

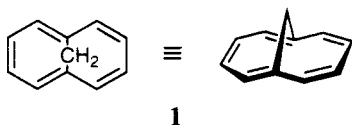
Institut für Organische Chemie der Universität zu Köln, Greinstr. 4, 50939 Köln, Germany

The cornucopia of novel porphyrinoid macrocycles that - as a result of a symbiotic link between annulene and porphyrin chemistry - has emerged from the Cologne laboratory over the last decade is reviewed.

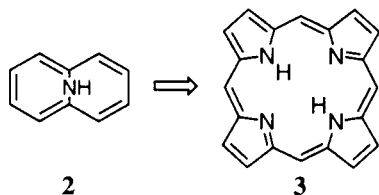
J. Heterocyclic Chem., **33**, 1461 (1996).

Introduction

It was at the 10th Congress of Heterocyclic Chemistry at Waterloo (Canada) in 1985 that I had the privilege to outline "The Heterocyclic Dimension of Bridged Annulene Chemistry" [1]. This facet of our research arose from the discovery, more than thirty years ago, of the Hückel-type aromatic hydrocarbon 1,6-methano[10]annulene **1** which is generally regarded as one of the best models yet for the hypothetical 10π -homologue of benzene [2].



1,6-Methano[10]annulene **1** - subsequently introduced into Organic Syntheses [3] - proved to be aromatic not only in the spectroscopic but, to a large extent, also in the classical chemical sense [4]. It thus occurred to us that this annulene might serve as a "Leitstruktur" for the development of novel heterocycles likely to be endowed with unusual properties. The viability of this concept was vindicated in due course by the synthesis of the chemically very versatile NH-bridged [10]annulene, 1,6-imino[10]annulene **2** [5]. Over the years, the advent of **2** was followed by the emergence of a host of other [10]- or [14]annulene-based heterocycles, a cross-section of which is given in the abstract (Fig. 1) of the 1985 lecture [1].



Apart from representing the key molecule among this class of heterocycles, 1,6-imino[10]annulene **2** plays a pivotal role in symbiotically linking the "bridged annulenes of the laboratory" to the "bridged annulenes of nature", the annulene chemist's view of the porphyrins [6].

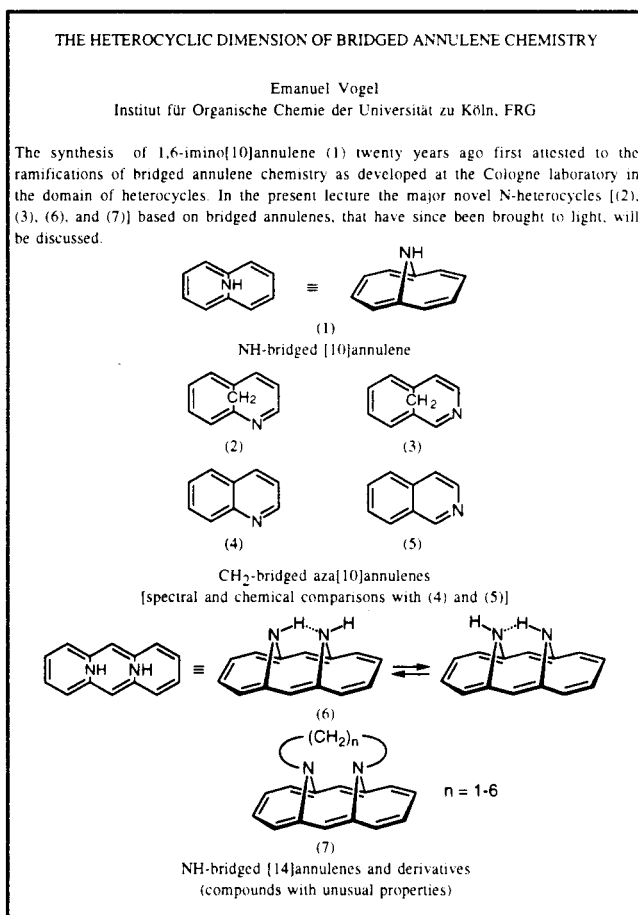
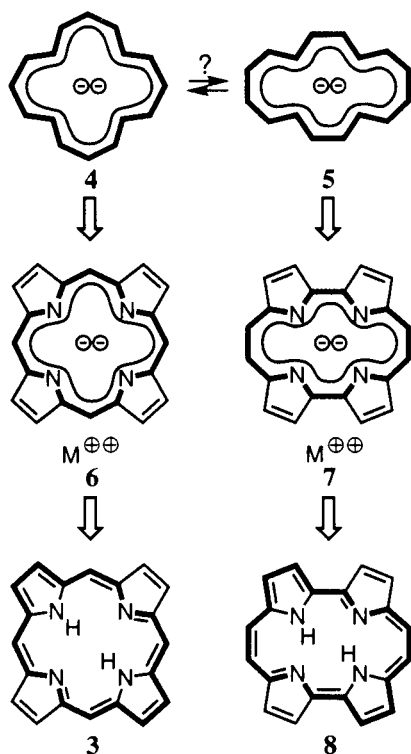


Figure 1. Abstract of the author's plenary lecture at the 10th Congress of Heterocyclic Chemistry (Waterloo, Canada, 1985).

As already pointed out at the time of its synthesis, **2** favorably compares with porphyrin **3** in ^1H NMR spectroscopic terms, especially with regard to ring current effects. This analogy made us receptive to the [18]annulene model of porphyrin [7] which, due to the presence of an 18π main conjugation pathway, invites the application of Hückel's $(4n+2)$ rule to the tetrapyrrolic macrocycle. Although the ramifications of this model had already been demonstrated by the landmark syntheses of the sapphyrins by R.B. Woodward [8] and of the corroles by A.W. Johnson [9] as early as 1965-70,

the cornucopia of novel porphyrinoid chromophores it entails has become fully apparent only in recent years. Guided by our experience in annulene chemistry, we set out a decade ago on a systematic exploration of potentially aromatic porphyrin structural variants that could be anticipated to generate interdisciplinary interest. Research programs complementary to ours had also independently been initiated at about the same time by the groups of B. Franck [10] and J.L. Sessler [11]. In this account the contributions from the Cologne laboratory to the field will be surveyed.

Porphyrin Isomers



The discovery of porphycene **8** at the Cologne laboratory in 1986 [12] has opened up a new avenue of research in porphyrin chemistry having great potential: the porphyrin isomers. Although such tetrapyrrolic macrocycles are among the most obvious porphyrin structural variants, surprisingly, not even a hint as to their possible existence could be found in the chemical literature prior to the synthesis of **8**. As revealed by pertinent methods of investigation, porphycenes qualify as porphyrin-like in many of their physical and chemical properties [6]. Additionally, their brilliant colors and general optical behavior - **8** and most of its derivatives are strongly fluorescent blue pigments exhibiting remarkable photostability - make these compounds a chemist's delight.

It is of interest to note that the idea of porphycene originated from investigations in [16]annulene chemistry, i.e., from our admittedly unsuccessful search for the presumed equilibrium between the well-known 18 π -electron [16]annulene dianion **4** [13] and the as yet hypothetical configurational isomer **5**. Having been aware of the structural and electronic relationship that **4** bears to the dianion **6** of porphyrin (as its magnesium complex) [14] it occurred to us that **5** is similarly related to dianion **7**, an isomer of **6**. To get to **8** requires only protonation of dianion **7**.

In simpler terms, **8** can be derived from porphyrin **3** by reshuffling the pyrrole and methine moieties of the latter in such a way as to maintain an N_4 coordination site. This conceptual approach to porphycene led us to the realization that **8** is but one member of a family of no less than seven porphyrin isomers - compounds **8-14** - having an N_4 core and one or two *cisoid* $C\equiv CH\equiv CH\equiv C$ units (arene fragments) as common features (Table 1) [15]. In order to get a feeling for the stabilities of the isomers, their relative energies - with **3** as the reference - were calculated employing the PM3 and BLYP/6-31G**//3-21G methods [16]. From these calculations the following may be deduced: 1) Porphycene matches porphyrin in energy although it is slightly strained; presumably, the strong N-H...N hydrogen bonds present in this isomer maintain the energetic balance. 2) The relative energies rise considerably as one goes from **3/8** to **14**; however, the increase remains modest for **9** and **10**. 3) Planarity of the ring skeleton applies to all of the isomers except **14**. - Based on the above considerations, among the isomers still awaiting synthesis, at least **9** and **10** seemed likely to be endowed with properties characteristic of porphyrins.

The synthesis of porphyrin isomers poses a challenge since it is obvious that methodology generally used in making porphyrins, such as biomimetic routes, would hardly provide access to these possibly non-natural target molecules. Viewing the generation of the formal double bond(s) - common to all of the isomers - as the key step of the synthesis, we reasoned that these molecules might best be approached by reductive carbonyl coupling of appropriate open-chain di- or tetrapyrrolic α,ω -dialdehydes (or diketones). Indeed, the McMurry coupling reaction [17], hitherto alien to porphyrin chemistry [18], has thus far proved to be the method of choice for the preparation of porphyrin isomers.

In the case of porphycene synthesis, which got all of the work in the field started, Woodward and Dolphin's 5,5'-diformyl-2,2'-bipyrrole **15** [8] appeared to be an ideal

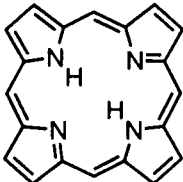
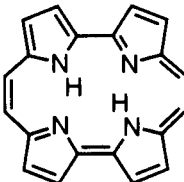
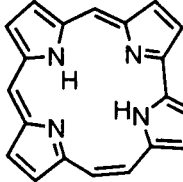
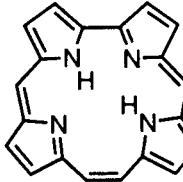
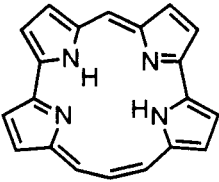
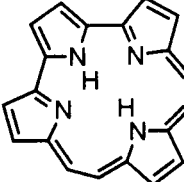
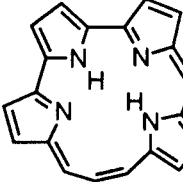
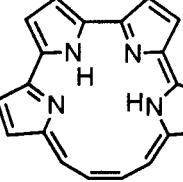
				
	-(1.1.1.1) Porphyrin 3	-(2.0.2.0) Porphycene 8	-(2.1.1.0) Hemiporphycene 9	-(2.1.0.1) Corrphycene 10
PM3	0.0	1.7	8.6	16.0
BLYP /6-31G** //3-21G	0.0	-1.5	5.1	12.0
				
	-(3.0.1.0) Isoporphycene 11	-(2.2.0.0) 12	-(3.1.0.0) 13	-(4.0.0.0) 14
PM3	23.6	33.3	39.7	53.9
BLYP /6-31G** //3-21G	19.0	30.6	38.7	70.6

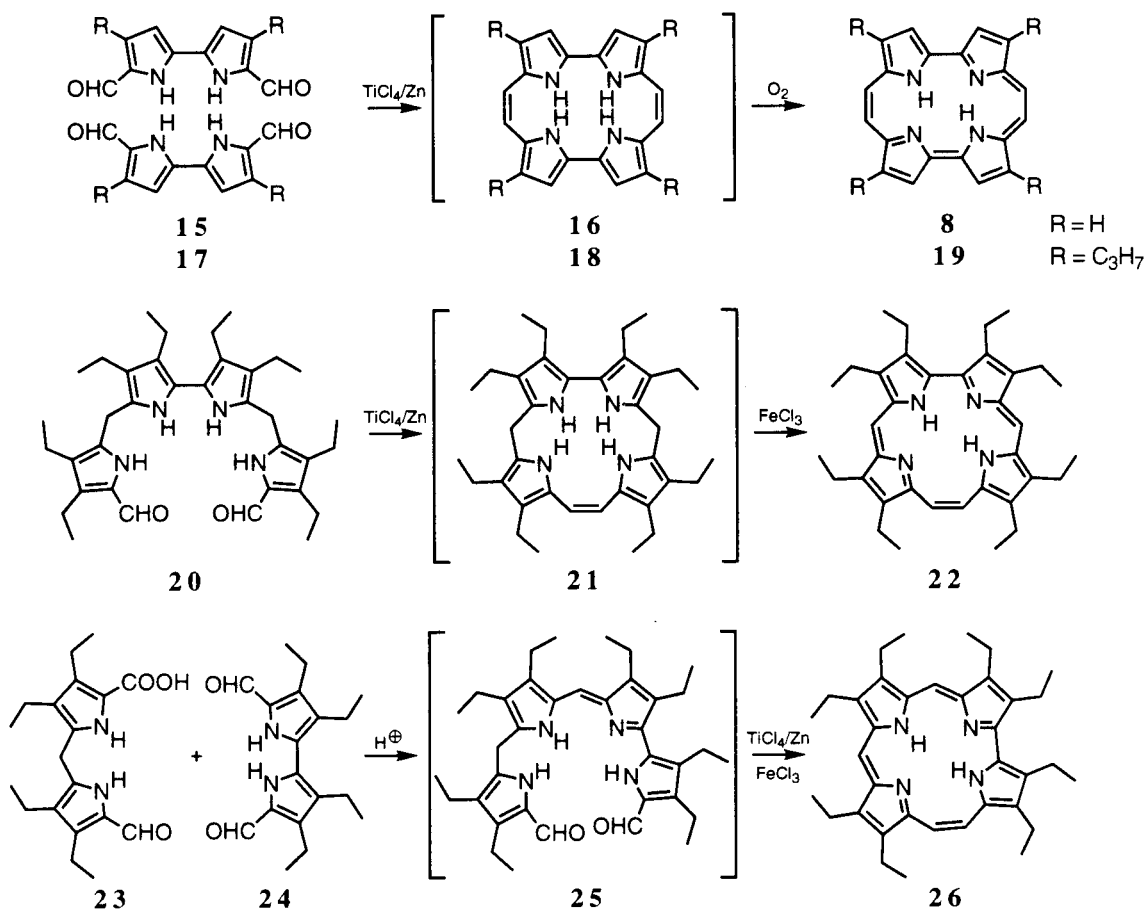
Table 1. The isomers of porphyrin **3** with an N₄ coordination site, [18]porphyrins-(·:·:·) **8-14**, and their relative energies (kcal mol⁻¹) calculated with **3** as the reference. The formulae represent the most stable among the respective NH tautomers.

building block. Indeed, reductive carbonyl coupling of **15** by means of titanium tetrachloride/zinc directly afforded porphycene **8** in low yield as the only non-polymeric product. Remarkably, the obligatory intermediate of the reduction, the *N,N'*-dihydroporphycene **16**, an NH-bridged [20]annulene, turned out to be so prone to oxidation that it escaped detection even when oxygen was excluded from the reaction medium. Embarking from the appropriate bipyrrole dialdehydes or diketones, McMurry coupling has since allowed the preparation of an entire host of alkyl- and aryl-substituted porphycenes (yields as high as 30%) [19]. Among these, the symmetrical 2,7,12,17-tetrapropylporphycene **19** (from **17** via **18**) stands out, for its favorable solubility properties have made it the "workhorse" in developing porphycene chemistry [19a].

The synthesis of porphycene inspired the idea that other porphyrin isomers, in particular [18]porphyrin-(2.1.1.0) **9** (hemiporphycene) and [18]porphyrin-(2.1.0.1) **10** (corrphycene), might be made. Recently, this expectation has been borne out in a joint project between J.L. Sessler

at the University of Texas at Austin and the Cologne group. Their collaborative effort resulted in successful approaches to both octaethylcorrphycene **22** [20] and octaethylhemiporphycene **26** by means of reductive coupling employing the tetrapyrrolic α,ω -dialdehydes **20** and **25** (the latter generated *in situ* from **23** and **24**), respectively, as strategic precursors. In contrast to **16/18** in the porphycene series, the primary product of coupling of **20** (i.e., **21**) and of its counterpart in the hemiporphycene series (not shown here) do not undergo spontaneous oxidation. Rather, these intermediates need to be treated with iron(III) chloride or other oxidizing agents in order to effect final conversion into the respective porphyrin isomer. Attesting to the interest porphyrin isomers have attracted, further syntheses of corrphycenes [21] and hemiporphycenes [22] have almost simultaneously been described.

In our previous studies on porphycene, encompassing the elaboration of its coordination chemistry (next section), we have shown that this tetrapyrrolic macrocycle



bears a surprisingly close relationship to porphyrin. As evidenced by very recent findings, the same is true for the new isomers corrophycene **22** and hemiporphycene **26**. Needless to say, the availability of porphyrin and three of

its isomers invites a wide range of comparative investigations (covering physical, chemical, medicinal and even material science aspects) on this intriguing set of compounds.

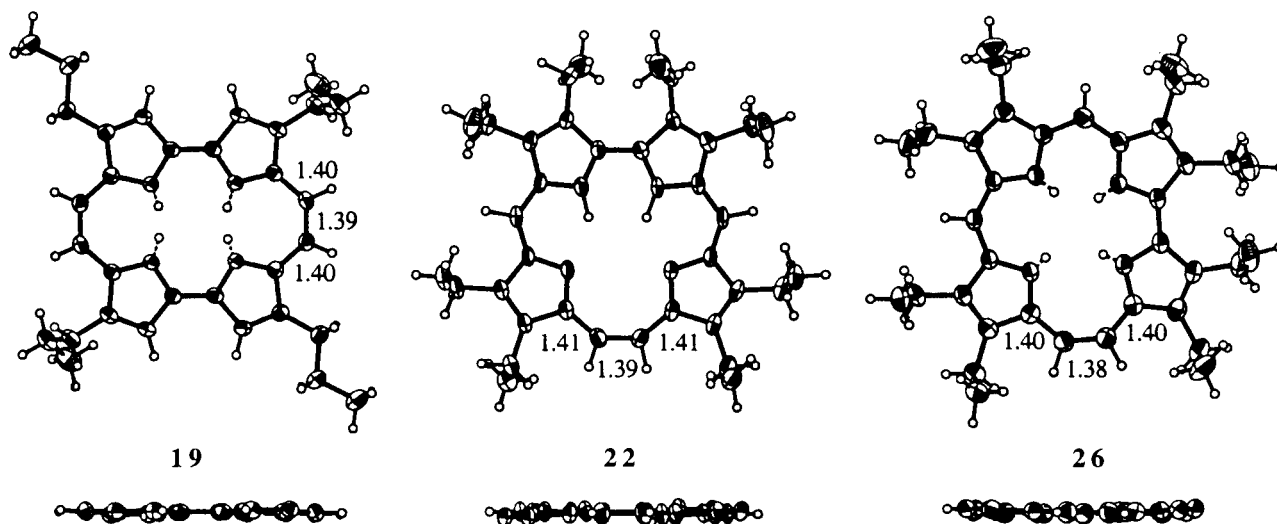


Figure 2. Molecular structures of tetrapropylporphyrin **19**, octaethylcorrophycene **22**, and octaethylhemiporphycene **26** in the solid state (top: top views, bottom: side views, substituents are omitted for clarity).

