Photoinduced Electron Transfer in Porphyrin-Quinone Cyclophanes, 10[1]

Zinc Complexes of Porphyrin-Quinone Cyclophanes: Syntheses, Structures and Electron-Transfer-Related Properties

Heinz A. Staab*, Claus Krieger, Christine Anders, and Andreas Rückemann

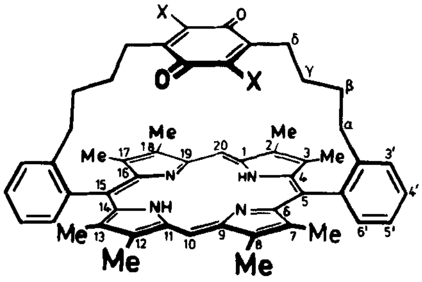
Abteilung Organische Chemie, Max-Planck-Institut für medizinische Forschung,
Jahnstraße 29, D-69120 Heidelberg, F.R.G.

Received August 30, 1993

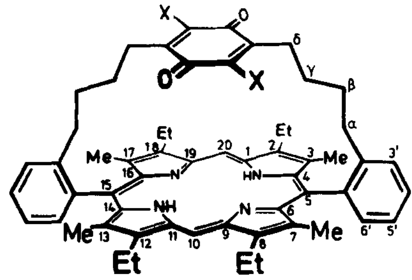
Key Words: Zinc porphyrin complexes / Porphyrin-quinone cyclophanes / Photoinduced electron transfer / Electron-transfer mechanism in metalloporphyrin-quinone cyclophanes

In order to increase the driving force for photoinduced electron-transfer reactions of porphyrin-quinone cyclophanes, the zinc complexes **3a**–**e** and **4a**–**e** were prepared from the corresponding cyclophanes of the **1** and **2** series. Electron-transfer-related properties like redox potentials and fluorescence spectra were determined for **3a**–**e** and **4a**–**e**. The X-ray structure analysis of **4a** indicates that for the very fast and solvent-independent electron transfer in these systems a specific mechanism involving an interaction of a quinone carbonyl group with the zinc might be considered as an alternative to through-space electron-transfer.

In preceding papers syntheses[2], structures, and conformational flexibilities[3] as well as photoinduced electron-transfer reactions[4,5] of porphyrin-quinone cyclophanes were described. For the quinone-bridged porphyrin systems **1** and **2** the driving force for intramolecular electron transfer was modified by changing gradually the electron affinities of the quinones by electron-donating and electron-withdrawing substituents while keeping unchanged the distance and the mutual orientation of the porphyrin and quinone units. This concept was realized by the cyclophane series **1a**–**d** and **2a**–**d** with the substituent sequence X = Me, MeO, H, and Cl[2] which recently was complemented by corresponding porphyrin-quinone cyclophanes with X = Br (**1e**)[1] and X = CF_3 (**2e**)[6].



1	X
a	Me
b	OMe
c	H
d	Cl
e	Br



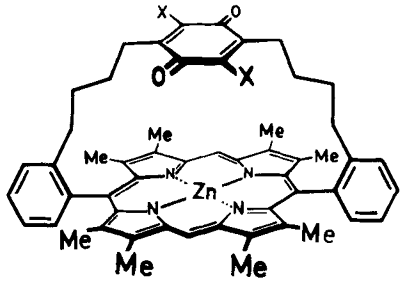
2	X
a	Me
b	OMe
c	H
d	Cl
e	CF_3

Since the driving forces $\Delta G'_{cs}$ of the photoinduced charge separation in these systems depends on the difference between the first oxidation potential E^1_{ox} of the porphyrin and the first reduction potential E^1_{red} of the quinone units, it was of interest to further expand the range of $\Delta G'_{cs}$ by increasing now the donor strength of the porphyrin part by including suitable metalloporphyrins into this study. As a first step in this direction, for comparison with the porphyrin-quinone cyclophanes **1a**–**e** and **2a**–**e**, the two series of the corresponding zinc complexes **3a**–**e** and **4a**–**e** were of interest. Of metalloporphyrin-quinone cyclophanes so far only **3a** and **3c** as well as the magnesium analogue of **3c** had been obtained[2]. Besides the preparation and characterization of the two sets of zinc porphyrin cyclophanes mentioned, electron-transfer reactions of these compounds were to be studied with reference to redox potentials and based on fluorescence spectra.

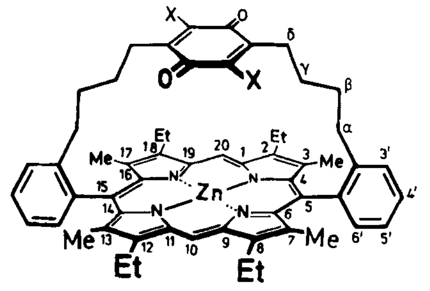
By ^{1}H-NMR spectra and possibly by X-ray structure analysis the question was to be answered whether these metalloporphyrin-quinone cyclophanes are analogous with regard to structure and conformation to the non-metallated parent compounds of the series **1** and **2** and, thus, represent indeed an appropriate extension of this series to systems with increased electron-transfer driving force.

