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SYNTHESIS OF RIGIDLY LINKED TRIAD MOLECULES BASED ON OCTAALKYLPORPHYRIN, CAPABLE OF MULTISTEP ELECTRON TRANSFER

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We have designed and carried out the synthesis of triad model systems containing octaalkylporphyrin, benzoquinone, and trichlorobenzoquinone with an oxidation–reduction potential gradient in the molecule. The quinone moieties are fixed relative to the porphyrin using spiro[4,4]nonane and methylene spacers.

We know that high-efficiency photoinduced charge separation to large distances at a photosynthetic reaction center is achieved as a result of multistep electron transfer through a whole series of donor and acceptor moieties when a redox-potential gradient exists in these moieties [1]. The same principles are used in triad and tetrad photosynthetic models, making it possible to achieve a long-lived state with separated charges with high quantum yields [1-5], i.e., using multistep electron transfer makes it possible to increase the efficiency and rate of electron transfer in model compounds. This was shown for the first time for the example of triads containing etioporphyrin II, benzoquinone, and trichlorobenzoquinone, covalently bonded to each other by two polyethylene chains [6, 7]. However, the presence of flexible polyethylene bridges may lead to conformations in which direct and back electron transfer can occur through space from the porphyrin to the secondary electron acceptor.

For a more detailed study of the process of charge separation, we chose the triad molecules Ia, b in which the primary acceptor is fixed relative to the porphyrin by a rigid spiro[4,4]nonane spacer, while the secondary acceptor is linked by a methylene bridge, which ensures a practically fixed distance from the other parts of the system. The distance between the porphyrin centers and the primary acceptor is 12.6 Å, while the secondary acceptor is 16.6-17.4 Å away from the porphyrin and the distance between centers in the quinones is 5.0 Å (the distances are determined using the program Chem 3D Plus 3.0). A spirobiindane spacer was successfully used in [8, 9], so we are interested in determining the effect of the secondary acceptor on the processes of electron transfer when an identical spacer is present. Trichlorobenzoquinone as the secondary acceptor was necessary to provide an oxidation–reduction potential gradient, in order to ensure efficient multistep electron transfer in triad systems Ia, b.

In order to construct the triad molecules Ia, we chose acid-catalyzed cyclization of 8,12-diethyl-2,3,7,13,17,18-hexamethyl-a,c-biladiene dihydrobromide (II) with the aromatic aldehyde III.

TABLE 1. Synthesis of 3,4,6-Trichloro-2,5-dimethoxybenzyl Alcohol (IX)

Reagent	Solvent	Conditions	Extent of conversion, %	Yield, %
Na_2CO_3	H_2O	100 °C/53 h	10 - 20	75
KO_2	DMSO–DMF	0 °C/1 h	80	55
AcOK/KOH	EtOH	78 °C/20 h	100	54

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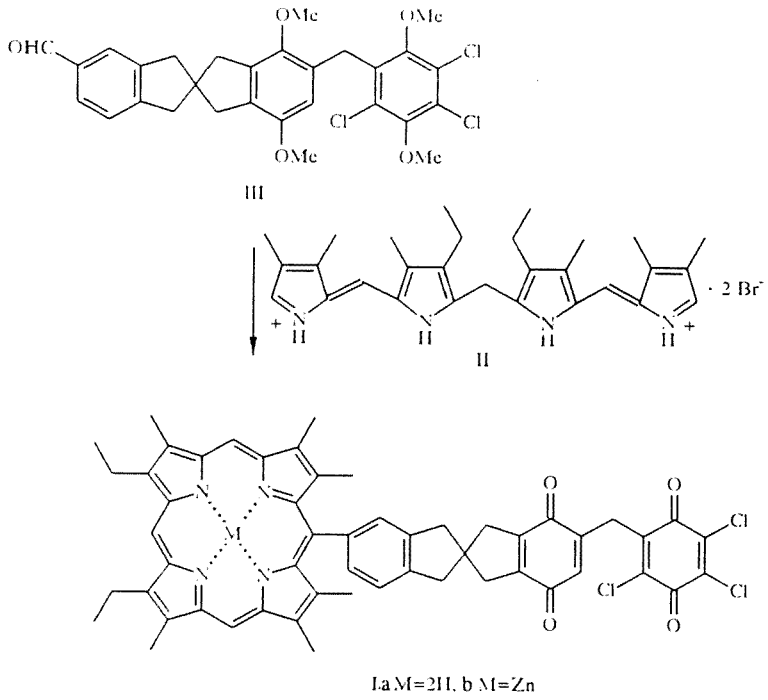
TABLE 2. Parameters of PMR Spectra of Compounds III, VIII, IX, XXI-XXIV

Compound	Chemical shift ($CDCl_3$), δ, ppm (spin–spin coupling constant J, Hz)					
	CH arom (1H)	CH_2 alkyl (2H)	OCH_3 (3H, s)	CH_2 spiro	CH_2OH (1H, t)	CHO (1H, s)
VIII	—	4,66 (s)	4,01, 3,90	—	—	—
IX	—	4,84 (d, J = 6,6)	3,92, 3,89	—	2,17 (J = 6,6)	—
XXI	7,0, 6,7 (d, J = 6,6)	—	3,90, 3,89	3,10 - 2,82, 2,74 - 2,55 (2H, m)	—	—
XXII	6,49 (s)	4,24 (s)	3,95, 3,89, 3,71, 3,68	2,96 - 2,64 (4H, m)	—	—
XXIII	7,33 (s), 7,27, 7,05 (d, J = 7,92), 6,52 (s)	4,25 (s)	3,98, 3,89, 3,74, 3,65	3,45, 3,39 (1H, d, J = 15,5), 2,99 (s, 2H), 2,80, 2,78 (1H, d, J = 15,5)	—	—
XXIV	7,31 (s), 7,27, 7,04 (d, J = 7,92), 6,10 (s)	4,20 (s)	3,89, 3,74, 3,68, 3,60	3,01, 2,96, 2,91, 2,88 (2H, s)	—	—
III	7,71 (s), 7,35, 7,18 (d, J = 7,92) 6,12 (s)	4,20 (s)	3,89, 3,76, 3,69, 3,60	3,04 (4H, s), 2,98, 2,90 (2H, s)	—	9,90

