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A new axially-chiral photochemical switch

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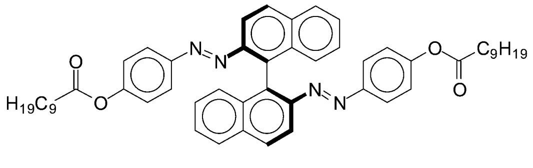
Axially chiral bis(azo) derivative 1 undergoes photochemical isomerisation, which can be seen with circular dichroism and pitch measurements of the induced cholesteric phases.

Molecular switches are a subject of continuous interest;[1] of these, chiral molecular switches seem particularly attractive. Under the influence of external factors, they undergo reversible transformations which are associated to changes in the chiral response of the system, which can be seen, for example, with chiroptical techniques (CD or optical rotation) or by measuring variation of the pitch of the cholesteric liquid crystals containing the switch.[2] In particular, photochemically driven chiral switches seem promising for several technological applications.[1]

Although the azo group, which undergoes light-driven, reversible, *E–Z* isomerisation, was used to obtain several photoswitchable systems (for example: photoresponsive crown ethers,[3] photoresponsive biomolecules,[4] molecular shuttles,[5] photoresponsive gels,[6] and azo solutes for lowering the electric field threshold in ferroelectric liquid crystals[7]), their employment for obtaining chiroptical molecular switches so far has been mainly limited to the use of achiral derivatives for modifying the pitch of classic cholesteric phases.[8]



(*R*,*E*,*E*)-**1**

A chiral switch acts as both a chiral agent to induce a cholesteric phase in a nematic liquid crystal and a photoresponsive dopant and, in principle, should have a more pronounced effect: the few cases investigated[9] were dealing with azobenzenes with chiral pendants attached to various positions of the aromatic rings, and the chiral response was not studied with chiroptical techniques, but only with induced cholesteric liquid crystals; in these examples, the values of the helical twisting powers[10] were low.[9] In this laboratory, we have synthetized several bis(azo) compounds containing chiral side groups, hoping to induce skewed chiral conformations of the molecules upon *E–Z* isomerisation, but the results obtained both in solution by CD, and in liquid crystals were very modest.[13]

Axially chiral binaphthyls have strong exciton CDs[14] and large helical twisting powers,[12,15] and both properties depend dramatically on the dihedral angle between the two aromatic moieties; we therefore decided to attach two azo groups to the 2,2′ positions of binaphthyl, hoping to obtain strong responses to the photochemical isomerisation. The presence of two azo groups maintains the C_2 symmetry[16] of binaphthyl, which is fundamental in asymmetric synthesis and gives strong exciton CD, hence a higher response to stereochemical variations.

The synthesis of compound **1** is straightforward, starting with commercial (*R*)-2,2′-diamino-1,1′-binaphtyl by diazotation and coupling with phenol; the simple bis(phenol) derivative does not give detectable *E–Z* isomerisation with an ordinary high-pressure Hg lamp;[17] compound (*R*)-**1** obtained by esterification with decanoyl chloride is instead photoswitchable: it was obtained, as a solid, in the pure (*E*,*E*) form.

The CD spectrum of 10^{-5} M acetonitrile solution of (*R*)-**1** changes markedly after irradiation with UV light (365 nm):[18] the strong $\pi\pi^*$ exciton couplet at 316 and 390 nm decreases dramatically and a new, strong, monosignated band appears at *ca.* 454 nm corresponding to the $n\pi^*$ transition (Fig. 1). The system can be switched back with visible light (546 nm) and the cycle can be repeated several times without apparent fatigue (Fig. 2) (we have chosen $\lambda = 412$ nm for reading the $\Delta\varepsilon$ values, as this wavelength, between the $n\pi^*$ and $\pi\pi^*$ transitions has very little influence on the isomerisation).

The thermic return to the initial state ([(*E*,*E*)] > 95%) is slow and, in the conditions used for CD measurements at 25 °C, the apparent half-time is *ca.* 10–13 h.

The possible isomers involved in the process are (*E*,*E*), (*E*,*Z*) and (*Z*,*Z*).[19] The compositions at the photostationary states (PPSs) were evaluated by CD spectroscopy after isolation of the pure isomers by preparative TLC (CD spectra of the pure isomers are reported in Fig. 1). The molar ratios (*E*,*E*)/(*E*,*Z*)/(*Z*,*Z*) were *ca.* 0.2/0.5/0.3 and 0.6/0.4/< 0.05 after irradiation with 365 and 546 nm light, respectively. The configurations were assigned by NMR.[20]

The (*E*,*E*) form was dissolved in the two different nematic solvents E7 (a mixture of cyanobiphenyl derivatives from Merck) and ZLI2359 (a mixture of cyanobicyclohexyl derivatives from Merck) and induces in both cases right-handed cholesteric phases. The twisting powers β are strong: +148 and +144 μm^{-1} in E7 and ZLI2359, respectively (constant values were observed in the low concentration interval used for the experiments). After irradiation with 365 nm light the β values decrease (the pitch length increases) considerably in both cases and the system can be switched back with visible light (546 nm). In the two nematic solvents the PSS after irradiation at 365 nm is richer in the (*E*,*E*) form with respect to the acetonitrile solution; as expected, the switching time is longer. The cycle could be repeated several times without changes of the twisting powers of the two PSSs (see Fig. 2).

