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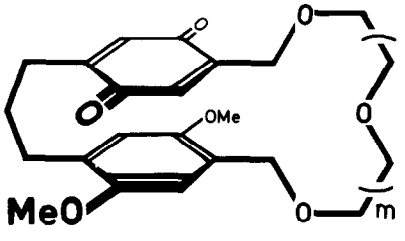
CATION-INDUCED CHARGE-TRANSFER ABSORPTIONS OF OLIGOOXA[n.n]PARACYCLOPHANE QUINHYDRONES [1)]

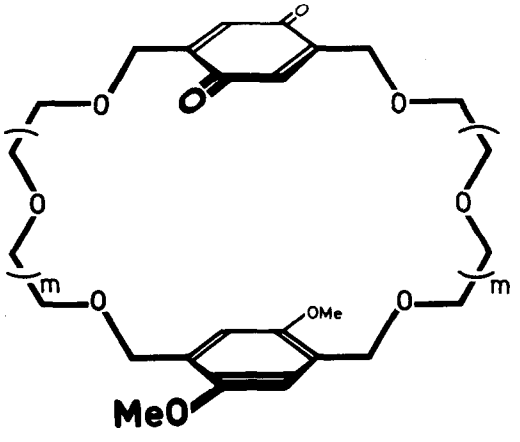
Helmut Bauer, Jan Briaire and Heinz A. Staab*

Abteilung Organische Chemie
Max-Planck-Institut für medizinische Forschung
Jahnstrasse 29, D-6900 Heidelberg

Summary: Intramolecular [n.n]paracyclophane quinhydrones with two oligo=oxaalkylene bridges 2a-e (m = 0,1,2,3 and 4, resp.) have been synthesized. The selective double complexation of these compounds with metal cations of suitable size (e.g. 7) is indicated by remarkable enhancements of the intensity of charge-transfer absorptions.

Investigations on the dependence of charge-transfer (CT) absorptions on distance, orientation and mutual fixation of donor and acceptor components in cyclophanes were extended recently to the intramolecular quinhydrones 1a-d (m = 1,2,3,4) [2)] where complexation of the crown-ether part of the molecules with suitably sized cations was expected to result in a mutual approach and fixation of donor and acceptor moieties. In fact, the complexation of these ligands was indicated by an increase of the intensity of CT-absorptions; for example, for the complex of 1c with sodium ion a (visually easily detectable) enhancement of the intensity of the CT-absorption by a factor of 3, as compared to the uncomplexed 1c, was observed. These first detections



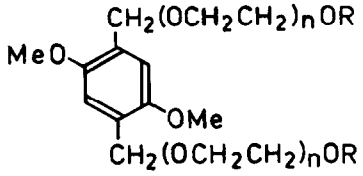


1a: m=1 1c: m=3
1b: m=2 1d: m=4

2a: m=0 2d: m=3
2b: m=1 2e: m=4
2c: m=2

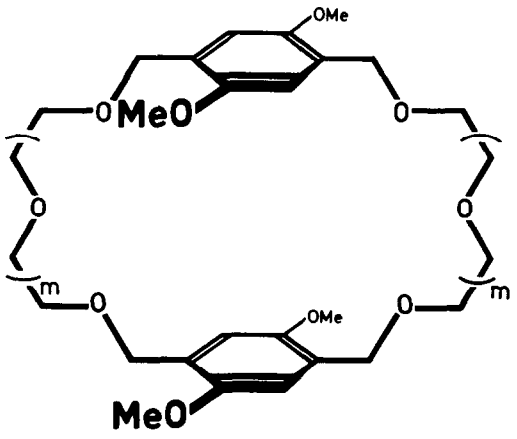
of selectively cation-induced CT-intensity changes were later followed by similar observations with other electron donor-acceptor systems [3]. In continuation of our previous work we now wish to report on the synthesis and complex formation of the intramolecular quinhydrones 2a-e (m = 0,1,2,3 and 4, resp.) where two oligooxaalkylene bridges should allow double complexation of cations of suitable size. Here an even stronger complexation effect on CT-absorptions was to be expected since for the uncomplexed systems, due to the long donor-acceptor distances, CT-absorptions, if at all detectable, should have very weak intensities.

Synthesis: The preparation of 2a-e was planned via the corresponding tetramethoxy-oligooxa[n.n]paracyclophanes 6a-e. Cyclization components for building up these macrocyclic ethers were 2,5-bis(bromomethyl)-1,4-dimethoxybenzene, 2,5-bis(hydroxymethyl)-1,4-dimethoxybenzene and the higher dialcohols 3b, 4b and 5b as well as the ditosylates 3c and 4c derived from 3b and 4b. Reaction of 2,5-bis(hydroxymethyl)-1,4-dimethoxybenzene with the corresponding tetrahydropyranyl(THP)-protected mono-, di- and triglycol monotosylates yielded the THP-derivatives 3a [4], 4a [4] and 5a [4] from which by hydrolysis 3b [4], 4b [4] and 5b [4] were obtained.



3a: n=1, R=THP 4a: n=2, R=THP 5a: n=3, R=THP
3b: n=1, R=H 4b: n=2, R=H 5b: n=3, R=H
3c: n=1, R=Tos 4c: n=2, R=Tos

Cyclization of 2,5-bis(bromomethyl)-1,4-dimethoxybenzene with 3b or of 3c with 2,5-bis(hydroxymethyl)-1,4-dimethoxybenzene (boil. tetrahydrofuran, sodium hydride, high dilution) yielded 6a [4] (m.p. 160-164°C). Although, according to an X-ray analysis [5], 6a does not show any significant molecular strain the yield (3%) of this smallest member of the series is rather poor due to the formation of the dimer which is the main product in spite of high-



6a: m=0
6b: m=1
6c: m=2
6d: m=3
6e: m 4

dilution conditions. Analogously, 6b [4] (m.p. 114-115°C; 32%) was obtained by cyclization of 3b with 3c, as were 6c [4] (m.p. 96-97°C; 40%) from 3b and 4c, 6d [4] (m.p. 87-88°C; 29%) from 4b and 4c, and 6e [4] (m.p. 69-71°C; 38%) from 5b and 4c.

