SYNTHESIS OF DIQUINONE DERIVATIVES OF DEUTEROPORPHYRIN IX FOR THE STUDY OF THE FIRST STAGE IN THE PROCESS OF PHOTOSYNTHESIS

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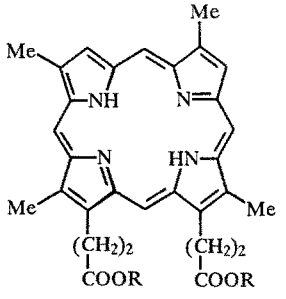
Diquinone derivatives of deuteroporphyrin IX containing covalent bridges of different lengths between the chromophores have been synthesized. The compounds were prepared by the condensation of hydroxy-quinones with deuteroporphyrin IX using a mixed anhydride method which employed the system di-tert-butylpyrocarbonate — 4-dimethylaminopyridine. A spectral study of the resulting porphyrin-quinones was carried out.

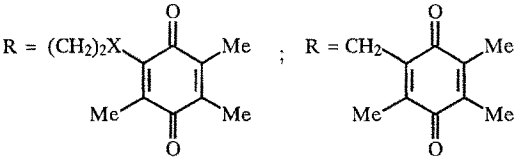
In recent years, attention has been directed to the study of the individual stages of the photosynthetic process in vitro. One promising approach is the modeling of the primary photosynthetic charge separation using prophyrin-quinone compounds [1, 2], in which the photosensitive porphyrin is covalently linked with the electron-acceptor quinone.

In earlier work, we synthesized some diquinone derivatives of deuteroporphyrin IX (Ia, b) [3, 4]. In these compounds, the benzoquinone structure is directly linked with the heteroatom (nitrogen or sulfur). This has a significant effect both on the acceptor properties of the quinone component and on the light-induced transfer of an electron from the porphyrin to the quinone [5]. To determine the role of the heteroatom in processes associated with photoinduced charge separation, compound Ic, which does not contain a heteroatom, was prepared.

This work describes the syntheses and spectral properties of the porphyrin-quinone Ic and its analog II with a shorter covalent bridge between chromophores. By varying the length of the chain between donor and acceptor, the effect of this factor on the three-dimensional structure of the model compounds and on the process of electron-transfer from the porphyrin to the quinone, can be determined.



Ia-c II



Ia-в II

Ia X=S; b X=NH; c X=CH_2

The photosensitizer was linked to the electron acceptor in the porphyrins Ic and II by means of the propionic acid groups of the porphyrin and the corresponding hydroxy-containing quinones III and IV.

The quinone components III and IV were obtained from trimethylhydroquinone V. Protective methyl groups were introduced into the hydroquinone V by boiling with Me_2SO_4 in the presence of K_2CO_3. In spite of the length (2 days) of the reaction, the yield of the dimethyl ether VII was 52.5%, which apparently is due to the steric hindrance of the hydroxyl group at position 4. In addition to the product VII, the monoether VI was isolated in 26% yield (the aim of this work was not the accurate determination of the position of the hydroxymethyl group), together with the starting hydroquinone V, which were subjected to repeated methylation under the same conditions with formation of the disubstituted VII. The dimethyl ether VII was converted to the chloromethyl derivative VIII (HCl gas, 40% formalin solution) [6] in 96.3% yield (see scheme below).

To prepare the alcohol III, the chloromethyl derivative VIII was condensed with the dimethyl ether of malonic acid (Na, MeOH, refluxing) [7]. The yield of the product IX after column chromatography was 39.7%. The main by-product of this reaction was the trimethyl ether X (yield 32%), the structure of which was determined by IR and PMR spectroscopic data and elemental analysis. Decarboxylation of compound IX by boiling in DMSO gave the monoether XI in 78.8% yield [7]. Reduction of the ester group in compound XI with lithium aluminum hydride in THF [7] gave the hydroxyderivative XII (99.9% yield). After