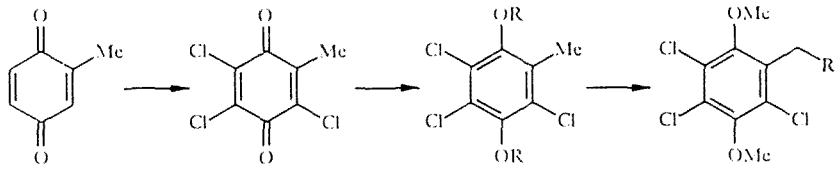
In order to synthesize the aldehyde III, first we needed to synthesize the bromo derivative VIII [10] starting from p-toluquinone (IV). Chlorination of the starting quinone IV in glacial acetic acid yielded the trichloroquinone V. Reduction of compound IV to the hydroquinone VI and treatment with dimethylsulfate led to compound VII. Bromination by bromosuccinimide made it possible to obtain the bromo derivative VIII in quantitative yield.

Scheme 1



I a M=2H, b M=Zn

Scheme 2



IV V VI, VII VIII, IX

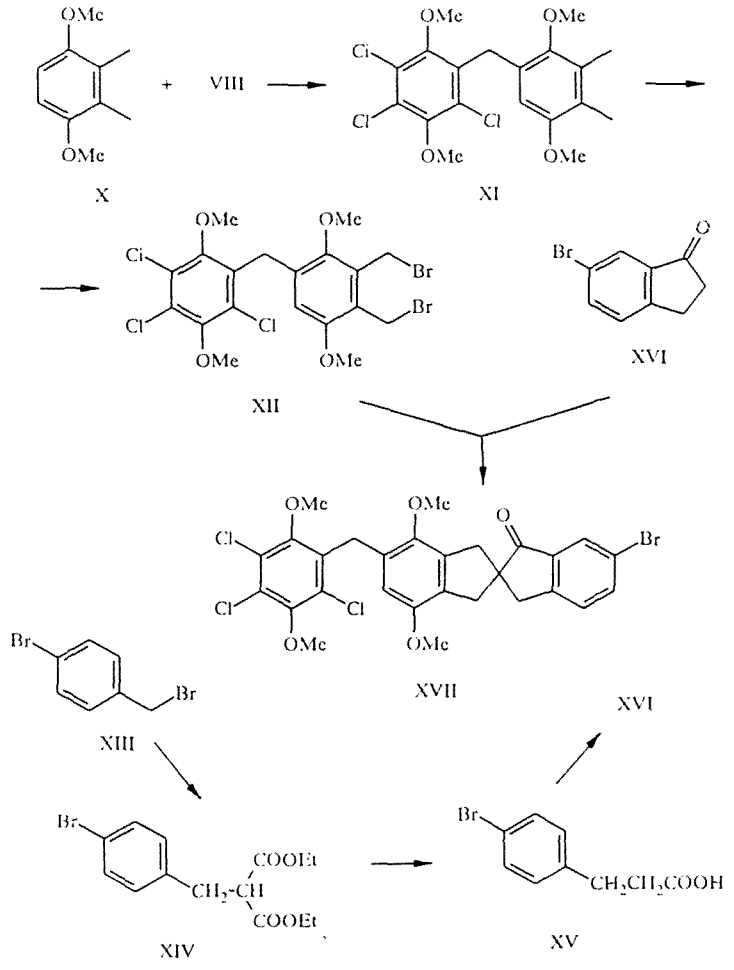
VI R=H; VII R=Me; VIII R=Br; IX R=OH

Then Friedel–Crafts alkylation of compound X by the bromo derivative VIII in the presence of Lewis acid ($AlCl_3$) yielded compound XI. Unfortunately, during the reaction partial removal of the methyl protective groups occurred, which caused the need for repeated treatment with dimethylsulfate and led to some reduction in the overall yield.

Treatment of compound XI with bromosuccinimide led to compound XII in only 24% yield due to formation of the mono- and tribromo derivatives as a result of undesired bromination of the methylene bridge. Then the dibromo derivative XII was condensed with 6-bromindanone (XVI). The bromindanone XVI was obtained from 4-bromobenzyl bromide XIII and malonic ester followed by Friedel–Crafts cyclization of the corresponding acid chloride of the acid XV in the presence of a Lewis acid [11].

Condensation of compounds XII and XVI in the presence of sodium hydride yielded the spirocyclic ketone XVII. The low yields in the later states and also the unsatisfactory results of removal of the carbonyl group in the ketone XVII forced us to choose another synthesis route.

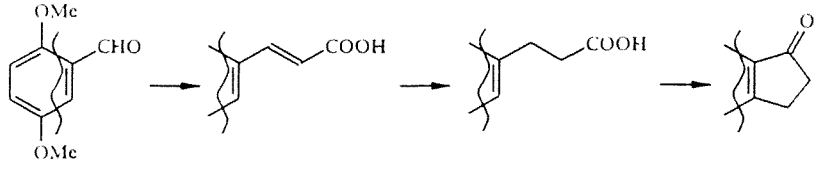
Scheme 3



X XI XII XVI XVII XIII XIV XV

In order to accomplish this, we needed to first synthesize 4,7-dimethoxyindanone (XXI) [12]. Starting from 2,5-dimethoxybenzaldehyde (XVIII), by the Knoevenagel reaction we obtained 2,5-dimethoxycinnamic acid (XIX), the catalytic hydrogenation of which yielded the substituted dihydrocinnamic acid (XX) with overall yield 80% (based on the starting benzaldehyde XVIII). For Friedel–Crafts intramolecular cyclization, we used polyphosphoric acid, which served as both the solvent and the Lewis acid [13]. In this case, removal of the protective groups did not occur as in the case of compound XI, which made it possible to obtain the indanone XXI. The principal requirement when carrying out this reaction was the need to maintain certain temperature conditions (57-60°C). With an increase in temperature, due to the exothermicity of the reaction, extremely undesirable polymerization of the starting material occurs.

