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## Chiroptical Molecular Switches 2; Resolution, Properties and Applications of Inherent Dissymmetric Alkenes

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## CHIROPTICAL MOLECULAR SWITCHES 2; RESOLUTION, PROPERTIES AND APPLICATIONS OF INHERENT DISSYMMETRIC ALKENES.

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**Abstract** The resolution and properties of various new inherent dissymmetric alkenes are described. A chiroptical molecular switch, based on these molecules, is presented in this paper.

### INTRODUCTION

Inherently dissymmetric alkenes<sup>1</sup> have attracted considerable attention due to their interesting stereochemical properties. Our research is focussed on the possible application of these molecules as active components for the construction of chiroptical molecular switches. In these switches a reversible photochemical transformation from a P- to a M-helical structure must be achieved. The principles of the envisaged molecular switch are outlined in the preceeding paper.

### COMPOUNDS INVESTIGATED

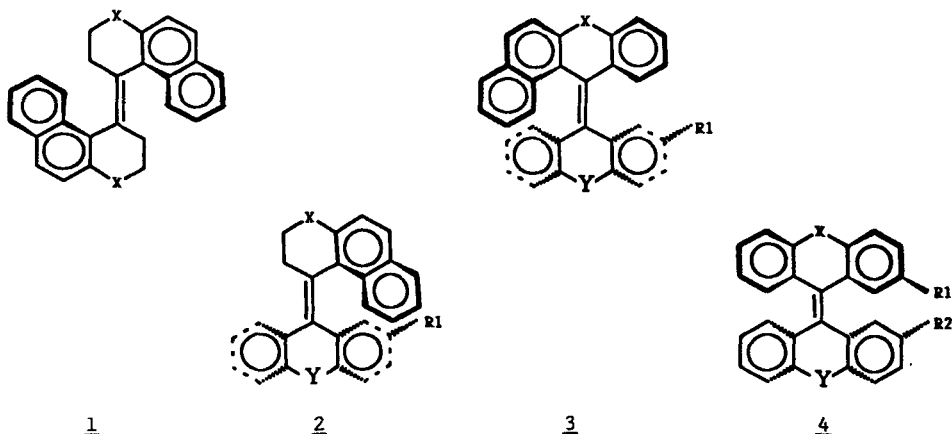


FIGURE 1

A large number of inherently dissymmetric alkenes have been synthesized. They can be divided in four classes as illustrated in figure 1. All these compounds are chiral due to a stable helical configuration.

### RESOLUTION

In order to investigate the chiroptical properties of the individual molecules, resolution as well as separation of geometrical isomers, is essential. Resolution was achieved by HPLC. Two types of Chiral Stationary Phases both coated on silica have been used; i TAPA<sup>2</sup>, 2-(2,4,5,7-tetranitro-9-fluorenylideneamino-oxy)propionic acid, a chiral fluorene based  $\pi$ -acceptor, and ii polytriphenylmethylmethacrylate<sup>3</sup>, a helical polymer containing triphenylmethyl groups for  $\pi$ - $\pi$  interactions. Surprisingly these methods were successful for the major part of type 1-4 alkenes. Even cis-trans mixtures could be fully resolved.

### SPECTROSCOPICAL DATA

TABLE 1 Spectroscopical data for selected alkenes.

compound	UV		CD		anisotropy factor $g \cdot 10^3$
	$\lambda(\text{nm})$	$\epsilon$	$\lambda(\text{nm})$	$\Delta\epsilon$	
<u>1a</u>	222.8	71900	224	281.3	3.9
X=Y=CH <sub>2</sub>	301.9	11300	240	222.0	4.5
(CIS)			257	-80.1	10.0
			282	11.9	2.4
			338	-14.0	2.8
<u>2a</u> :	222.9	78000	228	161.4	2.2
X=CH <sub>2</sub> Y=S	260.0	15400	260	-56.1	-5.1
<u>3a</u> :	203.3	82900	236	128.6	2.8
X=O Y=S	360.6	12500	314	-51.3	-6.4
			356	5.0	
<u>4a</u> :	206.4	66100	225	-13.7	-0.5
X= Y= S	238.5	41100	244	-13.7	-0.4
	267.2	17500	282	-10.6	-0.8
	351.6	9800	303	9.0	0.8

Spectroscopic characterization was achieved using NMR and (chir)optical techniques. Large Circular Dichroism effects were observed. UV and CD data of selected compounds of each class are presented in table 1.

