

Novel porphyrinoids

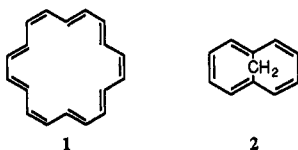
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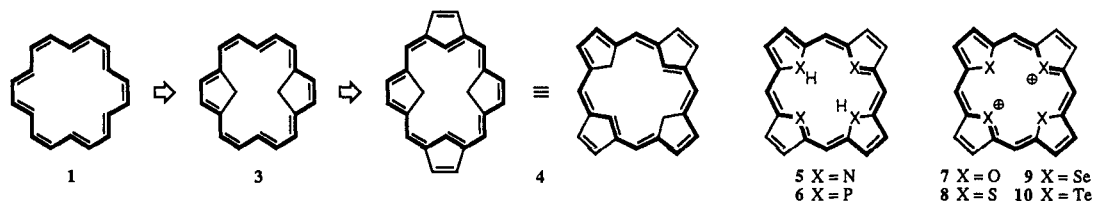
Abstract - The Porphyrins and their metal complexes, referred to as the pigments of life (Battersby), have developed into a major interdisciplinary area of research encompassing chemistry, physics (specifically photophysics), and medicine. Surprisingly, despite the plethora of work on these tetrapyrrolic macrocycles, quite a number of formally very simple porphyrin structural variants have hitherto eluded scientific attention and scrutiny. On looking at the porphyrins from the "annulene chemist's" point of view, i.e., by focusing on the interplay between molecular design and π -electron structure, one gets captivated by molecules such as porphycene and porphyrins in which the nitrogen atoms have been replaced by carbon, oxygen, chalcogen, or even phosphorus atoms. As reported three years ago, porphycenes can be prepared relatively easily and are found to resemble the porphyrins in many respects. Although porphycenes possess a coordination hole that is smaller than that of porphyrins, they are capable of complexation with many metal ions to give the respective metalloporphycenes. Very recently, the furan, thiophene, and the selenophene analogues of porphyrin, which exist as dications, have also yielded to synthesis (the selenium compound so far obtained only in solution). While these ionic species are reminiscent of pyrylium ions chemically, they clearly qualify as porphyrinoid in terms of spectral properties and molecular structure.

CONCEPTUAL APPROACH TO PORPHYRINOIDS FROM ANNULENES

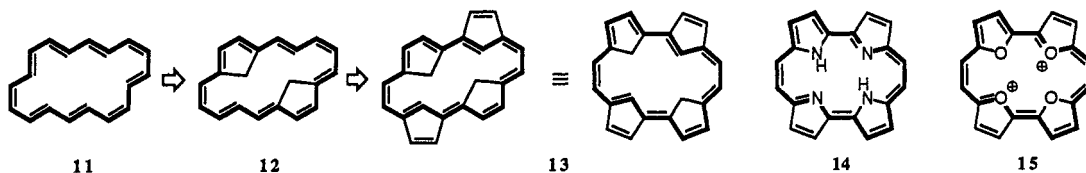
Sondheimer's [18]annulene (**1**) (ref. 1) and 1,6-methano[10]annulene (**2**) (ref. 2), that has emerged from the Cologne laboratory 25 years ago, are generally regarded as paradigms for $[4n+2]$ annulenes and their bridged variants, respectively. Both of these annulenes comply with the spectral and structural criteria for aromaticity, but it



is only the rigid bridged [10]annulene that exhibits benzenoid chemical properties. As a consequence of its conformational mobility (ref. 3), **1** is a highly reactive molecule that is more prone to polymerize than to undergo electrophilic substitution reactions. That **1**, despite these chemical shortcomings, may be regarded as a fundamental structural unit in organic chemistry, is largely due to the interesting molecules that derive from it by bridging.



It is easy to visualize that there are various bridging schemes by which **1**, by virtue of its favourable geometry, is transformed in a formal sense into "frozen" planar or near-planar 18π ring systems. Actually, several bridged [18]annulenes reported to be stable aromatic compounds have already been amenable to synthesis (ref. 4). One of the most effective schemes of imposing rigidity on **1** while maintaining planarity is the successive introduction into **1** of two internal CH_2 -bridges and two external etheno bridges (**1**→**3**→**4**). This transformation leads to the tetracyclopentadienic hydrocarbon **4**, which might be viewed as the parent structure of porphyrin (**5**). Approaching, conceptually, porphyrin from **1**, makes one realize that there should exist a host of porphyrin structural variants, such as the hydrocarbon **4**, tetraphosphaporphyrin (**6**) and the dicationic tetraoxa-, tetrathia-, tetraselena-, and tetratelluraporphyrins (**7-10**), which have as yet escaped the attention of the synthetic organic chemist.



