

Spectroscopic and thermal isomerization characteristics of 3,3'-dialkoxy and dialkanoyloxy azobenzenes

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The UV/visible spectra and activation parameters of thermal *Z*-to-*E* isomerization of several symmetrical 3,3'-dialkoxy and dialkanoyloxy azobenzenes were discussed in comparison to those of the corresponding 4,4'-disubstituted, unsubstituted and other substituted azobenzenes. It is shown that λ_{max} and molar extinction coefficient (ϵ) of the π - π^* bands of these 3,3'-disubstituted azobenzenes are similar to that of an azobenzene. Thermal isomerization rates of these azobenzenes were found to be relatively slower than those of 4,4'-disubstituted azobenzenes. The isokinetic plots in solutions suggested the inversion mechanism for these azobenzenes. It is also assumed from thermal isomerization in the glassy state that the *Z*-isomers of these azobenzenes were less strained, probably due to the conformation that consumes less space during isomerization.

Introduction

Researches on photofunctional molecular systems by means of azobenzenes cover huge aspects in opto-electronical, physico-chemical and biological fields.¹ Readily induced and reversible *E*-*Z* isomerization resulting in drastic changes in the absorption spectra and conformations is the key concept in tailoring the properties of these systems. Azobenzenes can, however, undergo thermal *Z*-to-*E* isomerization as well. This thermal process plays a crucial role, for example, in controlling the orientation direction of liquid crystal molecules or other processes that involve repeating *E*-*Z*-*E* conversion.

From the abundant literature, there are hardly any reports on the behavior of *meta*-substituted azobenzenes, whereas that of other substituted azobenzenes has been widely exploited.^{2,3} Such varieties of azobenzenes can be classified into three types, *i.e.* azobenzene, aminoazobenzene and pseudo-stilbene types, following the division by Rau, based on the relative energetic positions of the n - π^* and π - π^* states.⁴ The pseudo-stilbene type azobenzenes, such as a *p*-donor-*p*-acceptor (push-pull) azobenzene show extremely fast thermal isomerization rates (from seconds to milliseconds) whereas the azobenzene type, such as *ortho*- or *para*-alkylated azobenzenes, show relatively slow rates. There seems to be no clear information on which type *meta*-substituted azobenzenes belong to. The fact that azobenzene may have two isomerization mechanisms, rotation along the azo bond and in-plane inversion through sp hybridization of the azo nitrogens in the transition state, has long been known. The inversion mechanism is overwhelmingly favored over the rotation for thermal isomerization of azobenzenes.² However, several reports showed that push-pull azobenzene may favor the rotation mechanism.⁵

Recently, we have successfully prepared some novel azobenzenes having 3- and 3'-substituents with/without 2,2'-dimethyl groups at the azo-aromatic core. This type of azobenzenes was found to exhibit interesting photo-optical behaviors in liquid crystal materials, which were attributed to the unique elongated rod-like conformation of the *Z*-isomer.⁶ Stimulated by the lack of information of this type of azobenzenes as indicated above, we report here the spectro-

scopic and thermodynamic properties of some 3,3'-disubstituted azobenzenes (including those with 2,2'-dimethyl groups), **1m**–**4m**, in comparison to the analogues 4,4'-disubstituted azobenzenes, **1p** and **2p**, or unsubstituted azobenzene, **Az** (Fig. 1). The thermal *Z*-to-*E* isomerization was also studied in glassy polymeric materials.

Experimental

The preparation of azobenzene derivatives (**1m**–**4m**, **1p**, **2p**) has been reported previously.⁶ Unsubstituted azobenzene (**Az**) was purchased from Tokyo Chemical Industry. Solutions of the azobenzenes were adjusted to a concentration of approximately 10^{-3} mol dm⁻³. To these solutions were subjected 365 nm UV light from a Hg-Xe lamp combined with UV35 and UVD36 (Toshiba) glass filters toward the photostationary state. At this stage, the solutions contained 80–99% *Z*-isomers as determined from HPLC and the absorption spectra. The kinetics of the

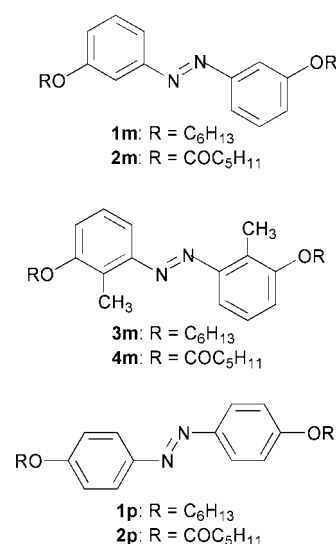


Fig. 1 Structures of 3,3'-disubstituted azobenzenes (**1m**–**4m**) and 4,4'-disubstituted azobenzene (**1p** and **2p**).

