhKM-3141 were used in the test of alignment properties of photooriented layers.

In order to compare the orienting ability of different azo-dyes the degree of orientation (S') were calculated as follows: $S'=A_{//}-A_{\perp}/A_{//}+2A_{\perp}$, where A is the absorbance of oriented layers or nematic LC.

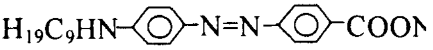
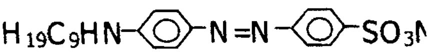
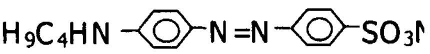
For avoiding the solubility of DD in LC the insoluble salts X - XII (Table 2) were synthesised.

RESULTS AND DISCUSSION

As one can see from Table 1, the compounds 4-(N-alkylamino)-4'-sulfoamidoazobenzene derivatives (II, IV, IX) and 4-(N-alkylamino)-4'-azobenzoic acid (I) possess the best photoanisotropic properties. Among them the best one is the dye (IX) with alkyl substituent C_9H_{19}.

For further investigations we have chosen the dyes with maximum value of photoinduced anisotropy (I, IV, IX). The photoanisotropic properties of sodium salts (Table 2) are worse than ones of the corresponding acid and sulphoamides (compounds I and X, IV and XII, IX and XI).

TABLE 2 Orientation ability of sodium salts of the azo-dyes

NN	DD	S' (DD)	LC orientation
X		- partial soluble	-
XI		0.01	homeotropic
XII		-	homeotropic

As it was expected[3-6], thin films of individual dyes (XI-XII) provide only homeotropic orientation due to long hydrophobic alkyl tails. In order to decrease the influence of the tails the dye (XI) was introduced into the polymeric matrix.

As polymeric matrix polyamidoacid (PAA) was used. The concentration of the dye in PAA was varied from 0 till 100%. The dependence of ZhKM-1630 degree of orientation on the concentration is shown in the Table 3.

As we expected, the polymeric matrix decreases the influence of the terminal alkyl tails. The best planar orientation was observed for dye concentration 20-25%. The homeotropic orientation appeared starting from dye concentration 50%.

TABLE 3 The dependence of ZhKM-1630 and ZhKM-3141 degree of orientation on the concentration of the dye XI in PAA.

Concentration Azodye XI in PAA	S' ZhKM-1630	S' ZhKM-3141
20	0.74	0.63
25	0.71	0.62
30	0.70	0.61

For comparison we have performed the same measurements for ZhKM-3141 at the concentration 20% of the dye XI in the polymeric matrix (compare S'=0.74 for ZhKM-1630 and S'=0.63 forZhKM-3141). The degree of orientation of ZhKM-3141 is less than the one of ZhKM-1630. This decreasing is possible due to the lateral positions of the polar substituents in the molecules of the substances composing ZhKM-3141 and to the complicate interaction with the composite film.

As it is known from the literature[6] the pretilt angle obtained by rubbing of polymer films depends on the presence and on the length of alkyl side-chains of polymer. We have studied the influence of the length of the terminal alkyl chain of dye molecules on the value of LC pretilt angle. We obtained for LC oriented by film containing 25% of dye XI in PAA the data reported in (Table 4).

TABLE 4 The dependence of the pretilt angle of ZhKM-1630 on the exposure time.

τ exposure (s)	Pretilt angle (°)
0	-
10	6.3
20	7
50	6
120	6

The best pretilt angles were obtained for compound XI, where alkyl chain is C_9H_{19}. Under the same conditions with dye XII the pretilt angle is absent, due to the short length of the terminal alkyl chain ($-C_4H_9$).

This is in agreement with the data obtained by authors[6,7] for different orienting films.

CONCLUSION

We have investigated the dependence of the photoinduced anisotropic properties on the structure of the dyes in films of both individual azo-dyes and their mixtures with polyamide acid.

It was shown that among the compounds investigated sulfoamidoazobenzenes with N-alkyl terminal substituents exhibit the best photoinduced anisotropy. The most efficient results were obtained on the azo-dye with terminal substituent $-C_9H_{19}$.

The best alignment of LC with pretilt angle about 6° - 7° was obtained with the films containing 20-30% of the dye XI in polyamide acid.

Acknowledgments

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