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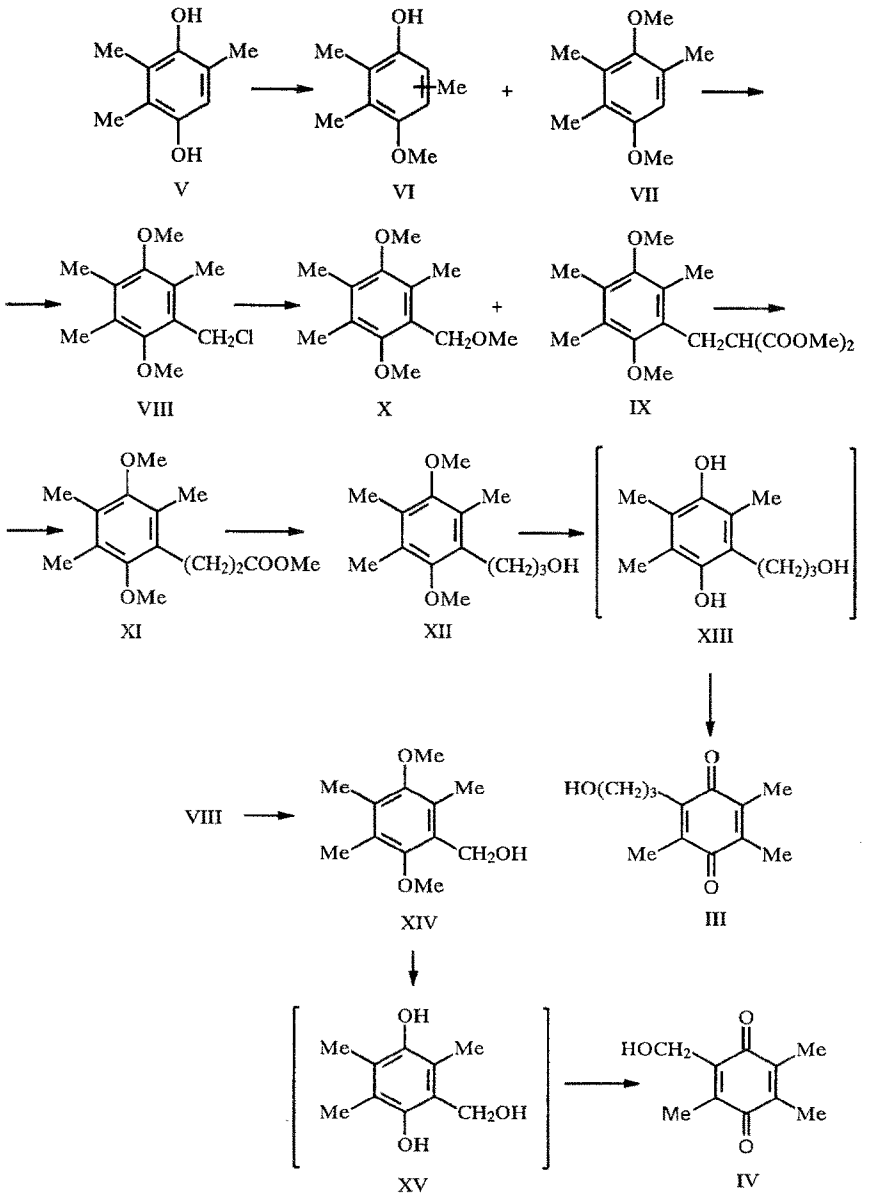

removal of the protective methyl group in compound XII with BBr_3 [8] and in situ oxidation of the resulting hydroquinone XIII with atmospheric oxygen, quinone III was isolated by column chromatography in 41.2% yield.

Quinone IV was obtained by alkaline hydrolysis of the chloromethylderivative VIII. The yield of the alcohol XIV was 91.8%. Demethylation of compound XIV with BBr_3 gave the hydroquinone XV, which without isolation was oxidized with PbO_2 [8]. The yield of quinone IV after chromatographic purification was 52.7%.

Deuteroporphyrin IX (DP IX), obtained from protohemin IX by Fischer's method [9], was used as the carboxyl component for the synthesis of the porphyrin-quinone Ic and II.

Condensation of deuteroporphyrin IX with the quinones III and IV was accomplished by the mixed anhydrides method. Earlier, we showed [3, 4] that di-tert-butylpyrocarbonate was effective as a condensing agent in the synthesis of diquinone derivative of prophyrins. Condensation of DP IX with the quinones III and IV in the presence of di-tert-butylpyrocarbonate and catalytic amounts of 4-dimethylaminopyridine in a mixture of pyridine and chloroform at 0°C gave mainly the diethers Ic and II. After purification by preparative TLC on kieselguhr 60 F_{254} (Merck), the yields of products Ic and II were 63.4 and 60.7%, respectively.

