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Photochromic Reactions of Two Azobenzene Chromophores in a Chiral Cyclohexane Moiety

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A chiral cyclohexane containing two photochromic azobenzene units, (1*R*,2*R*)-*N*, *N*′-bis[4-(phenylazo)benzylidene]-1,2-cyclohexanediamine, was synthesized in an attempt to construct a molecule which shows a large optical rotation change due to photoirradiation. The CD spectrum dramatically changed depending on the configuration of the two azobenzene units. The specific rotations of (*E*,*E*)-, (*E*,*Z*)- and (*Z*,*Z*)-isomers were −1400°, −940°, and −670°, respectivly, while that of the monosubstituted chiral cyclohexane, (1*R*, 2*R*)-*N*-[(4-phenylazo)benzylidene]-*N*′-benzylidene-1,2-cyclohexanediamine ((*E*)-isomer), was only −470°. There was no difference in the photoisomerization rates of the azobenzene chromophores attached to chiral and nonchiral cyclohexanes.

Although every effort to realize optical memory devices using photochromic compounds has been made, the photochromic memory devices still await practical applications.[1,2] One of the reasons is the lack of nondestructive readout capability. So far absorption spectral changes were used as the readout property change. In such systems, readout laser light destroys the memories.[3] One approach to avoid such inconvenience is to use optical rotation as the readout property change. The optical rotation can be detected using light which does not induce any photochromic reaction.[4,5]

A convenient way to construct a chiral photochromic compound which changes the optical rotation by photoirradiation is to incorporate a photochromic chromophore into a chiral moiety. An example is an amino acid having an azobenzene chromophore.[6] The specific rotation of β-[*p*-(phenylazo)]-L-phenylalanine is $[\alpha]_D^{20} = -42°$ in the *trans* form, and nearly zero in *cis* form. Another example is inherently chiral photochromic compounds.[7,8] The photoinduced specific rotation change as large as $\Delta[\alpha]_D = -421°$ has been reported.[8] Such optical rotation changes are not large enough for practical applications.[9] It is desired to develop chiral photochromic compounds which show larger optical rotation changes by to photoirradiation.

In this study we attempted to construct a chiral photochromic compound which shows a large optical rotation change. In order to amplify the optical rotation change we incorporated two azobenzenes into a chiral moiety. In such a system an exciton interaction of the two chromophores is expected to induce a large optical rotation change.

Results and Discussion

Chiral cyclohexanes, having one and two azobenzene chromophores, (1*R*,2*R*)-*N*, *N*′-bis[4-(phenylazo)benzylidene]-1,2-cyclohexanediamine (**1**) and (1*R*,2*R*)-*N*-[(4-phenylazo)benzylidene]-*N*′-benzylidene-1,2-cyclohexanediamine (**2**), were synthesized. A non-chiral cyclohexane, *N*-[(4-phenylazo)benzylidene]cyclohexanamine (**3**) was also synthesized as a reference compound (Chart 1).

Figure 1(a) shows the absorption spectral change of the compound **1** (5.2×10^{-4} mol dm^{-3}) in methanol by irradiation with 366 nm light (Chart 2). Upon irradiation with 366 nm light, the absorption peak at 330 nm decreased and the band at 420 nm increased. In the photostationary state under irradiation with 366 nm light, the absorption peak at 330 nm

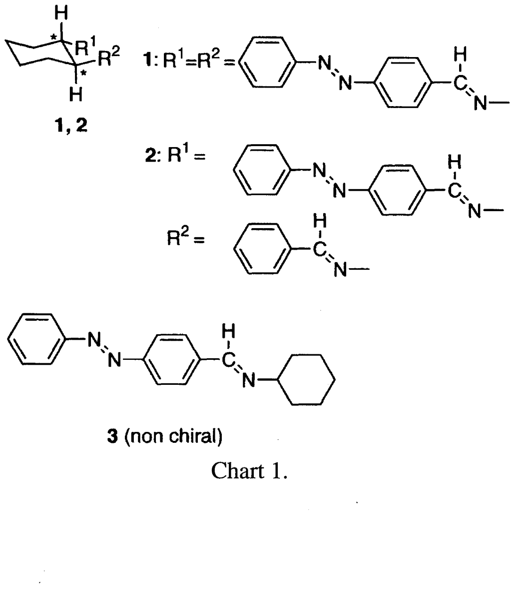

Chart 1.

