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Tetraoxa[24]porphyrinogen(4.0.4.0)/Tetraoxa[22]porphyrin(4.0.4.0) dication A further Isomer of the Aromatic 22π-Tetraoxaporphyrins

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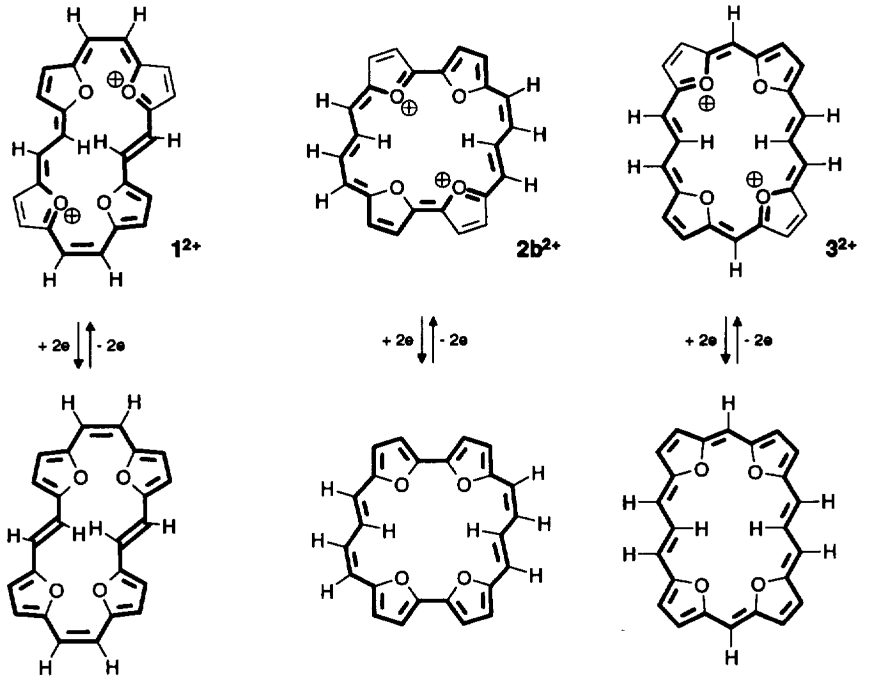
Abstract: While the antiaromatic tetraoxa[24]porphyrinogen(2.2.2.2) 1 (*trans,cis,trans,cis*) and the corresponding aromatic dication 1^{2+} have been published recently, the synthesis of the title compounds is described for the first time. Beside the *cis,trans,cis,trans*-tetraoxa[24]porphyrinogen(4.0.4.0) **2b** the isomeric porphyrinogens **2a** (*trans*, cis,*cis,trans*) and **2c** (all-*trans* in the *cisoid* conformation) could be isolated. The tetraoxa[22]porphyrin(4.0.4.0) dication is an aromatic 22π-system, it exists only in the *cis,trans,cis,trans*-configuration. The dication $\mathbf{2b}^{2+}$ can be reduced with tetrakis-N,N-dimethylaminoethene to give pure porphyrinogen **2b**. The electrochemistry of the system **2**/$\mathbf{2b}^{2+}$ and AM1 calculations are described.

Of the three isomeric, aromatic and dicationic tetraoxa[22]porphyrins $\mathbf{1}^{2+}$, $\mathbf{2}^{2+}$ and $\mathbf{3}^{2+}$, and their corresponding antiaromatic tetraoxa[24]porphyrinogens **1**, **2** and **3**, recently the [24]porphyrinogen(2.2.2.2)/[22]-porphyrin(2.2.2.2) dication redox pair **1**/$\mathbf{1}^{2+}$ has been described.[1]

The temperature-dependent ^{1}H NMR spectra indicate that the porphyrinogen **1** possesses a highly dynamic ring system, whereby the *trans* double bonds rotate around the adjacent sigma bonds at temperatures down to –80 °C.[2]

In light of these interesting findings, it appeared worthwhile to investigate the configurational, conformational and dynamic properties of the hitherto unknown isomeric tetraoxa[24]porphyrinogens **2** and **3**. These compounds are of additional interest because the corresponding porphyrins(4.0.4.0) and (3.1.3.1) are not yet known. Here we report on the system **2**/$\mathbf{2}^{2+}$. For the porphyrinogen **2** should exist six possible conformations in the all-*trans* configuration [3] {bis-*cisoid*: (aa), (ai), (ii); bis-*transoid*; *transoid*/*cisoid* (a); *transoid*/*cisoid* (i)} and two *cis*/*trans*-configurations {*trans,cis,cis,trans*, (**2a**); *cis,trans,cis,trans* (**2b**)}.

In contrast to **1**, which like the tetraoxa[20]porphyrinogen(2.0.2.0) [4] and the porphycen [5] is obtained by cyclization of the respective dialdehydes through a McMurry-type coupling reaction, the porphyrinogens **2** and **3** can not be prepared in this way. A successful synthesis of **2** can be achieved through use of a cyclizing double Wittig reaction,[6] whereby the bis-ylid, formed from the bisphosphonium salt **6**, reacts with the dialdehyde **7**.

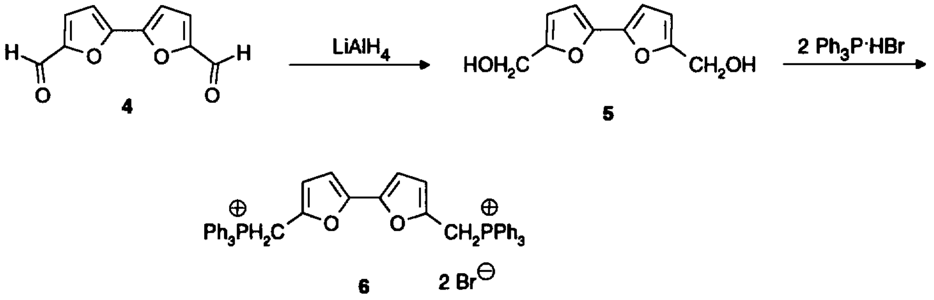


1^{2+} $2b^{2+}$ 3^{2+}

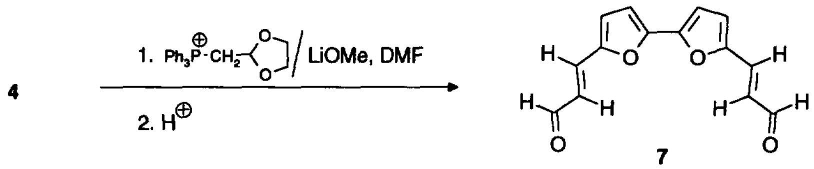
1 **2b** (cis,*trans*,*cis*,*trans*) **3**

Formation of the [24]Tetraoxaporphyrinogen(4.0.4.0) (2)

