Furan-Based Porphyrins: Tetraoxa[4n+2]porphyrin Dications with 18π-, 22π-, or 26π-Electron Systems[**]

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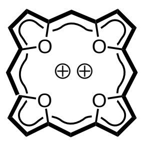
Dedicated to Professor Dieter Seebach

The D_{4h}-symmetric tetraoxa[18]porphyrin dication **1**,[1] which is isoelectronic with diprotonated porphyrin, and the *N*,*N'*,*N''*,*N'''*-tetramethyl[26]porphyrin-(3.3.3.3) dication (**3** with NCH_3 instead of O; as the octaethyl derivative) described by Franck et al.[2] are prototypes of chalcogenaporphyrins[3] and symmetrically expanded porphyrins, respectively.[4] These dicationic porphyrin variants should be viewed as resonance hybrids (carbenium and onium ion structures) in which special importance is attributed to carbenium ion structures with $4n+2$ π electrons on the $4(n+1)$ carbon perimeter—in agreement with both experiment and theory.[5]



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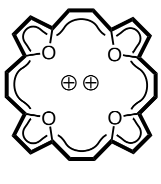

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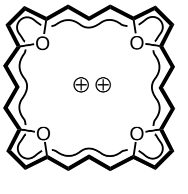

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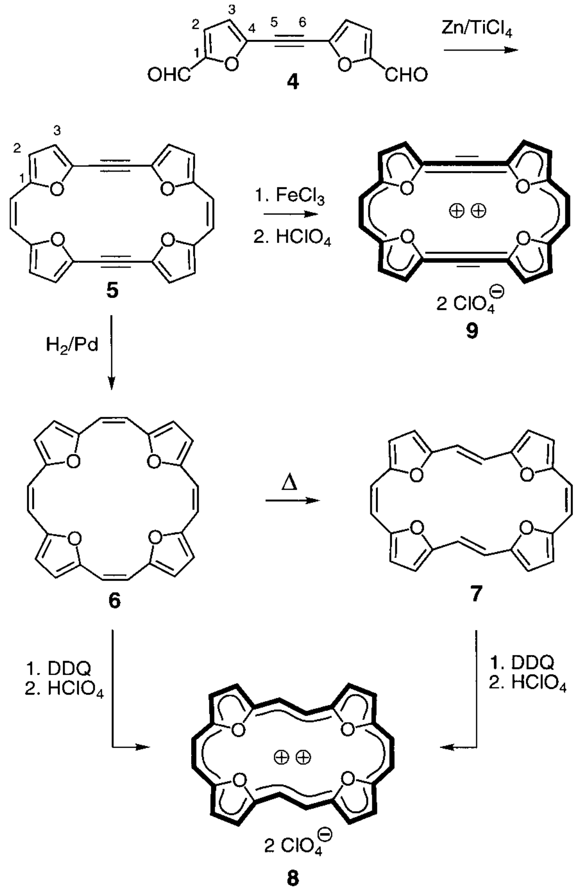
A combination of N/O exchange and symmetrical expansion conceptually transforms porphyrin into homologues of **1**, the all-*cis*-tetraoxa[22]porphyrin-(2.2.2.2) and the tetraoxa[26]porphyrin-(3.3.3.3) dications **2** and **3**, respectively. Our interest in **2** and **3** was stimulated by the exceptional spectroscopic properties of the *N*,*N'*,*N''*,*N'''*-tetramethyl[26]porphyrin dication from Franck et al., which prompted the authors to call the compound a super arene.[2]. If **2** and **3**—like **1**—were to exist as D_{4h}-symmetric molecules, the triad **1**–**3** would be ideally suited to provide meaningful spectroscopic correlations between the three members. However, the chance of obtaining a D_{4h}-symmetric all-*cis*-tetraoxa[22]porphyrin dication **2** seemed a priori fairly remote. According to calculations[6] the compound is no less than about 90 kcal mol^{-1} higher in energy than the di-*trans* isomer **8** in its preferred planar conformation. We describe here our attempts to prepare **2** and/or **8** as well as the synthesis of **3** (as the octaethyl derivative).[7]

We considered tetraepoxytetradehydro[24]annulene **5** (red-violet prisms from dichloromethane; decomposition above 300 °C; yield 50 %), which was obtained by reductive carbonyl coupling of the dialdehyde **4**[8] with Zn/CuCl and titanium tetrachloride in tetrahydrofuran, to be a key compound for preparation of tetraoxa[22]porphyrin-(2.2.2.2) dications (Scheme 1). Catalytic hydrogenation of **5** with Lindlar catalyst in tetrahydrofuran provided the all-*cis*-tetraepoxy[24]annulene **6** (violet crystals from tetrahydrofuran; decomposition above 270 °C; yield 35 %), a potential precursor of the all-*cis*-tetraoxa[22]porphyrin dication **2**.



