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PHOTORESPONSIVE COMPLEXING STILBENE α,α′ DISUBSTITUTED BY ETHYLENE DIOXY SIDE ARMS.

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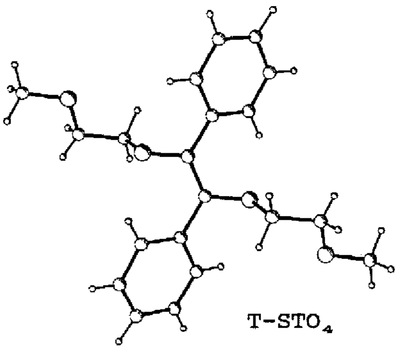
Summary: A photoresponsive stilbene molecule showing complexing ability has been synthesized. Its cis-trans isomerization under direct irradiation has been examined and the corresponding phenanthrene by-product has been prepared. The extracting ability versus Li, Na and K cations were measured. A stable complex with sodium thiocyanate has been isolated and characterized.

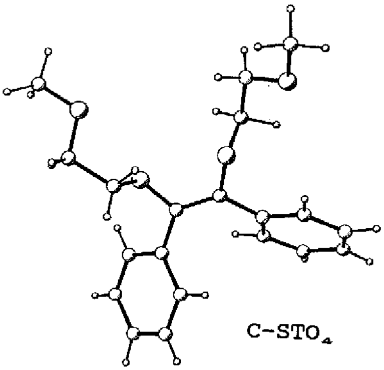
One of the recent developments in the use of macrocyclic ligands was the idea proposed by Shinkai to construct host molecules containing a photoresponsive chromophore ([1]). This could lead to a photocontrol of the binding ability of the host and models have been proposed, based on photoisomerization of azobenzenes ([2-4]) or olefins ([5]). Geometrical changes were also obtained by other mechanisms such as in the redox-switched crown ethers ([6]). Photocycloaddition was recently used in photoreversible cyclobutanocrown ethers ([7]).

In most of these examples, the geometrical modifications are not sufficient to generate an all-or-nothing change of the complexing ability. In a model recently proposed by Irie and Kato, a thioindigo derivative with ethylenedioxy side groups was used([8]), leaving the crown portion of the molecule in an open form. In order to test binding abilities, we synthesized a stilbene model bearing the complexing side arms directly on the double bond.

These compounds were prepared by a method similar to the one adopted by Merz ([9,10]) for the synthesis of stilbeno crown ethers: the tosylate of methoxy-2 ethanol was allowed to react with benzoin ([11]). The products were characterized by spectrometry and satisfactory data were obtained ([12]). The structures, as determined by X-ray diffraction, are given below and the crystallographic parameters are in reference ([13]).

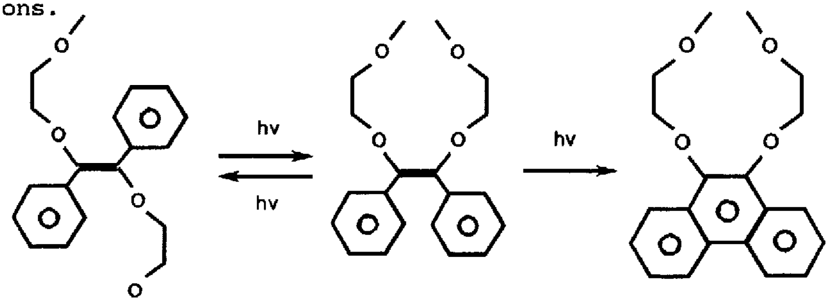


T-STO_4



C-STO_4

Cis-trans isomerization was performed by direct irradiation of C- or T-STO_4 ([16]). A photostationary state was not reached due to the expected photodehydrocyclization of C-STO_4 to the corresponding phenanthrene ($PheO_4$). After a carefully freeze-thaw degassing, the formation of the phenanthrene by-product was slowed down (by a factor of about 6) but not suppressed. In the presence of sodium perchlorate, the cis/trans ratio observed during the course of the isomerization was increased. The photocyclization of C-STO_4 was also found to be favoured in the presence of sodium cations.



T-StO4 C-StO4 PheO4

A reversible photocatalyzed isomerization, without interference with the dehydrocyclized $PheO_4$, may be obtained by irradiating with visible ligth a mixture of iodine and C- or T-STO_4 ([17]). The mixture was equilibrated when reaching a 2/1 T- to C-STO_4 ratio.

The $PheO_4$ by-product was prepared by photoisomerization starting from a mixture of C- and T-STO_4 in hexane solution ([18]). The product was spectrally characterized ([19]).

C or T-STO_4 do not show a measurable fluorescence: their emission spectrum is always dominated by the fluorescence of trace amounts of $PheO_4$ inevitably present in the stilbene samples. The UV spectra of these molecules are not strongly affected by the presence of salt and attempts to determine association constants have shown that their behaviour is not simple. Complexes with various stoechiometries are probably formed.

The extracting ability of the molecules synthesized has been tested by equilibrating a dichloromethane solutions of host molecules with an aqueous phase containing an alkaline picrate. The results are shown below.

