

Review

# Synthesis and Conformation of Substituted Chiral Binaphthyl-Azobenzene Cyclic Dyads with Chiroptical Switching Capabilities

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**Abstract:** Optically active binaphthyl-azobenzene cyclic dyads were synthesized to develop a photochromic switching molecule. Azobenzene moieties were *cis-trans* isomerized by photoirradiation. As a reflection of the structural change, the specific optical rotation and circular dichroism underwent significant shifts. Under certain conditions, the positive-negative and zero-positive (or zero-negative) signals were reversed. Optical rotation may potentially be applied in noise-cancelling nondestructive photoswitches. The conformations were studied by experimental and theoretical methods. The results revealed that the helical chirality, (*P*) or (*M*), of the *cis*-azobenzene moiety was induced by intramolecular axial chirality. The twist direction depended on the axial chirality as well as the azobenzene linkage position to the binaphthyls, but was independent of the identity of substituted groups. 2,2'-Linked-(*R*)-binaphthyl was found to induce *cis*-(*P*)-azobenzene, whereas symmetrically 7,7'-linked-(*R*)-binaphthyl was found to induce *cis*-(*M*)-azobenzene.

**Keywords:** optical rotation; circular dichroism; axial chirality; helical chirality; binaphthyl, azobenzene; DFT calculation; chiroptical switch

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## 1. Introduction

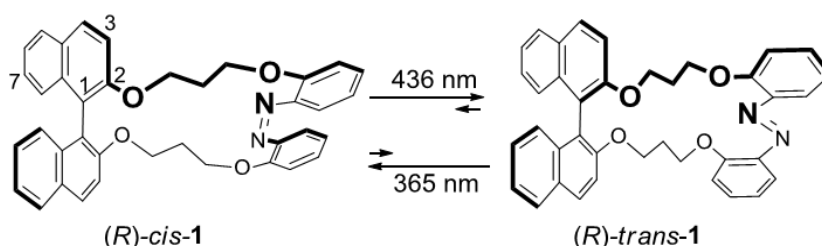
Molecular scaffolds designed for disparate purposes may be linked to enhance the properties of one component or to confer altogether new properties. Stimulus-driven chiroptical switches such as light-,

electrically-, pH-, ion-, and temperature-driven switches have received a great deal of attention in the past decade [1-11]. Their high sensitivity and fast response are of great interest for molecular devices. These molecular switches are expected to find application in the fields of noise cancellation data storage, display instrument, and modulator.

Meanwhile, the axially chiral 1,1'-binaphthyl skeletons represented by BINOL [12,13] and BINAP [14,15] have a wide, flexible asymmetric field. Therefore, binaphthyl skeletons have made great contributions to the fields of catalytic asymmetric synthesis [14-28], specific molecular recognition [29-41], helical twisting of liquid crystals [42-55], and computational chemistry [56-62]. Azobenzenes are frequently used as photochromic components due to their switchable absorption spectra, fluorescence properties, and association constants [63-86]. The *cis* and *trans* forms of the azobenzene skeleton differ significantly in length. Therefore, it was thought that the combination of binaphthyls and azobenzenes may lead to novel molecular switches with optical properties that are derived from the chirality of the components.

Previously, Kawamoto *et al.* described a basic binaphthyl-azobenzene dyad **1** (Figure 1) and its enantiomer [87]. The azobenzene moiety of **1** was efficiently photoisomerized to yield switching behavior, as observed in the intensity of the circular dichroism (CD) and the helical twisting power (HTP) against liquid crystal materials.

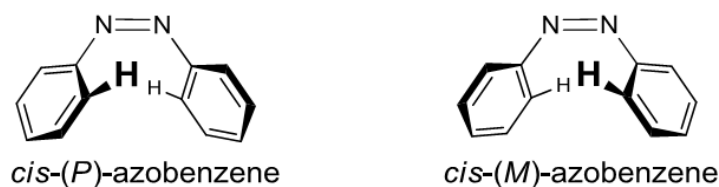
**Figure 1.** Photoisomerization of binaphthyl-azobenzene dyads **1**.



We have continued this work to analyze the photoswitchable optical properties, including absorption, CD, and optical rotation, using substituted binaphthyl-azobenzene dyads and their regioisomers [88,89]. Above all, we focused on the switching of the optical rotation, which can be detected at an unabsorbed wavelength, so that the target compounds did not degrade during measurements.

The *cis*-azobenzene isomers assume an inherent helicity, (*P*) or (*M*), caused by the steric hindrance of each of the two benzene rings (Figure 2). The properties of the helicity were not well understood with a notable exception [90], so we proceeded to investigate the twisting patterns of the *cis*-azobenzene moieties induced by intramolecular chirality transfer from the axial chirality of the binaphthyl units.