Scheme 1. Synthesis of the tetraoxa[22]porphyrin-(2.2.2.2) dications **8** and **9** as the bisperchlorates.

The ^{1}H NMR spectrum (room temperature) of **6** does not show the expected simple form consisting of a singlet each for the furan protons and the olefinic protons. Instead singlets appeared at $\delta = 7.60$ and 6.30 for the furan protons and there was an AB system at $\delta = 5.96$ and 5.85 with $^3J_{AB} = 13.1$ Hz (*cis* double bond) for the olefinic protons. This result is understandable only under the assumption that **6** exists in a relatively stable, nonplanar conformation in which the furan proton pairs are arranged alternately inside and outside the C_{24} ring.[9] As expected, the NMR spectrum is temperature dependent, but line broadening only occurs above 45 °C. From

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the coalescence temperature of the AB system (95 °C) it was possible to estimate that the free enthalpy of activation $\Delta G^{\neq}$ for the degenerate exchange of the furan rings is not less than 17 kcal mol^{-1}. The all-*cis*-tetraepoxy[24]annulene **6** is thermally labile, which became apparent from the occurrence of additional signals in the high-temperature ^{1}H NMR spectrum. A thermolysis study showed that **6** rearranges in boiling *o*-xylene (24 h) to form irreversibly the sterically uniform *cis,trans,cis,trans* isomer **7** (black-green crystals from ethyl acetate; decomposition above 300 °C; yield 65 %).[10]

While our investigations on tetraoxa[22]porphyrin-(2.2.2.2) dications were still in progress,[10] Märkl et al.[11] reported an independent synthesis of **7** and its successful oxidation to the dication **8**. Since the results of the two groups are in satisfactory agreement mention is made to reference [10] regarding the physical data of **7** and **8** determined here.

Oxidation of the stereoisomeric tetraepoxy[24]annulenes **6** and **7**[12] with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) in tetrahydrofuran and treatment of the resulting amorphous products with 70 % perchloric acid furnished the same tetraoxa[22]porphyrin dication: the sterically uniform *cis,trans,cis,trans* isomer **8** as the bisperchlorate (blue platelets from perchloric acid; decomposition above 270 °C; yield in both cases 20–25 %).

The presence of **8** was confirmed by the ^{1}H NMR spectrum, which, clearly as the result of a restricted mobility of the molecule compared to **6** and **7**, no longer exhibits any significant temperature dependency. Owing to the marked low- and high-field position of the signals of the outer and inner protons, respectively, of the formal *trans* double bonds, **8** is characterized by a pronounced diamagnetic ring current. The NMR investigations, however, do not allow a distinction to be made as to whether **8** exists in a ruffled or in a planar conformation (C_2 versus C_{2h} symmetry).

A clarification of the conformation of **8**—which is of interest because of the spectroscopic comparison with **1** and **3**—by X-ray structure analysis has hitherto failed because of crystal disorder. In contrast, the *cis,trans,cis,trans*-octaethyltetraoxa[22]porphyrin dication **8a** as the bisperchlorate (Figure 1, Table 1),[13] obtained analogously to our synthesis of **8**, was amenable to analysis. It emerged that the ring framework of **8a** is almost planar.

The usefulness of the tetraepoxytetradehydro[24]annulene **5** manifested itself not only in the *cis* hydrogenation to **6** but also in its two-electron oxidation with iron(III) chloride in acetonitrile. Treatment of the resulting solid with 70 % perchloric acid furnished the tetraoxatetradehydro[22]porphyrin-(2.2.2.2) dication **9** (as bisperchlorate), the oxygen analogue of diprotonated tetradehydro[22]porphyrin-(2.2.2.2) (blue needles from perchloric acid; decomposition above 280 °C; yield 24 %). The NMR and UV/Vis spectra of **9** correspond to those of the known octaethyltetradehydro[22]porphyrin-(2.2.2.2) in its doubly protonated form.[14]