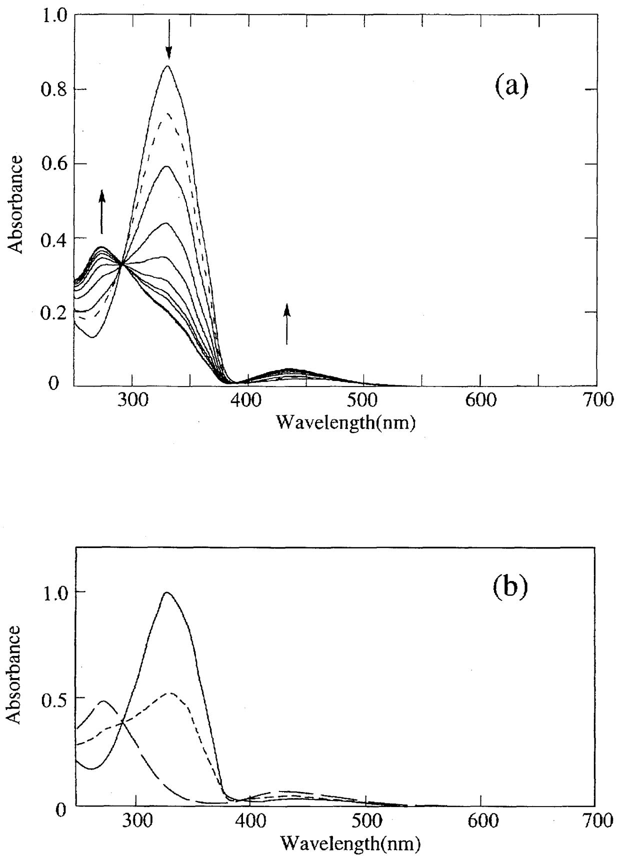

Fig. 1. (a) Absorption spectral change of **1** in methanol ($c = 1.5\times10^{-5}$ M). In the photostationary states by irradiation with 366 nm (——) and > 420 nm (- - -) light. (b) Absorption spectra of three isomers of **1** in methanol ($c = 1.8\times10^{-5}$ M). (*E*,*E*)- (——), (*E*,*Z*)- (- - -), and (*Z*,*Z*)-isomers (— —).

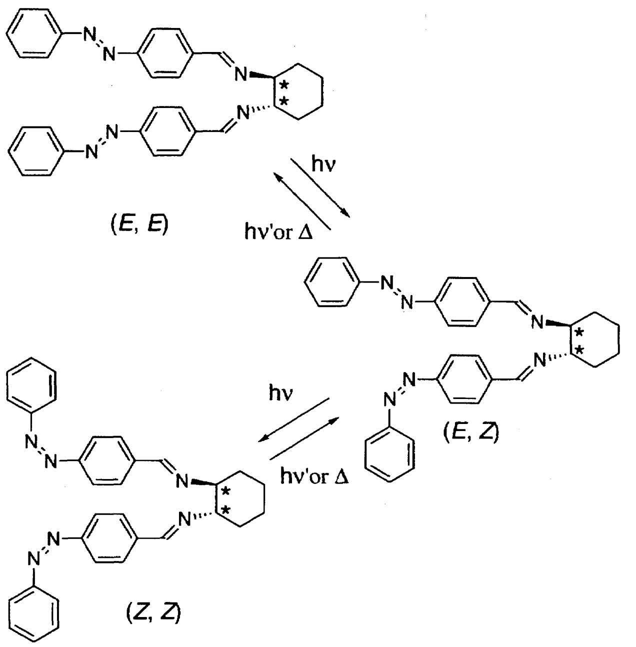

Chart 2.

almost disappeared. To determine the relative contributions of the three isomers, (*E*,*E*)-, (*E*,*Z*)-, and (*Z*,*Z*)-isomers, to the absorption spectrum, the three isomers were isolated by HPLC.[10] Figure 1(b) shows the spectra of these three isomers. The (*E*,*E*)-isomer of **1** ($\lambda_{\max}$ 330 nm; $\varepsilon_{\max}$ 5.9×10^4 $M^{-1}\,cm^{-1}$, M = mol dm^{-3}) converted to the (*E*,*Z*)- isomer ($\lambda_{\max}$ 330 nm; $\varepsilon_{\max}$ 3.1×10^4 $M^{-1}\,cm^{-1}$) and to the (*Z*,*Z*)-isomer ($\lambda_{\max}$ 270 nm; $\varepsilon_{\max}$ 2.9×10^4 $M^{-1}\,cm^{-1}$). The compound **2** ($\lambda_{\max}$ 330 nm; $\varepsilon_{\max}$ 3.1×10^4 $M^{-1}\,cm^{-1}$) showed a similar spectral change.