Scheme 4



XVIII XIX XX XXI

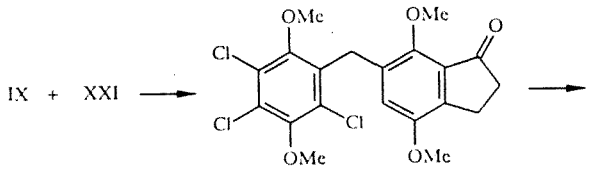
Attempts to accomplish Friedel–Crafts alkylation of the obtained indanone XXI with the bromo derivative VIII proved to be unsuccessful. Therefore from compound VIII we obtained the hydroxy derivative IX by three different methods (Table 1). Despite the fact that the yields of compound IX when using Na_2CO_3 and potassium peroxide [14] are higher than when using the AcOK–KOH system [15], the extent of conversion was much lower, which did not make it possible to obtain sufficient amounts of compound IX in a single cycle.

In the PMR spectrum of compound IX, substitution of the bromine by hydroxyl led to the appearance of a signal from the proton by the hydroxyl group in the form of a triplet with J = 6.6 Hz, a change in the signal from the protons of the methylene group (doublet, J = 6.6 Hz) and its downfield shift by 0.18 ppm (Table 2).

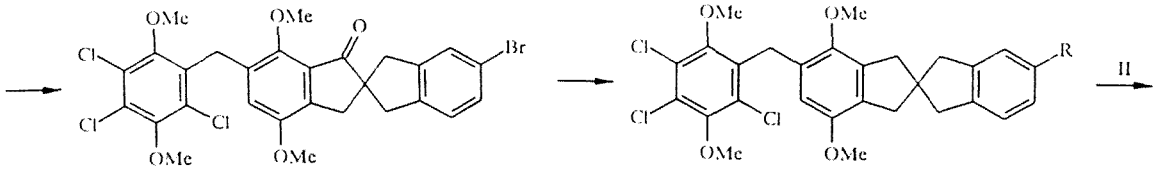
The next step in synthesis of the triad Ia was condensation of the derivatives IX and XXI in PPA with formation of compound XXIII. In the PMR spectrum of compound XXII, there were signals from the corresponding protons, and the signal from the protons of the methylene bridge was shifted upfield by 0.6 ppm (Table 2).

The spirocyclic compound XXIII was synthesized by condensation of compound XXII with 3,4-bis(bromomethyl)bromobenzene with boiling in anhydrous THF in the presence of sodium hydride. In the PMR spectrum of the compound obtained, the signals from the spirocyclic protons are resolved in the form of doublets with J = 15.5 Hz, except for the signal from the protons of the methylene group of the indanone ring, which appears as a singlet.

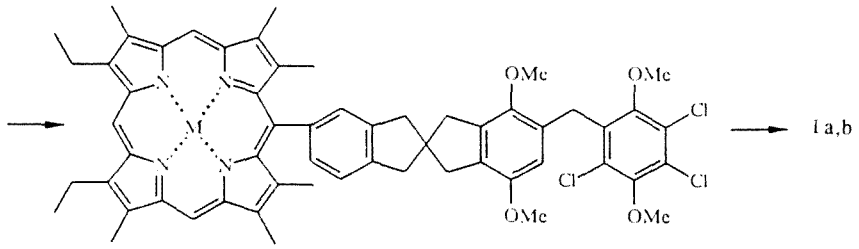
Scheme 5



XXII



XXIII XXIV, III



XXV a,b

XXIV R=Br; III R=CHO; XXVa M=2H, b M=Zn

Reductive removal of the keto group in ketone XXIII by triethylsilane in trifluoroacetic acid for 23 h leads to compound XXIV. In the IR spectrum of the reduced compound XXIV, there was no absorption band at 1720 cm^{-1} corresponding to vibrations of a carbonyl group.

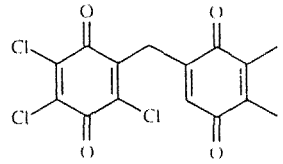
Substitution of the bromine by formyl (obtaining the aldehyde III) was achieved by treatment of XXIV with n-butyllithium and DMF in anhydrous THF at −78°C. In the PMR spectrum of compound III, the signal from the proton of the aldehyde appears at 9.9 ppm (Table 2).

In order to construct a porphyrin macrocycle, we synthesized a,c-biladiene II, starting from ethylacetoacetate using the previously described techniques in [16-23]; all the reaction conditions and the characteristics of the pyrroles are summarized in Table 3.

Condensation of the aldehyde III and the a,c-biladiene II by boiling in methanol in the presence of catalytic amounts of HBr for 24 h yields the porphyrin XXVa. Demethylation of porphyrin XXVa by boron tribromide followed by oxidation with lead dioxide leads to triad Ia. Zinc was quantitatively introduced into the porphyrin ring by treatment of compounds XXVa, Ia with zinc acetate in methylene chloride.

The electronic spectra of the porphyrin derivatives Ia, b, XXVa, b showed the absence of interaction between parts of the system in ground state [1-9].