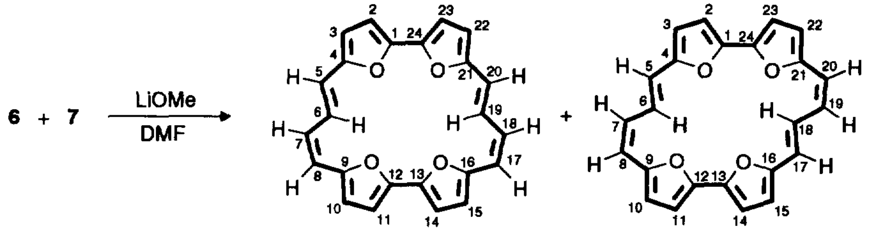
The key intermediate in this synthesis is 5,5'-diformyl-2,2'-difuran **4**,[7] which is prepared through an Ullmann coupling reaction of iodofurfural with Cu-bronze. Iodofurfural [8] is synthesized in a 78% yield from 5-bromofurfural,[9] which had been prepared from furfural in a 38% yield. The dialdehyde **4** can be reduced to 2,2'-difuryl-5,5'-biscarbinol **5** [10] with $LiAlH_4$ in nearly quantitative yield. By reacting **5** with $PPh_3 \times HBr$ in dry acetonitrile, 2,2'-difuryl-5,5'-diylbis(methylenetriphenylphosphonium bromide) **6** is formed. To obtain **7**, the second intermediate required for the synthesis of **2**, the dialdehyde **4** is allowed to react with 1,3-dioxolan-2-yl-methyltriphenylphosphonium bromide by Wittig reaction. The ^1H NMR spectrum (250 MHz, DMSO-d_6) of **7** shows a coupling constant of ^3J = 15.7 Hz for the α- and β-protons, which is consistent with a *trans*-configurated aldehyde.



4 **5** **6**



The successful formation of the cyclization product **2** is possible following the so called Ruggli-Ziegler-dilution principle by the very slow addition of MeOLi/methanol (30 h at 120 °C) to the reaction mixture of **6**/**7** in dry DMF. After allowing to continue the reaction an additional 24 h at 120 °C, the reaction-mixture is worked-up under hydrolyzing conditions and triphenylphosphine oxide is separated by silica gel chromatography (mobile phase of CH_2Cl_2) to give a red product (m.p. 220-225 °C) in 15% yield. The mass spectrum (70 eV) is in agreement with the structure of **2**, while the rather complex ^1H NMR spectrum (400 MHz, $CDCl_3$) (**Fig. 1a**) indicates a mixture of two tetraoxa[24]porphyrinogen (4.0.4.0) isomers as the main products and traces (1 and 3%) of two additional isomers.



2a (*trans,cis,cis,trans*) C_{2v} **2b** (cis,*trans,cis,trans*) C_{2h}

By chromatography on silica gel (mobile phase: ethyl acetate/*n*-hexane, v/v = 1:5), the main product is obtained as dark-red needles (m.p. 255-263 °C); the ^1H COSY spectra and NOE difference spectra confirm a 1:1 mixture of **2a** and **2b**. With the aid of the ^1H NMR spectrum of pure **2b** (see below), the ^1H NMR signals for **2a** and **2b** (**Fig. 1a**) can be assigned unequivocally. The signals centered at δ = 10.88 (m) and 11.91 (dd) ppm indicate that the protons H-6 and H-19 resp. H-18 are oriented towards the inside (the inner perimeter protons) of the paratropic, antiaromatic ring system of **2**.

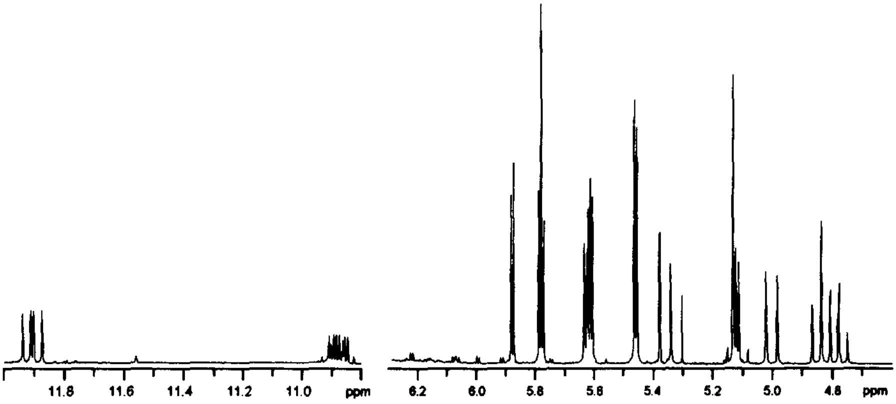


Fig. 1a: ^1H NMR spectra of the porphyrinogen-mixture **2** formed after 24 h reaction time (400 MHz, $CDCl_3$/TMS).

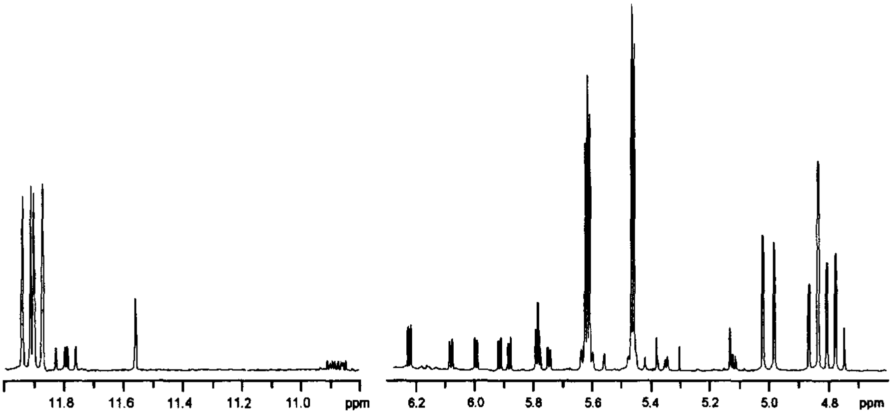


Fig. 1b: ^1H NMR spectra of the porphyrinogen-mixture **2** formed after 72 h reaction time (400 MHz, $CDCl_3$/TMS).

AM1 calculations[14] of the different possible *cis*/*trans*-isomers of **2** confirm that **2b** (*cis,trans,cis,trans*) is the energetically most stable isomer (ΔH_f^{AM1} = 94.87 kcal/mol). At 97.26 kcal/mol, the ΔH_f^{AM1} value of **2a** (*trans,cis,cis,trans*) is 2.4 kcal/mol higher than that of **2b**. Both minima deviate from a planar geometry, forming boat-like structures. In addition, a planar structure for **2b** with exact C_{2h} symmetry is found at only 0.47 kcal/mol above the energy minimum of **2b**. This planar structure is very likely the transition state for a degenerate ring inversion of **2b**. All the other calculated geometric isomers of **2** are lying energetically at least 9 kcal/mol above **2b**.