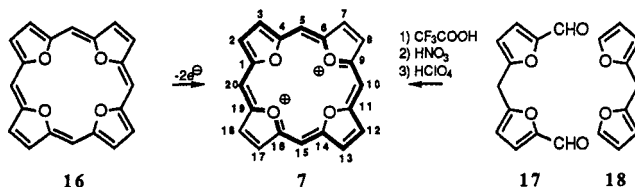
While the structural relationship among 1, 4, and porphyrin (5) has been discussed for some time (ref. 5), the analogous relationship that intertwines the fictitious [18]annulene of C_{2h} -symmetry (11), its bridged variants 12 and 13, and the porphyrin structural isomer 14 has been recognized only very recently (ref. 6). Among compounds 13-15, the tetrapyrrolic macrocycle 14 - henceforth termed porphycene (ref. 7) - commands special interest because it might possess properties reminiscent of those of porphyrin in many respects.

In this article, the novel porphyrinoid molecules encountered in our endeavours to link annulene chemistry and porphyrin chemistry are surveyed.

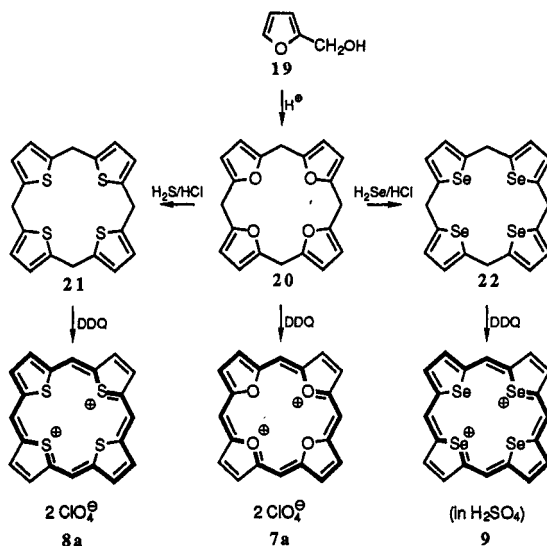
FURAN, THIOPHENE AND SELENOPHENE ANALOGUES OF PORPHYRIN

It was in pursuit of a programme intended to "assess the contribution of the bridging nitrogens to the aromaticity of the porphyrin structure" that A.W. Johnson and his group (ref. 8) prepared the first chalcogen porphyrins and thus initiated the development of a new realm of porphyrin structural variants. As shown by the British workers and, more recently, by several other groups (ref. 9), the established methodology of porphyrin synthesis also provides access to a host of porphyrins in which one or two of the nitrogen atoms have been replaced by oxygen, sulphur, selenium, and even tellurium atoms, respectively. While many of these novel macrocycles exhibit special features, such as unusual basicity or partial bonding across the hetero atom core etc., virtually all of them have retained the spectral and structural characteristics associated with porphyrins.

For reasons which are hard to explain, only sporadic efforts (ref. 10) have been undertaken to arrive at the molecules which one might consider to be the ultimate targets of this avenue of research in porphyrin chemistry: the dicationic tetraoxa-, tetrathia-, tetraseleno-, and tetratelluraporphyrins (7-10). After it had been shown at the Cologne laboratory that the tetraoxaporphycene dication (ref. 6) qualifies as a porphyrinoid aromatic species (see next chapter), there could be no doubt that the same would be true for its porphyrin counterpart, the tetraoxaporphyrin dication (7).



The most obvious approach to 7, i.e., the "annulene route", is by way of the as yet unknown oxygen-bridged [20]annulene 16, the furan analogue of isophlorin. Constituting a [4n]annulene, reminiscent of cyclobutadiene in some respects, 16 is likely to be prone to undergo a two-electron oxidation, be it chemically or electrochemically, with formation of the supposedly aromatic dication 7. As the polyenic 16 possesses quinodimethane-type furan structural units and might therefore be subject to ready polymerization, it appeared to us that the generation of 16 in situ under oxidizing conditions would offer the best chance of success. Following this strategy 5,5'-methylene-di-2-furaldehyd (17) was condensed with 2,2'-difurylmethane (18) in the presence of trifluoroacetic acid and the



(Fig. 1b). Rather than possessing the geometry predicted for it (dome-shaped), **8** is found to be centrosymmetric with the four thiophene rings tilted up and down from the mean molecular plane by 22.8° and 3.7°, respectively. If this conformation of **8** also applies to the dication in solution, then the simplicity of its NMR spectra (Table 1) must arise from a fast dynamic process conferring effective D_{4h} -symmetry on **8**.

