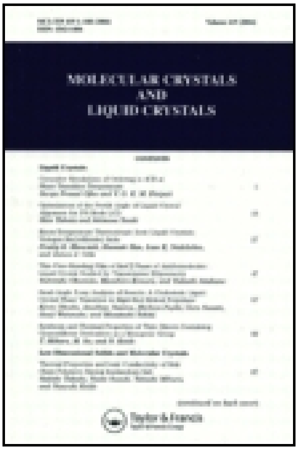

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Formation and Behavior of Monolayers of 3,3'- and 4,4'-Disubstituted Azobenzenes on a Water Surface

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The effect of changes in the molecular structure of 3,3'- and 4,4'-disubstituted azobenzenes, caused by the photoisomerization process, on both, capabilities of these compounds to form monolayers on a water surface and the behavior of their monolayers, are described and discussed. It has been found that their *Z*-isomers form monolayer whereas the *E*-isomers do not. Moreover it has been found also that the peculiar isomerization behavior of 3,3'-disubstituted azobenzenes, whose rodshape form is preserved during the photoisomerization process, result in a different behavior of the monolayers of these compounds from the ones of 4,4'-disubstituted azobenzenes. The bent form of the Z-isomers of 4,4'-disubstituted azobenzenes that favors the interaction of the azo polar group with a water surface has been pointed out as the origin of the remarkable stability of their monolayers. Finally, the results of this study have been successfully used for revealing the mechanism of so-called light-induced anchoring transition of nematics.

Keywords: 3,3'-disubstituted azobenzene; photoisomerization; air/water interface

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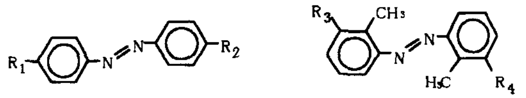
INTRODUCTION

The photofunctionalization of materials incorporating azobenzenes as photoreceptors stems from outstanding transformations of both molecular shape and molecular net dipole moment, due to photoisomerization process [1]. Recently, we have reported that the introduction of alkyl chains at 3- and 3'-positions of the azobenzene results in a peculiar photoisomerization behavior, *i.e.* *E*- and *Z*-isomers maintain the rod shape since the conformers with stretched alkyl chains are thermodynamically the most stable [2, 3]. As a result, nematic liquid crystals doped with a 3,3'-disubstituted azobenzene maintains the mesophase even after *E*-to-Z photoisomerization [2, 3] in contrast with a 4,4'-disubstituted azobenzene that induces nematic to isotropic phase transition upon *E*-to-*Z* photoisomerization [4]. This kind of different photoisomerization behavior of 3,3'- and 4,4'-disubstituted azobenzenes allowed us to evaluate the importance of the molecular shape and the molecular net dipole moment for the flexoelectric properties of liquid crystals [5]. In this work, we report the results of study on the formation and the behavior of monolayers of these azobenzenes on a water surface. The azobenzene monolayer/water surface has been used as a model system of liquid crystal/hydrophilic solid surface that has triggered the light-induced anchoring transition in doped azobenzene guest-host nematic photochromic mixtures [7, 8].

EXPERIMENTAL

Two types of azobenzenes were used in this work for π-A isotherm measurements. The first type of compounds (3,3'-AzoCOOH and 4,4'-AzoCOOH in Figure 1) possess an amphiphilic nature suitable for obtaining information concerning cross-sectional areas of the azobenzenes. Both were prepared in a conventional way starting from the corresponding hydroxyazobenzenes as follows. 3,3'-AzoCOOH was synthesized by the Williamson reaction of 3-hydroxy-3'-hexyloxy-2,2'-dimethylazobenzene with tetrahydropyranyl-6-bromohexanoate in the presence of K_2CO_3 in DMF, followed by acidic hydrolysis. m.p. 141-142 °C. ^{1}H-NMR (200 MHz, $CDCl_3$) δ: 0.92 (t, $J = 6.4$ Hz, 3 H), 1.36-1.92 (m, 14 H), 2.43 (t, $J = 7.3$ Hz, 2 H), 2.61 (s, 6 H), 4.02 (t, $J = 6.6$ Hz, 4 H), 6.88-7.26 (m, 6 H). Anal. Calcd. for $C_{26}H_{36}N_2O_4$; C: 70.87, H: 8.25, N: 6.36 %. Found C: 70.15, H: 8.30, N: 6.16 %. 4,4'-AzoCOOH was prepared in the same way. m.p. 185-186 °C. ^{1}H-NMR (200 MHz, DMSO) δ: 0.88 (t, *J* = 6.6 Hz, 3 H), 1.27-1.80 (m, 14 H), 2.23 (t, *J* = 7.3 Hz, 2 H), 4.05 (t, *J* = 6.5 Hz, 4 H), 7.09 (d, *J* = 9.2 Hz, 4 H). Anal. Calcd. for $C_{24}H_{32}N_2O_4$; C: 69.89, H: 7.83, N: 6.79 %. Found C: 69.88, H: 8.01, N: 6.75 %. The synthesis of 3,3'-Azo and 4,4'-Azo is described in ref [3].