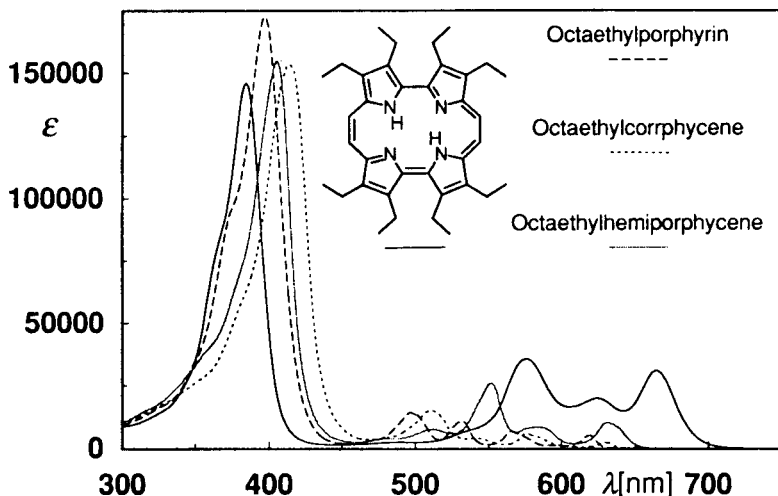


Figure 3. UV/vis spectra (in dichloromethane) of octaethylporphyrin, octaethylporphycene, octaethylcorphycene **22** and octaethylhemiporphycene **26**.

The basis for such investigations is laid by the structural finding that the three isomers, like porphyrin, are planar aromatic species (see Fig. 2). In each of the isomers, aromaticity manifests itself particularly clearly in the observation that the CC bonds of the C₄ unit containing the formal double bond do not alternate in length, but are typical benzenoid aromatic bonds (this analogy to the acenes was responsible for the ending "cene" in the names given to these isomers).

The similarities between porphyrin and its isomers found to exist with respect to molecular structure extend, as anticipated, to the electronic structure of these compounds [23]. The UV/vis spectra of all of the isomers (as octaethyl derivatives), shown together with the spectrum of octaethylporphyrin in Fig. 3, are distinctly porphyrin-like in that they exhibit the characteristic Soret band in the 400 nm region as well as a set of Q bands at longer wavelengths.

Qualitatively, the UV/vis spectrum of porphycene differs from those of its congeners in that it possesses a relatively strong Q band absorption at 560-680 nm, i.e., in the region where blood and body tissue are fairly translucent. This absorption pattern in conjunction with other photophysical properties of the compound [24], such as its stability towards photooxidation, its high quantum yields of fluorescence and singlet oxygen sensitization, render porphycenes promising agents for the detection and photodynamic therapy (PDT) of tumors [25]. In light of favorable toxicology tests on porphycenes and the potential these compounds might have not only in PDT but also in the treatment of diverse dermatological diseases, a chemical company (Cyto-

pharm, Inc., Menlo Park, CA) has been founded with the intention of developing this type of porphyrin isomer with regard to medicinal applications [26,27].

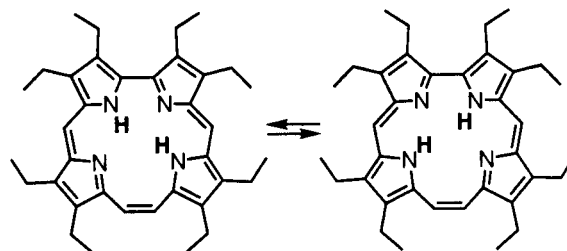


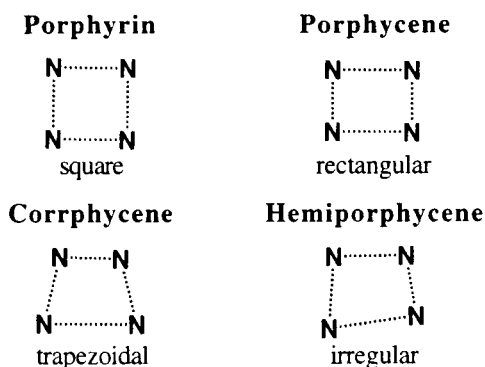
Figure 4. Isodynamic NH tautomerism in octaethylcorphycene **22**.

The observation that the ¹H NMR spectra of porphyrin and its three known isomers fully match with regard to ring current effects provides additional strong evidence in support of the contention that one is dealing with a set of closely related aromatic compounds. Moreover, NMR spectroscopy has allowed the evaluation of the NH tautomerism existing in these molecules [28]. A case in point is the ¹H NMR spectrum of octaethylcorphycene **22**. Here, from an observed temperature dependence, it can be deduced that **22** undergoes an isodynamic NH shift (Fig. 4) rapid on the NMR time scale ($\Delta G^\ddagger = 8.3 \text{ kcal mol}^{-1}$ [20] as compared to 10-15 kcal mol⁻¹ in porphyrins).

Metal Complexes of the Porphyrin Isomers

Taking into consideration the dominant role metalloporphyrins play in porphyrin chemistry, chemical

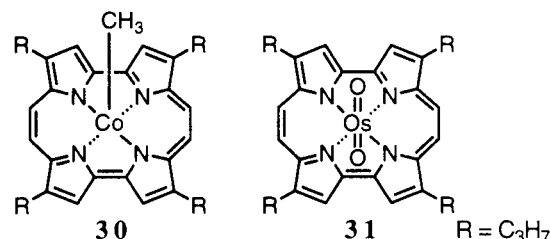
interest in porphyrin isomers naturally focuses on their metal complexation characteristics. Although these isomers exhibit geometries of the N_4 coordination site noticeably deviating from the ideal square shape of the porphyrin core - porphycene: rectangular; corphycene: pronouncedly trapezoidal; hemiporphycene: irregular - all of them prove to be good or even excellent ligands.



Apparently, the three isomers possess sufficient conformational flexibility as to satisfy the stereo-electronic coordination requirements of many metal ions to such an extent that the formation of stable complexes remains possible. In fact, the capability of the isomers to bind metal ions favorably compares, as far as small- or medium-sized ions are concerned, with that of the porphyrins. Insertion of large ions, however, meets with resistance that has as yet been overcome only in a few cases. In spite of this latter limitation, the study of the multifaceted metalloporphycenes [29], -corphycenes [30], and -hemiporphycenes [22,31] has already taken on a dimension that renders these complexes a chapter in itself. Hence, they will be reviewed here only briefly.

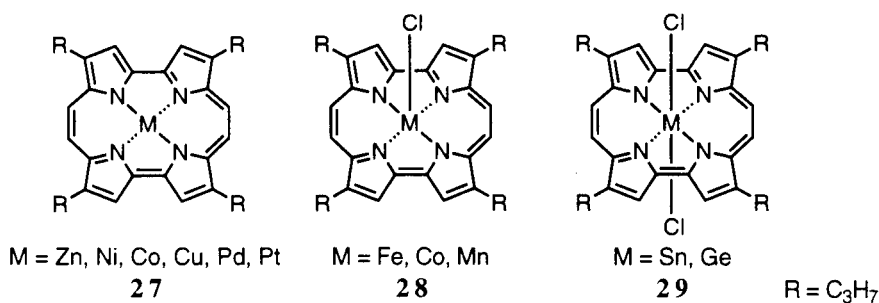
Porphycenes, on which our complexation studies have hitherto been concentrated, show a somewhat reduced tendency to form metal complexes (except with small cations) as compared to porphyrins. In all likelihood, this behavior is not only due to the smaller rectangular shape of their cavity, but also arises from the need to break the exceptionally strong $N-H\cdots N$ hydrogen bonds, typical of porphycenes, upon insertion of metal ions. Irrespective of

this, the spectrum of stable metalloporphycenes - using 2,7,12,17-tetrapropylporphycene **19** as the ligand - comprises complexes of the majority of the more important di-, tri-, and tetravalent metal ions. A representative cross-section of the metalloporphycenes already known and well characterized is given in formulae **27**, **28**, and **29** [29,32].

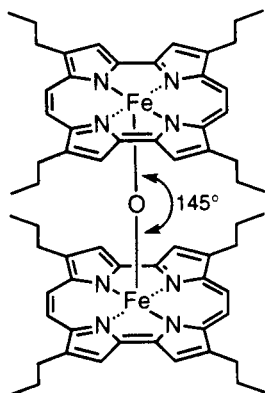
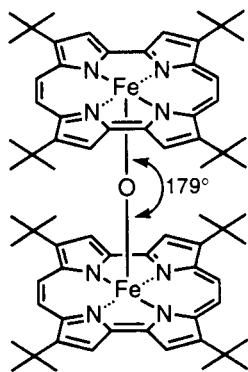


In some cases, complexes of type **28**, when treated with Grignard or organolithium compounds, smoothly underwent exchange of the axial chlorine substituent by alkyl or aryl groups. These transformations afforded stable σ -alkyl or aryl complexes, such as **30** [33], that warrant further examination. Additionally, the formation of the osmium complex **31** by C.-M. Che and C.K. Chang [34] has revealed that porphycenes, contrary to earlier findings, may also bind some of the larger metal ions.

It should be noted that the effectiveness of porphycenes as ligands can be modulated to some extent by peripheral alkyl groups. As inferred from molecular models, these groups can induce changes in the geometry of the porphycene skeleton as a result of non-bonded repulsions between the substituents [35]. Thus, while 2,7,12,17-tetrapropylporphycenatozinc tends to demetallate during chromatography, octaethyl- and etioporphycene form perfectly stable zinc complexes [19b]. This discrepancy is obviously attributable to relief of conformational strain upon metal insertion into the more highly alkyl-substituted porphycenes. Steric effects of alkyl groups in porphycenes, albeit of an entirely different kind, are also operative in the μ -oxo-diiron(III) complex **33** of 2,7,12,17-tetra-*t*-butylporphycene [36]. In contrast to the corresponding iron complex **32**, where the molecule can



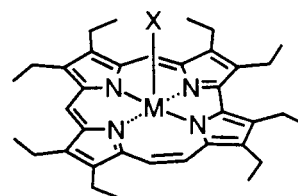
adopt an energetically favored Fe-O-Fe angle of 145° [37], the steric bulk of the substituents in **33** causes a widening of this angle to almost 180° .

**32****33**

Corrphycenes, possessing rather distorted trapezoidal-shaped cavities, were initially anticipated to be far less disposed to bind metal ions than their more symmetrical congeners. Surprisingly, however, it turned out that corrphycenes are excellent ligands, matching (if not exceeding) porphyrins in their tendency to form complexes, specifically with small- and medium-sized metal ions.

The efficacy of octaethylcorrphycene **22** as a ligand can hardly be demonstrated more convincingly than by the

"Periodic Table of Metalloctaethylcorrphycenes" (Fig. 5) [38] in which the metals (as ions) that have up to now been coordinated by **22** are indicated. X-ray crystallographic analyses performed on several of these complexes have provided insight into the geometric changes **22** experiences when serving as a ligand (to be detailed in forthcoming publications).

**34**

Metal-centered chirality

Hemiporphycenes have also been found to exhibit a great affinity for the binding of metal ions. While the first metallohemiporphycene, a nickel complex with diverse peripheral substituents, has recently been discovered serendipitously by H.J. Callot [22], a systematic study on the metal complexation of octaethylhemiporphycene **26** in collaboration with the Sessler group has since produced a sizable number of metalloctaethylhemiporphycenes [31]. The metal ions that to date have been inserted into **26** include: divalent magnesium (with pyridine as an axial ligand), zinc, nickel, and copper, trivalent iron, cobalt, and rhodium, and tetravalent tin. As

22

Li	Be											B	C	N
Na	Mg											Al	Si	P
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi

M

Metals already found to insert into octaethylcorrphycene **22**.

Figure 5. Periodic Table of Metalloctaethylcorrphycenes [30].

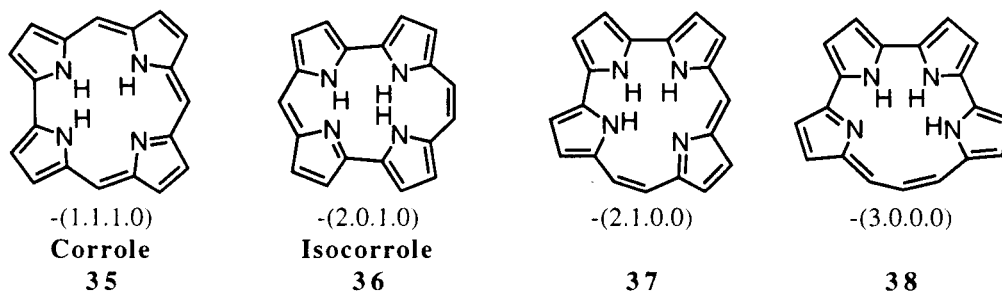
complexing partners, hemiporphycenes are unique among the porphyrinoid tetrapyrrolic macrocycles presently known in that metallohemiporphycenes bearing an axial substituent (e.g., **34**) are distinguished by "metal-centered" chirality and might therefore be separated into enantiomers.

Corrole and Isomers

The "Contracted Porphyrin" corrole **35**, first synthesized (as alkyl derivatives) by the British chemist A.W. Johnson [9], is structurally linked to vitamin B₁₂ [39] in

protons. Corrole, which is a very good ligand, has been reported to form complexes (metallocorroles) with a great variety of metal ions [9,40,41], in particular with cobalt(III), iron(III) [42], nickel(II), and copper(II).

In view of the history of porphyrin isomers it is hardly surprising that the possible existence of corrole isomers has likewise not been considered previously. As shown in Table 2, three isomers of **35**, i.e., compounds **36-38**, are theoretically feasible. Among these, corrole-(2.0.1.0) **36** (as the octaethyl compound **42**) was chosen as the prime target for synthesis because it is calculated by the PM3 and the BLYP/6-31G**//3-21G methods to be the

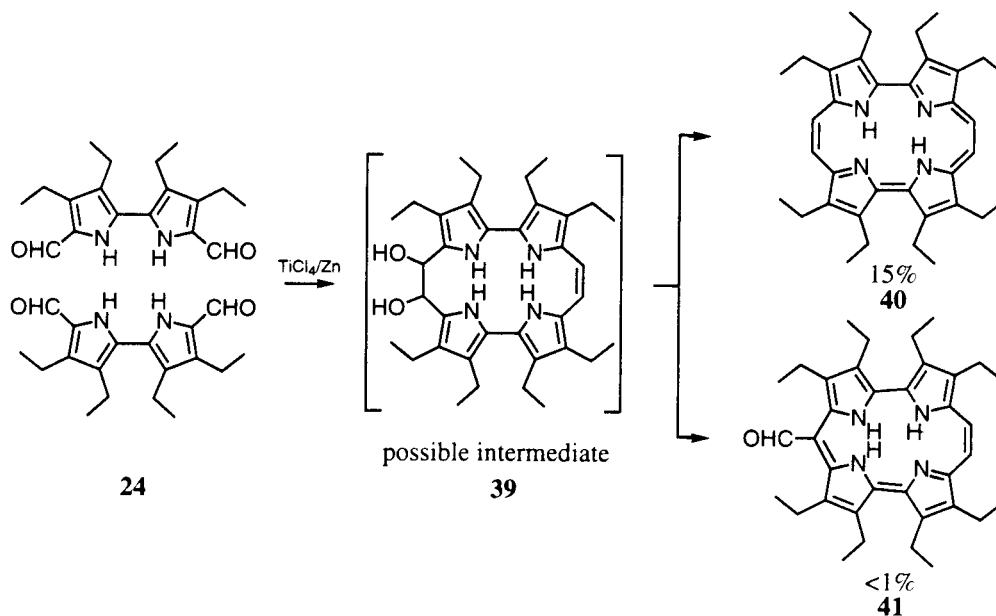


PM3	0.0	3.8	15.3	35.1
BLYP /6-31G** //3-21G	0.0	3.5	15.1	39.8

Table 2. The isomers of corrole **35** with an N₄ coordination site, [18]corroles-(·:·:·) **36-38**, and their relative energies (kcal mol⁻¹) calculated with **35** as the reference. The formulae represent the most stable among the respective NH tautomers.

