Tetrahedron Letters No. 27, pp 2513 - 2516. 0040-4039/79/0701-2513$02.00/0

ISOMERIC [2.2]METAPARACYCLOPHANE QUINHYDRONES [1)]

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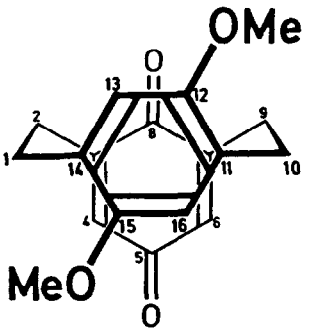
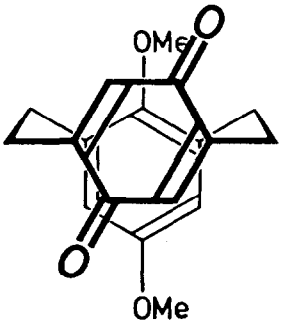
The two [2.2]metaparacyclophane quinhydrones 1 and 2 were synthesized. Structure, stereochemistry and charge-transfer absorptions are discussed.

The recent synthesis of [3.3]metaparacyclophane quinones and the discussion of their absorption spectra under the aspect of charge-transfer (CT) interactions [2)] induce us to report here results obtained in the synthesis of the two isomeric [2.2]metaparacyclophane quinhydrones 1 and 2. They represent the first examples of [2.2]metaparacyclophanes where fairly strong electron donor and acceptor units are linked together in the two different modes possible in this system. 1 and 2, due to the peculiar isomeric donor-acceptor orientations present, were of interest for comparison with quinhydrones of the meta- and paracyclophane series [1,3)].



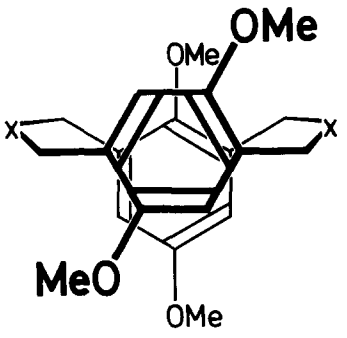
1



2

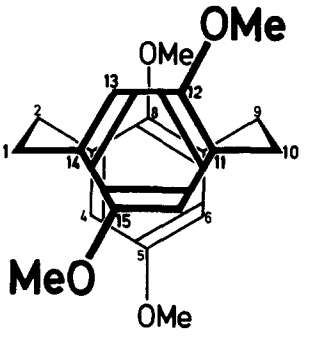
1,3-Bis(bromomethyl)-2,5-dimethoxybenzene and 1,4-bis(mercaptomethyl)-2,5-dimethoxybenzene were cyclized to 6,9,14,17-tetramethoxy-2,11-dithia[3.3]-metaparacyclophane (3) [4)] [slow simultaneous addition of 0.025 M solutions

of the components in tetrahydrofuran and N,N-dimethylformamide, resp., to a boiling 1:1 mixture of tetrahydrofuran and N,N-dimethylformamide, potassium carbonate; 43 % yield; m.p. 163.5° C]. 3 was converted into the disulfone 4 (hydrogen peroxide, dichloromethane/acetic acid, 90 %). From 4 by vacuum vapour phase pyrolysis [5] at 520° C/0.005 Torr the highly strained 5,8,12,15-tetramethoxy[2.2]metaparacyclophane (5)[4] was obtained in excellent yield (80 %; m.p. 113° C). ^{1}H-NMR [δ = 2.0 - 3.5 (m, 8 H), 3.20 (s, 3 H), 3.35 (s, 3 H), 3.72 (s, 3 H), 3.85 (s, 3 H), 5.50 (s, 1 H), 6.33 (s, 2 H), 6.56 (s, 1 H); $CDCl_3$], mass spectrum [m/e = 328 (M^+, 100 %), 313 (6), 297 (15), 177 (9), 164 (10), 149 (12)] as well as an X-ray analysis [6] are in accordance with structure 5.

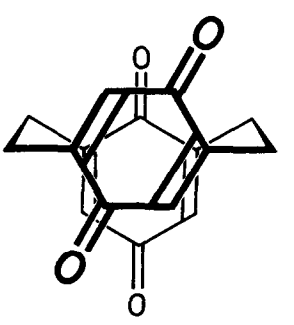


3: X = S

4: X = SO_2



5



6

Demethylation of 5 (BBr_3, dichloromethane, 30 min, 20° C) and subsequent oxidation (silver oxide, acetone, 24 h, 20° C) yielded the bis(quinone) 6 [4] in 60 % yield [yellow cubes, m.p. 197° C (dec.); ^{1}H-NMR ($CDCl_3$): δ = 2.1 - 3.5 (m, 8 H), 6.23 (s, 1 H), 6.37 (AB, J_{AB} = 2.5 Hz, 1 H), 6.48 (AB, 1 H), 6.51 (s, 1 H)]. Catalytic hydrogenation (1 equiv. H_2, $Pd/BaSO_4$, tetrahydrofuran) led to the deeply coloured quinhydrone stage, probably to a mixture of the two possible isomers (cf. 1 and 2) which were not yet obtained in a pure state.

