Z-Isomers of Azobenzenes Highly Compatible with Liquid Crystals

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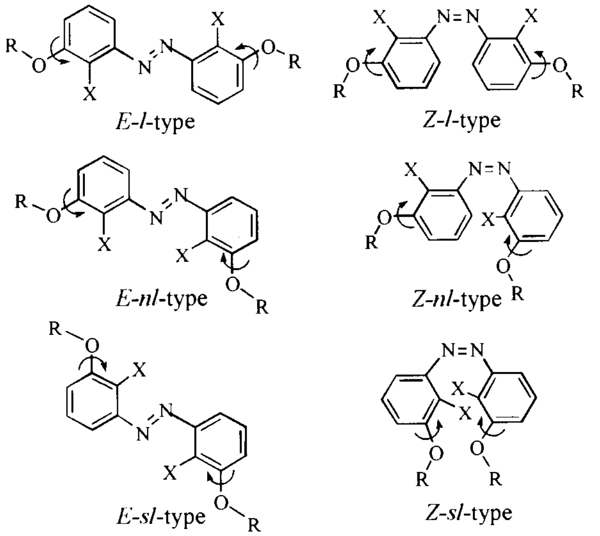
Novel guest-host liquid crystal systems containing 3,3-disubstituted azobenzenes as guests were prepared on the basis of molecular design by molecular calculations to achieve the improvement of compatibility of the chromophore with nematic phases. No phase change of nematic liquid crystals was induced by the *E*-to-*Z* photoisomerization of the guests even at doped concentrations as high as 20 wt%.

The phototriggered modification of liquid crystal (LC) phases by photoisomerizable guest molecules has attracted much attention because of providing access to wide variety of areas such as optical switching, holography and optical information storage systems.[1] Azobenzenes have been extensively employed for these purposes because of the excellent availability, reasonable photo-fatigue resistance and the marked transformation of their molecular shape upon *E*-to-*Z* photoisomerization.[2-6] It has been suggested that photoisomerized *Z*-isomers result in the disorganization of the molecular assemblage because of their bent structure, leading to mesophase changes. It has been reported recently that the flexoelectric effect is generated by *E-to-Z* configurational transformation of an azobenzene derivative doped in a nematic LC as a result of considerable alteration of dipole moment of the chromophore.[7] In this type of the photocontrol of LC properties, the compatibility of Z-isomer of azobenzenes with LC molecules is highly required in order to avoid photoinduced phase separation at a higher loading of Z-isomer.

Our interest has been focused on designing and developing photoresponsive LC systems that exhibit phase stability upon photoisomerization in a keen contrast to the conventional studies on photoinduced mesophase changes. We report here for the first time that the introduction of elongated substituents at both 3- and 3'-positions of azobenzenes enhances considerably the compatibility of the both geometrical isomers with nematic LCs. To our knowledge, detail studies emphasized on conformational changes of photoresponsive molecules with respect to the stability of LC phases have hardly been done.

Whereas the conformation of *E*-isomer of 4,4'-disubstituted azobenzenes is inherently restricted to give a rod-like shape, 3,3'-disubstituted counterparts may have three conformers for each geometrical isomer. The three conformers of *E*-isomer, named as *E-l-* (linear), *E-nl-* (non-linear) and *E-sl-* (semi-linear) type, respectively, are shown in Figure 1. The *l*-type is the most rod-like structure. 3,3-Disubstituted *Z*-isomers with a bent configuration have also three conformers, *Z-l-*, *Z-nl-* and *Z-sl-*type, as shown in Figure 1. The *Z-l*-type conformer with an elongated structure can been anticipated to be compatible with LCs. In this context, methyl residues are attached at 2- and 2'-positions under the expectation of the preference formation of *l*-type conformation to a greater extent.