The structures of the quinones III and IV and the porphyrin-quinones Ic and II were confirmed by UV, IR, PMR, and fluorescence spectroscopy and elemental analysis (Table 1 and Experimental).

PMR spectroscopic data both confirmed the structure of the synthesized compounds, and also provided some preliminary information about the spatial organization of the molecules Ic and II.

TABLE 1. Characteristics of Compounds Ic-IV, VI-XIV

Compound	Mp, °C	R_f (system)	IR spectrum in mineral oil, ν, cm^{-1}					Yield, %
			C=C	CH*	C = O quinone	C = O ester	OH**	
Ic***	—	0,63 (3)	1600	—	1627	1720	(3300)	60,7
II***	—	0,51 (3)	1600	—	1635	1730	(3295)	63,4
III	—	0,60 (2)	1600	2907	1630	—	3350	41,2
IV	75,5...77,0	0,39 (2)	1600	2900	1625	—	3350	52,7
VI	—	0,38 (2)	1590	—	—	—	3400	26,0
VII	31,5...33,0	0,75 (1)	1585	2920	—	—	—	52,5
VIII	63,0...65,0	0,65 (1)	1595	—	—	—	—	96,3
IX	85,0...87,0	0,39 (2)	1590	—	—	1745 1735	—	39,7
X	—	0,59 (2)	1560	2920	—	—	—	32,0
XI	46,5...47,0	0,53 (2)	1590	—	—	1730	—	78,8
XII	—	0,51 (2)	1580	2911	—	—	3400	99,9
XIV	121,0...123,0	0,42 (2)	1580	—	—	—	3350	91,8

*Compounds for which the spectra were taken using films without mineral oil.

**In parentheses ν_{NH}.

***Fluorescence spectra: λ_{max}^{emis} = 620 nm, λ_{excit} = 400 nm, C = 10^{-5} mole/liter, $I_{fl} \times 10^{-3}$ = 15.6 (for Ic) and 16.5 relative units (for II).

The position of signals from the protons of the porphyrin ring and its nearest substituent in compounds Ic and II are practically unchanged compared with the dimethyl ether of deuteroporphyrin IX. At the same time, the quinone proton signals are shifted toward the strong-field region compared to the starting quinones III and IV. This effect is caused by the magnetically anisotropic porphyrin ring which has a significant effect on the distance between chromophores. Such changes are characteristic for porphyrin-quinones with flexible covalent bridges and indicate localization of the quinone fragment under the plane of the porphyrin [1, 4, 10-12]. Singlets from the quinone methyl groups of Ic are shifted to the strong-field region of 0.42-1.52 ppm. A decrease of bond length of two methylene groups in compound II leads to a decrease in the effect of the magnetic anisotropic porphyrin ring on the protons of the quinone part. Moreover $\Delta\delta$ for the methyl groups of II is 0.54-0.94 ppm. Apparently, the longer chain allows the quinone fragment to approach nearer to the center of the prophyrine ring. As well, the mutual orientation of the fragments changes, which also affects the magnitude of $\Delta\delta$ of signals of the quinone part and increases the displacement of the signals from the methyl groups with increasing length of the covalent chain.

A shift of the signals of the protons of the methylene groups of the covalent bridge also occurs, and the shifts increase in proportion to the proximity of the quinone. Thus, for β-CH_2 group of the propyl group in Ic the magnitude of $\Delta\delta$ is 0.79 ppm, and for α-CH_2 group, 2.10 ppm. From PMR spectra, it appears that one methyl and the α-CH_2 group in Ic, and two methyl groups in II are closest to the plane of the porphyrin.

Comparing the spectra of compound Ic with that of the porphyrin-quinones Ia and b [4], the steric changes due to the geometry of the heteroatom can be clearly followed. From the magnitude of $\Delta\delta$, the effect of the heteroatom on the proximity of the quinone part to the plane of porphyrin can be determined. Thus, the amount of overlapping decreases in the series from Ic which has no heteroatom, through Ib which contains nitrogen as heteroatom, to Ia which contains sulfur.

The nonequivalence of the quinone substituents at position 6 and 7 of the porphyrin give rise to a complex spectrum. In compound Ic, signals from the quinone methyl group protons occur not as the expected triplet but as six peaks, in compound II as five singlets, and in Ic the propyl chain β-CH_2 group gives two triplets of triplets (J_1 = 5.5 Hz, J_2 = 7 Hz).

