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# [3.3]METACYCLOPHANE QUINHYDRONES

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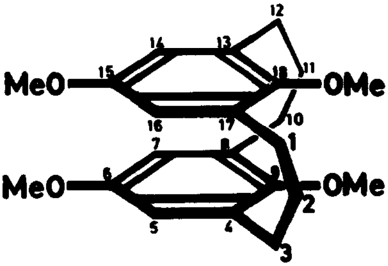
Via the stable stereoisomers 1 and 2 of 6,9,15,18-tetramethoxy[3.3]metacyclophane, by demethylation and oxidation, intramolecular quinhydrones of the [3.3]metacyclophane series were obtained the charge-transfer absorption of which is discussed.

Orientation and distance dependence of charge-transfer (CT) absorptions has been studied extensively by investigations on intramolecular donor-acceptor systems with well-defined geometry (1). In this connection we tried to determine the effect of a parallel translation of donor and acceptor units by comparing *syn*- and *anti*-[3.3]metacyclophane quinhydrones.

The two stereoisomeric 7,10,17,20-tetramethoxy-2,13-dithia[4.4]metacyclophanes (2), by pyrolysis (570° C, $10^{-4}$ Torr) of the disulfones derived therefrom, yielded *syn*- and *anti*-6,9,15,18-tetramethoxy[3.3]metacyclophanes which were separated by chromatography: 1 (3) (m.p. 115 - 116° C, 26 % yield) and 2 (3) (m.p. 89.5° C, 21 % yield) the assignment of which is proved by $^1$H-NMR [1: $\delta$ = 1.6 - 3.4 (m, 12 H), 3.46 (s, 6 H), 3.67 (s, 6 H), 6.12 (s, 4 H); 2: $\delta$ = 1.9 - 2.9 (m, 12 H), 3.14 (s, 6 H), 3.78 (s, 6 H), 6.54 (s, 4 H), $CDCl_3$]. 1 and 2 are remarkably stable stereoisomers; no isomerisation was detectable even after prolonged heating (e.g., 25 h at 190° C in decalin).



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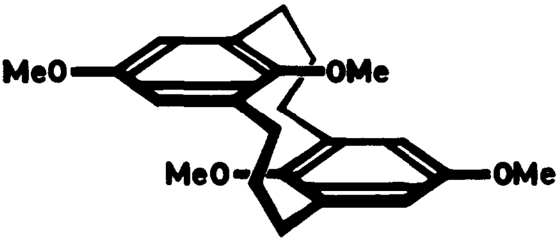

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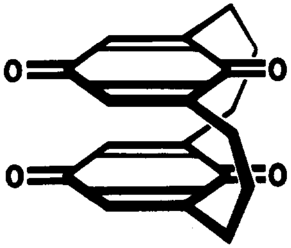
From 1 as well as 2 by demethylation (methylmagnesium iodide, 30 min, 180° C) and subsequent oxidation (silver oxide, acetone) the same [3.3](2,6)-p-benzoquinonophane (3)[3] was obtained (yellow needles, m.p. 236° C, dec.; 60 % yield). $^1$H-NMR data [$\delta$ = 1.5 - 3.2 (m, 12 H), 6.38 (s, 4 H), $CDCl_3$] and the photochemical conversion into the 'cage' isomer 4 [3] [dec. > 280° C; $^1$H-NMR: $\delta$ = 1.6 - 2.3 (m, 12 H), 3.33 (s, 4 H)] suggest the syn constitution for 3. The loss in sterical stability when going from 1/2 to 3 is explained as resulting from smaller size of intraanular substituents and higher flexibility of quinoid rings. Catalytic hydrogenation of 3 (Pd/C, dioxane, 20° C) yielded the quinhydrone 5 [3] [dark-violet crystals, m.p. 245 - 246° C (dec.); 82 % yield] the CT absorption of which [$\lambda_{max}$ 447 nm ($\varepsilon$ 2740), in dioxane] is very similar to the CT absorption of pseudogeminal [3.3]paracyclophane quinhydrone [1] suggesting an analogous donor-acceptor orientation.



