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Helical Chirality of Azobenzenes Induced by an Intramolecular Chiral Axis and Potential as Chiroptical Switches

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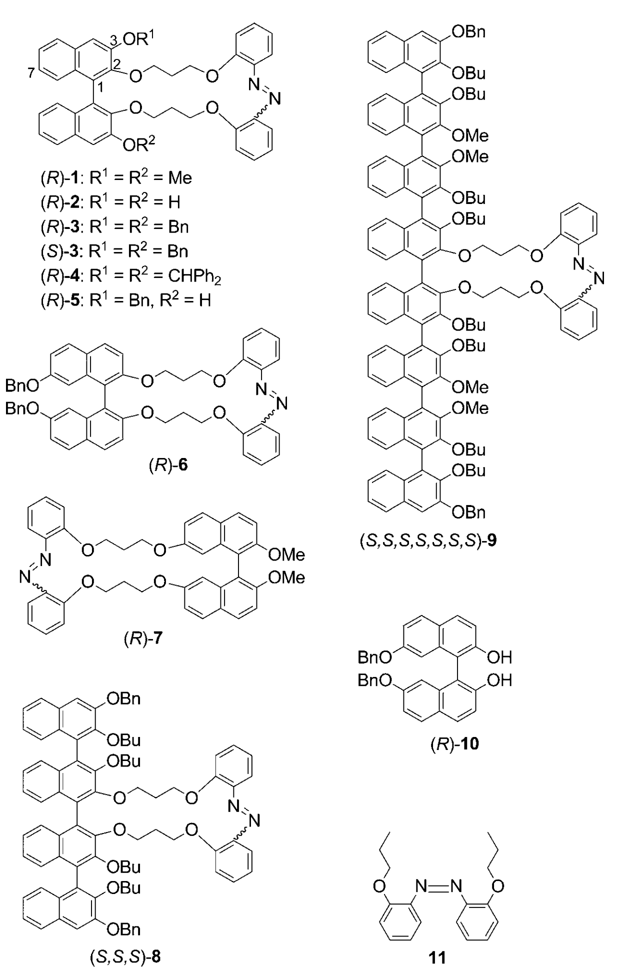
The *cis* and *trans* forms of the azobenzene skeleton differ significantly in length and therefore are frequently used as photochromic parts[1] for changing absorption and fluorescence properties,[2] in addition to association constants when they are hosts.[3] Although optically active compounds with azobenzene adducts have been reported,[4–6] few studies have examined the asymmetry of the azobenzene moiety itself. Haberhauer and Kallweit have investigated the twisting direction of the *cis*-azobenzene moiety by studying the helical chirality linked to a chiral cyclic imidazole tetrapeptide, possessing four asymmetric centers.[7] The axially chiral binaphthyl is rigid in the rod direction, but around the axis has a wide and flexible asymmetric field. Thus, binaphthyl skeletons have been employed in asymmetric organocatalysis,[8] molecular recognition,[9] and chiral doping of liquid crystals.[10]

In addition to studying the half-life of the *cis*-azobenzene moieties, we have previously investigated photoswitching of the optical properties, including absorption, circular dichroism (CD), and optical rotation of axially chiral binaphthyl–azobenzene cyclic dyads.[11] Although this study included compounds **1**–**5**, their extensive steric structures were elusive (Scheme 1).[11b] Herein, we investigate the twisting patterns of the *cis*-azobenzene moieties induced by the axial chirality of the binaphthyl units in **1**–**7**, and oligonaphthyls linked to azobenzenes **8** and **9**, with an emphasis on changes in the chiroptical properties due to *cis*–*trans* photoisomerization. In particular, we have examined the optical rotation because of its relationship to noise cancellation and nondes-



Scheme 1. Compounds **1**–**11**; Bn = Benzyl.