	H2 $^3J(^1H, ^1H)$	H5	C1	C2 $^1J(^{13}C, ^1H)$	C5
7a	11.17	12.13	157.03	139.61	104.87
	$J(2,3)=4.71$		-	188	168
8a	10.52	12.46	163.90	142.20	136.47
	$J(2,3)=5.23$		-	180	171
9	9.90	11.81	-	142.89	147.05
	-	-	-	177	167

TABLE 1. 1H NMR (300 MHz) and ^{13}C NMR data (75.5 MHz) of **7a** and **8a** (68% $DClO_4$, CH_2Cl_2 int.) and of **9** (98% D_2SO_4 , CH_2Cl_2 int.). Chemical shifts δ_H and δ_C , and coupling constants J [Hz].

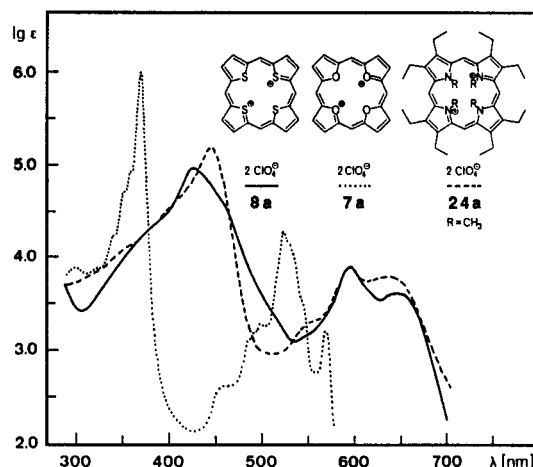
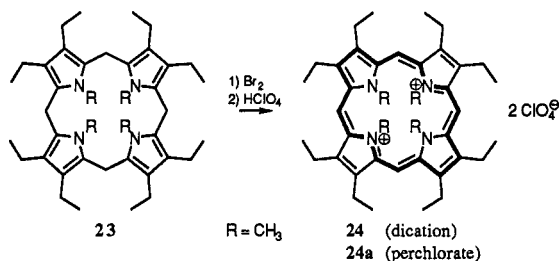


Fig. 2. UV/VIS spectra of **8a**, **7a**, and **24a** (96% H_2SO_4).

The synthetic scheme that led to **8a** has more recently also allowed generation of the tetraselenaporphyrin dication (**9**) (ref. 14). Although **9** has as yet evaded full characterization due to the difficulty of obtaining the compound in crystalline form (e.g., as a perchlorate), it is apparent from the available data on **9** (Table 1) that one is still dealing with a true porphyrinoid molecule.

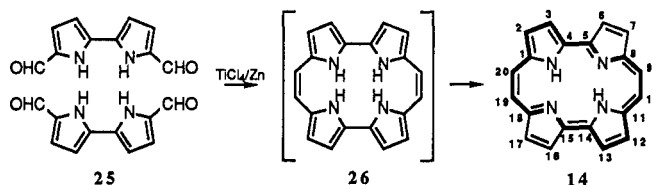


An interesting aspect of **8a** is the close agreement of its UV/VIS spectrum (Fig. 2) with those of the dicationic N,N',N'',N''' -tetraalkylporphyrins (as bromides) elegantly synthesized by Franck (ref. 15), a type of porphyrin thought to be forbiddingly deformed because of nonbonded steric interactions of the alkyl groups. In order to get insight into the molecular structure of such unconventional porphyrins, N,N',N'',N''' -tetramethyl-octaethylporphyrinogen (**23**) (ref. 16) was converted into the N,N',N'',N''' -tetramethyl-octaethylporphyrin dication (**24**) as its perchlorate **24a** (ref. 14), which, as anticipated, proved to be amenable to X-ray crystallographic analysis (Fig. 1c). From this analysis it is evident that **24**, while approximating the high symmetry D_{2d} , exhibits an extremely ruffled conformation. The pyrrole rings are tilted alternately up and down from the mean molecular plane, the angle of tilt amounting to 39°. Although **24** probably holds a record among porphyrins with regard to the level of deviation from planarity (ref. 17), the spectral (specifically 1H NMR) and structural (bond lengths) indications are that the reduction of the aromaticity of **24** is within limits.