The values of the oxidation−reduction potentials of trimethylbenzoquinone, trichlorotoluquinone, and diquinone XXVI, measured as the polarographic halfwave potentials ($E_{1/2}$) in acetonitrile and characterizing the electron-acceptor activity of the quinones, showed that in compound XXVI there is no interaction between parts of the molecule. These data also indicate that in triads Ia, b there exists an oxidation−reduction potential gradient, necessary for multistep photoinduced electron transfer. The corresponding values of $E_{1/2}$ are −0.73, −0.13 V for trimethylbenzoquinone, trichlorotoluquinone, and −0.75, −0.20 V for the diquinone XXVI.



XXVI

In studying the fluorescence spectra of compounds Ia, b we observed strong quenching of the porphyrin fluorescence, connected with photoinduced intramolecular electron transfer from the porphyrin to the quinone [1-9]. The relative fluorescence quantum yield of the porphyrin in Ia, b was 12% and 0.8% respectively.

All these data allow us to conclude that photoinduced multistep electron transfer is possible in the synthesized triads Ia, b, and that their further investigation as photosynthetic model systems using time-resolved spectroscopy is feasible.

EXPERIMENTAL

The condensations were carried out in anhydrous solvents. The materials were purified by column chromatography on Wakogel C-200 silica gel (100-200 mesh) and Kieselgel 60F (230-400 mesh). Preparative TLC was carried out on glass

plates (20 × 20 cm^2) with Kieselgel 60F (Merck, layer thickness 2 mm and 0.2 mm) and Whatman (layer thickness, 1 mm). The purity of the compounds obtained and the course of the reactions were monitored by TLC in the systems: Kieselgel 60F (Merck), chloroform–methanol, 20:1 (1), chloroform–methanol (40:1 (2), chloroform–methanol, 100:1 (3), chloroform (4), chloroform–hexane, 2:1 (5), chloroform–hexane, 1:2 (6).

The electronic spectra and the fluorescence spectra of the porphyrin–quinone compounds were measured on the Hitachi-150 spectrophotometer and the Hitachi-850 spectrofluorimeter respectively. The IR spectra of the compounds obtained were measured on the Shimadzu IR-435. The PMR spectra were recorded in $CDCl_3$ on the JEOL JNM EX-270; the PMR spectra of porphyrins were recorded on the Brucker AM-360 with TMS as the internal standard.

The mass spectra of the compounds were obtained on the ESCO EMD-59 mass spectrometer with ionization by electron impact; the mass spectra of the porphyrins were obtained on the JEOL DX-300 mass spectrometer by bombardment with accelerated atoms (Ar atoms as the primary source of ions with energy 6 eV, accelerating potential 10 kV, 3-nitrobenzyl alcohol as the matrix). The redox potentials of the quinones were measured in acetonitrile relative to the silver chloride electrode, with Bu_4NClO_4 as the auxiliary electrolyte.

2,4,5-Trichloro-3,6-toluquinone (V). A solution of 25 g p-toluquinone (0.2 mole) and 10.3 g I_2 (0.08 mole) in 260 ml glacial acetic acid were heated at 100°C and dry Cl_2 was bubbled through for 5 h. After cooling the reaction mass down to 20°C, 300 ml saturated aqueous solution of $KBrO_3$ was added with vigorous stirring and the mixture obtained was filtered. The filtrate was extracted with chloroform (4 × 700 ml), the chloroform extract was washed with saturated aqueous solutions of $NaHCO_3$ (3 × 1.5 liters), NaCl (1 × 2 liters), and water (2 × 1 liter) and then dried over anhydrous Na_2SO_4. After removal of the solvent under vacuum, the residue was recrystallized from chloroform. Yield, 39.4 g (86%). R_f 0.6 (5). mp 233-236°C. According to data in [10], mp 234-235°C. Mass spectrum, m/z: 224 (M^+).

2,4,5-Trichloro-3,6-dihydroxytoluene (VI). A solution of 10 g (45 mmole) compound V in 200 ml chloroform at 20°C was added dropwise with stirring to a solution of 35 g (0.2 mole) $Na_2S_2O_4$ in 300 ml of a 1:1 chloroform–water mixture. This was allowed to stand (with stirring) overnight. The reaction mass was diluted with 1 liter of water and extracted with chloroform (5 × 400 ml), washed with water (2 × 1.5 liters) and a saturated solution of NaCl (2 liters), and then dried over anhydrous Na_2SO_4. Then the solvent was removed under vacuum. The residue was recrystallized from ethanol. Yield, 8.9 g (88%). R_f 0.46 (4). mp 198-200°C. According to the data in [10], mp is 198°C. Mass spectrum, *m/z*; 226 (M^+).

2,4,5-Trichloro-3,6-dimethoxytoluene (VII). An aqueous solution (50 ml) of 17.4 g KOH was slowly added with stirring to a solution of 8.9 g (39 mmoles) compound VI in 140 ml THF; 5 min later, 13.3 ml Me_2SO_4 (0.14 mole) was added. The reaction mass was boiled with a reflux condenser for 12 h. After cooling, the inorganic impurities were filtered off and it was poured into 200 ml water, extracted with chloroform (3 × 200 ml), washed with water (500 ml) and a saturated aqueous solution of NaCl (500 ml), and then dried over anhydrous Na_2SO_4. After removal of the solvent under vacuum, the residue was recrystallized from a benzene–hexane mixture. Yield, 9.1 g (92%). R_f 0.74 (5). mp 136-138°C. According to data in [10], mp 134-135°C. Mass spectrum, *m/z*: 254 (M^+).

2,4,5-Trichloro-3,6-dimethoxybenzyl bromide (VIII). Compound VII (9 g, 35 mmoles), 6.3 g (35 mmoles) N-bromosuccinimide, 150 ml dry CCl_4, and catalytic amounts of benzoyl peroxide were placed into the reaction flask. The reaction mass was boiled with a reflux condenser with irradiation by a tungsten lamp for 1 h. After cooling, this was poured into 300 ml water and extracted with chloroform (3 × 150 ml), washed with a 10% aqueous solution of $Na_2S_2O_3$ (300 ml) and a saturated aqueous solution of NaCl (300 ml), and then dried over anhydrous Na_2SO_4. After removal of the solvent under vacuum, compound IV was obtained as a colorless oil. Yield, 11.7 g (quantitative). R_f 0.52 (6). Mass spectrum, *m/z*: 333 (M^+).