Preparation and Characterization of Zinc Porphyrin-Quinone Cyclophanes

For zinc complexation the respective metal-free porphyrin-quinone cyclophanes were heated with excess zinc acetate dihydrate in trichloromethane/methanol or in dichloromethane/methanol. The zinc complexes were purified by MPLC on silica gel with cyclohexane/ethyl acetate and crystallized from trichloromethane/methanol (for details see Ex-



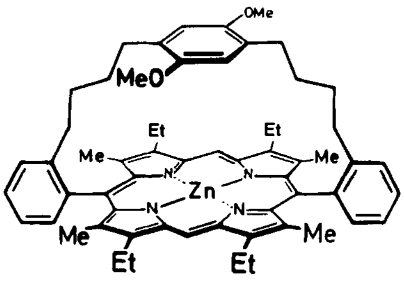
3	X
a	Me
b	OMe
c	H
d	Cl
e	Br



4	X
a	Me
b	OMe
c	H
d	Cl
e	CF_3

perimental). **3a**–**e** and **4a**–**e** form dark red to violet crystals with melting points between 265°C and 350°C, respectively. The characterization of all zinc complexes was made by mass spectrometry including high-resolution MS and by ^{1}H-NMR spectra. The latter (500 MHz, CD_2Cl_2, 303 K; assignment by COSY) show signal patterns similar to those of the corresponding non-metallated parent compounds. Only rather small differences of chemical shifts are observed for the central parts of the quinone bridges and for 10,20-H of the porphyrin rings; they can be attributed to the different shielding effect of zinc porphyrins as compared to porphyrins themselves. Thus, from ^{1}H-NMR spectra no reliable indication can be derived for different conformational arrangements of the zinc complexes in comparison with the corresponding parent compounds. ^{1}H-NMR measurements at low temperatures as reported in ref.[3], however, are not yet available; they are of special interest in view of the recent results of the X-ray structure analysis of **4a** (see below).

For comparison with the quinone systems **3** and **4** the non-quinoid zinc porphyrin cyclophane **5** was prepared in analogy to the syntheses of **3** and **4** (for the corresponding compound of the octamethylporphyrin series see ref.[2]).



5

Physical Properties Related to Photoinduced Electron Transfer

Oxidation and Reduction Potentials of Zinc Porphyrin-Quinone Cyclophanes

The redox potentials of **3a**–**d** and **4a**–**e** were measured by cyclovoltammetry under the same conditions as those of the corresponding porphyrin-quinone cyclophanes of type **1** and **2**[5] (dichloromethane, "glassy carbon electrode" vs. Ag/AgCl). The potentials referred to ferrocene E (Fc/Fc$^+$) are listed in Table 1.

Table 1. Redox potentials in V (±0.01) of zinc porphyrin-quinone cyclophanes [in dichloromethane, potentials quoted with reference to ferrocene E (Fc/Fc$^+$ ≡ 0.0 V); for details see Experimental]

	E^2_{ox} (P^+/P^{2+})	E^1_{ox} (P/P^+)	E^1_{red} (Q/Q^-)	E^2_{red} (Q^-/Q^{2-})
3a	+0.39	+0.16	−1.17	−1.79
3b	+0.39	+0.14	−1.05	(ca. −2.01, 2e)
3c	+0.40	+0.14	−0.93	−1.58
3d	+0.36	+0.17	−0.72	−1.43
4a	+0.40	+0.17	−1.17	−1.99
4b	+0.40	+0.16	−1.04	−1.85
4c	+0.41	+0.16	−0.93	−1.75
4d	+0.36	+0.17	−0.73	−1.49
4e	+0.35	+0.16	−0.70	−1.49

As expected, the zinc porphyrin subunits in **3a**–**d** and **4a**–**e** with $E^1_{ox}(P/P^+) = +0.14$ to $+0.17$ V are considerably stronger electron donors than the zinc-free porphyrins of the compounds **1a**–**d** and **2a**–**d** [$E^1_{ox}(P/P^+) = +0.33$ to $+0.36$ V]. Obviously, the first oxidation potentials of the zinc porphyrin-quinone cyclophanes are not significantly influenced by the neighboring quinone units since for the non-quinoid zinc porphyrin cyclophane **5** under the same conditions $E^1_{ox}(P/P^+) = +0.15$ V was obtained. The first reduction potentials E^1_{red} of the quinone units in the series **3** and **4** show very similar graduations as found for the corresponding porphyrin-quinone cyclophanes of the series **1** and **2**; the E^1_{red} values, however, are less negative by 260 to 320 mV. This effect had been observed already for **3a** and **3c**[5] and was ascribed to specific transannular interactions between the semiquinone radical anion and the zinc cation. The structure analysis of **4a** (see below) now supports an explanation along this line.

Based on the potentials E^1_{ox} and E^1_{red}, the driving force $\Delta G'_{cs}$ of the photoinduced electron transfer can roughly be approximated by the equation $\Delta G'_{cs} = (E^1_{ox} - E^1_{red}) - E_{00}$ where E_{00} is the $S_0 \rightarrow S_1$ excitation energy amounting to 2.14 eV for the zinc porphyrin chromophores present in the series **3** and **4**. Within the porphyrin-quinone cyclophane series these approximated $\Delta G'_{cs}$ values as a relative measure for comparing electron-transfer processes might be especially justified: the ignoring of Coulomb energy terms and any other electronic interactions for the process of charge separation seems less serious here due to the corresponding sterical situation which in these series of compounds is enforced by the cyclophane structure common for all these systems.

