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Photoswitching of Dextro/Levo Rotation with Axially Chiral Binaphthyls Linked to an Azobenzene

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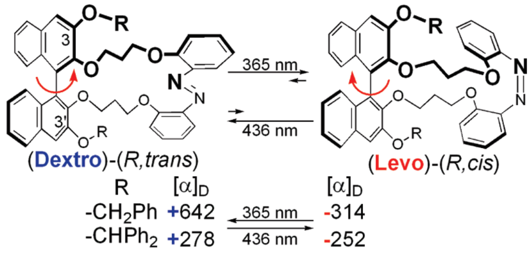

To examine the reversible photoisomerization and subsequent change of asymmetric field, we synthesized optically active 3,3′-disubstituted-1,1′-binaphthyls with an azobenzene moiety. Reflecting the structural change, the specific rotation and circular dichroism underwent significant variations. Under certain conditions, the positive−negative signals were reversible. Furthermore, the magnitude of these changes showed a 3,3′-substituent dependency. Dibenzyloxy or bis(diphenylmethyloxy) derivatives were better suited for sign interconversion of the optical properties. In contrast, the hydroxy group(s) lacked both optical signals and durability.

Axially chiral binaphthyls have a wide, flexible asymmetric field. Hence, they have been extensively used in catalytic asymmetric syntheses,[1] specific molecular recognition,[2] and helical twisting of liquid crystallines,[3] and have been selected as objects in computational chemistry.[4] Moreover, reflecting their chirality, some axially chiral binaphthyls exhibit relatively large optical rotations and circular dichroism (CD).[5] The large positive-negative-reversible changes of such optical properties have been evaluated with promising results in the development of novel photoswitching materials. Moreover, optical rotation can be detected at an unabsorbed wavelength, so target compounds do not degrade during measurement. Hence, a switch for dextro (positive)/levo (negative) rotation will lead to the development of noise-cancellation, nondestructive reading of memory devices.[6c] Although practical recording-reproduction systems have been designed by using optical rotation, practical applications have yet to emerge due to the lack of appropriate compounds.[6d,e] Irie, Branda, Wang, and Yokoyama et al. have independently reported changes using helicenoids via photochroism,[7] but the CD variations are not large or unreported and the change in optical rotations at the sodium D-line, the universal wavelength (589 nm), does not involve a sign inversion. Our research strives to change the CD variations and optical rotations using axially chiral binaphthyl derivatives.

We have reported basic compound (*R*)-**1** (Figure 1), which is composed of binaphthyl and azobenzene skeletons.[8] Azobenzene skeletons are heavily used photochromic parts,[9] and show a significant change in length between the cis and trans forms. The azobenzene moiety of (*R*)-**1** can be reasonably cis−trans photoisomerized. Additionally, isomerization can be detected by the change in CD intensity, which is likely due to the change in the dihedral angle formed by the two naphthalene rings because the dihedral angle is related to the CD intensity. This change is reversible, but the change is small and sign reversal is not detected. Although we have attempted to shorten the linkers so that the structural change of the azobenzene moiety can be more directly transmitted to the binaphthyl, our attempts have been unsuccessful. As an alternative, herein we investigate whether the 3,3′-substituents of the binaphthyl moiety can produce large conformation changes between the cis and trans forms as well as initiate subsequent changes in optical rotation and CD.

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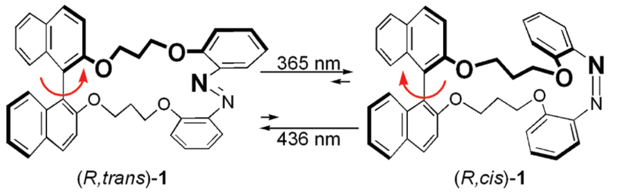
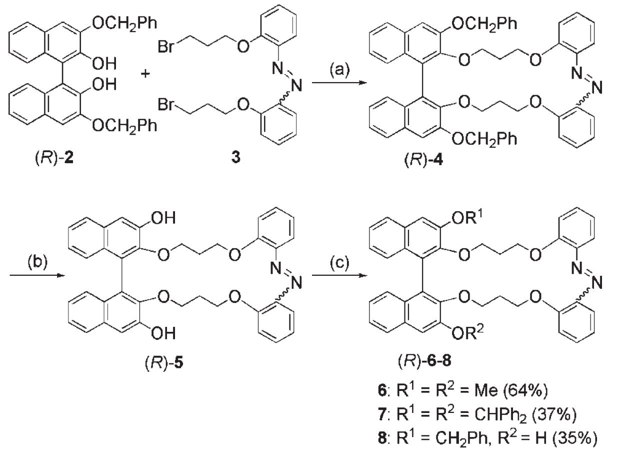


FIGURE 1. (*R*)-**1** and its photoisomerization.

