

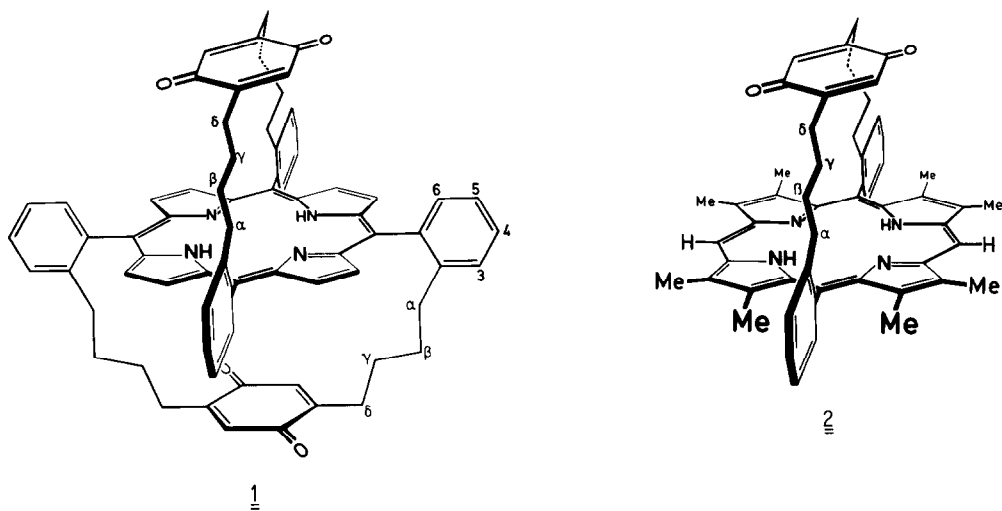
## A NEW BENZOQUINONE-BRIDGED PORPHYRIN

Jürgen Weiser and Heinz A. Staab\*

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

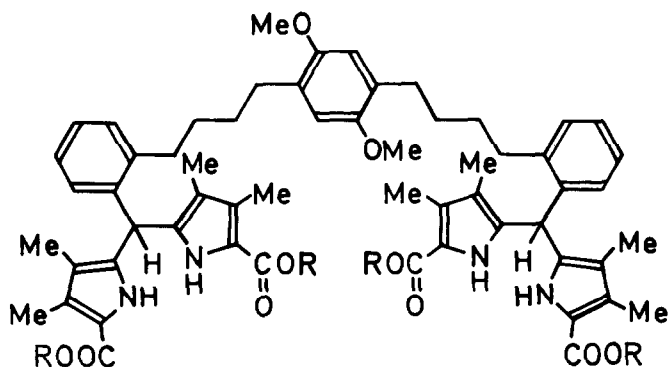
**Summary:** The bridged porphyrin 6 was prepared via the bis(dipyrrylmethane) compounds 3, 4 and 5; by demethylation of 6 and oxidation the benzoquinone/porphyrin system 2 was obtained. The strong fluorescence quenching of 2, as compared to 6, is explained on the basis of an electron-transfer from porphyrin to quinone in the  $S_1$  state.

In connection with the biochemical importance of electron-transfer reactions between porphyrins and *para*-benzoquinones <sup>1)</sup> the doubly benzoquinone-bridged porphyrin 1 was synthesized <sup>2)</sup>, and its molecular structure and fluorescence behaviour were determined recently <sup>3)</sup>. As compared to other porphyrin-quinone model systems described lately <sup>4)</sup>, 1 is the first model with a precisely defined sterical arrangement of porphyrin and benzoquinone moieties in parallel and exactly centered position. To supplement the results on 1 where the porphyrin is shielded from both sides by benzoquinone units, the single-bridged analogue 2 was of interest for which, due to the same carbocyclic structure of the quinone bridge, a corresponding mutual arrangement of porphyrin and benzoquinone rings was to be expected.



For the synthesis of 2, from 2,2'-[2,5-dimethoxy-1,4-phenylene-bis(tetramethylene)]-dibenzaldehyde <sup>2)</sup> the bis(dipyrrylmethane) system 3 <sup>6)</sup> was obtained in 78% yield by conden=

sation with 2-ethoxycarbonyl-3,4-dimethylpyrrole <sup>5)</sup> (ethanol, conc. hydrochloric acid, 1 h, reflux) after chromatography (silica, toluene/ethyl acetate, 10:1). Transesterification with benzylalcohol (sodium, 4 h reflux at 15 Torr) yielded the corresponding benzyl ester 4 <sup>6)</sup> (82%) from which by catalytic hydrogenation (Pd/C, tetrahydrofuran, 20°C) tetracarboxylic acid 5 <sup>6)</sup> (m. p. 140°C, dec.; 91%) was obtained.