**Figure 2.** Helicity of the *cis*-azobenzenes.

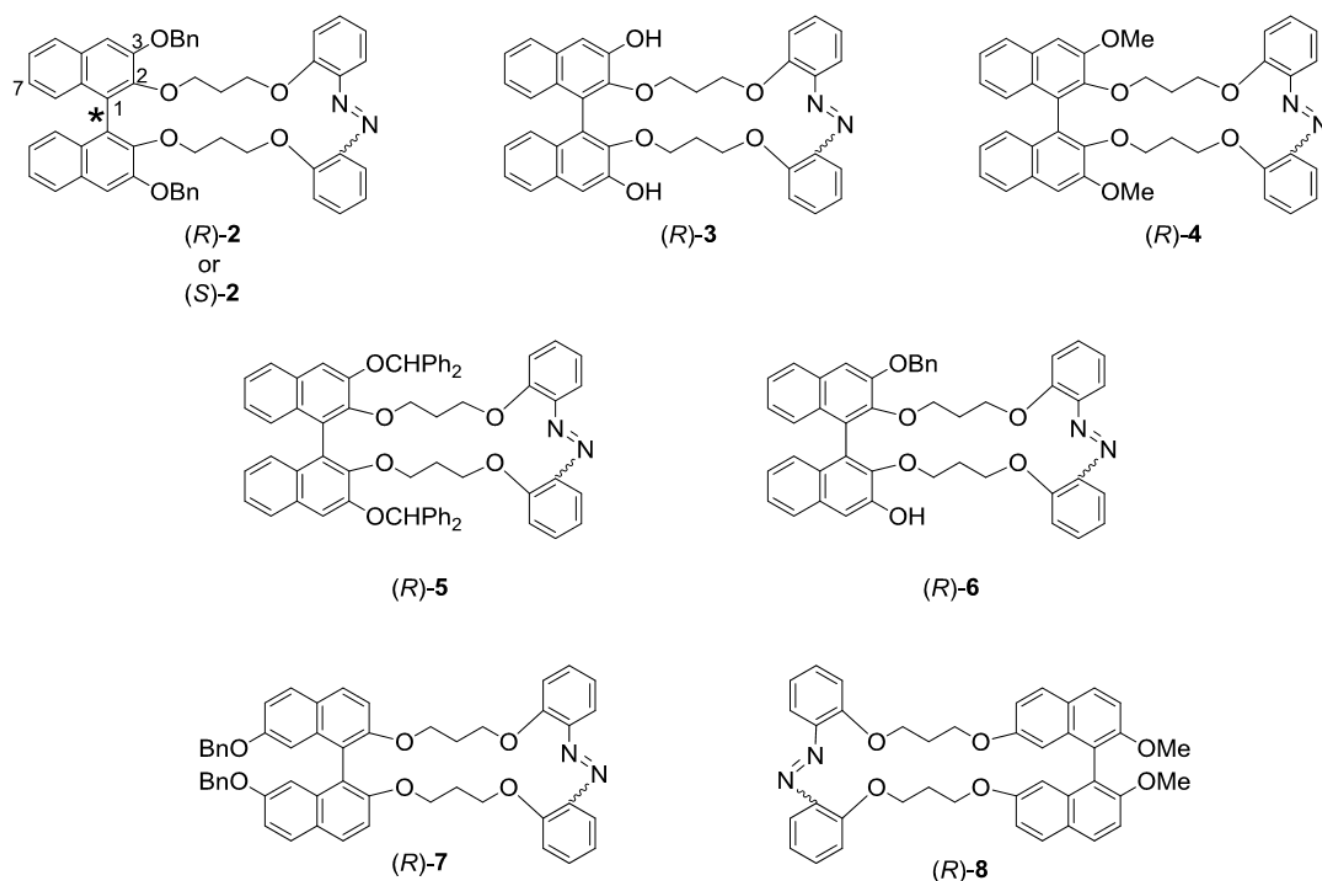


## 2. Results and Discussion

### 2.1. Binaphthyl-Azobenzene Cyclic Dyads

Binaphthyl-azobenzene cyclic dyads **2–8** used in this study are shown in Figure 3. Their binaphthyl moieties are the axially chiral parts, and the azobenzene moieties are the photochromic parts. Compounds **2–6** have various substituents – benzyloxy, hydroxy, methoxy, and diphenylmethoxy groups – at the 3,3'-positions of the 1,1'-binaphthyl moiety and are linked circularly to the azobenzene moiety at the 2,2'-positions. In contrast, compound **7** has dibenzyloxy groups at the 7,7'-positions, while compound **8** is substituted by 2,2'-dimethoxy groups and is linked to an azobenzene moiety through the 7,7'-positions.

**Figure 3.** Optically active binaphthyl-azobenzene cyclic dyads **2–8**.

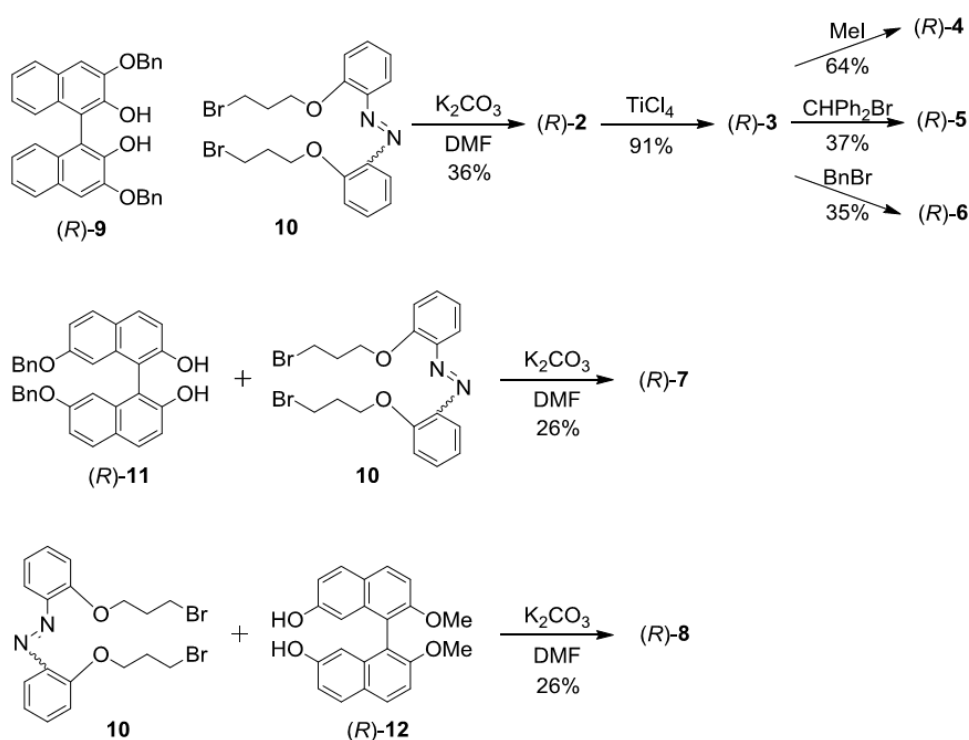


### 2.2. Synthesis of **2–8**

As shown in Scheme 1, 3,3'-disubstituted binaphthyl-azobenzene dyads (*R*)-**2–6** were synthesized starting from optically active (*R*)-**9** [91]. Tandem Williamson synthesis of diol (*R*)-**9** and dibromide **10** afforded cyclic compound (*R*)-**2** in 36% yield. Then debenzoylation of (*R*)-**2** with titanium tetrachloride [92–94] for 5 min gave (*R*)-**3** in high yield (91%). Using a higher temperature, longer reaction time, or other Lewis acids (e.g. aluminum trichloride or niobium pentachloride) resulted in an extremely low yield (<5%). Additionally, generalized deprotection using palladium-activated carbon (Pd/C) and hydrogen was unsuccessful due to the concomitant reduction of the azobenzene moiety. (*R*)-**4–6** were

prepared in moderate yields by coupling (*R*)-**3** with the appropriate halide. In the synthesis of (*R*)-**4** and **-5**, excess methyl iodide (MeI) and  $\alpha$ -bromodiphenylmethane were used, respectively. Although in the synthesis of nonsymmetrical (*R*)-**6**, 1.1 equivalents [based on (*R*)-**3**] of benzyl bromide were used for preferential monobenylation, mixtures of desired (*R*)-**6** (35%), unreacted (*R*)-**3** (25%), and dibenzylated (*R*)-**2** (29%) were obtained; they were easily separated by gel permeation chromatography (GPC). (*R*)-**7** and **-8** were synthesized by similar manner of synthesis of (*R*)-**2** from **10** and binol (*R*)-**11** [95,96] and **-12** [97,98], respectively in moderate yield. Moreover, (*S*)-**2** was prepared from (*S*)-**9** and **10** using the foregoing procedure.