The position of the UV absorption bands in the spectra of the porphyrin-quinones Ic and II are virtually the same as those for the dimethyl ether deuteroporphyrin IX. The spectra correspond to the superimposed spectra of the porphyrin and quinone parts. This suggests the absence of any significant interaction between chromophores in the basic compound [1, 4, 8, 13].

The fluorescence spectra of compounds Ic and II do not differ from the spectra of the dimethyl ether of deuteroporphyrin IX. However, the fluorescence of the porphyrin is strongly quenched. The ratios of the intensities of the fluorescence of the porphyrin-quinone to that of the starting dimethyl ether of deuteroporphyrin IX in acetone is 1:64.2 for Ic and 1:60.7 for II. This suggests the presence of an effective channel for quenching the porphyrin fluorescence, associated with electron transfer

from the light-excited photosensitizer to the quinonoid electron acceptor [1, 2, 10, 13]. The less effective quenching of fluorescence for compound II, which has a shortened covalent chain, is probably due to the large increase in the distance of the quinone from the plane of the porphyrin (confirmed by PMR spectral data), which makes the transfer of an electron from the porphyrin to the quinone difficult.

From these photochemical studies, quantitative parameters have been obtained for electron transfer in the model compounds Ic and II.

EXPERIMENTAL

Condensations were carried out in anhydrous solutions. The purity of the compounds and the course of the reaction were monitored by TLC using Silufol UV-254 (Kavalier) with acetone—hexane, 1:19(1) or acetone—hexane, 6:19(2), and kieselguhr 60 F_{254} (Merck) with chloroform—methanol, 15:1(3). IR spectra were taken on a Shimadzu IR-435 spectrophotometer, UV spectra on a Shimadzu UV-240 and a Beckman DU-8 spectrophotometer. PMR spectra were recorded on a Bruker WM-250 instrument with a working frequency of 250 MHz, internal standard HMDS. Fluorescence spectra were taken in acetone on a Shimadzu RF-540. The trimethylhydroquinone V was obtained from Aldrich (USA) and used without further purification.

Elemental analysis data for compounds Ic-IV, VI-XII, and XIV were in good agreement with calculated values.

1,4-Dimethoxy-2,3,5-trimethylbenzene (VII, $C_{11}H_{17}O_2$). To a solution of trimethylhydroquinone (V) (25 g, 164.3 mmole) in acetone (250 ml) was added dimethylsulfate (31 ml, 327 mmole) and potash (25 g). The reaction mixture was stirred under reflux for 48 h. The acetone was evaporated, the residue extracted with petroleum ether (300 ml), and the extract passed through a layer of aluminum oxide (5 cm, neutral, activity grade IV). The solvent was evaporated and the residue chromatographed on a column (2 × 20 cm) of silica gel L 100 × 160, fraction A with R_f 0.75 (1) was eluted with hexane, and fraction B with R_f 0.38 (2) with a 10:1 mixture of hexane and chloroform. The solvent was evaporated from fraction A, the residue refluxed in 10% potassium hydroxide solution (200 ml) for 2 h, extracted with hexane (3 × 100 ml), washed with water (3 × 300 ml), dried with sodium sulfate, and passed through a layer of silica gel L 100 × 160 (5 cm). The solvent was evaporated, and the oil dried in vacuum over paraffin and phosphorus pentoxide to give VII. PMR spectra in C_6D_6: 6.42 (1H, s, aromatic C—H), 3.43 (3H), 3.41 (3H, all s, OCH_3), 2.29 (3H), 2.23 (3H), 2.17 ppm (3H, all s, CH_3 aromatic).

1(4)-Methoxy-4(1)-hydroxy-2,3,5-trimethylbenzene (VI, $C_{10}H_{15}O_2$). From fraction B from the previous reaction the solvent was evaporated, and the residue recrystallized from heptane. The crystals were dried in vacuum over paraffin and phosphorus pentoxide to give VI. PMR spectrum in C_6D_6: 6.40 (1H, s, C—H aromatic), 3.42 (3H, s, OCH_3), 2.30 (3H), 2.22 (3H), 2.11 ppm (3H, all s, aromatic CH_3).

