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Syntheses of a Fourfold-Bridged Porphyrin-Quinone Cyclophane and its Zinc Complex[1]

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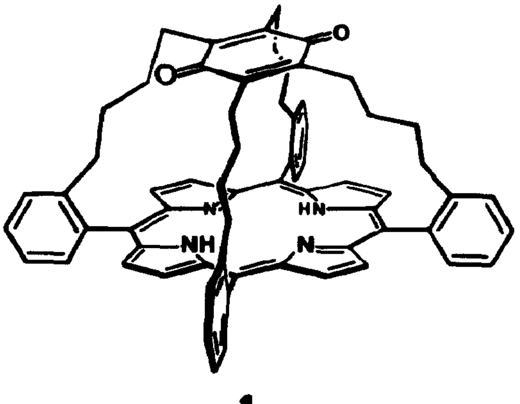
Abstract: Porphyrin-quinone cyclophane **1**, in which a tetraphenylporphyrin is linked to a benzoquinone unit by four tetramethylene chains in a face-to-face orientation, was prepared in a multistep synthesis. The structure of **1** and its zinc complex **10** are discussed based on ^{1}H-NMR and in view of photoinduced electron-transfer reactions.

A series of porphyrin-quinone cyclophanes with gradually varied porphyrin-quinone distances was recently synthesized in order to examine experimentally the distance dependence of the rates of photoinduced electron-transfer reactions[1]. The concept applied made use of aryl substituents in the 5,15-positions of the porphyrin unit acting as spacers into which tetramethylene-quinone-tetramethylene bridges are linked in spatially fixed orientations. The insertation of the same bridges into the 2-positions of phenyl and the 7-positions of 1-naphthyl, 1-biphenylenyl and 1-anthryl groups was expected to result in a parallel shift of the quinone-containing bridges with porphyrin-quinone distances increasing from about 350 pm to the order of 900 pm. Although these systems represent comparatively rigid and well-defined structures, low-temperature ^{1}H-NMR as well as X-ray structure analyses revealed[2] that there are still some conformational interconversions possible making it difficult to relate electron-transfer rates to specific conformations. In order to further reduce this residual flexibility the synthesis of cyclophanes was started in which porphyrin



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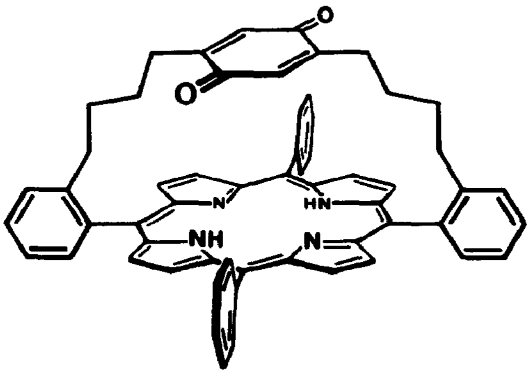

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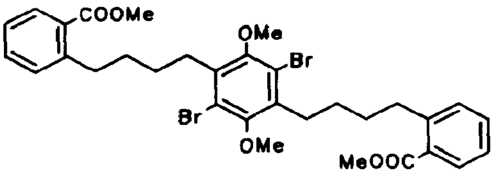
and quinone units are linked by four (instead of two) bridges containing again the sequence of benzene, naphthalene, biphenylene and anthracene spacers. In the present paper we report on the synthesis of the first member of this family, the fourfold benzene-spacered porphyrin-quinone cyclophane **1** which was to be compared with the twofold quinone-bridged tetraphenylporphyrin **2**[2,3].

The synthesis of **1** started from 1,4-dibromo-3,6-dimethoxy-2,5-bis[4-(2-methoxycarbonylphenyl)butyl] benzene (**3**)[3] which in a Heck reaction[4] with acrylic acid yielded **4** (60%)[5]. Reduction of **4**[6] to the corresponding 2,5-bis(3-hydroxypropenyl) compound[5] and immediately following oxidation with barium manganate in dichloromethane yielded the dialdehyde **5** (yield 90%)[5] which in a double Wittig reaction with (2-methoxycarbonylbenzyl)triphenylphosphonium bromide[7] yielded **6** (mixture of *cis-trans* isomers, ca. 90% yield) which without further purification was hydrogenated (Pd/C, ethyl acetate/methanol; yield 95%) to the tetracarboxylic ester **7**[5]. Reduction of **7** with lithium aluminium hydride in THF yielded the corresponding hydroxymethyl compound (95%)[5] which with barium manganate (boiling dichloromethane) was oxidized to the tetraaldehyde 1,2,4,5-tetrakis[4-(2-formylphenyl)butyl]-3,6-dimethoxybenzene (**8**, colourless needles, m. p. 134.5 - 136.5 °C, from ether)[5].