SCHEME 1. Synthetic Route to (*R*)-4−8[a]



[a]Conditions: (a) K_2CO_3, 36%, (b) $TiCl_4$, 91%, (c) RX, base, 35−64%.

As shown in Scheme 1, 3,3′-disubstituted binaphthyl-azobenzene diads (*R*)-**4**−**8** were synthesized starting from optically active (*R*)-**2**.[10] Williamson synthesis of diol (*R*)-**2** and dibromide **3** afforded cyclic compound (*R*)-**4** in 36% yield. Then debenzylation of (*R*)-**4** with titanium tetrachloride for 5 min gave (*R*)-**5** in high yield (91%). Using a higher temperature, longer reaction time, or another Lewis acid (e.g., aluminum trichloride or niobium pentachloride) resulted in an extremely low yield (<5%) because some of the other O−alkyl bonds of (*R*)-**4** were also disconnected, and subsequent polymerization was also detected. Additionally, generalized deprotection with palladium-activated carbon (Pd/C) and hydrogen was unsuccessful under the reduction of the azobenzene moiety. (*R*)-**6**−**8** were prepared in moderate yields by coupling (*R*)-**5** with the appropriate halide. In the synthesis of (*R*)-**6** and -**7**, excess methyl iodide (MeI) and α-bromodiphenylmethane were used, respectively. Although in the synthesis of (*R*)-**8**, 1.1 equiv (based on (*R*)-**5**) of benzyl bromide was used for preferential monobenzylation, mixtures of desired (*R*)-**8**, unreacted (*R*)-**5**, and dibenzylated (*R*)-**4** were obtained; they were easily separated by gel permeation chromatography (GPC).

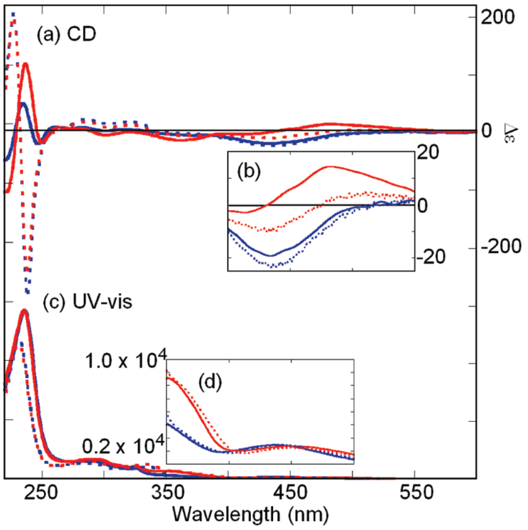


FIGURE 2. (a, b) CD spectra of (*R*)-**4** and (*R*)-**1**. (c, d) Absorption spectra of (*R*)-**4** and (*R*)-**1** (horizontal scales are common). (*R*)-**4** after 365 nm irradiation (blue solid line), (*R*)-**4** after 436 nm irradiation (red solid line), (*R*)-**1** after 365 nm irradiation (blue dotted line), and (*R*)-**1** after 436 nm irradiation (red dotted line). Conditions: 1,4-dioxane (1.0×10^{-5} M), 20 °C, light path length = 10 mm, irradiation wavelength = 365 nm (10 mW/cm^2, 100 s) and 436 nm (10 mW/cm^2, 100 s).

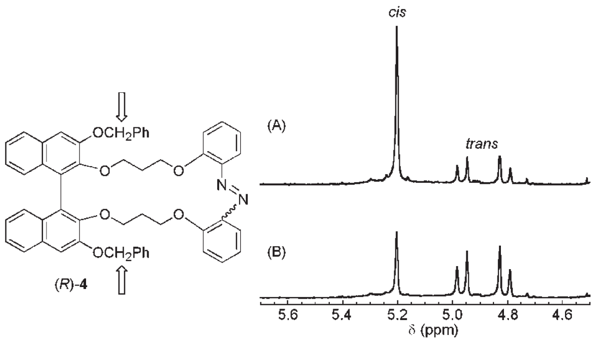


FIGURE 3. ^{1}H NMR spectra of the benzyl protons of (*R*)-**4** after (A) 365 nm irradiation and (B) 436 nm irradiation. Conditions: $CDCl_3$ (1×10^{-3} M), 300 MHz, 22 °C, irradiation 365 nm (10 mW/cm^2, 500 s) and 436 nm (10 mW/cm^2, 500 s) in an NMR test tube (ϕ = 5 mm).