1,4-Dimethoxy-2-chloromethyl-3,5,6-trimethylbenzene (VIII, $C_{12}H_{17}O_2Cl$). Hydrogen chloride was bubbled through a solution of compounds VII (7.2 g, 39.9 mmole) in dioxane (60 ml) at 20°C and a 40% solution of formalin (8.4 ml) was added in 3 portions at 3-min intervals. Stirring was continued for 5 h with passage of hydrogen chloride and the mixture then left for 12 h at 20°C. Concentrated HCl (58 ml) was added and the mixture cooled to 0°C. The precipitate which separated was filtered off, dried in vacuum over potassium hydroxide, and recrystallized from heptane. The crystals were dried under vacuum over paraffin and phosphorus pentoxide to give VIII. PMR spectrum in C_6D_6: 4.57 (2H, s, CH_2Cl), 3.54 (3H), 3.28 (3H, all s, OCH_3), 2.27 (3H), 2.04 (3H), 2.00 ppm (3H, all s, CH_3 aromatic).

Dimethyl Ether of 2-(2,5-Dimethoxy-3,4,6-trimethylphenylmethyl)malonic Acid (IX, $C_{17}H_{24}O_6$). To a refluxing solution of sodium methoxide in methanol, obtained by dissolving sodium (405 mg, 17.6 mg atom) in methanol (40 ml), was added dropwise during 10 min a solution of dimethyl malonate (2.22 ml, 19.4 mmole) in methanol (10 ml). The mixture was refluxed for 20 min, a solution of compound VIII (4.3 g, 18.8 mmole) added dropwise over a period of 20 min and refluxing continued for 3 h. The methanol was evaporated, the residue chromatographed on a column (2.8 × 35 cm) with silica gel L 100 × 160, and eluted with a 1:2 mixture of ether and heptane. Fraction A with R_f 0.59 (2) was collected, followed by fraction B with R_f 0.39 (2). The solvent was evaporated from fraction B, and the residue recrystallized from heptane. The crystals were dried in vacuum over paraffin and phosphorus pentoxide to give IX. PMR spectrum in C_6D_6: 4.13 (1H, t, J = 7.5 Hz, CH_2CH), 3.44 (2H, d, J = 7.5 Hz, CH_2CH), 3.27 (3H), 3.25 (3H, all s, OCH_3), 3.18 (6H, s, OCH_3), 2.27 (3H), 1.96 (3H), 190 ppm (3H, all s, aromatic CH_3).

1,4-Dimethoxy-2-methoxymethyl-3,5,6-trimethylbenzene (X, $C_{12}H_{20}O_3$). From fraction A of the preceding reaction, the solvent was evaporated, and the oil remaining dried in vacuum over paraffin and phosphorus pentoxide to give X. PMR spectrum in C_6D_6: 4.55 (2H, s, CH_2OCH_3), 3.63 (3H), 3.47 (3H, both s, OCH_3), 2.46 (3H), 2.10 ppm (6H, both s, aromatic CH_3).

Methyl Ester of 3-(2,5-dimethoxy-3,4,6-trimethylphenyl)propionic Acid (XI, $C_{15}H_{22}O_4$). A solution of sodium chloride (1.25 g) in water (1.25 ml) was added to a solution of compound IX (770 mg, 2.37 mmole) in DMSO (20 ml). The mixture was refluxed for 4 h, then poured into ice-water (300 ml), and extracted with ether (3 × 50 ml). The extract was washed with water (5 × 100 ml), dried over sodium sulfate, and the solvent evaporated. The residue was passed through aluminum oxide (5 cm), eluted with a 2:1 mixture of pentane and ether, and the solvent evaporated. The oil remaining was triturated with methanol, the crystals obtained washed with water, recrystallized from pentane, and dried in vacuum over paraffin and phosphorus pentoxide to give XI. PMR spectrum in C_6D_6: 3.44 (3H), 3.41 (3H, all s, $OC\underline{H}_3$), 3.20-3.12 (2H, m, $C\underline{H}_2CH_2CO$), 2.64-2.56 (2H, m, $CH_2C\underline{H}_2CO$), 2.24 (3H), 2.14 (3H), 2.10 ppm (3H, all s, $C\underline{H}_3$ aromatic).

