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The synthesis of aminoazobenzenes and the effect of intermolecular hydrogen bonding on their photoisomerization

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Abstract

Two series of azobenzene derivatives were synthesized so as to investigate the effects of intermolecular hydrogen bonding on their photochemistry. Photoisomerization in polymer matrices was investigated under various irradiation conditions using UV pulsed laser light. Rate constants were calculated according to equations for reversible photoisomerization. Although aminoazobenzenes exhibited faster photoisomerization and larger integral rate constants than the corresponding acetylamino derivatives, the latter compounds displayed faster conversion from the *trans* to the *cis* form owing to potential intermolecular hydrogen bonding interaction between the acetylamino groups. Long alkyl chain azobenzenes possessed faster photoisomerization rates than those with short alkyl chains.

Keywords: Azobenzene; Synthesis; Intermolecular hydrogen bonding; Dynamic equilibrium; Photoisomerization; Substitute effect

1. Introduction

In the past years, azo dyes have been attracting intensive interest for their potential use in optical data storage [1], optical switching [2], polarization holography [3,4], optical modulation [5], nonlinear optics [6], and photolabile surfactants [7]. Recently, most works are investigating the photoinduced motions resulting from photoisomerization of the azo moieties, which are connected to the side chain of the polymer or doped into the polymer matrix [8,9].

It is well known that the substituents of azo chromophores play an important role in molecular motion during photoisomerization. Many efforts have been made to investigate the motion of azobenzene derivatives by introducing substituents, such as chloro atom into the 2′-position [1], naphthalene [10,11] or carbazole moiety [12] into the azobenzene chromophore, even extending the chromophore by two azo moieties [13]. According to the classification by Rau [14], azobenzene derivatives can be divided into three groups based on their photochemical behavior. One of these is *aminoazobenzene* group. They possessed longer *cis* lifetimes than "*pseudostilbene*" group, although their extinction coefficient is smaller than that of *pseudostilbenes*. Consequently, aminoazobenzenes are also treated as good candidates for photoinduced birefringence materials when a blue or green laser is used as a pump source [14]. Moreover, potential hydrogen bondings in azobenzenes also influence their properties. Intramolecular hydrogen bonding (H-bonding), formed by introducing *o*-hydroxyl phenyl moiety into azobenzene, has significant effect on liquid crystalline properties [15]. It is also reported that azobenzenes with intramolecular H-bonding possess a longer *cis* isomer lifetime and have potential application in photoswitching [16].

Our attention was given to the intermolecular H-bonding effect on the photochemical behavior of aminoazobenzenes. In this paper, two kinds of aminoazobenzene derivatives $\mathbf{I_{a-c}}$ and $\mathbf{II_{a-c}}$ were designed and synthesized to understand the

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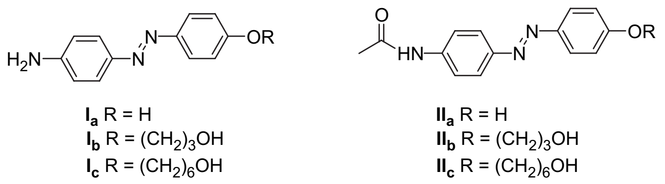

Scheme 1. The molecular structures of $\mathbf{I_{a-c}}$ and $\mathbf{II_{a-c}}$.

substituents' effect on the photoisomerization process (Scheme 1). The photoisomerization behaviors of the polymer matrix (PMMA) doped with $\mathbf{I_{a-c}}$ and $\mathbf{II_{a-c}}$ were investigated by varying the irradiating laser power and the doping concentration of azobenzenes. Furthermore, the substituent and concentration effects on the rate constant of photoisomerization are discussed.

2. Experimental detail

2.1. Materials

4-Acetylaminoaniline, phenol, sodium nitrite, hydrochloric acid (36–38%), sodium hydroxide, tetrahydrofuran and chloroform-*d* were purchased from Beijing Chemical and Reagent Company. 3-Chloropropan-1-ol and 6-chlorohexan-1-ol were obtained from J&K Chemicals. All the reagents and solvents were used as-received without further purification.

2.2. Synthesis and characterizations

Compounds $\mathbf{I_{a-c}}$ and $\mathbf{II_{a-c}}$ used in this paper were synthesized according to previously reported procedure [17,18]. ^{1}H NMR spectra were recorded on a Varian Jemini-300/Brucker AV 400 spectrometer using $CDCl_3$ as a solvent and all shifts are referenced to tetramethylsilane (TMS). The fine splitting of phenyl ring patterns is ignored and the signals are reported as simple doublets, with J values referring to the two most intense peaks. Infrared spectra were recorded on an FT/IR-410 spectrophotometer (JASCO Corp.) and mass spectra were measured on a ZAB-HS (Micromass, UK). All data of $\mathbf{I_{a-c}}$ and $\mathbf{II_{a-c}}$ are listed below.

2.2.1. 4-Hydroxy-4′-aminoazobenzene ($\mathbf{I_a}$)

Yield = 96%; m.p. 184–186 °C (lit. [18] m.p. 185–186 °C); ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): 7.82 (dd, 4H, $J_1 = 9.3$ Hz, $J_2 = 8.7$ Hz), 6.94 (d, 2H, $J = 9.3$ Hz), 6.77 (d, 2H, $J = 8.7$ Hz), 5.04 (s, 1H), 4.02 (s, 2H); IR (KBr, cm^{-1}): 3371, 3284, 1594, 1497, 1470, 1235, 841; HRMS (ESI$^+$) (M + Na$^+$): calcd 236.0794, found: 236.0786 (−3.4 ppm).