The molecular calculation[8] revealed that the heat of formations of the *E-l*-type conformers are lower than the other two types. In the model compound with no methyl substituents in the 2 and 2'-positions, there were only slight differences in the heat of formation among *l*-, *nl*- and *sl*-type conformations in *Z*-isomer, although the *E*- *l* and *E-nl*-types were somewhat more stable than the *E-sl*-type. The molecular calculation predicted that, to our expectation, the rod-like-generating effect is intensely pronounced when methyl substituents are introduced to the 2- and 2'-positions, indicated by low heat of formation of the *l*-type conformers as shown in Table 1.



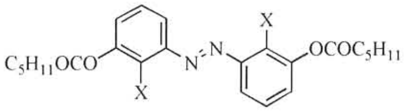
R= $COCH_3$, X= H or CH_3

Figure 1. Three conformational structures of *E*- and *Z*-isomer of 3,3'-disubstituted azobenzenes and model compounds used in molecular calculations.

Table 1. Calculated heat of formation [kcal / mole] of each stable conformer

	R= $COCH_3$, X= H		R= $COCH_3$, X= CH_3	
Conformer	*E*-isomer	*Z*-isomer	*E*-isomer	*Z*-isomer
l-type	-69.62	-63.50	-78.30	-78.37
nl-type	-67.55	-64.94	-76.67	-74.81
sl-type	-68.04	-62.94	-75.29	-73.45

Encouraged by the simulation results, 3,3'-disubstituted azobenzenes were prepared, starting from the corresponding 3,3'-dihydroxyazobenzenes[9] which were esterified to give desired compounds, **1a** and **1b**, as showed in Figure 2. For comparison, 4,4'-dihexanoyloxyazobenzene (**2**) was also prepared[10]. The *E/Z* photoisomerizability of all the compounds was confirmed by tracing the spectral change of n-π* band. *Z* fractions at 350 nm light photostationary state were more than 0.9 and 0.8 in methanol and in nematic LCs, respectively.



1a: X= H
1b: X= CH$_3$

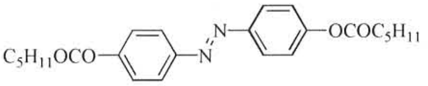


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Figure 2. Chemical structures of 3,3'-disubstituted azobenzenes (**1a**, **1b**) and a 4,4'-disubstituted azobenzene (**2**).

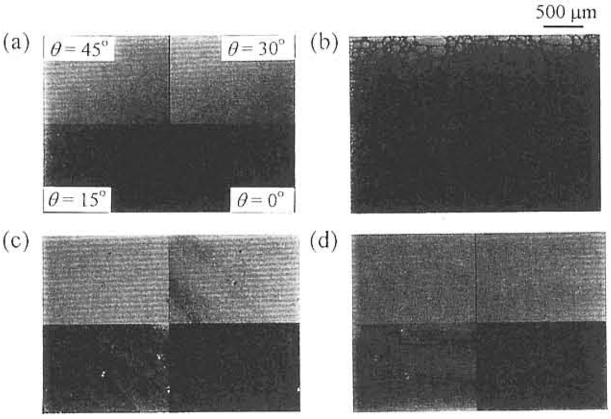

Figure 3. Polarized optical micrographs of 20 wt% (a) **2** / DON-103 at 75 °C before UV light exposure and (b) at 20 °C after UV light exposure, (c) **1b** / DON-103 at 46 °C before UV light exposure and (d) at 30 °C after UV light exposure. θ indicates the angle between analyzer and rubbing directions.

The effect of highly doped azo-compounds in nematic systems on phase changes upon UV light irradiation was determined by dissolving the guests in DON-103 (nematic-isotropic phase transition temperature, T_{NI} = 73.4 °C, $\Delta\varepsilon$ = -1.4) in concentrations of 5, 10 and 20 wt%, followed by injecting these binary systems to empty LC cells. In 5 wt % and 10 wt% doped systems, no clear visible changes after UV light irradiation were observed. In systems containing 20 wt% of **2**, phase separation was induced during UV light irradiation. On the other hand, in the systems with 3,3'-disubstituted azobenzenes **1a** and **1b**, the LC phases were maintained even after UV light irradiation (Figure 3). These systems showed amazingly stable nematic phase maintenance during photoisomerization. These results suggest that Z-isomer correlates well with the host. For the systems showing phase separation (**2** / DON-103), cooling down the systems ended up with the appearance of crystalline domains.