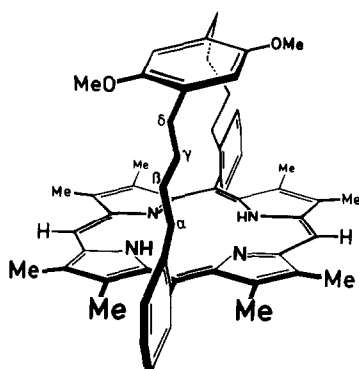


3: R = Et

4: R = Bz

5: R = H

Decarboxylation and ring-closing condensation <sup>7)</sup> of 5 was achieved with trichloroacetic acid and triethoxymethane in dichloromethane (14 h, 20°C, exclusion of light). The 'capped porphyrin' 6 <sup>6)</sup> was separated from oligomers and decomposition products by chromatography (silica, toluene/ethyl acetate, 15:1) and crystallisation from dichloromethane/methanol and methylcyclohexane: violet needles, m. p. 319 - 320°C (11% yield). The mass spectrum supports structure 6 [m/z 820 (M<sup>+</sup>, 100%), 806 (47), 410 (M<sup>++</sup>, 60)]. <sup>1</sup>H-NMR data indicate a sterical arrangement corresponding to that derived for 1 by <sup>1</sup>H NMR and X-ray structure analysis <sup>3)</sup> [ $\delta$  = -2.45 (s, 2H), -0.09 - 0.11 (m, 4H), 0.29 - 0.33 (m, 4H), 0.79 - 0.88 (m, 4H), 1.94 - 1.98 (m, 4H), 2.05 (s, 6H), 2.46 (s, 12H), 3.52 (s, 12H), 4.15 (s, 2H), 7.55 - 7.57 (m, 2H), 7.61 - 7.66 (m, 2H), 7.69 - 7.74 (m, 2H), 8.20 - 8.22 (m, 2H), 10.13 (s, 2H); 360 MHz, in [D<sub>2</sub>]dichloromethane]. As in 1, the decreasing shielding by the porphyrin ring for the bridge-methylene protons is observed when proceeding from  $\delta$ - via  $\gamma$ - and  $\beta$ - to  $\alpha$ -methylene groups. The sharp singlets observed for the two ring-protons as well as for the two methoxy



groups of the central ring suggest a parallel and centered position of this ring with regard to the porphyrin system (or, in any case, conformations close to this arrangement averaging in time for  $^1\text{H}$  NMR).

Demethylation with boron tribromide in dichloromethane (3 h,  $-40^\circ\text{C}$ , exclusion of light) and subsequent oxidation by 1,2-dichloro-4,5-dicyano-*p*-benzoquinone (dichloromethane/methanol, 1:1, 1 h,  $20^\circ\text{C}$ ) yielded, after chromatography (neutral alumina; toluene/ethyl acetate, 10:1), the quinone-bridged porphyrin 2 <sup>6</sup> in 54% yield: violet crystals (from ethyl acetate/methylcyclohexane), m. p.  $> 330^\circ\text{C}$ . The structure suggested is in accordance with the mass spectrum [ $m/z$  790 ( $\text{M}^+$ , 85%), 775 (68), 395 ( $\text{M}^{++}$ , 100), a. o.] and  $^1\text{H}$  NMR data [(360 MHz,  $[\text{D}_2]$ dichloromethane)  $\delta = -2.41$  (s, 2H; NH),  $-0.05 - 0.08$  (m, 4H;  $\delta\text{-CH}_2$ ),  $0.17 - 0.20$  (m, 4H;  $\gamma\text{-CH}_2$ ),  $0.86 - 0.91$  (m, 4H;  $\beta\text{-CH}_2$ ),  $1.96 - 2.01$  (m, 4H;  $\alpha\text{-CH}_2$ ),  $2.47$  (s, 12H; pyrrole-Me),  $3.56$  (s, 12H; pyrrole-Me),  $4.06$  (s, 2H; quinone-H),  $7.54 - 7.57$  (m, 2H; arom. H),  $7.61 - 7.65$  (m, 2H; arom. H),  $7.70 - 7.74$  (m, 2H; arom. H),  $8.16 - 8.18$  (m, 2H; arom. H),  $10.21$  (s, 2H; meso-H)].