Figure 2 shows the formation process of (*E*,*Z*)- and (*Z*,*Z*)-isomers. The transformation of (*E*,*E*)-isomers to (*E*,*Z*)-isomers and then to (*Z*,*Z*)-isomers was clearly observed. In the photostationary state under irradiation with 366 nm light, (*Z*,*Z*)-isomers were the main product (80%) and the rest were (*E*,*Z*)-isomers. In the photostationary state under irradiation with 420 nm light, (*E*,*E*)-isomers were the main product (70%) and the rest were (*E*,*Z*)-isomers or (*Z*,*Z*)-isomers.

The photogenerated (*Z*,*Z*)-isomer converted to the (*E*,*E*)-isomer in the dark via the (*E*,*Z*)-isomer. The thermal isomerization rates from (*Z*,*Z*)- to (*E*,*Z*)-isomers and from (*E*,*Z*)- to (*E*,*E*)-isomers were determined to be 0.0245 (h^{-1}) and 0.0123 (h^{-1}), respectively. The thermal isomerization rate of (*Z*,*Z*)-isomers was twice as large as that of (*E*,*Z*)-isomers. This is simply due to the fact that the (*Z*,*Z*)-isomer has two azobenzene units.

Figure 3 shows the circular dichroism (CD) spectra of three isomers of **1** in methanol. The CD spectrum was found to change the shape and intensity depending on the configuration of the two azobenzene units. The (*E*,*E*)-isomer exhibits an intense exciton-split CD curve.[11] The negative exciton couplet with negative first at a longer wavelength indicates the negative chirality between the two C–N bonds. The exciton splitting in the circular dichroism (CD) of the Schiff base and salicyldene derivatives of (1*R*,2*R*)-(−)-1,2-cyclohexanediamine[12,13] has been utilized to determine the

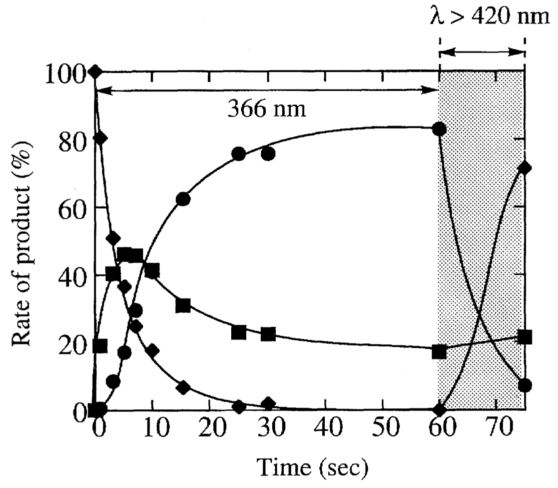

Fig. 2. Photoisomerization of compound **1** (2.0×10^{-5} M) from (*E*,*E*)-(◆) to (*Z*,*Z*)- (●) isomers through (*E*,*Z*)- (■) isomers by irradiation with 366 nm and > 420 nm light. The (*Z*,*Z*)-isomers returned to (*E*,*E*)-isomers by irradiation with > 420 nm light.

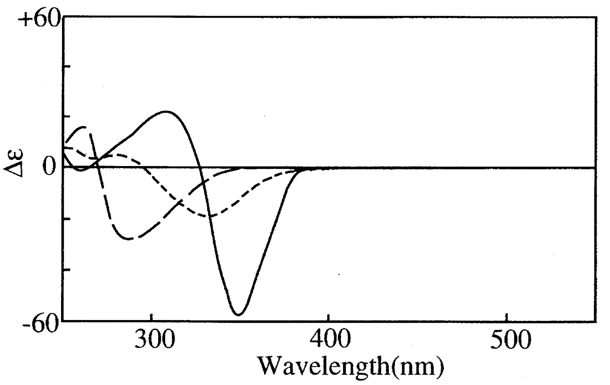

Fig. 3. CD spectra of the three isomers of compound **1** in methanol, (*E*,*E*)- (—), (*E*,*Z*)- (- - -), and (Z,Z)-isomers (— —).

chiral structure. The sign of the long wavelength band has the same sign as the chirality (right-handed screw for positive chirality).

