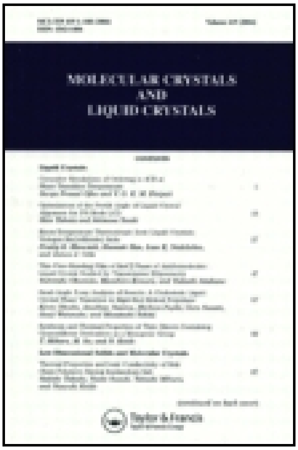

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Photochromic Azobenzenes Which are Stable in the Trans and cis Forms

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PHOTOCHROMIC AZOBENZENES WHICH ARE STABLE IN THE TRANS AND CIS FORMS

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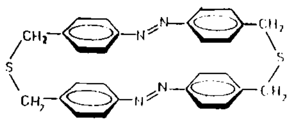
Abstract Azobenzenophanes with three-carbon bridges can be photoisomerized in both trans to cis and cis to trans directions. Contrary to other aromatic azo compounds the cis,cis form is stable at room temperature with a half life of about a year.

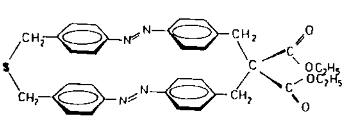
INTRODUCTION

Photochromism is the consequence of a light-induced molecular transformation $A \rightleftarrows B$. Stilbenes and azobenzenes are prototypes of cis-trans-photochromes. Contrary to other photochromic systems like spyropyrenes, fulgides or others[1], where a new band is developed in the molecular transformation, in the cis-trans isomerization intensity changes of bands common to both the cis and trans forms are observed. Azobenzene has an additional feature which can be used for practical purposes[2]: the molecule is shortened, measured by the 4-4'-distance, by 40 % on transformation from trans to cis. Material properties are changed by light when azobenzene units are incorporated in these materials[2].

Cis-azobenzene with a half life of some 1.5 days is one of the most stable aromatic compounds. Substitution by alkyl, electron donating and electron withdrawing groups decreases the lifetime of the cis compounds, in some cases to less than seconds. We report on photo- and thermal reactions of new azobenzenophanes with surprising properties.



2S



SC

RESULTS

Trans,trans azobenzenophanes are characterized by a phane band near 380 nm which is absent in azobenzene spectra (Fig. 1). 366 and 436 nm irradiation of the phanes induces predominantly trans ⟶ cis isomerization. The analysis is performed by Mauser[3] AD- and ADQ diagrams. In the AD diagram (Fig. 2) the end points represent the photostationary states at 366 nm (low left, nearly pure cis)