Table 2. Approximated $\Delta G'_{cs}$ values for photoinduced electron transfer in porphyrin-quinone cyclophanes

$\Delta G'_{cs}$ [5]	$\Delta G'_{cs}$ [5]	$\Delta G'_{cs}$	$\Delta G'_{cs}$
1a: −0.15	**2a**: −0.15	**3a**: −0.80	**4a**: −0.80
1b: −0.31	**2b**: −0.29	**3b**: −0.94	**4b**: −0.94
1c: −0.37	**2c**: −0.35	**3c**: −1.07	**4c**: −1.05
1d: −0.65	**2d**: −0.61	**3d**: −1.25	**4d**: −1.24
	2e: −0.73		**4e**: −1.28

Table 2 shows that by inclusion of the zinc porphyrin-quinone cyclophanes a considerable extension of $\Delta G'_{cs}$ in the direction of increased driving forces for charge separation was achieved. From −0.15 up to −1.28 V one of the widest ranges of $\Delta G'_{cs}$ within a series of structurally closely related compounds was obtained. This result is of interest with regard to the experimental test of certain theoretical predictions on electron-transfer reactions, provided the electron transfer in the whole group of porphyrin-quinone cyclophanes follows a common mechanism (the latter reservation gained special significance by the structure analysis of **4a** which is reported below).

Absorption and Emission Spectra; Fluorescence Lifetimes

For all zinc porphyrin-quinone cyclophanes **3a**–**e** and **4a**–**e** the wavelengths of absorption maxima are nearly identical for the Soret as well as for the Q bands (range of λ_{max}: 411–415, 537–542, and 573–576 nm, in dichloromethane). As the corresponding data for toluene solutions show (λ_{max} = 412–417, 539–544, and 574–578 nm, respectively) the solvent dependence is negligible. For the non-quinoid porphyrin cyclophane **5** [λ_{max} = 415, 542, and 577 nm (dichloromethane); 416, 543, and 577 nm (toluene)], for the corresponding zinc octamethylporphyrin cyclophane[2,5] and even for the simple 2,3,7,8,12,13,17,18-octamethyl-5,15-diphenylporphyrin zinc[2,5] almost congruent absorption data were observed. These results demonstrate that for this whole set of compounds the zinc porphyrin chromophore is not perceivably disturbed – neigter by the incorporation of this chromophore into the cyclophane skeleton nor even by transanular donor-acceptor interactions with the quinone units.

On excitation in the Soret bands all zinc porphyrin cyclophanes including the nonquinoid reference compound **5** show two fluorescence bands in the rather narrow ranges of λ = 579–585 and 632–640 nm (in toluene) and 572–585 and 626–639 nm (in dichloromethane), respectively. The relative quantum yield of fluorescence as referred to **5**, however, is drastically reduced for all zinc porphyrin-quinone cyclophanes to the order of 10^{-3}. Small differences in the fluorescence quenching which are observed within the two series **3a**–**d** and **4a**–**e** show a common trend to reduced quenching for the compounds with the strongest acceptors; due to the margins of error of these measurements of rather weak fluorescence intensities it seems, however, unjustified to try to interpret these differences in terms of electron-transfer rates. So far, fluorescence lifetime data by time-resolved laser spectroscopy are available only for **3d**, the zinc porphyrin-quinone cyclophane with the strongest electron acceptor in this series. For this compound a monoexponential fluorescence decay (99%) with lifetimes shorter than 1 ps was found, not depending on the polarities and dielectric relaxation properties of the solvents; the measurements were made in *n*-hexane, toluene, dichloromethane, acetonitrile, *n*-butanol, *n*-octanol, and in glycerol triacetate (at 300 and 210 K)[7].

X-ray Structure Analysis of 4a

The molecular structure of **4a**, at first glance, looks similar to those of the quinone-bridged, yet metal-free porphyrin cyclophane **2b** and two other single-bridged porphyrin cyclophanes the structures of which were reported recently[3]: The quinone ring is neither parallel nor centered with regard to the porphyrin system. Yet, the inclination between the two ring planes in **4a** with 40° is found considerably larger than for **2b** (26°), as the side-view in Figure 1(A) shows. The vertical distance from the quinone center to the porphyrin plane is 427 pm (**2b**: 448 pm), the center-to-center distance between the quinone and porphyrin units amounts to 461 pm (**2b**: 474 pm). The most remarkable feature of the structure of **4a**, however, manifests itself in the orientation and distance of the nearest quinone carbonyl group to the porphyrin: whereas in **2b** the distance between the oxygen of this group (O39′) to the porphyrin