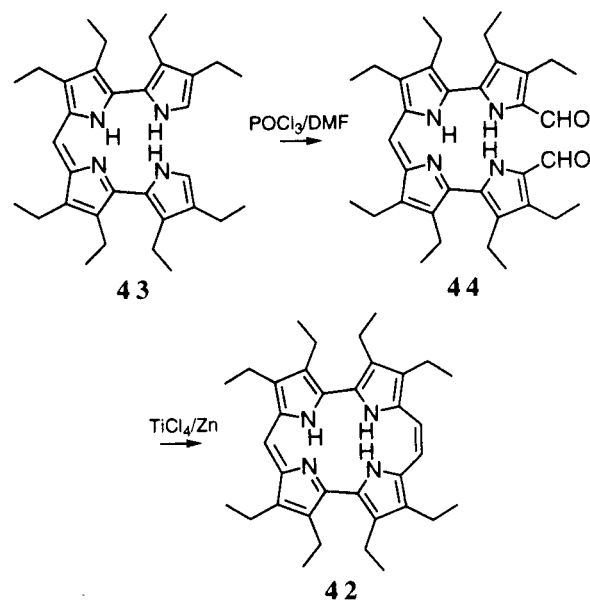
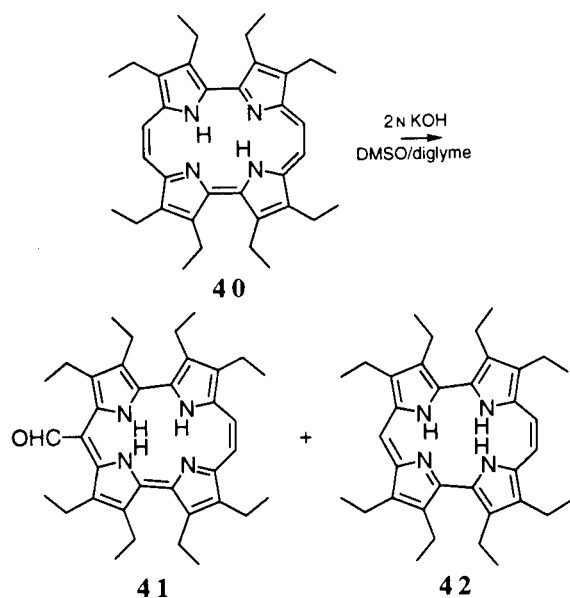
that it constitutes the aromatic parent of corrin. Similar to porphyrin, **35** features an 18 π conjugation pathway, but in contrast to the latter contains three inner NH

most stable of the isomers [43]. Moreover, **42** is inferred from retrosynthetic analysis to be accessible fairly straightforwardly. Work on **42** had hardly gotten under-

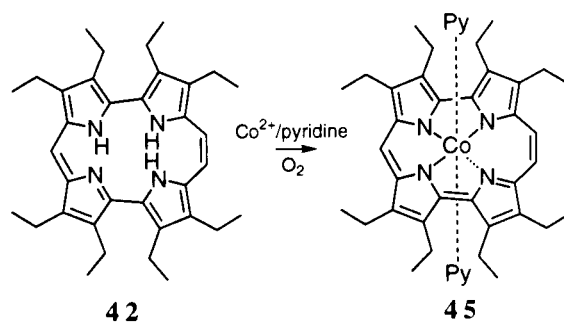


way when we accidentally encountered corroles-(2.0.1.0) (henceforth called isocorroles) on two occasions: firstly, as minor side products in the McMurry reaction of tetraalkyl-substituted 5,5'-diformyl-2,2'-bipyrroles such as **24**, and secondly, in base-induced rearrangements of octaethylporphycene **40**, etioporphycene and 3,6,13,16-tetrabromo-2,7,12,17-tetrapropylporphycene [44].

Chromatography of octaethylporphycene **40** from the reductive carbonyl coupling of **24** gave a well-separated small fraction from which a carbonyl compound, identified as the octaethylisocorrole aldehyde **41** (differing from **42** with respect to its preferred NH tautomer!), was isolated. As shown by control experiments, **41** does not arise from a subsequent rearrangement of **40**. Formation of **41** might best be explained if one invokes the 1,2-glycol **39** as an intermediate in the coupling of **24**; the aldehyde **41** would then be the product of a Wagner-Meerwein rearrangement of **39** [45], presumably brought about by the Lewis acid titanium tetrachloride.



Capitalizing on experience gained in the synthesis of porphyrin isomers, we were able to prepare octaethylisocorrole **42** in a more straightforward manner from the linear tetrapyrrole **43** [46,47] by a sequence involving reductive carbonyl coupling of the tetrapyrrolic α,ω -dialdehyde **44** as the crucial step. In accord with expectation, **42** is similar to octaethylcorrole **46** in spectral and structural respects.

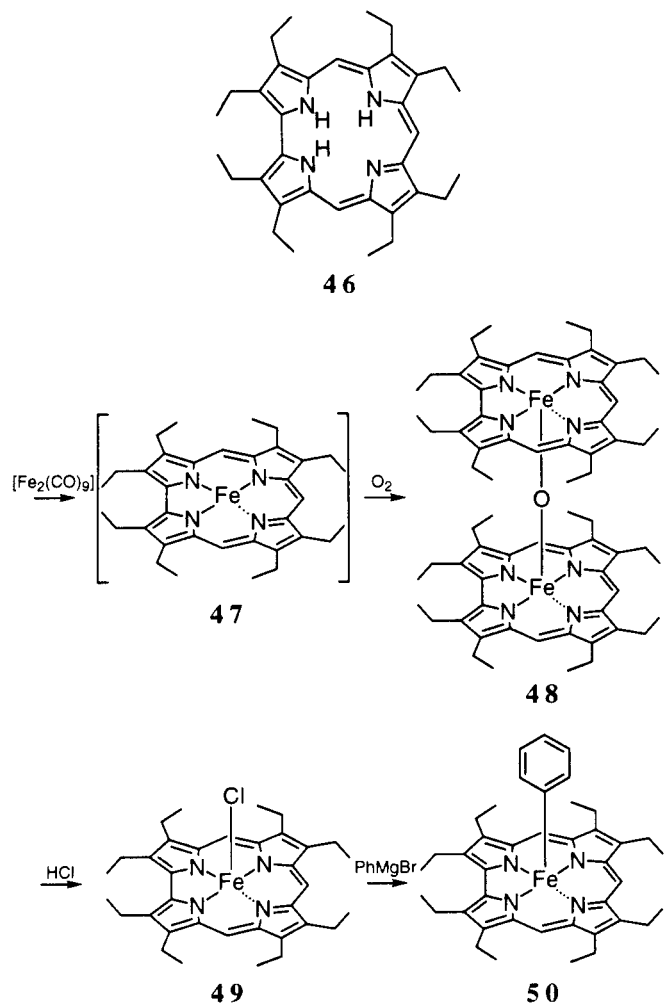


While the contraction of a porphyrin into a corrole has, to our knowledge, not yet been observed, octaethylporphycene **40** was found to be subject to conversion into a mixture of octaethylisocorrole aldehyde **41** and octaethylisocorrole **42** when heated with aqueous potassium hydroxide in dimethylsulfoxide/diglyme. The ratio of compounds **41** and **42** varied depending on reaction conditions. Analogously, 3,6,13,16-tetrabromo-2,7,12,17-tetrapropylporphycene furnished the aldehyde corresponding to **41**, but no decarbonylated product was observed in this case. The mechanism of these intriguing contractions of porphycenes into isocorroles still needs to be unraveled.

Octaethylisocorrole **42** readily forms a cobalt(III) complex **45** containing two molecules of pyridine as axial ligands, but failed (initially) to afford a defined iron(III) complex on treatment with diverse iron(III) transfer agents.

The difficulties encountered in obtaining an iron(III) complex of **42** prompted us to reinvestigate the alleged isolation of iron(III) corrole complexes [42]. In pursuit of this side-line we made the striking discovery that corroles are capable of stabilizing iron in the formal oxidation state IV [48]. As it turned out, reaction of octaethylcorrole **46** with nonacarbonyldiiron, followed by work-up

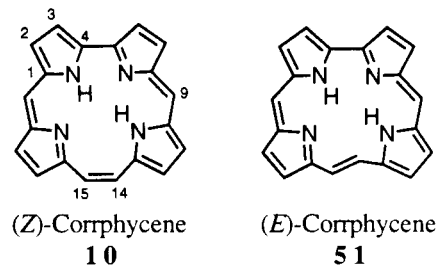
with admission of air, yielded as the only defined product the oxygen-bridged binuclear iron(IV) complex **48**, μ -oxo-bis[octaethylcorrolatoiron(IV)]. This new iron(IV) complex, a stable compound, must have arisen from the spontaneous air oxidation of the iron(III) octaethylcorrole **47**, the assumed primary product. By analogy to the chemical behavior of μ -oxo-bis[octaethylporphyrinatoiron(III)] [49], complex **48** could, in turn, be converted into the mononuclear iron(IV) octaethylcorrole complexes **49**, **50**, and others.



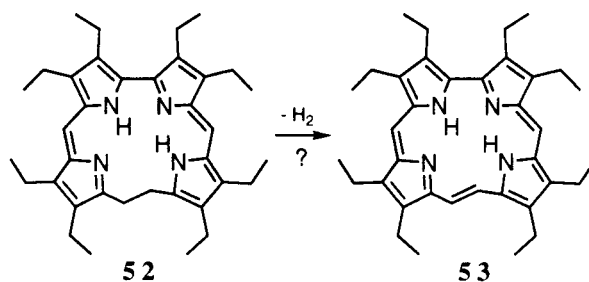
Extension of the aforementioned complexation studies to octaethylisocorrole **42** as a ligand have since shown that **42** parallels **46** in forming binuclear and mononuclear iron(IV) complexes. Due to crystal disorders, however, iron(IV) octaethylisocorroles, do not lend themselves to structural investigations as readily as iron(IV) corroles. To characterize these new complexes other pertinent physical methods were employed [50].

Cyclooctapyrroles - Octaphyrins

Cyclooctapyrroles or octaphyrins-(.....), molecules attracting interest as potentially versatile ligands (e.g., for the formation of bimetallic complexes) [51] are a most recent outgrowth of our synthetic pursuits in the domain of porphyrin isomers and corroles. As already indicated, the isomers have in common the structural feature that they contain one or two formal double bonds. Consequently, these molecules should give rise to geometrical isomerism, i.e., the (*Z*)-forms shown in Table 1 might have (*E*)-counterparts. While (*E*)-porphycene almost certainly suffers from too severe steric constraints to be of more than fleeting existence, (*E*)-forms of the other isomers, notably of hemiporphycene, corphycene, and isoporphycene, are possibly stable enough to be isolable compounds.



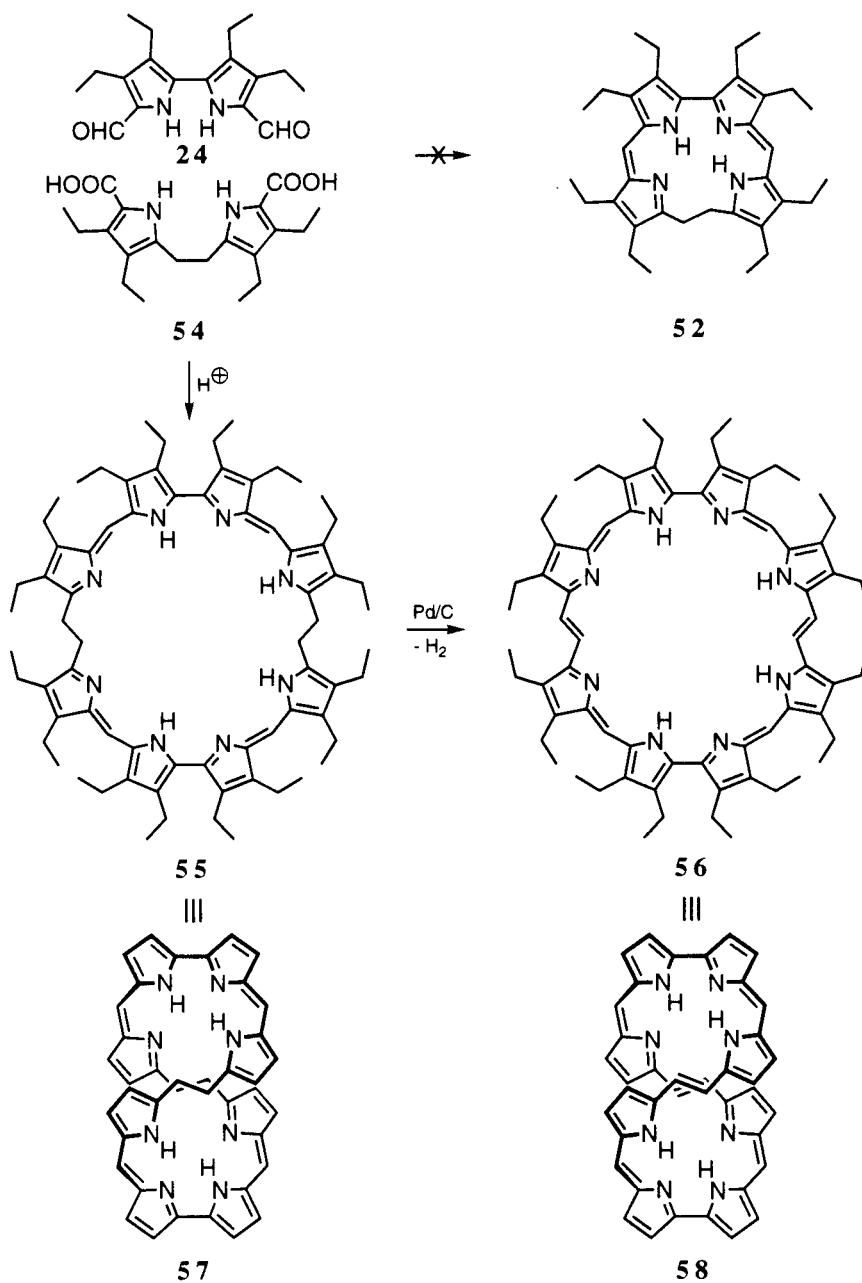
Our interest in the hitherto uncharted territory of (*E*)-configured porphyrin isomers (for reasons of solubility as octaethyl derivatives) has focused on (*E*)-corphycene **51**. As inferred from Stuart-Briegleb models, **51** possesses an essentially strain-free chiral conformation in which the double bond is rigidly held orthogonal to the tetrapyrrolic structural moiety. That this conformation of **51** is preferred also follows from PM3 calculations [according to these, **51** is 8 kcal mol⁻¹ higher in energy than planar (*Z*)-corphycene **10**]. Being deprived of cyclic conjugation due to steric hindrance, **51** is expected to constitute a rather unique non-aromatic porphyrinoid. As such, it invites interesting comparisons of its structural and spectroscopic properties with those of its aromatic counterpart.



On pondering the synthesis of (*E*)-octaethylcorrphycene **53** it occurred to us that this molecule might be obtained by dehydrogenation of 14,15-dihydrocorrphycene **52**. The intended formation of **53** in this reaction derives from model considerations according to which **52** closely resembles **53** in its conformation, with the CH₂CH₂ unit arranged in such a way as to be conducive to the generation of an (*E*)-double bond.

Unfortunately, this conceptual approach to **53** could not be tested because the strategically important dihydro compound **52** has as yet failed to materialize. To our

surprise, the planned route to **52** via the acid-catalyzed MacDonald condensation [52] of the bipyrrrole dialdehyde **24** with the dipyrroethane dicarboxylic acid **54** was completely suppressed by an admittedly equally welcome competition reaction, namely the condensation of two molecules of **24** and **54** each to give the cyclooctapyrrole **55**, an octaphyrin-(2.1.0.1.2.1.0.1), as the only defined product isolated. On heating in the presence of Pd/C in refluxing toluene, **55** experiences dehydrogenation with formation of the fully conjugated cyclooctapyrrole **56** possessing (*E*)-double bonds [16].



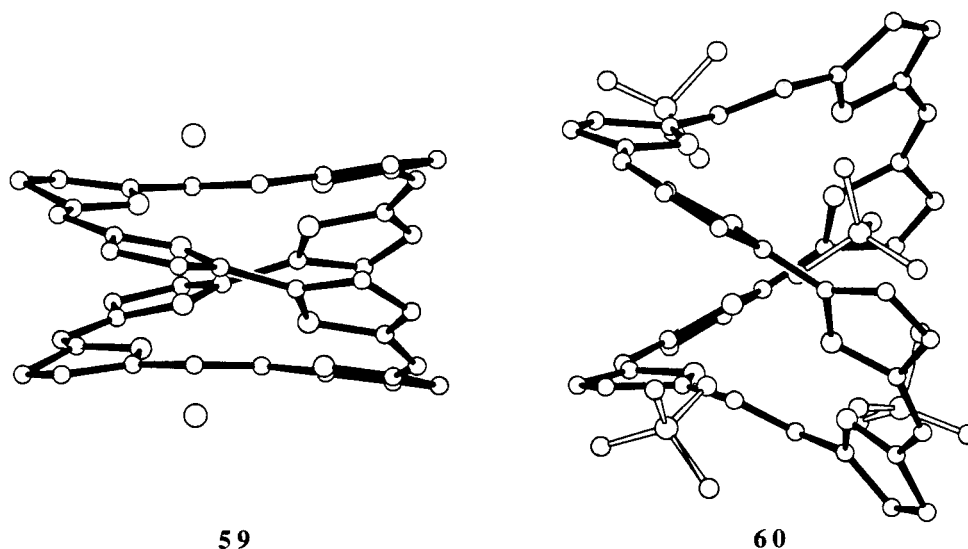


Figure 6. Molecular structure of the bis(hydrochloride) **59** and the tetrakis(hydroperchlorate) **60** of the cyclooctapyrrole **58** in the solid state (side views; substituents are omitted for clarity).

Clearly, formulae **55** and **56** only serve to illustrate the gross structures of these cyclooctapyrroles. As concluded from NMR spectroscopic studies, compounds **55** and **56** have non-planar ring systems that adopt the chiral figure-eight conformations **57** and **58**, respectively, approximating D_2 -symmetry. In view of the finding that the CH_2 protons of the ethyl groups in **57** and **58** exhibit diastereotopicity, which is maintained even at high temperature, the two cyclooctapyrroles must be fairly rigid, thus opening the prospect of being resolvable into enantiomers. The inferred presence of these molecules in figure-eight conformations derives additional support from X-ray crystallographic analyses of the bis(hydrochloride) **59** and the tetrakis(hydroperchlorate) **60** of **58** (Fig. 6) [16]. For obvious steric and electronic reasons ($4n$ conjugation pathway), **58** bears only a formal relationship to porphyrins.

The expectation that **57** and **58** might qualify as ligands capable of forming binuclear metal complexes has already been realized as far as **58** is concerned. Treatment of **58** with copper(II) acetate monohydrate in dichloromethane/methanol leads to the incorporation of two copper(II) ions to give the helical complex **61**, the structure of which could be determined by X-ray analysis (Fig. 7) [53]. Copper(II) complexation of **58** is found to be associated with significant conformational changes in the ligand resulting in the movement of the two (*E*) double bonds into an almost parallel arrangement. Featuring a relatively large Cu-Cu distance (7.48 Å), complex **61** is complementary to the bis-copper(II) complex of the cyclohexapyrrole amethyrin, recently described by Sessler [54], in which the copper(II) ions are

in relatively close proximity (2.76 Å). Apart from copper(II) ions, zinc and palladium ions have also been incorporated into **58** yielding the respective binuclear complexes; these, however, still await structural characterization.