**Scheme 1.** Synthetic route to (*R*)-**2-8**.

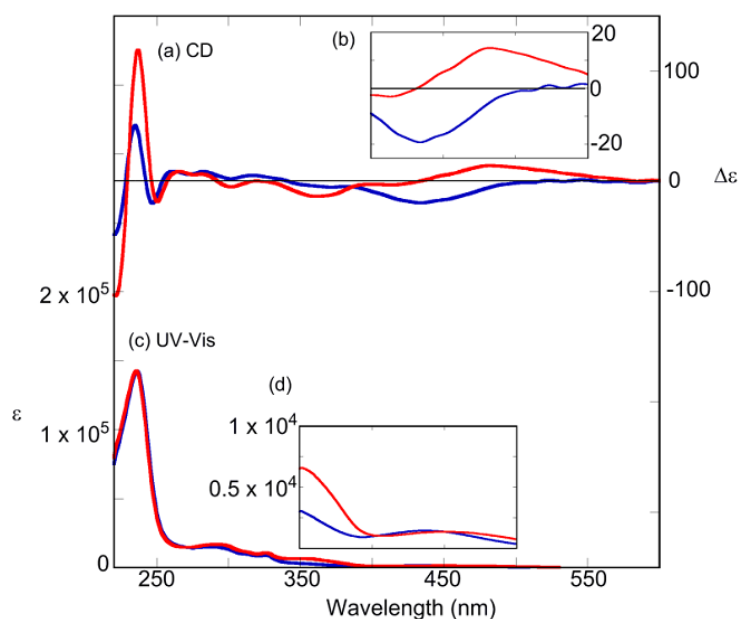


### 2.3. Photoswitching of Absorption, CD, and NMR Spectra

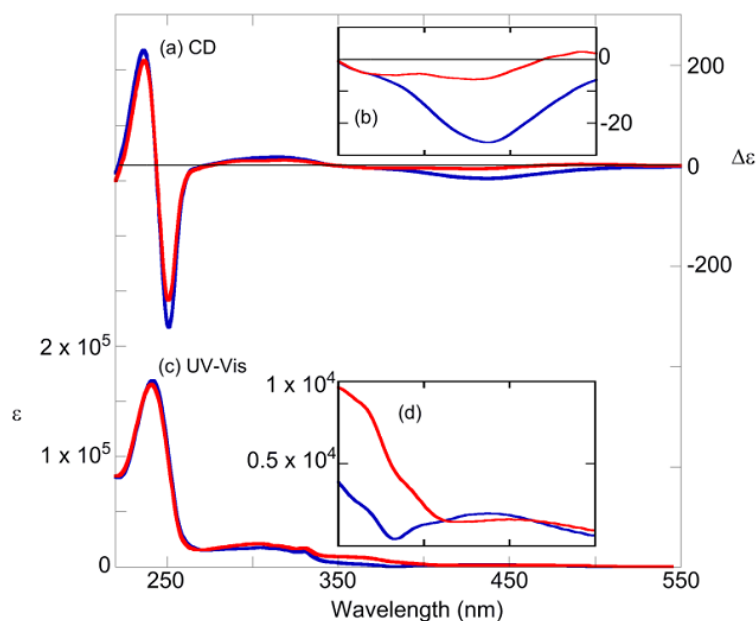
The change in absorption near 360 nm, which indicated a  $\pi$ - $\pi^*$  transition of the *trans* form, confirmed the *cis-trans* isomerization of the azobenzene moiety. The absorption regions of the binaphthyl moiety were below 350 nm [95-100]. Hence, every compounds efficiently photoisomerized. As an example, Figures 4c-d and 5c-d show the change in the absorption spectrum of (*R*)-**2** and (*R*)-**7** after irradiation with 365 nm or 436 nm light, respectively. Irradiation at 365 nm caused *trans*→*cis* isomerization, whereas irradiation at 436 nm caused the reverse *cis*→*trans* isomerization. Both wavelengths gave the same *cis-trans* isomerization rates of 0.7–0.8 in all compounds. Figures 4a-b and 5a-b show the CD spectra of (*R*)-**2** and (*R*)-**7** after photoirradiation, respectively. The split CD at a short wavelength (around 250 nm), which is attributed mainly to the  $^1\text{B}_b$  transition moment of naphthalene rings, reflects the dihedral angle of two naphthalene rings of binaphthyl [101-103]. CD spectra of (*R*)-**2** mean the dihedral angles are varied with the compounds and the isomerism. However, further investigation on the short wavelength side is extremely difficult because the azobenzene units also absorb in this region. Meanwhile, the positive/negative region appeared on the long wavelength

(400–500 nm) and absorbed only an azobenzene moiety,  $n\text{-}\pi^*$  band, of (*R*)-**2**. Additionally, about (*R*)-**7**, the negative/flat region appeared on same wavelength. Hence, we hypothesized that their *cis*-azobenzene moieties were preferentially-twisted as either (*P*) or (*M*) along with the chiral axis of the binaphthyls. This point is discussed later in detail (Section 2.6).

**Figure 4.** (a, b) CD spectra of (*R*)-**2**. (c, d) Absorption spectra of (*R*)-**2**. After 365-nm irradiation (blue line), after 436-nm irradiation (red line). Conditions: 1,4-dioxane ( $1.0 \times 10^{-5}$  M), 20 °C, light path length = 10 mm, irradiation wavelength = 365 nm ( $10 \text{ mW/cm}^2$ , 100 s) and 436 nm ( $10 \text{ mW/cm}^2$ , 100 s).

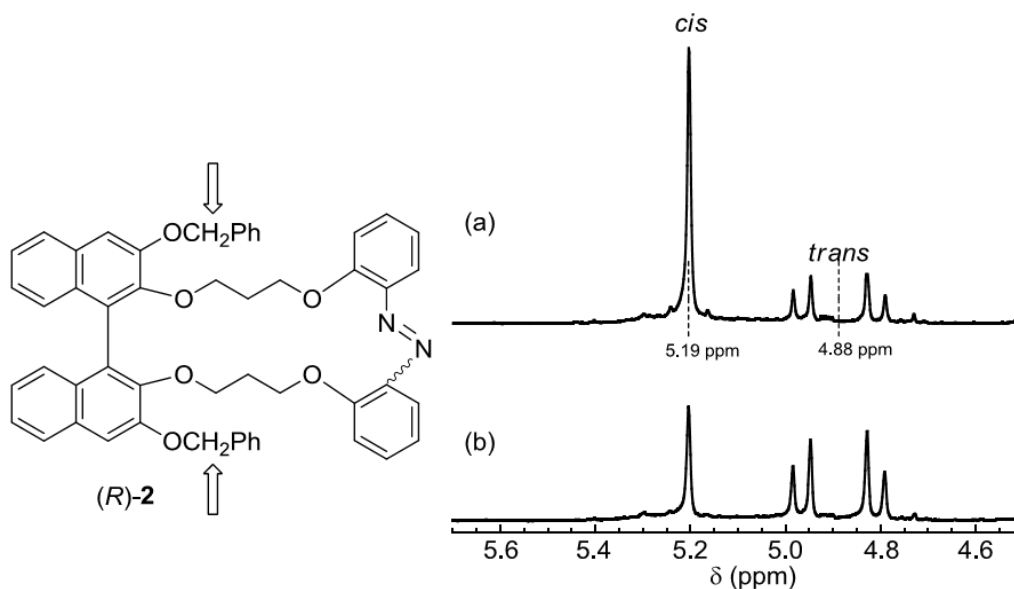


**Figure 5.** (a, b) CD spectra of (*R*)-**7**. (c, d) Absorption spectra of (*R*)-**7**. After 365-nm irradiation (blue line), after 436-nm irradiation (red line). Conditions: 1,4-dioxane ( $1.0 \times 10^{-5}$  M), 20 °C, light path length = 10 mm, irradiation wavelength = 365 nm ( $10 \text{ mW/cm}^2$ , 100 s) and 436 nm ( $10 \text{ mW/cm}^2$ , 100 s).