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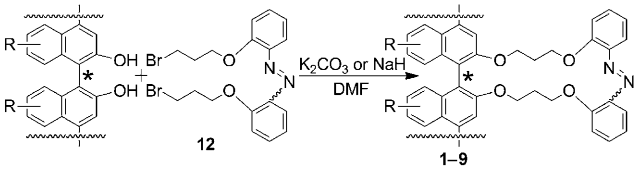
tructive photoswitches; both of which have applications in memory devices.[12]

In compounds **1**–**5**, the 3,3′-positions of the binaphthyl are substituted and circularly linked to the azobenzene moiety at the 2,2′-positions. Compound **6** has dibenzyloxy groups at the 7,7′-positions, however compound **7** is linked to the azobenzene moiety at the 7,7′-positions, but is also substituted by 2,2′-dimethoxy groups. Compounds **8** and **9** are oligonaphthyl–azobenzene dyads with multiple chiral axes. Compounds (*R*)-**10** and **11** are model structures, which were selected for comparison by using computational chemistry. Compounds **1**–**9** were synthesized by a tandem Williamson reaction,[11] with the appropriate axially chiral binol[13] or oligonaphthalene–diol[14] derivative and 2,2′-bis(3-bromopropoxy)azobenzene (**12**, Scheme 2).



Scheme 2. Synthesis of **1**–**9** (Compound **7** is a regioisomer of the above structure).

The change in absorption near 360 nm indicated a π–π* transition of the *trans* form, which confirmed the *cis*–*trans* isomerization of the azobenzene moiety. The absorption regions of the binaphthyl and oligonaphthyl moieties were less than 350 nm,[13,14] hence most compounds were efficiently photoisomerized. As an example, Figure 1 c–d shows the changes in the absorption spectra of (*R*)-**6** after irradiation with 365 and 436 nm light, respectively. Irradiation at 365 nm caused *trans*→*cis* isomerization, whereas the reverse reaction occurs upon irradiation at 436 nm. According to the integral of the HPLC chromatograms for (*R*)-**6**, both wavelengths gave the same *cis*–*trans* isomerization rate of 0.8 (Table 2, entry 1). Figure 1 a–b shows the CD spectra of (*R*)-**6** after photoirradiation. Although the *cis* and *trans* forms varied slightly, the negative split CD at a short wavelength (around 250 nm) had a typical shape for (*R*)-1,1′-binaphthyls. This shape was largely attributed to the ^1B_b transition moment.[15] However, further investigation on the short wavelength side was extremely difficult because the azobenzene units also exhibited CD signals in this region. In addition, the negative/flat region, which appeared at the long wavelengths (400–500 nm), absorbed in the n–π* band of the azobenzene moiety. Hence, we hypothesized that the *cis*-azobenzene moiety of (*R*)-**6**, preferentially twisted as either (*P*) or (*M*) along with the chiral axis of a binaphthyl, displayed a negative Cotton effect in the long-wavelength region, whereas the *trans*-azobenzene moiety maintained planarity without preferential asymmetry.

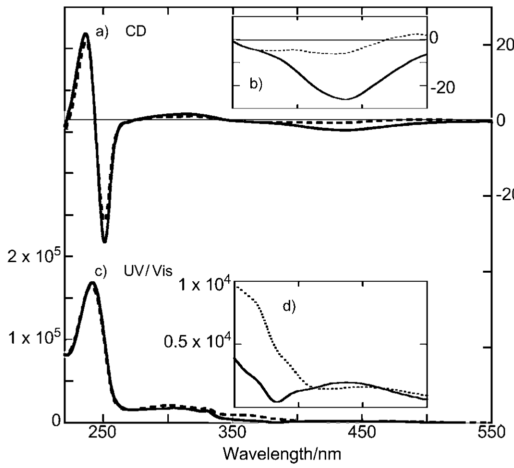


Figure 1. a) and b) CD spectra of (*R*)-**6**. c) and d) absorption spectra of (*R*)-**6** (horizontal scales are the same) after 365 nm irradiation (solid line) and after 436 nm irradiation (dashed line). Conditions: 1,4-dioxane (1.0×10^{-5} M), 20 °C, light path length = 10 mm, irradiation wavelengths = 365 nm (10 mW/cm^2, 100 s) and 436 nm (10 mW/cm^2, 100 s).