1,4-Dimethoxy-2-(3-hydroxypropyl)-3,5,6-trimethylbenzene (XII, $C_{14}H_{22}O_3$). Lithium aluminum hydride (300 mg, 7.9 mmole) was added portionwise over a period of 10 min to a stirred solution of compound XI (595 mg, 2.23 mmole) in THF (10 ml). Ethyl acetate (10 ml) was then gradually added (1 h). After stirring for a further 30 min, the reaction mixture was poured into 2% HCl (300 ml) extracted with chloroform (3 × 300 ml), the extract washed with water (3 × 300 ml), and dried over sodium sulfate. Evaporation of the solvent yielded an oil which was dried in vacuum over paraffin and phosphorus pentoxide to give XII. PMR spectra in C_6D_6: 3.50 (2H, t, J = 7 Hz, $CH_2CH_2C\underline{H}_2OH$), 3.39 (3H), 3.34 (3H, all s, $OC\underline{H}_3$), 2.76 (2H, t, J = 7 Hz, $C\underline{H}_2CH_2CH_2O$), 2.23 (3H), 2.12 (3H), 2.06 (3H, all s, aromatic $C\underline{H}_3$), 1.74 ppm (2H, q, J = 7 Hz, $CH_2C\underline{H}_2CH_2OH$).

2-(3-Hydroxypropyl)-3,5,6-trimethyl-1,4-benzoquinone (III, $C_{12}H_{16}O_3$). Boron tribromide (2.5 ml) was added to a cooled (—40°C) and stirred solution of compound IX (265 mg, 1.1 mmole) in methylene chloride (12 ml). Stirring was continued for a further 24 h at 20°C, the reaction mixture poured into ice (500 g), and extracted with chloroform (3 × 100 ml). The extract was washed with saturated sodium carbonate, water (3 × 300 ml), saturated sodium chloride (300 ml), and dried over sodium sulfate. The solvent was evaporated, the residue chromatographed on a column (3.2 × 35 cm) with silica gel L 100 × 160, and eluted with a 3:1 mixture of chloroform and hexane. The fraction with R_f 0.6 (2) was collected, and the solvent evaporated. The oil remaining was dried in vacuum over paraffin and phosphorus pentoxide to give III. PMR spectrum in $CDCl_3$: 3.58 (2H, t.t, J_1 = 6.25 Hz, J_2 = 7.38 Hz, $CH_2C\underline{H}_2CH_2O$). PMR spectrum in C_6C_6: 3.33 (2H, t, J = 6 Hz, $CH_2C\underline{H}_2O$), 2.40 (2H, t, J = 7.5 Hz, $C\underline{H}_2CH_2O$), 1.86 (3H), 1.73 (3H), 1.71 (3H, all s, $C\underline{H}_3$), 1.48 ppm (2H, t.t, J_1 = 6 Hz, J_2 = 7.5 Hz, $CH_2CH_2C\underline{H}_2O$).

1,4-Dimethoxy-2-hydroxymethyl-3,5,6-trimethylbenzene (XIV, $C_{12}H_{18}O_3$). A mixture of compound VIII (831 mg, 3.63 mmole), water (25 ml), and sodium carbonate (6.25 g) was refluxed for 48 h. The reaction mixture was extracted with ether (300 ml), the extract washed with 2% HCl (100 ml), water (3 × 200 ml), and dried with sodium sulfate. The solvent was evaporated and the residue recrystallized from heptane. The crystals were dried in vacuum over paraffin and phosphorus pentoxide to give XIV. PMR spectrum in C_6D_6: 4.64 (2H, s, $C\underline{H}_2OH$), 3.44 (3H), 3.34 (3H, all s, OCH_3), 2.28 (3H), 2.10 (3H), 2.06 ppm (3H, all s, aromatic $C\underline{H}_3$).

2-Hydroxymethyl-3,5,6-trimethyl-1,4-benzoquinone (IV, $C_{10}H_{12}O_3$). A solution of compound XIV (700 mg, 3.88 mmole) in methylene chloride (28 ml) was cooled to —40°C, and boron tribromide (7 ml) added. The reaction mixture was stirred at 20°C for 48 h, then poured onto ice (500 g), and extracted with chloroform (3 × 100 ml). The extract was washed with saturated sodium carbonate, water (3 × 100 ml), and saturated sodium chloride (300 ml), and dried over sodium sulfate. The solvent was evaporated, the residue dissolved in a 1:1 mixture of chloroform and benzene (100 ml), lead oxide (7 g) added, and stirred for 24 h. The solution was filtered, the solvent evaporated, and the residue chromatographed on a column (3.2 × 40 cm) of silica gel L 100 × 160, and eluted with a 1:1 mixture of chloroform and hexane. The fraction with R_f 0.39 (2) was collected. After evaporation of the solvent, the residue was dried in vacuum over paraffin and phosphorus pentoxide to give IV. PMR spectrum in $CDCl_3$: 4.52 (2H, d, J = 6.5 Hz, $C\underline{H}_2OH$), 2.64 (1H, t, J = 6.5 Hz, $CH_2O\underline{H}$), 2.08 (3H), 2.03 (3H), 2.02 ppm (3H, all s, $C\underline{H}_3$). PMR spectrum in C_6D_6: 4.27 (2H, s, $C\underline{H}_2OH$), 2.46 (1H, broad s, $CH_2O\underline{H}$), 1.80 (3H), 1.64 ppm (6H, all s, $C\underline{H}_3$).