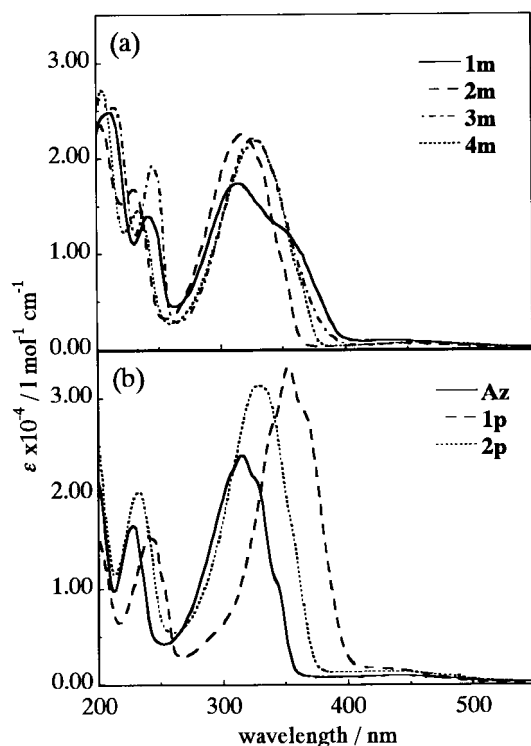


Fig. 2 Absorption spectra of (a) 3,3'-disubstituted azobenzenes (**1m–4m**), (b) unsubstituted azobenzene (**Az**) and 4,4'-disubstituted azobenzenes (**1p** and **2p**) in hexane.

thermal isomerization were followed spectroscopically in the dark by using a diode array spectrometer (HP8452A) in a quartz cell with a path length of 1.0 cm, set in a cell holder equipped with a water jacket and thermostated by a temperature controller (Coolnics Circulator CTE-24W). X-Ray crystallography was performed on a Rigaku AFC5R diffractometer with graphite monochromated Mo-K α radiation and a rotating anode generator.

Isomerization in the glassy state was carried out by dispersing dilute azobenzenes in PMMA (from Aldrich, $T_g = 114^\circ\text{C}$). The concentrations of azobenzenes in PMMA were made in the order of 10^{-3} mol dm $^{-3}$ by mixing a 20 wt% PMMA solution and a 0.2 wt% solution of the azobenzenes in toluene at a ratio of 4:1. Within this concentration, no aggregation of azo-chromophores occurs.⁷ These solutions were cast onto quartz plates and allowed to dry slowly in a capped Petri dish at room temperature overnight before being subjected to a vacuum oven at 120°C for 2 h to obtain films of about 20–40 μm thick and absorption of less than 0.6 at λ_{max} of the $\pi\text{--}\pi^*$ band. After exposure of UV light toward the photostationary state (*Z*-fraction of 75–93%), the film was set in a hot stage (Mettler FP 800) and the spectral changes were traced with time.

Table 1 λ_{max} /nm and molar extinction coefficients $\epsilon/\text{l mol}^{-1} \text{cm}^{-1}$ of azobenzenes in solutions

Compound	In hexane		In methanol	
	$\pi\text{--}\pi^*$ ($\epsilon \times 10^{-4}$)	$n\text{--}\pi^*$ ($\epsilon \times 10^{-2}$)	$\pi\text{--}\pi^*$	$n\text{--}\pi^*$
Az	318 (2.20)	448 (4.0)	318	442
1m	314 (1.65)	442 (5.7)	318	—
2m	318 (2.30)	446 (4.4)	318	442
3m	326 (2.18)	464 (5.2)	328	460
4m	328 (2.17)	464 (5.2)	328	460
1p	354 (3.25)	—	358	—
2p	328 (3.13)	440 (7.1)	328	440
Az1^a	330 (2.70)	—	—	—
Az2^b	328 (1.75)	455 (8.5)	—	—
Az3^b	313 (1.60)	465 (14.0)	—	—

^aAz1 is 4,4'-dimethylazobenzene in cyclohexane (from reference 2(c)).

^bAz2 and Az3 are 2,2',4,4',6,6'-hexamethylazobenzene and 2,2',4,4',6,6'-hexaethylazobenzene, respectively (from reference 3).