To confirm the hypothesis that the axial chirality of binaphthyl induces the helical chirality of *cis*-azobenzene, we calculated the optimized geometries and corresponding CD spectra of two diastereomers, the (*P*) and (*M*) forms at the azobenzene moiety.[16] Figure 2 shows the optimized structures of (*R*)-*cis*-(*P*)-**6** and (*R*)-*cis*-(*M*)-**6** obtained by the DFT calculations at the B3LYP/6-31G(d) level. By using these optimized structures, the CD in the "azobenzene region" (350–600 nm) was predicted (Figure 3). It should be noted that the CD of (*R*)-**10**, the corresponding binaphthyl skeleton, was silent. Time-dependent (TD)DFT methods at the B3LYP/6-31G(d) level indicated that (*R*)-*cis*-(*P*)-**6** displayed a negative Cotton-effect pattern whereas (*R*)-*cis*-(*M*)-**6** exhibited a positive Cotton-effect pattern. The experimental CD indicated that the preferential configuration of (*R*)-*cis*-**6** was the (*P*) form. By the same method, compound (*R*)-*cis*-**7** was assigned the (*M*) configuration (Figure 4).

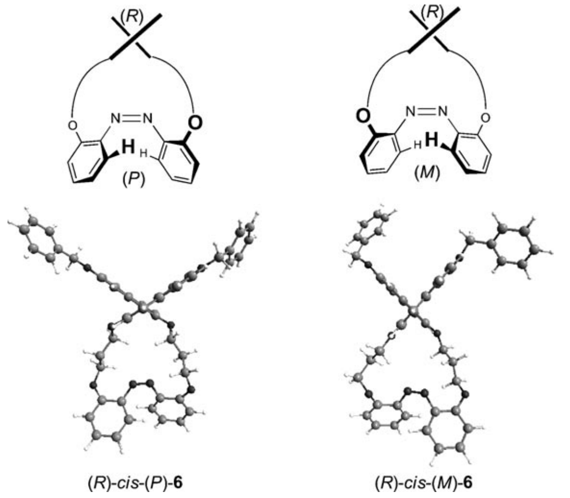


Figure 2. Optimized structures of (*R*)-*cis*-(*P*)-**6** and (*R*)-*cis*-(*M*)-**6** obtained by DFT calculations at the B3LYP/6-31G(d) level.

Table 1. Experimental and calculated CDs and estimated helical chirality of the *cis*-azobenzene moiety in **1**–**9** and **11**.

		Sign of $\Delta\varepsilon$[a,b]			
Entry	Compound	Experimental	Calcd *cis*-(*P*)	Calcd *cis*-(*M*)	Chirality of *cis*-azobenzene[c]
1	(*R*)-**1**	−	−	+	(*P*)
2	(*R*)-**2**	−	−	+	(*P*)
3	(*R*)-**3**	−	−	+	(*P*)
4	(*R*)-**4**	−	−	+	(*P*)
5	(*R*)-**5**	−	−	+	(*P*)
6	(*R*)-**6**	−	−	+	(*P*)
7	(*R*)-**7**	+	−	+	(*M*)
8	(*S*)-**3**	+	−	+	(*M*)
9	(*S*,*S*,*S*)-**8**	+			(*M*)
10	all-(*S*)-**9**[d]	+			(*M*)
11	**11**		−	+	

[a] Sign of $\Delta\varepsilon$ at 350–600 nm. [b] Calculated by using the TD-DFT method with B3LYP/6-31G(d). [c] For entries 1–8, the chirality was determined by comparing the signs between the experimental and computational CD. For entries 9 and 10, the chirality observed was due to the experimental Cotton effect. [d] (*S*,*S*,*S*,*S*,*S*,*S*,*S*)-**9**.