Next, the NMR spectra of the *cis*- and *trans*-forms were investigated. In compounds 2–8, isomerism resulted in a pronounced change in the signals of the protons of the binaphthyl parts and their substituents far from the light-driven parts. For example, the chemical shift and signal splitting pattern of the benzyl protons far from the light-driven part of (*R*)-2 in the  $^1\text{H}$ -NMR differed vastly between the *cis* and *trans* forms because the signal of (*R*)-*cis*-2 appeared as a singlet (5.19 ppm), whereas that of (*R*)-*trans*-2 was an AB quartet (4.88 ppm,  $\Delta\nu_{AB} = 61.7$  Hz,  $J_{AB} = 11.2$  Hz) with  $\Delta\delta$  of 0.3 ppm (Figure 6). Like in the examples above, the 3,3'-substituents of binaphthyls played an important role in the overall conformation of these compounds.

**Figure 6.**  $^1\text{H}$ -NMR spectra of the benzyl protons of (*R*)-2 after (a) 365 nm-irradiation, (b) 436 nm-irradiation. Conditions:  $\text{CDCl}_3$ ,  $1 \times 10^{-3}$  M, 300 MHz, 22 °C, Irradiation: 365 nm ( $10 \text{ mW/cm}^2$ , 500 s), 436 nm ( $10 \text{ mW/cm}^2$ , 500 s) in an NMR test tube ( $\phi = 5$  mm).



#### 2.4. Photoswitching of Optical Rotation

Isomerization also influenced the optical rotation. Table 1 shows the specific optical rotations at the sodium D-line,  $[\alpha]_D$ , of (*R*)-2–8 after photoirradiation until the values were constant (500 seconds). Generally,  $[\alpha]_D$  after 365-nm irradiation reflects the CD intensity and Cotton effect pattern at longer wavelengths. The *cis*-*trans* ratios were same as those shown in Table 1. The absolute values of  $[\alpha]_D$  were lower than those of helicenes and other chiral metallic compounds [104–106], but were greater than general axially chiral binaphthyls. Furthermore,  $[\alpha]_D$  of (*R*)-2, -4, and -5 resulted in a sign inversion; (*R*)-2 showed the largest change (ca.  $1,000^\circ$ ). The absolute values of  $[\alpha]_D$  of compound (*R*)-5 remained nearly constant, but the sign was reversed. From the result of (*R*)-6, both 3- and 3'-substituents, which are bulkier than the hydroxy group, are necessary to realize a sufficient sign inversion.  $[\alpha]_D$  of (*R*)-7 is suited as a switch for zero-rotation/levo-rotation, although the values of (*R*)-8 remained relatively constant despite efficient isomerization. Hence, a selection of appropriate compounds could yield any type of sign-changing pattern. Moreover, absorption at the sodium D-line (589 nm) did not occur despite analysis at high concentrations and long path-lengths (Figure 7). Thus, target compounds did not degrade during measurement of  $[\alpha]_D$ . Hence, a switch for large  $\alpha$

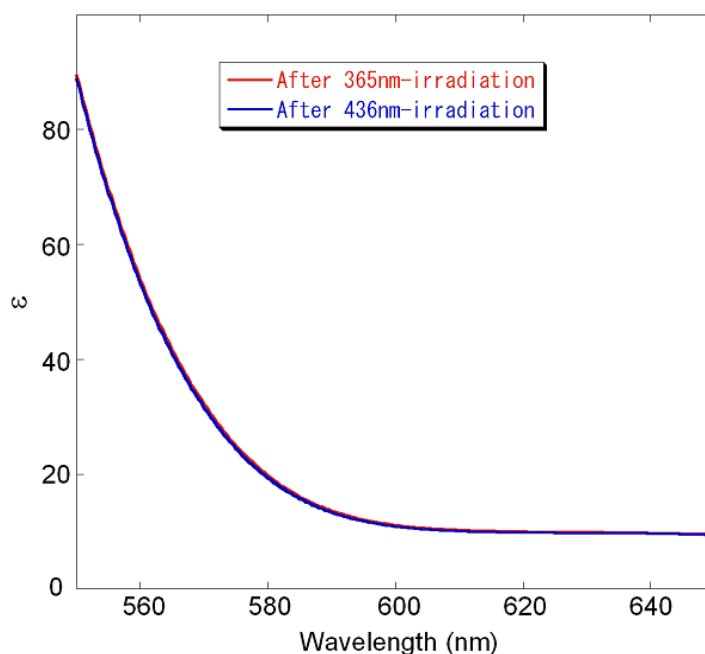
adapted from these compounds should realize the development of nondestructive reading of memory devices [107-109].

**Table 1.**  $[\alpha]_D$  and *cis-trans* ratio after photoirradiation of (*R*)-2-8.

Compound	$[\alpha]_D$ after 365 nm irradiation (deg)	$[\alpha]_D$ after 436 nm irradiation (deg)	<i>cis:trans</i> after 365 nm irradiation	<i>cis:trans</i> after 436 nm irradiation
( <i>R</i> )-2	-314	+642	71:29	31:69
( <i>R</i> )-3	-427	-490	65:35	31:69
( <i>R</i> )-4	-370	+248	72:28	22:78
( <i>R</i> )-5	-252	+278	69:31	35:65
( <i>R</i> )-6	-415	-285	68:32	29:71
( <i>R</i> )-7	-544	-7	80:20	20:80
( <i>R</i> )-8	+358	+282	80:20	26:74

Conditions: chloroform,  $c = 0.10$  g/dL, 20 °C, light path length = 10 cm, irradiation wavelength = 365 nm (10 mW/cm<sup>2</sup>, 500 s) and 436 nm (10 mW/cm<sup>2</sup>, 500 s)

**Figure 7.** Absorption spectra of concentrated (*R*)-2 after photo-irradiation; after 365 nm-irradiation (blue line), after 436 nm-irradiation (red line). Conditions: CHCl<sub>3</sub>, 0.0126 M (0.01 g/dL), light path length = 10 mm, 20 °C, Irradiation wavelength: 365 nm (10 mW/cm<sup>2</sup>, 500 s), 436 nm (10 mW/cm<sup>2</sup>, 500 s).



### 2.5. Thermodynamic Parameters of *Trans* to *cis* Isomerization Process

The thermodynamic parameters, including rate constants ( $k$ ), enthalpy of activation ( $\Delta H^\ddagger$ ), entropy of activation ( $\Delta S^\ddagger$ ), and half-life ( $t_{1/2}$ ) at 298 K of 2-8 for the *cis* to *trans* thermal isomerization were measured or calculated. These parameters were determined according to Eyring equation [110] as discussed in more detail below, and were first-order reactions. For the thermal *cis-trans* isomerization:

$$\ln \frac{[cis]_t}{[cis]_0} = -kt \quad (1)$$

where  $[cis]_t$  and  $[cis]_0$  are the concentrations of the *cis*-azobenzene at time  $t$  and time zero, respectively, and  $k$  is the rate constant for the thermal *cis-trans* isomerization. The first-order rate constant was determined by fitting the experimental data to the equation:

$$\ln \frac{A_\infty - A_t}{A_\infty - A_0} = -kt \quad (2)$$

where  $A_t$ ,  $A_0$  and  $A_\infty$  are the absorbance at 365 nm at time  $t$ , time zero and infinite time, respectively. The first order plots according to equation (2) for the *cis-trans* thermal isomerization at various temperatures and resulting rate constants are shown in Figure 8 and Table 2, respectively.