PORPHYCENES

On examination of porphyrin (**5**) from the "annulene chemist's" point of view, i.e., by focusing on the interplay between molecular design and π -electron structure rather than on biochemical aspects, it occurred to us that the porphyrin isomer porphycene (**14**) - derived from **5** by a mere reshuffling of the pyrrole and methine moieties - might be endowed with porphyrin-like physical and chemical properties. Surprisingly, not even a hint of the possible existence of **14** could be found in the chemical literature, although the development of pyrrolic porphyrin structural variants, spurred by the growing interdisciplinary interest in porphyrins (ref. 18), has been pursued in many laboratories.

The synthesis of **14** turned out to be very simple since the compound was obtained as the only nonpolymeric product from the known 5,5'-diformyl-2,2'-bipyrrole (**25**) in a single step, i.e., by reductive coupling of the



dialdehyde with the titanium tetrachloride/zinc/pyridine system (Mukaiyama variant of the McMurry reaction) (ref. 7). In accord with expectation, **14** - a fascinating, strongly fluorescent blue pigment - qualifies as an aromatic porphyrinoid molecule resembling **5** in structural, spectral, and chemical respects.

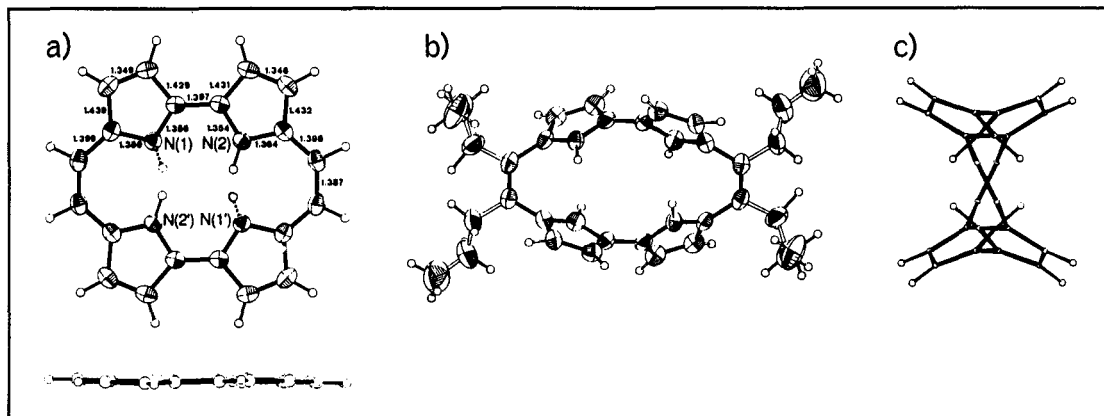
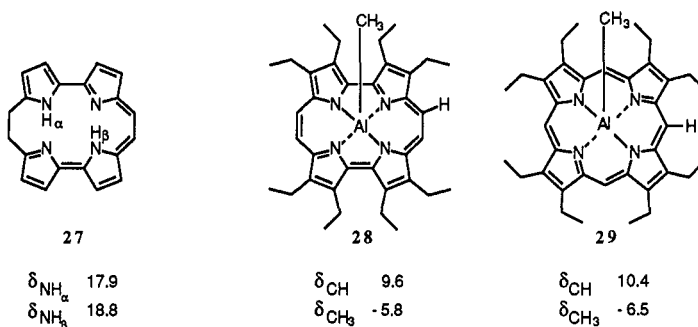
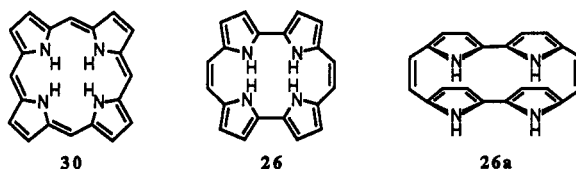


Fig. 3. a) Structure of **14**. Viewed from the top and from one side. b) Structure of **14**. Viewed in the direction of the C_2 -axis. c) Structure of **14**. Viewed in the direction perpendicular to the C_2 -axis along the bipyrrrole units (propyl groups omitted).