Table 2. $[\alpha]_D$ of **6**–**9** after photoirradiation.[a]

	$[\alpha]_D$ [°]		*cis*/*trans* ratio[b]	
Compound	After 365 nm irradiation	After 436 nm irradiation	After 365 nm irradiation	After 436 nm irradiation
(*R*)-**6**	−544	−7	80:20	20:80
(*R*)-**7**	+358	+282	80:20	26:74
(*S*,*S*,*S*)-**8**	+233	+141	83:17	41:59
all-(*S*)-**9**[c]	−2	−26	83:17	40:60

[a] Conditions: chloroform, $c = 0.10\,\mathrm{g\,dL^{-1}}$, 20 °C, light path length = 10 cm, irradiation wavelengths = 365 nm (10 mW cm^{-2}, 500 s) and 436 nm (10 mW cm^{-2}, 500 s). [b] Determined by HPLC (column: Inertsil SIL 100 A (GL science)), eluent: $CHCl_3$/*n*-hexane 1:1. [c] (*S*,*S*,*S*,*S*,*S*,*S*,*S*)-**9**.

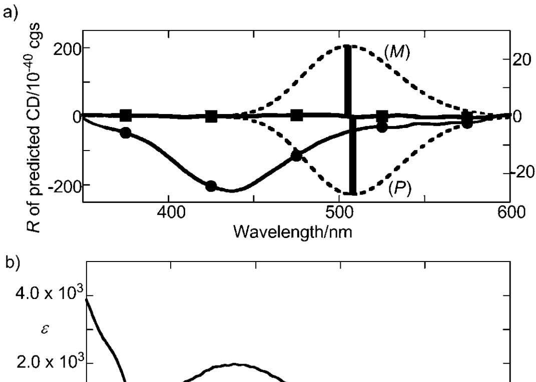


Figure 3. a) CD (calculated by the TD-DFT method at the B3LYP/6-31G(d) level) of (*R*)-*cis*-(*P*)-, (*R*)-*cis*-(*M*)-**6** (dashed lines), and experimental CD spectra of (*R*)-**6** after 365 nm irradiation (solid line with circles, 1×10^{-5} M in 1,4-dioxane, 20 °C) and (*R*)-**10** (solid line with squares, 1×10^{-5} M in 1,4-dioxane, 20 °C). Gaussian bands with a half-band width of 2500 cm^{-1} were used to produce the calculated spectra. b) Absorption spectra of (*R*)-**6** after 365 nm irradiation (1.0×10^{-5} M, 1,4-dioxane, 20 °C).

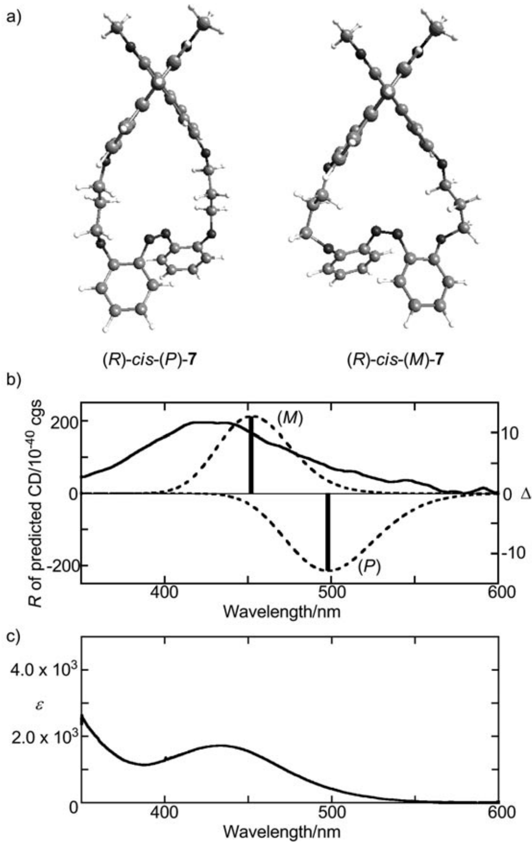
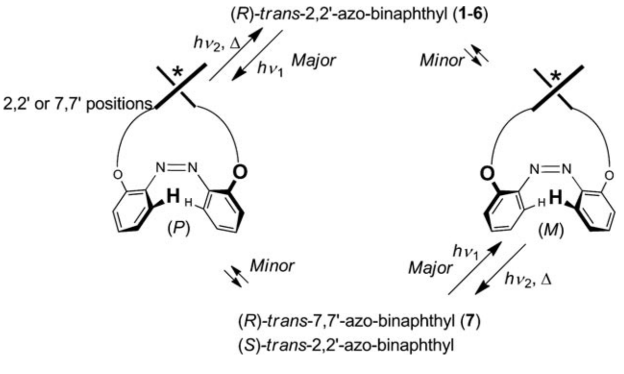