A solution of *E*-isomer of an azobenzene carboxylic acid in a 1:1 (v/v) mixture of THF and chloroform was spread on a water subphase (Milli-Q) filled in a LAUDA FW-II film balance. Chloroform was used as a spreading solution for the azobenzenes (3,3'-Azo, 4,4'-Azo and C6Azo in Figure 1). After the evaporation of the solvents for 10 min, a monolayered film was compressed at a speed of 25 cm^2 min^{-1} and π-A isotherms were taken at 20 °C. The same solution of *E*-isomer was irradiated with 365 nm light to obtain the *Z*-isomer as a predominant component, followed by spreading of the solution on a subphase to record π-A isotherms of the *Z*-isomer. Characterization of floating monolayer was performed by UV-visible absorption spectroscopy (MCPD-2000; Ohtsuka Electronics) and Brewster angle microscopic (BAM) observation (NLE-EMM633; Nippon Laser Electronics).



	R1	R2	R3	R4
4,4'-Azo-COOH	$-O(CH_2)_5COOH$	$-OC_6H_{13}$		
4,4'-Azo	$-OC_6H_{13}$	$-OC_6H_{13}$		
C6Azo	$-C_6H_{13}$	$-C_6H_{13}$		
3,3'-Azo-COOH			$-O(CH_2)_5COOH$	$-OC_6H_{13}$
3,3'-Azo			$-OC_6H_{13}$	$-OC_6H_{13}$

FIGURE 1 Structural formula of azobenzene derivatives.

The deposition of LB films on the solid substrates was done in a LAUDA FW-II system. The film was transferred onto a clean hydrophilic quartz substrate by vertical dipping. The dipping rate was 5 mm min^{-1}. Electronic absorption spectra of the LB films were taken on a JASCO

MAC-1 spectrophotometer.

RESULTS AND DISCUSSION

As seen in Figure 2, the molecular occupied area of *E*-3,3'-AzoCOOH estimated by the extrapolation at a steep rise is *ca.* 0.38 nm^2 and much larger than that of 4,4'-AzoCOOH (*ca.* 0.25 nm^2). This is evidently due to the presence of two *o*-methyl groups of the former. This situation was also supported by UV-vis absorption spectra of floating monolayers of both *E*-isomers at 10 mN m^{-1}. As shown in Table 1, the level of blue shift of λ_{max} of *E*-3,3'-AzoCOOH as a result of H-aggregation in a densely packed monolayer is far less than that of *E*-4,4'-AzoCOOH. BAM observation of floating monolayers indicated that a monolayer of *E*-4,4'-AzoCOOH forms island-sea domain structures, whereas that of the 3,3'-counterpart gives rise to a homogeneous morphology. Consequently, *o*-methyl groups of *E*-3,3'-AzoCOOH suppress effectively the close packing of azobenzene moieties in a floating monolayer even though the stability of the monolayer is quite high.