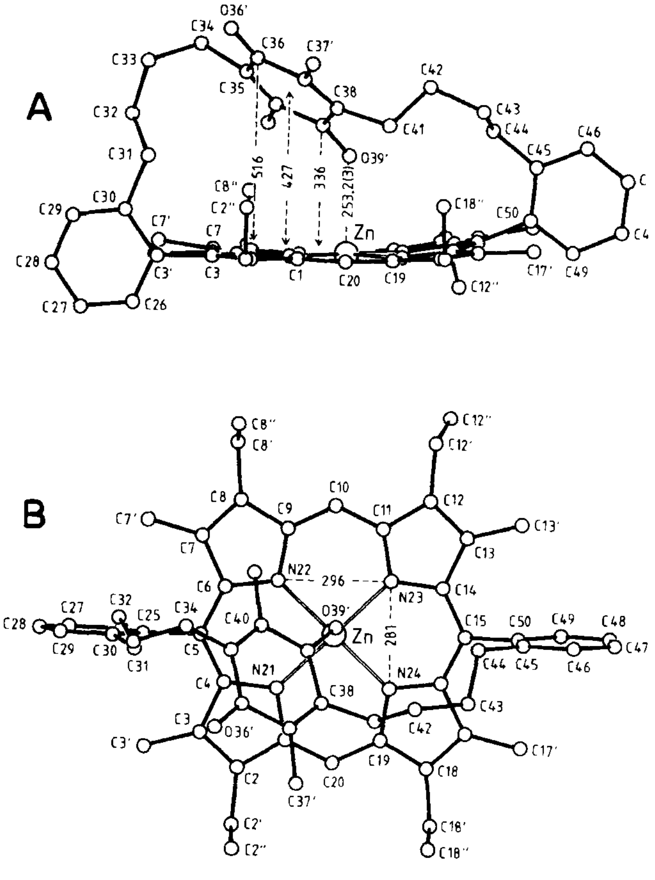


Figure 1. Molecular structure of **4a** in a side view along the C10···C20 axis (A) and in a top view onto the mean plane of the porphyrin (B)

is 429 pm, the corresponding distance in **4a** is only 257 pm. Actually O39′ is placed exactly above the zinc, as the top-view in Figure 1(B) shows. That the close O···Zn distance of 253.2(2) pm is an indication for an attractive coordination is supported by the fact that the oxygen deviates for 6° from the quinone plane in the direction to Zn, and the Zn atom itself deviates for 4 pm toward the oxygen out of the mean plane through the four nitrogen atoms of the porphyrin.

With the exception of this very specific zinc-oxygen connection, the molecular structure of **4a** is in analogy to those of the other porphyrin cyclophanes: The two tetramethylene chains with regard to the torsional angles with the exception of C31−C32−C33−C34 [89.4(5)°] and C41−C42−C43−C44 [87.4(5)°] correspond to energetically favourable conformations; the pyrrole rings are nearly planar the maximal deviation from the mean planes being only 2 pm; the C−C−C angles at the unsubstituted methine carbons C10 and C20 are widened to 129.6(4)°, the planes of the phenyl substituents on C5 and C15 are, as a result of the four methyl groups at C3,7,13,17, kept in a nearly orthogonal position to the planes formed by the bonds at C5 and C15.

An obvious result of the Zn complexation is that the distance of the two sets of N···N pairs in the nitrogen rectangle of the porphyrin differ less than in metal-free porphyrins (**4a**: N21···N22: 281, N22···N23: 296 pm; **2b**: N21···N22: 271, N22···N23: 314 pm). As found for **2b**, too, three of the four ethyl groups are turned to the "inside" which is certainly due to the packing of the molecules in the crystal; the packing of **4a**-molecules in the crystal again is very similar to that of **2b**[3].

Conclusion

Within the family of porphyrin-quinone cyclophanes the preparation of the zinc complexes **3a**−**e** and **4a**−**e**, due to increased donor strength of the zinc porphyrins extend the range of the driving force for photoinduced electron transfer considerably. The molecular structure as determined for the zinc porphyrin-quinone cyclophane **4a** leaves some doubts, however, as to whether the same mechanisms for an electron transfer can be assumed for the two groups of zinc-complexes and metal-free porphyrin-quinone cyclophanes. For the latter essentially a "through-space" mechanism can be expected. On the other hand, for the zinc porphyrin-quinone cyclophanes the observed interaction and the relatively short distance between the quinone carbonyl group and the zinc of the porphyrin unit suggests that for these compounds an alternative pathway for the electron transfer might be possible. Of course, this argument so far is based on evidence from a crystal structure. Nevertheless, it seems very likely that conformations with direct quinone-zinc coordination should also be preferred in solution, unless such an interaction is blocked by structural and sterical factors. Porphyrin-quinone cyclophanes which meet this requirement have recently been synthesized and will be published as soon as electron-transfer data are available.

Experimental

Melting points: Büchi SMP20 and 512, Bock Monoskop M. − UV/Vis: Varian Cary 2300; 10^{-5} M solutions in dichloromethane and toluene. − Fluorescence spectra: Fluorolog F112 XE (Spex, Grassbrunn); 10^{-5} M solution in dichloromethane and toluene. − MS: FAB spectra (LSI-MS: Liquid Secondary Ion MS, positive; 3-nitrobenzylic alcohol, 1% trifluoroacetic acid); HR-MS (LSI-MS, 3-nitrobenzylic alcohol, 2% polyethyleneglycol 1000, 1% trifluoroacetic acid); VG Analytical ZAB 2E/70SE. − ^{1}H-NMR: Bruker Physik HX-360, AM 500 (internal reference tetramethylsilane). − Cyclic voltammetry: Potentiostat PAR 362 (EG & G Princeton Applied Research); "glassy carbon electrode", reference electrode Ag/AgCl (3.5 M KCl/water); 0.2 M solution of tetrabutylammonium perchlorate (puriss., Fa. Fluka) in dichloromethane (washed with conc. sulfuric acid, dried with calcium hydride, fractional distillation under argon); concentration of measured compounds 10^{-3}−10^{-4} M; voltage increase rate 200 $\mathrm{mVs^{-1}}$; all measurements at 20°C; reference ferrocene [$E_{ox}(Fc/Fc^+) = +0.54 \pm 0.01$ V].