Figure 4. a) Optimized structures of (*R*)-*cis*-(*P*)-**7** and (*R*)-*cis*-(*M*)-**7** obtained by DFT calculations at the B3LYP/6-31G(d) level) under C_2 symmetry. b) CD (calculated by the TD-DFT method at the B3LYP/6-31G(d) level of (*R*)-*cis*-(*P*)-, (*R*)-*cis*-(*M*)-**7** (dashed line), and the experimental CD of (*R*)-**7** after 365 nm irradiation (solid line, 1×10^{-5} M in 1,4-dioxane at 20 °C). Gaussian bands with a half-band width of 2500 cm^{-1} were used to produce the calculated spectra. c) Absorption spectra of (*R*)-**7** after 365 nm irradiation (1.0×10^{-5} M, 1,4-dioxane at 20 °C).

The coequal data concerning the asymmetry of the compounds **1**–**11** (Table 1),[17] illustrates three points regarding chirality: 1) (*R*)-2,2′-azobenzene-linked-binaphthyls induced the (*P*) azobenzene conformation (Table 1, entries 1–6), 2) (*S*)-2,2′-analogues induced the (*M*) azobenzene conformation (Table 1, entry 8), and 3) 7,7′-analogues acted as pseudo-enantiomers of 2,2′-analogues (Table 1, entry 7). The size of oligonaphthyls **8** and **9** prevented the fine optimization of their structures, however the central (*S*)-axial chirality induced the *cis*-(*M*)-azobenzene conformation (Table 1, entries 9 and 10). Additionally, the CDs of just the azobenzene moieties in *cis*-(*P*)-**11** and *cis*-(*M*)-**11** (extracted from the optimized structures of corresponding (*R*)-*cis*-**6**) were calculated. Similar to (*R*)-*cis*-**6**, compound *cis*-(*P*)-**11** exhibited a negative Cotton effect, with *cis*-(*M*)-**11** showing a positive Cotton effect (Table 1, entry 11). Therefore, the CD patterns described herein are derived from the innate CD of azobenzene itself and not from binaphthyl-related induced CD.[18,19] The relationship between the twisting patterns of the *cis*-azobenzene moieties and the sign of the Cotton effect are consistent with those reported by Haberhauer and Kallweit.[7]

Isomerization was also shown to influence the optical rotation. Table 2 shows the specific optical rotations at the sodium D-line (589 nm), $[\alpha]_D$, in addition to the *cis–trans* ratios of **6**–**9**, after photoirradiation until the values became constant. Generally, the $[\alpha]_D$ value after 365 nm irradiation reflects the CD intensity and the Cotton-effect pattern at longer wavelengths. In other words, the $[\alpha]_D$ value reflects the twist of the *cis*-azobenzene moieties. The $[\alpha]_D$ value of (*R*)-**6** exhibited the largest change (537°), and consequently (*R*)-**6** is a suitable switch for zero-/levo-rotation. In contrast, the values of **7**–**9** remained relatively constant despite efficient isomerization. Hence, 2,2′-azobenzene-substituted binaphthyls are more effective in altering $[\alpha]_D$ than the 7,7′-analogues. However, oligonaphthyls are unsuitable for α-changes because their structural changes only occur in the vicinity of the azobenzenes, and subsequent structural changes do not occur throughout the entire molecule. Dextro/levo rotation switching has already been realized for (*R*)-**1**, −**3**, and −**4**.[11b] Hence, selecting the appropriate compound may control the type of sign-changing pattern. Moreover, absorption of the sodium D-line did not occur, and consequently the target compounds did not degrade during the measurement of $[\alpha]_D$. Therefore, a switch for α, adapted from these compounds, should realize the nondestructive reading of memory devices. Furthermore, at 298 K, the half-lives for most of these cyclic *cis*-compounds was longer than 100 h, which is extraordinary for azobenzene derivatives. These long half-lives, which are due to the cyclic structures, provide a practical advantage for future applications (see Table S3 in the Supporting Information).