Cis-trans isomerization[11] was confirmed by the change in absorption near 360 nm, which indicated a π-π^* transition of the trans form. On the whole, the absorption spectra of (*R*)-**4** and (*R*)-**1** were similar (Figure 2). On the other hand, the CD spectra differed; the CD spectral shape of (*R*)-**4** was atypical in three ways: (1) the cis and trans forms differed significantly, (2) a positive-negative-reversible region was observed on the long-wavelength side (around 450−500 nm) for the trans form, which unlike (*R*)-**1**, exhibited a positive Cotton effect, and (3) the Cotton effect at a short wavelength (around 230 nm), which was attributed mainly to the ^1B_b transition moment and reflected twisting of two naphthalene rings,[12] did not resemble that of (*R*)-**1**.[13] Meca, et al. have calculated the racemization barriers of select 2,2′-disubsituted-1,1′-binaphthyl derivatives; all the values are greater than 38 kcal/mol. Hence, racemizations of these binaphthyls are atypical.[14] Racemization or epimerization

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[11] $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for cis−trans isomerization of (*R*)-**4** and **7** have been experimentally determined to be 22 kcal/mol and −13 cal/(mol·K) for (*R*)-**4** and 20 kcal/mol and −17 cal/(mol·K) for (*R*)-**7**.

[12] Harada, N.; Nakanishi, K. *Acc. Chem. Res.* **1972**, *5*, 257–263.

[13] Although Bari et al. used calculations to determine that the Cotton effect of the CD was inverted at a naphthalene dihedral angle of 110°, no exceptions have yet to be reported for this empirical rule: (a) Bari, L. D.; Pescitelli, G.; Marchetti, F.; Salvadori, P. *J. Am. Chem. Soc.* **2000**, *122*, 6395–6398. (b) Bari, L. D.; Pescitelli, G.; Salvadori, P. *J. Am. Chem. Soc.* **1999**, *121*, 7998–8004.

[14] Meca, L.; Reha, D.; Havlas, Z. *J. Org. Chem.* **2003**, *68*, 5677–5680.

TABLE 1. CD Data and Cis−Trans Ratio of (*R*)-4−8[a]

entry	compd	CDλ after 365 nm irradiation (nm)	$\Delta\varepsilon$ after 365 nm irradiation	cis:trans after 365 nm irradiation[b]	CDλ after 436 nm irradiation (nm)	$\Delta\varepsilon$ after 436 nm irradiation	cis:trans after 436 nm irradiation[b]
1	(*R*)-**4**	235.0	+50.7	71:29	237.0	+119.3	31:69
		434.0	−19.3		482.0	+14.4	
2	(*R*)-**5**	230.5	+50.0	65:35	232.0	+51.7	31:69
		436.5	−16.7		426.5	−10.5	
3	(*R*)-**6**	233.5	+53.3	72:28	234.5	+87.3	22:78
		436.5	−14.5		485.5	+7.2	
4	(*R*)-**7**	234.0	+37.0	69:31	238.0	+93.3	35:65
		435.5	−19.8		486.5	+14.2	
5	(*R*)-**8**	233.0	+48.2	68:32	235.0	+86.7	29:71
		435.0	−19.4		488.5	+9.4	

[a] Conditions: 1,4-dioxane (1.0×10^{-5} M), 20 °C, light path length = 10 mm, irradiation wavelength = 365 nm (10 mW/cm^2, 100 s) and 436 nm (10 mW/cm^2, 100 s). [b] Determined by HPLC (column, Inertsil SIL 100-A (GL science, Inc.); eluent, $CHCl_3$:*n*-hexane = 1:1 for (*R*)-**4**, **6**, **7**, **8**, $CHCl_3$ for (*R*)-**5**).

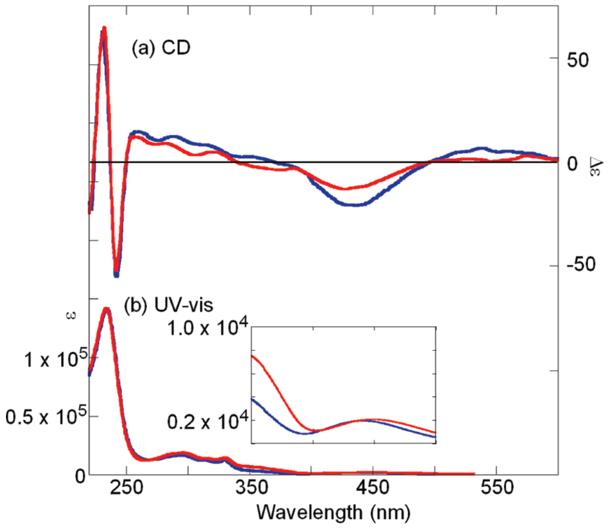

FIGURE 4. (a) CD spectra of (*R*)-**5** and (b) absorption spectra of (*R*)-**5**; after 365 nm irradiation (blue line) and after 436 nm irradiation (red line). Conditions: 1,4-dioxane (1.0×10^{-5} M), 20 °C, light path length = 10 mm, irradiation wavelength = 365 nm (10 mW/cm^2, 100 s) and 436 nm (10 mW/cm^2, 100 s).

