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 CB2 1EZ (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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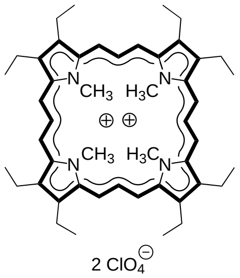
Dedicated to Professor Burchard Franck

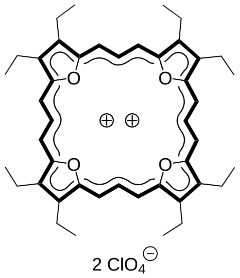
The interdisciplinary interest in porphyrins and their metal complexes has made the development of structural variants of the basic tetrapyrrole macrocycle one of the main lines of current porphyrin research. As a recently published monograph on this topic has demonstrated,[1] the number of new porphyrinoid 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 1 b) 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.

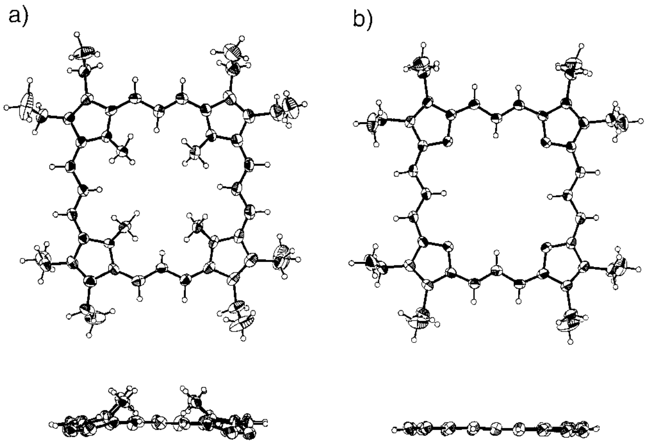


Figure 1. Molecular structures of the 26π porphyrinoids **1** and **2** in the crystal. a) **1**; top: plan view; bottom; side view. b) **2**; top: plan view; bottom: side view (the ethyl groups have been omitted in the side views).

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

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solution of the bis(trifluoroactate) in acetonitrile with 70% perchloric acid (green platelets with a metallic sheen with incorporation of acetonitrile in a ratio of 1:1), were also suitable for X-ray structure analysis.[4] This analysis revealed the dication as an approximately C_4-symmetric molecule whose ring skeleton assumes the shape of a flat bowl (Figure 1a). The slight deviation of the framework from planarity, which should not be too detrimental to the delocalization of the π-electron system in the C_{28} perimeter, arises because the four pyrrole rings are tilted by 16–19° out of the plane formed by the C_3 segments towards the same side of the molecule. As a result of pyramidalization at the nitrogen atoms the N-methyl groups protrude an additional 21–25° from the described reference plane (Figure 2).

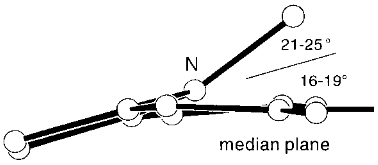
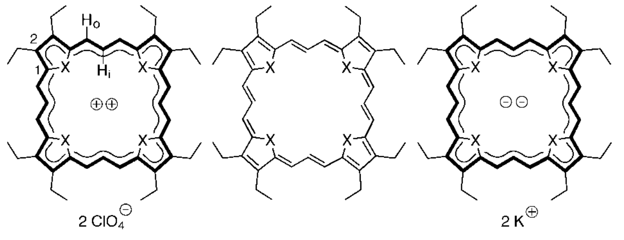


Figure 2. Partial structure of **1** (schematic) as viewed from the side. Illustration of the deviation of the pyrrole rings from the median plane and pyramidalization at the nitrogen atoms.

As determined from molecular models and calculations,[6] the steric interaction of the N-methyl groups with the respective neighboring inner perimeter hydrogen atoms—and not a mutual hindrance—is responsible for their displacement from the interior of the molecule. With respect to the bond lengths in the C_3 perimeter segments and the bond-length relationship in the five-membered heterocyclic rings, **1** resembles the tetraoxa[26]porphyrin dication **2**. In anticipation of the NMR results, it should be mentioned here that **1** exhibits dynamics which are interpreted on the basis of an inversion process.