In summary, we have revealed the conformation of several binaphthyl–azobenzene dyads and oligonaphthyl–azobenzene dyads with a focus on the twist pattern of the *cis*-azobenzene moiety. The 2,2′-linked-(*R*)-binaphthyl induced the *cis*-(*P*) conformation of the azobenzene, whereas symmetrically 7,7′-linked-(*R*)-binaphthyl induced the *cis*-(*M*) conformation of the azobenzene (Scheme 3). A systematic and simple induction of asymmetrical azobenzenes was realized by using common binaphthyl skeletons. Moreover, photoswitching of zero-/levo- rotation was achieved with (*R*)-**6**. These conformational and chiroptical results should assist in the future study of asymmetric azobenzene and chiroptical switches. Studies to investigate the relationship between conformation and linker length are currently underway in our laboratory.



Scheme 3. Twisting pattern of *cis*-azobenzenes induced by axial chirality of the binaphthyls.

Experimental Section

Full experimental details, characterization data, and computational results are given in the Supporting Information.

Synthesis of (*R*)-6: A suspension of diol (*R*)-**10** (200 mg, 0.401 mmol), K_2CO_3 (166 mg, 1.20 mmol, 3.0 equiv), and 2,2′-bis(3-bromopropoxy)azobenzene (**12**, 183 mg, 0.401 mmol, 1.0 equiv) in DMF (30 mL) was stirred for 22 h at room temperature. 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 under vacuum to give a residue, which was purified by silica gel column chromatography (with chloroform as the eluent) and gel permeation chromatography (GPC) to afford (*R*)-**6** (83 mg, 0.105 mmol, 26 %) as a red amorphous solid.

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Keywords: azo compounds · binaphthyl · chirality · isomerization · photochromism

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[1] a) B. L. Feringa, *Molecular Switches*, Wiley-VCH, Weinheim, **2001**; b) V. Balzani, M. Venturi, A. Credi, *Molecular Devices and Machines*, Wiley-VCH, Weinheim, **2003**; c) E. R. Kay, D. A. Leigh, F. Zerbetto, *Angew. Chem.* **2007**, *119*, 72–196; *Angew. Chem. Int. Ed.* **2007**, *46*, 72–191; d) R. Siewertsen, H. Neumann, B. Buchheim-Stehn, R. Herges, C. Näther, F. Renth, F. Temps, *J. Am. Chem. Soc.* **2009**, *131*, 15594–15595.

[2] For recent examples, see: a) S. Uno, C. Dohno, H. Bittermann, V. L. Malinovskii, R. Häner, K. Nakatani, *Angew. Chem.* **2009**, *121*, 7498–7501; *Angew. Chem. Int. Ed.* **2009**, *48*, 7362–7365; b) J. Han, D. Yan, W. Shi, J. Ma, H. Yan, M. Wei, D. G. Evans, X. Duan, *J. Phys. Chem. B* **2010**, *114*, 5678–5685; c) M. Liu, X. Yan, M. Hu, X. Chen, M. Zhang, B. Zheng, X. Hu, S. Shao, F. Huang, *Org. Lett.* **2010**, *12*, 2558–2561.