Results and discussion

The UV/visible absorption spectra of the 3,3'-disubstituted azobenzenes (**1m–4m**) possess smaller ϵ in comparison to **1p** or **2p** as shown in Fig. 2. In general, we can also observe that the λ_{max} of the $\pi\text{--}\pi^*$ bands of 3,3'-disubstituted azobenzenes are hypsochromically shifted with respect to those of 4,4'-disubstituted azobenzenes. Table 1 shows the spectroscopic features of these azobenzenes in solutions. There is not much effect of solvent polarity on λ_{max} of the spectra, although some slight shifts occur for azobenzenes with ether substituents. The variation of substituents from ether to ester for 3,3'-disubstituted azobenzenes (**1m** to **2m** or **3m** to **4m**) has very little or even no effect on the energy of the transition bands, although the spectral shape of **1m** is somewhat peculiar when compared to the others. In a keen contrast, the 4,4'-disubstituted azobenzenes show a significant change of λ_{max} upon variation of the substituents (from 328 nm for **1p** to 354 nm for **2p**). The interplay of the *meta*-substituents does not influence the electronic system of the azo-bridge as that of the *para*-substituents does.

The conformational structures in the crystal state are of importance and closely related to the observed spectroscopic features. It is well known that an *E*-unsubstituted azobenzene has a planar structure in its crystal state and introduction of bulky groups at the *ortho*-positions induced rotation of the phenyl ring as a result of steric effects. This will emerge in the hypsochromic shift of the absorption spectra (see also cited data in Table 1). However, it is also reported that a methyl group is not bulky enough to affect the planar structure of a *para*-substituted azobenzene such as in a 2,2',4,4',6,6'-hexamethylazobenzene.^{3,8} We suspect also that introduction of methyl substituents at the *ortho*-positions of 3,3'-disubstituted azobenzenes (resulting in **3m** and **4m**) does not essentially affect the planar conformation of the two phenyl rings; otherwise, their spectra would show a hypsochromic shift when compared

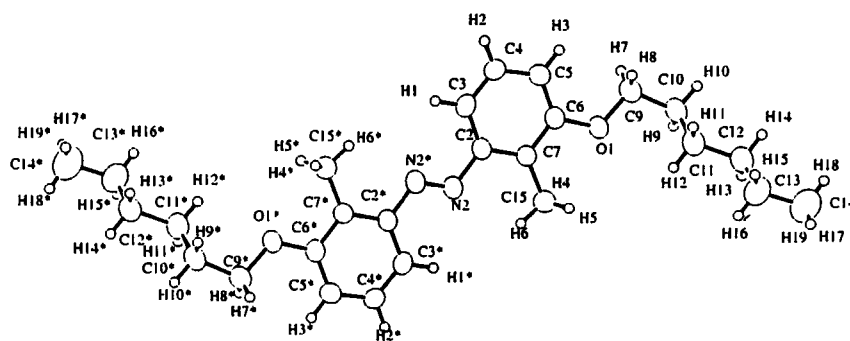


Fig. 3 The molecular structure of **3m** from single crystal X-ray analysis.

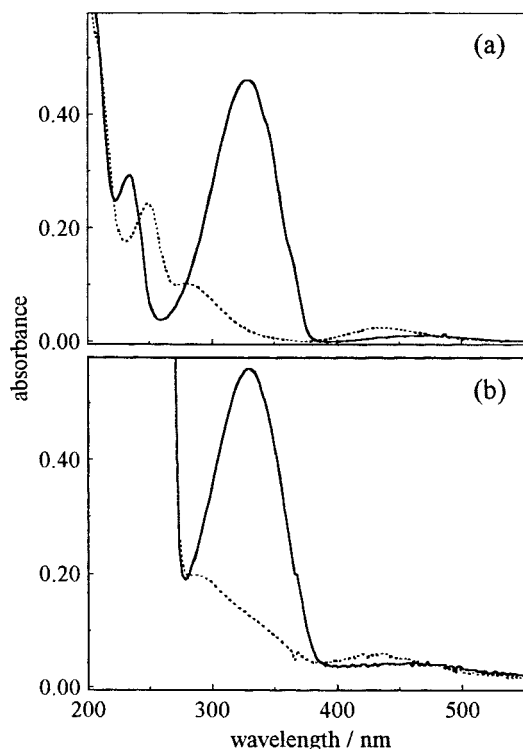


Fig. 4 Spectra of **4m** at initial state (solid line) and photostationary state of UV light (dotted line) in (a) hexane solution and (b) glassy state of PMMA at room temperature.

to **1m** and **2m**, respectively. Thus, the observed bathochromic shifts in **3m** and **4m** are due to electronic effects attributed to the additional substitution at the *ortho*-positions. The crystal structure of **3m**⁹ from X-ray crystallography (Fig. 3) gives supportive information on the planarity of this compound. Notice that the C(2)–N=N–C(2*), N–C(2)–C(7)–C(15) and N–C(2*)–C(7*)–C(15*) dihedral angles are 180°, 1.7° and 1.7°, respectively.

