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ANTI-[3.3]METACYCLOPHANE QUINHYDRONES: SYNTHESIS, CHARGE-TRANSFER ABSORPTION AND THERMAL REARRANGEMENT TO SYN-STEREOISOMERS [1)]

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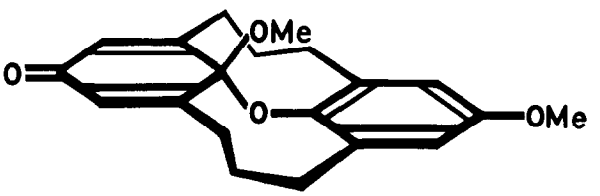
The synthesis of anti-[3.3]metacyclophane quinhydrones and their thermal rearrangement to syn-stereoisomers are described. Charge-transfer absorptions are discussed under the aspect of different donor-acceptor orientations.

We recently reported on the synthesis of syn-[3.3]metacyclophane quinhydrones starting from syn-6,9,15,18-tetramethoxy[3.3]metacyclophane [1)]. From the corresponding anti-tetramethoxy[3.3]metacyclophane, too, via thorough demethylation, oxidation to the bis(quinone) and catalytic hydrogenation only syn-[3.3]metacyclophane quinhydrone was obtained whereas partial demethylation and subsequent oxidation yielded a compound the elemental composition and the ^{1}H-NMR absorption of which were compatible with the structure of anti-15,18-dimethoxy[3](2,6)-p-benzoquinono[3]metacyclophane (2) [1)]. On the basis of mass spectra, however, the structure of the isomeric quinol 1 had to be adopted the formation of which consists also with the reaction conditions mentioned.



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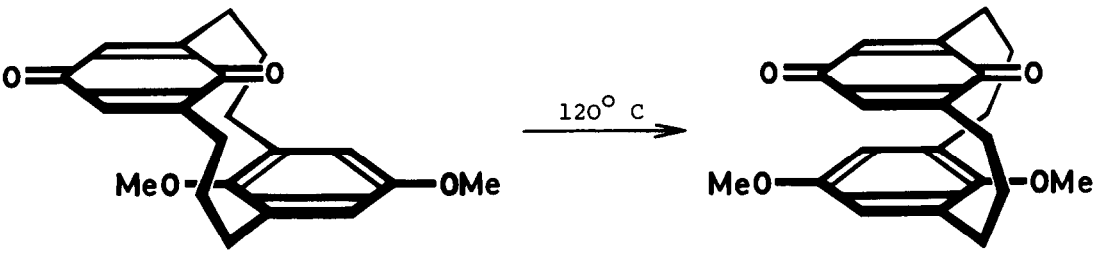
The true anti-15,18-dimethoxy[3](2,6)-p-benzoquinono[3]metacyclophane (2) was now obtained from anti-6,9,15,18-tetramethoxy[3.3]metacyclophane [1)] by

partial demethylation with chlorotrimethylsilane/sodium iodide in acetonitrile (5 h, 40° C) and subsequent oxidation with silver oxide in acetone (30 % yield). The structure of 2 (orange platelets, m.p. 136° C) is supported by ^{1}H-NMR [δ = 1.5 - 3.0 (m, 12 H), 3.40 (s, 3 H), 3.82 (s, 3 H), 6.46 (s, 2 H) 6.55 (s, 2 H), $CDCl_3$] and the mass spectrum which for 2, in contrast to 1, shows close similarity to that of the syn-stereoisomer 3 described previously [1] [m/e = 326 (M^+, 100 %), 164 (7), 162 (9), 149 (8), 136 (5)].



2 3

As can be followed by recording the ^{1}H-NMR spectra in [D_6]dimethylsulfoxide at 120° C, 2 on heating rearranges completely to the syn-stereoisomer 3 [1]. Considering the strong sterical strain in 3 (evident from ring deformations and short transanular distances as determined by X-ray analysis [2]) and the sterically less crowded structure of 2 the complete isomerisation 2 (anti) ⟶ 3 (syn) suggests a considerably stronger ground state stabilisation by electron-donor-acceptor interactions for 3 than for 2. This result agrees well with MO-calculations on CT ground state stabilisation of quinhydrone [3] according to which a parallel-translocated donor-acceptor arrangement as in 2 would result in only about 50 % of the ground state stabilisation present in the ecliptic face-to-face arrangement which is closely approximated in 3.

In contrast to the strong orientation dependence found for pseudogeminal and pseudo-ortho paracyclophane quinhydrones [4], the CT absorptions of the syn-anti isomers 2 and 3 are, in spite of the very different donor-acceptor overlap, surprisingly similar in wavelength and band shape (fig.). The CT absorption intensity is found to be significantly higher for the anti-isomer

2 than for the syn-compound 3 [2: λ_{max} = 402 nm (ε 3230), 3: 402 (2670), in chloroform; 2: 387 (3410), 388 (2520), in dioxane]. MO-calculations of transition energies and transition moments [5] so far do not account satisfactorily for the experimental absorption wavelengths and intensities of 2 and 3. As is clearly demonstrated by the pair of stereoisomers 2 and 3 there exists no general correlation between ground state stabilisation by electron donor-acceptor interaction and the wavelengths and/or the intensities of CT absorptions which frequently has been taken for granted.