Preparation of Zinc Porphyrin-Quinone Cyclophanes **3** *and* **4**: The following is a general procedure for which specific conditions, amounts, yields, characterization data etc. are given for the individual compounds below: The corresponding porphyrin-quinone cyclophanes of series **1** and **2**[2] in 50 or 60 ml of trichloromethane/methanol (5:1 or 4:1) were heated with excess of zinc acetate dihydrate to reflux for 1.5 h. The reaction mixture then was washed with 50 ml of water, 50 ml of saturated ammonium chloride solution and again with 50 ml of water (procedure 1), or with 50 ml of saturated sodium carbonate solution and then twice with 50 ml each of water (procedure 2). After drying over magnesium sulfate the solvent was distilled off on a rotatory evaporator and the remaining red oil was purified by MPLC (d = 3.7 cm, h = 48 cm; silica gel 60, 20−45 μm; flow rate 40 ml/min) from cyclohexane/ethyl acetate. The product was dissolved in a small quantity of trichloromethane (**4e**: in dichloromethane) and, after adding the threefold volume of methanol, crystallized at 4°C.

5,15-[3,6-Dimethoxy-p-benzoquinone-1,4-diylbis(4,1-butanediyl-2,1-benzeno)]-2,3,7,8,12,13,17,18-octamethylporphyrin Zinc (**3b**): 16 mg (18 μmol) of **1b**[2], 50 ml of trichloromethane/methanol (5:1), 400 mg (1.82 mmol) of zinc acetate dihydrate, procedure 1; R_f = 0.35 (silica gel, cyclohexane/ethyl acetate, 30:1): 16.0 mg (97%) of **3b**, violet crystals, m.p. 321°C. − ^{1}H-NMR (500 MHz, CD_2Cl_2, assignment by COSY): δ = −0.11 ("t", J ≈ 7.1, 4H, δ-CH_2), 0.39−0.41 (m, 4H, γ-CH_2), 0.94−0.98 (m, 4H, β-CH_2), 1.77 (s, 6H, OCH_3), 1.91 (t, J = 8.2 Hz, 4H, α-CH_2), 2.43 (s, 12H, 3,7,13,17-CH_3), 3.47 (s, 12H, 2,8,12,18-CH_3), 7.54 ("d", J ≈ 8.2 Hz, 2H, ar-3′-H), 7.59−7.62 (m, 2H, ar-5′-H), 7.69−7.73 (m, 2H, ar-4′-H), 8.18−8.20 (m, 2H, ar-6′-H), 10.09 (s, 2H, 10,20-H). − MS (LSI-MS): m/z (%) = 917 (66), 916 (75), 915 (100), 914 (90), 913 (91) [MH^+]. − $C_{56}H_{57}N_4O_4Zn$: calcd. 913.3671, found 913.3644 (MS: MH^+).

5,15-[3,6-Dichloro-p-benzoquinone-1,4-diylbis(4,1-butanediyl-2,1-benzeno)]-2,3,7,12,13,17,18-octamethylporphyrin Zinc (**3d**): 18 mg (21 μmol) of **1d**, 50 ml of trichloromethane/methanol (5:1), 250 mg (1.14 mmol) of zinc acetate dihydrate, procedure 2; R_f = 0.31 (silica gel, cyclohexane/ethyl acetate, 20:1): 17.0 mg (88%) of **3d**, violet crystals, m.p. >330°C. − ^{1}H-NMR (500 MHz, CD_2Cl_2, assignment by COSY): δ = 0.17−0.25 (m, 4H, γ-CH_2), 0.49−0.56 (m, 4H, δ-CH_2), 0.86−0.95 (m, 4H, β-CH_2), 1.86−1.93 (m, 4H, α-CH_2), 2.42 (s, 12H, 3,7,13,17-CH_3), 3.50 (s, 12H, 2,8,12,18-CH_3), 7.54 ("d", J ≈ 7.8 Hz, 2H, ar-3′-H), 7.63 ("dt", J ≈ 1.3 and 7.4 Hz, 2H, ar-5′-H), 7.72 ("dt", J ≈ 1.3 and 7.4 Hz, 2H, ar-4′-H), 8.20 (dd, J = 7.30 Hz, J ≈ 1.1 Hz, 2H, ar-6′-H), 10.14 (s, 2H, 10,20-H). – MS (LSI-MS): *m/z* (%) = 928 (43), 927 (65), 926 (77), 925 (100), 924 (79), 923 (94), 922 (44), 921 (42) [MH$^+$], 920 (8) [M$^+$]. – $C_{54}H_{53}Cl_2N_4O_2Zn$: calcd. 923.2837, found 923.2885 [MS: (M + 3H)$^+$].