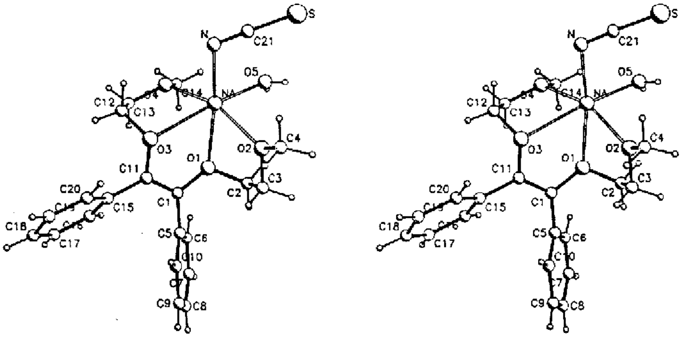
Table 1: Extraction of alkaline picrates .

	Alkali picrates extracted^a:		
	Li$^+$	Na$^+$	K$^+$
T-STO$_4$	1.4	0.7	5.7
C-STO$_4$	2.5	8.8	7.0
PheO$_4$	1.2	5.2	0.9
DB18C6^b		96.1	

a) In % of the aqueous alkali picrate as measured spectrophotometrically. Possible error: ±0.05 . Aqueous phase: 3.3 10^{-4} M in alkali picrate, 1 10^{-2} M in alkali hydroxide. Organic phase: 7 10^{-2} M in host molecule.
b) Dibenzo-18-crown 6.

The comparison with a powerful known crown ether shows that our molecules are poor extractants. However, a strong variation of the complexing property between C- and T-STO$_4$ was found in the case of the sodium extraction. This may be favourably compared with other cases presented in the litterature (5,20). Among the alkali cations, sodium is preferentially extracted by the C-STO$_4$. It is known that Li is the preferred one when the comparable 12-crown-4 is used (21). This difference must be attributed to a more loose cavity provided by the open C-STO$_4$ compound.

The complexing ability of the C-STO$_4$ was further demonstrated by the isolation af a complex formed between this compound and sodium thiocyanate. In this complex, the sodium cation is binded to the ethylenedioxy sidearms, to the thiocyanate anion and to a water molecule. This complex, stereoscopically shown below, was crystallographically characterized (22).



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(11) The yields (unoptimized) in crystallized products are at least of 60%. (Cis and trans are obtained in a 3/7 mixture separated by flash chromatography (Ethyl acetate/petroleum ether 2/1, 0.1% in triethylamine) and crystallized. M.p.: 46° ($C-StO_4$) and 56°($T-STO_4$).

(12) $C-StO_4$: NMR 200 MHz, δ(ppm). ^1H: 3.42(6H,s), 3.68(4H,t), 3.91((4H,t), 7.2(10H,m). ^{13}C: 58.7, 69.6, 71.8, 142.8, 127.4, 127.5, 127.7, 128.6, 129.7, 135.1, 142.8. UV(CH_3CN): λ_{max}:299 nm.
$T-STO_4$: NMR. ^1H: 3.24(6H,s), 3.43(4H,t), 3.62(4H,t), 7.36-7.82 (10H,m). ^{13}C: 58.6, 69.7, 71.4, 127.5, 127.6, 127.8, 128.3, 128.6, 134.2, 144.4. UV(CH_3CN) λ_{max}: 295 nm.

(13) The crystallographic data were obtained with a Huber 4 cycle diffractometer using CuKα graphite monochromatized radiation (λ =1.5418 Å), solution by SHELXS-86 (14), refinement by SHELX-76 (15). The structure of C-STO4 is discussed elsewhere (22).
$C-STO_4$: monoclinic, P21/a, a = 20.640(4), b = 9.542(1), c = 9.400(2)Å, β = 96.17(2)°, V = 1840.6(6)$Å^3$, Z = 4, Dx = 1.19 gcm^{-3}, final R index 0.060 for 2545 observed reflections.
T-STO4: monoclinic, P21/c, a = 9.541(2), b = 10.597(4), c = 9.109(3)Å, β = 93.32(2)°, V = 919.4(4) $Å^3$, Z = 2, Dx = 1.19 gcm^{-3}, final R index 0.056 for 1452 observed reflections. The list of atomic coordinate and molecular dimensions has been deposited with the Cambridge Data Center.

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(16) Irradiation in pyrex tubes with UV light from high pressure Hg lamp (Q300 Hanau burner); STO_4 in CH_3CN solvent.

(17) Irradiation with 2 visible lamps (150W) in heptane. $T-STO_4$ was 3.10^{-3} M and I_2 was 7.10^{-5} M.

(18) A 2 10^{-3} M solution of $T-STO_4$ in heptane was irradiated in the presence of 2 10-4 M I_2(quartz tube and 150 W high pressure Hg lamp. After reaching a 99% of $T-STO_4$ consumption, the residual $C-STO_4/PheO_4$ mixture was chromatographed with ethyl acetate/hexane eluent (1:1) containing 0.1% of triethylamine. The yield of $PheO_4$ (pale yellow liquid) was 70%.

(19) $PheO_4$: NMR 200 MHz, δ(ppm), ^1H: 3.49(6H,s), 3.80(4H,t), 4.39(4H,t), 7.61(4H,m), 8.34(2H,m), 8.62(2H,m). UV(CH_3CN): the spectrum shows the characteristic shape and wavelength of a phenanthrene aromatic.

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