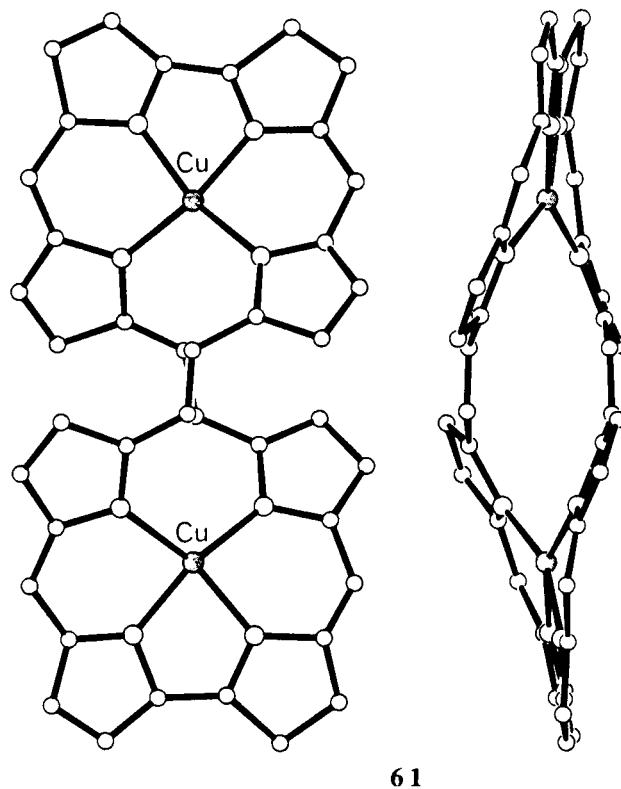
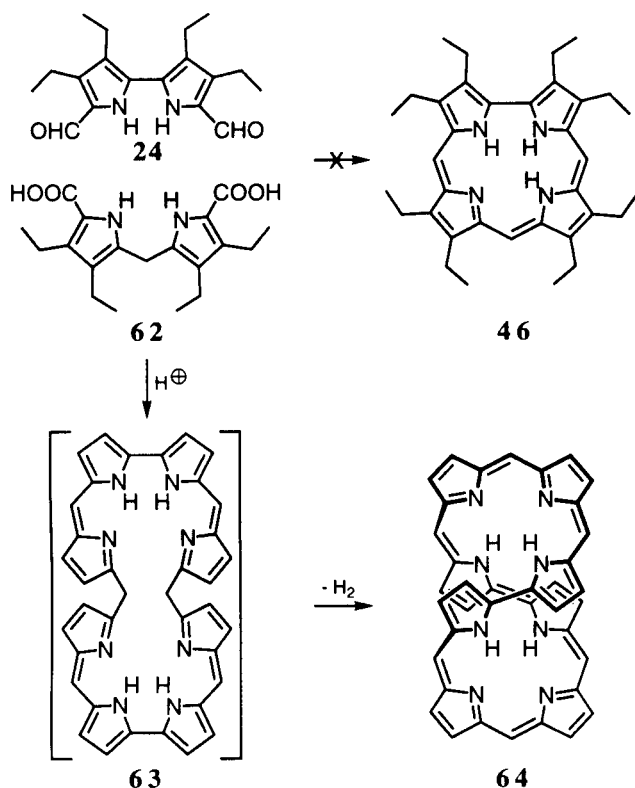


Figure 7. Molecular structure of the binuclear copper(II) complex **61** of the cyclooctapyrrole **58** in the solid state (top and side view; substituents are omitted for clarity).



In light of the formation of the cyclooctapyrrole **57** from **24** and **54**, it is hardly surprising that attempts at the synthesis of octaethylcorrole **46** by MacDonald condensation of **24** and dipyrromethane dicarboxylic acid **62** likewise did not afford the expected cyclotetrapyrrole but led to the cyclooctapyrrole **64**, an octaphyrin-(1.1.1.0.1.1.1.0) [16]. For reasons presumably more steric (release of conformational strain) than electronic in origin, the primary condensation product of **24** and **62**, i.e., **63** or its NH tautomer, turned out to be so prone to dehydrogenation that it has as yet defied isolation. By analogy to **57** and **58**, cyclooctapyrrole **64** was also shown to exist in a figure-eight conformation both in solution and in the solid state (Fig. 8). As resonance in **64** is impaired sterically, the molecule is non-aromatic even though it contains a $(4n+2)\pi$ conjugation pathway.

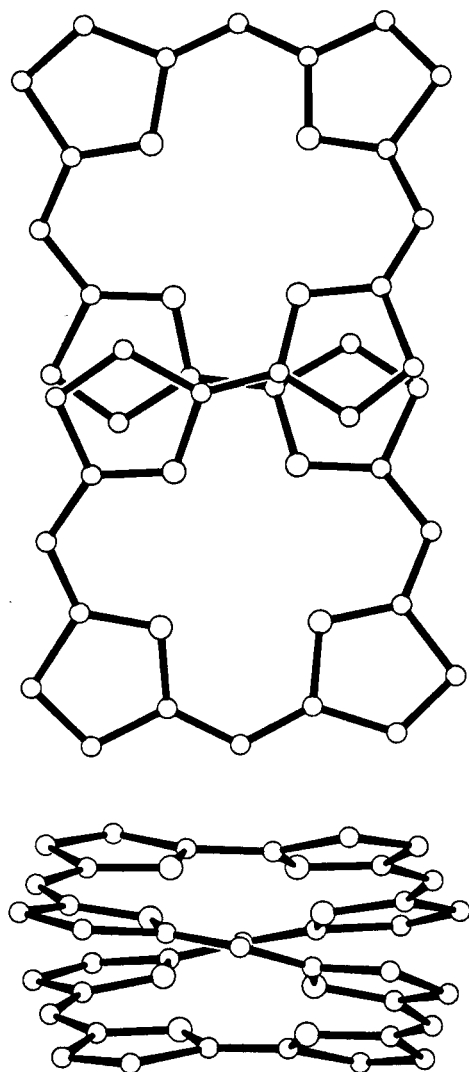
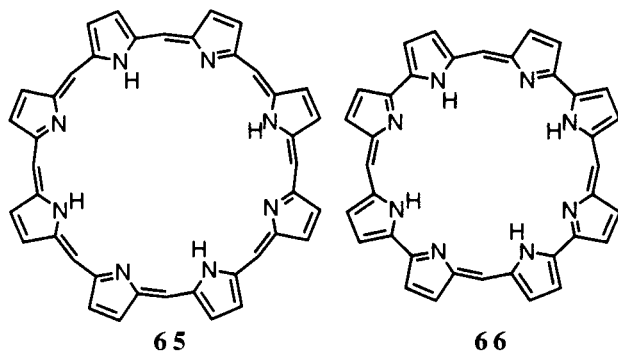


Figure 8. Molecular structure of the cyclooctapyrrole **64** in the solid state (top: top view, bottom: side view; substituents are omitted for clarity).

In pursuit of determining the scope and limitations of cyclooctapyrrole synthesis, octaphyrin-(1.1.1.1.1.1.1.1) **65** and octaphyrin-(1.0.1.0.1.0.1.0) **66**, to be regarded as major representatives of the class, became obvious target molecules. In a formal sense, octaphyrin **65** constitutes a homologue of porphyrin. However, **65** substantially differs from the latter in electronic respects in that its main conjugation pathway involves $4n$ (36) rather than $(4n+2)$ π -electrons. Octaphyrin **66** is also related to porphyrin since it derives from it by replacement of the four pyrrole rings by four bipyrrole units. Its conjugation pathway, like that of **65**, is made up of $4n$ (32) π -electrons. Calculations (PM3) leave no doubt that **65** and **66**, which in their hypothetical planar conformations exhibit effective D_{8h} - and D_{4h} -symmetry, respectively,



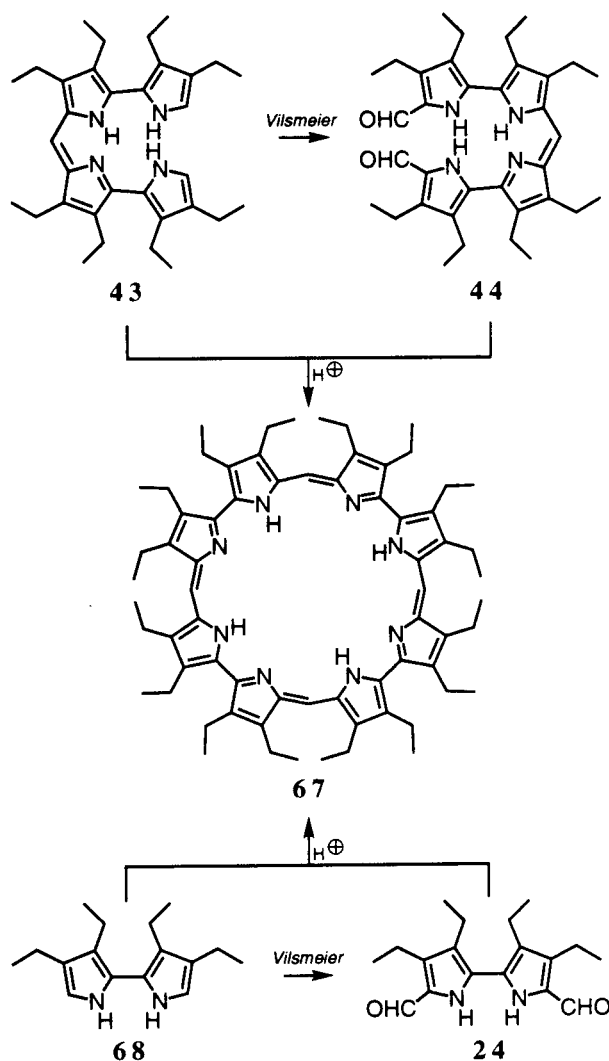
resemble their predecessors **57**, **58**, and **64** in their figure-eight topologies. While **65** remains a challenge, **66** has recently been prepared as its hexadecaethyl derivative **67** by two independent routes [55].

The availability - from the synthesis of isocorroles [47] - of the linear tetrapyrrole **43** and the α,ω -dialdehyde **44**, obtained from **43** by Vilsmeier formylation, invited attempts to synthesize octaphyrin **67** in straightforward fashion by a MacDonald condensation of the two tetrapyrrolic compounds. Indeed, when **43** and **44** were treated with trifluoroacetic acid in dichloromethane, the desired cyclooctapyrrole **67** is the only non-polymeric product isolated (yield 11%). Subsequently, it was found that **67** is obtained more expediently (fewer steps) if two equivalents each of bipyrrrole **68** and bipyrrrole dialdehyde **24** are condensed with acid catalysis (yield 14%).

It is interesting to note that the condensation of tetraalkyl-substituted bipyrrroles (unsubstituted α,α' -positions) with aromatic aldehydes under oxidizing conditions which - being patterned after Rothmund's synthesis [56] of tetra-*meso*-substituted porphyrins - might also have led to octaphyrins-(1.0.1.0.1.0.1.0), is reported by Sessler [57] to afford the expanded porphyrins named rosarins, i.e., hexaphyrins-(1.0.1.0.1.0), exclusively.

The ^1H NMR spectrum (300 MHz, CDCl_3) of octaphyrin **67** is relatively simple in that it consists only of a singlet ($\delta = 6.57$, *meso*-protons), a broad singlet ($\delta = 13.30$, NH protons) and two ABX_3 systems (ethyl groups with diastereotopic CH_2 protons). With $[\text{D}_8]$ toluene as solvent, no significant changes occur in the spectrum in the temperature range between -100°C and 100°C . These NMR observations might best be explained by one of the two following scenarios, both of which are consistent with the constant diastereotopicity of the CH_2 protons: 1) octaphyrin **67** exists in an achiral tub conformation resembling cyclooctatetraene and does not invert on the NMR time scale. 2) **67** consists of two enantiomeric figure-eight conformers that interconvert rapidly *via* a tub conformation (Fig. 9).

To answer the question of whether octaphyrin **67** is static (excluding NH tautomerism) or dynamic, a force field conformational analysis of the molecule was performed. Based upon this analysis, scenario 2 is most probable, and the barrier to racemization is too low ($<10 \text{ kcal mol}^{-1}$) to allow separation of enantiomers. Additionally, the study shows that the conformational change is coupled to NH tautomerism [58].



An X-ray analysis of the free base octaphyrin **67** reveals a figure-eight conformation of the molecule in the solid state (Fig. 10). As can be seen from the structural parameters, **67** is made up of four nearly planar dipyrrole (pyrromethene) [59] subunits (torsional angles between 1 and 10°). The observed conformation of the molecule arises mainly because the pyrrole rings of the bipyrrrole units are rotated about their linking bond (the torsional angles are in the range of 43 to 52°).

Preliminary chemical investigations on **67** indicate that this polypyrrolic macrocycle is not only capable of metal complexation to give both mono- and binuclear complexes but is also endowed with other interesting host-guest properties. In hindsight, it is hard to understand that the assembly of figure-eight cyclooctapyrroles in acid-catalyzed condensation reactions of appropriate pyrrolic building blocks has escaped detection for so long. Apparently, formation of such macrocycles is

avored over that of cyclotetrapyrroles if ring-closure to afford the latter is impaired by conformational rather than

thermodynamic (product stability) reasons [60].

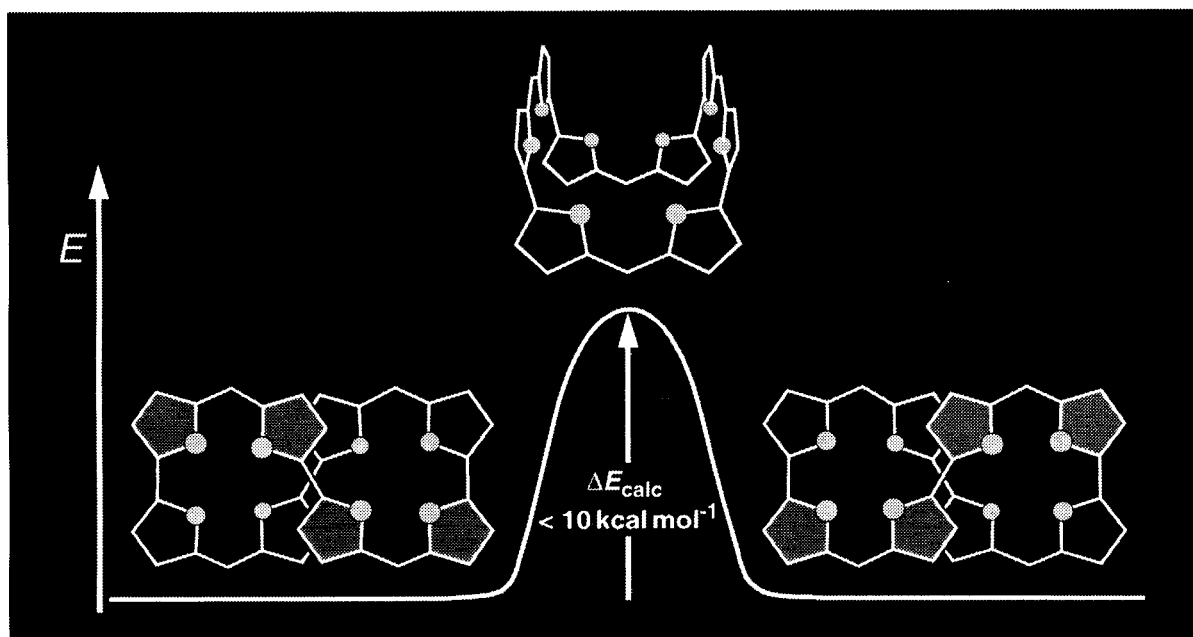


Figure 9. Energy profile of the interconversion of the enantiomers of the octaphyrin **67** (substituents are omitted for clarity).

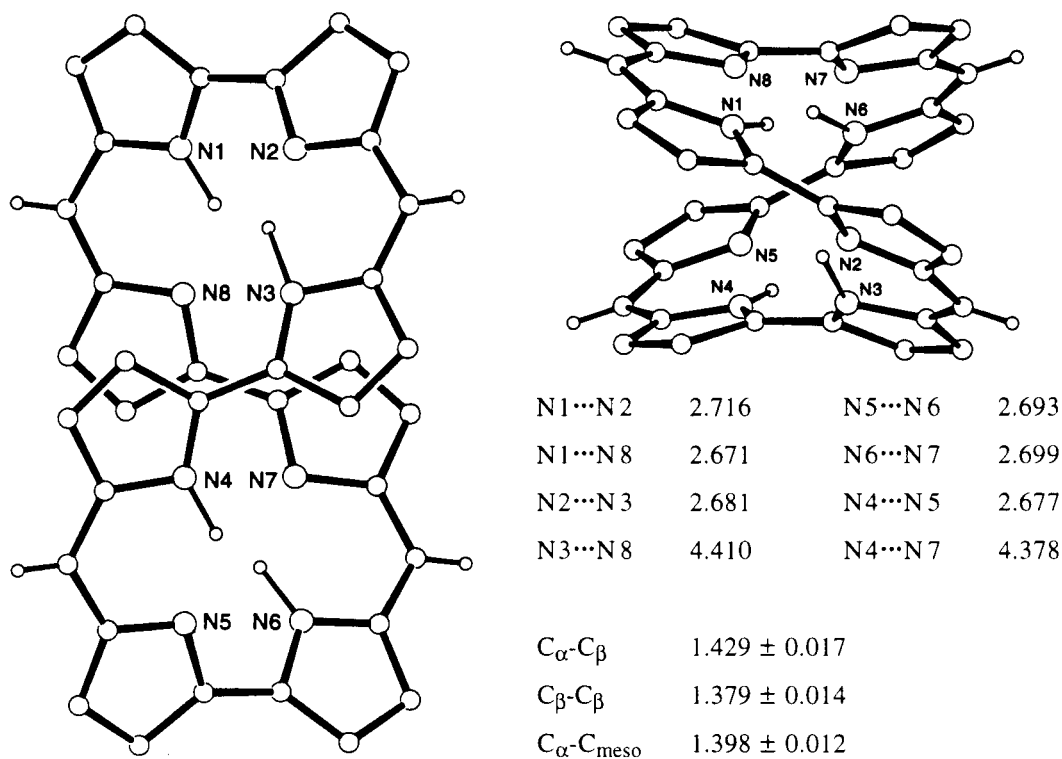


Figure 10. Molecular structure of the octaphyrin **67** in the solid state (left: top view, right: side view; N...N-distances and bond lengths in Å; substituents are omitted for clarity).