5,15-[3,6-Dibromo-p-benzoquinone-1,4-diylbis(4,1-butanediyl-2,1-benzeno)]-2,3,7,8,12,13,17,18-octamethylporphyrin Zinc (**3e**)[8]: 17 mg (17.9 μmol) of **1e**[1], 50 ml of trichloromethane/methanol (5:1), 250 mg (1.14 mmol) of zinc acetate dihydrate, procedure 2; R_f = 0.82 (silica gel, toluene/ethyl acetate, 30:1); crystallized from dichloromethane/methanol; 16.6 mg (92%) of **3e**. – ^{1}H-NMR (500 MHz, CD_2Cl_2, assignment by COSY): δ = 0.24–0.31 (m, 8H, δ- and γ-CH_2), 0.87–0.93 (m, 4H, β-CH_2), 1.94–1.96 (m, 4H, α-CH_2), 2.40 (s, 12H, 3,7,13,17-CH_3), 3.48 (s, 12H, 2,8,12,18-CH_3), 7.54 ("d", *J* ≈ 7.7 Hz, 2H, ar-3'-H), 7.63 ("dt", *J* ≈ 1.2 and 7.4 Hz, 2H, ar-5'-H), 7.72 ("dt", *J* ≈ 1.3 and 7.1 Hz, 2H, ar-4'-H), 8.17 (dt, *J* = 1.0 and 7.1 Hz, 2H, ar-6'-H), 10.11 (s, 2H, 10,20-H). – MS (LSI-MS): *m/z* (%) = 1015 (52), 1014 (73), 1013 (80) [MH$^+$], 1012 (100) [M$^+$]. – $C_{54}H_{50}Br_2N_4O_2Zn$: calcd. 1012.21, found 1012.30 [MS: M$^+$].

5,15-[3,6-Dimethyl-p-benzoquinone-1,4-diylbis(4,1-butanediyl-2,1-benzeno)]-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin Zinc (**4a**): 18 mg (20 μmol) of **2a**[2], 50 ml of trichloromethane/methanol (5:1), 400 mg (1.83 mmol) of zinc acetate dihydrate, procedure 1; R_f = 0.40 (silica gel, cyclohexane/ethyl acetate, 30:1): 17.5 mg (93%) of **4a**, red-violet crystals (from trichloromethane/methanol), m.p. 303°C. – ^{1}H-NMR (500 MHz, CD_2Cl_2, assignment by COSY): δ = 0.00 (s, 6H, quin-CH_3), 0.08–0.11 (m, 4H, δ-CH_2), 0.20–0.26 (m, 4H, γ-CH_2), 0.86–0.92 (m, 4H, β-CH_2), 1.74 (t, *J* = 7.6, 12H, 2,8,12,18-CH_2CH_3), 1.80–1.84 (m, 4H, α-CH_2), 2.45 (s, 12H, 3,7,13,17-CH_3), 4.00 (q, *J* = 7.6 Hz, 8H, 2,8,12,18-CH_2CH_3), 7.54 ("d", *J* ≈ 7.6 Hz, 2H, ar-3'-H), 7.62–7.65 (m, 2H, ar-5'-H), 7.72–7.75 (m, 2H, ar-4'-H), 8.24 ("d", *J* ≈ 7.2 Hz, 2H, ar-6'-H), 10.14 (s, 2H, 10,20-H). – MS (LSI-MS): *m/z* (%) = 941 (64), 940 (69), 939 (94), 938 (91), 937 (100) [MH$^+$]. – X-Ray structure analysis of **4a** see above. – $C_{60}H_{65}N_4O_2Zn$: calcd. 937.4399, found 937.4371 [MS: MH$^+$].

5,15-[3,6-Dimethoxy-p-benzoquinone-1,4-diylbis(4,1-butanediyl-2,1-benzeno)]-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin Zinc (**4b**): 23 mg (25 μmol) of **2b**[2], 60 ml of trichloromethane/methanol (5:1), 500 mg (2.28 mmol) of zinc acetate dihydrate, procedure 1; R_f = 0.30 (silica gel, cyclohexane/ethyl acetate, 30:1): 22.7 mg (91%) of **4b**, violet crystals, m.p. 310°C. – ^{1}H-NMR (500 MHz, CD_2Cl_2, assignment by COSY): δ = −0.08 to −0.05 (m, 4H, δ-CH_2), 0.41–0.45 (m, 4H, γ-CH_2), 0.99–1.05 (m, 4H, β-CH_2), 1.66–1.76 (m, 18H, OCH_3 + 2,8,12,18-CH_2CH_3), 1.85–1.89 (m, 4H, α-CH_2), 2.45 (s, 12H, 3,7,13,17-CH_3), 3.96–4.01 (m, 8H, 2,8,12,18-CH_2CH_3), 7.55 ("d", *J* ≈ 7.4, 2H, ar-3'-H), 7.59–7.62 (m, 2H, ar-5'-H), 7.69–7.73 (m, 2H, ar-4'-H), 8.23 ("d", *J* ≈ 6.9 Hz, 2H, ar-6'-H), 10.10 (s, 2H, 10,20-H). – MS (LSI-MS): *m/z* (%) = 974 (46), 973 (74), 972 (78), 971 (100), 970 (84), 969 (85) [MH$^+$], 968 (11) [M$^+$]. – $C_{60}H_{65}N_4O_4Zn$: calcd. 969.4297, found 969.4338 [MS: MH$^+$].