The thermal *Z*-to-*E* isomerization in solutions satisfied the first order kinetics according to eqn. (1).

$$\ln \frac{A_{\infty} - A_0}{A_{\infty} - A_t} = kt \quad (1)$$

Here, A_{∞} , A_0 , and A_t are the absorption of an *E*-azobenzene (before being subjected to UV light), absorption at which measurement started (at the photostationary state of UV light) and the absorption at time t , respectively, whereas k and t are the rate constant and reaction time, respectively. It is to be noticed that the *Z*-fractions at the photostationary state of UV light are dependent on the nature of the compounds represented by their spectroscopic features and the surroundings where the reactions occur. However, the difference in *Z*-fractions here does not essentially affect the thermal isomerization behavior.¹⁰ Fig. 4 shows an example of a comparison

Table 2 Activation parameters of thermal *Z*-to-*E* isomerization of azobenzenes in hexane

Compound	$A \times 10^{-10}/s^{-1}$	$E_a/kcal\ mol^{-1}$	$t_{1/2}^a/min$	$\Delta H/kcal\ mol^{-1}$	$\Delta S/cal\ K^{-1}\ mol^{-1}$
Az	27.8	23.3	5240	22.7	-8.34
1m	11.5	22.8	5460	22.2	-10.1
2m	0.37	20.8	5150	20.1	-16.9
3m	37.1	23.8	8430	23.1	-7.76
4m	0.44	20.5	2770	19.8	-16.6
1p	15.5	21.6	520	20.9	-9.48
2p	6.11	21.9	2010	21.2	-11.3
Az4^b	—	—	0.58 ^c	15.0 ^d	-19.0 ^d

^aExtrapolated from Arrhenius plot at 298 K. ^b**Az4** is 4-nitro-4'-dimethylaminoazobenzene. ^cCited from reference 5(b) in benzene. ^dCited from reference 5(a).

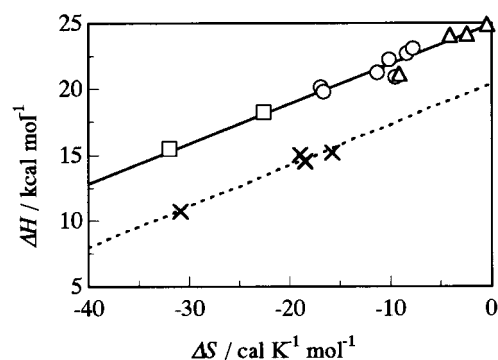


Fig. 5 Isokinetic plots for ΔH and ΔS of azobenzenes in solutions; azobenzenes in this work (○), *para* and/or *ortho*-substituted azobenzenes (△),^{2b} azobenzene-bridged crown ethers (□),^{5a} push-pull azobenzenes (×).^{5a}

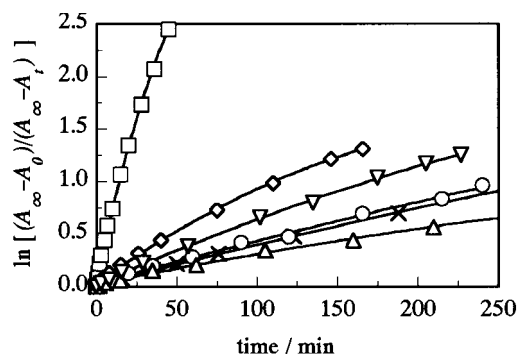


Fig. 6 Thermal isomerization kinetics of **1m** (×), **2m** (○), **3m** (△), **4m** (▽), **1p** (□) and **2p** (◇) in glassy PMMA at 60°C.