Oxygen and Sulfur Analogues of Porphyrin

A structural variation of porphyrin even more obvious than the reorganization of the tetrapyrrolic macrocycle to yield porphycene and its congeners is the partial or complete replacement of the nitrogen atoms of porphyrin by other heteroatoms, specifically by oxygen, sulfur and selenium. One thus arrives at various types of chalcogen analogues of porphyrin. It was in pursuit of a program intended to "assess the contribution of the bridging nitrogen atoms to the aromaticity of the porphyrin structure" that A.W. Johnson and his group [9b,c]

For reasons hard to explain, previous workers did not take into consideration the existence of the molecules which might be viewed as the ultimate targets of this avenue of research in porphyrin chemistry: the dicationic tetraoxa-, tetrathia-, and tetraselenaporphyrins (as salts). In fact, the only clear reference to such species to be found in the chemical literature is in a theoretical paper by J. Michl [7b]. These dications can be described by oxonium, sulfonium, or selenonium resonance structures, as well as by structures with a dicationic C₂₀ perimeter (Fig. 11) - the latter ones assumed to be the major contributors to the resonance hybrid.

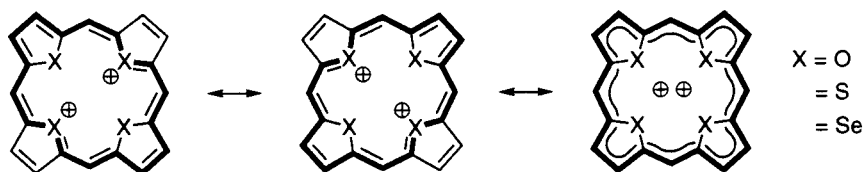
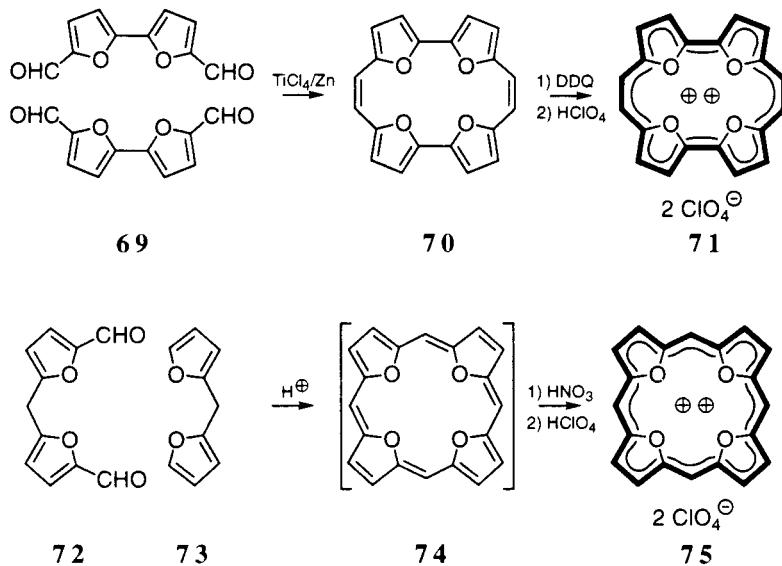
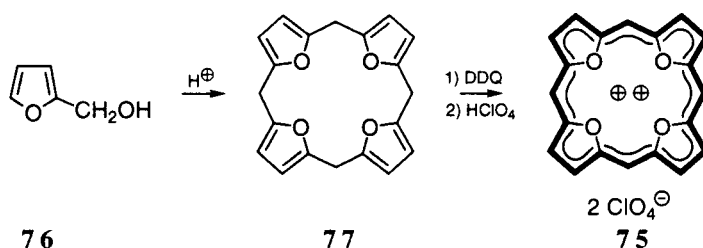


Figure 11. Resonance structures of the tetraoxa-, tetrathia-, and tetraselenaporphyrin dications.

initiated the development of this new line in porphyrin chemistry. As shown by the British chemists and, more recently, by several other groups [61], the established methods of porphyrin synthesis also provide access to a host of porphyrins in which one or two of the nitrogen atoms have been replaced by chalcogen atoms. While many of these novel macrocycles exhibit special features, such as unusual basicity or partial bonding across the heteroatom core, virtually all of them have retained the spectral and structural characteristics associated with porphyrins.

After it had been shown at the Cologne laboratory that the tetraoxaporphycene dication **71** (as its perchlorate) [62], obtained by two-electron oxidation of the oxygen-bridged [20]annulene **70** (product of the reductive carbonyl coupling of 5,5'-diformyl-2,2'-bifuran **69**), qualifies as a porphyrinoid aromatic species, there could be no doubt that the same would be true for its porphyrin counterpart, the tetraoxaporphyrin dication **75**. In parallel to the conversion of **70** into **71**, the most obvious approach to **75** is by the "annulene route", i.e., by oxidation of the as yet unknown [20]annulene **74**, the





oxygen analogue of the hitherto elusive isophlorin (*N,N'*-dihydroporphyrin) **79** [63]. Since the polyenic **74** possesses quinodimethane-type furan structural units it appeared to us that generation of **74** *in situ* under oxidizing conditions would offer the best chance of success. Following this strategy, 5,5'-diformyl-di-2-furylmethane **72** was condensed with di-2-furylmethane **73** in the presence of trifluoroacetic acid, and the resulting product, assumed to contain **74** in latent form, treated successively with nitric acid (oxidation) and perchloric acid (formation of a readily crystallizing salt). Although this sequence of reactions may have an alchemistic touch it lived up to our expectations in that it afforded **75** in the form of its stable perchlorate [64].

The impressive progress in the synthesis of natural and non-natural porphyrinoid compounds by biomimetic routes achieved in recent years inspired an alternative approach to **75**, namely from furfuryl alcohol **76** *via* the crown ether tetraoxaporphyrinogen **77** (not reported previously). A reexamination of the acid-catalyzed

condensation of **76** revealed that this reaction indeed produces **77**, albeit in only 1-2% yield [65]. As one might have expected, **77** - in contrast to porphyrinogen - is fairly stable towards molecular oxygen. While the chemical properties of **75** preclude its oxidative generation from **77** under the conditions of porphyrin biosynthesis, reaction of **77** with oxidants such as DDQ or cerium(IV) salts followed by treatment of the products formed with perchloric acid smoothly gives **75**. In view of the relatively ready availability of **77** (despite the low yield), the latter procedure is the method of choice in preparing **75**.

As a dication bearing some resemblance to pyrylium ions, **75** is stable in strongly acidic media but shows great sensitivity towards nucleophilic solvents and agents. The study of the presumed addition reactions was rendered difficult due to the poor solubility of **75**. Evidence regarding the aromatic nature of **75** is provided by spectral and structural findings. The ^1H NMR spectrum is consistent with the presence of a strongly diatropic dicationic species, and the UV/vis spectrum (Fig. 13) resembles that of a porphyrin-type molecule in

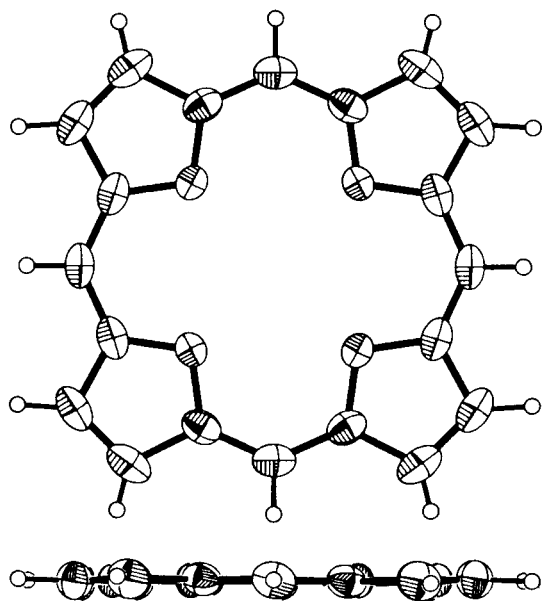


Figure 12. Molecular structure of the tetraoxaporphyrin dication **75** (as its perchlorate) in the solid state (top: top view, bottom: side view).

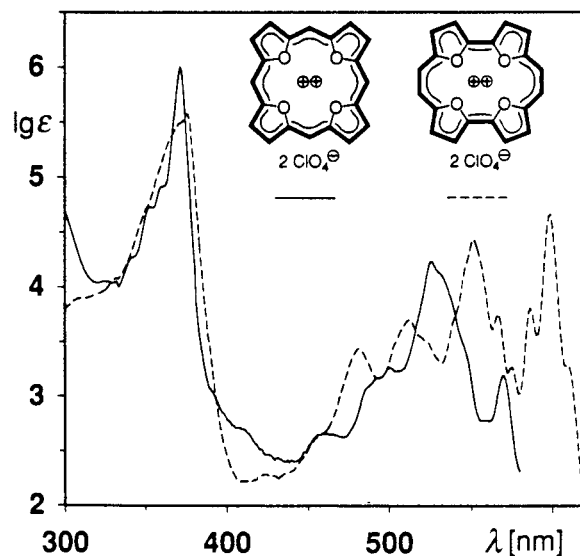
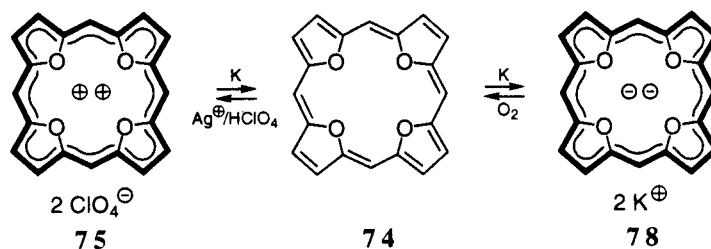


Figure 13. UV/vis spectra of the tetraoxaporphyrin dication **75** (in 96% sulfuric acid) and the tetraoxaporphycene dication **71** (in 70% perchloric acid) (each as its perchlorate).

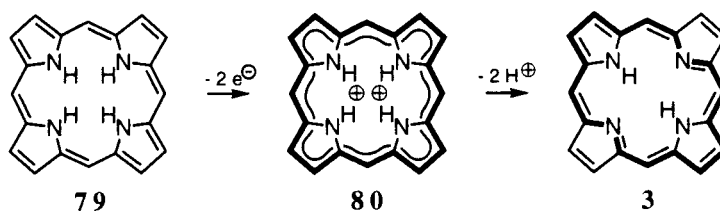


that it exhibits a remarkably sharp Soret-band and a set of Q-bands in the expected region. As borne out by an X-ray crystallographic analysis of **75** (Fig. 12), the dication is planar, possesses approximate D_{4h} -symmetry, and shows a bond length pattern matching that in porphyrins. It should be noted that the O...O distances almost exactly agree in length with the N...N distances in the parent porphyrin. Attesting to the close electronic relationship between **75** and the tetraoxaporphycene dication **71**, the ^1H NMR and UV/vis spectra of **75** are similar to the corresponding spectra of the latter but have experienced simplification due to the increase in symmetry - from D_{2h} to D_{4h} - on going from **71** to **75**.

Despite poor solubility, the tetraoxaporphyrin dication **75** (as its perchlorate) has been found to be amenable to useful chemical transformations. Among these, the elaboration of the redox system comprising the dication **75**, the radical cation, tetraoxaisophlorin **74**, the radical anion, and the dianion **78** (uptake of a total of four

Tetraoxaisophlorin **74**, in contrast to the parent compound **79**, is presumed to be planar, or at least nearly so, and thus to possess D_{4h} or D_{2h} symmetry, depending on whether the π -bonds are delocalized or not. In light of such properties, **74** - which, according to simple Hückel theory might be a diradical - qualifies, like cyclobutadiene [67] and cycl[3.3.3]azine [68], as a $[4n]$ annulene model compound.

The direct synthesis of tetraoxaisophlorin **74** from **75** by two-electron reduction utilizing potassium in tetrahydrofuran met with only partial success because the reaction could not be arrested at the stage of **74**, but proceeded further to give the aromatic 22π -tetraoxaporphyrin dianion **78**. This result prompted attempts to prepare the supposedly highly reactive **74** by partial oxidation of **78**. The method of choice in bringing about this oxidation proved to be molecular oxygen applied at low temperature. Tetraoxaisophlorin produced in this fashion is isolated as air-sensitive black crystals.



electrons) stands out [66]. A particularly interesting aspect of this system is the possible two-electron reduction of the dication to give tetraoxaisophlorin. As far as we are aware, the only reference to the parent isophlorin **79** - a formally very simple porphyrin derivative - in the chemical literature is by R.B. Woodward [63]. In the course of his ingenious synthesis of chlorophyll, he pointed out that **79** is a true non-Hückel $[20]$ annulene that should be very conducive to oxidation to porphyrin (presumably *via* **80**). For us, isophlorins and their analogues with other heteroatoms hold special fascination, since their discovery would demonstrate in a most telling way how intricately porphyrin and annulene chemistry can be intertwined.

As indicated by the occurrence of sharp lines in its ^1H and ^{13}C NMR spectra and the absence of signals in the ESR spectrum, tetraoxaisophlorin **74** exists in the singlet ground state. However, the HOMO-LUMO energy gap in **74** must be very small since the ^1H NMR spectrum of this molecule (Fig. 14), consisting of two singlets at $\delta = 1.98$ and $\delta = -0.64$ for the furanoid and *meso*-protons, respectively, exhibits a most marked paramagnetic ring current. To our knowledge, the up-field chemical shifts of the tetraoxaisophlorin protons are the highest ones ever recorded for hydrogen bound to olefinic carbon. Remarkably, the ^1H and ^{13}C resonances (three lines) of **74** remain sharp down to -135°C (the lowest temperature reached so far) showing that the isodynamic

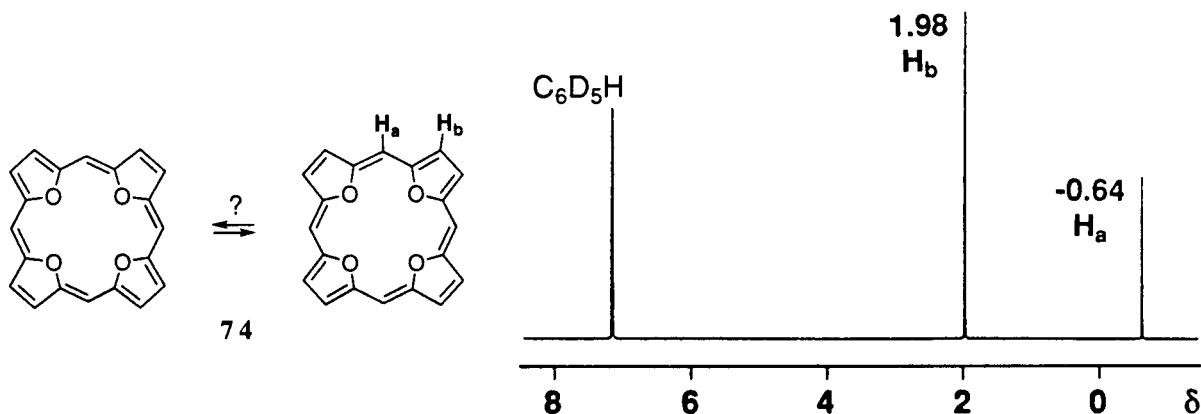
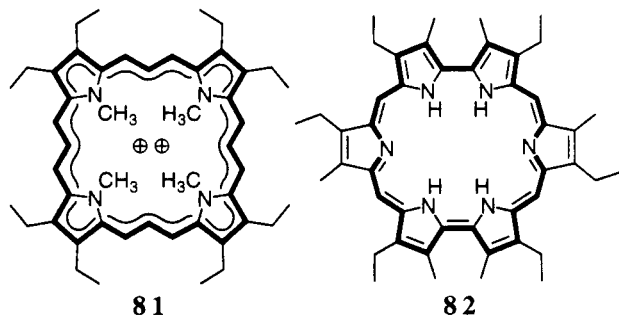


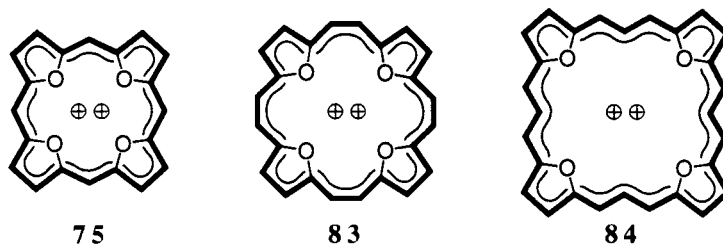
Figure 14. ^1H NMR spectrum (300 MHz, benzene- d_6) of tetraoxaisophlorin **74**.

π -bond shift assumed to take place in the molecule must be extremely fast. Bearing in mind that the free energy of activation (ΔG^\ddagger) of the π -bond shift in some bridged [12]annulenes [69], which noticeably deviate from planarity, is on the order of only 4-5 kcal mol $^{-1}$, ΔG^\ddagger for this dynamic process in **74** is presumably too small to be accessible by NMR spectroscopic methods. The UV/vis spectrum of **74** exhibits, in addition to relatively intense bands at 310-350 nm, a very weak and broad long-wave absorption (600-900 nm) that is characteristic of $(4n)\pi$ -electron systems in which such a transition involves alternating compression and expansion of adjacent bonds. An X-ray crystallographic analysis of **74** confirmed that the molecule is planar, but, due to static and possibly also dynamic disorder, the analysis has as yet remained inconclusive regarding the nature of bonding along the C_{20} -perimeter. At present, evidence for π -bond alternation in **74** mainly rests upon MO theoretical arguments [66].

metry can only be attained by homologues in which the number, n , of the carbon atoms of the $(\text{CH})_n$ segments connecting the pyrrole rings is odd.