For the synthesis of the tetraoxa[26]porphyrin-(3.3.3.3) dication, as the octaethyl derivative **13** for reasons of solubility, we followed the route illustrated in Scheme 2, which was based on porphyrin chemistry methodology.[2] The starting aldehyde **10** was obtained by vinylogous Vilsmeier formylation of 3,4-diethylfuran with 3-(*N,N*-dimethylamino)acrolein and phosphorus oxychloride in dichloromethane at 0 °C (pale yellow crystals; m.p. 53–54 °C; yield 65 %). Reduction of **10** with sodium borohydride in tetrahydrofuran/water (25/1) gave the alcohol **11** (oily liquid) in almost quantitative yield. Because of its instability it was used immediately. Compound **11** unexpectedly showed only a slight tendency towards cyclotetracondensation under normal acidic conditions, but it was possible to obtain **12** by treating **11** with citric acid (equimolar amounts) in nitromethane at 70 °C (colorless crystals; m.p. 212 °C (decomposition); yield 3 % (based on **10**)). The method of choice for the oxidation step proved to be the reaction of **12** with bis(trifluoroacetoxy)iodo(III)benzene) in benzene (RT); the 26π-electron dication precipitated out as the microcrystalline bis(trifluoroacetate). It was purified by chromatography on silica gel with acetonitrile (containing 2 % trifluoroacetic acid) and then converted into the bisperchlorate **13** with 70 % perchloric acid. Crystallization of **13** from formic acid resulted in green rhomboids with a metallic sheen which trapped solvent (suitable for X-ray structure analysis). This material gave the analytically pure compound (dark green powder; decomposition above 300 °C; yield 50 %) when heated at 140 °C (0.2 Torr; 48 h).

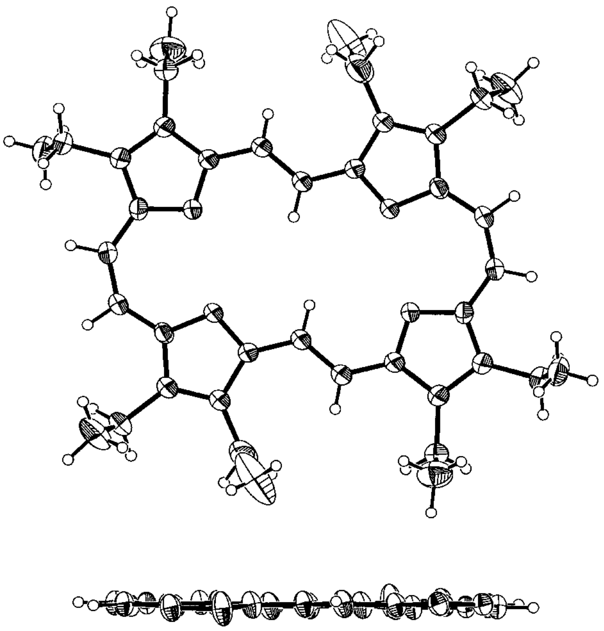


Figure 1. Crystal structure of the *cis,trans,cis,trans*-octaethyltetraoxa[22]porphyrin-(2.2.2.2) dication **8a** as the bisperchlorate. Top: plan view; bottom: side view without ethyl substituents.

Within the limits of comparison the ^{1}H NMR spectrum of **13** agreed remarkably well with that of the octaethyl-*N,N′,N″,N‴*-tetramethyl[26]porphyrin-(3.3.3.3) dication.[2] As with its NCH_3 analogue, **13** is characterized by an unusually strong diamagnetic ring current which is manifested in the position of the signals of the outer- and inner-perimeter protons at extremely low and high field: $\delta = 14.61$ (H_o), -10.92 (H_i). The presence of a D_{4h}-symmetric dication can be inferred from a combination of the ^{1}H and ^{13}C NMR spectra (six signals) and the finding that the structure of **13** exhibits a planar ring framework (see the following communication[19]).

Table 1. Selected physical data for **4–6**, **8a**, **9**, **10**, **12**, **13**, and **15** (^{1}H NMR: 300 MHz; ^{13}C NMR: 75.5 MHz).[a]

4: ^{1}H NMR ([D$_6$]DMSO): $\delta = 9.64$ (s, 2H; CHO), 7.66 (d, 2H; H-2,9; $^3J_{2,3} = 3.8$ Hz), 7.37 (d, 2H; H-3,8); ^{13}C NMR ([D$_6$]DMSO): $\delta = 178.4$ (CHO), 153.1, 138.2, 123.0, 120.3, 84.7; MS (EI, 70 eV): *m/z* (%): 214 (78) [M^+], 157 (100), 129 (70); IR (KBr): $\tilde{\nu} = 3105$, 1669, 1526, 1399, 1248, 1034, 962, 814, 781, 705 cm^{-1}; UV/Vis (CH$_2$Cl$_2$): λ_{max} (ε) = 227 (10200), 343 (30800), 367 nm (27300)