Fluorescence measurements ( $1 \cdot 10^{-6}$  molar solutions in degassed toluene, excitation at 410 nm) show for 6 typical porphyrin emission maxima at 637 and 703 nm; for 2, however, a nearly complete quenching of the fluorescence of the porphyrin chromophore is observed (Fig=

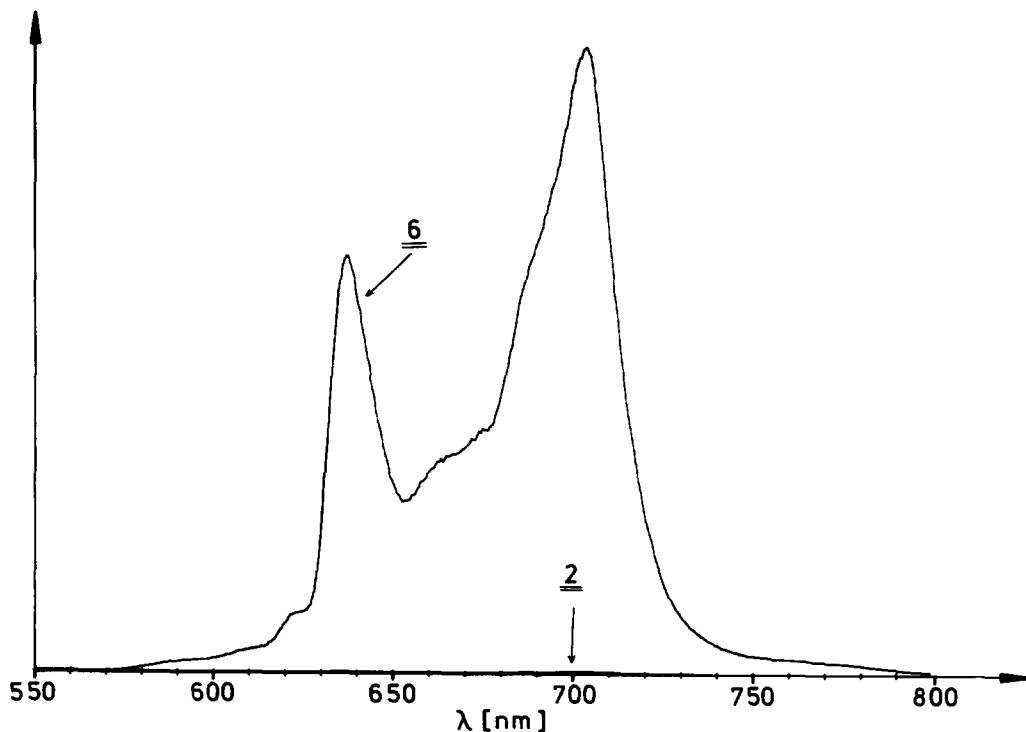


Figure. Fluorescence Spectra of 2 in Comparison with 6 ( $1 \cdot 10^{-6}$  Molar Solutions in Degassed Toluene; Excitation at 410 nm)

ure). By comparing the integrated fluorescence intensities of 2 and 6 the fluorescence quenching of 2 is approximately estimated to > 99.5% in relation to 6. This result indicates in the S<sub>1</sub> state an efficient intramolecular electron-transfer from the porphyrin to the quinone.

- 
- 1) See, e.g., J. J. Katz, J. R. Norris, L. L. Shipman, M. C. Thurnauer and M. R. Wasielewski, Annu. Rev. Biophys. Bioeng. 7, 393 (1978); L. V. Natarajan and R. E. Blankenship, Photochem. Photobiol. 37, 329 (1983); L. V. Natarajan, J. E. Rieker, R. E. Blankenship and R. Chang, Photochem. Photobiol. 39, 301 (1984).
  - 2) J. Weiser and H. A. Staab, Angew. Chem. 96, 602 (1984); Angew. Chem. Int. Ed. Engl. 23, 623 (1984).
  - 3) C. Krieger, J. Weiser and H. A. Staab, Tetrahedron Lett., in press (preceding paper).
  - 4) For references see l.c. <sup>2)</sup> (footnote 1); M. R. Wasielewski and M. P. Niemczyk, J. Am. Chem. Soc. 106, 5043 (1984); A. D. Joran, B. A. Leland, G. G. Geller, J. J. Hopfield and P. B. Dervan, ibid. 106, 6090 (1984); J. R. Bolton, Te-Fu Ho, S. Liauw, A. Siemiarczuk, C. S. K. Wan, and A. C. Weedon, J. Chem. Soc. Chem. Commun. 1985, 559.
  - 5) G. G. Kleinspehn, J. Am. Chem. Soc. 77, 1546 (1955).
  - 6) For these compounds correct elemental analyses and spectroscopic data are in accordance with the structures suggested.
  - 7) Cf. A. H. Jackson, G. W. Kenner and J. Wass, J. Chem. Soc. Perkin Trans 1 1972, 1475; J. E. Baldwin, T. Klose and M. Peters, J. Chem. Soc. Chem. Commun. 1976, 881.

(Received in Germany 20 September 1985)