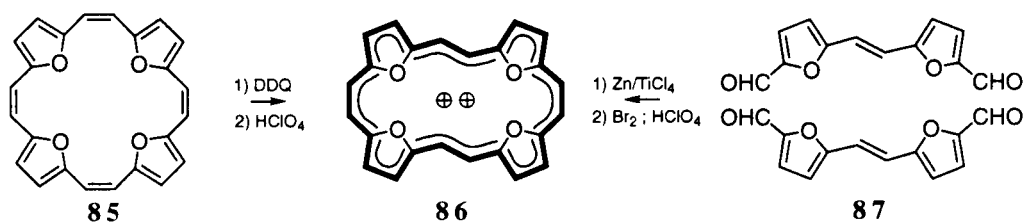


Major synthetic inroads into neutral porphyrin-related macrocycles containing more than four pyrrole rings, such as rubein **81** [70], rosarin [57], and amethyrin [11d], have been made by J.L. Sessler.



In pioneering work (1982 to date) B. Franck (University of Münster) has shown that the N,N,N',N'' -tetramethyloctaethyl[18]porphyrin dication, which is isoelectronic to **75**, possesses symmetrically expanded aromatic homologues featuring peripheral 26π - (e.g., **81**) and 34π -electron systems, respectively [10]. These novel porphyrin structural variants have become accessible by pathways patterned after the biosynthesis of porphyrins. Evidently, an essentially strain-free porphyrin-like geo-

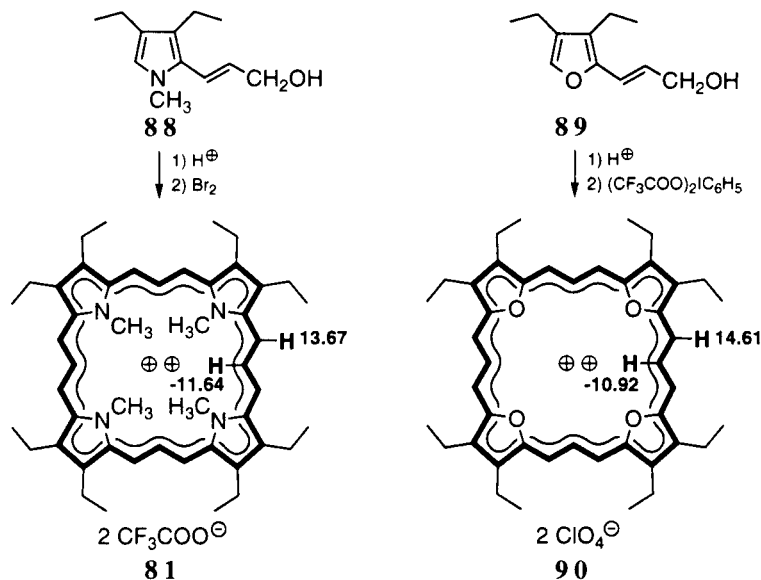
The extraordinary spectroscopic properties of Franck's expanded porphyrins (extreme ^1H NMR chemical shifts and exorbitant molar extinction coefficients of the Soret band) [71] which prompted him to denote his molecules as "superaromatic", were an incentive for us to explore the synthesis of the two next higher homologues of **75**, the tetraoxa[22]porphyrin-(2.2.2.2) dication **83** (even number of n) and the tetraoxa[26]porphyrin-(3.3.3.3) dication **84**.



In geometrical respects, the tetraoxa[22]porphyrin-(2.2.2.2) dication **83** is a special case since the all-*cis*-configuration and planar conformation of the molecule, required to render it a homologue of **75** and **84** in terms of symmetry, imposes severe angular strain on **83**. In contrast to **83**, its less symmetric *cis,trans,cis,trans*-isomer **86** can adopt a nearly strain-free planar conformation. It thus seems very likely that **83**, if it ever were formed, will readily isomerize to give the *cis,trans,cis,trans*-isomer.

One possibility to obtain **83** is offered by the two-electron oxidation of the oxygen-bridged [24]annulene **85**, a non-planar, atropic molecule that has recently become available [72]. However, when **85** is sequentially treated with DDQ and perchloric acid, the only dicationic product isolated was the *cis,trans,cis,trans*-isomer **86** (as its perchlorate). As evidenced by its spectra, **86** is closely related to the aromatic diprotonated *cis,trans,cis,trans*-[22]porphyrin-(2.2.2.2). An X-ray study of **86** has shown the molecule to be planar, but did not allow determination of the bond lengths accurately due to crystal disorders. While our studies on **86** were still in progress an independent synthesis of **86** employing the McMurry reaction of the dialdehyde **87** was achieved by G. Märkl (University of Regensburg) [73].

The successful synthesis by biomimetic schemes of the *N,N',N'',N'''*-tetramethyloctaethyl[26]porphyrin-(3.3.3.3) dication **81** (as its trifluoroacetate) from the *N*-methylpyrrolepropenal **88** on the one hand (B. Franck) [71], and of the octaethyltetraoxa[18]porphyrin dication **91** (as its perchlorate) from 2-hydroxymethyl-3,4-diethylfuran on the other (this group) [74], made it appear likely that the tetraoxa[26]porphyrin dication **90** could analogously be prepared from the alcohol **89**. Indeed, treatment of **89** in nitromethane with citric acid brings about cyclotetracondensation with formation of the corresponding porphyrinogen (yield 3%), which furnished the desired dication **90** as its perchlorate salt upon oxidation with bis(trifluoroacetoxy)iodobenzene followed by addition of 70% perchloric acid. The presumed close structural and electronic relationship of **90** to Franck's dication **81** is borne out most strikingly by a spectroscopic comparison of the two compounds. In the ¹H NMR spectra, **90** and **81** not only show the same absorption pattern, but also exhibit good agreement in the values of the chemical shifts (indicated in the formulae) of the perimeter protons. The parallelism between **90** and **81** further extends to their UV/vis spectra, except for the astounding finding that the already extremely high value of ε_{Soret} for **81** - hitherto a record - is surpassed by the corresponding value for **90** by a considerable margin: 900 000 vs. 1 600 000.



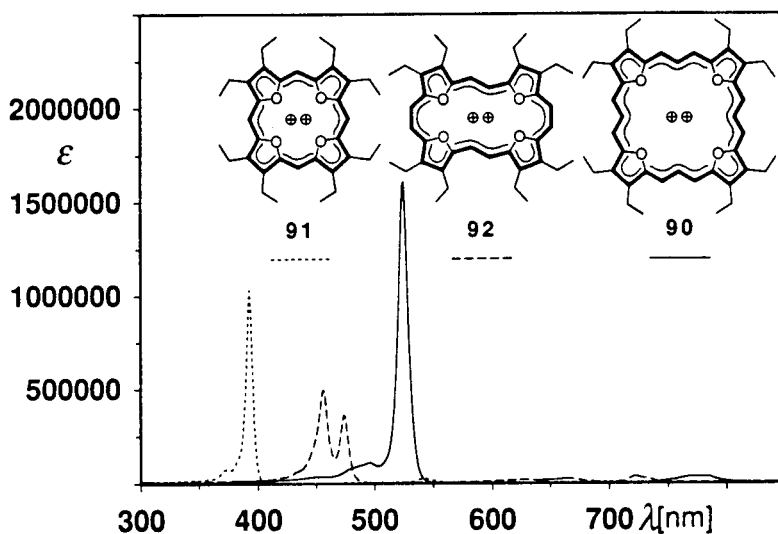


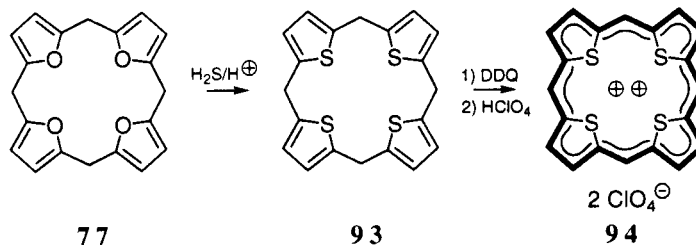
Figure 15. UV/vis spectra (in formic acid) of the octaethyltetraoxa[18]porphyrin-(1.1.1.1) dication **91**, the *cis,trans,cis,trans*-octaethyltetraoxa[22]porphyrin-(2.2.2.2) dication **92**, and the octaethyltetraoxa[26]porphyrin-(3.3.3.3) dication **90** (as their perchlorates).

It would seem appropriate to conclude the discussion of the homologous tetraoxa[4*n*+2]porphyrin dications by a joint presentation of the UV/vis spectra of the octaethyltetraoxa[18]-, *cis,trans,cis,trans*-octaethyltetraoxa[22]- and octaethyltetraoxa[26]porphyrin dications **91**, **92**, and **90** (all as their perchlorates), respectively, because these spectra demonstrate in a telling fashion the importance of symmetry in UV/vis spectroscopy. While the main absorption band (Soret) of the three dications moves to longer wavelengths as the (4*n*+2) π -electron system gets larger, the sharpness of the band observed for **91** and **90** yields to splitting in the case of **92** due to reduced symmetry of the molecule (Fig. 15).

The sulfur analogues of porphyrin, alternatively to be regarded as porphyrins based on thiophene, derive their attractiveness to a large extent from the important role that thiophene has attained in recent years as a structural component of advanced materials (organic conductors and semiconductors, functional dyes, and others) [75]. This background provided added incentive for us to extend our work on the tetraoxaporphyrin dication **75** (as its perchlorate) to its sulfur analogue, the tetrathiaporphyrin dication **94** (as its perchlorate).

Knowledge of **75** did not allow a safe guess as to the properties of **94** since the thia compound would be anticipated to deviate from planarity due to the steric interference of the relatively large sulfur atoms. Force field calculations (MM2) imply that **94** is dome-shaped with all four of the sulfur atoms protruding out of the C₂₀ perimeter on the same side. Initial attempts at the synthesis of **94** by routes analogous to those that proved to be successful in preparing **75**, i.e., the "annulene route" and the "biomimetic route", did not lead to the desired product. This deadlock was, however, overcome by the observation that tetraoxaporphyrinogen **77** readily experiences oxygen/sulfur exchange to give **93** when treated with hydrogen sulfide in the presence of hydrogen chloride. Subsequent conversion of **93** into **94** (as its perchlorate) was effected by oxidation with DDQ under conditions similar to those employed in the synthesis of **75** [65].

The ¹H NMR spectrum of the thia compound **94** corresponds to that of **75** in that it only shows two signals in the resonance region to be expected for a dicationic and aromatic porphyrin-type compound. Very distinct differences are observed, however, in the UV/vis



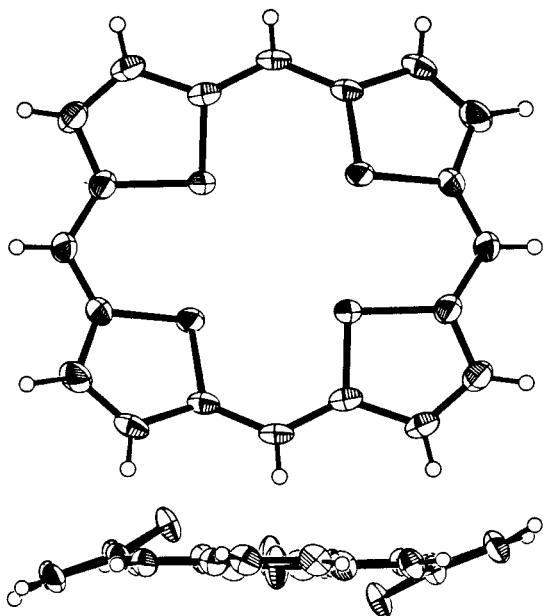
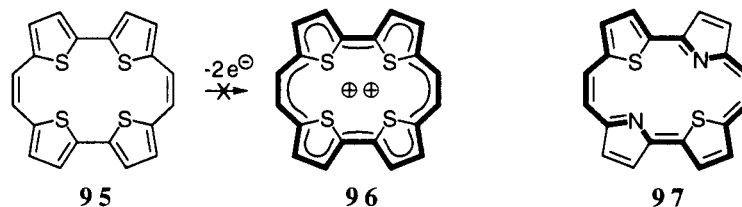


Figure 16. Molecular structure of the tetrathiaporphyrin dication **94** (as its perchlorate) (top: top view, bottom: side view taken from the above projection, rotated by 45°).

spectra of **94** and **75**. While the spectrum of **94** still resembles that of **75** in type, it no longer exhibits a sharp Soret-band with high extinction and fairly resolved Q-bands. Instead, all absorption bands of **94** are strongly broadened and shifted to longer wavelengths. The UV/vis spectroscopic findings on **94** are indicative of the presumed non-planarity of this dication, which has since been confirmed by an X-ray analysis (Fig. 16). Remarkably, rather than possessing the geometry predicted for it (dome-shaped), **94** is found to be centrosymmetric with two of the thiophene rings tilted up and down from the mean molecular plane as depicted.



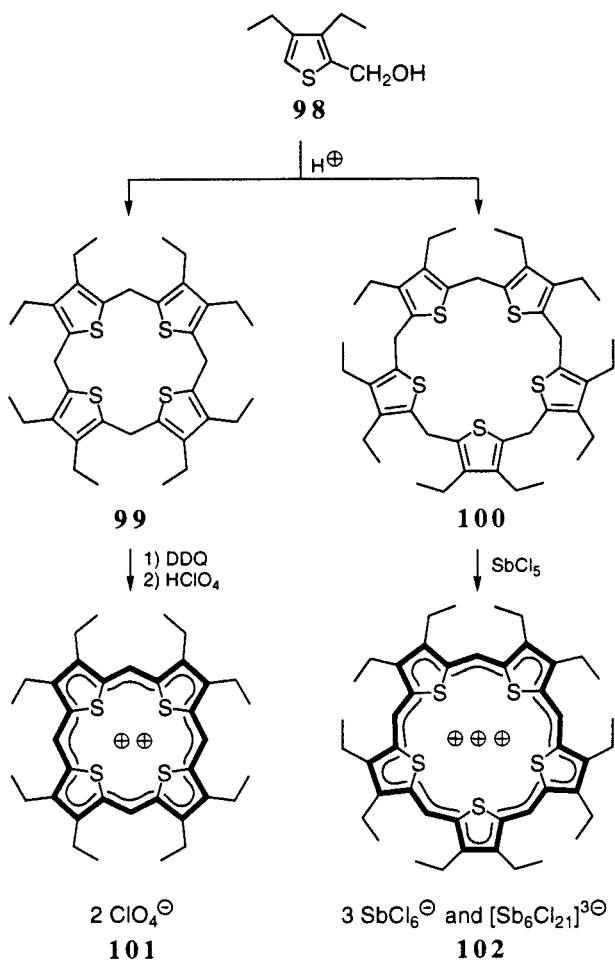
At this point, a brief comment on the counterpart of **94** in the porphycene series, i.e., the tetrathiaporphycene dication **96** seems appropriate. In the case of **96**, the distortion imposed on the ring system by the steric demand of the four sulfur atoms is such as to render this dication extremely unstable, if it exists at all. Oxidation

studies on the [20]annulene **95**, which, in contrast to its planar oxygen analogue, is compelled to adopt a plane conformation, resulted in the formation of undefined products only [76]. In view of this observation it is somewhat surprising that the dithiaporphycene **97**, recently synthesized by R. Neidlein (University of Heidelberg), is found to be entirely planar [77].

The poor solubility and relative instability of the parent tetrathiaporphyrin dication **94**, which hampered chemical exploration of the compound, prompted us to try to prepare its octaethyl derivative **101**. As it turned out, 2-hydroxymethyl-3,4-diethylthiophene **98** (in striking contrast to 2-hydroxymethylthiophene itself) was amenable to cyclocondensation in acidic medium to afford not only the tetra- but also the pentacyclocondensation products, **99** and **100**, respectively, in about equal amounts (total yield 46%) [78]. In line with expectation, **99** could be smoothly converted into the desired octaethyl tetrathiaporphyrin dication **101** (as its perchlorate) using proven methodology. According to an X-ray analysis of **101**, its ring system, like **94**, is non-planar. Presumably due to crystal forces, however, **101** differs from **94** in conformation in that its thiophene rings are tilted with respect to the mean molecular plane in an *up, up, down, down* fashion. The ethyl substituents of **101** bestow upon the molecule the anticipated good solubility in polar non-prototropic solvents such as dichloromethane and acetonitrile, and thus should render it a suitable candidate for chemical studies.

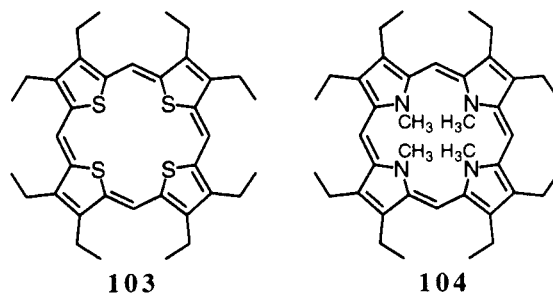
The formation of the cyclocondensation product **100** on treatment of **98** with acids was equally welcome as that of **99** since **100** also promised to undergo interesting chemical transformations. Thus, exhaustive oxidation of **100** offered the chance of generating the pentathiapentaphyrin trication **102**, a potentially aromatic 22π -electron system that represents the sulfur analogue of A. Gossauer's pentaphyrin (described as alkyl

derivatives) [79] in its triprotonated form. When **100** was treated with iron(III) chloride, an oxidation product could in fact be isolated, but this proved to be a π - π -dimer of the monocation [as a bis(tetrachloroferrate)]. However, employment of the more powerful oxidizing agent antimony pentachloride did produce the desired trication



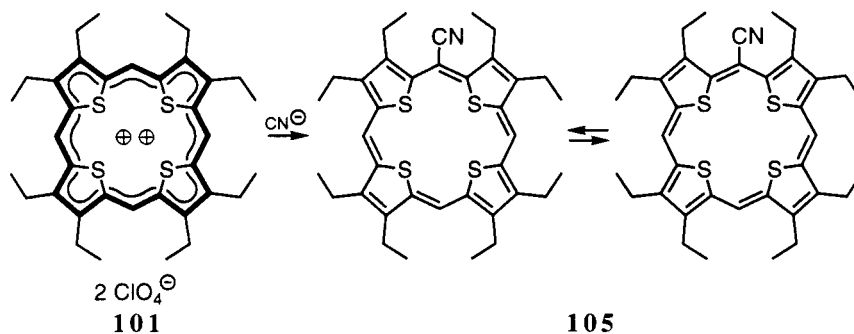
102. This is obtained as a mixture of salts differing in the nature of the antimony-based counterions: three $SbCl_6^-$, the cluster $[Sb_6Cl_{21}]^{3-}$, and possibly others. Although this mixture has as yet defied separation on a preparative scale, crystals solely consisting of the tris(hexachloroantimonate) and the cluster salt, respectively, could be isolated and subjected to X-ray analysis. The structural investigation revealed that the ring skeleton of the trication is planar and that it possesses approximate D_{5h} symmetry. In accord herewith, the 1H NMR spectrum (in CD_3NO_2) shows a

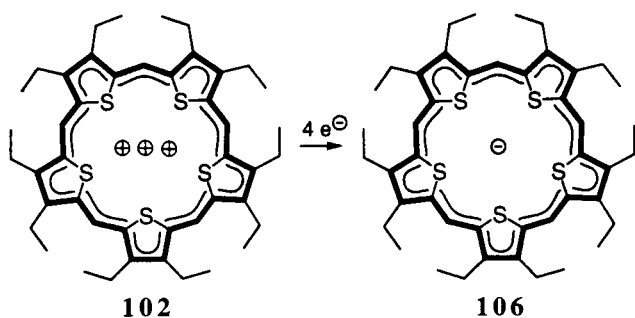
sharp singlet for the *meso*-protons that, due to its location at extremely low field ($\delta=14.8$), is clearly indicative of the presence of an aromatic trication [78]. In order to allow for a more detailed investigation of the trication, current efforts are concentrated on finding a practical way to separate the mixture of salts.