5: ^{1}H NMR (CD$_2$Cl$_2$): $\delta = 6.30$ (d, 4H; H-3,8,15,20; $^3J_{2,3} = 3.5$ Hz), $\delta = 5.99$ (d, 4H; H-2,9,14,21), 5.48 (s, 4H; H-11,12,23,24); ^{13}C NMR (CD$_2$Cl$_2$): $\delta =$ 154.4, 137.0, 119.1, 115.8, 113.9, 85.3; MS (EI, 70 eV): *m/z* (%): 364 (100) [M^+], 182 (9) [M^{2+}]; IR (CsI): $\tilde{\nu} = 3125$, 2197, 1715, 1573, 1354, 1272, 1021, 946, 799 cm^{-1}; UV/Vis (CH$_2$Cl$_2$): λ_{max} (ε) = 230 (20100), 312 (65900), 326 (106000) 332 (99000), 346 (72500) 430 nm (1800)

6: ^{1}H NMR ([D$_8$]THF, 295 K): $\delta = 7.60$ (s, 4H; H-8,9,20,21, inward pointing furan protons), $\delta = 6.30$ (s, 4H; H-2,3,14,15, outward pointing furan protons), 5.96 (d, 4H; H-6,11,18,23; $^3J_{5,6} = 13.1$ Hz), 5.85 (d, 4H; H-5,12,17,24); ^{13}C NMR ([D$_8$]THF, 295 K): $\delta = 154.7$, 151.7, 117.0, 115.2, 114.9, 114.3; MS (EI, 70 eV): *m/z* (%): 368 (100) [M^+], 184 (24) [M^{2+}]; IR (CsI): $\tilde{\nu} = 3125$, 3030, 1708, 1623, 1598, 1551, 1240, 1168, 1023, 949, 794, 648 cm^{-1}; UV/Vis (THF): λ_{max} (ε) = 337 (124000), 354 (179000), 505 nm (1200)

8a: ^{1}H NMR (CF$_3$COOD, CH$_2$Cl$_2$ int.) $\delta = 13.15$ (d, 2H; H-5,17; $^3J_{5,6} =$ 14.9 Hz), -8.20 (d, 2H; H-6,18), 11.26 (d, 2H; H-11,23; $^3J_{11,12} = 12.3$ Hz), 11.21 (d, 2H; H-12,24), 5.28 (q, 4H; H-8a,20a), 4.80 (q, 4H; H-3a,15a), 4.73 (q, 4H; H-9a,21a), 4.65 (q, 4H; H-2a,14a), 2.61 (t, 6H; H-8b,20b), 2.35 (t, 6H; H-3b,15b), 2.20 (t, 6H; H-9b,21b), 2.16 (t, 6H; 2b, 14b); ^{13}C NMR (CF$_3$COOD): $\delta = 161.3$, 158.3, 156.9, 156.8, 156.4, 154.6, 151.4, 149.3, 119.1, 115.8, 112.0, 111.6, 24.2, 22.4, 22.3, 22.2, 18.7, 18.5, 18.4, 14.8; MS (EI, 70 eV): *m/z* (%): 592 (100) [$(M - 2\,ClO_4)^+$], 296 (16); IR(CsI): $\tilde{\nu} = 2967$, 2933, 2871, 1550, 1449, 1205, 1127, 1083, 842, 624 cm^{-1}, UV/Vis (HCOOH): λ_{max} (ε) = 270 nm (37300), 433 (63200) sh, 456 (518000), 474 (380000), 615 (4300), 665 (20000), 722 (36100), 730 (25800) sh

9: ^{1}H NMR (98%. D$_2$SO$_4$, CH$_2$Cl$_2$ int.): $\delta = 11.66$ (d, 4H; H-2,9,14,21; $^3J_{2,3} = 3.7$ Hz), 11.22 (d, 4H; H-3,8,15,20), 11.61 (s, 4H; H-11,12,23,24); ^{13}C NMR (98% D$_2$SO$_4$, CH$_2$Cl$_2$ int.): $\delta = 157.6$, 143.9, 139.3, 137.8, 117.9, 109.6; IR (CsI): $\tilde{\nu} = 3104$, 1530, 1399, 1352, 1242, 1099, 1004, 958, 919, 776, 624 cm^{-1}; UV/Vis (98%. H$_2$SO$_4$): λ_{max} (ε) = 419 (200100), 436 sh (121900), 660 (6700), 675 (6900), 706 (41500), 721 nm (88600)