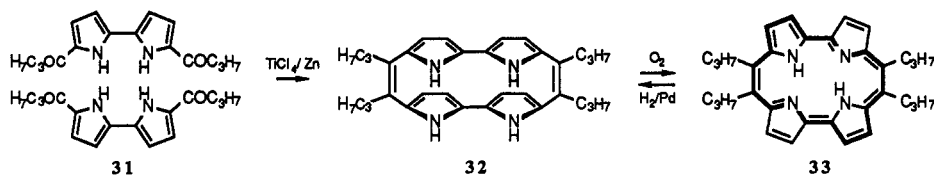
According to an X-ray crystallographic analysis (Fig. 3a), **14** is planar and, as a consequence of fast NH-tautomerism, possesses effective D_{2h} -symmetry. In order to attain planarity **14** adopts $N(1)\cdots N(2')$ and $N(2)\cdots N(1')$ distances as short as 2.63 Å ($N\cdots N$ distances in **5**: 2.89 Å) which, while allowing exceptionally strong $N-H\cdots N$ hydrogen bonds to be formed, cause the bond angles in the CHCH segments connecting the α,α' -bipyrrrole units to widen to 132° .



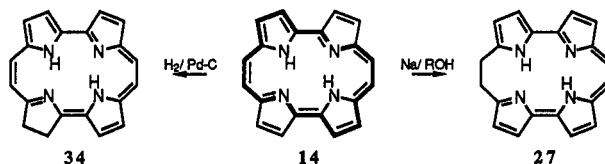
The presence of strong $N-H\cdots N$ hydrogen bonds in **14** manifests itself also in the 1H NMR spectrum, namely by the finding that the NH signal, when compared to that of **5**, has shifted downfield by no less than 7 ppm. Significantly, the resonances of the peripheral protons of **14** and **5** occur in the same region. That **14** and **5** sustain diamagnetic ring currents very similar in magnitude independently follows from the striking analogies observed in the spectra of the methylaluminum complexes **28** and **29** as well as from the dramatic deshielding of the NH protons in the spectrum of 9,10-dihydroporphycene (**27**) (ref. 19). As shown by ^{15}N CPMAS NMR spectroscopy (ref. 20), the $N-H\cdots N$ hydrogen bridges in **14**, despite their shortness, are unsymmetrical and to be described by a double minimum potential. An additional important argument in favour of the porphyrin-like nature of **14** is provided by the UV/VIS spectrum since this consists of a Soret-band and a set of Q-bands. Qualitatively, the UV spectrum of **14** differs from that of **5** mainly in that it shows higher absorption for the Q-bands. The latter spectral finding on **14**, in conjunction with other photophysical properties of the compound (ref. 21), such as its stability towards photooxidation, its high quantum yields of fluorescence, and singlet oxygen sensitization, suggest that this novel porphyrinoid and its alkyl derivatives are potential agents for tumor marking and photodynamic therapy. In view of the important role that porphyrins play in photochemical and photobiological processes a more detailed investigation of the photoexcited triplet states of **14** and derivatives employing time-resolved EPR spectroscopy and other techniques was initiated (ref. 22). In the same context, the anion radical of **14**, generated both chemically and electrochemically, was characterized by ESR and ENDOR (ref. 23).



An intriguing facet of the synthesis of porphycene is the invoked intermediacy of *N,N'*-dihydroporphycene (26) and the extreme ease with which it experiences dehydrogenation to give 14. That 26 has as yet defied all attempts at its isolation becomes plausible if one realizes that 26 is the counterpart in the porphycene series of the equally elusive *N,N'*-dihydroporphyrin (30), also termed isophlorin. As pointed out by Woodward (ref. 24) in connection with the synthesis of chlorophyll, 30 is a non-Hückel [20]annulene that should be very susceptible to a two-electron oxidation affording resonance-stabilized diprotonated porphyrin. Notwithstanding the obvious relationship between 26 and 30, the virtually spontaneous dehydrogenation of 26 remains astounding since this compound being a cyclophane (26a) can be assumed to be geometrically remote from 14.