5,15-[p-Benzoquinone-1,4-diylbis(4,1-butanediyl-2,1-benzeno)]-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin Zinc (**4c**): 26 mg (31 μmol) of **2c**[2], 60 ml of trichloromethane/methanol (5:1), 500 mg (2.28 mmol) of zinc acetate dihydrate, procedure 1; R_f = 0.44 (silica gel, cyclohexane/ethyl acetate, 16:1): 20.7 mg (74%) of **4c**, violet crystals, m.p. 293°C. – ^{1}H-NMR (500 MHz, CD_2Cl_2, assignment by COSY): δ = 0.15–0.22 (m, 4H, γ-CH_2), 0.45–0.51 (m, 4H, δ-CH_2), 1.02–1.10 (m, 4H, β-CH_2), 1.72 (t, *J* = 7.6 Hz, 12H, 2,8,12,18-CH_2CH_3), 2.04–2.08 (m, 4H, α-CH_2), 2.44 (s, 12H, 3,7,13,17-CH_3), 3.68 (s, 2H, quin-H), 3.99 (q, *J* = 7.6 Hz, 8H, 2,8,12,18-CH_2CH_3), 7.57 (dd, *J* = 7.7 and 1.2 Hz, 2H, ar-3'-H), 7.62 (mc, 2H, ar-5'-H), 7.72 (mc, 2H, ar-4'-H), 8.19 (dd, *J* = 7.4 and 1.2 Hz, 2H, ar-6'-H), 10.09 (s, 2H, 10,20-H). – MS (LSI-MS): *m/z* (%) = 914 (53), 913 (68), 912 (89), 911 (100), 910 (86), 909 (72) [MH$^+$], 908 (13) [M$^+$]. – $C_{58}H_{62}N_4O_2Zn$: calcd. 910.4164, found 910.4125 [MS: (M + 2H)$^+$].

5,15-[3,6-Dichloro-p-benzoquinone-1,4-diylbis(4,1-butanediyl-2,1-benzeno)]-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin Zinc (**4d**): 16 mg (17 μmol) of **2d**[2], 50 ml of trichloromethane/methanol (5:1), 250 mg (1.14 mmol) of zinc acetate hydrate, procedure 2; R_f = 0.37 (silica gel, cyclohexane/ethyl acetate, 20:1): 9.0 mg (53%) of **4d**, violet crystals, m.p. 294–296°C. – ^{1}H-NMR (500 MHz, CD_2Cl_2, assignment by COSY): δ = 0.26–0.35 (m, 4H, γ-CH_2), 0.39–0.46 (m, 4H, δ-CH_2), 0.90–0.99 (m, 4H, β-CH_2), 1.76 (t, *J* = 7.7 Hz, 12H, 2,8,12,18-CH_2CH_3), 1.86–1.93 (m, 4H, α-CH_2), 2.45 (s, 12H, 3,7,13,17-CH_3), 3.94–4.08 (m, 8H, 2,8,12,18-CH_2CH_3), 7.55 ("d", *J* ≈ 7.4 Hz, 2H, ar-3'-H), 7.63 ("dt", *J* ≈ 1.3 and 7.4 Hz, 2H, ar-5'-H), 7.73 ("dt", *J* ≈ 1.4 and 7.5 Hz, 2H, ar-4'-H), 8.23 ("d", *J* ≈ 7.1 Hz, 2H, ar-6'-H), 10.16 (s, 2H, 10,20-H). – MS (LSI-MS): *m/z* (%) = 984 (48), 983 (77), 982 (74), 981 (100), 980 (70), 979 (80), 978 (30), 977 (20) [MH$^+$]. – $C_{58}H_{61}Cl_2N_4O_2Zn$: calcd. 979.3463, found 979.3480 [MS: (M + 3H)$^+$].

5,15-[3,6-Bis(trifluoromethyl)-p-benzoquinone-1,4-diylbis(4,1-butanediyl-2,1-benzeno)]-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin Zinc (**4e**): 14 mg (14 μmol) of **2e**[6], 50 ml of dichloromethane/methanol (4:1), 200 mg of (0.91 μmol) of zinc acetate dihydrate, procedure 2; R_f = 0.37 (silica gel, cyclohexane/ethyl acetate, 20:1): 8.0 mg (54%) of **4e**, violet crystals, m.p. 266–269°C. – ^{1}H-NMR (500 MHz, CD_2Cl_2, assignment by COSY): δ = 0.05–0.15 (m, 4H, δ-CH_2), 0.21–0.31 (m, 4H, γ-CH_2), 0.78–0.92 (m, 4H, β-CH_2), 1.76 (t, *J* = 7.6 Hz, 12H, 2,8,12,18-CH_2CH_3), 1.93–2.00 (m, 4H, α-CH_2), 2.43 (s, 12H, 3,7,13,17-CH_3), 3.92–4.07 (m, 8H, 2,8,12,18-CH_2CH_3), 7.55 ("d", *J* ≈ 7.7 Hz, 2H, ar-3'-H), 7.64 ("dt", *J* ≈ 1.4 and 7.4 Hz, 2H, ar-5'-H), 7.72 ("dt", *J* ≈ 1.4 and 7.5 Hz, 2H, ar-4'-H), 8.19 (dd, *J* = 7.6 and 1.3 Hz, 2H, ar-6'-H), 10.15 (s, 2H, 10,20-H). – MS (LSI-MS): *m/z* (%) = 1050 (48), 1049 (76), 1048 (78), 1047 (100), 1046 (63), 1045 (67) [MH$^+$], 1044 (8) [M$^+$]. – $C_{60}H_{60}F_6N_4O_2Zn$: calcd. 1046.3912, found 1046.3890 [MS: (M + 2H)$^+$].