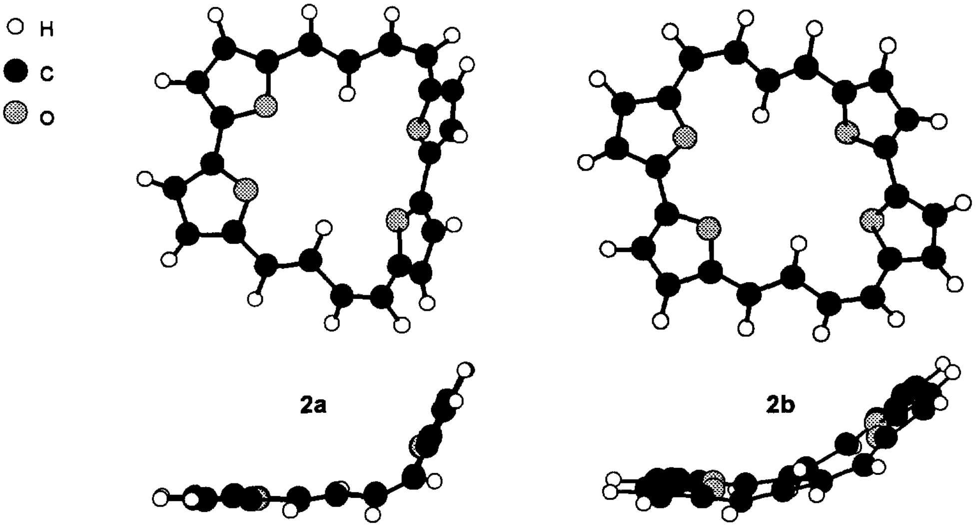
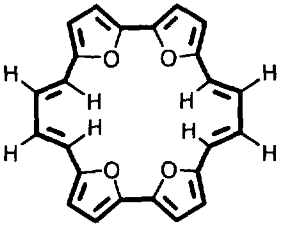


Fig. 2: Plot drawing of the structural minima for **2a** (*trans,cis,cis,trans*) and **2b** (*cis,trans,cis,trans*) obtained from semiempirical calculations.

These by calculations defined configurationally and conformationally isomeric relationships are confirmed by the experimental result, that the ratio of **2a** to **2b** depends on the length of the reaction time. With the help of 400 MHz ^{1}H NMR, it was possible to follow the ratio of **2a/2b** as a function of time. While the relative yields of both **2a** and **2b** were 48% 24 h after the addition of Li-methanolate (with the other two isomers at 1 and 3%), it was found, that after an additional 72 h reaction period the yield of **2a** dropped to just 7% and that of **2b** rose to 73%, while the yields of the other two isomers increased to 10% each (**Fig. 1b**).

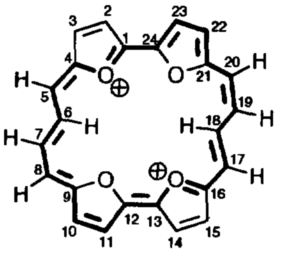
It can be assumed that during the Wittig reaction of **6** and **7** the expected isomer **2a** forms initially (by carbonyl olefination with non resonance stabilized alkylidene phosphoranes preferentially the *cis*-alkenes are formed [11]), which then rearranges to the thermodynamically more stable isomer **2b**. Spectroscopic data indicate in all probability that the isomer that forms with the original 3% yield is the all-*trans* compound **2c** (i.e., a *cis/trans*-isomerization of both *cis* bonds in **2a**).



2c

Formation of the [22]Tetraoxaporphyrin(4.0.4.0)dication ($2b^{2+}$)

The oxidation of the isomeric mixture of **2a** and **2b** with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) in dichloromethane at 0 °C, followed by the addition of perchloric acid, yields as the sole product the aromatic *cis,trans,cis,trans*-tetroxa[22]porphyrin(4.0.4.0)-bisperchlorate $\mathbf{2b^{2+}}$ $(ClO_4^-)_2$ in the form of blue, shiny metallic needles, m.p. > 300 °C (decomp.) with a yield of 90%.



$\mathbf{2b^{2+}}$ *(cis,trans,cis,trans)*

The 1H-NMR-Spectrum of $\mathbf{2b^{2+}}$ (**Fig. 3**) confirms the *cis,trans,cis,trans*-configuration with C_{2h} symmetry, the UV/VIS spectrum (Fig. 4) with the SORET-bands proofs the porphyrin character.

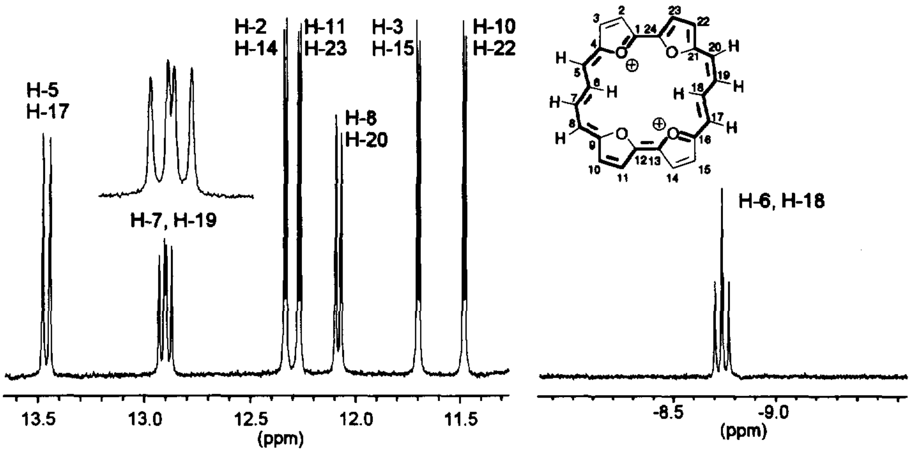


Fig. 3: ^{1}H NMR spectrum of **2b**$^{2+}$ (400 MHz, CF_3COOD/TMS).

The assignments of the ^{1}H NMR signals (experimental section) were made possible with NOE-difference spectra and COSY experiments. The chemical shifts of the protons oriented towards the outside (outer perimeter protons) (δ = 12.91-13.46 ppm) and those oriented towards the inside (inner perimeter protons) (i.e. H-6 and H-18, δ = –8.73 ppm) of the ring, with $\Delta\delta$ values of 21.64 and 22.19 ppm, respectively, indicate the presence of the expected aromatic, diatropic system.

In **Fig. 4** the UV/VIS spectrum of **2b**$^{2+}$ is compared with that from the tetraoxa[22]porphyrin(2.2.2.2) dication **1**$^{2+}$. The UV/VIS spectra of both bridged 22π-annulenes are very similar, however, the long wavelength absorption maxima in **2b**$^{2+}$ are shifted bathochromic by approximately 50 nm relative to **1**$^{2+}$.

Considering that the DDQ oxidation of the isomeric mixture of **2a** and **2b** leads solely to the dication **2b**$^{2+}$, it is reasonable to assume that the *cis/trans*-isomerization occurs on the oxidation level of the initially formed radical cation **2**$^{+\bullet}$ which results in the formation of the thermodynamically most stable dication **2b**$^{2+}$.