The intense peaks at 350 and 303 nm of the (*E*,*E*)-isomers correlate with the maximum at 330 nm in the UV spectra. The (*Z*,*Z*)-isomer has peaks at 290 and 255 nm, which correlate with the maximum at 270 nm in the UV spectra. The CD spectrum intensity of (*Z*,*Z*)-isomer is larger than that of (*E*,*Z*)-isomer.

The CD spectrum of the (*E*,*Z*)-isomer did not show any clear splitting and is assigned to an induced CD spectrum. Figure 4 shows the absorption and CD spectra of (*E*)-isomer of compound **2** in methanol. This CD spectrum has two bands: at 330 nm (Δε: −9.5) and at 261 nm (Δε: −17.5). The CD spectral peaks agree with the absorption spectral peaks. The CD spectrum of compound **2** is assigned to an induced spectrum. Upon irradiation with 366 nm light the UV absorption peak at 330 nm decreased along with the decrease of the CD spectrum at 330 nm.

Figure 5 shows the optical rotation $[\alpha]_D^{25}$ ($c = 1$, CH_3CN) changes by irradiation with 366 and > 420 nm light in acetonitrile ($c = 1.1\times10^{-4}$ M). In this experiment acetonitrile was used as the solvent, because of high solubility of compound **1** in acetonitrile. The alternate irradiation of UV and of visible light reversibly changes the optical rotation. This is due to the difference in the ratio of the three isomers. Specific rotations of each isomer, (*E*,*E*)-, (*E*,*Z*)-, and (Z,Z)-isomer, were estimated from the content of the isomers, which was measured by HPLC after irradiation with 366 nm light. It was impossible to mesure directly each optical rotation value of (*E*,*Z*)-isomer and (*Z*,*Z*)-isomer isolated by HPLC, because an optical rotation measurement requires high solute concentration and the azobenzenes thermally isomerized during the concetration process. Under the present high concentration condition, the content of the (*Z*,*Z*)-isomer after irradiation with 366 nm light for 2.5 h was only 58% and the rest were (*E*,*E*)- and (*E*,*Z*)-isomers. The specific rotation values were evaluated to be −1400° ((*E*,*E*)-isomer), −940° ((*E*,*Z*)-isomer) and −670° ((*Z*,*Z*)-isomer). On the other hand, the specific rotation values of compound **2** ((*E*) and (*Z*)-isomers), which has only one azobenzene chromophore, were mea-

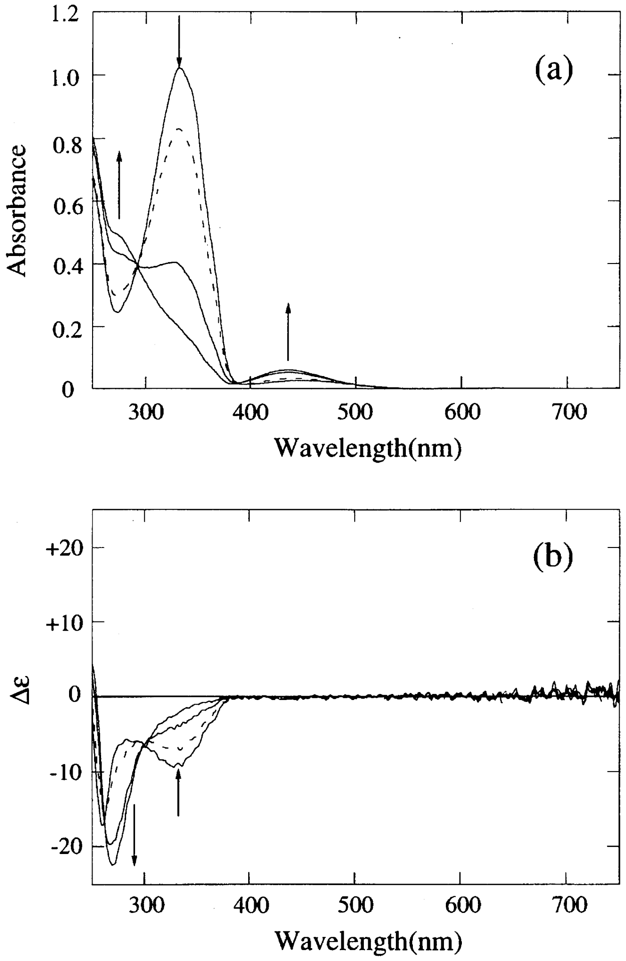

Fig. 4. (a) Absorption spectral change of **2** in methanol ($c = 3.8\times10^{-5}$ M). In the photostationary states by irradiation with 366 nm (—) and > 420 nm (- - -) light. (b) CD spectral change of **2** in methanol ($c = 3.8\times10^{-5}$ M). In the photostationary states by irradiation with 366 nm (—) and > 420 nm (- - -) light.