Initial chemical studies on the octaethyltetrathia-porphyrin dication **101** were aimed at its conversion into the [20]annulene octaethyltetrathiaisophlorin **103** by two-electron reduction. While attempts to obtain this annulene electrochemically provided inconclusive results, it could be generated, albeit not in a pure state, by employing samarium(II) iodide as the reducing agent. Proof of the presence of the highly reactive tetrathia-isophlorin **103** unequivocally follows from the NMR spectra of the compound.

In order to get to tetrathiaisophlorins stable enough to be isolated, it appears sufficient to introduce an electronegative substituent into just one of the *meso*-positions. A case in point is 5-cyano-octaethyltetra-thiaisophlorin **105** which is formed when **101** is treated with sodium cyanide in ethanol [78]. This reaction has precedent in earlier work devoted to the synthesis of *N,N',N'',N'''*-tetramethyloctaethylisophlorin **104** [80]. The [20]annulene **105** exhibits temperature dependent NMR spectra from which it could be deduced that the compound undergoes a fast π -bond shift with $\Delta G^{\#}_{190K} = 8.9 \text{ kcal mol}^{-1}$, as compared to $\Delta G^{\#}_{298K} = 13.2 \text{ kcal mol}^{-1}$ for **104** and $\Delta G^{\#}_{138K} < 6 \text{ kcal mol}^{-1}$ for the practically planar tetraoxaisophlorin **74** [66].





In the case of the pentathiapentaphyrin trication **102** a four- rather than a two-electron reduction attracted our interest since transfer of four electrons onto **102** should lead to the aromatic 26π -monoanion **106**. In view of the fact that the antimony-based counteranions of **102** are electrochemically active, efforts at effecting the conversion of **102** to **106** by taking advantage of electrochemistry seemed problematic. However, according to recent findings that will be reported in a forthcoming publication, a formal four-electron reduction of **102** to give **106** can be accomplished by chemical means. The anion **106** is convincingly characterized by its NMR spectra as being an aromatic species.

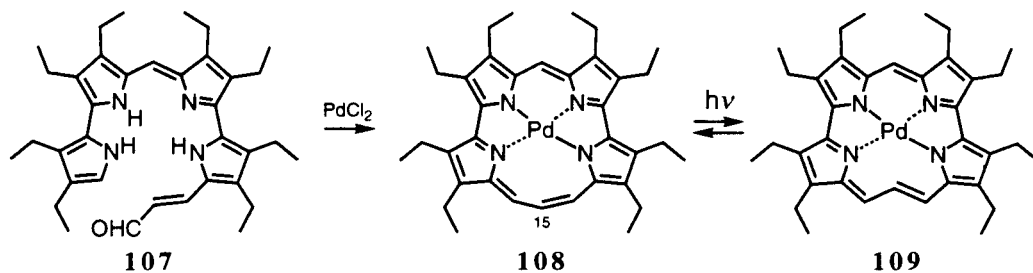
Conclusion

Porphyrins and metalloporphyrins - due to their multifaceted biological functions [81], their importance in medicine [10,25], and last but not least their utilization as components of supramolecular structures [82] - rank among the most fascinating molecules known to organic chemistry. The interdisciplinary interest these

porphyrins, has been brought to light during the last decade. Among these chromophores, the porphyrin isomers - porphycene, hemiporphycene, and corphycene (the latter two resulting from a joint project with J.L. Sessler) - stand out in potential since they share the capacity of the porphyrins to form complexes with a large number of metal ions.

The question whether there are further porphyrin isomers existing as stable molecules is a matter of speculation because of the fairly high relative energy of the as yet unknown isomers [four (*Z*)-isomers and several (*E*)-isomers]. That the search for these isomers is an endeavour worthwhile is evident from the most recent discovery (after the Congress of Heterocyclic Chemistry) of thermally stable yet photosensitive metal complexes of [18]porphyrin-(3.0.1.0), termed isoporphycene. Significantly, this isomer brings stereochemistry into the game. As will be reported in a forthcoming publication, palladium(II) chloride is capable of inducing cyclization of the tetrapyrrolic aldehyde **107** to give a mixture (still to be separated) of the photochemically equilibrating palladium complexes **108** and **109** of (*Z*)- and (*E*)-octaethylisoporphycene, respectively. In addition to **108** and **109**, the 15-formyl derivative of **108** is obtained in this palladium-mediated reaction.

Taking also into account the intriguing inverted or confused porphyrins that have emerged from work of Japanese [83] and Polish [84] chemists, porphyrin isomers and their metal complexes are bound to add a new dimension to research on tetrapyrrolic macrocycles [85]. Apart from porphyrin isomers, the equally interesting figure-eight cyclooctapyrroles are currently under active



molecules engender, in conjunction with the idea of symbiotically linking annulene and porphyrin chemistry, has provided the incentive to us to employ porphyrin as a "Leitstruktur" for the design and synthesis of structural variants of this prototype of tetrapyrrolic macrocycles. As a result of our systematic efforts to manipulate the porphyrin structure, a cornucopia of novel chromophores, some of them to be regarded as fundamental non-natural

investigation at this laboratory, especially with respect to metal complexation. While cyclooctapyrroles have already been shown to form binuclear complexes with metals of the same kind, their conversion into complexes with mixed metals, that would render them models for enzymes containing two different metal centers [86], still poses a challenge.

There remains the tantalizing question whether porphyrin isomers are exclusive products of the laboratory or whether any of these cyclotetrapyrroles may eventually be uncovered in nature.

Dedicated to Professor Richard Neidlein on the occasion of his 65th birthday.

Acknowledgements

It is a pleasure to express my appreciation to a group of highly motivated associates and students - names cited in the references - for their contributions to the development of this research program. The support of our work by the Deutsche Forschungsgemeinschaft, by the German-Israeli Foundation for Scientific Research & Development, and by the Otto-Bayer-Fonds is gratefully acknowledged. I am also indebted to Dr. B. Binsack and Dr. S.J. Weghorn for their technical assistance in preparing this manuscript.

REFERENCES AND NOTES

- [1] E. Vogel, Lectures in Heterocyclic Chemistry, Vol VIII, Hetero Corporation, Tampa, USA, 103 (1985).
- [2] E. Vogel and H.D. Roth, *Angew. Chem. Int. Ed. Engl.*, **3**, 228 (1964); *Chem. Eng. News*, **42** (23), 40 (1964); H.M. Sulzbach, P. von Ragué Schleyer, H. Jiao, Y. Xie, and H.F. Schaefer III, *J. Am. Chem. Soc.*, **117**, 1369 (1995); for a fluxional 1,6-methano[10]annulene, see: R. Neidlein, W. Wirth, A. Gieren, V. Lamm, and T. Hübner, *Angew. Chem. Int. Ed. Engl.*, **24**, 587 (1985).
- [3] E. Vogel, W. Klug, and A. Breuer, *Org. Synth.*, **54**, 11 (1974).
- [4] E. Vogel, Aromaticity, *Chem. Soc., Spec. Publ.*, **21**, 113 (1967); *Chimia*, **22**, 21 (1968); *Robert A. Welch Found. Conf. Chem. Res.*, **XII**, Organic Synthesis, 215 (1969); *Pure Appl. Chem.*, **28**, 355 (1971); *Internat. Congr. Pure Appl. Chem.*, Vol I, Boston, USA, 1971, p 275; *Isr. J. Chem.*, **20**, 215 (1980); *Pure Appl. Chem.*, **54**, 1015 (1982); E. Vogel, Current Trends in Organic Synthesis, H. Nozaki, ed, Pergamon Press, Oxford, 1983, p 379.
- [5] E. Vogel, W. Pretzer, and W.A. Böll, *Tetrahedron Lett.*, 3613 (1965).
- [6] a) E. Vogel, *Pure Appl. Chem.*, **62**, 557 (1990); b) *ibid.*, **65**, 143 (1993).
- [7] a) M. Gouterman, The Porphyrins, Vol III, D. Dolphin, ed, Academic Press, New York, 1978, p 1; b) J. Michl, *J. Am. Chem. Soc.*, **100**, 6801 (1978); c) C.H. Reynolds, *J. Org. Chem.*, **53**, 6061 (1988).
- [8] First reported by R.B. Woodward at the Aromaticity Conference, Sheffield, UK, 1966; V.J. Bauer, D.L.J. Clive, D. Dolphin, J.B. Paine III, F.L. Harris, M.M. King, J. Loder, S.-W.C. Wang, and R.B. Woodward, *J. Am. Chem. Soc.*, **105**, 6429 (1983).
- [9] a) A.W. Johnson and I.T. Kay, *J. Chem. Soc.*, 1620 (1965); b) A.W. Johnson, *Pure Appl. Chem.*, **28**, 195 (1971); c) A.W. Johnson, Porphyrins and Metalloporphyrins, K.M. Smith, ed, Elsevier, Amsterdam, 1975, p 729.
- [10] B. Franck, *Angew. Chem. Int. Ed. Engl.*, **21**, 343 (1982); *Chimia*, **48**, 490 (1994); B. Franck and A. Nonn, *Angew. Chem. Int. Ed. Engl.*, **34**, 1795 (1995); for related work see: R.A. Berger and E. LeGoff, *Tetrahedron Lett.*, 4225 (1978); E. LeGoff and O.G. Weaver, *J. Org. Chem.*, **52**, 711 (1987).
- [11] a) J.L. Sessler, T. Murai, V. Lynch, and M. Cyr, *J. Am. Chem. Soc.*, **110**, 5586 (1988); b) J.L. Sessler and A.K. Burrell, *Top. Curr. Chem.*, **161**, 177 (1991); c) J.L. Sessler, *Angew. Chem. Int. Ed. Engl.*, **33**, 1348 (1994); d) J.L. Sessler, G. Hemmi, T.D. Mody, T. Murai, A. Burrell, and S.W. Young, *Acc. Chem. Res.*, **27**, 43 (1994); e) J.L. Sessler, S.J. Weghorn, Y. Hiseada, and V. Lynch, *Chem. Eur. J.*, **1**, 56 (1995).
- [12] E. Vogel, M. Köcher, H. Schmickler, and J. Lex, *Angew. Chem. Int. Ed. Engl.*, **25**, 257 (1986); *Chem. Eng. News*, **64** (23), 27 (1986).
- [13] J.F.M. Oth, H. Baumann, J.-M. Gilles, and G. Schröder, *J. Am. Chem. Soc.*, **94**, 3498 (1972); see also: K. Müllen, T. Meul, E. Vogel, U. Kürschner, H. Schmickler, and O. Wennerström, *Tetrahedron Lett.*, **26**, 3091 (1985).
- [14] J.-H. Fuhrhop, *Angew. Chem. Int. Ed. Engl.*, **13**, 321 (1974).
- [15] The set of porphyrin isomers was first discussed by J. Waluk and J. Michl in connection with studies of the MCD spectra of porphyrinoid compounds: *J. Org. Chem.*, **56**, 2729 (1991).
- [16] E. Vogel, M. Bröring, J. Fink, D. Rosen, H. Schmickler, J. Lex, K.W.K. Chan, Y.-D. Wu, D.A. Plattner, M. Nendel, and K.N. Houk, *Angew. Chem. Int. Ed. Engl.*, **34**, 2511 (1995).
- [17] T. Mukaiyama, T. Sato, and J. Hanna, *Chem. Lett.*, 1041 (1973); J.E. McMurry, *Acc. Chem. Res.*, **16**, 405 (1983); *Chem. Rev.*, **89**, 1513 (1989).
- [18] In recent years further novel porphyrinoid macrocycles have been synthesized by employing the McMurry reaction: M.G.H. Vicente and K.M. Smith, *J. Org. Chem.*, **56**, 4407 (1991); M.R. Johnson, D.C. Miller, K. Bush, J.J. Becker, and J.A. Ibers, *ibid.*, **57**, 4414 (1992); D.C. Miller, M.R. Johnson, J.J. Becker, and J.A. Ibers, *Heterocycl. Chem.*, **30**, 1485 (1993); D.C. Miller, M.R. Johnson, and J.A. Ibers, *J. Org. Chem.*, **59**, 2877 (1994); Z. Hu, C. Scordilis-Kelley, and M.P. Cava, *Tetrahedron Lett.*, **34**, 1879 (1993); Z. Hu and M.P. Cava, *ibid.*, **35**, 3493 (1994).
- [19] a) E. Vogel, M. Balci, K. Pramod, P. Koch, J. Lex, and O. Ermer, *Angew. Chem. Int. Ed. Engl.*, **26**, 928 (1987); b) E. Vogel, P. Koch, X.-L. Hou, J. Lex, M. Lausmann, M. Kisters, M.A. Aukauloo, P. Richard, and R. Guillard, *ibid.*, **32**, 1600 (1993); c) W. Hennig, Dissertation, University of Cologne, 1992; d) S. Nonell, N. Bou, J.I. Borrell, J. Teixidó, A. Villanueva, A. Juarranz, and M. Cañete, *Tetrahedron Lett.*, **36**, 3405 (1995); R. Guillard, M.A. Aukauloo, C. Tardieux, and E. Vogel, *Synthesis*, 1480 (1995).
- [20] J.L. Sessler, E.A. Brucker, S.J. Weghorn, M. Kisters, M. Schäfer, J. Lex, and E. Vogel, *Angew. Chem. Int. Ed. Engl.*, **33**, 2308 (1994); this citation refers to the synthesis of etiochorrphycene: the octaethyl compound **22** was prepared analogously.
- [21] a) M.A. Aukauloo and R. Guillard, *New J. Chem.*, **18**, 1205 (1994); b) H. Falk and Q.-Q. Chen, *Monatsh. Chem.*, **127**, 69 (1996).
- [22] H.J. Callot, A. Rohrer, T. Tschamber, and B. Metz, *New J. Chem.*, **19**, 155 (1995).
- [23] J. Waluk, M. Müller, P. Swiderek, M. Köcher, E. Vogel, G. Hohlneicher, and J. Michl, *J. Am. Chem. Soc.*, **113**, 5511 (1991).
- [24] P.F. Aramendia, R.W. Redmond, S. Nonell, W. Schuster, S.E. Braslavsky, K. Schaffner, and E. Vogel, *Photochem. Photobiol.*, **44**, 555 (1986); H. Ofir, A. Regev, H. Levanon, E. Vogel, M. Köcher, and M. Balci, *J. Phys. Chem.*, **91**, 2686 (1987); H. Levanon, M. Toporowicz, H. Ofir, R.W. Fessenden, P.K. Das, E. Vogel, M. Köcher, and K. Pramod, *ibid.*, **92**, 2429 (1988); J. Waluk and E. Vogel, *ibid.*, **98**, 4530 (1994).
- [25] R. Bonnett, *Chem. Soc. Rev.*, **24** (1), 19 (1995); T.J. Dougherty, *Pharmaceutical News*, **1** (3), 15 (1994).
- [26] K. Schaffner, E. Vogel, and G. Jori, Biological Effects of Light 1993, E.G. Jung and M.F. Holick, eds, Walter de Gruyter,

Berlin, New York, 1994, p 312; C. Richert, J.M. Wessels, M. Müller, M. Kisters, T. Benninghaus, and A.E. Goetz, *J. Med. Chem.*, **37**, 2797 (1994).

[27] G. Jori, M. Köcher, E. Vogel, and A.D. Cross, US Patent 4.913.907 (1990), *Chem. Abstr.*, **113**, 145334y (1990); E. Vogel, P. Koch, A. Rahbar, and A.D. Cross, US Patent 5.244.671 (1993), *Chem. Abstr.*, **118**, 80731g (1993); E. Vogel, T. Benninghaus, C. Richert, M. Müller, and A.D. Cross, US Patent 5.179.120 (1993), *Chem. Abstr.*, **119**, 72432r (1993).

[28] B. Wehrle, H.-H. Limbach, M. Köcher, O. Ermer, and E. Vogel, *Angew. Chem. Int. Ed. Engl.*, **26**, 934 (1987); for recent publications on NH tautomerism in porphyrin, see: J. Braun, M. Schlabach, B. Wehrle, M. Köcher, E. Vogel, and H.-H. Limbach, *J. Am. Chem. Soc.*, **116**, 6593 (1994); J.R. Reimers, T.X. Lü, M.J. Crossley, and N.S. Hush, *ibid.*, **117**, 2855 (1995); A. Ghosh and J. Almlöf, *J. Phys. Chem.*, **99**, 1073 (1995).