A comparison of the ^{1}H NMR spectra (room temperature) of dications **1** and **2** (Table 1) shows that the deviation of the ring framework from planarity detected in the structural analysis of **1** is too small to manifest itself in a weakening of the diamagnetic ring current effect. This finding is in accordance with the observation that the lower homologue of **1**, the octaethyl-*N,N′,N″,N‴*-tetramethyl[18]porphyrin dication (as the bisperchlorate),[7a,b] in which the ring framework is markedly deformed, still exhibits a considerable ring current effect. As can be seen from Table 1, a conspicuously good agreement exists between the chemical shifts of the outer- and inner-perimeter protons H_o and H_i of **1** and **2**—and thus also for the $\Delta\delta$ value ($\delta(H_o) - \delta(H_i)$), which may be regarded as an indicator of the ring current effect. The low- and high-field shifts of H_o and H_i in **1** and **2**, which at a first glance appear abnormal (for comparison: the signal for H_o in **2** is shifted to lower field by about 2.8 ppm relative to that for the *meso* protons in the octaethyltetraoxa[18]porphyrin dication[8]), may be rationalized in part if it is considered that the strength of the diamagnetic ring current effect increases with the number of π electrons and with the area of the molecule.[9]

Table 1. Characteristic ^{1}H NMR data of **1** and **2** (in CD_3CN) as well of **3**–**6** (in $[D_8]$THF).



1, 2 **3, 4** **5, 6**

X = NCH_3	**1**		**3**	**5**
$\delta(H_o)$	14.06	$\Delta\delta = 26.0$	2.53	12.27
$\delta(H_i)$	–11.98		16.48	–11.78
$\delta(NCH_3)$	–9.46		10.23	–8.89
X = O	**2**		**4**	**6**
$\delta(H_o)$	14.42	$\Delta\delta = 25.5$	2.58	12.78
$\delta(H_i)$	–11.12		15.94	–12.21

In light of the structural findings the ^{1}H NMR spectrum of **1** at room temperature, which suggests the presence of a D_{4h}-symmetric and thus planar molecule, can only be explained by the assumption that the NCH_3 groups oscillate through the ring framework very quickly on the NMR time scale. In agreement with this a splitting of the signals for the diastereotopic CH_2 ethyl protons occurs in the low-temperature spectrum (in CD_2Cl_2/CF_2Br_2 at –135 °C) of the bis(trifluoroacetate) of the dication, which was used instead of the bisperchlorate because of improved solubility. By using the Eyring equation an activation barrier of $\Delta G^{\neq} = 8.6\,\text{kcal}\,\text{mol}^{-1}$ for the inversion process of the NCH_3 groups was derived from the coalescence temperature of the CH_2 signals (–93 °C).

The comparison of the NMR spectra of **1** and **2** is appropriately complemented by inclusion of the spectra of the neutral [28]annulenes **3** and **4** ($4n\pi$ systems) and the 30π dianions **5** and **6** [$(4n+2)\pi$ systems] (Table 1), which can be generated from the corresponding dications by chemical two- or four-electron reduction with potassium in tetrahydrofuran.[10] The tetraepoxy[28]annulene **4** (blue, microcrystalline solid; decomposition above 0 °C) could be isolated with some effort by reoxidation of the readily formed dianion **6** (obtained at room temperature) with atmospheric oxygen at –78 °C. In contrast **3**, which is formed without significant overreduction by reduction of **1** at –78 °C, was characterized by NMR spectroscopy only. The final reduction products **5** and **6** are, as expected, completely stable in solution. According to Table 1 the transition from the diatropic dications **1** and **2** to the paratropic annulenes **3** and **4**, respectively, causes a spectacular reversal (kind of "umpolung") of the chemical shifts of the inner- as well as the outer-perimeter protons. In the case of **1**/**3**, regardless of the slight deformation of the ring framework, this umpolung is similar in magnitude as that for **2**/**4**. The latter finding is remarkable in that the paratropy of [4*n*]annulenes is relatively sensitive to deviations from planarity in the ring framework.[7c] Apart from the observation that the increased electron density in **5** and **6** causes a moderate high-field shift of the signals for the perimeter protons, the spectra of the diatropic dianions **5** and **6** are analogous to those of the dications **1** and **2**.[11]