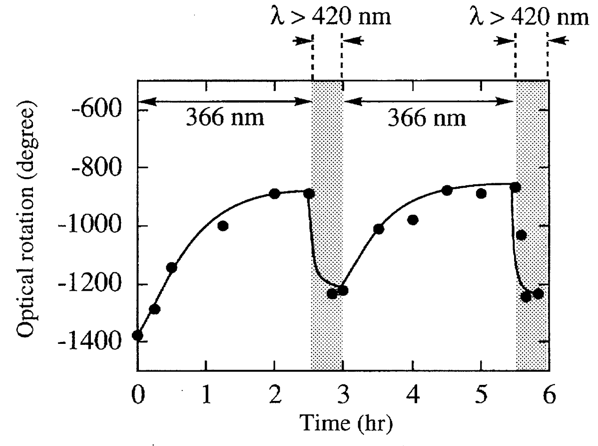

Fig. 5. Reversible optical rotation $[\alpha]_D^{25}$ ($c = 1$, CH_3CN) change of compound **1** by alternate irradiation with 366 nm and > 420 nm light. Concentration of compound **1**: 1.1×10^{-4} M.

Table 1. Relative Quantum Yields of the Photoisomerization of Compound **1** from *E–E* to *E–Z*
The quantum yield of **3** from *E* to *Z* was normalized to 1.

Irradiation wavelength	Relative quantum yield
313 nm	0.491
334 nm	0.485
350 nm	0.501
366 nm	0.469

sured to be −470° ((*E*)-isomer) and −280° ((*Z*)-isomer) in acetonitrile. The specific rotation change of the mono-chromophoric compound is much lower than the bichromophoric compound. This result suggests that some interactions of two azobenzene chromophores, such as exciton coupling, play a role to enhance the specific rotation value.

Table 1 shows the relative quantum yields of the isomerizations for **1** and **3**. The quantum yield of compound **3** from (*E*)- to (*Z*)-isomer was normalized to 1. Compound **1** has two azobenzene units. If the two azobenzene chromophores in compound **1** have no special interaction with each other, the relative quantum yields should be 0.5. Although the values are slightly smaller than 0.5, the difference is in the experimental error. This result indicates that the exciton coupling can not (or only slightly) affect the quantum yield of (*E*) to (*Z*) photoisomerization.

Conclusion

A chiral cyclohexane containing two azobenzene units, (*R*,*R*)-*N*,*N*′-bis[(4-phenyl-azophenyl) methylene]-1,2-cyclohexanediamine, was synthesized and its chiral property change by photoirradiation was examined. Upon irradiation with 366 nm light both azobenzene units isomerized. In the photostationary state under dilute condition, (2.0×10^{-5} M), (*Z*,*Z*)-isomers were the main product (80%) and the rest were (*E*,*Z*)-isomers. The CD spectrum was found to change the shape and intensity depending on the configuration of the two azobenzene units. The compound also showed a large optical rotation change, as large as 730° at 589 nm when photoisomerized from (*E*,*E*)- to (*Z*,*Z*)-isomer. This value is, however, still too small to apply for the practical optical disk memories.

Experimental

General. Solvents used were spectrograde and were purified by distillation before use. Absorption spectra were measured with an absorption spectrophotometer (Hitachi, U-3410). A mercury lamp (Ushio, 500 W) and a xenon lamp (Ushio, 1 kW) were used as the light sources. Monochrometric light was obtained by passing the light through a Toshiba cut-off filter (L-42). ^{1}H NMR spectra were recorded on a Gemini 200 (200 MHz) spectrometer. The signals were expressed as ppm downfield from tetramethylsilane, used as an internal standard (δ value). Mass spectra were taken with a LUCY (Version 2.22) mass spectrometer. Circular dichromism was measured with a JASCO J-720S spectrometer. The optical rotation was measured using a Union GIKEN PM-101 (589 nm light). HPLC was carried out on a Shimadzu LC-6AD liquid chromatograph coupled with a Shimadzu SPD-10AV spectrophotomeric detector.