[3] For recent examples, see: a) F. Puntoriero, G. Bergamini, P. Ceroni, V. Balzania, F. Vögtle, *New J. Chem.* **2008**, *32*, 401–406; b) J. Chen, T. Serizawa, M. Komiyama, *Angew. Chem.* **2009**, *121*, 2961–2964; *Angew. Chem. Int. Ed.* **2009**, *48*, 2917–2920; c) Y. Oka, N. Tamaoki, *Inorg. Chem.* **2010**, *49*, 4765–4767.

[4] For examples of axially chiral compounds, see; a) T. Muraoka, K. Kinbara, T. Aida, *Nature* **2006**, *440*, 512–515; b) M. Kawamoto, T. Sassa, T. Wada, *J. Phys. Chem. B* **2010**, *114*, 1227–1232; c) W. C. Chen, Y. W. Lee, C. T. Chen, *Org. Lett.* **2010**, *12*, 1472–1475.

[5] For examples of planar chiral compounds, see; a) B. Jousselme, P. Blanchard, M. Allain, E. Levillain, M. Dias, J. Roncali, *J. Phys. Chem. A* **2006**, *110*, 3488–3494; b) M. Mathews, N. Tamaoki, *J. Am. Chem. Soc.* **2008**, *130*, 11409–11416; c) M. C. Basheer, Y. Oka, M. Mathews, N. Tamaoki, *Chem. Eur. J.* **2010**, *16*, 3489–3496.

[6] For examples of helical oligomers, supramolecules, and liquid crystals, see: a) F. Vera, R. M. Tejedor, P. Romero, J. Barberá, M. B. Ros, J. L. Serrano, T. Sierra, *Angew. Chem.* **2007**, *119*, 1905–1909; *Angew. Chem. Int. Ed.* **2007**, *46*, 1873–1877; b) M. Z. Alam, T. Yoshioka, T. Ogata, T. Nonaka, S. Kurihara, *Chem. Eur. J.* **2007**, *13*, 2641–2647; c) S. W. Choi, S. Kawauchi, N. Y. Ha, H. Takezoe, *Phys. Chem. Chem. Phys.* **2007**, *9*, 3671–3682; d) E. D. King, P. Tao, T. T. Sanan, C. M. Hadad, J. R. Parquetted, *Org. Lett.* **2008**, *10*, 1671–1674; e) O. Sadovski, A. A. Beharry, F. Zhang, G. A. Woolley, *Angew. Chem.* **2009**, *121*, 1512–1514; *Angew. Chem. Int. Ed.* **2009**, *48*, 1484–1486; f) G. Zou, J. H. Hao, H. Kohn, T. Manaka, M. Iwamoto, *Chem. Commun.* **2009**, 5627–5629.

[7] G. Haberhauer, C. Kallweit, *Angew. Chem.* **2010**, *122*, 2468–2471; *Angew. Chem. Int. Ed.* **2010**, *49*, 2418–2421.

[8] For recent examples, see: a) J. M. Fraile, J. I. Garcia, J. A. Mayoral, *Chem. Rev.* **2009**, *109*, 360–417; b) J. M. Blacquiere, R. McDonald, D. E. Fogg, *Angew. Chem.* **2010**, *122*, 3895–3898; *Angew. Chem. Int. Ed.* **2010**, *49*, 3807–3810.

[9] a) H. Miyaji, S. J. Hong, S. D. Jeong, D. W. Yoon, H. K. Na, J. Hong, S. Ham, J. L. Sessler, C. H. Lee, *Angew. Chem.* **2007**, *119*, 2560–2563; *Angew. Chem. Int. Ed.* **2007**, *46*, 2508–2511; b) T. Ema, K. Hamada, K. Sugita, Y. Nagata, T. Sakai, A. Ohnishi, *J. Org. Chem.* **2010**, *75*, 4492–4500; c) X. Chen, Z. Huang, S. Y. Chen, K. Li, X. Q. Yu, L. Pu, *J. Am. Chem. Soc.* **2010**, *132*, 7297–7299.