2,3,5-Trichloro-3,6-dimethoxybenzyl Alcohol (IX). A). Na_2CO_3 (50 g) and 180 ml water were added to 11.9 g (35 mmoles) compound VIII and boiled with a reflux condenser for 53 h. The reaction mixture was diluted with water and extracted with chloroform (3 × 200 ml), washed with 600 ml 2% HCl and a saturated aqueous solution of NaCl (600 ml), and then dried over anhydrous Na_2SO_4. After removal of the solvent under vacuum, the residue was purified using column chromatography (chloroform–hexane, 1:1). Yield, 1.1 g (75%, based on the reacted compound VIII).

B). A solution of 11 g (33 mmoles) compound VIII in 100 ml of a 1:1 DMF–DMSO mixture was added dropwise at 0°C with stirring to a solution of 9.4 g (132 mmoles) KO_2 and 17.4 g (66 mmoles) 18-crown-6 in 200 ml of a 1:1 DMF–DMSO mixture. After stirring for 1 h at 0°C, ice water was added to the reaction mass and then it was filtered. The filtrate was extracted with chloroform (3 × 250 ml), washed with a saturated aqueous solution of NaCl (300 ml) and water (6 × 300 ml) and then dried over anhydrous Na_2SO_4. After removal of the solvent under vacuum, the residue and the filtered residue were purified using column chromatography (chloroform). Yield, 4.9 g (55%, based on reacted compound VIII).

TABLE 3. Synthesis of 4,5-Diethyl-1,2,3,6,7,8-hexamethyl-a,c-biladiene

Compound	Reagent	Solvent	Conditions	Yield, %	T_{mp} (T_{mp} [lit.]) °C
Benzylacetoacetate*	Benzyl alcohol, ethylacetoacetate	–	160...170 °C/45 min	83	142 - 44/11 mm Hg (162 - 167/15 mm Hg [16])
2-Benzyloxycarbonyl-4-ethyl-3,5-dimethylpyrrole	1. $NaNO_2$ 2. acac, Zn	AcOH (glacial)	1. 0 °C/3 h, 20 °C 12 h 2. Boiling/3 h	51	133 - 135 (135, [17])
2-Benzyloxycarbonyl-4-ethyl-3,5-dimethylpyrrole	$NaBH_4/Et_2O \cdot BF_3$	THF (anhydr.)	20 °C/3 h	89	103 - 105 (104 - 105, [18])
2-Benzyloxycarbonyl-3-methyl-4-ethyl-5-acetoxymethylpyrrole	$Pb(OAc)_4$	AcOH (glacial)	20 °C/2,5 h	85	122 - 124 (122, [20])
5,5'-Bis(benzyloxycarbonyl-4-,4'-dimethyl-3,3'-diethyl-2,2'-dipyrrolylmethane	–	AcOH (80%)	90 °C/1 h	78	127 - 128 (126 - 27, [20])
5,5'-Dicarboxy-4,4'-dimethyl-3,3'-diethyl-2,2'-dipyrrolylmethane	H_2/10% Pd/C	THF (anhydr.)	20 °C/24 h	100	166 (170, [19])
5,5'-Diformyl-4,4'-dimethyl-3,3'-diethyl-2,2'-dipyrrolylmethane	1. – 2. PhCOCl 3. Na_2CO_3	1. DMF 2. DMF 3. EtOH/H_2O (1 : 1)	1. Boiling/2 h 2. 20 °C/1 h 3. 70 °C/2 h	62	203 - 204 219 - 222, [21])
8,12-Diethyl-2,3,7,13,17,18-hexamethyl-a,c-biladiene dihydrobromide	3,4-Dimethylpyrrole 47% HBr	MeOH	1. 80 °C/8 min 2. 20 °C/2 h	95	–

*The boiling point at reduced pressure is given in the table.

C). A solution of 5.66 g (17 mmoles) compound VIII and 1.96 g (20 mmoles) potassium acetate in 100 ml 95% ethanol was boiled with a reflux condenser for 15 h. After cooling the reaction mass, the salt was filtered off; 5.5 g KOH was added to the filtrate and the solution was boiled with a reflux condenser for 8 h. Then the reaction mass was neutralized with 600 ml 5% HCl and filtered. The residue on the filter was washed with water and recrystallized from chloroform–hexane. Yield, 2.45 g (54%). R_f 0.53 (1). mp 130-132°C. Mass spectrum, m/z: 270 (M^+).

1-(2,4,5-Trichloro-3,6-dimethoxybenzyl)-2,5-dimethoxy-3,4-dimethylbenzene (XI). $AlCl_3$ (1.8 g, 13.5 mmoles) was added to a solution of 3 g (9 mmoles) compound VIII and 2.24 g (13.5 mmoles) X in 40 ml CS_2 and boiled with a reflux condenser for 2 h. After removal of the solvent under vacuum, the residue was dissolved in 200 ml chloroform, washed with water (2 × 200 ml), and then dried over anhydrous Na_2SO_4. The solvent was removed under vacuum, the residue was dissolved in 100 ml 95% EtOH, and then 10 ml of a 3 N solution of NaOH was added. After cooling down to 20°C, 2.8 ml (11.8 mmoles) Me_2SO_4 was added and this was boiled with a reflux condenser for 3 h. Then 10 ml of a 3 N solution of NaOH was added and this was stirred at 20°C for 12 h. The reaction mass was poured into 200 ml water and filtered. The filtrate was extracted with ether (2 × 200 ml) and washed with water (2 × 300 ml). After removal of the solvent under vacuum, the residue was recrystallized from ethanol. Yield 1.78 g (47%). R_f 0.58 (4). Mass spectrum, *m/z*: 418 (M^+). ^{1}H-NMR spectrum ($CDCl_3$, δ, ppm): 6.06 (1H, s, CH_{arom}); 4.23 (2H, s, CH_2); 3.89, 3.76, 3.65, 3.58 (3H, all s, OCH_3); 2.23, 2.10 (3H, all s, CH_3).