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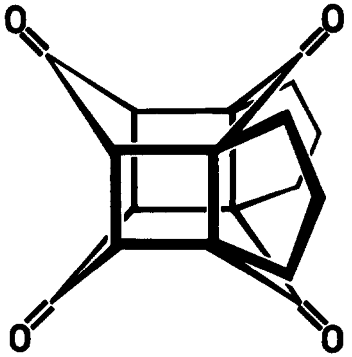

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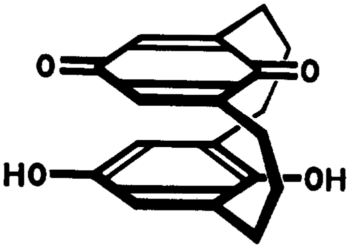
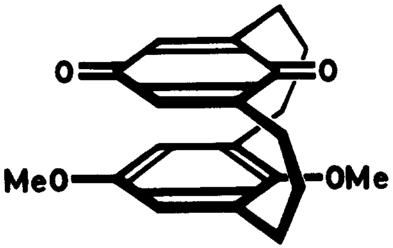


5

In an attempt to obtain quinhydrones both of the syn- and of the anti-[3.3]metacyclophane series the partial demethylations of 1 and 2 were studied. Treatment of 1 with chlorotrimethylsilane/sodium iodide in acetonitril [4] (2 d, 40° C) after oxidation with silver oxide led in 38 % yield to syn-15,18-dimethoxy[3](2,6)-p-benzoquinono[3]metacyclophane (6)[3] [red prisms, m.p. 195 - 197° C; $^1$H-NMR ($CDCl_3$): $\delta$ = 1.7 - 3.1 (m, 12 H), 3.58 (s, 3 H), 3.63 (s, 3 H), 5.96 (s, 2 H), 6.35 (s, 2 H)]. The strong CT absorption of 6 [$\lambda_{max}$ 400 nm ($\varepsilon$ 2740), in chloroform] supported again the assumption of a close resemblance of mutual donor-acceptor orientations in syn-[3.3]metacyclophane and [3.3]paracyclophane quinhydrones which definitely was confirmed by X-ray structure analysis of 6 5): in the projection of the quinone ring onto the benzene ring the ring centers show a transanular distance of 3.19 Å and are only slightly dislocated; the inclination of the C(4)-C(5)-C(7)-C(8) and C(13)-C(14)-C(16)-C(17) planes is only 15°.

As a by-product in the 6-synthesis a monomethyl ether of 1 has been obtained (red crystals, dec. > 184° C; 11.5 % yield) the CT absorption of which [$\lambda_{max}$ 438 nm ($\varepsilon$ 2610), in dioxane] is nearly congruent with that of 1.



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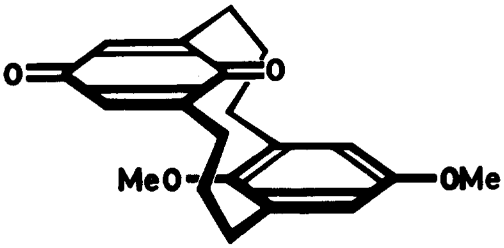

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Preliminary experiments on partial demethylation of 2 (methylmagnesium iodide, 160° C) led, after oxidation with silver oxide, to an isomer of 6 of m.p. 168 - 169° C ($M^+$: calc. 326.1518, obs. 326.1522). $^1$H-NMR data [$\delta$ = 2.2 - 3.2 (m, 12 H), 3.12 (s, 3 H), 3.69 (s, 3 H), 6.12 (s, 2 H), 6.40 (s, 2 H), in $CDCl_3$] agree well with the structure of the anti-15,18-dimethoxy[3](2,6)-p-benzoquinono[3]metacyclophane (7). However, alternative structures (e.g., a quinol isomer of 7) have not yet been ruled out definitely. The compound obtained does not at all show a CT absorption extending beyond 380 nm. Thus, in case we are really dealing with 7, the pair of stereoisomers 6/7 would offer an especially striking demonstration of the orientation dependence of CT absorptions.

1) W. Rebafka and H. A. Staab, *Angew. Chem.* **85**, 831 (1973); **86**, 234 (1974); *Angew. Chem. Int. Ed. Engl.* **12**, 776 (1973); **13**, 203 (1974); H. A. Staab and W. Rebafka, *Chem. Ber.* **110**, 3333 (1977); H. A. Staab and C. P. Herz, *Angew. Chem.* **89**, 839 (1977); *Angew. Chem. Int. Ed. Engl.* **16**, 799 (1977); R. Reimann and H. A. Staab, ibid. **90**, 385 (1978), and **17**, 374 (1978), resp.; H. A. Staab and V. Schwendemann, ibid. **90**, 805 (1978), and **17**, 756 (1978), resp.; H. A. Staab and U. Zapf, ibid. **90**, 807 (1978), and **17**, 757 (1978), resp.; further references are given there.

2) H. A. Staab, C. P. Herz and A. Döhling, *Chem. Ber.* (in press).

3) Elemental analyses, mass spectra, and other spectroscopic properties are in agreement with the structures given.

4) Cf. T. Morita, Y. Okamoto and H. Sakurai, *J. C. S. Chem. Comm.* **1978**, 874.

5) C. Krieger and H. A. Staab, to be published.

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