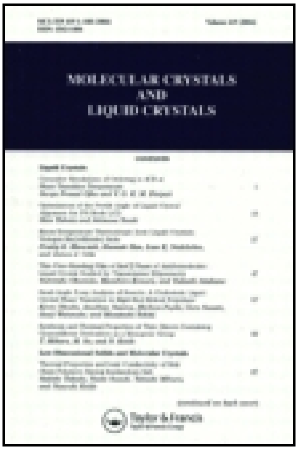

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A Novel Donor Acceptor Substituted Chiroptical Molecular Switch: Physical Properties and Photoisomerization Behavior

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A Novel Donor Acceptor Substituted Chiroptical Molecular Switch: Physical Properties and Photoisomerization Behavior

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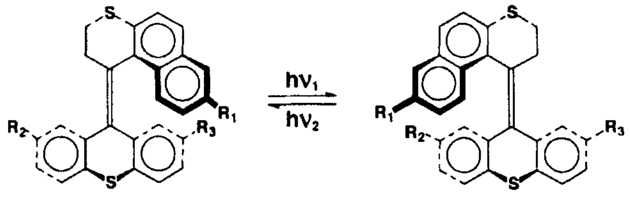
A novel donor acceptor substituted sterically overcrowded alkene was synthesized and characterized. Photoisomerization experiments it showed that this system could be converted with high efficiency towards a *cis* photostationary state and although the reverse isomerization towards the *trans* state was not as efficient this compound can function as a chiroptical molecular switch.

Keywords: Molecular Switches; Chirality; Photochromism

INTRODUCTION

Helically shaped sterically overcrowded alkenes can function as chiroptical molecular switches [1]. The switching process is based on a photoinduced *cis-trans* isomerization of the central double bond. The pseudoenantiomeric *cis* and *trans* state constitute a binary element which can be used for optical data storage and as a chiroptical trigger in for example LCD technology [2]. For example, with the donor-acceptor (DA) substituted switch **1** (Figure 1) switching between two photostationary states (PSS) of 70% **P** *trans* and 90% **M** *cis*, respectively using 365 and 435 nm light is possible [3].



M *cis* **P** *trans*

1: $R_1 = H$; $R_2 = NMe_2$; $R_3 = NO_2$
2: $R_1 = NMe_2$; $R_2 = H$; $R_3 = NO_2$

FIGURE 1 Switching of sterically overcrowded alkenes

The relatively high efficiency for compound **1** can be ascribed to the DA substitution pattern. The substituents hardly influence the pseudo-enantiomeric character of the two forms but they cause subtle differences in the UV absorptions resulting in an efficient photoisomerization process. To further improve the switching behavior alkene **2** was synthesized. In this system a through-space interaction of the electron-rich upper part and the electron-poor lower part can be expected in *cis* **2** whereas in *trans* **2** this donor acceptor interaction should be absent. This feature might result in large differences in absorption spectra and therefore high selectivities in the photochemical switching process.

MATERIALS

The synthesis of **2** is based on the diazo-thioketone coupling approach [4]. The synthesis of this compound is described elsewhere [5]. The enantiomers of **2** were resolved by chiral HPLC using a Daical Chiralpak OT+ column and hexane/isopropanol 9:1 as eluent. Absolute configurations of the four stereoisomers were assigned by CD spectroscopy by comparison with described switches [2],[3]. The enantiomers of **2** are stable under ambient conditions. Thermal racemization of *cis*-**2**, as determined by CD spectroscopy in *p*-xylene (85°C) shows first order kinetics with a barrier of 107 kJ / mol. No thermal *cis-trans* isomerization was observed during any of the described experiments.

CRYSTAL STRUCTURE OF *TRANS* 2

From the crystal structure of *trans*-**2** it was shown that the arrangement around the central double bond shows a strong deviation from planarity (dihedral angles: C12-C11-C14-C26 = 6.8(5)°; C10-C11-C14-C15 = 2.7(8)°; Figure 2).

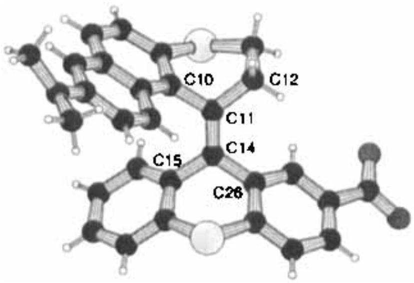


FIGURE 2 Crystal structure of *trans* **2**.

The bond length obtained for the central double bond (1.338(4) Å) is, quite unexpectedly, characteristic for a simple non-conjugated double bond. The molecule has an anti-folded helical structure in which the upper and lower halves are tilted in opposite directions relative to the plane of the central double bond. The heterocyclic ring in the upper part of *trans*-**2** adopts a boat conformation, unlike the heterocyclic rings in the upper parts of **1** which show twisted-boat conformations in their crystal structures. PM3 (gas phase) calculations showed that a twist-boat conformation was favorable. Therefore, it seems plausible to ascribe the observed boat conformation of **2** to crystal packing effects.