Strong fluorescence was found for type 3 and type 4 compounds, and fluorescence quantum yields, relative to 9,10- diphenylanthracene, between 0.2 and 0.6 have been measured.

#### THERMAL BEHAVIOUR

The thermal behaviour of the alkenes was investigated by heating enantiomerically pure compounds and monitoring the process on HPLC. The kinetics of the racemization process and the energy barriers could be determined by polarimetry, using p-xylene as solvent.

Surprisingly most compounds were conformationally stable at room temperature. The racemization barriers of a selected number of alkenes of type 2, 3 and 4 are displayed in table 2.

A clear correlation between the aryl-X and aryl-Y bond length and the racemization barrier is observed.

TABLE 2 Racemization barriers for selected alkenes.

Compound	X	Y	$\Delta^\ddagger G^\ominus$	
<u>2b-d</u>	O/CH <sub>2</sub> /S	-	>30	
<u>2e</u>	O	S	21.7	
<u>2a</u>	CH <sub>2</sub>	S	26.3	
<u>2f</u>	S	S	28.9	
<u>3a</u>	O	S	26.7	
<u>3b</u>	S	O	25.9	
<u>3c</u>	S	S	28.4	
Compound	X	Y	R1	R2
<u>4a</u>	S	NCH <sub>3</sub>	CH <sub>3</sub>	H
<u>4b</u>	S	S	CH <sub>3</sub>	H

By heating the unsymmetrical substituted alkenes 1-4 (R1,R2 ≠ H), molecules that exist as cis and trans geometrical isomers, the mechanism of the racemization process could be revealed. The results are

interesting. Type 1 and type 2 compounds only show racemization eg M-cis into P-cis. Compounds of type 3 show a specific conversion of a M-cis to a P-trans form. Compounds of type 4 show both racemization and cis-trans isomerization with comparable rates.

#### PHOTOCHEMICAL BEHAVIOUR

All compounds resolved so far were irradiated in hexane ( $\lambda = 300$  nm). All symmetrically substituted molecules ( $R_1 = H$ ) of type 2, 3 and 4 racemize under these conditions. Quantum yields, determining the kinetics of the racemization process, were measured. Values between 0.15 and 0.30 were obtained.

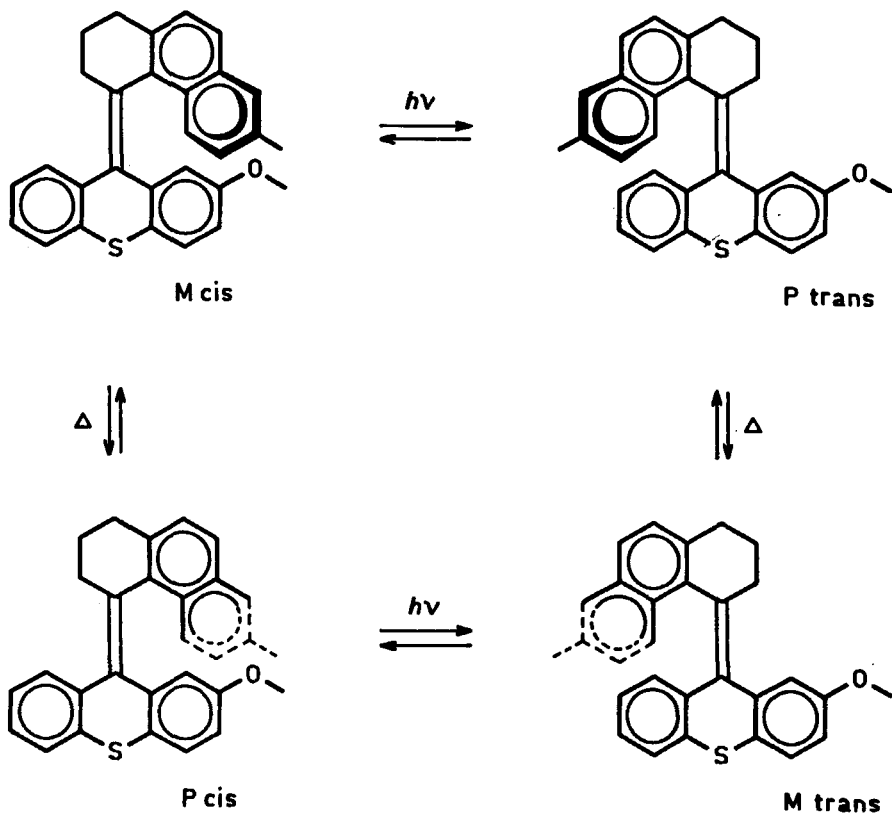


FIGURE 2 Conformational behaviour of a type 2 alkene.