1-(2,4,5-Trichloro-3,6-dimethoxybenzyl)-3,4-bis(bromomethyl)-2,5-dimethoxybenzene (XII). A mixture of 1 g (2.4 mmoles) compound XI, 0.85 g (4.8 mmoles) N-bromosuccinimide, 25 ml dry CCl_4, and catalytic amounts of benzoyl peroxide were boiled with a reflux condenser with irradiation by a tungsten lamp for 20 min. After cooling, this was poured into 100 ml water and extracted with chloroform (3 × 50 ml), washed with a 10% aqueous solution of $Na_2S_2O_3$ (100 ml) and a saturated aqueous solution of NaCl (100 ml), and dried over anhydrous Na_2SO_4. After removal of the solvent under vacuum, the residue was purified using column chromatography (chloroform–hexane). Yield, 0.31 g (24%). R_f 0.75 (4): Mass spectrum, *m/z*: 576 (M^+). PMR spectrum ($CDCl_3$, δ, ppm): 6.26 (1H, s, CH_{arom}); 4.77, 4.73 (2H, all s, CH_2–Br); 4.23 (2H, s, CH_2); 3.96, 3.89 (3H, all s, OCH_3); 3.66 (6H, s, OCH_3).

1-Bromo-4-(2,2′-diethoxycarbonyl)ethylbenzene (XIV). This was obtained according to the technique in [11] from 25 g (0.1 mole) 4-bromobenzyl bromide XIII and 51.2 g (0.32 moles) of the diethyl ester of malonic acid. Yield, 20 g (61%). bp 188°C/11 mm Hg. According to the data in [11], bp is 176°C/4 mm Hg.

3-(4-bromophenyl)propionic Acid (XV). Hydrolysis and decarboxylation of compound XIV was done using the technique in [11] starting from 20 g (60 mmoles). Yield, 11.1 g (81%). mp 133-136°C. According to the data in [11], mp is 132-135°C.

6-Bromoindanone (XVI). Friedel–Crafts cyclization was done according to the technique in [11] from 4 g (17 mmole) compound XV. Yield, 2.9 g (81%). mp 108-110°C. According to the data in [11], mp is 109-110°C. Mass spectrum, *m/z*: 211 (M^+).

6′-Bromo-4,7-dimethoxy-6-(2,4,5-trichloro-3,6-dimethoxybenzyl)-2,2′-spirobiindan-1′-one (XVII). 0.03 g (0.75 mmole) 60% NaH was added to a solution of 0.28 g (0.5 mmole) compound XII and 0.1 g (0.5 mmole) XVI in 25 ml anhydrous THF and boiled with a reflux condenser for 2 h. Then 0.03 g NaH was added again and boiling was continued for 4 h. After cooling, ice water (50 ml) was added to the reaction mass and this was extracted with chloroform (2 × 75 ml), washed with a saturated aqueous solution of NaCl (100 ml), and then dried over anhydrous Na_2SO_4. After removal of the solvent under vacuum, the residue was purified by preparative TLC (chloroform–hexane). Yield, 0.05 g (16%). R_f 0.50 (4). Mass spectrum, *m/z*: 625 (M^+). IR spectrum (Vaseline oil, KBr), ν, cm^{-1}: 1710 (C=O), 1600, 1496 (V=C_{arom}). PMR spectrum ($CDCl_3$, δ, ppm): 7.58-7.30 (2H, m, CH_{arom}); 7.20 (1H, m, CH_{arom}); 6.24 (1H, s, CH_{arom}); 4.24 (2H, s, CH_2); 3.92 (3H, s, OCH_3); 3.89 (6H, s, OCH_3); 3.87 (3H, s, OCH_3); 3.70-3.45 (6H, s, spiro-CH_2).

2,5-Dimethoxycinnamic acid (XIX). A solution of 25 g (0.15 mole) 2,5-dimethoxybenzaldehyde, 21 g (0.2 mole) malonic acid, and 3 ml piperidine in 60 ml pyridine were heated at 110°C for 4 h. After cooling, the reaction mass was poured into a mixture of 250 ml concentrated hydrochloric acid and 250 g ice. The residue was filtered off and recrystallized from ethanol. Yield, 29.8 g (79.5%). R_f 0.76 (1). mp 151-152°C. According to the data in [12], mp 153-154°C.

3-(2,5-Dimethoxyphenyl)propionic acid (XX). 5% Pd/C (1.3 g) was added to a solution of 8.4 g (42 moles) compound XIX in 200 ml anhydrous THF and stirred for 24 h under a hydrogen atmosphere. The suspension was filtered through Hyflo Super Gel and the solvent was removed under vacuum. The residue was recrystallized from benzene–hexane. Yield, 8.5 g (100%). R_f 0.3 (1). mp 63-63.5°C. According to the data in [12], mp is 65-66°C.

4,7-Dimethoxyindanone (XXI). A mixture of 8 g (38 mmoles) compound XX and 80 g polyphosphoric acid were stirred at 57-60°C for 30 min. After cooling, 100 ml water was added dropwise maintaining the temperature of the reaction mass to at most 60°C. After this, the reaction mass was poured into 300 ml water and extracted with chloroform (3 × 150 ml), washed with saturated aqueous solutions of $NaHCO_3$ (300 ml) and NaCl (300 ml), and then dried over anhydrous Na_2SO_4. After removal of the solvent under vacuum, the residue was purified by column chromatography (chloroform). Yield, 4.6 g (63%). R_f 0.51 (1). mp 125-126°C. According to the data in [12], mp is 124.5-125°C.