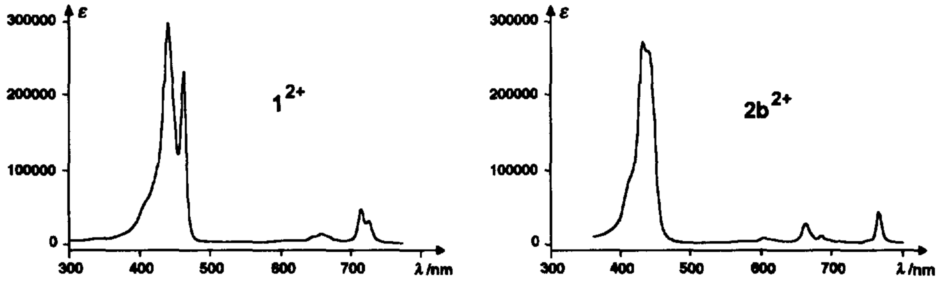
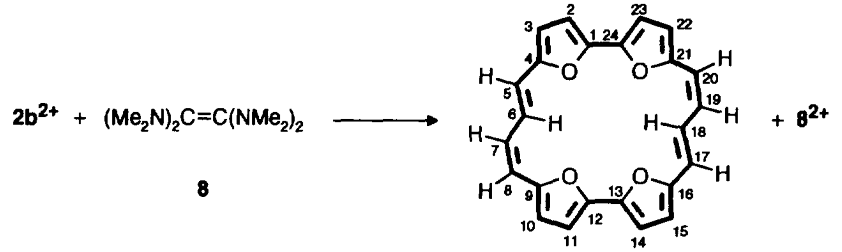


Fig. 4: UV/VIS spectra of **1**$^{2+}$ and **2b**$^{2+}$ (70% $HClO_4$).

Formation of *cis,trans,cis,trans*[24]Tetraoxaporphyrinogen(4.0.4.0) (2b) by Reduction of $2b^{2+}$

Because it had not been possible to separate the mixture of the porphyrinogens **2a**/**2b**, we tried to reduce the dication $2b^{2+}$ which has a defined *cis,trans,cis,trans* structure, to the [24]porphyrinogen **2**. We found that tetrakis-N,N-dimethylaminoethene [12] **8** is particularly well suited for reducing the porphyrinogen dication, in this case $2b^{2+}$ even at 0 °C, in fact, $2b^{2+}$ can be titrated with **8**. Under these particularly mild reducing conditions, it was expected that the stereochemistry of $2b^{2+}$ would be maintained in the porphyrinogen **2**; the ^{1}H NMR spectrum (**Fig. 5**) confirms that $2b^{2+}$ is converted to isomerically pure *cis,trans,cis,trans*-**2b**.



2b (*cis,trans,cis,trans*)

The assignment of the ^{1}H NMR signals for **2b** is based on the NOE difference spectra and on COSY experiments.

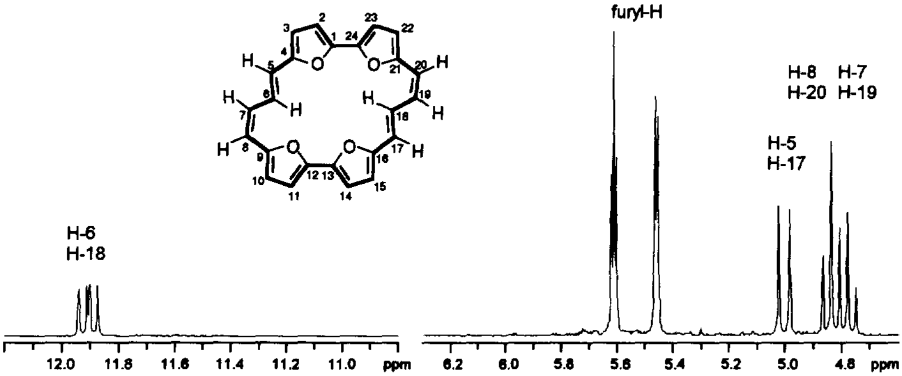


Fig. 5: ^{1}H NMR spectrum of the porphyrinogen **2b** (400 MHz, $CDCl_3$/TMS).

Upon conversion of the paratropic, antiaromatic porphyrinogen **2b** into the diatropic, aromatic dication $2b^{2+}$, the inner perimeter protons H-6 and H-18, which are oriented towards the inside of the ring, are high-field shifted by $\Delta\delta = 20.64$ ppm, while the three sets of protons that are oriented towards the outside of the ring (outer perimeterprotons); that is H-5 and H-17, H-7 and H-19, and H-8 and H-20, are low-field shifted by $\Delta\delta$ = 8.45, 8.11 and 7.23 ppm, respectively.

The ^{13}C NMR spectrum of **2b** (**Table 2**) shows the expected 4 signals for the quaternary and 8 signals for the tertiary C-atoms.

With the ^1H NMR data for the pure porphyrinogen **2b** (**Table 2** and **Fig. 5**), it was now possible to unequivocally identify the spectrum of **2a** in the ^1H NMR spectrum of the mixture of **2a**/**2b**. The NMR data for the *trans,cis,cis,trans*-isomer **2a**, which was obtained by subtracting the spectrum of **2b** from that of the mixture of **2a**/**2b** are listed in the experimental section.

In agreement with the antiaromatic, paratropic properties of **2a**, the inner perimeter protons H-6 and H-19 are at 11.19 ppm, while the outer perimeter protons H-5 and H-20, H-7 and H-18, and H-8 and H-17 are located at 5.08, 4.95 and 4.94 ppm, respectively. In contrast to the [24]porphyrinogen(2.2.2.2) **1**, the porphyrinogens **2a** and **2b** are conformationally stable; that is the ^1H NMR spectra show no temperature dependency in the range between –50 °C and 120 °C.

Electrochemistry of the Tetraoxa[24]porphyrinogens 2 and the Dication 2^{2+}

The electrochemical properties of the porphyrinogens **1** and **2b**, as well as the dications $\mathbf{1}^{2+}$ and $\mathbf{2b}^{2+}$, were investigated by cyclovoltammetry (CV) and spectroelectrochemistry. As can be seen in **Fig. 6**, the cyclovoltammograms of the (4.0.4.0)porphyrinogen **2b** and of the (2.2.2.2)porphyrinogen **1**, as well as of the dications $\mathbf{2b}^{2+}$ and $\mathbf{1}^{2+}$, are very similar.

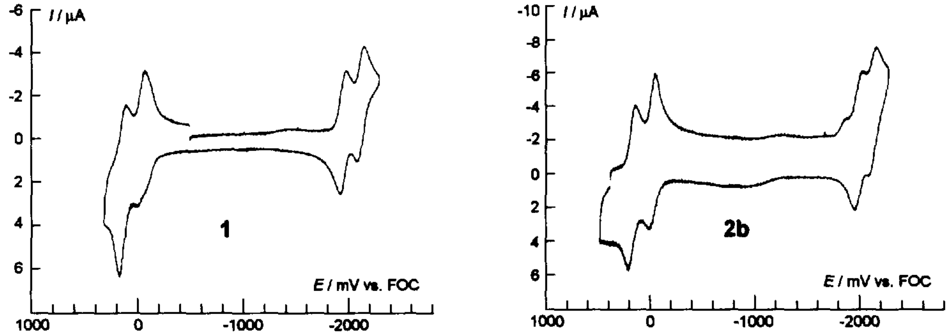


Fig. 6: Cyclovoltammograms of **1** and **2b**.