required strong acids or metallic catalysts.[15] Therefore, (*R*)-**4** maintains its original configuration. As a precautionary measure, (*R*)-**4** was derivatized to a known compound to verify that inversion did not occur (see the Supporting Information). Hence, the approximate inversion of the Cotton effect near 230 nm likely caused the defferences between the dihedral angle of naphthalene rings or the wavelength of maximum absorption for (*R*)-**4** and that of (*R*)-**1**.

The chemical shift and signal splitting of the benzyl protons far from the light-driven part of (*R*)-**4** in the ^{1}H NMR vastly differed between the cis and trans forms because the signal of (*R*,*cis*)-**4** appeared as a singlet, whereas that of (*R*,*trans*)-**4** was an AB quartet with $\Delta\delta$ of 0.3 ppm (Figure 3). Similar to the examples above, the 3,3′-dibenzyl groups played an important role in the entire conformation of these compounds.

Table 1 shows the CD data and isomer ratio at the points of (*R*)-**4**−**8**. The three tendencies described above were true for (*R*)-**6**−**8**, but the intensities varied. The 3-substituent does not have to be aromatic because the CD movement of (*R*)-**6**, which possesses methoxy groups, was similar to that of (*R*)-**4**, but with a smaller variation. Thus, we speculated that although bulkier is not necessarily better, the steric effect is important. Dihydroxy groups were too small to exibit unique properties (Figure 4).[16] This photoisomerization can be cycled numerous times without decomposition by using (*R*)-**4**, -**6**, and -**7**, but (*R*)-**5** and -**8**, which possess hydroxy group(s), degraded slightly after 20 irradiation cycles.

TABLE 2. $[\alpha]_D$ and $[\Phi]_D$ of (*R*)-4−8 after Photoirradiation[a]

entry	compd	$[\alpha]_D$ ($[\Phi]_D$[b]) after 365 nm irradiation (deg)	$[\alpha]_D$ ($[\Phi]_D$) after 436 nm irradiation (deg)
1	(*R*)-**4**	−314 (−2500)	+642 (+5100)
2	(*R*)-**5**	−427 (−2600)	−490 (−3000)
3	(*R*)-**6**	−370 (−2400)	+248 (+1600)
4	(*R*)-**7**	−252 (−2400)	+278 (+2600)
5	(*R*)-**8**	−415 (−2900)	−285 (−2000)

[a] Conditions: chloroform, *c* = 0.10 g/dL, 20 °C, light path length = 10 cm, irradiation wavelength = 365 nm (10 mW/cm^2, 500 s) and 436 nm (10 mW/cm^2, 500 s). [b] $[\Phi]_D = [\alpha]_D/100 \times$ (molecular weight).

Table 2 shows the specific optical rotations ($[\alpha]_D$) and molar optical rotations ($[\Phi]_D$) of (*R*)-**4**−**8** after photoirradiation until the values were constant. Absorption at the sodium D-line (589 nm) did not occur despite analysis at high concentrations and long path lengths. The cis−trans ratios were the same as those shown in Table 1. The absolute values of $[\alpha]_D$ were lower than those of helicenes and other chiral metallic compounds,[17] but were greater than general axially chiral compounds. Furthermore, $[\alpha]_D$ of (*R*)-**4**, -**6**, and -**7** resulted in a sign inversion; (*R*)-**4** showed the largest change (ca. 1000°). The absolute values of $[\alpha]_D$ of compound (*R*)-**7** remained nearly constant, but the sign was reversed. From the result of (*R*)-**8**, both 3- and 3′-substitents, which are bulkier than the hydroxy group, are necessary to realize a sufficient sign inversion. $[\Phi]_D$, which is the molecular weight-adjusted value, of (*R*)-**4**−**8** after 365 nm irradiation was similar. Thus, the conformation around the azobenzene moiety about the cis form has a negligible difference, and consequently, the 3,3′-substituent is key to the conformation of the trans form.