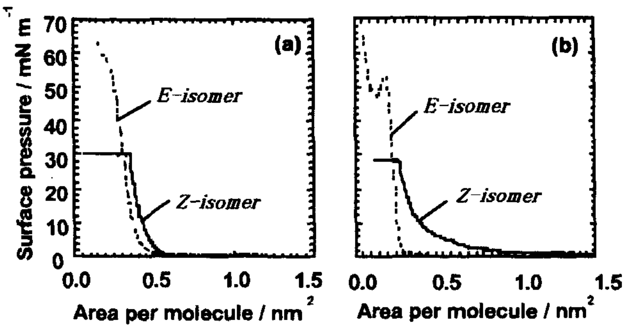


FIGURE 2 π-A isotherm of *E*- and *Z*-isomers of (a) 3,3'-AzoCOOH and (b) 4,4'-AzoCOOH.

On the other hand, the π-A isotherms of *Z*-isomers of both azobenzenes were quite different. Although surface pressures of a monolayer of *Z*-4,4'-AzoCOOH increases gradually under compression, surface pressures of *Z*-3,3'-AzoCOOH rose rather steeply in a manner similar to the case of its *E*-isomer. An occupied area of the *Z*-3,3'-AzoCOOH estimated by the extrapolation at a steep rise was *ca.* 0.45

nm^2, being slightly larger than the *E*-3,3-AzoCOOH probably because of the contribution of the azo group which goes away from the molecular axis.

TABLE 1 Absorption maxima of 3,3'-AzoCOOH and 4,4'-AzoCOOH in solution and monolayer.

	Solution a)	Monolayer b)
3,3'-Azo-COOH	330 nm	310 nm
4,4'-Azo-COOH	359 nm	305 nm

a) $CHCl_3$ / THF = 1 (v/v); b) 10 mN m^{-1}.

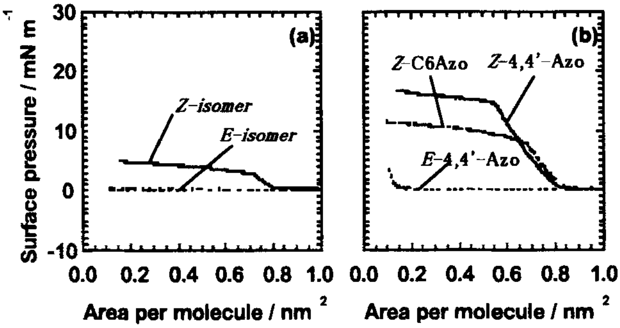


FIGURE 3 π-A isotherms of *E*- and *Z*-isomers of (a) 3,3'-Azo and (b) 4,4'-Azo and C6Azo.

The second type of the compounds subjected to π-A isotherm measurements is the dihexyloxyazobenzenes (3,3'-Azo and 4,4'-Azo) and 4,4'-dihexylazobenzene (C6Azo). The results are shown in Figure 3. No distinct π-A isotherm was observed for *E*-isomers of the three compounds because the monolayer formation is inhibited on a water surface due to the hydrophobic nature of the molecules, leading to the formation of droplets. On the other hand, a rise in π-A isotherms was observed at an area per molecule of *ca.* 0.8 nm^2 for their *Z*-isomers, suggesting that the azo groups of *Z*-isomer acts as a polar site that interacts directly with a water surface to form floating monolayers. It should be noticed that there is a significant difference in collapse pressures between both of them. Collapse pressures of monolayers of *Z*-

4,4'-Azo and *Z*-C6Azo were relatively large and about 10 mN m^{-1}, whereas a floating monolayer of *Z*-3,3'-Azo was far unstable and collapsed at a surface pressure of *ca.* 3 mN m^{-1}. The higher stability of the monolayers of *Z*-4,4'-Azo and *Z*-C6Azo is evidently due to the azo-moiety acting as a polar head which interacts efficiently with a water surface [9,10]. On the other hand, the presence of two methyl groups at the *ortho*-positions and the linear-shape of *Z*-3,3'-Azo inhibit sterically the direct interaction of the polar azo-group with a water surface.