The reductions of the annulene dications $\mathbf{2b}^{2+}$ and $\mathbf{1}^{2+}$ to their corresponding dianions are both reversible and proceed through 4 separate one-electron transfer steps, as shown in the following scheme:

$$1^{2+}, 2b^{2+} \overset{\mathbf{a}}{\underset{-1e}{\overset{+1e}{\rightleftarrows}}} 1^{+\bullet}, 2b^{+\bullet} \overset{\mathbf{b}}{\underset{-1e}{\overset{+1e}{\rightleftarrows}}} 1, 2b \overset{\mathbf{c}}{\underset{-1e}{\overset{+1e}{\rightleftarrows}}} 1^{-\bullet}, 2^{-\bullet\,*)} \overset{\mathbf{d}}{\underset{-1e}{\overset{+1e}{\rightleftarrows}}} 1^{2-}, 2^{2-\,*)}$$

*) The stereochemistry is not defined in the case of the radical anions and dianions of **2**.

From the position of the half-wave potentials it is clear that both **1** and **2** have nearly identical electrochemical behavior. The difference in the potential of the redox steps (b) and (c) is an estimation of the HOMO/LUMO energy difference. For **2b** this difference is $\Delta E = 1970$ mV. The half-wave potentials and the potential differences for the individual redox processes for compounds **1** and **2b** are given in **Table 1**.

Table 1: Half-wave potentials for **1** and **2b** (potentials are given in mV vs FOC/FOC$^+$) (FOC = Ferrocene).

E	**1** (2.2.2.2)	ΔE	**2b** (4.0.4.0)	ΔE
$E_{1/2}$Ox II (a)	+150		+170	
		180		190
$E_{1/2}$Ox I (b)	–30		–20	
		1910		1970
$E_{1/2}$Red I (c)	–1940		–1990	
		170		130
$E_{1/2}$Red II (d)	–2110		–2120	

The spectroelectrochemical investigations [13] confirm the four-step reduction of $\mathbf{2b}^{2+}$ to $\mathbf{2}^{2-}$. The changes in the UV/VIS absorption bands during the individual electron transfer steps are listed in **Table 2**. **Fig. 7** shows the formation of the radical cation $\mathbf{2b}^{+\bullet}$ from $\mathbf{2b}^{2+}$ as well as the radical anion $\mathbf{2}^{-\bullet}$ from the oxygen bridged [24]annulen **2b**. The reversibility of the processes (a) to (c) are further confirmed by the presence of isosbestic points. The further reduction of the radical anion $\mathbf{2}^{-\bullet}$ leads to the formation of the dianion $\mathbf{2}^{2-}$, however, its formation is observed only initially since it undergoes rapidly an irreversible succeeding reaction. The reason is the very low velocity of the potential change in the spectrochemical technique compared to the CV technique.

Table 2: Summary of the changes in the UV/VIS absorption bands from the spectroelectrochemical experiments.

	position of the maxima [nm]*
$\mathbf{2b}^{2+} \rightarrow \mathbf{2b}^{+\bullet}$	346 (↑), 428 (↓), 600 (↓), 658 (↓), 683 (↓), 765 (↓), 810 (↑), ca. 1350 (↑)
$\mathbf{2b}^{+\bullet} \rightarrow \mathbf{2b}$	343 (↑), 428 (↓), 808 (↓), ca. 1335 (↓)
$\mathbf{2b} \rightarrow \mathbf{2}^{-\bullet}$	254 (↑), 331, 343 (↓), 391, 417, 484 (↑), 850, 980, 1155 (↑)
$\mathbf{2}^{-\bullet} \rightarrow \mathbf{2}^{2-}$	262 (↑), 390, 416 (↓), 488 (↑), 707, 769, 805 (↑), 990, 1155 (↓)

*) (↑): increasing bands; (↓): decreasing bands

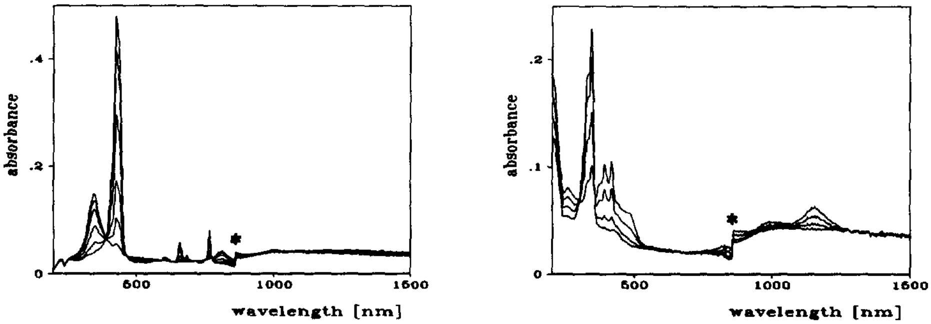


Fig. 7a: Spectroelectrograms of **2b**; left: reduction of $\mathbf{2b}^{2+}$ to $\mathbf{2b}^{+\bullet}$; right: reduction of **2b** to $\mathbf{2}^{-\bullet}$; (* an artefact from the detector change of the spectrometer).

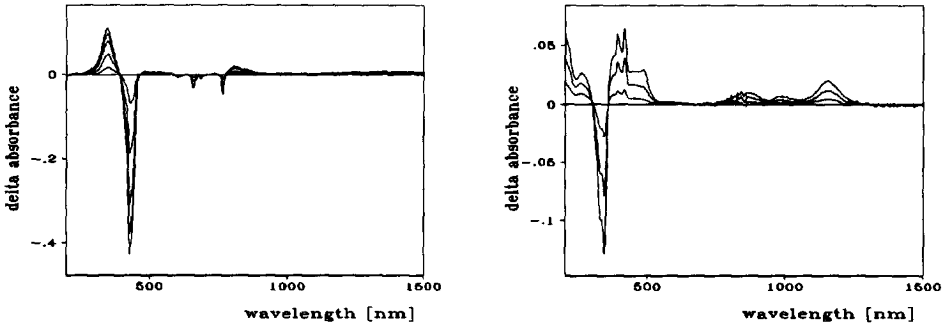


Fig. 7b: Difference spectroelectrograms of **2b**; left: reduction of $\mathbf{2b}^{2+}$ to $\mathbf{2b}^{+\bullet}$; right: reduction of **2b** to $\mathbf{2}^{-\bullet}$.

The spectroelectrograms of the tetraoxa[22]porphyrin(2.2.2.2) dication $\mathbf{1}^{2+}$ [15] and of the tetraoxa[22]porphyrin(4.0.4.0) dication $\mathbf{2b}^{2+}$ are nearly identical (**Fig. 8a and 8b**).