**Figure 8.** First-order plots for *cis* to *trans* thermal isomerization of (*R*)-2-8. (a) 35 °C, (b) 45 °C, (c) 55 °C, (d) 65 °C. Conditions: 1,4-dioxane,  $1.0 \times 10^{-5}$  M.

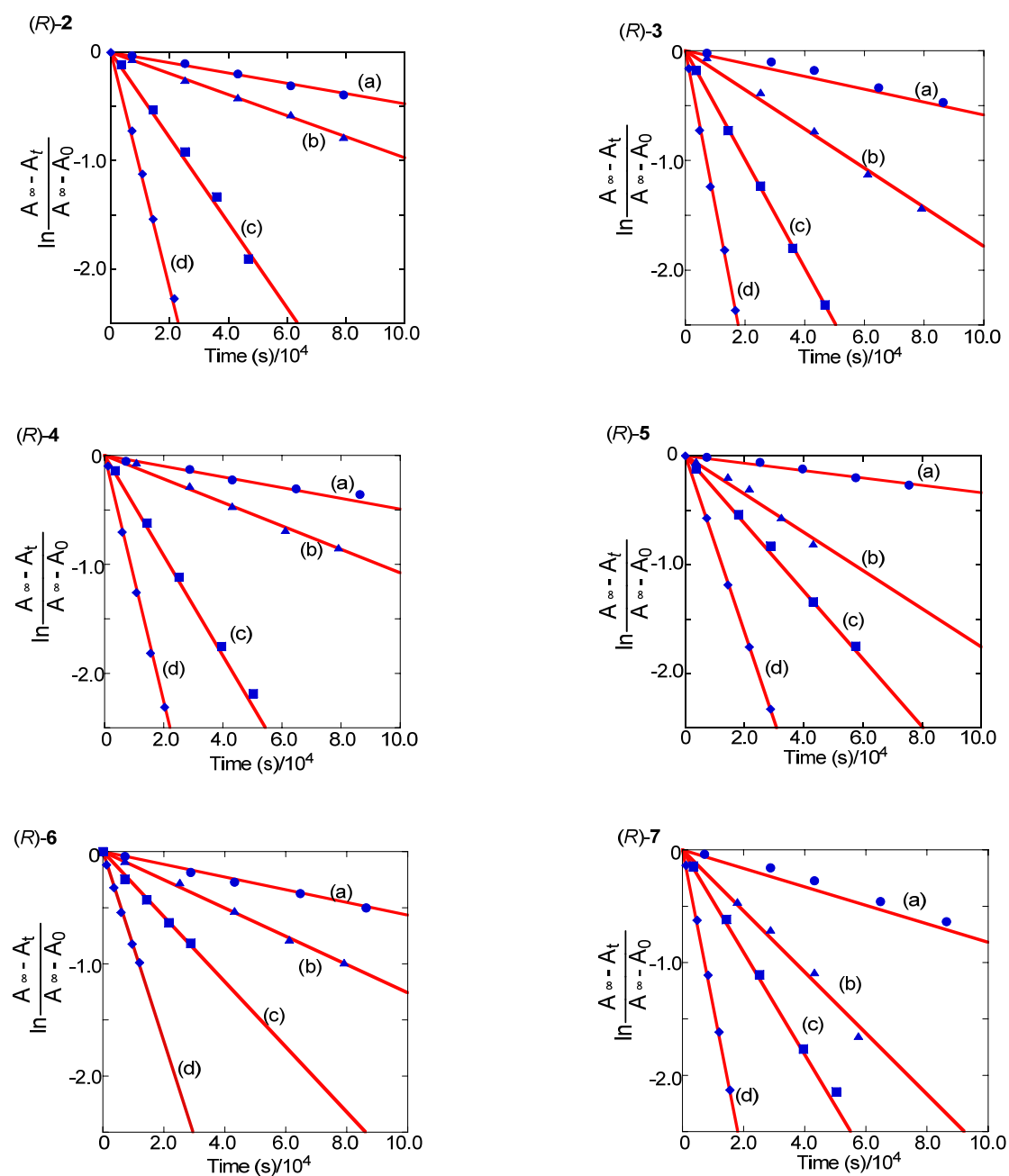
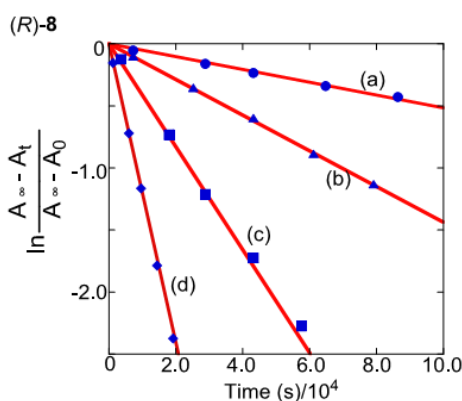




Figure 8. Cont.

Table 2. Rate constants  $k$  ( $s^{-1}$ ) of *cis* to *trans* isomerization of (R)-2-8.

Compound	$k$ at 35 °C	$k$ at 45 °C	$k$ at 55 °C	$k$ at 65 °C
(R)-2	$4.7 \times 10^{-6}$	$9.8 \times 10^{-6}$	$4.0 \times 10^{-5}$	$1.1 \times 10^{-4}$
(R)-3	$5.9 \times 10^{-6}$	$1.8 \times 10^{-5}$	$5.0 \times 10^{-5}$	$1.4 \times 10^{-4}$
(R)-4	$5.0 \times 10^{-6}$	$1.1 \times 10^{-5}$	$4.6 \times 10^{-5}$	$1.1 \times 10^{-4}$
(R)-5	$3.4 \times 10^{-6}$	$1.8 \times 10^{-5}$	$3.1 \times 10^{-5}$	$8.1 \times 10^{-5}$
(R)-6	$5.7 \times 10^{-6}$	$1.3 \times 10^{-5}$	$2.9 \times 10^{-5}$	$8.5 \times 10^{-5}$
(R)-7	$8.2 \times 10^{-6}$	$2.7 \times 10^{-5}$	$4.5 \times 10^{-5}$	$1.4 \times 10^{-4}$
(R)-8	$5.2 \times 10^{-6}$	$1.4 \times 10^{-5}$	$4.2 \times 10^{-5}$	$1.2 \times 10^{-4}$

Conditions: 1,4-dioxane,  $1.0 \times 10^{-5}$  M.