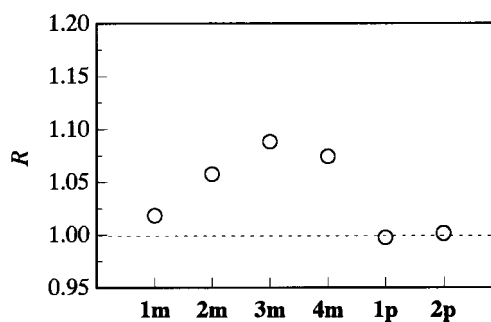


Fig. 7 The ratio R for the thermal kinetics of azobenzenes in glassy PMMA (see the text for the definition of R).

between the spectra taken in a hexane solution and in a glassy state of PMMA at the initial state and the photostationary state of UV light for compound **4m**. The rates at different temperatures allow us to derive the activation parameters from Arrhenius and Eyring plots. Table 2 summarized these parameters in solutions for all the azobenzenes used. The

half-life times of the *Z*-isomers of 4,4'-disubstituted azobenzenes **1p** and **2p** are shorter than those of 3,3'-disubstituted azobenzenes although they are still much longer (three to four order in magnitude) than a push-pull azobenzene such as 4-nitro-4'-dimethylaminoazobenzene (see also Table 2). It is interesting to notice that the longer lifetimes of the ester substituted 3,3'-disubstituted azobenzenes (**2m** and **4m**) are not due to higher activation energy (E_a) since their E_a are rather low when compared to those of the others. Their lifetimes are characterized by small pre-exponential factors A which are one order smaller in magnitude. Their larger negative entropy (ΔS) may be an indication of rather severe coulombic interactions between the azo electronic systems and the ester groups in the activated complexes or degree of steric restriction, which are plausible explanations considering the results of Brown and Granneman on pyridyl analogs of azobenzenes.^{2c}

Isokinetic plots for ΔH and ΔS for azobenzenes of this work were compared to those in the literature to evaluate the mechanisms of the reactions (Fig. 5). The plots of azobenzenes of this work are all in line with other non-push-pull azobenzenes, indicating that the inversion mechanism occurs for the thermal isomerization. Using a more polar solvent such as acetone resulted in small decrease of reaction rates, which is also characteristic of this mechanism.^{5b}

In the glassy state of PMMA, the thermal isomerization shows a deviation from eqn. (1) as is depicted in Fig. 6 for reactions at 60 °C. A portion of the initial reaction proceeds faster than the rest. This fast reaction has been interpreted as the relaxation of strained *Z*-isomers trapped in the matrix.¹¹ This behavior can be expressed as a sum of two simultaneous first order kinetics.¹⁰ However, this is not applied here due to extremely slow isomerization of some of the samples for which the relaxation times were spectroscopically traced only until a little longer than the half-life times. Instead, by defining the ratio (R) between the apparent activation energy at the half- and quarter-life times, where $(A_\infty - A_t)/(A_\infty - A_0)$ are 0.75 and 0.50, respectively, a relative comparison among the behaviors of these azobenzenes in glassy states can be done, noting that at the quarter-life times, most fast reactions with low activation energies were still in progress (the ordinate in Fig. 6 being less than 0.30 and exactly 0.69 at the quarter- and half-life times, respectively). Fig. 7 compares the ratio R for the azobenzenes. It is found here that **1m–4m** have $R > 1.00$, suggesting that the portion of fast reactions are relatively smaller than those for **1p** or **2p**. This may be attributed to the difference in the conformations of the *Z*-isomers that affect the space for isomerization. The *Z*-isomers of some 3,3'-disubstituted azobenzenes have been indicated to prefer rod-like conformations, enhanced more by the presence of methyl substituents at *ortho*-positions and need less space to isomerize with respect to 4,4'-disubstituted analogs.⁶ As a consequence, the formation of

strained *Z*-isomers should be suppressed, resulting in relatively less portion of the fast isomerization.

Conclusion

The spectroscopic features and *Z*-to-*E* thermal isomerization kinetics of some 3,3'-disubstituted azobenzenes have been studied in comparison with other azobenzenes. From spectral analysis and thermal isomerization behaviors, the 3,3'-disubstituted azobenzenes here seem to belong to "azobenzene type" azobenzenes,⁴ characterized by a large energy gap between $n-\pi^*$ and $\pi-\pi^*$ bands, insensitivity to solvent polarity, and relatively slow reaction rates. The inversion mechanism occurs most likely for these azobenzenes as was shown by the isokinetic plots. The differences in the conformations of the *E*- and *Z*-isomers, as a consequence of different positional substitutions of an azobenzene, affect the thermal *Z*-to-*E* kinetics behaviors in the glassy states of polymeric systems.

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