

CROWN ETHERS CONTAINING TRANS DOUBLE BONDS

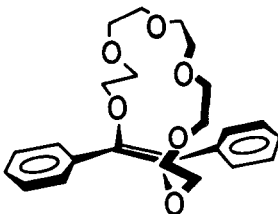
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Summary: The synthesis and spectroscopic properties of 18-crown-6-derivatives containing the E- α,β -dialkoxystilbene moiety as a ring member are described. These crown ethers are chiral but their complexing ability is drastically reduced as compared with the corresponding Z-isomers.

In an accompanying paper [1] we have reported the formation of 2,3-(9,10-phenanthro)-E-11,12-diphenyl-11,12-dehydro-18-crown-6 4c as a side product in the oxidative photolysis of 2,3,11,12-tetraphenyl-2,3,11,12-didehydro-18-crown-6 [2]. The structure of 4c attracted our attention for the following reasons:

CPK space filling molecular models suggest a best conformation such that the E-stilbene unit is oriented in a plane tangential to the crown ether ring with the phenyl groups slightly twisted (Fig.1). Due to the rigidity of the double bond system the vinylic oxygen atoms are forced to the outer sphere of the ring; instead, the C=C- π -bond points towards its center as do the remaining four oxygen atoms. This will not only change the normal 18-crown-6-geometry but also the electronic situation. Furthermore, the conformation in Fig.1 has C_2 symmetry with a chiral plane; since the bulky stilbene moiety cannot be rotated through the ring, enantiomers should be stable. We report here the synthesis of three more crown species containing E-stilbene units and some preliminary results in the study of their properties.

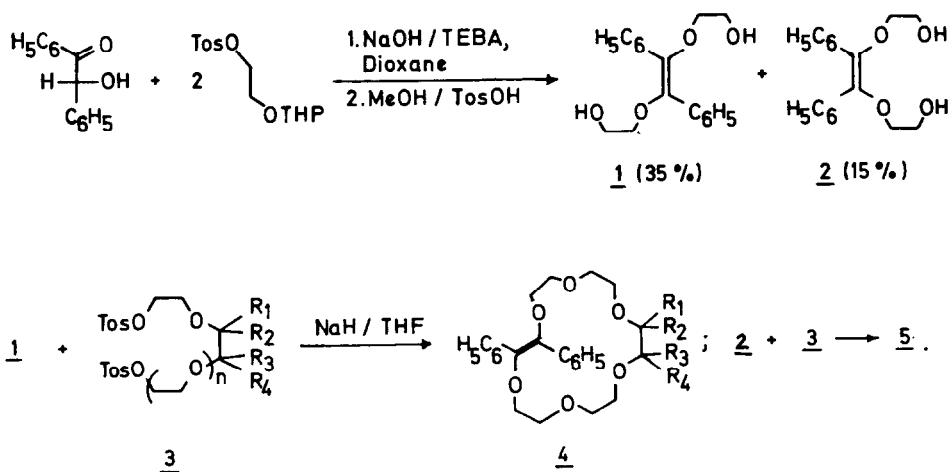
Fig.1



The key intermediate in our synthetic approach is E- α,β -(2-hydroxyethoxy)-stilbene 1 which is obtained together with its Z-isomer 2 by phase transfer catalyzed bis-alkylation of benzoin [3] with O-THP protected ethylene glycol monotosylate [4]. Cycloalkylation of 1 by suitable ditosylates with sodium hydride in THF [5] leads to the crown ethers 4a-c in moderate to fair yields. Reaction of 1 with diethylene-glycol ditosylate did not give the trans-15-crown-6 4d but instead the 30-crown-10 species 6 with two E-stilbene groups. For comparison, the corresponding crown ethers 5a-e with the Z-configured double bond were also synthesized using 2 as a starting material, or by cyclization of benzoin with suitable ditosylates [4].