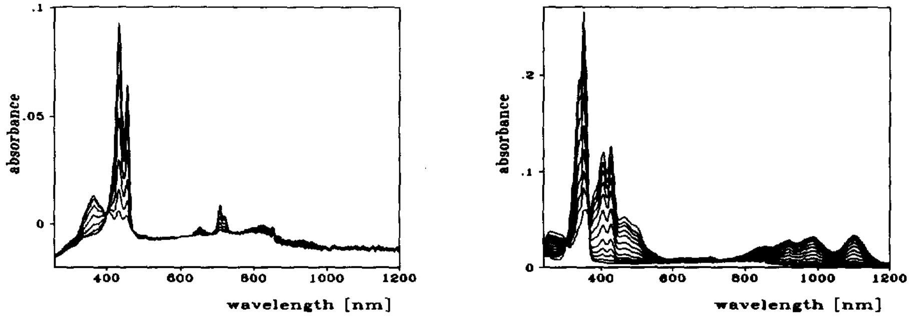


Fig. 8a: Spectroelectrograms of **1**; left: reduction of $\mathbf{1}^{2+}$ to $\mathbf{1}^{+\bullet}$; right: reduction of **1** to $\mathbf{1}^{-\bullet}$.

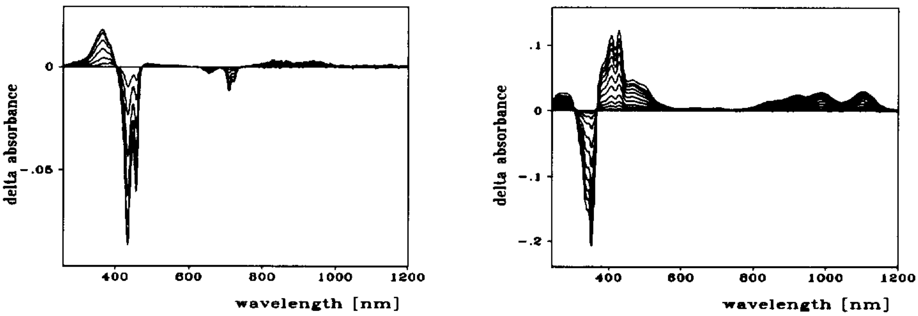
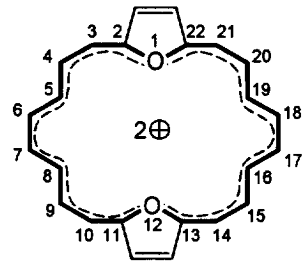


Fig. 8b: Difference spectroelectrograms of **1**; left: reduction of $\mathbf{1}^{2+}$ to $\mathbf{1}^{+\bullet}$; right: reduction of **1** to $\mathbf{1}^{-\bullet}$.

The electronic spectra of $\mathbf{1}^{2+}$ and $\mathbf{2b}^{2+}$, as well as the electrochemical data of **1** and **2b**, show that the positions of the epoxi-bridges in the ethylene bridged dioxa[22]perimeter dication **9** (**Fig. 9**) are irrelevant with regard to the electronic properties of these compounds.



9

Epoxi-bridges in **9**
→ **1**: 5,8; 16,19;
→ **2**: 3,6; 14,17;
→ **3**: 4,7; 15,18;

Fig. 9: Epoxi-bridges in the [22]perimeter dication **9** (the stereochemistry of **9** is arbitrarily chosen) to the tetraoxa[22]porphyrin dications **1**, **2** and **3**.

EXPERIMENTAL

The ^{1}H NMR spectra were measured on a Bruker ARX 400 spectrometer at a frequency of 400.13 MHz (samples **2**, **2a**, **2b**, $\mathbf{2b}^{2+}$, **6**) and on a Bruker AC 250 spectrometer at 250.13 MHz (samples **5** and **7**). In all cases TMS was added for chemical shift reference. The ^{13}C NMR spectra were measured on a Bruker ARX 400 spectrometer at a frequency of 100.61 MHz, the ^{31}P NMR spectra were recorded on a Bruker ARX 400 spectrometer at a frequency of 162 MHz, shift reference H_3PO_4 85perc., extern. Due to the extremely different solubility of the mentioned compounds a various number of solvents has been used for recording the NMR spectra.

The computational studies were carried out with the VAMP 5.01 [14] software running on a SGI INDY R 4600 workstation. All semiempiric quantum mechanical calculations were done using the AM1 method as a closed-shell according to the RHF formalism without symmetry restrictions. The minimum structures and transition states were characterized by vibrational analysis using the keyword FORCE.

Electrochemical measurements were carried out in acetonitrile/tetra-*n*-butyl-ammonium-hexafluorophosphate (0.1 M) with a pseudo-reference electrode of Ag/AgCl. Internal calibration was done by using the first reduction of anthraquinone and converted to the potential for FOC. Cyclovoltammetry: Amel System 5000, working electrode: Pt-plate electrode; spectroelectrochemistry: Potentiostat/Galvoanostat Amel 550, UV/VIS/NIR Spectrometer Perkin-Elmer Lambda 9, working electrode: minigrid-gold mesh [13].

5,5'-Diformyl-2,2'-difuran (4) [7]

In a 100 mL round bottom flask fitted with a water-cooled condenser, 15.5 g (70.0 mmol) of 5-iodofurfural and 4.45 g (70.0 mmol) of activated copper-bronze were made to react in 27 mL DMF at 100 °C for 3 d. The progress of the reaction was followed by TLC. Following the removal of the solvent under reduced pressure, the brown residue was sublimed (200 °C/ 0.05 Torr) to give 3.18 g (48% yield) **4** as a yellow powder, m.p. 260-262 °C. (lit.: m.p. 263-265 °C, yield 50%); IR (KBr): $\bar{\nu}$ [cm^{-1}] = 1660 (C=O, s).

2,2'-Difuryl-5,5'-biscarbinol (5)

In a 250 mL three-necked flask fitted with a water-cooled condenser and dropping funnel, 0.91 g (24.0 mmol) $LiAlH_4$ was stirred in 20 mL dry THF under an atmosphere of N_2 and protection from light. While the flask was cooled in an ice-bath, a suspension of 1.90 g (10.0 mmol) 5,5'-diformyl-2,2'-difuran (**4**) in 100 mL dry THF was added dropwise, after which the reaction was refluxed for 1 h. Following the addition of water, the hydrolyzed reaction mixture was extracted with ether and the solvent removed to yield 1.88 g (97% yield) of the carbinol **5** in the form of light-yellow needles, m.p. 142-143 °C. ^{1}H NMR (250 MHz, acetone-d_6): δ [ppm] = 6.51 (AB, ^3J(H/H) = 3 Hz, 2H, furyl-H), 6.37 (AB, ^3J(H/H) = 3 Hz, 2H, furyl-H), 4.56 (d, ^3J(H/H) = 6 Hz, 4H, $C\underline{H}_2OH$), 4.30 (t, ^3J(H/H) = 6 Hz, 2H, $CH_2O\underline{H}$); IR (KBr), $\bar{\nu}$ [cm^{-1}] = 3500 - 3000 (OH, s, broad); UV/VIS (ether): λ_{max} [nm] (ε) = 306 (15500), 291 (21500), 284 (21000).