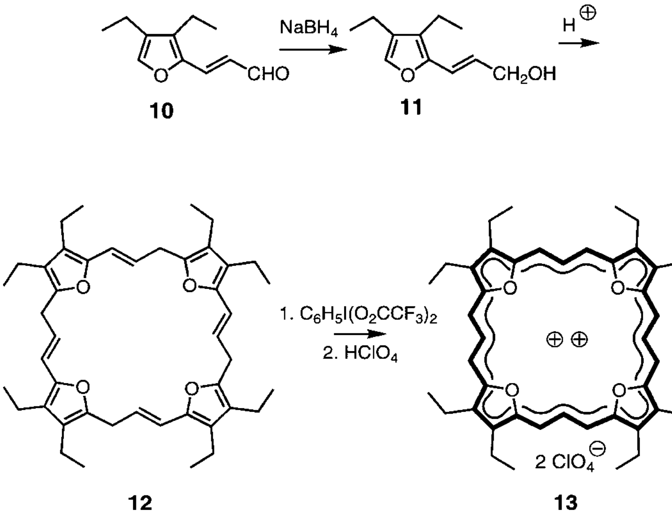
10: ^{1}H NMR (CDCl$_3$): $\delta = 9.58$ (d, 1H; CHO), 7.26 (s, 1H, H-5), 7.19 (d, 1H; H-2a; $^3J_{2a,2b} = 15.4$ Hz), 6.49 (dd, 1H; H-2b), 2.53 (q, 2H; H-3a), 2.40 (q, 2H; H-4a), 1.20 (t, 3H; H-4b), 1.15 (t, 3H; H-3b); ^{13}C NMR (CDCl$_3$): $\delta = 192.8$, 146.6, 142.0, 136.0, 134.4, 129.8, 124.3, 17.1, 16.7, 15.1, 13.6; MS (EI, 70 eV): *m/z* (%): 178 (78) [M^+], 149 (100); IR (CsI): $\tilde{\nu} = 3129$, 3007, 2970, 2877, 1657, 1581, 1520, 1462, 1398, 1376 cm^{-1}; UV/Vis (CH$_2$Cl$_2$): λ_{max} (ε) = 259 (3100), 333 nm (32000)

12: ^{1}H NMR (CDCl$_3$): $\delta = 6.22$ (d, 4H; H-5,12,19,26; $^3J_{5,6} = 15.6$ Hz), 6.02 (m, 4H; H-6,13,20,27), 3.38 (d, 8H; H-7,14,21,28), 2.37 (q, 8H; H-3a,10a,17a,24a), 2.31 (q, 8H; H-2a,9a,16a,23a), 1.09 (t, 12H; H-3b,10b,17b,24b), 1.07 (t, 12H; H-2b,9b,16b,23b); ^{13}C NMR (CDCl$_3$): $\delta = 147.9$, 146.3, 123.7, 122.7, 122.1, 118.5, 30.1, 16.8, 16.6, 15.7, 15.6; MS (EI, 70 eV): *m/z* (%): 648 (88) [M^+], 485 (100); IR (CsI): $\tilde{\nu} = 3038$, 2970, 2826, 1655, 1549, 1465, 1322, 1292, 1227, 1101, 995, 953 cm^{-1}; UV/Vis (CH$_2$Cl$_2$): λ_{max} (ε) = 285 (84800), 302 nm (41000)

13: ^{1}H NMR (CF$_3$COOD, CH$_2$Cl$_2$ int.): $\delta = 14.61$ (d, 8H; H-5,7,12,14,19,21,26,28; $^3J_{5,6} = 13.4$ Hz), -10.92 (t, 4H; H-6,13,20,27), 5.73 (q, 16H; H-2a,3a,9a,10a,16a,17a,23a,24a), 2.92 (t, 24H; H-2b,3b,9b,10b,16b,17b,23b,24b); ^{13}C NMR (CF$_3$COOD, CH$_2$Cl$_2$ int.): $\delta = 154.6$, 150.9, 122.8, 121.9, 22.7, 18.9; MS (FAB, matrix: nitrobenzyl alcohol): *m/z* (%): 743 (9) [$(M - ClO_4)^+$], 644 (100) [$(M - 2\,ClO_4)^+$]; IR (CsI): $\tilde{\nu} = 2972$, 2660, 1472, 1377, 1314, 1249, 1082, 1052, 974, 700, 671, 624 cm^{-1}; UV/Vis (HCOOH): λ_{max} (ε) = 496 (117500), 525 (1600000), 705 (2200), 772 (35100), 783 (34100), 846 nm (3500)

15: ^{1}H NMR (CDCl$_3$): $\delta = 7.43$ (dd, 2H; H-1,10), 6.69 (dd, 2H; H-3,8), 6.41 (dd, 2H; H-2,9); $^3J_{1,2} = 1.8$, $^3J_{2,3} = 3.4$ Hz; ^{13}C NMR (CDCl$_3$): $\delta = 144.2$, 136.4, 116.4, 111.0, 83.1; MS (EI, 70 eV): *m/z* (%): 158 (100) [M^+], 102 (31); IR (film): $\tilde{\nu} = 3132$, 2205, 1494, 1376, 1282, 1075, 1015, 913, 816, 742 cm^{-1}; UV/Vis (CH$_2$Cl$_2$): λ_{max} (ε) = 258 (12600), 295 (19900), 315 nm (13200)

[a] Correct elemental analyses are available for **4–10**, **8a, 13**, and **15**.