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(15) Tsubaki, K.; Tanaka, H.; Takaishi, K.; Miura, M.; Morikawa, H.; Furuta, T.; Tanaka, K.; Fuji, K.; Sasamori, T.; Tokitoh, N.; Kawabata, T. *J. Org. Chem.* **2006**, *71*, 6579–6587.

(16) Because the CD spectral shape of (*R*)-**5** in methanol and that in 1,4-dioxane are the same, it is likely that hydrogen bonds do not contribute much to its conformation.

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In summary, we synthesized a series of 3,3′-disubstituted-1,1′-binaphthyls with an azobenzene moiety, and the variation of their CD spectra and optical rotations were detected before and after photoisomerization. The optical properties of the axially chiral compounds changed greatly. Moreover, novel, reversible positive−negative signals were detected. This result may be useful in designing molecular switches, binaphthyl-type catalysts, and their leads. Studies on the substituent effect are currently underway.

Experimental Section

Synthesis of (*R*)-4. A suspension of (*R*)-**2** (2.00 g, 4.02 mmol), K_2CO_3 (1.22 g, 8.83 mmol, 2.2 equiv) and **3** (1.92 g, 4.02 mmol, 1.0 equiv) in DMF (300 mL) was stirred for 12 h at 50 °C. Then the reaction mixture was poured into a mixed solvent of chloroform and water. The organic layer was separated and washed successively with 0.1 N hydrochloric acid solution, water (twice), and brine. After drying over sodium sulfate, the solvent was evaporated in vacuo to give a residue, which was purified by column chromatography (SiO_2; *n*-hexane/chloroform = 1/9) and GPC to afford (*R*)-**4** (1.15 g, 1.45 mmol, 36%): red amorphous; IR (KBr) 2959, 1439, 1281, 1250, 1017, 748 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.2−2.1 (m, 4H), 3.2−4.3 (m, 8H), 4.88, 5.19 (ABq, ν_{AB} = 61.7 Hz, J_{AB} = 11.2 Hz, s, 4H), 6.4−7.5 (m, 26H), 7.73, 7.78 (two d, *J* = 8.4, 8.4 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 29.5, 29.7, 64.8, 65.1, 68.9, 70.1, 70.5, 70.6, 108.4, 108.4, 113.1, 113.9, 119.4, 120.2, 124.0, 124.2, 125.0, 125.6, 125.7, 125.2, 126.3, 127.8, 127.9, 128.2, 128.5, 128.8, 128.8, 130.5, 130.6, 130.8, 136.4, 136.5, 142.6, 143.7, 145.9, 146.4, 151.1, 151.3, 152.8 (some peaks overlapped); HRMS (ESI^+) calcd for $C_{52}H_{45}N_2O_6$ $(M + H)^+$ 793.3278, found 793.3303; LR MS (FAB^+) 793.4 $(M + H)^+$.

Synthesis of (*R*)-5. A suspension of (*R*)-**4** (400 mg, 0.504 mmol) and $TiCl_4$ (111 μL,1.01 mmol, 2.0 equiv) in CH_2Cl_2 (20 mL) was stirred for 5 min at 0 °C. Then the reaction mixture was poured into a mixed solvent of chloroform, ethyl acetate, and water. The organic layer was separated and washed successively with water (twice) and brine. After drying over sodium sulfate, the solvent was evaporated in vacuo to give a residue. The residue was purified by column chromatography (SiO_2; *n*-hexane/chloroform/ethyl acetate = 2/3/1) to afford (*R*)-**5** (281 mg, 0.459 mmol, 91%): red amorphous; IR (KBr) 3374, 1439, 1283, 1250, 752 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.4−1.9 (m, 4H), 3.5−4.0 (m, 8H), 6.54 (br s, 2H), 6.7−7.5 (m, 16H), 7.62, 7.73 (two d, *J* = 8.4, 8.4 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 29.0, 29.5, 67.2, 67.4, 69.8, 71.1, 111.1, 111.5, 114.4, 115.4, 119.6, 120.7, 120.8, 121.1, 123.6, 123.9, 124.5, 124.7, 125.2, 125.3, 125.7, 125.8, 126.6, 128.2, 128.5, 128.6, 129.2, 130.9, 131.6, 143.4, 144.9, 145.2, 145.7, 147.9, 148.3, 148.3, 149.0, 153.2; HRMS (ESI^+) calcd for $C_{38}H_{32}N_2O_6Na$ $(M + Na)^+$ 635.2158, found 635.2147; LR MS (FAB^+) 613.2 $(M + H)^+$, 635.2 $(M + Na)^+$.

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Supporting Information Available: CD and UV−vis spectra of **4**−**8**, including select overlapping displays, full experimental details, and characterization data of all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.