The UV/Vis spectra of **1** and **2** (Figure 3) show the expected similarity with respect to the position and appearance of the Soret and Q bands. Surprisingly, however, the spectra differ dramatically in terms of the molar extinction coefficients ε of the Soret band in that $\varepsilon_{\text{Soret}}$, which exhibits the unusually high value of almost $1 \times 10^6\,\text{M}^{-1}\,\text{cm}^{-1}$ for **1**, is increased still further to the record value of $1.6 \times 10^6\,\text{M}^{-1}\,\text{cm}^{-1}$ for **2**. This result is all the more remarkable since the oscillator strength of the Soret band of **2** (3.8) is only marginally greater than that of **1** (3.6). The occurrence of only one Soret band in the spectra of **1** and **2** shows that the two Soret transitions are degenerate, as required by the presence of fourfold symmetry. For both **1** and **2** the Soret band exhibits only a weakly developed vibrational structure, which indicates that the molecular geometry in the electronic ground state S_0 and in the singlet state S_2 is almost identical. The extremely high $\varepsilon_{\text{Soret}}$ value found for **2** corresponds with the considerable reduction in the half-peak width of the Soret band to 600 cm^{-1} compared to about 1000 cm^{-1} observed for **1**. The relatively large half-peak width of this band for **1** most likely results from a perturbation of the fourfold symmetry, which is caused by the different degree of twisting of the pyrrole rings and the associated scattering of the conformational alignment of the NCH_3 groups. The slight increase in the oscillator strength of **2** in comparison to **1** suggests that the frontier orbitals of **2** are more strongly located at the C_{28} perimeter than is the case for **1**.

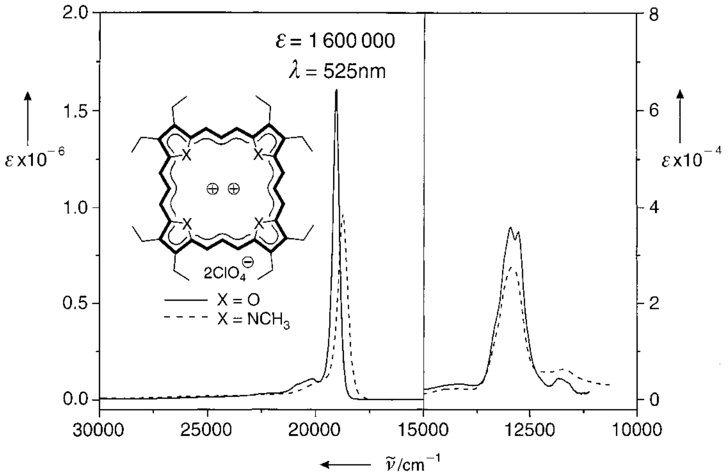


Figure 3. UV/Vis spectra (in HCOOH) of **1** (----) and **2** (——).

Because of the fourfold molecular symmetry, the degenerate Q transitions[12] are allowed for **1** and **2** in addition to the degenerate Soret transitions. However, the 0-0 transition of the Q band occurring at 11 800 cm^{-1} for both molecules is relatively weak ($\varepsilon \approx 4000$; Figure 3). The low intensity of this transition can be attributed to the S_1 state having negative pseudoparity.[13] Since Soret and Q transitions in porphyrinoid systems with fourfold symmetry belong to the same irreducible representation a strong vibrational coupling results, which leads to a marked increase in the intensity at 12 800 cm^{-1}.