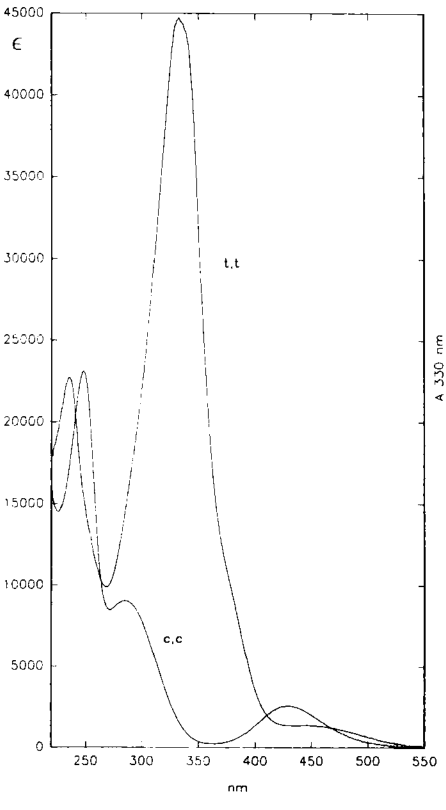


FIGURE 1 Absorption of SC

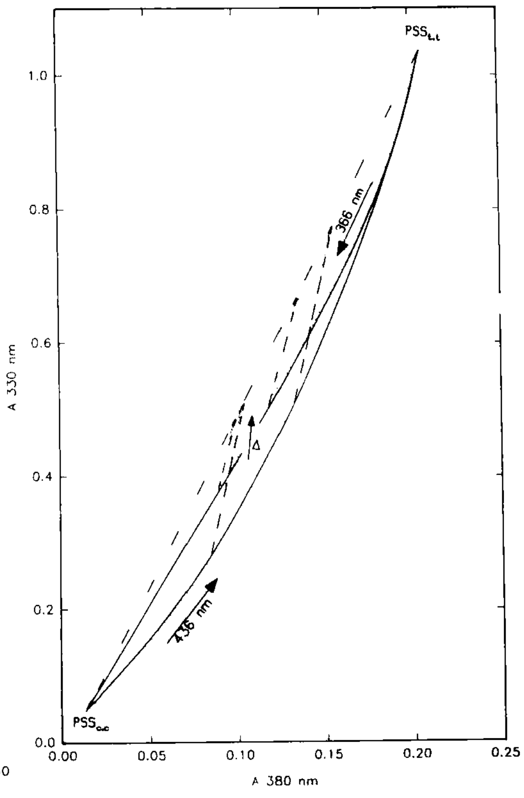


FIGURE 2 Mauser AD diagram of SC

and at 436 nm (upper right, rich in trans). The curved absorbance difference $[A_\lambda(t) - A_\lambda(0)]$ plots indicate two photoreactions and the linear plots ending at the line connecting the two photostationary states indicates one thermal reaction combined in the scheme

$$\mathrm{tt} \underset{h\nu,\Delta}{\overset{h\nu}{\rightleftharpoons}} \mathrm{ct} \underset{h\nu}{\overset{h\nu}{\rightleftharpoons}} \mathrm{cc}$$

We infer that the thermal reaction is from the highly strained ct to tt, the cc form of the three-carbon-bridged phanes is thermally stable. We have kept a cc sample at room temperature for several months and can give a lower value for its half life of 1 year.

On 313 nm irradiation the molecular system escapes from the above reaction scheme. Irreversible rupture of the ring structure occurs, the typical phane absorption disappears and additional absorption is built up around and below 300 nm. We take this a a further hint that the tetrazetidine ring may be a byproduct of isomerization and an intermediate in the short wavelength photolysis[3].

DISCUSSION

In Fig. 3 we give an artist's view of the potential surfaces in the system, compared to azobenzene. Fig. 3 repre-

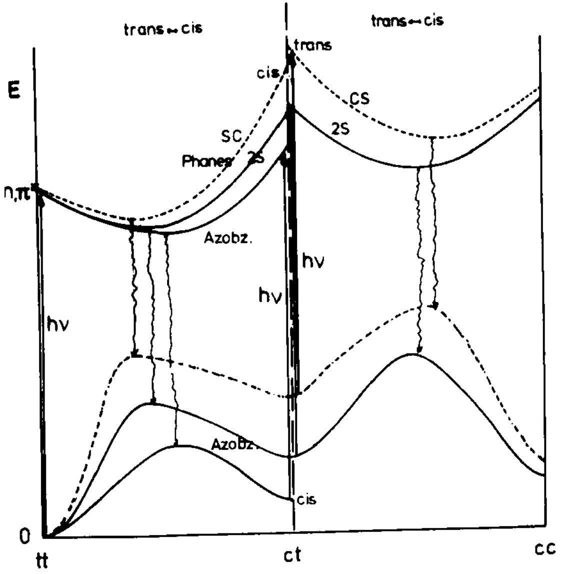


FIGURE 3 Potential energy curves of Azobenzene, 2S and CS phane (schematic)

sents two steps of isomerization, the ct form appears on irradiation of the tt form, absorption by the cis unit in ct leads back to tt, absorption of the cis unit on to cc. The strain of the ring system lifts the energy of the ct form with the consequence that the activation energy of ct → tt in the ground state (78 kJ/mole) is smaller than that in azobenzene (96 kJ/mole). The cc form also is higher in energy than azobenzene but lower than ct. There are differences between the phanes, cc → ct is still possible in a 2S-phane ($t_{1/2}$ = 5 days) but no longer in the SC-phane.

So the azobenzenophane with three-carbon bridge display four properties which are important for potential use. (1) the cis,cis and trans,trans forms can be interconverted by intense 366 and 436 nm irradiation, respectively. The molecule is photostable. (2) There is a spectral region (350-370 nm) where the absorbance of the trans,trans and cis,cis forms are very different up to a factor of 75, the cis,cis form nearly non-absorbing. (3) In this spectral region low light intensities as used for probing convert the absorbing trans,trans form to the trans,cis form which quickly re-isomerizes thermally to the trans,trans form. On the other hand low intensity light causes negligible loss of the non-absorbing cis,cis form. Thus probing is possible with a minimum loss of information. (4) Both the trans,trans and cis,cis forms are thermally stable.

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