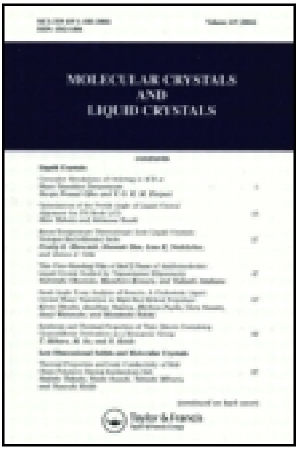

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Influence of Chemical Structure on the Aligning Power of Photo-Oriented Films

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Influence of Chemical Structure on the Aligning Power of Photo-Oriented Films

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The orienting ability of different azo-dyes has been investigated in films organized by individual dyes or by mixtures of a dye either with polyamide acid or with a specially synthesized dopant based on phenylquinoxalinone as well[1]. It was shown that the replacement of the functional group in the azo-dye molecules plays a very important role in the appearance or disappearance of the photo-anisotropy. The orienting films always were prepared using the spin-coating technique. Sometimes, the appearance of either planar or homeotropic orientation was dependent only on the solvent used during the spin-coating procedure. In all cases there was a good correlation between the arising of planar alignment and the existence of hydrogen bonds. We would like to underline that hydrogen bonding plays a very important role not only in the formation of mesophase[2], but also in the interactions at the surface.

Keywords: chemical structure; azo-dyes; alignment; liquid crystals; photo-anisotropy; hydrogen bonding

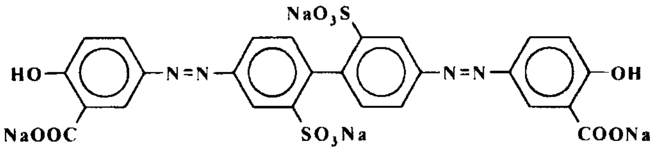
INTRODUCTION

The proper orientation of liquid crystals in a cell is a prerequisite condition for the correct performance of any liquid crystalline device. The aligning methods without rubbing were intensively investigated during the last years, due to the reason that they have many advantages. The photo-induced orientation is the most promising among the contactless methods[3-5]. It gives the most successful repeatability of the liquid crystal alignment. Recently this method was extended to the area of the pretilt angle generation of liquid crystals in the bulk[6]. The azo-dyes with linear structure[7-9] often are used as agents for photo-induced orientation. Several mechanisms of the photo-orientation effect have been proposed. The most popular among them is *trans-cis* isomerization under UV-light[10]. But no one of these mechanisms can explain the fact that p-alkylamino-substituted derivative of azo-dye shows the photo-anisotropic effect, but the substitution of alkylamino-group with alkyloxy-group in the same azo-dye leads to the disappearance of the effect[8].

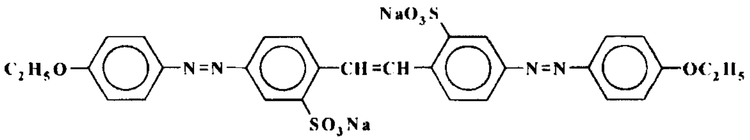
In this work we deal with the development of the photoinduced anisotropic films for planar and inclined nematic liquid crystal (LC) alignment. It should be stressed that there exist two aspects of the alignment uniformity: the homogeneity of nematic LC molecules orientation and the predetermination of a certain value of the pretilt angle. To obtain the desirable nematic LC alignment by the anisotropic films, one needs to choose:

a) the molecular design of azo-dye;
b) the correct preparation of orienting film;
c) the proper solvent for spin-coating.

In the present work several azo-dyes were investigated (see Figure 1). The substances analysed either were used as individual compounds or were introduced into polyamic acid (PAA) - composition films. A commercially available polyamic acid (code AD-9103) was used.



Dye I



Dye II

FIGURE 1 Chemical formulae of the dyes investigated.

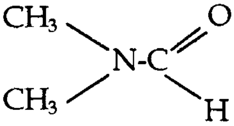
For the preparation of photoinduced anisotropic films we used the well known "bistep" method[11]: the isotropic thin films were exposed to polarised (first stage) and nonpolarised light (second stage).

The main goals of the present work are:

- to investigate the orienting ability of different azo-dyes, both as individual substances and in the mixtures either with polyamic acid, or with a specially synthesized dopant based on phenyl-quinoxalinone as well.
- to investigate the influence of hydrogen bonds on the orienting ability of different azo-dyes.

EXPERIMENT

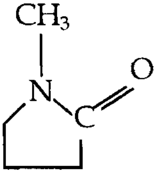
The azo-dyes I and II (see Figure 1) were used as materials for preparation of photo-oriented films. The thin (100 - 150 nm) films of individual azo-dyes or polymer (PAA)- azo-dyes compositions were prepared by spin-coating technique; the cell plates were made of glass with ITO electrodes. To obtain the films of various anisotropic materials we used 1-2% solutions of azo-dyes (I and II) in three different solvents, namely: dimethylformamide (DMF), N-methylpirrolydone (N-MPD) and ethylcellosolve (ECS) - see Figure 2 - and polymer-azodye compositions in DMF. After spin-coating the films were dried at 80°C during 30 min.