In respect to the relationship between UV/Vis spectroscopy and molecular symmetry, the discussion of the UV/Vis spectra of **1** and **2** is closely associated with the previous investigation of tetraoxa[4n+2]porphyrin dications ($n = 4-6$).[3c] While in that case the dependency of the habitus of the spectrum on the geometry of the respective planar C_{4n+2} perimeter was demonstrated, it could be shown here how a perturbation of the D_{4h} symmetry in [26]porphyrin dications affects the spectra of such molecules.

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[4] Crystal structure data for **1**: $C_{48}H_{64}N_4 \cdot 2\,ClO_4 \cdot CH_3CN$, $M = 936.99\ \text{g mol}^{-1}$; crystals from acetonitrile/perchloric acid, crystal dimensions $0.35 \times 0.30 \times 0.25$ mm; orthorhombic, space group $P2_12_12_1$, $a = 11.783(1)$, $b = 17.576(1)$, $c = 24.358(1)$ Å, $V = 5044.5(6)$ Å^3; $Z = 4$, $\rho_{\text{calcd}} = 1.234\ \text{g cm}^{-3}$; $F(000) = 2000$; $\mu_{\text{Mo}} = 0.185\ \text{mm}^{-1}$; 11 006 measured, 10 564 independent, 6412 observed reflections ($F_o^2 > 2\sigma F_o^2$); $\Theta_{\max} = 27°$; $R1 = 0.065$, $wR2 = 0.140$. Crystal structure data for **2**: $C_{44}H_{52}O_4 \cdot 2\,ClO_4 \cdot 2\,HCOOH$, $M = 935.81\ \text{g mol}^{-1}$; crystals from acetonitrile, crystal dimensions $0.30 \times 0.20 \times 0.20$ mm; triclinic, space group $P\bar{1}$, $a = 12.592(1)$, $b = 13.143(1)$, $c = 16.464(1)$ Å, $\alpha = 110.80(1)$, $\beta = 107.09(1)$, $\gamma = 97.04(1)°$, $V = 2354.9(3)$ Å^3; $Z = 2$, $\rho_{\text{calcd}} = 1.320\ \text{g cm}^{-3}$; $F(000) = 988$; $\mu_{\text{Mo}} = 0.207\ \text{mm}^{-1}$; 20 159 measured, 9992 independent, 6497 observed reflections ($F_o^2 > 2\sigma F_o^2$); $\Theta_{\max} = 27.00°$; $R1 = 0.066$, $wR2 = 0.175$. Nonius-Kappa-CCD diffractometer, room temperature, $\text{Mo}_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). The structures were 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); $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$. Programs used: for structure determination SHELXS-86 and for refinement SHELXL-93 (G. M. Sheldrick, Universität Göttingen). Calculations were carried out at the data processing systems of the regional computer center, Universität Köln. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-119092 and-119093. 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).

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[11] A triad of $(4n+2)\pi$ dications, $[4n]$annulenes, and $(4n+2)\pi$ dianions analogous to **1**/**3**/**5** and **2**/**4**/**6** has been reported by K. Müllen, T. Meul, E. Vogel, U. Kürschner, H. Schmickler, O. Wennerström, *Tetrahedron Lett.* **1985**, 3091–3094.

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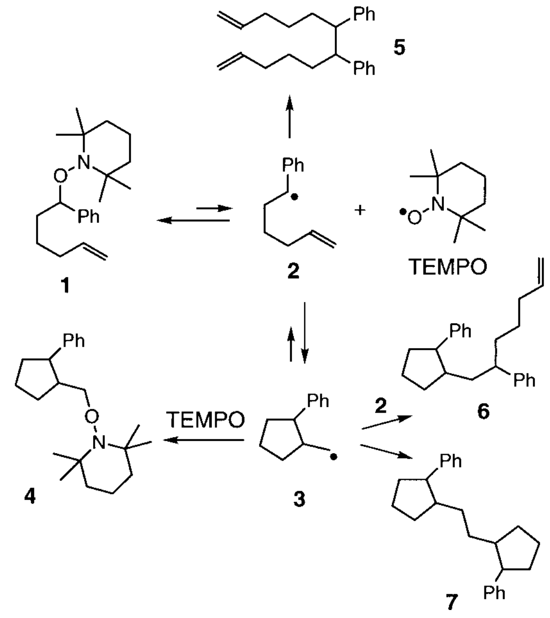

Scheme 1. Radical 5-*exo*-cyclization with use of the persistent 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO) radical.