The synthesis of the biscarbinol **5** was first reported by Cresp and Sargent [10a] through the $LiAlH_4$ reduction of the corresponding di-*n*-butyl ester, however, they did not characterize the product. The catalytic reduction of **4** with Pd/C in ethanol or by a Meerwein-Ponndorf-Verley reduction of **4**, by Osipov et al.[10b] likewise did not yield pure dialcohol (reported m.p. 132-137 °C).

2,2'-Difuryl-5,5'-diylbis-(methylenetriphenylphosphonium bromide) (6)

In a 250 mL round bottom flask, 1.17 g (6.00 mmol) 2,2'-difuryl-5,5'-biscarbinol (**5**) and 4.12 g (12.0 mmol) triphenylphosphonium bromide were made to react in 85 mL of dry acetonitrile by refluxing for 5 d under an atmosphere of N_2 and protected from light. The reaction was cooled to room temperature and the precipitated phosphonium salt was collected by filtration. The light brown powder was dried under oil-pump vacuum and recrystallized from ethanol to yield 2.79 g (55%) of **6**, m.p. > 300 °C. MS (FAB, ethanol): *m/z* = 683 ($[M\text{-}2\ Br - H]^+$, 8%), 421 ($[M\text{-}2\ Br - PPh_3]^+$, 100%), 342 ($[M\text{-}2\ Br]^{2+}$, 33%); $^{1}H\{^{31}P\}$ NMR (400 MHz, CD_3OD): δ[ppm] = 7.72 (m, 30H, phenyl-H), 6.32 (AB, ^3J(H/H) = 3 Hz, 2H, furyl-H), 6.04 (AB, ^3J(H/H) = 3 Hz, 2H, furyl-H), 5.21 (s, 4H, $-C\underline{H}_2{}^{\oplus}PPh_3$); $^{31}P\{^{1}H\}$ NMR (162 MHz, CD_3OD): δ [ppm] = 21.53 (s). Elementary analysis: $C_{46}H_{38}Br_2O_2P_2$(844.6), Calc. Br 19.96 Found Br 19.97.

The formation of the bisphosphonium salt **6** by reacting the carbinol **5** with $Ph_3P \times HBr$ (55% yield) was also previously postulated by Cresp and Sargent (22% yield);[10a] however, because the starting carbinol was not pure, the purity of **6**, which was also not characterized, is questionable.

5,5'-Bis(formylethene)-2,2'-difuran (7)

In a 500 mL three-necked flask fitted with a water-cooled condenser and dropping funnel, 1.91 g (10.0 mmol) 5,5'-diformyl-2,2'-difurane (**4**) and 9.40 (22.0 mmol) 1,3-dioxolan-2-yl-methyl-triphenylphosphonium bromide were stirred in 100 mL dry DMF under an atmosphere of N_2. The flask was warmed to 90 °C and a freshly prepared solution of lithium-methonalate, prepared from 0.21 g (30.0 mmol) lithium in 100 mL dry methanol, was added dropwise over 1.5 h. The reaction turned deep red. To assure that the reaction went to completion, it was stirred overnight at 90 °C. After cooling to room temperature, 600 mL water was added and a brown product precipitated out of solution. The precipitate, which was soluble in ether, was extracted 3 times with a total of 450 mL ether. The organic phases were combined, washed 3 times each with 80 mL of a saturated NaCl solution, and dried over Na_2SO_4. The solvent was removed under reduced pressure and the brown oil that remained was taken up in 50 mL THF, to which 50 mL 10% HCl solution was added. After 2 h of stirring, 500 mL water was added and **7** fell out as a dark-brown powder, which was recrystallized from nitromethane to give 1.43 g (59% yield) **7** as red-brown crystals, m.p. 231-232 °C. Elementary analysis: $C_{14}H_{10}O_4$ (242.2) Calc. C 69.42 H 4.16; Found C 69.46 H 4.23.

MS (EI, 70 eV): *m/z* = 242 (M^+, 100%), 121 ($M^+/2$, 58%); ^1H NMR (250 MHz, DMSO-d_6): δ [ppm] = 9.64 (d, ^3J(H/H) = 8.0 Hz, 2H, H-1,1'), 7.62 (d, ^3J(H/H) = 15.7 Hz, 2H, H-3,3'), 7.28 (d, ^3J(H/H) = 3.7 Hz, 2H, AB spectrum, H-5,5'), 7.20 (d, ^3J(H/H) = 3.7 Hz, 2H, AB spectrum, H-6,6'), 6.63 (dd, ^3J(H/H) = 15.7 Hz, 8.0 Hz, 2H, H-2,2'); ^{13}C NMR (101 MHz, DMSO-d_6): δ [ppm] = 193.6 (C-1,1'), 151.2 (C-4,4'), 147.4 (C-7,7'), 137.8 (C-3,3'), 126.2 (C-2,2'), 120.0 (C-6,6'), 111.6 (C-5,5'); IR (KBr) $\bar{\nu}$ [cm^{-1}] = 3120, 3040 (CH arom., m), 2820, 2750, 2730 (CH aliph., m) 1670 (C=O, s); UV/VIS (nitromethane): λ_{max} [nm] (ε) = 411 (30.500).

Bis-Wittig reaction of 7 with 6 to give the isomeric mixture of tetraoxa[24]porphyrinogen(4.0.4.0) (2)

In a 1000 mL three-necked flask fitted with a water-cooled condenser and a Mariott dropping funnel, 484 mg (2.00 mmol) 5,5'-bis(formylethene)-2,2'-difurane **7** and 1.69 g (2.00 mmol) bisphosphonium salt **6** were stirred in 400 mL dry DMF under an atmosphere of N_2 and with protection from light. The flask was warmed to 120 °C and a freshly prepared lithium methoxide solution in methanol, made by reacting 34.7 mg (5.00 mmol) lithium with 100 mL dry methanol, was added dropwise over a period of 30 h, whereby the reaction mixture immediately became red. After allowing the reaction to proceed an additional day at 120 °C, it was cooled to room temperature. The methanol and approx. 300 mL of the DMF were distilled off under reduced pressure, and to the residue was added 100 mL of a saturated NH_4Cl solution and 400 mL of a saturated NaCl solution. The red solution was extracted 8-10 times with a total of approx. 2.5 L ether, the ether phases combined, and dried over Na_2SO_4. After removing the solvent under reduced pressure, a dark-red oil remained. To separate the triphenylphosphine oxide from the product, silica gel chromatography with a mobile phase of dichloromethane was used. Following the removal of dichloromethane, 104 mg (15% yield) of **2** was obtained, which according to spectroscopic data was a mixture of 4 isomers. MS (EI, 70 eV): *m/z* = 368 (M^+, 100%), 366 ($[M-2\,H]^+$, 29%), 184 (M^{2+}, 29%); UV/VIS (CH_2Cl_2): λ_{max} [nm] (ε) = 332 (52.500), 349 (56.000).