Partial oxidative demethylation of 6a-e with diammonium hexanitratocerate (acetonitrile, 20 min, 20°C) [2] yielded as orange crystals (from acetone) 2a [4] (m.p. 202°C; 55% yield), 2b [4] (m.p. 169°C; 51%), 2c [4] (m.p. 120-121°C; 62%) and 2d [4] (m.p. 99-101°C; 52%); 2e [4] was obtained as orange oil (65%).

Complexation: The macrocyclic quinhydrones 2a-e show only small absorption intensities in the wavelength range where the CT-absorption of quinhydrones is to be expected (λ_{max} ~ 450 nm). For example, for 2d λ_{max} = 447 nm with ϵ = 98 (in chloroform) is observed. When 2d, however, is complexed with sodium ion by adding solid sodium thiocyanate to a 2d-solution in chloroform, this absorption band shows a fivefold increase in intensity to ϵ = 476 and a bathochromic shift to λ_{max} = 477 nm (Figure). This spectral change can be reversed by adding the stronger complex ligand 4,7,13,16,21-pentaoxa-1,10-diazabicyclo[8.8.5]tricosane ('Kryptofix 221'). The strong CT-absorption of the sodium complex of 2d is explained by assuming a structure as shown in 7 in which a double complexation induces a stacking of the donor-acceptor rings at considerably shorter distances as in 2d [6]. This structure is also supported by ^{1}H-NMR which shows for 7, in comparison to 2d, a high-field shift of $\Delta\delta$ = - 0.38 ppm for the signal of the quinoid protons as would be expected on

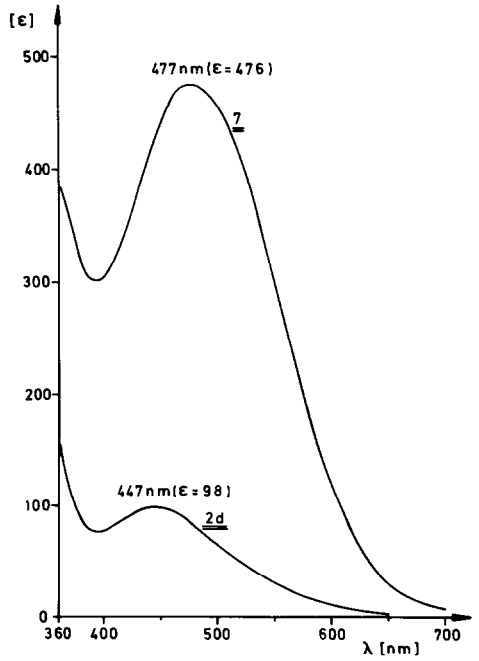
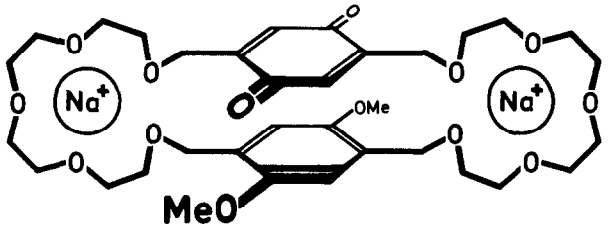


Figure.
Intensity Enhancement of CT-Absorption by Double Sodium Complexation of a Crown Ether [15.15]Paracyclophane Quinhydrone (in Chloroform)

the basis of an enhanced transanular anisotropy effect of the benzenoid ring. From a boiling solution in acetone of 2d and sodium thiocyanate in a molar ratio 1:2 the complex 7 [4] was isolated as red needles (m.p. 133-135°C, from ethyl acetate).

Addition of NaSCN to chloroform solutions of the smaller ring systems 2a-2c does not change significantly the absorption intensity of the CT band; a small hypsochromic shift of this band is observed with 2b and 2c. With the larger ring system 2e, complexation with sodium ions does not result in a similar intensity increase of the CT-absorption as with 2d, whereas for 2e potassium ions show a much stronger complexation effect than sodium ions [2e: λ = 430 (sh, ϵ = 51); 2e + KSCN: λ_{max} = 455 nm (ϵ = 268), in chloroform].



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Surprisingly, an especially strong complexation effect of barium ions on the CT-absorption was observed for 2d which in chloroform on addition of barium thiocyanate shows a tenfold intensity increase to ϵ = 1054 and, in contrast to the sodium effect, a hypsochromic shift of the CT-absorption maximum to 435 nm. This hypsochromic shift as well as a different complexation effect on ^{1}H-NMR (compared to the one reported above for the sodium complex of 2d) suggest that the binding of the doubly charged barium ion includes interactions with the oxygens on the aromatic and/or quinoid rings. This would also explain the irregularity of the binding with regard to the ionic radii (Na^+ 97, K^+ 133, Ba^{++} 134 pm). The barium complex, due to its high stability, was also obtained from 7 and barium thiocyanate in chloroform.

Further quantitative studies on the cation-selectivity of these complex ligands with 'built-in CT-indicators' are going on.

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4) Elemental analysis and spectroscopic data are in accordance with the structures suggested.

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6) See also the recent X-ray analysis of a disodium complex of a related [13.13]paracyclophane crown ether: J.D. Owen, Acta Cryst. C 40, 951 (1984).

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