In summary, the computational molecular design and the synthesis of a novel type photoresponsive dopants, 3,3'-disubstituted azobenzenes, were performed, aiming at the development of photoresponsive nematic LC systems that performs phase stability during photoisomerization. We discovered that 3,3'-dialkanoyloxy azobenzenes, **1a** and **1b,** are the best candidates since they, in both *E*- and *Z*-conformers, exhibit a considerable stability of the LC system upon photoirradiation, which is not observable in the case of 4,4'-disubstituted azobenzenes at all.

References and Notes

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8 Stable conformation and heat of formation of both isomers were calculated by using the Molecular Mechanics calculation with the MM2 parameter and the Molecular Orbital calculation with the semi-empirical MOPAC PM3 parameter, successively, which are packed in the CAChe (Computer Aided Chemistry) version 3.0.

9 Reductive coupling by $LiAlH_4$ of *m*-nitrophenol or 2-methyl-3-nitrophenol which were protected by 3,4-dihydro-2H-pyrane gave the corresponding 3,3'-dihydroxyazobenzene in a 19% or 32% overall yield.

10 Data for **1a**: ^1H NMR ($CDCl_3$) δ 0.94 (t, J = 6.6 Hz, 6H), 1.38-1.86 (m, 12 H), 2.59 (t, J = 7.2 Hz, 4 H), 7.19-7.56 (m, 8 H). ^{13}C NMR ($CDCl_3$) δ 13.9, 22.3, 24.6, 31.3, 34.4, 115.0, 121.8, 124.3, 129.8, 151.5, 153.4, 172.1. UV (hexane, λ_{max} (ε)) 318 nm (23000 dm^{-3} mol^{-1} cm^{-1}). Anal. Found: C, 70.07; H, 7.66; N, 6.67%. Calcd for $C_{24}H_{30}N_2O_4$: C,70.21; H,7.38; N, 6.82%. Data for **1b**: ^1H NMR ($CDCl_3$) δ 0.95 (t, 6 H), 1.35-1.90 (m, 12 H), 2.55 (s, 6 H), 2.64 (t, J = 7.4, 4 H), 7.11-7.53 (m, 6 H). ^{13}C NMR ($CDCl_3$) δ 10.6, 14.0, 22.4, 24.8, 31.4, 34.3, 113.6, 124.4, 126.3, 131.0, 150.4, 152.0, 172.0. UV (hexane, λ_{max} (ε)) 328 nm (21700 dm^{-3} mol^{-1} cm^{-1}). Anal. Found: C, 70.87; H, 8.01; N, 6.22%. Calcd for $C_{26}H_{34}N_2O_4$: C, 71.19; H, 7.83; N, 6.39%. Data for **2**: ^1H NMR ($CDCl_3$) δ 0.94 (t, J = 7.2, 6 H), 1.38-1.86 (m, 12 H), 2.59 (t, J = 7.6 Hz, 4 H), 7.24 (d, J = 8.8 Hz, 4 H), 7.94 (d, J = 9.0 Hz, 8 H). ^{13}C NMR ($CDCl_3$) δ 13.9, 22.4, 24.6, 31.3, 34.4 . 122.3, 124.1, 150.1, 152.9, 172.0. UV (hexane, λ_{max} (ε)) 328 nm (31300 dm^{-3} mol^{-1} cm^{-1}). Anal. Found: C, 70.11; H, 7.42; N, 6.86%. Calcd for $C_{24}H_{30}N_2O_4$: C, 70.21; H, 7.38; N, 6.82%.