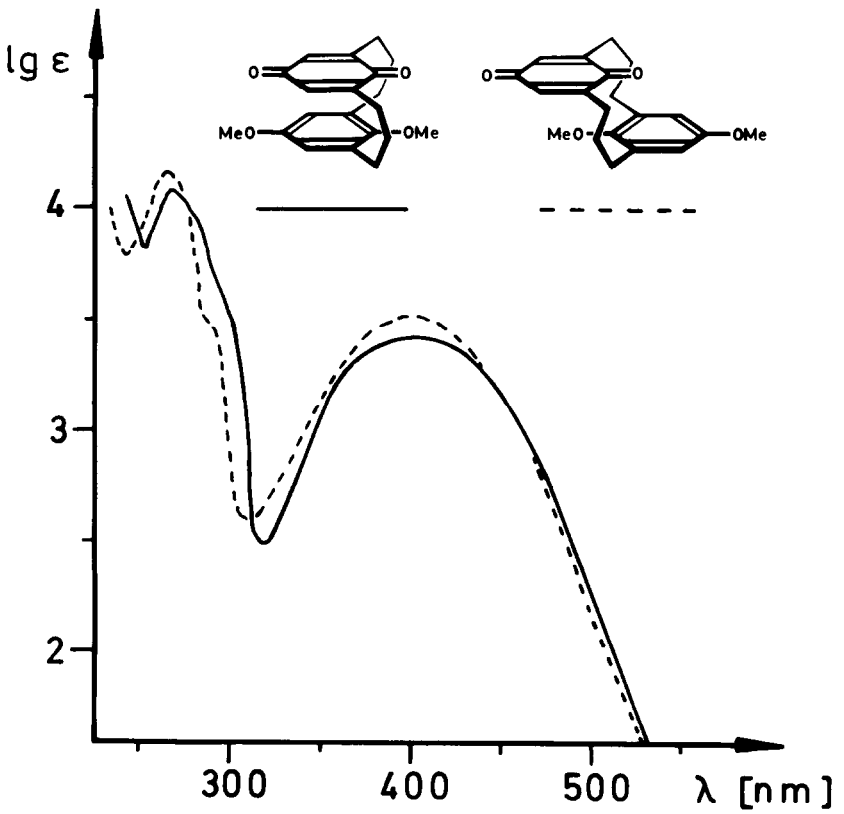
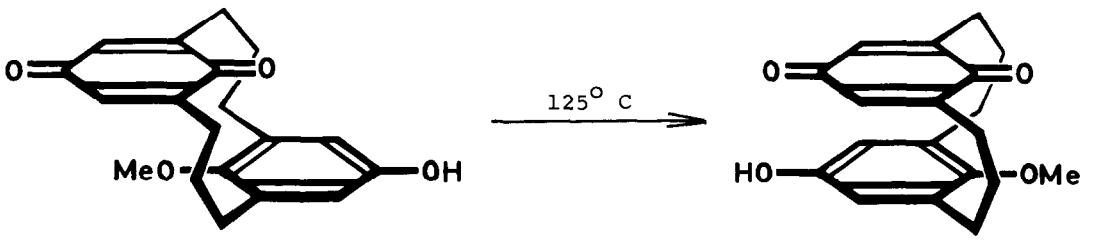


Fig. CT absorption of 2 and 3 (in chloroform)

In addition to 2, by partial demethylation of anti-6,9,15,18-tetramethoxy[3.3]metacyclophane and subsequent oxidation, an anti-[3.3]metacyclophane quinhydrone monomethylether was obtained (red needles; m.p. 190° C, dec.). ^{1}H-NMR data [δ = 1.9 - 3.0 (m, 12 H), 3.38 (s, 3 H), 6.45 (s, 2 H),

6.49 (s, 2 H), $CDCl_3$] support the structure of anti-15-hydroxy-18-methoxy-[3](2,6)-p-benzoquinono[3]metacyclophane (4). Under similar conditions as with 2 a complete thermal isomerisation of 4 is observed yielding the corresponding syn-isomer 5 [orange-red crystals; m.p. 240° C, dec.; ^{1}H-NMR: δ ≈ 1.5 - 3.1 (m, 12 H), 3.57 (s, 3 H), 6.00 (s, 2 H), 6.33 (s, 2 H), $CDCl_3$]. 4 and 5 form a second set of syn-anti-isomeric [3.3]metacyclophane quinhydrones the ground state stability ratio as well as the CT absorptions of which correspond very much to those of the pair 2/3 [4: λ_{max} = 393 nm (ε 3390); 5: 394 (2430), in dioxane].



4 5

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1) Electron-Donor-Acceptor Compounds, Part 22. - Part 23: H. A. Staab, C. P. Herz and A. Döhling, Tetrahedron Lett. 1979, 791.

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

3) B. Mayoh and C. K. Prout, J. Chem. Soc., Faraday Trans. II 1972, 1072.

4) W. Rebafka and H. A. Staab, 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, C. P. Herz and H.-E. Henke, ibid. 110, 3351 (1977); H. A. Staab and C. P. Herz, Angew. Chem. Int. Ed. Engl. 16, 799 (1977).

5) H. Vogler, unpublished.

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