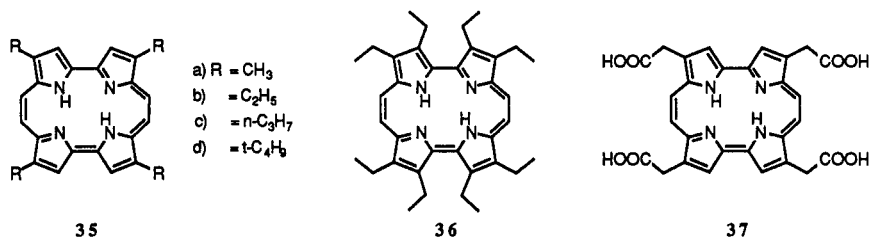


The intermediate formation of *N,N'*-dihydroporphycenes in the synthesis of porphycenes was eventually demonstrated by the isolation of 9,10,19,20-tetrapropyl-*N,N'*-dihydroporphycene (32) (ref. 25) in the reductive coupling of 31. Although 32 is still readily oxidized, its reaction with oxygen, presumably for steric reasons, is markedly slower than that of 26a. The cyclophane-type structure of 32 which was already suggested by the fact that the compound is colourless, rigorously follows from an X-ray crystallographic analysis (Fig. 3b and 3c). As found most recently, oxidation of 32 to 33 can be reversed by catalytic hydrogenation of 33 with palladium.



The course of this hydrogenation, which makes the pair 32/33 a most unusual redox system, was unexpected because the chlorin-type 2,3-dihydroporphycene (34) (ref. 26) rather than 26 is obtained when 14 is hydrogenated catalytically. That porphycene may also take up hydrogen with formation of 9,10-dihydroporphycene (27), bearing some structural relationship to phlorin, will be shown in a forthcoming publication (ref. 19).

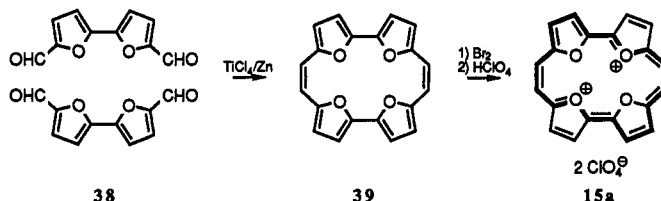
Porphycene (14) is more soluble in organic solvents than porphyrin presumably because it is the less polar isomer. However, many of its derivatives (as is the case with those of 5), such as the majority of its products of substitution and its metal complexes, lack solubility and crystallinity and are therefore not as open to physical and chemical investigations as one would wish. Accordingly, development of porphycene chemistry depends on the availability of porphycenes possessing solubilizing alkyl or aryl groups. This demand can easily be met since the method of synthesis of 14 has been found not only to be very versatile but also to be particularly well adapted to the preparation of alkyl porphycenes of various substitution patterns.



Among the alkyl porphycenes presently known, the symmetrical 2,7,12,17-tetrapropylporphycene (35c) (ref. 27), in view of its properties, would seem predestined to play the role as counterpart to H₂(OEP) in opening up porphycene chemistry. 2,3,6,7,12,13,16,17-Octaethylporphycene (36) (ref. 19), though no longer planar due to steric interference of the substituents at the 3,6- and 13,16-positions, has proven to be an interesting ligand in complexation. The synthesis of the tetraacid 37 (ref. 28) was prompted by the expectation that solubility in water (as sodium salt) might be advantageous to the use of porphycenes as agents in photodynamic therapy and to other possible applications in medicine.

The experimental verification of the "porphycene concept" made it imperative to include the furan and thiophene analogues of 14, the dicationic tetraoxaporphycene (15) and tetrathiaporphycene, respectively, as targets of our search for novel porphyrin structural variants. While 15 was expected to have properties similar to those of 7, the

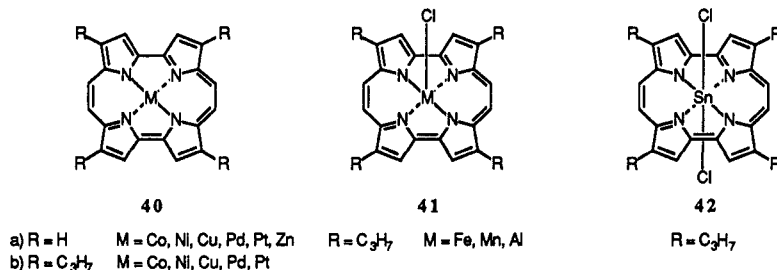
chance that tetrathiaporphycene would exist as a stable porphyrinoid molecule seemed very small because of the distortions imposed on the ring skeleton by the steric demand of the sulphur atoms.