Furthermore thermodynamic parameters such as enthalpy of activation ( $\Delta H^\ddagger$ ) and entropy of activation ( $\Delta S^\ddagger$ ) were determined according to the Eyring equation:

$$k = \frac{k_B T}{h} \exp\left(\frac{\Delta S^\ddagger}{R}\right) \exp\left(-\frac{\Delta H^\ddagger}{RT}\right) \quad (3)$$

where  $R$ ,  $k_B$ , and  $h$  are gas constant, Boltzmann constant, and Planck's constant, respectively. Substituting into equation (3):

$$\ln\left(\frac{kh}{k_B T}\right) = -\frac{\Delta H^\ddagger}{RT} + \frac{\Delta S^\ddagger}{R} \quad (4)$$

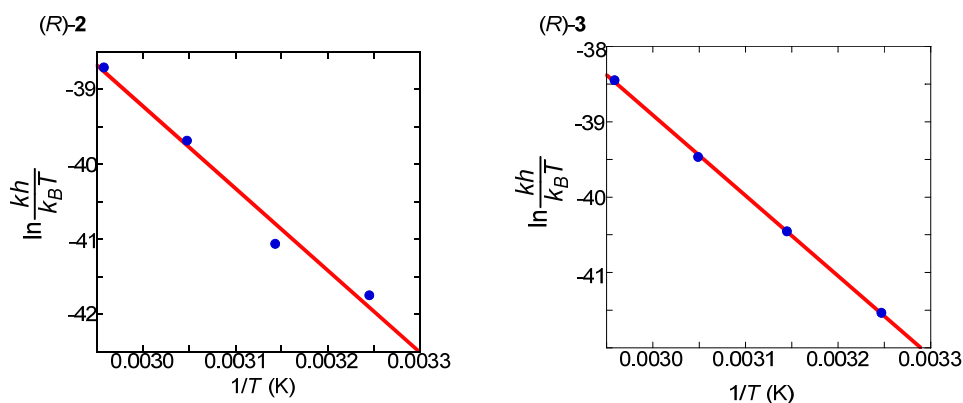
Figure 9. Eyring plots for *cis* to *trans* thermal isomerization of (R)-2-8.

Figure 9. Cont.

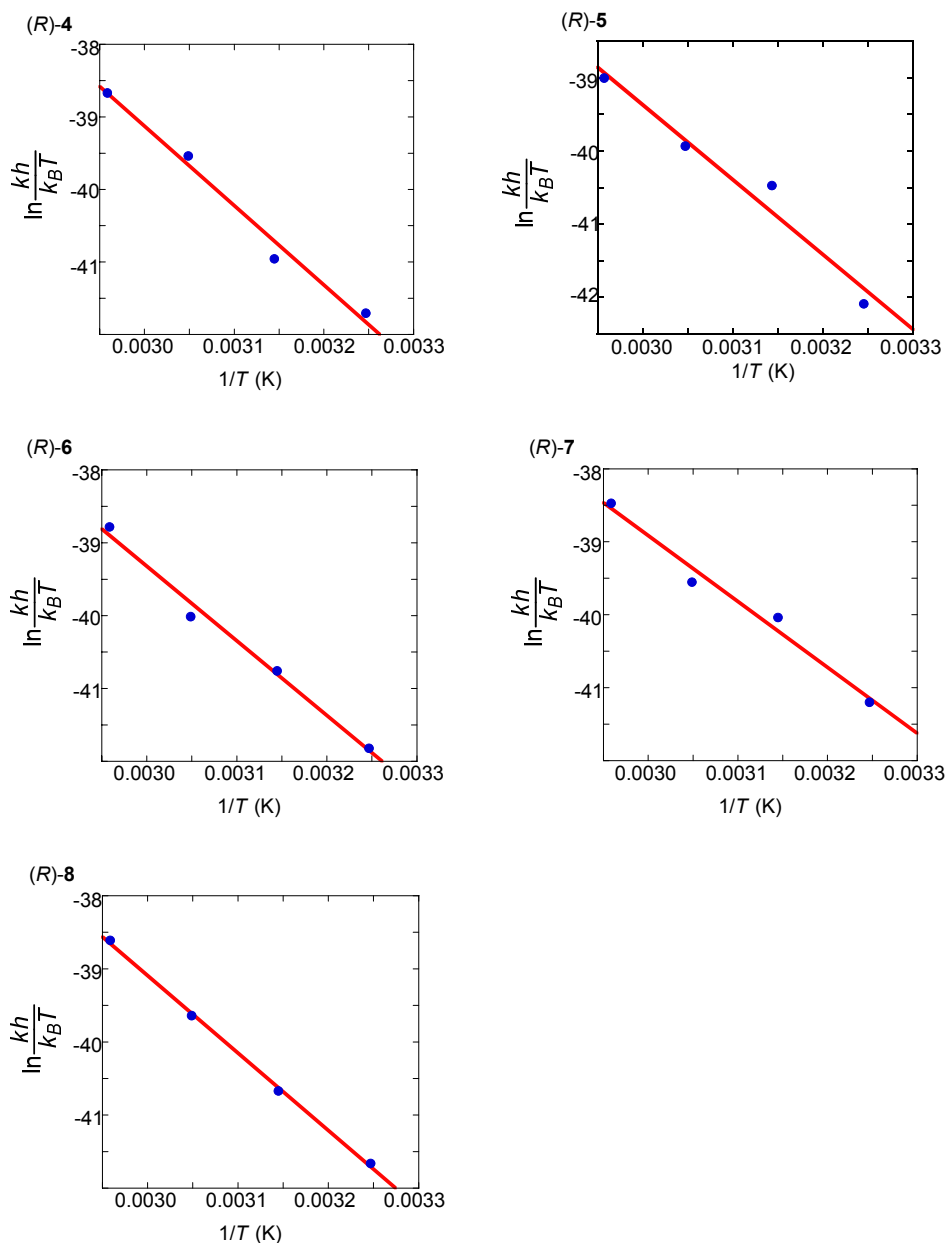


Figure 9 shows Eyring plots for *cis* to *trans* thermal isomerization. The values of  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  were obtained from intersect and a slope, respectively, of the linear plot of  $\ln(kh/k_B T)$  versus  $1/T$  extrapolated to  $T \rightarrow \infty$  (Table 3).

**Table 3.** Enthalpy of activation, entropy of activation, and half-life of (R)-2-8.

Compound	$\Delta H^\ddagger$ (kcal/mol)	$\Delta S^\ddagger$ (cal/mol·K)	$t_{1/2}$ at 298 K (h)
(R)-2	22	-13	157
(R)-3	21	-14	120
(R)-4	22	-13	163
(R)-5	20	-17	148
(R)-6	18	-25	101
(R)-7	18	-23	61
(R)-8	21	-15	128

Conditions: 1,4-dioxane,  $1.0 \times 10^{-5}$  M.

Both  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  derived from the rate constants varied slightly for each compound. Although the isomer ratios differ slightly, it is more than probable that the isomerization mechanism is the same for all compounds. Furthermore, most of these compounds had the half-lives at 298 K longer than 100 h, which is extraordinary for azobenzene derivatives. These long lives provide practical advantages for future application.

## 2.6. Helical Chirality of *cis*-Azobenzenes

To confirm the hypothesis that the axial chirality of binaphthyl induces the helical chirality of *cis*-azobenzene (Figure 10), we calculated the optimized geometries and corresponding CD spectra of two diastereomers, the (*P*)- and (*M*)-forms at the azobenzene moiety.