Materials. 4-(Phenylazo)benzaldehyde (4). 4-(Phenylazo)benzoylchloride (0.500 g) in 15 ml of THF was cooled at −78 °C under nitrogen gas. The solution of lithium tri-*t*-butoxyhydroaluminate (0.625 g) in 20 ml of dry THF was added dropwise to this solution. The solution was stirred for 1 h at −78 °C. The reaction mixture was poured into 1 M hydrochloric acid. The product was extracted with diethyl ether, and dried over sodium sulfate. The solvent was removed, and the residue was purified by column chromatography to give **4** in 75% yield: Mp 119—120 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.53—7.57 (m, 3H), 7.94—7.99 (m, 2H), 8.05 (s, 4H), 10.12 (s, 1H); IR 1698 cm^{-1} (C=O); MS *m*/*z* M$^+$ 210. Anal. Calcd for $C_{13}H_{10}N_2O$: C, 74.27; H, 4.79; N, 13.32%. Found: C, 74.33; H, 4.76; N, 13.19%.

(1*R*,2*R*)-*N*,*N*′-Bis[4-(phenylazo)benzylidene]-1,2-cyclohexanediamine (1). 4-(Phenylazo)benzaldehyde **4** (0.150 g) in 10 ml of methanol and excess magnesium sulfate were added to (1*R*,2*R*)-(−)- cyclohexanediamine (0.0407 g), and the solution was stirred for 24 h. The magnesium sulfate was filtered, and the solvent was removed to give **1** in quantitative yield: Mp 180—181 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ = 1.53 (s, br, 2H), 1.93 (s, br, 6H), 3.48 (t, *J* = 4.8 Hz, 2H), 7.44—7.52 (m, 3H), 7.74 (d, *J* = 8 Hz, 2H), 7.85—7.90 (m, 4H), 8.29 (s, 2H); IR 1637 cm^{-1} (C=N); MS *m*/*z* M$^+$ 498, M$^+$ 498. Anal. Calcd for $2C_{32}H_{30}N_6+CH_3OH$: C, 75.99; H, 6.13; N, 16.41%. Found: C, 75.85; H, 6.27; N, 16.33%.

(1*R*,2*R*)-*N*-[(4-Phenylazo)benzylidene]-*N*′-benzylidene-1,2-cyclohexanediamine (2). Benzaldehyde (0.255 g) in 10 ml of methanol and excess magnesium sulfate were added to (1*R*,2*R*)-(−)- cyclohexanediamine (0.500 g), and the solution was stirred for 24 h. Subsequently, 4-(phenylazo)benzaldehyde **4** (0.150 g) was added to the solution, and the solution was stirred for 24 h. The magnesium sulfate was filtered, and the solvent was removed to give **2** (yield: 35%): Mp 118—119 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ = 1.50 (s, br, 2H), 1.86—1.90 (s, br, 6H), 3.40—3.48 (m, 2H), 7.30—7.32 (m, 2H), 7.46—7.52 (m, 3H), 7.57—7.59 (m, 2H), 7.72—7.75 (m, 2H), 7.85—7.90 (m, 4H), 8.20 (s, 1H), 8.27 (d, *J* = 3 Hz, 1H); MS *m*/*z* M$^+$ 395, M$^+$ 395. Anal. Calcd for $C_{26}H_{26}N_4$: C, 79.16; H, 6.64; N, 14.20%. Found: C, 79.24; H, 6.71; N, 14.05%.

***N*-[(4-Phenylazo)benzylidene]cyclohexanamine (3).** 4-(Phenylazo)benzaldehyde **4** (0.150 g) in 10 ml of methanol and excess magnesium sulfate were added to cyclohexandiamine (0.0407 g), and the solution was stirred for 24 h. The magnesium sulfate was filtered, and the solvent was removed to give **3** in quantitative yield: Mp 117—118 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ = 1.23—1.89 (m, 10H), 3.19—3.28 (m, 1H), 3.48 (s, 1H), 7.48—7.56 (m, 3H), 7.85—7.97 (m, 6H), 8.38 (s, 1H). Anal. Calcd for $C_{19}H_{21}N_3$: C, 78.32; H, 7.26; N, 14.42%. Found: C, 78.25; H, 7.24; N, 14.31%.

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