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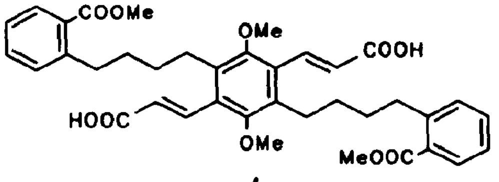

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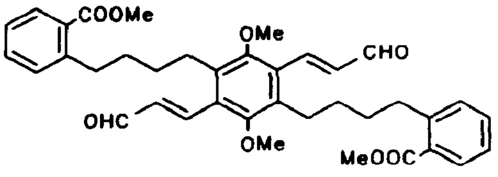

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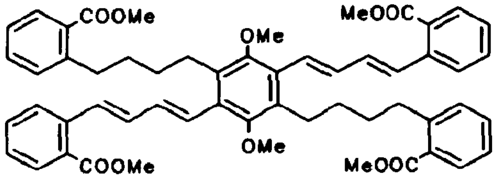

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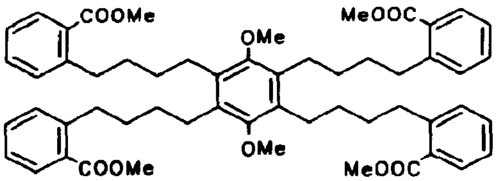

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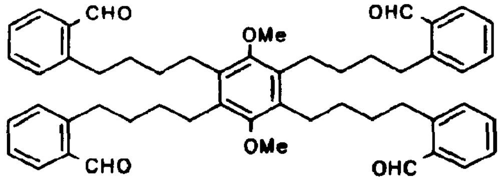

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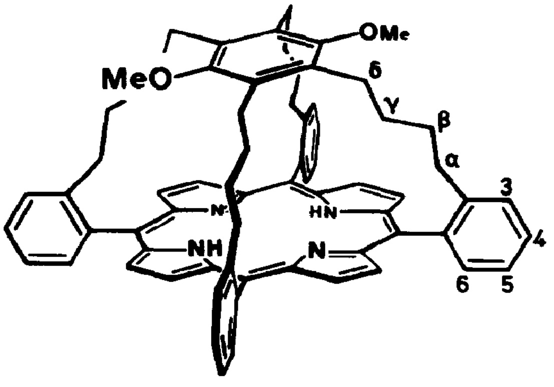
For the synthesis of **1**, the most critical step was the fourfold condensation of the tetraaldehyde **8** with pyrrole to the sterically unfavourable 'cage' compound **9**. By a series of 'trial and error' experiments the following procedure proved eventually successful (although in yields of only 1%): To a diluted solution of **8** (2.0 millimolar) in propionic acid at 100 °C a threefold excess of pyrrole was added in small portions within 1 h. After 2 h heating under reflux the propionic acid was distilled off and the porphyrin fraction was worked up in analogy to lit.[7]. Chromatography (silica gel, toluene, $R_f \approx 0.75$) and further purification of the porphyrin-containing fraction by HPLC (silica gel, cyclohexane/ethyl acetate, 60:1) yielded **9** (red-violet microcrystals, m. p. > 300 °C). The structure **9** was confirmed by high-resolution MS (LSIMS positive, 3-nitrobenzyl alcohol/1% trifluoroacetic acid, 2% PEG 1000: $[MH]^+$ calc. for $C_{68}H_{65}N_4O_2$ 969.5108, found 969.5134) and by ^{1}H-NMR [δ = -2.81 (s, 2H, NH), -0.15 to -0.17 (m, 4H, δ_1-H), 0.22 - 0.29 (m, 8H, β_1,γ_1-H), 0.51-0.55 (m, 4H, δ_2-H), 0.79 - 0.84 (m, 4H, γ_2-H, 1.06-1.09 (m, 4H, β_2-H), 2.41-2.48 (m, 10H, OCH_3 + α_1-H), 2.58-2.65 (m, 4H, α_2-H), 7.54-7.59 (m, 8H, ar-3,4-H), 7.70 ('t', $J \approx 7.3$ Hz, 4H, ar-5-H), 8.13 ('d', $J \approx$ 7.2 Hz, 4H, ar-6-H), 8.58 (s, 4H, pyr-H), 8.68 (s, 4H, pyr-H); 360 MHz, [1,2-D_2]tetrachloroethane, 352 K].



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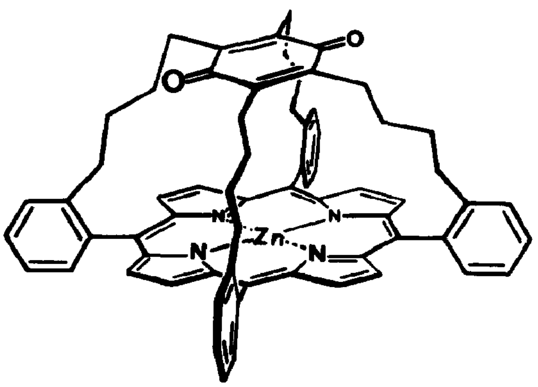