[10] a) K. Akagi, S. Guo, T. Mori, M. Goh, G. Piao, M. Kyotan, *J. Am. Chem. Soc.* **2005**, *127*, 14647–14654; b) Q. Li, L. Green, N. Venkataraman, I. Shiyanovskaya, A. Khan, A. Urbas, J. W. Doane, *J. Am. Chem. Soc.* **2007**, *129*, 12908–12909; c) A. Yoshizawa, K. Kobayashi, M. Sato, *Chem. Commun.* **2007**, 257–259; d) Y. Han, K. Pacheco, C. W. M. Bastiaansen, D. J. Broer, R. P. Sijbesma, *J. Am. Chem. Soc.* **2010**, *132*, 2961–2967.

[11] a) M. Kawamoto, T. Aoki, T. Wada, *Chem. Commun.* **2007**, 930–932; b) K. Takaishi, M. Kawamoto, K. Tsubaki, T. Wada, *J. Org. Chem.* **2009**, *74*, 5723–5726; c) M. Kawamoto, N. Shiga, K. Takaishi, T. Yamashita, *Chem. Commun.* **2010**, *46*, 8344–8346.

[12] a) M. Irie, *Chem. Rev.* **2000**, *100*, 1685–1716 and references therein; b) T. J. Wigglesworth, D. Sud, T. B. Norsten, V. S. Lekhi, N. R. Branda, *J. Am. Chem. Soc.* **2005**, *127*, 7272–7273; c) Z. Y. Wang, E. K. Todd, X. S. Meng, P. J. Gao, *J. Am. Chem. Soc.* **2005**, *127*, 11552–11553; d) T. Okumura, Y. Tani, K. Miyake, Y. Yokoyama, *J. Org. Chem.* **2007**, *72*, 1634–1638.

[13] a) F. Diederich, M. R. Hester, M. A. Uyeki, *Angew. Chem.* **1988**, *100*, 1775–1777; b) T. Horiuchi, T. Ohta, M. Stephan, H. Takaya, *Tetrahedron: Asymmetry* **1994**, *5*, 325–328; c) J. Reeder, P. P. Castro, C. B. Knobler, *J. Org. Chem.* **1994**, *59*, 3151–3160; d) M. Bandini, S. Casolari, P. G. Cozzi, G. Proni, E. Schmohel, G. P. Spada, E. Tagliavini, A. Umani-Ronchi, *Eur. J. Org. Chem.* **2000**, 491–497; e) K. Tsubaki, H. Morikawa, H. Tanaka, K. Fuji, *Tetrahedron: Asymmetry* **2003**, *14*, 1393–1396.

[14] a) K. Tsubaki, H. Tanaka, K. Takaishi, M. Miura, H. Morikawa, T. Furuta, K. Tanaka, K. Fuji, T. Sasamori, N. Tokitoh, T. Kawabata, *J. Org. Chem.* **2006**, *71*, 6579–6587; b) D. Sue, K. Takaishi, T. Harada, R. Kuroda, T. Kawabata, K. Tsubaki, *J. Org. Chem.* **2009**, *74*, 3940–3943; c) K. Takaishi, D. Sue, S. Kuwahara, N. Harada, T. Kawabata, K. Tsubaki, *Tetrahedron* **2009**, *65*, 6135–6140.

[15] a) N. Harada, K. Nakanishi, *Acc. Chem. Res.* **1972**, *5*, 257–263; b) L. Di Bari, G. Pescitelli, F. Marchetti, P. Salvadori, *J. Am. Chem. Soc.* **2000**, *122*, 6395–6398.

[16] Computational calculations were performed with Gaussian 09, Revision A.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian, Inc., Wallingford CT, **2009**.

[17] See the Supporting Information for values (Table S1).

[18] The induced CD of the azobenzene moiety in a hydrogel was detected, see; X. Ma, Q. Wang, D. Qu, Y. Xu, F. Ji, H. Tian, *Adv. Funct. Mater.* **2007**, *17*, 829–837.

[19] The induced CD of related binaphthyls was detected and calculated, see: N. Kobayashi, R. Higashi, B. C. Titeca, F. Lamote, A. Ceulemans, *J. Am. Chem. Soc.* **1999**, *121*, 12018–12028.

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