Using type 1, and unsymmetrical substituted molecules of type 2 and 3 ( $R_1, R_2 \neq H$ ) the mechanism of the photochemical isomerization process could be revealed. A selective cis-trans isomerization simultaneously reversing the helicity of the molecules was observed, eg M-cis to P-trans. Figure 2 summarizes the thermal and photochemical behaviour of a type 2 compound.

#### BUILDING A SWITCH

Since, for unsymmetrically substituted alkenes 1-3, a cis-trans isomerization is accompanied by a reversal of the helicity of the molecule a molecular switch can be constructed<sup>4</sup>. Using cis- or trans-4-[9'-(2'-methoxythioxanthylidene)]-7-methyl-1,2,3,4-tetrahydrophe-nanthrene 2g and 2h the feasibility of such a chiroptical switch was demonstrated.

A solution of optically pure M-cis 2g, showed two distinguishable photostationary states after irradiating with 250 and 300 nm UV light, see figure 3. Detection of these photostationary states was achieved by CD spectroscopy.

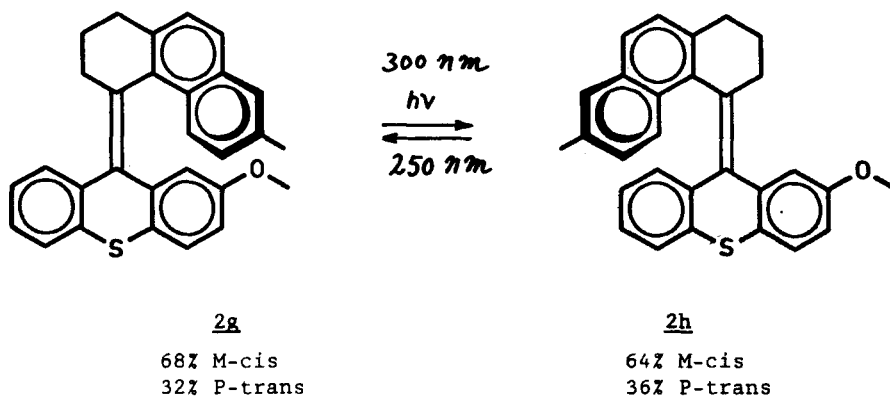


FIGURE 3

Alternated irradiation at 250 and 300 nm resulted in a modulated CD signal. This process could be repeated at least 10 times without racemization or changes in CD or UV spectra, see figure 4.

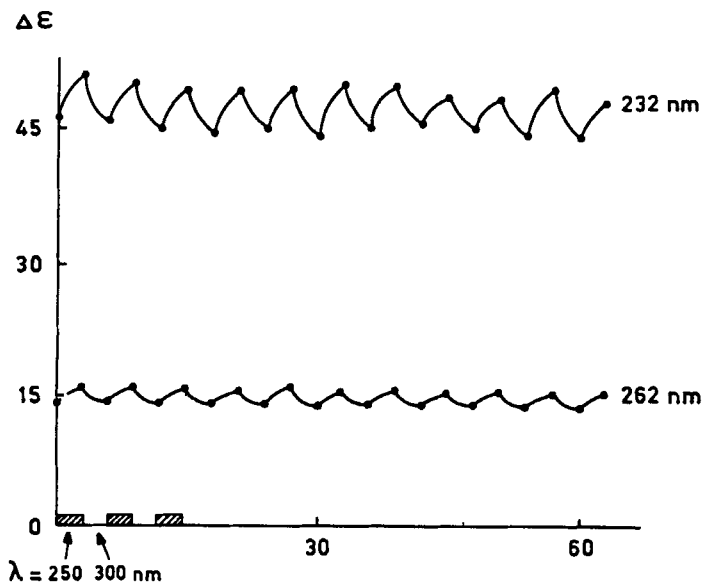


FIGURE 4. CD signal of the chiroptical switch.

#### CONCLUSIONS

The research described here demonstrated that all four types of inherent dissymmetric alkenes 1-4 are thermally stable at room temperature. Photochemical racemization or isomerization turned out to be a selective and highly specific process. The principle of a molecular switch using 2g light of 250 and 300 nm has been demonstrated.

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