4,7-Dimethoxy-6-(2,4,5-trichloro-3,6-dimethoxybenzyl)indanone (XXII). A mixture of 0.05 g IX (0.18 mmole), 0.07 g XXI (0.37 mmole), and 10 g PPA were stirred at 60°C for 45 min. After cooling, 30 ml water was added dropwise, maintaining the temperature of the reaction mass to at most 60°C. The reaction mass was diluted with water and extracted with chloroform (3 × 50 ml), washed with saturated aqueous solutions of $NaHCO_3$ (200 ml) and NaCl (200 ml), and then dried over anhydrous Na_2SO_4. After removal of the solvent under vacuum, the residue was purified by preparative TLC (chloroform). Yield, 0.07 g (85%). R_f 0.4 (3). Mass spectrum, *m/z*: 444 (M^+). IR spectrum (in Vaseline oil, KBr), ν, cm^{-1}: 1718 (C=O), 1598, 1502 ($C=C_{arom}$).

6′-Bromo-4,7-dimethoxy-6-(2,4,5-trichloro-3,6-dimethoxybenzyl)-2,2′-spirobiindan-1-one (XXIII). 0.1 g (2.5 mmole) 60% NaH was added to a solution of 0.75 g (1.7 mmoles) compound XXII and 0.58 g (1.7 mmoles) 3,4-bis(bromomethyl)bromobenzene in 70 ml anhydrous THF and boiled with a reflux condenser for 2 h. Then 0.1 g NaH was added again and boiling was continued for 12 h. After cooling, ice water (100 ml) was added to the reaction mass and this was extracted with chloroform (3 × 50 ml), washed with a saturated aqueous solution of NaCl (200 ml), and then dried over anhydrous Na_2SO_4. After removal of the solvent under vacuum, the residue was purified by preparative TLC (chloroform–hexane). Yield, 0.54 g (72%). R_f 0.42 (4). Mass spectrum, *m/z*: 625 (M^+). IR spectrum (in Vaseline oil, KBr), ν, cm^{-1}: 1720 (C=O), 1596, 1494 ($C=C_{arom}$).

6′-Bromo-4,7-dimethoxy-6-(2,4,5-trichloro-3,6-dimethoxybenzyl)-2,2′-spirobiindane (XXIV). Triethylsilane (0.31 g g, 2.7 mmoles) was added to a solution of 0.67 g (1.07 mmoles) compound XXIII in 30 ml trifluoroacetic acid and stirred at room temperature for 23 h. After removal of the trifluoroacetic acid at reduced pressure, the residue was dissolved in 100 ml chloroform and washed with saturated aqueous solutions of $NaHCO_3$ (2 × 100 ml) and NaCl (200 ml), and then dried over anhydrous Na_2SO_4. After removal of the solvent under vacuum, the residue was purified by preparative TLC (chloroform–hexane). Yield, 0.61 g (94%). R_f 0.53 (5). Mass spectrum, *m/z*: 611 (M^+). IR spectrum (in Vaseline oil, KBr), ν, cm^{-1}: 1598, 1502 ($C=C_{arom}$).

6′-Formyl-4,7-dimethoxy-6-(2,4,5-trichloro-3,6-dimethoxybenzyl)-2,2′-spirobiindane (III). A solution of 1.15 g (1.9 mmoles) compound XXIV in 70 ml anhydrous THF was cooled down to −78°C and 2.4 ml (3.8 mmoles) n-butyllithium was added with stirring under a nitrogen atmosphere. After 5 min, 1.6 ml (21 mmoles) freshly distilled DMF was added and this was stirred at −78°C for 1 h. After the temperature of the reaction mass reached 20°C, 50 ml of a saturated aqueous solution of NH_4Cl was added. This was extracted with chloroform (3 × 100 ml), washed with a saturated aqueous solution of NaCl (2 × 200 ml), and then dried over anhydrous Na_2SO_4. After removal of the solvent under vacuum, the residue purified by column chromatography on silica gel (chloroform–hexane). Yield, 0.6 g (65%). R_f 0.31 (4). Mass spectrum, *m/z*: 560 (M^+).

5-[4,7-dimethoxy-6-(2,4,5-trichloro-3,6-dimethoxybenzyl)-2,2′-spirobiindan-6′-yl]-13,17-diethyl-2,3,7,8,12,18-hexamethylporphyrin (XXVa). 2 drops of 30% HBr in AcOH was added to a solution of 48 mg (0.09 mmole) compound III and 58 mg (0.1 mmole) a,c-biladiene II in 40 ml dry methanol. This was boiled with a reflux condenser for 24 h. After cooling the reaction mass was poured into 200 ml water, extracted with methylene chloride (3 × 100 ml), washed with a saturated aqueous solution of $NaHCO_3$ (2 × 200 ml) and water (4 × 200 ml) and dried over anhydrous Na_2SO_4. After removal of the solvent under vacuum, the residue was purified by preparative TLC (CH_2Cl_2). Yield, 7 mg (8%). R_f 0.64 (2). Mass spectrum, *m/z*: 983 $[M+3H]^+$. Electronic spectrum (acetone), λ_{max}, nm (log ε): 623.0 (3.66), 570 (3.90), 530 (3.92), 498.9 (4.23), 398 (5.23). PMR spectrum ($CDCl_3$, δ, ppm): 10.15, 10.14, 9.93 (1H, all s, meso-H), 7.85-7.81 (2H, m, CH_{arom}); 7.53 (1H, d, J = 7.3 Hz, CH_{arom}); 6.18 (1H, s, CH_{arom}); 4.26 (2H, s, CH_2); 4.07 (4H, q, J = 7.63 Hz, $\underline{CH_2}CH_3$); 3.91, 3.87, 3.72, 3.69 (3H, all s, OCH_3); 3.64 (6H, s, $CH_{3\ porph}$); 3.54, 3.53 (3H, all s, $CH_{3\ porph}$); 3.34 (2H, s, spiro-CH_2); 3.28, 3.27 (1H, s, spiro-CH_2); 3.23 (2H, s, spiro-CH_2); 3.13, 3.11 (1H, s, spiro-CH_2); 2.52 (6H, s, 3-, 7-CH_{3porph}); 1.83 (6H, t, J = 7.63 Hz, $CH_2\underline{CH_3}$); −3.19 (2H, br.s, NH_{porph}).