**Figure 10.** Structures of *cis*-(*P*)-azobenzene and *cis*-(*M*)-azobenzene linked to a 1,1'-binaphthyl.

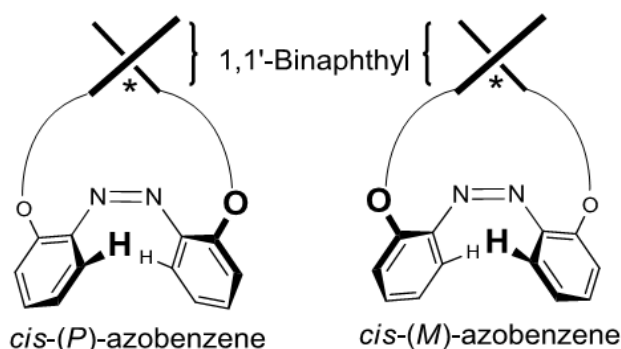
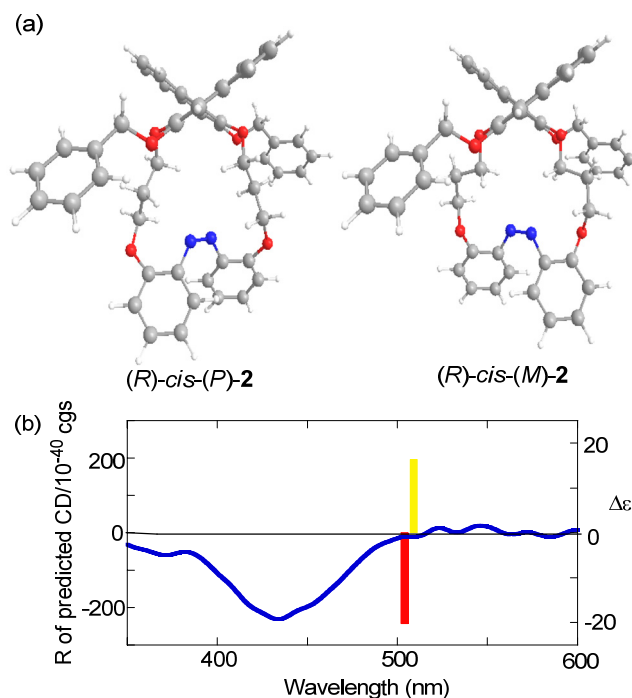


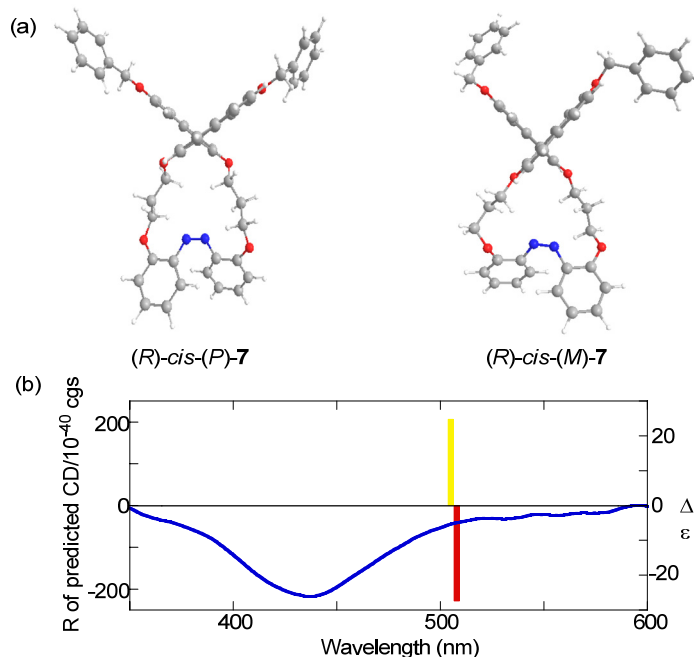
Figure 11a shows the optimized structures of (*R*)-*cis*-(*P*)- and (*R*)-*cis*-(*M*)-**2** obtained by the DFT calculations at the B3LYP/6-31G(d) level [101]. Figure 11b shows the CD in the “azobenzene region” (350–600 nm) predicted using these optimized structures by TD-DFT methods at the B3LYP/6-31G(d) level. These results indicated that the (*R*)-*cis*-(*P*)-**2** exhibited a negative Cotton effect pattern and (*R*)-*cis*-(*M*)-**2** exhibited a positive Cotton effect pattern.

The experimental CD indicated that the preferential configuration of (*R*)-*cis*-**2** was the (*P*)-form. Using the same method, (*R*)-*cis*-**7** was also determined to assume (*P*)-configuration (Figure 12). In contrast, (*R*)-*cis*-**8** was determined to assume (*M*)-configuration (Figure 13). Additionally, the CDs of just the azobenzene moieties in *cis*-(*P*)- and *cis*-(*M*)-**13** were calculated (Figure 14). Similar to (*R*)-*cis*-**2** -**7**, and -**8**, *cis*-(*P*)-**13** (*cis*-(*M*)-**13**) exhibited a negative (positive) Cotton effect. Therefore, the CD patterns described herein are derived from the innate CD of azobenzene itself and not from binaphthyl-related induced CD [112,113]. Most of the optimized structures were obtained by a calculation under  $C_2$  symmetry. However, the obtained structure of (*R*)-*cis*-(*M*)-**7** calculated under  $C_2$  symmetry had an imaginary frequency. Hence, the symmetry was ignored during the optimization of (*R*)-*cis*-(*M*)-**7**. Additionally, some of the obtained structures using M06/6-31G(d) [114] were unacceptable as it was based on an imaginary frequency.

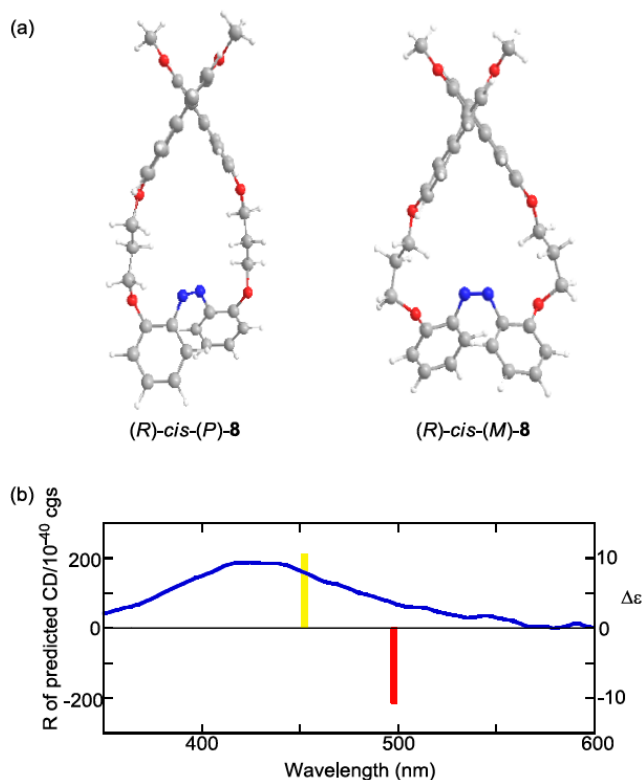
**Figure 11.** (a) Optimized structures of (*R*)-*cis*-(*P*)-2 and (*R*)-*cis*-(*M*)-2 obtained by the DFT calculations at the B3LYP/6-31G(d) level under  $C_2$  symmetry. (b) CD calculated by the TD-DFT method with the B3LYP/6-31G(d) level of (*R*)-*cis*-(*P*)-2 (red bar), (*R*)-*cis*-(*M*)-2 (yellow bar), and experimental CD of (*R*)-2 after 365-nm irradiation (blue line,  $1 \times 10^{-5}$  M in 1,4-dioxane, 20 °C).