TABLE 2 Photoisomerization of azobenzene moieties in monolayers.

compound	cross sectional area of *E*-isomer (nm^2)$^{a)}$	area per molecule (nm^2)	filling ratio (%) $^{b)}$	*Z*-isomer conversion $^{c)}$
4,4'-Azo-COOH	0.25	0.30	83	0.09
		0.40	63	0.28
		0.60	42	0.45
3,3'-Azo-COOH	0.38	0.38	100	0.17
		0.43	88	0.33
		0.50	76	0.46

a) estimated from π-A isotherm; b) (cross sectional area)/(area per molecule);
c) estimated by absorbances at λ_{max} of azobenzene moiety after UV irradiation.

Densely packed monolayers of amphiphilic azobenzene derivatives exhibit no or scarce photoisomerization because of a relatively large sweep volume needed for *E*-to-*Z* photoisomerization of azobenzene. The peculiar behavior of 3,3'-disubstituted azobenzenes is demonstrated by the studies of the effect of regioisomerism of azobenzene carboxylic acids on the photoisomerizability in organized molecular films. For these studies, LB films of azobenzene carboxylic acids were prepared at various areas per molecule. Note that the transfer of floating monolayers on substrate plates was conducted by spreading solutions of *Z*-isomers on a subphase, since *E*-isomers form island-see domains even before thorough compression to give heterogeneous morphology as stated above. Transferred films were kept standing in the dark for thermal recovery of *E*-isomers, followed by irradiation with 365 nm light to be subjected to UV-vis spectral measurements. A filling ratio defined as (molecular area at transfer)/(cross-sectional area) displays a level of packing of the molecules in LB films. Experimental conditions and results are listed in Table 2. The contents of *Z*-isomer increase with the decrement of the filling ratios, reflecting that the isomerization by the π–

π^* excitation of azobenzene proceeds through the rotation mechanism requiring a large sweep volume. Levels of *E*-to-*Z* photoconversion for 3,3'-Az-COOH are significantly higher than the ones of the 4,4'-counterpart. The 3,3'-counterpart exhibits 17% of the photoisomerization even in a densely packed monolayer (with 100% filling ratio), whereas only 9% of the photoisomerization occurs for 4,4'-Az-COOH in a 83% filling ratio. As estimated from the results shown in Figure 2-(a), cross-sectional areas of 3,3'-Az-COOH are not far different between both rod-shaped isomers so that it is anticipated that reversible photoisomerization occurs even in densely packed molecular films without marked molecular shape alterations. The results were not the case and suggest consequently that the rotation mechanism works specifically for *E*-to-*Z* photoisomerization in molecular films.

The results of the present study can be summarized as follows. The *Z*-isomers of both 3,3'- and 4,4'-disubstituted azobenzenes have a distinct polar head that promotes formation of monolayer of these isomers on a water surface. This observation fits well with the suggested selective absorption of *Z*-isomers of 3,3'- and 4,4'-disubstituted azobenzenes dopants, dissolved in a nematic host, on the hydrophilic substrate surfaces of a sandwich liquid crystal cell; the hydrophilic surface and the water surface are quite the same in a physicochemical meaning [7, 8]. The different molecular shape of the *Z*-isomers, linear in the case of 3,3'-, and bent, in the case of 4,4'-disubstituted azobenzenes, has also been clearly manifested by the behavior of their monolayers. The results of the present study, indicating the higher polarity of the *Z*-isomers of both 3,3'- and 4,4'-disubstituted azobenzenes and a different molecular shape, are in accordance with the suggested possible origin of the light-induced anchoring transition in photochromic guest-host nematic mixtures containing such azobenzene dyes [7, 8].

CONCLUSION

The study of the formation of monolayers from 3,3'-disubstituted and 4,4'-disubstituted azobenzenes on a water surface revealed the polar character of their *Z*-isomers. The marked differences in their monolayer behavior arose from the peculiarity of the *Z*-isomer of 3,3'-disubstituted azobenzenes that exhibited a rod-like form as a thermodynamically stable conformer. This observation explains why the light-induced anchoring transition from planar to homeotropic does not take place in the case of

guest-host nematic mixtures containing 3,3'-disubstituted azobenzenes dopant [8]. Moreover, the photoisomerization behavior of this kind of dopant is a demonstration of the enhancement of molecular polarity with minor changes in the molecular shape. Such photo-induced change in the molecular polarity might be of interest for applications that are based on light-induced change in the volume properties of liquid crystals.

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