5,15-[2,5-Dimethoxybenzene-1,4-diylbis(4,1-butanediyl-2,1-benzeno)]-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin Zinc (**5**): 27 mg (31 μmol) of 5,15-[2,5-dimethyoxybenzene-1,4-diylbis(4,1-butanediyl-2,1-benzeno)]-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin[2], 60 ml of trichloromethane/methanol (5:1), 500 mg (2.28 mmol) of zinc acetate dihydrate, procedure 1; R_f = 0.65/silica gel, cyclohexane/ethyl acetate (16:1): 21.5 mg (74%) of **5**, violet crystals, m.p. 265°C. – ^{1}H-NMR (500 MHz, CD_2Cl_2, assignment by COSY): δ = 0.10–0.27 (m, 4H, γ-CH_2), 0.40–0.52 (m, 4H, δ-CH_2), 1.06–1.19 (m, 10H, β-CH_2, OCH_3), 1.65 (m, 12H, 2,8,12,18-CH_2-CH_3), 1.90–2.04 (m, 4H, α-CH_2), 2.45 (s, 12H, 3,7,13,17-CH_3), 3.90–4.04 (m, 8H, 2,8,12,18-CH_2CH_3), 4.12 (s, 2H, central ar-H), 7.55–7.64 (m, 4H, ar-3',5'-H), 7.70 (m, 2H, ar-4'-H), 8.20 (dd, *J* = 7.3 and 1.0 Hz, 2H, ar-6'-H), 10.02 (s, 2H, 10,20-H). – MS (LSI-MS): *m/z* (%) = 943 (43), 942 (63), 941 (81), 940 (100), 939 (98), 938 (100) [M$^+$]. – $C_{60}H_{68}N_4O_2Zn$: calcd. 940.4633, found 940.4591 [MS: (M + 2H)$^+$].

X-ray Structure Analysis of 5,15-[3,6-Dimethyl-p-benzoquinone-1,4-diylbis(4,1-butanediyl-2,1-benzeno)]-2,8,12,18-tetraethyl-3,7 13,17-tetramethylporphyriatozinc (**4a**): Crystals of **4a** were obtained by recrystallization from cyclohexane as dark-red triclinic needles (0.05 · 0.05 · 0.15 mm). Enraf-Nonius CAD 4 (Mo-K_α radiation, graphite monochromator, ω-2Θ-scan technique); $C_{60}H_{64}N_4O_2Zn$

(938.57); space group $P\bar{1}$ (No. 2, Intern. Tables); a = 1441.8(4), b = 1448.7(4), c = 1460.2(8) pm; α = 75.16(3), β = 61.72(3), γ = 65.51(2)°; V = 2438(2) · 10^6 pm^3; Z = 2; D_x = 1.279 g · cm^{-3}; no. of reflections measured: 5951 up to $\sin\Theta/\lambda$ = 5.3 nm^{-1}, observed reflections included 3465 with $I \geqslant 3.0\sigma(I)$; R = 0.042. The structure solution was done by means of the heavy-atom method (Patterson). For the refinement all non-hydrogen atoms were included with anisotropic temperature factors; hydrogen atoms were located and refined isotropically. For further details see ref.[9].

---

[1] Part 9: H. A. Staab, T. Carell, A. Döhling, *Chem. Ber.* **1994**, *127*, 223–229, preceding paper.

[2] H. A. Staab, J. Weiser, E. Baumann, *Chem. Ber.* **1992**, *125*, 2275–2283; H. A. Staab, J. Weiser, M. Futscher, G. Voit, A. Rückemann, C. Anders, *Chem. Ber.* **1992**, *125*, 2285–2301.

[3] C. Krieger, M. Dernbach, G. Voit, T. Carell, H. A. Staab, *Chem. Ber.* **1993**, *126*, 811–821.

[4] H. Heitele, F. Pöllinger, K. Kremer, M. E. Michel-Beyerle, M. Futscher, G. Voit, J. Weiser, H. A. Staab, *Chem. Phys. Lett.* **1992**, *188*, 270–278; W. Frey, R. Klann, F. Laermer, T. Elsaesser, E. Baumann, M. Futscher, H. A. Staab, ibid. **1992**, *190*, 567–573.

[5] H. A. Staab, G. Voit, J. Weiser, M. Futscher, *Chem. Ber.* **1992**, *125*, 2303–2310.

[6] H. A. Staab, C. Anders, to be published.

[7] F. Pöllinger, H. Heitele, M. E. Michel-Beyerle, C. Anders, M. Futscher, H. A. Staab, *Chem. Phys. Lett.* **1992**, *198*, 645–652.

[8] For the synthesis and characterization of **3e** we thank A. Döhling from our group.

[9] Further details of the crystal structure investigation are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, Postfach 2465, 76012 Eggenstein-Leopoldshafen, on quoting the depository number CSD-57691, the names of the authors, and the journal citation.

[289/93]