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Cleavage of the methoxy groups of **9** with boron triiodide (dichloromethane, under argon, darkness; 1.5 h at 20 °C; then hydrolysis with satd. aqueous potassium hydrogencarbonate), oxidation of the hydroquinone formed by DDQ (20 min, 20 °C) and working up by chromatography (silica gel, chloroform) produced **1** ($R_f \approx 0.58$; silica gel, cyclohexane/ethylacetate 5:1). MS (LSIMS, as for **9**): $[M]^+$ calcd. for $C_{66}H_{58}N_4O_2$ 938.4560, found 938.4564; ^{1}H-NMR (measurement conditions as for **9**): δ = -2.79 (s, 2H, NH), -0.71 to -0.67 (m, 4H, δ_1-H), - 0.05-0.03 (m, 4H, γ_1-H), 0.34-0.40 (m, 4H, β_1-H), 0.69-0.76 (m, 4H, δ_2-H), 0.81-0.89 (m, 4H, γ_2-H), 0.96-1.05 (m, 4H, β_2-H), 2.46-2.55 (m, 8H, α_1, β_2-H), 7.57-7.62 (m, 8H, ar-3,4-H), 7.73 ('t', $J \approx 7.5$ Hz, 4H, ar-5-H), 8.18 ('d', $J \approx 7.3$ Hz, 4H, ar-6-H), 8.65 (s, 4H, pyr-H), 8.73 (s, 4H, pyr-H).

For the preparation of the zinc complex **10**, the porphyrin-quinone cyclophane **1** was heated to reflux for 1 h in trichloromethane/methanol (5:1) in the presence of excess zinc(II) acetate dihydrate. MPLC (silica gel, cyclohexane/ethyl acetate, 30:1) and filtration from cyclohexane through silica gel yielded **10** as pink-violet powder which was recrystallized from methanol/trichloromethane (3:1) at 4 °C: yield 44% (based on **9**); m. p. > 330 °C; R_f (silica gel, cyclohexane/ethyl acetate) = 0.17. MS (LSIMS): $[M]^+$ calcd. for $C_{66}H_{56}N_4O_2$ Zn 1000.3595, found 1000.3727; ^{1}H-NMR (360 MHz, [1,2-D_2]tetrachloroethane, 403 K): δ = -0.65 to -0.55 (m, 4H, δ_1-H), -0.02-0.03 (m, 4H, γ_1-H), 0.56-0.61 (m, 4H, β_1-H), 0.87-10.3 (m, 12H, δ_2, γ_2, β_2-H), 2.10-2.18 (m, 4H, α_1-H), 2.38-2.47 (m, 4H, α_2-H), 7.58 ('d', $J \approx 7.6$ Hz, 4H, ar-3-H), 7.64 ('t', $J \approx 7.4$ Hz, 4H, ar-4-H), 7.75 ('t', $J \approx 7.6$ Hz, 4H, ar-5-H), 8.32 ('d', $J \approx 7.3$ Hz, 4H, ar-6-H), 8.76 (s, 4H, pyr-H), 8.83 (s, 4H, pyr-H); assignment by comparison with ^{1}H-NMR of **1**.

The absorption wavelengths of **1** (Soret band at 420 nm, Q-bands at 515, 550, 590, and 647 nm) and of **2** (418, 515, 549, 591 and 647 nm, respectively) and their intensities are very similar as the fluorescence wavelengths are (**1**: 650, 717 nm; **2**: 651, 719 nm; excitation in Soret band); the porphyrin chromophore in **1**, thus, is not significantly affected by the fourfold bridging. As low-temperature ^{1}H-NMR measurements showed, for twofold-bridged porphyrin-quinone cyclophanes there are in general three intramolecular dynamic processes[2]: besides the NH/N-tautomerism these are the rotation of the quinone rings around the axis through the bridgeheads, and the interconversion of two unsymmetrical conformations by the so-called 'swinging bridge' process. For **1**, the NH/N-tautomerism, of course, should not essentially be affected, the quinone-ring rotation, on the other hand, is impossible, and for the 'swinging-bridge' process in accordance with molecular dynamic calculations there is left only limited scope due to the stronger rigidity of the fourfold bridging. Preliminary results of low-temperature ^{1}H-NMR show indeed splittings of β-pyrrole- and NH-signals at $T_C = 240$ and 252 K, respectively, the Δν-values of which lead to a barrier $\Delta G_{T_C} \approx 11.5$ kcal/mol similar to those found for the NH/N-tautomerization of more simple porphyrin-quinone cyclophanes. Surprisingly, already at room temperature exclusively for the methylene signals of the four tetramethylene chains a broadening is observed which may be due to hindered torsional libration modes of the closely adjacent methylene groups. Further temperature-dependent ^{1}H-NMR measurements are in progress as are conformational studies of the zinc complex **10**. For the twofold-bridged zinc porphyrin-quinone cyclophanes a coordinative interaction between quinone oxygen and zinc has been derived from the strong inclination of the quinone to the porphyrin plane and the short O···Zn distance of 253 pm[8]. This specific quinone-zinc interaction may open up an alternative electron-transfer pathway from porphyrin to quinone, thus explaining the very fast and solvent-independent electron-transfer rates[9]. This assumptions can now be checked by fluorescence-lifetimes measurements on **10** where a similar approach of quinone oxygen to zinc seems impossible due to the steric situation of the fourfold-bridged cyclophane.

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