PHYSICAL PROPERTIES

The absorption spectra (Figure 3) of *cis*-**2** and *trans*-**2** are clearly different. Especially in the short wavelength region pronounced differences are observed. In the longer wavelength region *cis*-**2** shows a weaker absorption at 328 nm (ε=7700) and *trans*-**2** at 344 nm (ε=5000).

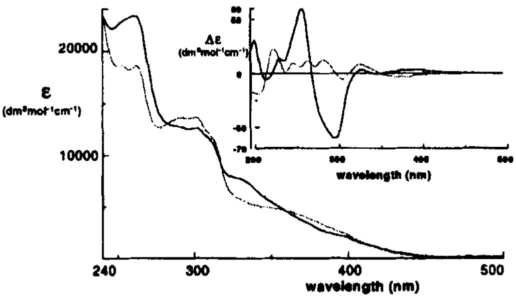


FIGURE 3 UV-VIS and CD characteristics of **2** in *n*-hexane (**M** *cis*-**2**: solid; **P** *trans*-**2**: dashed).

The CD spectra of **M** *cis*-**2** and **P** *trans*-**2** (Figure 3, inset) are completely different and the two forms cannot be considered pseudoenantiomers. In the region of 250–350 nm **P** *trans*-**2** exhibits several positive and one negative absorption with moderate intensities. **M** *cis*-**2** shows two strong absorptions (Δε(254) = 59.3 and Δε(295) = -62.2) which can be assigned as the positive and negative Cotton effects due to a chiral exiton coupling [6]. The pronounced CD spectrum of **M** *cis*-**2** can be explained by a strong through-space interaction of the electron-rich upper part with the electron-poor lower part of the molecule influencing the helix conformation and transition moments.

PHOTOISOMERIZATION BEHAVIOR

Irradiation of enantiomerically pure **P** *trans*-**2** in different solvents resulted in photostationary states as shown in Table 1.

λ (nm)	**M** *cis*-**1** / **P** *trans*-**1**	**M** *cis*-**2** / **P** *trans*-**2**		
	n-hexane	*n*-hexane	toluene	CH_2Cl_2
313	50/50	80/20	67/33	45/55
365	30/70	82/18	74/26	56/44
405	47/53	93/7	90/10	76/24
435	90/10	94/6	99/1	-

TABLE 1 Photostationary states for **2** in different solvents (determined by HPLC analysis and CD measurements; the data for alkene **1** in *n*-hexane are added for comparison).

The stereoselectivity of the photoisomerization proved to be strongly solvent dependent but at all wavelengths an excess of **M** *cis*-**2** is found at the photostationary states (except at 313 nm in dichloromethane). The selectivity of **2** towards the *cis* isomer is larger than for **1**: In toluene almost complete selectivity for the *cis* isomer (99%) is achieved. Since the absorption spectra of the two forms differ greatly the preference for the *cis* state in all cases can be ascribed to the relative stability of the *cis* state leading to a low quantum yield for the *cis* to *trans* isomerization. The relative stability can be explained by the favorable DA interaction in the *cis* state. The fact that in more polar solvents the PSS shift further towards the *trans* state is in accordance with this theory since more polar solvents diminish the effect of the intramolecular DA interaction.

The photostationary states are in most cases achieved within 2 min. of irradiation. However, the required irradiation times at 435 nm are strongly solvent dependent. In more polar solvents irradiation at 435 nm will only very slowly lead to isomerization (1,4-dioxane) or does not lead to isomerization at all (dichloromethane). Formation of a CT complex with more polar solvents can account for these observations [7]. Protonation of *cis*-**2** in order to disrupt the DA interaction lead to a non-isomerizable quartenary ammonium compound.

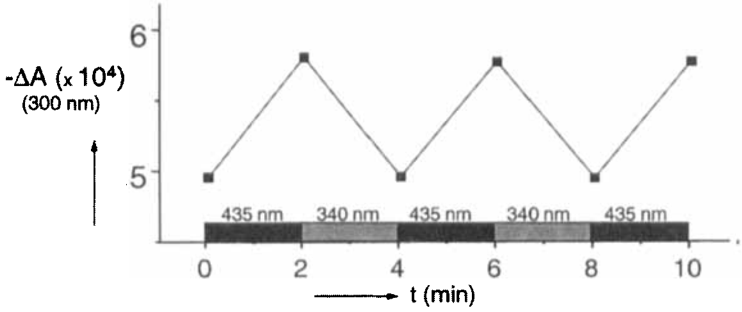


FIGURE 4 Modulation of CD signal of **2** (at 300 nm) upon alternate irradiation at 435 and 340 nm in *n*-hexane solution.

A typical switching experiment of this alkene in *n*-hexane is shown in Figure 4. The CD signal at 300 nm of **M** *cis*-**2** and **P** *trans*-**2** in *n*-hexane is monitored upon alternated irradiation at 435 and 340 nm. The process is completely reversible and compound **2** can thus in principle function as a molecular switch.

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