DIMETHYLFORMAMIDE

$C_2H_5O\text{-}CH_2\text{-}CH_2\text{-}OH$

ETHYLCELLOSOLVE



N-METHYLPIRROLYDONE

FIGURE 2 Chemical formulae of the solvents used for spin coating.

Two glass plates prepared in such manner were assembled as LC cell with the gap 15 μm. In order to orient the films the empty cell was exposed to 250 W high-pressure mercury lamp radiation. The Glan prism was used to obtain linearly polarised light. We found that the optimal exposure time for the preparation of photoanisotropic films was 15 min at 20-30 mW/cm^2 light intensity (for polarised light).

Before the exposure to nonpolarised light, the cell was cured for 15 min at 160°C. The exposure time for nonpolarised light was 1- 120 s. The cell was filled with LC by capillarity. The commercially available nematic LC material ZhKM-1630 (produced by SSC RF "NIOPIK") was used as sample to be aligned.

The degree of ordering (S') of photo-oriented films and of nematic LC were calculated as follows:
$S' = (A_{\parallel}\ A_{\perp})/(A_{\parallel} + 2\,A_{\perp})$, where $A_{\parallel}$ and $A_{\perp}$ are the absorbances of the dye in the direction parallel and perpendicular, respectively, to the electric field of the polarised light beam - easy axis of the dye orientation (in the case of perfect alignment, S' will coincide with the order parameter S of the dichroic dye).

In order to measure S' of the nematic LC, it was doped (0.2% wt) with a special spectral mark, namely: the dichroic dye KD-184 (also produced by SSC RF "NIOPIK"). The absorption spectrum of this mark (λ_{max}= 530 nm) differs from that of the photoanisotropic materials (λ_{max}= 390 - 400 nm): in particular, the latter spectrum levels off asymptotically for wavelengths λ higher than 500 nm.

The dependences of S', θ on the exposure time were measured. In order to detect the absorbence under polarised light, the UV-VIS spectrophotometer "Spekord-M40" was used. The measurements of the pretilt angle θ were made by means of the common "crystal rotating" technique[17].

RESULTS AND DISCUSSION

On the first stage of the experiment the photosensitive films were exposed to the polarised light. The parameters $A_{\parallel}$, $A_{\perp}$, $\Delta A = A_{\parallel} - A_{\perp}$ and the degree of ordering (S') strictly depend on the exposure time. The maximum value of ΔA was achieved for exposure time $t = 5$ min. A further irradiation led to a small decrease of ΔA. We suppose that this was caused by a small percentage (less than 10% in 20 min) of photodestruction of Dye II.

Nevertheless, as was shown by experiment, the best alignment of nematic LC was obtained by using photo-oriented films which were irradiated during 15 min.

TABLE I Dependence of the degree of ordering S' of the photo-oriented dye film on the nonpolarised light exposure time and on the nature of the solvent used for spin-coating. S' accuracy was calculated as 0.01.

Dye	t (s)	Degree of ordering S'		
		Solvent		
		N-MPD	ECS	DMF
I	0	0.11	0.36	0.22
	10	0.03	0.24	0.09
	20	0.01	0.15	0.06
	60	0.01	0.08	0.04
	120	0.01	0.08	0.01
II	0	0.03	0.11	0.09
	10	0.02	0.09	0.06
	20	0.02	0.06	0.05
	60	0.01	0.03	0.03
	120	0.01	0.01	0.01

Dyes I and II were used for anisotropic films preparation both as individual dyes and as polymer-dye compositions. The latter samples were prepared as 1:1 mutual solutions of the dye in PAA. This concentration was chosen as the optimal one after a preliminary study of the pretilt angle dependence on the dye concentration.

At the second experimental stage both the individual dyes and the composition films were exposed to nonpolarised light.

The results of the experiments are presented in Tables 1-3.

It is evident from Table 1 that in all cases the irradiation by nonpolarised light diminishes the degree of ordering of the photo-oriented dye films. Comparing *S'* of Dye I and Dye II obtained with different solvents, which where used for spin-coating, one can see that the greatest degree of ordering occurs with ECS. This solvent, due to the presence of hydroxyl, is able to form hydrogen bonds with ITO covering a glass plate. Comparing Dye I with Dye II it is easy to see that Dye I has much higher degree of ordering than Dye II before treatment under nonpolarised light: and this happens for all the three solvents. This fact also can be explained in terms of hydrogen bonding. Dye I has two terminal hydroxy substituents and due to this reason it is able to form hydrogen bonds with all of the investigated solvents and with ITO as well. The disordering under nonpolarised light is more dramatic for Dye I. Probably under this condition also the breaking of hydrogen bonds occurs.