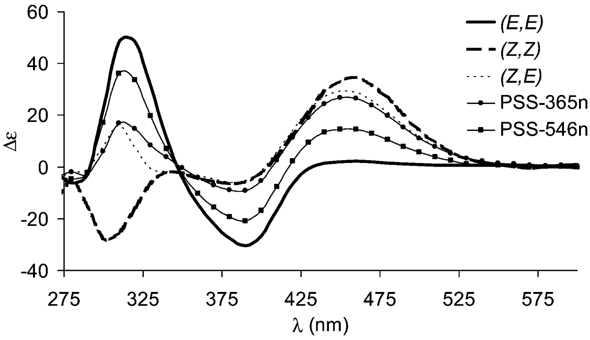


Fig. 1 CD spectra of the pure (*E*,*E*), (*Z*,*Z*), and (*Z*,*E*) isomers of (*R*)-**1** and of the 365 nm (PSS-365 nm) and 546 nm (PSS-546 nm) photostationary states.

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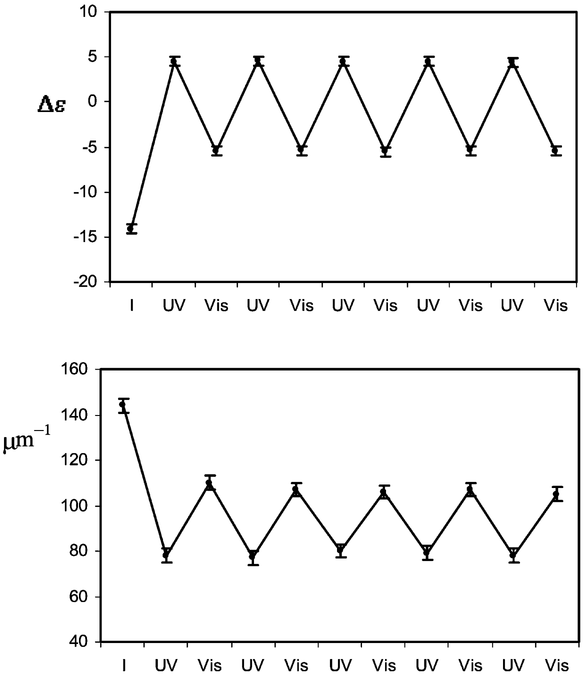

Fig. 2 Photoinduced alteration of Δ*ε* at 412 nm in a 10^{-5} M acetonitrile solution of (*R*)-**1**, $T = 25$ °C (top) and of *β* of (*R*)-**1** in ZLI2359, $c = 3 \times 10^{-4}$ mol mol^{-1}, $T = 17$ °C (bottom), upon irradiation with 365 and 546 nm light. I, UV, and Vis refer to the initial, 365 nm photostationary, and 546 nm photostationary states, respectively. Irradiation time at 365 and 546 nm: 20 and 70 min, respectively, in acetonitrile solution and 70 and 100 min, respectively, in ZLI2359.

The dependence of pitch with temperature was also investigated, as suggested in ref. 9*c*, as the decrease of *β* after irradiation could be connected to the disorder induced by the *Z* forms, rather than to the change in molecular chirality; in actual fact, the value of *β* depends on both a chirality and an orientational factor which can be calculated,[21] but not singled out experimentally. In all cases, *β* decreases with increasing temperature, but this effect is much smaller than the effect of the light. We also measured the clearing temperatures before and after irradiation: they are identical, indicating that there are not important changes in the order of the cholesteric matrix. A confirmation of the fact that the increase of the pitch after 365 nm irradiation is a consequence of the different chiral structures of the stereoisomers has been obtained by the calculation of their helical twisting powers according to the "Shape Chirality Model":[21] the *β*s calculated for the more stable conformations of the (*Z*,*Z*) and (*E*,*E*) isomers have opposite signs,[22] positive for (*R*,*E*,*E*)-**1** and negative for (*R*,*Z*,*Z*)-**1**.

To summarize, we have synthesized a new axially-chiral azo-switch with strong helical twisting power and CD. Photochemical isomerisation can be very easily read with CD and pitch measurements giving in both cases neat responses. The high value of *β* allows one to modulate the cholesteric pitch to a desired value even with low dopant concentration and also to obtain coloured phases. There is no apparent fatigue of the dopant, which seems very robust and resistant in the experimental conditions. The irradiation time needed to reach the PPSs is, unfortunately, rather long; however, this problem should be overcome by introducing appropriate substituents.[2]

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