5[6-(2,4,5-trichloro-1,4-cyclohexadiene-3,6-dion-1-yl)methyl-2,2′-spirobiindane-4,7-dion-6′-yl]-13,17-diethyl-2,3,7,8,12,18-hexamethylporphyrin (Ia). A solution of 0.7 ml (7.5 mmoles) BBr_3 in 5 ml dry CH_2Cl_2 at 0°C was added to a solution of 34 mg (0.04 mmole) porphyrin XXV in 20 ml dry CH_2Cl_2. This was stirred for 21 h at 20°C. The reaction mass

was poured into 100 ml water and extracted with methylene chloride (3 × 50 ml), washed with saturated aqueous solutions of $NaHCO_3$ (2 × 200 ml) and NaCl (200 ml), and then dried over anhydrous Na_2SO_4. After removal of the solvent under vacuum, the residue was dissolved in 20 ml CH_2Cl_2 and 0.45 g (1.9 mmoles) lead dioxide was added with stirring. After stirring for 19 h at 20°C, the reaction mass was filtered. After removal of the solvent, the residue was purified by preparative TLC (CH_2Cl_2). Yield, 7 mg (22%). R_f 0.41 (2). Mass spectrum, *m/z*: 921 $[M+H]^+$. Electronic spectrum (acetone), λ_{max}: 623.0, 570.1, 531, 499, 397.6 nm. PMR spectrum ($CDCl_3$): 10.12 (2H, s, meso-H); 9.91 (1H, s, meso-H); 7.78 (1H, d, J = 7.3 Hz, CH_{arom}); 7.67 (1H, s, CH_{arom}); 7.43 (1H, d, J = 7.3 Hz, CH_{arom}); 6.13 (1H, s, CH_{arom}); 4.05 (2H, s, CH_2); 4.04 (4H, q, J = 7.63 Hz, $\underline{CH_2}CH_3$); 3.61 (6H, s, $CH_{3\ porph}$); 3.51, 3.50 (3H, all s, $CH_{3\ porph}$); 3.21-2.86 (8H, m, spiro-CH_2); 2.41 (6H, s, 3-, 7-$CH_{3\ porph}$); 1.86 ppm. (6H, t, J = 7.63 Hz, $CH_2\underline{CH_3}$).

General Technique for Obtaining Zinc Complexes (Ib, XXVb). A saturated solution (2 ml) of zinc acetate in methanol was added to a solution of 5.1 mmoles of porphyrin in 20 ml CH_2Cl_2, and the reaction mass was stirred at 30°C for 1 h, washed with water (3 × 30 ml), and dried over anhydrous Na_2SO_4. After removal of the solvent under vacuum, the residue was purified by column chromatography on silica gel, eluting with CH_2Cl_2; the zinc complex was obtained in quantitative yield.

XXVb. R_f 0.59 (4). Mass spectrum, *m/z*: 1044 $[M+H]^+$. Electronic spectrum (acetone), λ_{max} (log ε): 573, 536.9, 407.8 nm. PMR spectrum ($CDCl_3$): 10.17, 10.16, 10.07 (1H, all s, meso-H), 7.88-7.82 (1H, m, CH_{arom}); 7.83 (1H, s, CH_{arom}); 7.53 (1H, d, J = 7.83 Hz, CH_{arom}); 6.18 (1H, s, CH_{arom}); 4.27 (2H, s, CH_2), 4.11 (4H, q, J = 7.56 Hz, $\underline{CH_2}CH_3$); 3.91, 3.88, 3.72, 3.70 (3H, all s, OCH_3), 3.65 (6H, s, $CH_{3\ porph}$); 3.56, 3.55 (3H, all s, $CH_{3\ porph}$); 3.35 (2H, s, spiro-CH_2); 3.29, 3.28 (1H, s, spiro-CH_2); 3.23 (2H, s, spiro-CH_2); 3.15, 3.13 (1H, s, spiro-CH_2); 2.53 (6H, s, 3-, 7-$CH_{3\ porph}$); 1.90 ppm. (6H, t, J = 7.63 Hz, $CH_2\underline{CH_3}$).

Ib. R_f 0.25 (4). Mass spectrum, *m/z*: 983 (M^+). Electronic spectrum (acetone), λ_{max}: 573.0, 537.2, 407.4 nm. PMR spectrum ($CDCl_3$): 10.17 (2H, s, meso-H); 10.07 (1H, s, meso-H); 7.87 (1H, d, J = 7.3 Hz, CH_{arom}); 7.85 (1H, s, CH_{arom}); 7.58-7.50 (1H, m, CH_{arom}); 6.10 (1H, s, CH_{arom} of quinone); 4.20 (2H, s, CH_2); 4.11 (4H, q, J = 7.56 Hz, $\underline{CH_2}CH_3$); 3.65 (6H, s, $CH_{3\ porph}$); 3.55 (6H, s, $CH_{3\ porph}$); 3.36 (2H, s, spiro-CH_2); 3.24 (2H, s, spiro-CH_2); 3.12 (2H, s, spiro-CH_2); 3.11 (2H, s, spiro-CH_2); 2.50 (6H, s, 3-, 7-$CH_{3\ porph}$); 1.90 ppm. (6H, t, J = 7.56 Hz, $CH_2\underline{CH_3}$).

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