Tin-Free Radical Cyclization Reactions Using the Persistent Radical Effect**

Armido Studer*

Organotin compounds have found widespread application in conducting various types of radical reactions.[1] Despite this important utility, there are drawbacks associated with tin-based radical chemistry, namely, toxicity of organostannanes that necessitate special handling of disposal, and in many instances problems with product purification. Therefore, various research groups have been looking for alternatives.[2] Herein we report new tin-free radical cyclization reactions based on the persistent radical effect (PRE).

The PRE[3, 4] is a general principle that explains the highly specific formation of the cross-coupling product (R^1–R^2) between two radicals R^1 and R^2 when one species is persistent (long-lived) and the other transient; the two radicals must be formed at equal rates. The initial buildup in concentration of the persistent species, caused by self-termination of the transient radical, steers the reaction to follow a single pathway for the cross-reaction. The PRE has already been used in various chemical systems[3, 5] and is important in stable free radical polymerization (SFRP).[6]

In Scheme 1, an application of the PRE for a 5-*exo* cyclization with the 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO) radical as persistent species is suggested. It is known that α-phenyl-substituted alkoxyamines such as **1** have weak C–O bonds which are homolytically cleaved upon heating.[6, 7] C–O bond homolysis in **1** will therefore lead to the persistent TEMPO radical and the transient radical **2**.[6–10] Radical **2** can either be trapped by TEMPO to reform **1**, or it can undergo a 5-*exo* cyclization (the 6-*endo* cyclization is omitted in Scheme 1) to form a new radical **3**, which after trapping with TEMPO affords **4**. The trapping of **3** with TEMPO is irreversible, because the C–O bond in an alkoxyamine derived from TEMPO and a primary alkyl radical is too strong to be homolytically cleaved.[7] Due to the low concentration of TEMPO during the isomerization,[6b] **3** is long-lived and the cyclization from **2** to **3** is probably reversible.[11] According to the PRE, the coupling products **5**–**7** from the transient radicals **2** and **3** should be formed in very low yields, and the isomerization of **1** should occur almost quantitatively.[4] Furthermore, degenerate radical reactions (reversible initial C–O bond homolysis in our system) have been shown to suppress potential side reactions by reforming starting material when the desired cyclization does not proceed effectively.[5b]

To test the concept of the PRE in cyclization reactions, alkoxyamine **1** was prepared from 1-bromo-1-phenyl-5-hexene and the Ca alkoxide (2 equiv) of 1-hydroxy-2,2,6,6-tetramethylpiperidine in refluxing THF (14 h, 80%).[12, 13] The isomerization reaction depicted in Scheme 1 was studied under different conditions (Table 1). In *tert*-butylbenzene and *N*,*N*′-dimethyl-*N*,*N*′-propylene urea (DMPU), no isomerization was observed (entries 1 and 2). In DMF after 16 h, **4** was isolated in 56% yield (*trans*:*cis* = 2.5:1)[14] along with the 6-*endo* product **8** (10%, *trans*:*cis* = 1:1; entry 3). In *t*BuOH (0.1 M) clean but slower isomerization occurred (entry 4) and lowering the concentration (0.1 M → 0.01 M) has no significant effect (entry 5). Interestingly, the reaction was accelerated by addition of camphorsulfonic acid (CSA, entry 6),[15] with the best results obtained in *t*BuOH (0.02 M) with 10% CSA (entry 7). The isomerization products were isolated in 83% yield along with **9** (2%).[16]

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