**Figure 12.** (a) Optimized structures of (*R*)-*cis*-(*P*)-7 and (*R*)-*cis*-(*M*)-7 obtained by the DFT calculations at the B3LYP/6-31G(d) level. (b) CD calculated by the TD-DFT method with the B3LYP/6-31G(d) level of (*R*)-*cis*-(*P*)-7 (red bar), (*R*)-*cis*-(*M*)-7 (yellow bar), and experimental CD of (*R*)-7 after 365-nm irradiation (blue line,  $1 \times 10^{-5}$  M in 1,4-dioxane, 20 °C).



**Figure 13.** (a) Optimized structures of (*R*)-*cis*-(*P*)-**8** and (*R*)-*cis*-(*M*)-**8** obtained by the DFT calculations at the B3LYP/6-31G(d) level under  $C_2$  symmetry. (b) CD calculated by the TD-DFT method with the B3LYP/6-31G(d) level of (*R*)-*cis*-(*P*)-**8** (red bar), (*R*)-*cis*-(*M*)-**7** (yellow bar), and experimental CD of (*R*)-**8** after 365-nm irradiation (blue line,  $1 \times 10^{-5}$  M in 1,4-dioxane, 20 °C).



**Figure 14.** (a) Structures of *cis*-(*P*)-**13** and *cis*-(*M*)-**13**. (b) CD calculated by the TD-DFT method with the B3LYP/6-31G(d) level of *cis*-(*P*)-**13** (red bar), *cis*-(*M*)-**13** (yellow bar).

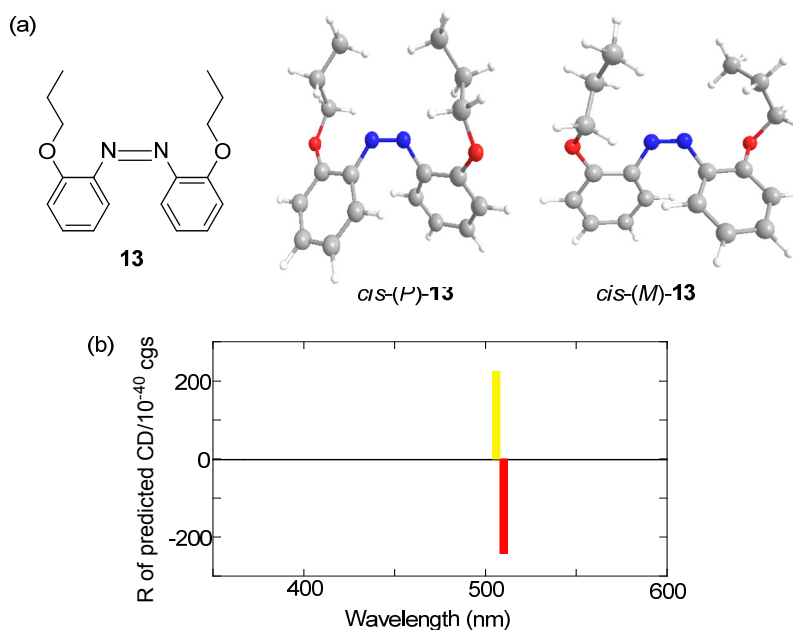


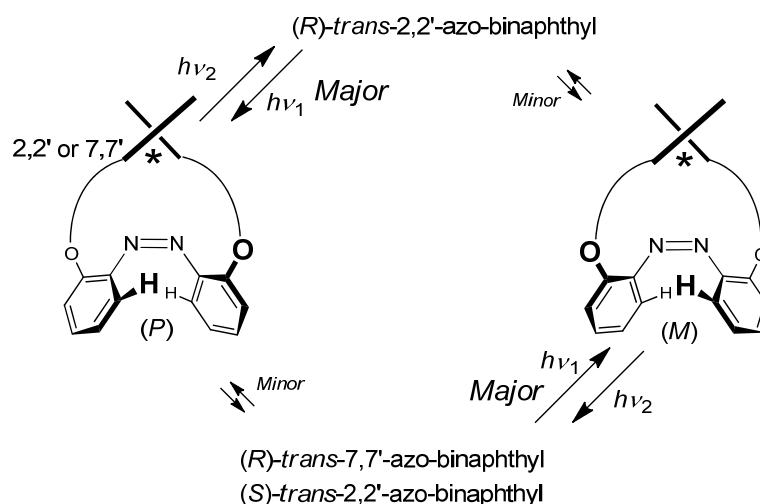
Table 4, which shows the data regarding the asymmetry of the compounds (*R*)-**2–8**, (*S*)-**2**, and **13**, illustrates three points regarding chirality: (1) (*R*)-2,2'-azobenzene-linked-binaphthyls induced (*P*)-azobenzene, (2) (*S*)-2,2'-analogues induced (*M*)-azobenzene, and (3) 7,7'-analogues acted as pseudo-enantiomers of 2,2'-analogues. A systematic and simple induction of asymmetrical *cis*-azobenzenes (Figure 15) was structured using common binaphthyl skeletons. These conformational results should assist in future studies on asymmetric azobenzenes.

**Table 4.** Sign of experimental and calculated CD, and helical chirality of the *cis*-azobenzene moiety in **2–8** and **13**.

Compound	Sign of $\Delta\epsilon$ <sup>[a][b]</sup>			Chirality of <i>cis</i> -azobenzene <sup>[c]</sup>
	Experimental	Calculated <i>cis</i> -( <i>P</i> )-form	Calculated <i>cis</i> -( <i>M</i> )-form	
( <i>R</i> )- <b>2</b>	–	–	+	( <i>P</i> )
( <i>R</i> )- <b>3</b>	–	–	+	( <i>P</i> )
( <i>R</i> )- <b>4</b>	–	–	+	( <i>P</i> )
( <i>R</i> )- <b>5</b>	–	–	+	( <i>P</i> )
( <i>R</i> )- <b>6</b>	–	–	+	( <i>P</i> )
( <i>R</i> )- <b>7</b>	–	–	+	( <i>P</i> )
( <i>R</i> )- <b>8</b>	+	–	+	( <i>M</i> )
( <i>S</i> )- <b>2</b>	+	–	+	( <i>M</i> )
<b>13</b>		–	+	

[a] Sign of  $\Delta\epsilon$  at 350–600 nm; [b] Calculated using the TD-DFT method with B3LYP/6-31G(d); [c] These chiralities were determined by comparing the signs between the experimental and computed CD.

**Figure 15.** Twisting pattern of *cis*-azobenzenes induced by axial chirality of binaphthyls.



### 3. Conclusions

Several axially chiral binaphthyl-azobenzene dyads with substituents were synthesized to examine their reversible photoisomerization and subsequent changes in optical properties. The chiroptical properties of the dyads, CD and optical rotation, changed dramatically. It is notable that reversible positive-negative and zero-positive (zero-negative) chiroptical signals were detected. Moreover,

intramolecular chiral transfer from the chiral axis to the helix of the *cis*-azobenzene moiety was studied empirically and computationally. 2,2'-Linked-(*R*)-binaphthyl was found to induce *cis*-(*P*)-azobenzene, whereas the symmetrical 7,7'-linked-(*R*)-binaphthyl was found to induce *cis*-(*M*)-azobenzene without exception. These results may be useful in designing chiroptical switches as well as in the study of azobenzene helicity. Additionally, this work provides a novel use for axially chiral binaphthyls. We are currently studying the development, conformation, and application of specific binaphthyl-azobenzene systems with interesting functions.

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*Sample Availability:* Samples of the compounds **2–8** are available from the authors.

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