[29] M.W. Renner, A. Forman, W. Wu, C.K. Chang, and J. Fajer, *J. Am. Chem. Soc.*, **111**, 8618 (1989); H. Ofir, H. Levanon, E. Vogel, M. Köcher, K. Pramod, and R.W. Fessenden, *Photochem. Photobiol.*, **50**, 37 (1989); L.R. Furenlid, M.W. Renner, K.M. Smith, and J. Fajer, *J. Am. Chem. Soc.*, **112**, 1634 (1990); J.P. Gisselbrecht, M. Gross, M. Köcher, M. Lausmann, and E. Vogel, *ibid.*, **112**, 8618 (1990); W.A. Oertling, W. Wu, J.J. Lopez-Garriga, Y. Kim, and C.K. Chang, *ibid.*, **113**, 127 (1991); A. Berman, A. Michaeli, J. Feitelson, M.K. Bowman, J.R. Norris, H. Levanon, E. Vogel, and P. Koch, *J. Phys. Chem.*, **96**, 3041 (1992); K.M. Kadish, E. Van Caemelbecke, P. Boulas, F. D'Souza, E. Vogel, M. Kisters, C.J. Medforth, and K.M. Smith, *Inorg. Chem.*, **32**, 4177 (1993); C. Bernard, J.P. Gisselbrecht, M. Gross, E. Vogel, and M. Lausmann, *ibid.*, **33**, 2393 (1994); K.M. Kadish, F. D'Souza, E. Van Caemelbecke, P. Boulas, E. Vogel, A.M. Aukauloo, and R. Guillard, *ibid.*, **33**, 4474 (1994); K.M. Kadish, P. Boulas, F. D'Souza, M.A. Aukauloo, R. Guillard, M. Lausmann, and E. Vogel, *ibid.*, **33**, 471 (1994); F. D'Souza, P. Boulas, A.M. Aukauloo, R. Guillard, M. Kisters, E. Vogel, and K.M. Kadish, *J. Phys. Chem.*, **98**, 11885 (1994); C.-M. Che, K.-K. Cheung, Z.-Y. Li, K.-Y. Wong, C.-C. Wang, and Y. Wang, *Polyhedron*, **13**, 2563 (1994); C.-M. Che, Z.-Y. Li, C.-X. Guo, K.-Y. Wong, S.-S. Chern, and S.-M. Peng, *Inorg. Chem.*, **34**, 984 (1995); Chi K. Chang, I. Morrison, W. Wu, S.-S. Chern, and S.-M. Peng, *J. Chem. Soc., Chem. Commun.*, **11**, 1173 (1995).

[30] E. Vogel and J.L. Sessler (joint project), manuscript in preparation.

[31] J.L. Sessler and E. Vogel (joint project), manuscript in preparation.

[32] M. Lausmann, Dissertation. University of Cologne, 1993; T. Souquet, Dissertation, University of Cologne, 1992.

[33] H. Bormann, Dissertation, University of Cologne, 1993.

[34] Z.-Y. Li, J.-S. Huang, C.-M. Che, and C.K. Chang, *Inorg. Chem.*, **31**, 2670 (1992).

[35] E. Vogel, M. Köcher, J. Lex, and O. Ermer, *Isr. J. Chem.*, **29**, 257 (1989).

[36] M. Lausmann, I. Zimmer, J. Lex, H. Lueken, K. Wieghardt, and E. Vogel, *Angew. Chem. Int. Ed. Engl.*, **33**, 736 (1994).

[37] K. Tatsumi and R. Hoffmann, *J. Am. Chem. Soc.*, **103**, 3328 (1981).

[38] The Periodic Table of Metalloporphyrins, see: J.W. Buchler, *The Porphyrins*, Vol I, D. Dolphin, ed., Academic Press, New York, 1978, p 389.

[39] A. Eschenmoser, *Angew. Chem. Int. Ed. Engl.*, **27**, 5 (1988); A. I. Scott, *ibid.*, **32**, 1223 (1993); F. Blanche, B. R. Cameron, J. Crouzet, L. Debussche, D. Thibaut, M. Vuilhorgne, F.J. Leeper, and A.R. Battersby, *ibid.*, **34**, 383 (1995); B. Kräutler and C. Kratky, *ibid.*, **35**, 167 (1996).

[40] a) R. Grigg, *The Porphyrins*, Vol II, D. Dolphin, ed., Academic Press, New York 1978, p. 327; b) R. Paolesse, S. Licocchia, M. Fanciullo, E. Morgante, and T. Boschi, *Inorg. Chim. Acta*, **203**, 107 (1993); c) R. Paolesse, S. Licocchia, G. Bandoli, A. Dolmella, and T. Boschi, *Inorg. Chem.*, **33**, 1171 (1994); d) S. Licocchia and R. Paolesse, *Structure and Bonding*, **84**, J.W. Buchler, ed., Springer Verlag, Berlin, 1995, p. 71.

[41] Y. Murakami, Y. Matsuda, K. Sakata, S. Yamada, Y. Tanaka, and Y. Aoyama, *Bull. Chem. Soc. Jpn.*, **54**, 163 (1981).

[42] M. Conlon, A.W. Johnson, W.R. Overend, D. Rajapaksa, and C.M. Elson, *J. Chem. Soc., Perkin Trans.*, **1**, 2281 (1973); Y. Murakami, Y. Aoyama, and M. Hayashida, *J. Chem. Soc., Chem. Commun.*, 501 (1980); T. Boschi, S. Licocchia, R. Paolesse, P. Tagliatesta, M.A. Tehran, G. Pelizzi, and F. Vitali, *J. Chem. Soc., Dalton Trans.*, 463 (1990); S. Licocchia, M. Paci, R. Paolesse, and T. Boschi, *ibid.*, 461 (1991).

[43] These calculations were carried out by Prof. Y.-D. Wu, Department of Chemistry, HKUST, Clear Water Bay, Kowloon (Hong Kong).

[44] S. Will, A. Rahbar, H. Schmickler, J. Lex, and E. Vogel, *Angew. Chem. Int. Ed. Engl.*, **29**, 1390 (1990).

[45] H.G. Raubenheimer and D. Seebach, *Chimia*, **40**, 12 (1986).

[46] S. Sepulveda-Boza and E. Breitmaier, *Liebigs Ann. Chem.*, 894 (1983).

[47] B. Binsack, H. Bormann, M. Bröring, Y. Hellwig, J. Lex, H. Schmickler, T. Souquet, B. Walther, Y.-D. Wu, and E. Vogel, manuscript in preparation.

[48] E. Vogel, S. Will, A. Schulze Tilling, L. Neumann, J. Lex, E. Bill, A.X. Trautwein, and K. Wieghardt, *Angew. Chem. Int. Ed. Engl.*, **33**, 731 (1994).

[49] J.W. Buchler and H.H. Schneehage, *Z. Naturforsch.*, **28b**, 433 (1973); B. Cheng, J.D. Hobbs, P.G. Debrunner, J. Erlebacher, J.A. Shelnut, and W.R. Scheidt, *Inorg. Chem.*, **34**, 102 (1995).

[50] Unpublished results with C. Erben.

[51] J.P. Collman, P.S. Wagenknecht, and J.E. Hutchison, *Angew. Chem. Int. Ed. Engl.*, **33**, 1537 (1994); J.-C. Chambron, C. Dietrich-Buchecker, and J.P. Sauvage, *Top. Curr. Chem.*, **165**, 131 (1993); H. Adams, N.A. Bailey, D.E. Fenton, S. Moss, C.O. Rodriguez de Barbarin, and G. Jones, *J. Chem. Soc., Dalton Trans.*, 693 (1986); F.V. Acholla, F. Takusagawa, and K.B. Mertes, *J. Am. Chem. Soc.*, **107**, 6902 (1985); F.V. Acholla and K.B. Mertes, *Tetrahedron Lett.*, **25**, 3269 (1984); P. Comba, A. Fath, T.W. Hambley, and D.T. Richens, *Angew. Chem. Int. Ed. Engl.*, **34**, 1883 (1995).

[52] G.P. Arsenault, E. Bullock, and S.F. MacDonald, *J. Am. Chem. Soc.*, **82**, 4384 (1960); J.A.S. Cavaleiro, A.M. d'A. Rocha Gonsalves, G.W. Kenner, and K.M. Smith, *J. Chem. Soc., Perkin Trans.*, **1**, 1771 (1974).

[53] Unpublished results with D. Rosen, M. Michels, and J. Lex.

[54] S.J. Weghorn, J.L. Sessler, V. Lynch, T.F. Baumann, and J.W. Sibert, *Inorg. Chem.*, **35**, 1089 (1996).

[55] M. Bröring, J. Jendry, L. Zander, H. Schmickler, J. Lex, Y.-D. Wu, M. Nendel, J. Chen, D.A. Plattner, K.N. Houk, and E. Vogel, *Angew. Chem. Int. Ed. Engl.*, **34**, 2515 (1995).

[56] P. Rothmund, *J. Am. Chem. Soc.*, **58**, 625 (1936); P. Rothmund and A.R. Menotti, *ibid.*, **63**, 267 (1941).

[57] J.L. Sessler, S.J. Weghorn, T. Morishima, M. Rosingana, V. Lynch, and V. Lee, *J. Am. Chem. Soc.*, **114**, 8306 (1992).

[58] K.N. Houk, M. Nendel, J. Chen, Y.-D. Wu, E. Vogel, and L.M. Tolbert, manuscript in preparation.

[59] H. Falk, *The Chemistry of Linear Oligopyrroles and Bile Pigments*, Springer Verlag, Wien, 1989.

[60] The cyclopolypyrroles described here have precedent in the fascinating blue-violet pigment turcasarin, a cyclodecapyrrole that

has emerged from the laboratory at the University of Texas at Austin: J.L. Sessler, S.J. Weghorn, V. Lynch, and M.R. Johnson, *Angew. Chem. Int. Ed. Engl.*, **33**, 1509 (1994).

[61] A. Ulman and J. Manassen, *J. Am. Chem. Soc.*, **97**, 6540 (1975); A. Ulman, J. Manassen, F. Frolow, and D. Rabinovich, *ibid.*, **101**, 7055 (1979); R.L. Hill, M. Gouterman, and A. Ulman, *Inorg. Chem.*, **21**, 1450 (1982); L. Latos-Grażyński, J. Lisowski, M.M. Olmstead, and A.L. Balch, *J. Am. Chem. Soc.*, **109**, 4428 (1987); L. Latos-Grażyński, J. Lisowski, L. Szterenber, M.M. Olmstead, and A.L. Balch, *J. Org. Chem.*, **56**, 4043 (1991); P.J. Chmielewski and L. Latos-Grażyński, *Inorg. Chem.*, **31**, 5231 (1992); R.P. Pandian and T.K. Chandrashekar, *ibid.*, **33**, 3317 (1994).

[62] E. Vogel, M. Sicken, P. Röhrig, H. Schmickler, J. Lex, and O. Ermer, *Angew. Chem. Int. Ed. Engl.*, **27**, 411 (1988).

[63] R.B. Woodward, *Angew. Chem.*, **72**, 651 (1960); *Ind. Chim. Belge*, **27**, 1293 (1962); R.B. Woodward, W.A. Ayer, J.M. Beaton, F. Bickelhaupt, R. Bonnett, P. Buchschacher, G.L. Closs, H. Dutler, J. Hannah, F.P. Hauck, S. Itô, A. Langemann, E. Le Goff, W. Leimgruber, W. Lwowski, J. Sauer, Z. Valenta, and H. Volz, *Tetrahedron*, **46**, 7599 (1990).

[64] E. Vogel, W. Haas, B. Knipp, J. Lex, and H. Schmickler, *Angew. Chem. Int. Ed. Engl.*, **27**, 406 (1988); W. Haas, B. Knipp, M. Sicken, J. Lex, and E. Vogel, *ibid.*, **27**, 409 (1988).

[65] E. Vogel, P. Röhrig, M. Sicken, B. Knipp, A. Herrmann, M. Pohl, H. Schmickler, and J. Lex, *Angew. Int. Ed. Engl.*, **28**, 1651 (1989); R.M. Musau and A. Whiting, *J. Chem. Soc., Chem. Commun.*, 1029 (1993).

[66] R. Bachmann, F. Gerson, G. Gescheidt, and E. Vogel, *J. Am. Chem. Soc.*, **114**, 10855 (1992).

[67] G. Maier, *Angew. Chem. Int. Ed. Engl.*, **27**, 309 (1988).

[68] R.P. Cunningham, D. Farquhar, W.K. Gibson, and D. Leaver, *J. Chem. Soc. (C)*, 239 (1969).

[69] E. Vogel, H. Königshofen, K. Müllen, and J.F.M. Oth, *Angew. Chem. Int. Ed. Engl.*, **13**, 281 (1974); E. Vogel, H. Königshofen, J. Wassen, K. Müllen, and J.F.M. Oth, *ibid.*, **13**, 732 (1974).

[70] J.L. Sessler, T. Morishima, and V. Lynch, *Angew. Chem. Int. Ed. Engl.*, **30**, 977 (1991).

[71] M. Gosmann and B. Franck, *Angew. Chem. Int. Ed. Engl.*, **27**, 1100 (1986).

[72] T. Pelster, Dissertation, University of Cologne, 1992.

[73] G. Märkl, H. Sauer, P. Kreitmeyer, T. Burgemeister, F. Kastner, G. Adolin, H. Nöth, and K. Polborn, *Angew. Chem. Int. Ed. Engl.*, **33**, 1151 (1994).

[74] E. Vogel, J. Dörr, A. Herrmann, J. Lex, H. Schmickler, P. Walgenbach, J.P. Gisselbrecht, and M. Gross, *Angew. Chem. Int. Ed. Engl.*, **32**, 1597 (1993).

[75] F. Garnier, G. Horowitz, X. Peng, and D. Fichou, *Adv. Mater.*, **2**, 592 (1990); G. Heywang and F. Jonas, *ibid.*, **4**, 116 (1992); J. Guay, A. Diaz, R. Wu, and J.M. Tour, *J. Am. Chem. Soc.*, **115**, 1869 (1993); L.F. Lindoy, *Nature*, **364**, 17 (1993); J. Roncali, *Chem. Rev.*, **92**, 711 (1992); F. Geiger, M. Stoldt, H. Schweizer, P. Bäuerle, and E. Umbach, *Adv. Mater.*, **5**, 922 (1993); F. Effenberger and F. Würthner, *Angew. Chem. Int. Ed. Engl.*, **32**, 719 (1993); S. Gilmour, S.R. Marder, J.W. Perry, and L.-T. Cheng, *Adv. Mater.*, **6**, 494 (1994); R.E. Gill, G.G. Malliaras, J. Wildeman, and G. Hadziioannou, *ibid.*, **6**, 132 (1994); P. Bäuerle, T. Fischer, B. Bidlingmeier, A. Stabel, and J.P. Rabe, *Angew. Chem. Int. Ed. Engl.*, **34**, 303 (1995); M.J. Marsella, P.J. Carroll, and T.M. Swager, *J. Am. Chem. Soc.*, **117**, 9832 (1995); M.J. Marsella, R.J. Newland, P.J. Carroll, and T.M. Swager, *ibid.*, **117**, 9842 (1995); P. Dyreklev, M. Berggren, O. Inganäs, M.R. Andersson, O. Wennerström, and T. Hjertberg, *Adv. Mater.*, **7**, 43 (1995).

[76] P. Röhrig, Dissertation, University of Cologne, 1991; F. Ellinger, A. Gieren, Th. Hübner, J. Lex, F. Lucchesini, A. Merz, R. Neidlein, and J. Salbeck, *Monatsh. Chem.*, **124**, 931 (1993).

[77] G. De Munno, F. Lucchesini, and R. Neidlein, *Tetrahedron*, **49**, 6863 (1993).

[78] E. Vogel, M. Pohl, A. Herrmann, T. Wiß, C. König, J. Lex, M. Gross, and J.P. Gisselbrecht, *Angew. Chem. Int. Ed. Engl.*, in press.

[79] H. Rexhausen and A. Gossauer, *J. Chem. Soc., Chem. Commun.*, 275 (1983); R. Charrière, T.A. Jenny, H. Rexhausen, and A. Gossauer, *Heterocycles*, **36**, 1561 (1993).

[80] M. Pohl, H. Schmickler, J. Lex, and E. Vogel, *Angew. Chem. Int. Ed. Engl.*, **30**, 1693 (1991).

[81] The Porphyrins, Vol VI, Part A, and Vol VII, Part B, D. Dolphin, ed. Academic Press, New York, 1978.

[82] J.-M. Lehn, Supramolecular Chemistry, Verlag Chemie, Weinheim, 1995; J. Weiser and H.A. Staab, *Angew. Chem. Int. Ed. Engl.*, **23**, 623 (1984); D. Gust and T.A. Moore, *Top. Curr. Chem.*, **159**, 103 (1991); Y. Sakata, H. Tsue, M.P. O'Neil, G.P. Wiederrecht, and M.R. Wasielewski, *J. Am. Chem. Soc.*, **116**, 6904 (1994); M.J. Crossley and P.L. Burn, *J. Chem. Soc., Chem. Commun.*, 1569 (1991); J. Seth, V. Palaniappan, T.E. Johnson, S. Prathapan, J.S. Lindsey, and D.F. Bocian, *J. Am. Chem. Soc.*, **116**, 10578 (1994); S. Anderson, H.L. Anderson, A. Bashall, M. McPartlin, and J.K.M. Sanders, *Angew. Chem. Int. Ed. Engl.*, **34**, 1096 (1995).

[83] H. Furuta, T. Asano, and T. Ogawa, *J. Am. Chem. Soc.*, **116**, 767 (1994).

[84] P.J. Chmielewski, L. Latos-Grażyński, K. Rachlewicz, and T. Głowiak, *Angew. Chem. Int. Ed. Engl.*, **33**, 779 (1994); P.J. Chmielewski, L. Latos-Grażyński, and K. Rachlewicz, *Chem. Eur. J.*, **1**, 68 (1995); see also: A. Ghosh, *Angew. Chem. Int. Ed. Engl.*, **34**, 1028 (1995).

[85] The most recent syntheses of Oxybenzporphyrin [T.D. Lash, *Angew. Chem. Int. Ed. Engl.*, **34**, 2533 (1995)] and of a carbaporphyrin [E. Breitmaier, personal communication] are further notable manifestations of the many ways the porphyrin structure can be varied.

[86] I. Bertini, H.B. Gray, S.J. Lippard, and J.S. Valentine, Bioinorganic Chemistry, University Science Books, Mill Valley, California, 1994.