Partial demethylation of 5 (methylmagnesium iodide, 1 h, 160° C) led, after oxidation (silver oxide, acetone), in 30 % yield to 1 [4] (dark-red platelets, m.p. 142° C); isomer 2 could not be isolated under these conditions. 1 and an

isomeric compound, however, were obtained as minor by-products (about 0.5 % each) of the pyrolysis of the disulfone 4 (see above); chromatography on silica from dichloromethane resulted in the separation of 1 and the slower moving isomer (orange-red crystals, m.p. 171° C) [4]. The assignment of the two isomers to the structures 1 and 2, resp., was first made tentatively on the basis of mass spectra and NMR data. In the mass spectrum of 1 [m/e = 298 (M^+, 100 %), 283 (4), 267 (10), 164 (20), 151 (7), 134 (20)] the most prominent fragments are those of m/e = 164 and 134 which can be assigned to the dimethoxy-1,4-quinodimethane fragment $C_{10}H_{12}O_2$ of 2 and the fragment $C_8H_6O_2$ derived therefrom by O-methyl cleavage. These fragments which are indicative of the dimethoxy-substituted paracyclophane part of the molecule do not show up in the mass spectrum of the isomer [m/e = 298 (M^+, 100 %), 283 (6), 267 (4), 184 (6), 151 (45), 149 (19)]. In ^{1}H-NMR it is especially the different shielding of the methoxy groups which supports the assignment made [1: δ = 3.55 (s, 3 H), 3.90 (s, 3 H); 2: δ = 2.14 (s, 3 H), 3.75 (s, 3 H); $CDCl_3$]. Whereas the 12,15-dimethoxy[2](2,6)-p-benzoquinono[2]paracyclophane structure 1 was definitely confirmed by X-ray analysis, structure 2 of the isomer - considering also the unusual way of its only formation - is less firmly established though very plausible.

In addition to at least two crystal modifications of the racemate, 1 crystallizes also as separated enantiomers in orthorhombic prisms of the chiral space group $P2_12_12_1$ [a = 7.698(1), b = 8.205(1), c = 24.024(5)]. For this modification the structure analysis was carried out which reveals the following essential structural features [6]: The benzenoid paracyclophane unit shows a boat-type deformation with an inclination of about 11° for the planes C(12)-C(11)-C(16) and C(13)-C(14)-C(15) against the bottom plane of the boat [C(12)-C(13)-C(15)-C(16)]. The meta-bridged quinone unit exhibits a much stronger deformation the angle between C(3)-C(8)-C(7) and C(3)-C(4)-C(6)-C(7) being 21°. The carbonyl carbon C(8) is closely below the center of the benzenoid ring with a transanular distance of 287 pm. The quinone ring, too, forms a boat conformation the less crowded side, however, being only slightly distorted from planarity [angle C(4)-C(5)-C(6)/C(3)-C(4)-C(6)-C(7): 7°]. The

inclination between the bottom planes of the quinoid and the benzenoid rings is about 19°. Whereas for the unsubstituted [2.2]metaparacyclophane due to the rocking motion of the meta-substituted ring a high internal mobility was found [7] the structure analysis of 1 shows clearly that the tetrasubstituted [2.2]metaparacyclophanes dealt with in this paper have very rigid structures.

By picking out crystals of the chiral 1-modification it has been possible to obtain levorotatory as well as dextrorotatory enantiomers of 1. For example, for two crystals (optical purity not yet known) the rotations $[\alpha]_{334}^{20}$ = - 11800°, $[\alpha]_{460}^{20}$ = - 1750° and $[\alpha]_{334}^{20}$ = + 14000°, $[\alpha]_{460}^{20}$ = + 1950°, resp., have been observed (in chloroform). These systems offer, apparently for the first time, the opportunity of measuring ORD and CD related to a charge-transfer chromophore with well-defined and rigid donor-acceptor orientations.

As was to be expected on the basis of the different donor-acceptor arrangements, for 1 and 2 strong differences of the charge-transfer absorptions are observed: The absorption spectrum of 1 shows a broad CT band from 400 to 630 nm with λ_{max} = 490 nm (ε 590, in chloroform) whereas the CT absorption of 2 occurs at considerably shorter wavelength beginning at about 550 nm and with λ_{max} = 420 nm (ε 800, in chloroform).

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1) Electron-Donor-Acceptor-Compounds, Part 24. - Part 23: H. A. Staab and A. Döhling, Tetrahedron Lett. (in press).

2) T. Shinmyozu, T. Inazu and T. Yoshino, Chem. Lett. 1978, 1319.

3) W. Rebafka and H. A. Staab, Angew. Chem. Int. Ed. Engl. 12, 776 (1973); 13, 203 (1974); H. A. Staab, C. P. Herz and H.-E. Henke, Tetrahedron Lett. 1974, 4393; H. A. Staab and H. Haffner, ibid. 1974, 4397; H. A. Staab and W. Rebafka, Chem. Ber. 110, 3333 (1977); H. A. Staab and C. P. Herz, Angew. Chem. Int. Ed. Engl. 16, 799 (1977); R. Reimann and H. A. Staab, ibid. 17, 374 (1978); H. A. Staab and V. Schwendemann, ibid. 17, 756 (1978); H. A. Staab, C. P. Herz and A. Döhling, Tetrahedron Lett. 1979, 791; and further references given therein.

4) Elemental analyses, mass spectra and other spectroscopic data agree with the structures given.

5) M. Haenel and H. A. Staab, Tetrahedron Lett. 1970, 3585; H. A. Staab and M. Haenel, Chem. Ber. 106, 2190 (1973).

6) For details see C. Krieger, M. Jörns and H. A. Staab, forthcoming paper.

7) Cf. F. Vögtle, Chem. Ber. 102, 3077 (1969); S. Akabori, S. Hayashi, M. Nawa and K. Shiomi, Tetrahedron Lett. 1969, 3727; D. T. Hefelfinger and D. J. Cram, J. Am. Chem. Soc. 93, 4754 (1971).

(Received in Germany 9 April 1979)