The spectroscopic properties of the new crowns are listed in Table 1. The general differences of E- and Z-stilbene derivatives are also reflected in the spectra of the crown ethers; in the nmr-spectra, the phenyl protons of the trans species appear as two multiplets (3:2) while only singlets are observed in the cis-species [3]. In the UV-spectra, the intensities of the A- (ca. 300 nm) and B-bands (ca. 225 nm) of the stilbene moiety are reversed in the cis- and trans-isomers [6]. The mass spectra of E/Z-pairs generally have an identical fragmentation pattern, but the parent peak is higher in the trans isomer (cf. also ref. [1]).

4a was subjected to enantioselective low pressure liquid chromatography on triacetyl cellulose [7] on an analytical scale. Partial separation was observed by UV and polarimetric detection, the optical rotation being changed from - to + during the chromatography. It is thus proved, that 4a does exist in stable enantiomers at ambient temperature. Attempts of optical resolution on a preparative scale are underway.



The cis configurated crown ethers 5a-d readily form crystalline complexes with alkali and ammonium thiocyanates. Complexes of 4a are stable only in solution in equilibrium with suspended salt.

Complex association constants of the crown ethers 4a, 5a and 5e with Li, Na, K and NH₄ picrates, which were determined by the extraction method of Cram et al [5] are given in Table 2.

Tab.1: Physical and spectroscopic properties of the new crown ethers

	R ₁ ,R ₂	m.p.	¹ H-NMR (CDCl ₃)	UV (CH ₃ CN)	MS (70 eV)
	R ₃ ,R ₄	°C (yield)	δ [ppm] vs. TMS	λ _{max} [nm] (ε)	m/Z (rel.%); * = M ⁺
<u>4a</u>	H n=1	98 (28)	3.41-4.04, m, 16H 3.77, s, 4H 7.17-7.50, m, 6H 7.70-7.94, m, 4H	298 (16 250) 228 (8 590)	414* (57), 238 (19) 105 (100)
<u>5a</u>	H n=1	73 (42)	3.73, s, 8H 3.80, s, 12H 7.10, s, 10H	298 (9 500) 245s(5 900) 220s(12 400)	414* (44), 238 (15) 105 (100)
<u>4b</u>	benzo n=1	148 (25)	3.54-3.90, m, 12H 4.13-4.22, m, 4H 6.90, s, 4H 7.27-7.40, m, 6H 7.64-7.94, m, 4H	298 (16 300) 284 (15 900) 220 (1 900)	426* (100), 238 (15) 136 (50), 105 (15)
<u>5b</u>	benzo n=1	117 (45)	3.90, s, 8H 3.83-4.06, 4.06-4.30, symm. m, 8H 6.85, s, 4H 7.15, s, 10H	301 (10 800) 285 (11 100)	462* (53), 238 (77) 136 (76), 105 (100)
<u>4c</u> <u>5c</u>	9,10-phenanthro (1)			see ref. [1]	
<u>5d</u>	H n=0	80 (38)	3.73, s, 8H 3.80, s, 8H 7.10, s, 10H	297 (9 700) 244s(6 000) 220 (12 000)	370* (50), 238 (10) 105 (100)
<u>6</u>	a)	95-96 (15)	3.39-3.64, m, 32H 7.15-7.45, m, 12H 7.68-7.82, m, 8H	295 (26 500) 225 (24 000)	740* (70), 370** (29) 238 (34), 149 (65) 105 (100)

a) 6: E,E-2,3,17,18-tetraphenyl-2,3,17,18-didehydro-30-crown-10

Table 2: Complex association constants of some crown ethers with alkali and ammonium picrates.

Crown	$M^+ \text{-Picrate}^- (x10^{-3})$			
	Li	Na	K	NH_4
<u>4a</u>	0.6	4.1	26	5.8
<u>5a</u>	7.8	860	19000	1800
<u>5d</u>	19	1100	650	18

The cis-crown ethers show a normal complexing behavior, 5a being very similar to dibenzo-18-crown-6 [4,8] and 2,3-naphtho-18-crown-6 [5]; also, the smaller crown ether 5d matches the expected sodium selectivity. The crown ether 4a with the trans-double bond, however, has a drastically reduced complexing ability; since the selectivity sequence is roughly the same as in the cis isomer it seems likely that this is caused rather by the unfavorable combination of the "hard" oxygen and "soft" olefinic donor centers than by the ring size of the crown ether.

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