The isomeric mixture was subjected once again to silica gel chromatography, this time with ethyl acetate/*n*-hexane (v/v = 1:5) as the mobile phase. After concentrating the red fractions, which contained the product, the isomeric mixture of **2a/2b** were obtained as red needles, m.p. 255-263 °C (from dichloromethane).

Oxidation of the isomeric mixture of 2a/2b with DDQ to *cis,trans,cis,trans*-tetraoxa[22]porphyrin (4.0.4.0) dication (2b^{2+})

In a 50 mL round bottom flask, 8.0 mg (0.02 mmol) of the tetraoxa[24]porphyrinogen(4.0.4.0) isomeric mixture **2a/2b** was dissolved in 25 ml dichloromethane. With the flask cooled in an ice-bath, 5.00 mg (0.02 mmol) DDQ was added in portions to the deep-red solution of **2a/2b**, whereby the color immediately turned black. The precipitate was collected by centrifugation and washed twice with dichloromethane. The product was taken up in 15 mL 70% perchloric acid, the deep-green solution was filtered under N_2 in the presence of dry silica gel, and then diluted dropwise with water. A blue, microcrystalline powder precipitated, which was washed several times with water to give 11.0 mg (90% yield) of a shiny, metallic powder, m.p. > 300 °C.

Spectroscopic data of **2b**$^{2+}$ $(ClO_4^-)_2$: MS(FAB): *m/z* (%): 368 [M^+-2 ClO_4] (100); UV/VIS (70-perc. $HClO_4$): λ_{max}[nm] (ε) = 432 (280000), 440 (266500), 602 (7500), 662 (28500), 684 (11500), 697 sh (4500), 715 (3500), 750 (5000), 765 (44000); ^{1}H NMR (400 MHz, CF_3COOD, 21 °C); δ = 13.46 (d, ^3J(H-5,H-17 / H-6,H-18) = 13.6 Hz, H-5, H-17), 12.91 (dd, ^3J(H-7,H-19 / H-8/H-20) = 10.2 Hz, ^3J(H-7,H-19 / H-6,H-18) = 13.6 Hz, H-7, H-19), 12.34 (AB, ^3J(H-2,H-14 / H-3,H-15)= 4.8 Hz, H-2, H-14), 11.70 (AB, ^3J(H-2,H-14 / H-3,H-15)= 4.8 Hz, H-3, H-15), 12.27 (AB, ^3J(H-11,H-23 / H-10,H-22) = 4.8 Hz, H-11, H-23), 11.49 (AB, ^3J(H-11,H-23 / H-10,H-22) = 4.8 Hz, H-10, H-22), 12.09 (d, ^3J (H-8,H-20 / H-7,H-19) = 10.2 Hz, H-8, H-20), –8.73 (pt, ^3J(H-6,H-18 / H-5,H-17) = ^3J(H-6,H-18 / H-7,H-19) = 13.7 Hz), H-6, H-18).

Reduction of 2b^{2+} to *cis,trans,cis,trans*-tetraoxa[24]porphrinogen (4.0.4.0) (2b)

In a 25 mL round bottom flask, 20.0 mg (0.04 mmol) of tetraoxa[22]porphyrin(4.0.4.0) dication **2b**$^{2+}$ was dissolved in 5.0 mL dry nitromethane under an inert atmosphere. The green solution was titrated dropwise (approx. 5 drops) with a solution of 15.0 mg tetrakis-(dimethylamino)ethene **8** in 5.0 mL dichloromethane until a complete red coloration indicated the end point, after which a further small amount of reductant was added. After stirring for 1 h, the solvent was removed under reduced pressure and the remaining orange residue was taken up in dichloromethane. The tetrakis-(dimethylamino)ethene bisperchlorate **8**$^{2+}$ was filtered off under an atmosphere of N_2 and washed generously with dichloromethane. The filtrate, a clear, red solution, yielded a red oil following the removal of the solvent. The crude product was chromatographed on silica gel with dichloromethane as the mobile phase. The removal of the dichloromethane under reduced pressure led to 8.00 mg (62% yield) of tetraoxa[24]porphyrinogen(4.0.4.0) **2b** in the form of a red-brown, microcrystalline solid, m.p. > 300 °C.

Spectroscopic data of the porphyrinogen **2b**: reddish brown, microcrystalline product, m.p. > 300 °C (dec.), yield 62% (from **2b**$^{2+}$); UV/VIS (dichloromethane): λ_{max} [nm] (ε) = 333 (72500), 349 (88500); ^{1}H NMR (400 MHz, CDCl$_3$): δ = 11.91 (dd, ^3J(H-6,H-18 / H-5,H-17) = 15.3 Hz, ^3J(H-6,H-18 / H-7,H-19) = 11.6 Hz, H-6, H-18), 5.62, 5.46 (AB, ^3J(H,H) = 3.5 Hz, furyl-H), 5.61, 5.46 (AB, ^3J(H,H) = 3.5 Hz, furyl-H), 5.01 (d, ^3J(H-5,H-17 / H-6,H-18) = 15.3 Hz, H-5, H-17), 4.86 (d, ^3J(H-8,H-20 / H-7,H-19) = 12.0 Hz, H-8, H-20), 4.80 (dd, ^3J(H-7,H-19 / H-6,H-18) = 11.6 Hz, ^3J(H-7,H-19 / H-8,H-20) = 12.0 Hz, H-7, H-19). ^{13}C NMR (100.6 MHz, CDCl$_3$): δ = 156.3, 155.1, 147.8, 147.7 (*quaternary* C-atoms) 128.3, 126.6, 123.7, 116.4, 114.5, 114.4, 109.3, 109.0 (*tertiary* C-atoms).

NMR data of the trans,cis,cis,trans-tetraoxa[22]porphyrinogen(4.0.4.0) (**2a**): ^{1}H NMR (400 MHz, C$_6$D$_6$): δ = 11.19 (dd, ^3J(H-6,H-19 / H-5,H-20) = 15.5 Hz, ^3J(H-6,H-19 / H-7,H-18) = 10.9 Hz, H-6,H-19), 5.49, 5.39 and 5.41, 5.26 two AB-spectra (^3J(H,H) = 3.5 Hz, furyl-H), 5.08 (d, ^3J(H-5,H-20 / H-6,H-19) = 15.5 Hz, H-5, H-20), 4.95 (dd, ^3J(H-7,H-18 / H-8,H-17) = 12.0 Hz, ^3J(H-7,H-18 / H-6,H-19) = 10.9 Hz, H-7, H-18), 4.94 (d, ^3J(H-8,H-17 / H-7,H-18) = 12.0 Hz, H-8, H-17).

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Dedicated to Professor Manfred Regitz on the Occasion of his 60th Anniversary

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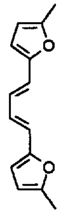

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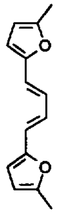

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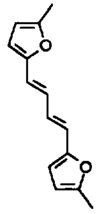

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