Access to **15a** proved to be straightforward due to the ready availability of the oxygen-bridged [20]annulene **39** (analogue to the elusive **26**) by reductive coupling of 5,5'-bi-2,2'-furaldehyde (**38**) using low-valent titanium. Compound **39**, representing a [4n]annulene, sustains a pronounced paramagnetic ring current in the ^1H NMR spectrum as indicated by the occurrence of all the ^1H -resonances at relatively high field. An X-ray analysis of **39** bears out the anticipated marked alternation of the bond lengths in the ring segment C8-C9-C10-C11. The analysis, moreover, reveals that **39**, in notable contrast to the isoelectronic N,N'-dihydroporphycenes, does not exist as a cyclophane but is an almost planar molecule. In accord with the finding that the base peak in the mass spectrum of **39** is the doubly positively charged molecular ion, **39** smoothly undergoes a two-electron oxidation to give **15** as the perchlorate **15a** when treated successively with bromine and perchloric acid (ref. 6). The dication **15** is shown by spectral and structural investigations of **15a** (and of the hydrogen dinitrate salt of the dication) to qualify, indeed, as the "porphycene counterpart" of the tetraoxaporphyrin dication (7).

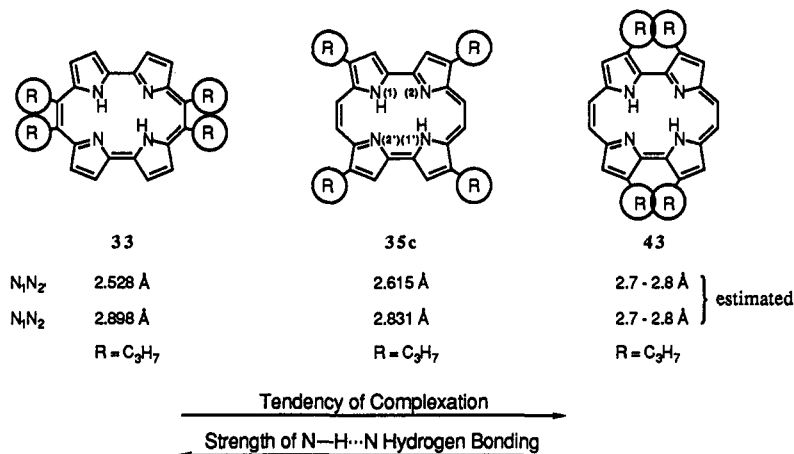
METALLOPORPHYCENES – AN OUTLOOK

Porphycenes, constituting porphyrin-like tetrapyrrolic macrocycles, promise rich and colourful chemistry that is likely to attract interdisciplinary interest. Taking into account the dominant role metalloporphyrins play in porphyrin chemistry, it should be particularly rewarding to explore the syntheses of metalloporphycenes and to relate the properties of such complexes to those of their metalloporphyrin counterparts. As our first studies already revealed, porphycene and its alkyl derivatives are capable of forming metal complexes with a great number of metal ions. A compilation of the metalloporphycenes that readily yielded to synthesis, following conventional procedures of metalation of porphyrins, is given in formulae **40**, **41**, and **42**.



In general, the propensity of porphycenes to undergo complexation is, except for small cations, somewhat reduced as compared to that of porphyrins because the cavity is smaller and slightly rectangular in shape, and, perhaps even more so, because the electron lone pairs on the nitrogen atoms are not oriented precisely towards the center of the molecule. The observation that 2,7,12,17-tetrapropylporphycene (**35c**) forms nickel and aluminum complexes with great ease whereas it has as yet failed to coordinate with the relatively large osmium ion lend support to this proposition.

Scheme 1



In conclusion it should be noted that **35c**, currently the major porphycene ligand utilized, and its structural isomers **33** and **43** differ rather markedly in the geometry of the N_4 -coordination hole as a consequence of steric interactions of alkyl substituents. According to the $N \cdots N$ distances observed (or estimated) for these alkylporphycenes (Scheme 1), the tendency of complexation should increase as one goes from **33** to **43** due to improved "tuning" of the shape of the hole to the stereoelectronic requirements of the metal ion. In line herewith octaethylporphycene (**36**), which corresponds to **43**, has been found to be superior to **33** and **35c** in binding zinc ion and some other metal ions. The availability of alkylporphycene ligands, differing in the pattern of substitution, may therefore be instrumental in developing the still virgin field of metalloporphycenes.

Acknowledgement

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