As it is shown in Table 2, the nematic LC oriented by the film of Dye I which was irradiated by linearly polarised light has high degree of ordering with all the three solvents, but with solvent N-MPD it is enough to illuminate the film during 10 s with nonpolarised light to delete the orientation. With the two other solvents, the degree of ordering of the nematic LC investigated decreases very slowly, but the pretilt angles are higher with DMF. By using the solvent N-MPD with Dye II (neither one is able to organise hydrogen bonds), we succeeded to obtain pretilt angles only with special dopants based on phenylquinoxalinone[11] (see Figure 3). These dopants have bent molecules and can form hydrogen bonds, due to the presence of free carboxyl moieties.

TABLE 2 Dependence of the degree of ordering S' and of the pretilt angle θ of the LC (ZhKM-1630) on the nonpolarised light exposure time and on the nature of the solvent used for spin-coating. S' accuracy is 0.01, θ accuracy is 0.2°

Dye	*t* (s)	Degree of ordering S'			Pretilt angle θ(°)		
		Solvent			Solvent		
		N-MPD	ECS	DMF	N-MPD	ECS	DMF
I	0	0.79	0.80	0.84	0.0	0.0	0.0
	10	*	0.79	0.73	*	2.2	6.0
	20	*	0.78	0.58	*	3.5	7.0
	60	*	0.77	0.56	*	4.8	7.5
	120	*	0.77	0.55	*	6.0	7.5
II	0	**	0.30	**	**	0.0	**
	10	**	0.30	**	**	0.5	**
	20	**	0.30	**	**	0.8	**
	60	**	0.30	**	**	1.5	**
	120	**	0.30	**	**	2.5	**

*orientation practically absent; ** homeotropic orientation.

Nematic LC, oriented by Dye II with aprotic N-MPD and with DMF gave only homeotropic orientation. We succeeded to obtain planar and inclined orientation of LC only with solvent ECS, which has hydrogen

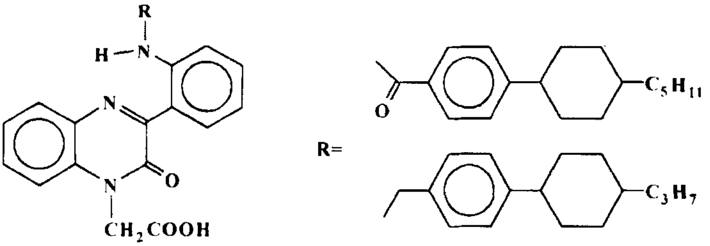


FIGURE 3 Aminophenylquinoxalinone

bonds with the surface, but both degree of ordering and pretilt angle turned out to be smaller than in the case of Dye I. These results are also demonstrating the important role of hydrogen bonding. Nevertheless for complete understanding of the nature of orientation it is necessary to take into account all cooperative interactions in-between ITO, solvent, dye and LC as well. For the investigation of the polymeric matrix influence on the orientation of LC we prepared as aligning layer a composite mixture, containing 50% of PAA and 50% of Dye II. It is necessary to stress that it was impossible to orient individual (pure) PAA by UV-light. DMF was used as a solvent for spin-coating of this composite mixture. The results of such experiment are presented in Table 3.

From Table 3 one can see that the irradiation of orienting film by linearly polarised light leads to planar alignment of nematic LC. On the contrary, with DMF and individual Dye II, it was possible to obtain only homeotropic orientation (see Table 2).

This result can be explained due to the fact that PAA is able to organize hydrogen bonds with the surface. Under the irradiation by nonpolarised light the degree of ordering of the orienting film decreased as usually, whereas the orientation of nematic LC remained homogeneous with high degree of ordering and small pretilt angle.

TABLE 3 Dependence of the degree of ordering *S'*, of the pretilt angle θ of LC (ZhKM-1630) and of the degree of ordering *S'* of the orienting film (50% Dye II and 50% PAA) on the nonpolarised light exposure time. Accuracies as in Table 2.

t (s)	Degree of ordering *S'*		Pretilt angle θ(°)
	Orienting film	Nematic LC	
0	0.14	0.76	0.0
10	0.07	0.75	1.0
20	0.04	0.74	1.8
60	0.03	0.73	2.5
120	0.02	0.73	3.0

CONCLUSION

In this work we demonstrated the strong influence of the chemical structure of azo-dye and of the solvent used for spin-coating on the aligning power of the orienting films, and on the degree of ordering and pretilt angle of NLC as well. The explanation was given in terms of hydrogen bonding, suggesting the necessity to take into account all cooperative interactions in-between ITO, solvent, dye and LC.

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