1,3,5,8-Tetramethyl-6,7-di[2-(3-(3,5,6-trimethyl-1,4 benzoquinone-2-yl) propyl)oxycarbonylethyl]porphyrin (Ic, $C_{54}H_{58}N_4O_8$). To a solution of deuteroporphyrin IX (100 mg, 0.18 mmole) in a mixture of chloroform (25 ml) and pyridine (5 ml) was added quinone III (94 gm, 0.45 mmole), followed by di-tert-butylpyrocarbonate (100 mg, 0.45 mmole) at 0°C. After 10 min, 4-dimethylaminopyridine (5 mg, 0.04 mmole) was added, the mixture stirred for 2 h at 20°C, poured into 2% HCl (300 ml), and extracted with chloroform (3 × 30 ml). The extract was washed with water (3 × 300 ml) and dried with sodium sulfate. The solvent was evaporated, the residue chromatographed on plates (20 × 20 cm) of kieselguhr 60 F_{254} (Merck), and eluted with a 100:1 mixture of chloroform and methanol. The main porphyrin fraction was eluted with a 3:2 mixture of chloroform and heptane, the solvent evaporated, and the residue triturated with pentane. The product was dried in a vacuum over paraffin and phosphorus pentoxide. Electronic spectrum in chloroform, λ_{max} (log ε): 621.1 (3.59), 567.5 (3.84), 530.5 (393), 497.1

(4.18), 399.1 nm (5.29) (Sore). PMR spectrum in $CDCl_3$: 10.08 (1H), 10.04 (1H), 9.95 (1H), 9.91 (1H, all s, Meso-H), 9.02 (1H), 9.01 (1H, both s, β – H, 4.46 (4H, t, J = 7 Hz, $CH_2CH_2C_2O$), 3.76 (4H, t, J = 5.5 Hz, $CH_2CH_2CH_2O$), 3.72 (3H), 3.69 (3H), 3.65 (3H), 3.63 (3H, all s, porph. CH_3), 3.29 (4H, t, J = 7 Hz, CH_2CH_2CO), 1.63 (3H), 1.62 (3H), 1.34 (3H), 1.43 (3H), 0.55 (3H), 0.50 (3H, all s, quinone CH_3), 0.91 (2H), 0.89 (2H, both t.t, J_1 = 5.5 Hz, J_2 = 7 Hz, $CH_2CH_2CH_2O$), 0.50 ppm (4H, t, J = 7 Hz, $CH_2CH_2CH_2O$).

1,3,5,8-Tetramethyl-6,7-di[2-(3,5,6-trimethyl-1,4-benzoquinone-2-yl)methoxycarbonylethyl]porphyrin(II,$C_{50}H_{50}N_4O_8$) was synthesized by the method used for the preparation of compound Ic from deuteroporphyrin IX (100 mg, 0.18 mmole). Electronic spectrum in chloroform, λ_{max} (log ε): 620.5 (3.58), 567.1 (3.83), 529.7 (3.91), 497.3 (4.17), 399.1 nm (5.26) (Sore). PMR spectrum in $CDCl_3$: 10.11 (1H), 10.08 (1H), 10.00 (2H, all s, meso-H), 9.11 (1H), 9.09 (1H, both s, β–H), 4.84 (4H, s, CH_2O), 4.39 (2H), 4.38 (2H, both t, J = 7 Hz, CH_2CH_2CO), 3.77 (3H), 3.75 (3H), 3.64 (3H), 3.61 (3H, all s, porphyrin CH_3), 3.32 (4H, t, J = 7 Hz, $CH_2CH_2CO_2O$), 1.54 (6H), 1.18 (3H), 1.14 (3H), 1.10 (3H), 1.08 ppm (3H, all s, quinonne CH_3).

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