Scheme 2. Synthesis of octaethyltetraoxa[26]porphyrin-(3.3.3.3) dication **13** as the bisperchlorate.

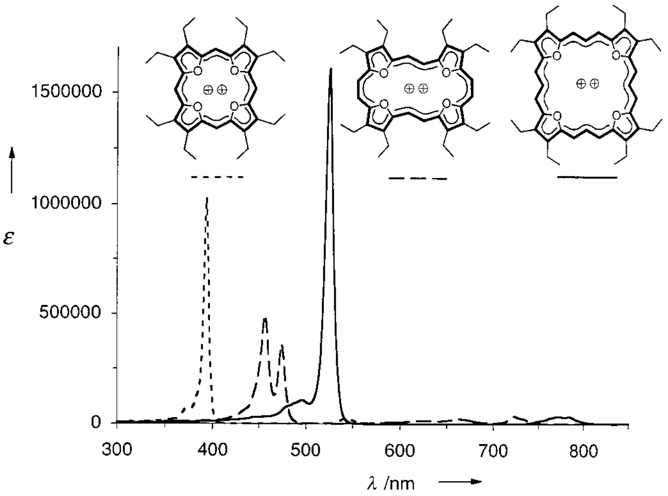


Figure 2. UV/Vis spectra (in HCOOH) of the octaethyltetraoxa[18]porphyrin-(1.1.1.1) dication **1a** (----), the *cis,trans,cis,trans*-octaethyltetraoxa-[22]porphyrin-(2.2.2.2) dication **8a** (– – –), and the octaethyltetraoxa[26]-porphyrin-(3.3.3.3) dication **13** (——) as the bisperchlorates.

A comparison of the UV/Vis spectrum of **13** with those of the octaethyl derivatives **1a**[15] and **8a**[13] of **1** and **8** is particularly informative. Characteristic of the spectra of **13** and **1a** is that each displays an extraordinarily sharp Soret band which exhibits almost no vibrational structure (half peak width ca. 600 cm^{-1} for **13** and 400 cm^{-1} for **1a**). The very narrow widths of these bands lead to record extinctions ε of 1.6×10^6 and 1×10^6 M^{-1}cm^{-1} for **13** and **1a**, respectively, although the oscillator strengths for the two dications (3.8 and 2.9) are of the same order of magnitude as for diprotonated porphyrins (2.1). Two important conclusions may be drawn from the narrow widths of the Soret bands: 1) Compounds **13** and **1a** possess fourfold symmetry, which causes a degeneracy of the two Soret transitions (B transitions in the Platt nomenclature)[16] and hence excludes π-bond fixation on the time scale of optical excitation ($< 10^{-13}$ s), and 2) when the weak vibrational progression is considered **13** and **1a** must be very rigid molecules whose geometry remains almost unchanged on excitation. In the case of **8a**, whose ring framework exhibits only C_{2h} symmetry, the two Soret transitions are no longer degenerate so that a splitting of the Soret band and a reduced maximum extinction is observed in comparison with **1a** and **13**. Based on the absence of significant vibrational structure, a rigid ring framework and thus extensive cyclic π-electron delocalization can also be inferred for **8a**. The oscillator strength of the Soret band region of **8a** (2.3) is smaller than that of **1a** rather than being intermediate between the values of **1a** (2.9) and **13** (3.8) as would have been expected for the all-*cis* compound **2**. The ratio between the transition moments M derived from the experimental oscillator strengths of the dications **1a, 8a**, and **13** is reproduced quantitatively by INDO/S calculations.[17] The fact that the squares of the transition moments of the three cations show the same ratios as the areas within the molecules suggests that the highest occupied and the lowest unoccupied orbitals are almost completely located on the carbon perimeter, in agreement with theoretical expectations.[5, 18]

The meaningfulness of the UV/Vis spectroscopic comparison reported here is attributed to the existence of the tetraoxa[22]porphyrin-(2.2.2.2) dication as the planar *cis,trans,-cis,trans* isomer **8** or **8a**. Since the Soret bands in the spectra of **8a** and **1a/13** differ quite dramatically—the former having a split band with a relatively low extinction, and the others a sharp band with very high extinction—the outcome of the comparison may be regarded as a reference example of the significance of molecular symmetry on the shape of UV/Vis spectra.