2.2.2. 4-Amino-4′-3-hydroxy-propoxyazobenzene ($\mathbf{I_b}$)

Yield = 98%; m.p. 127–129 °C; ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): 7.86 (d, 2H, $J = 8.8$ Hz), 7.80 (d, 2H, $J = 8.6$ Hz), 7.01 (d, 2H, $J = 8.8$ Hz), 6.76 (d, 2H, $J = 8.6$ Hz), 4.22 (m, 2H), 3.78 (m, 2H), 2.21 (s, 1H), 2.11 (m, 2H); HRMS (ESI$^+$) (M + Na$^+$): calcd 294.1213, found: 294.1230 (+5.8 ppm).

2.2.3. 4-Amino-4′-6-hydroxy-hexyloxyazobenzene ($\mathbf{I_c}$)

Yield = 97%; m.p. 131–133 °C; ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.84 (d, 2H, $J = 8.9$ Hz), 7.76 (d, 2H, $J = 8.6$ Hz), 6.98 (d, 2H, $J = 8.9$ Hz), 6.75 (d, 2H, $J = 8.6$ Hz), 4.05 (t, 2H, $J = 6.5$ Hz), 3.98 (br s, 2H), 3.70 (m, 2H), 1.87 (m, 2H), 1.66 (m, 2H), 1.56 (s, 1H), 1.53 (m, 2H); HRMS (ESI$^+$) (M + H$^+$): calcd 314.1863, found: 314.1856 (−2.2 ppm).

2.2.4. 4-Hydroxy-4′-acetaminoazobenzene ($\mathbf{II_a}$)

Yield = 88%; m.p. 194–198 °C; ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): 7.90 (dd, 4H, $J_1 = 8.5$ Hz, $J_2 = 8.6$ Hz), 7.68 (d, 2H, $J = 8.5$ Hz), 6.97 (d, 2H, $J = 8.6$ Hz), 2.24 (s, 3H); IR (KBr, cm^{-1}): 3428, 3325, 1663, 1594, 1551, 1508, 1382, 1266, 847; HRMS (ESI$^+$) (M + Na$^+$): calcd 278.0900, found: 278.0892 (−2.9 ppm).

2.2.5. 4-Acetamino-4′-(3-hydroxypropoxy)azobenzene ($\mathbf{II_b}$)

Yield = 97%; m.p. 178–180 °C; ^{1}H NMR (300 MHz, CD_3OD, δ ppm): 7.86 (m, 4H), 7.72 (d, 2H, $J = 8.8$ Hz), 7.06 (d, 2H, $J = 8.8$ Hz), 4.19 (t, 2H, $J = 6.2$ Hz), 3.78 (t, 2H, $J = 6.2$ Hz), 2.15 (s, 3H), 2.04 (m, 2H); HRMS (ESI$^+$) (M + Na$^+$): calcd 336.1318, found: 336.1308 (−3.0 ppm).

2.2.6. 4-Acetamino-4′-(6-hydroxyhexyloxy)azobenzene ($\mathbf{II_c}$)

Yield = 76%; m.p. 174–175 °C; ^{1}H NMR (300 MHz, CD_3OD, δ ppm): 8.32 (s, 1H), 7.73 (d, 2H, $J = 9.0$ Hz), 7.62 (d, 2H, $J = 8.8$ Hz), 7.05 (d, 2H, $J = 9.0$ Hz), 6.66 (d, 2H, $J = 8.8$ Hz), 4.05 (t, 2H, $J = 6.5$ Hz), 3.42 (m, 2H), 2.54 (s, 3H), 2.09 (s, 1H), 1.75 (m, 2H), 1.46 (m, 6H); HRMS (ESI$^+$) (M + Na$^+$): calcd 378.1788, found: 378.1773 (−4.0 ppm).

2.3. Sample preparation and physical measurements

The $CHCl_3$ solution of azobenzenes **I** and **II** was used for the absorption spectra measurements with a concentration of 5.0×10^{-5} M. All the films used in the photoisomerization experiments were prepared by spin coating a solution onto a cleaned glass slide; the concentration of azobenzenes in solvent ($CHCl_3$ or THF) was 0.01 M. The doped concentration of azobenzenes in PMMA was 10% except for those specially marked. The films were heated at 60 °C for 1 h and allowed to stand in vacuum overnight to remove residual solvent. The IR spectra of the films were recorded on a 3100 FT-IR (Varian).

For the photoisomerization experiments, a laser beam from an Nd:YAG laser was employed as the light source at a wavelength of 355 nm with a pulse width of 8 ns and repetition rate of 10 Hz. The diameter of the laser beam was 1 cm. Photoirradiation was carried out until the photoisomerization reached its photostationary state. The ultraviolet–visible (UV–vis) spectra were recorded by a UV-2550 Shimadzu UV–vis spectrophotometer.

3. Results

3.1. IR spectra

Infrared spectrum presented rich information about the azobenzene-doped PMMA film. As shown in Fig. 1A, $\mathbf{I_b}$ in