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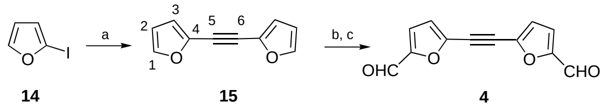
[7] Complementary to our investigations on **1/1a**, **8/8a**, and **13**, Märkl and co-workers have developed a whole series of tetraoxa-[4n+2]porphyrin-(x.0.x.0) dications with up to $n = 9$, the tetraoxa-[38]porphyrin-(12.0.12.0) dication, and demonstrated impressively that the Hückel rule still applies in the case of the latter compound: G. Märkl, T. Knott, P. Kreitmeier, T. Burgemeister, F. Kastner, *Helv. Chim. Acta* **1998**, *81*, 1480–1505; G. Märkl, M. Hafner, P. Kreitmeier, T. Burgemeister, F. Kastner, M. Porsch, J. Daub, *Tetrahedron* **1996**, *52*, 1981–1996; G. Märkl, T. Knott, P. Kreitmeier, T. Burgemeister, F. Kastner, *Tetrahedron* **1996**, *52*, 11763–11782.

[8] The new compound **4** can be obtained from 2-iodofuran as illustrated in Scheme 3 (T. Kauffmann, H. Lexy, R. Kriegesmann, *Chem. Ber.* **1981**, *114*, 3667–3673).



Scheme 3. a) Bubbling acetylene through a solution of **14**, $[\{(C_6H_5)_3P\}_2Pd^{II}Cl_2]$, and CuI in diethylamine, 6 h, RT. **15**: colorless oil, b.p. 70 °C/0.3 torr (yield 75 %), method of K. Sonogashira, Y. Tohda, N. Hagihara, *Tetrahedron Lett.* **1975**, 4467–4470; b) addition of *n*-butyllithium in *n*-hexane to a solution of **15** and *N,N,N′,N′*-tetramethylethylendiamine (TMEDA) in *n*-hexane at 0 °C, then 3 h at RT; c) DMF, 0 °C then 1 h at RT. **4**: colorless crystals; m.p. 210–211 °C (from dichloromethane, then dichloromethane/*n*-hexane; yield 50 %).

[9] In contrast to **6**, its long-established sulfur analogue, the all-*cis*-tetraepithia[24]annulene, is conformationally so flexible that the protons of the four heterorings appear as a singlet in the ^1H NMR spectrum, even at −60 °C; A. Straud, B. Thulin, O. Wennerström, *Acta Chem. Scand. B* **1977**, *31*, 521–523; F. Gerson, W. Huber, O. Wennerström, *Helv. Chim. Acta* **1978**, *61*, 2763–2772; Z. Hu, J. L. Atwood, M. P. Cava, *J. Org. Chem.* **1994**, *59*, 8071–8075.

[10] The syntheses of **5**–**9** as well as the X-ray structure analysis of **6** have already been described in the dissertation of T. Pelster, Universität Köln, **1992**, but were not published then since the structure analysis of **8a** and the investigations on **13** were still in progress.

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[12] J. A. Elix (*Aust. J. Chem.* **1969**, *22*, 1951–1962) first reported two stereoisomeric tetraepoxy[24]annulenes. According to the opinion of the Australian author these were the *cis,trans,cis,trans* isomer **7** and the all-*trans* isomer. However, it has hitherto not been possible to assign the configuration to the two compounds unequivocally in spite of a comparison of their physical data with those of authentic **6** and **7**.

[13] Crystal structure data for **8a**: $C_{40}H_{48}O_4 \cdot 2\,ClO_4$; $M = 791.68\ g\,mol^{-1}$; crystals from formic acid/perchloric acid, crystal dimensions $0.30 \times 0.20 \times 0.20$ mm; triclinic, space group $P\bar{1}$, $a = 8.157(1)$, $b = 8.849(1)$, $c = 14.055(1)$ Å, $\alpha = 73.56(1)$, $\beta = 87.68(1)$, $\gamma = 83.90°$, $V = 967.5(2)$ Å^3; $Z = 1$, $\rho_{calcd} = 1.359\ g\,cm^{-3}$; $F(000) = 418$; $\mu_{Mo} = 0.231\ mm^{-1}$; 8544 measured, 4348 independent, 3340 observed reflections ($F_o^2 > 2\sigma F_o^2$); $\Theta_{max} = 27.48°$; $R1 = 0.059$, $wR2 = 0.153$. Nonius-Kappa-CCD diffractometer, room temperature, $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å); the structure was solved with direct methods and refined against F^2 for all independent reflections (heavy atoms with anisotropic temperature factors, H atoms with isotropic temperature factors); $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$. Program used: SHELXS-86 for structure determination and SHELXL-93 for refinement (G. M. Sheldrick, Universität Göttingen). Calculations were carried out on the data processing systems of the regional computer center, Universität Köln. Crystallo-

graphic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-119094. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk). The synthesis of **8a**—analogous to that of **8**—is described in the dissertation of H.-S. Böhm, Universität Köln, **1993**.

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Porphyrinoids with 26 π Electrons: Molecules with Exceptional Spectroscopic Properties**

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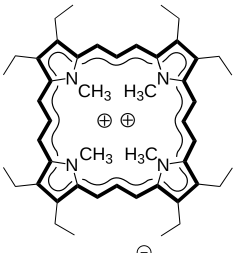
Dedicated to Professor Burchard Franck

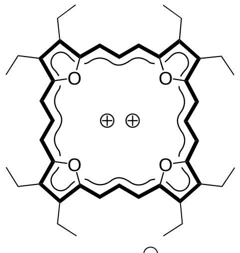
The interdisciplinary interest in porphyrins and their metal complexes has made the development of structural variants of the basic tetrapyrrole macrocycle one of the main lines of current porphyrin research. As a recently published monograph on this topic has demonstrated,[1] the number of new porphyrinoid macrocycles which have emerged from the expansion, contraction, reorganization, or other modifications of the porphyrin ring system is now legion. From the outset, considerable attention has been paid to expanded porphyrins because it was anticipated that the enlargement of the π-electron system and hence of the cavity would give rise to unusual physical and chemical properties of the molecules involved.

Exceptional spectroscopic properties were indeed encountered with the *N,N′,N″,N‴*-tetramethyl- and tetraoxa[26]porphyrin-(3.3.3.3) dications **1** (originally as the bis(trifluoroacetate)) and **2**, which were synthesized in complementary investigations by the groups of Franck[2] and Vogel.[3] Although the dications **1** and **2** are closely related, the two compounds surprisingly exhibit marked differences in part of their spectra. It therefore seemed attractive to us to perform a comparative study of the structures and spectra of **1** and **2**.



2 $ClO_4^{\ominus}$

1



2 $ClO_4^{\ominus}$

2

The octaethyltetraoxa[26]porphyrin dication as the bisperchlorate **2** gave crystals suitable for X-ray crystallographic analysis from anhydrous formic acid[4] into which solvent molecules—necessary for maintenance of a stable crystal lattice—were incorporated. According to the analysis (Figure 1b) the alkyl groups are arranged in such a way that the molecule as a whole becomes almost centrosymmetric. In agreement with this the ring system of **2** is nearly planar (a slight deviation of the framework from the implied D_{4h} symmetry is presumed to be caused by packing effects). The porphyrinoid, aromatic nature of **2** is reflected not only in an essential equalization of the C–C bond lengths in the C_3 segments, but is also inferred from the length relationship C_α–C_β > C_β–C_β in the five-membered heterocyclic rings.[5] The two perchlorate ions, which are located at different distances above and below the ring system, are each associated with one formic acid molecule.

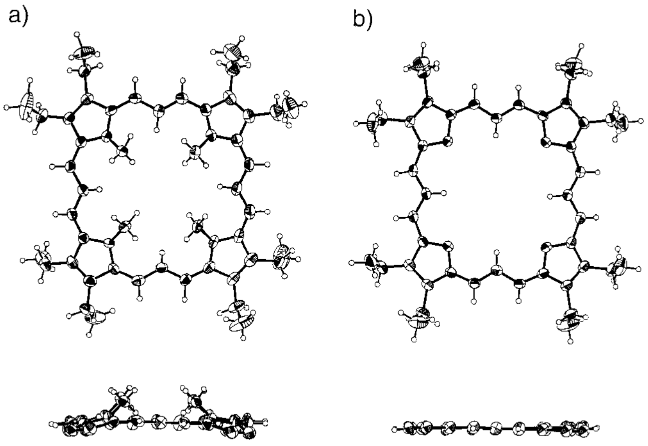


Figure 1. Molecular structures of the 26π porphyrinoids **1** and **2** in the crystal. a) **1**; top: plan view; bottom; side view. b) **2**; top: plan view; bottom: side view (the ethyl groups have been omitted in the side views).

Crystals of the *N,N′,N″,N‴*-tetramethyl[26]porphyrin dication as the bisperchlorate **1**, obtained by treatment of a

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