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The porphyrins from the 'annulene chemist's' perspective

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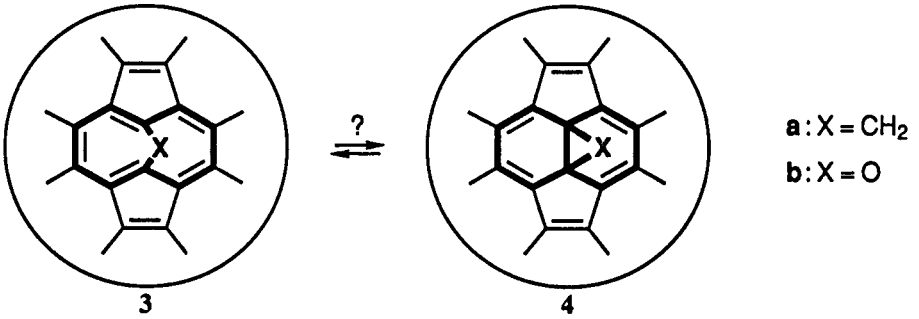
Abstract - The [18]annulene model of porphyrin, emphasizing the presence of an 18π main conjugation pathway in the molecule, invites the application of Hückel's 4n+2 rule to the tetrapyrrolic macrocycle. Although the usefulness of this model had already been demonstrated in the late sixties by the landmark syntheses of sapphyrins by R. B. Woodward and of corroles by A. W. Johnson, the cornucopia of novel porphyrinoid chromophores it entails became apparent only in recent years. Guided by experience in annulene chemistry, we embarked some time ago on a systematic exploration of potentially aromatic porphyrin structural variants that could be expected to generate interdisciplinary interest. As a result, the porphycenes and metalloporphycenes as well as the tetraoxa-, tetrathia- and tetraselenaporphyrin dications were discovered. In this account our latest contributions to the field - homologues of porphyrin, of porphycene and of the tetraoxaporphyrin dication, isophlorins, isocorroles and metalloisocorroles - will be surveyed.

PROLOGUE

The chemistry encompassed by this progress report represents the latest outgrowth of a research programme that, under the common denominator "Aromaticity - Hückel's Rule", has evolved over more than 25 years from annulenes of various types to porphyrinoids. Our investigations in these domains originated from the serendipitous discovery in 1964 of the Hückel-aromatic hydrocarbon 1,6-methano[10]annulene (**1**) which, exhibiting benzenoid chemical properties (formation of a host of substitution products) and being available in quantity, constitutes the most widely studied (4n+2)π-homologue of benzene.[1]

1 **2**

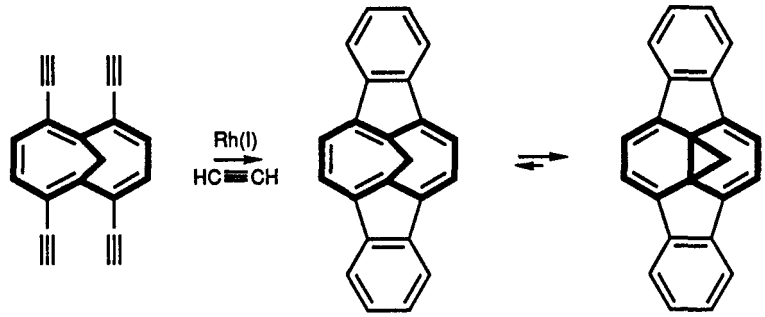
A particularly intriguing aspect of 1,6-methano[10]annulene (π-homonaphthalene), subject to continued debate, is the subtlety of its π-electron structure - peripheral cyclic conjugation blended with 1,6-homoconjugation - in connection with valence tautomerism involving the σ-homonaphthalene form (**2**).[2] In a dramatic new development, this kind of tautomerism was found by several groups to be instrumental in establishing a fascinating linkage between 1,6-bridged [10]annulene and buckminsterfullerene chemistry.



3 **4**

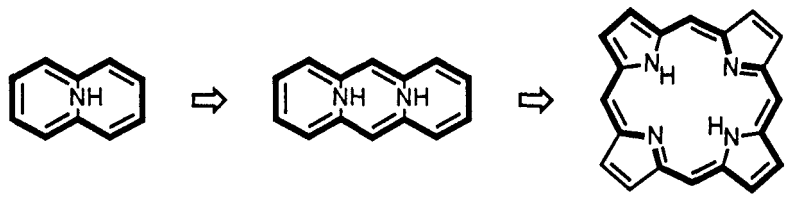
As described in a series of publications, C_{60} reacts with diazoalkanes[3] (by 1,3-dipolar addition followed by loss of nitrogen) and with various oxidants[4] at the central π-bond of the pyracylene substructure to give adducts containing a 1,6-bridged [10]annulene-type and/or a σ-homonaphthalene-type unit (**3a**/**4a** and

3b/4b, respectively) embedded into the buckminsterfullerene framework. While the structures of the diazoalkane-mediated CX_2-adducts to C_{60} have not yet been proven rigorously, except in the case of $C_{60}C(C_6H_4Br\text{-}p)_2$ where a 1,6-methano[10]annulene unit with an exceptionally short $C_1\cdots C_6$ distance (1.84 Å vers. 2.24 Å in **1**) was shown to be present by an X-ray crystallographic analysis, $C_{60}O$ was determined to be of the σ-homonaphthalene-type (**4b**).



5 **6** **7**

It occurred to us that the dibenzohomopyracylene **6/7**, for which a one-step synthesis from 2,5,7,10-tetraethinyl-1,6-methano[10]annulene (**5**) by a metal-catalyzed two-fold [2+2+2]cycloaddition with acetylene can be envisaged, might serve as a reference compound for the still elusive **3a/4a** regarding 1,6-methano[10]annulene - σ-homonaphthalene valence tautomerism. The anticipated approach to **6/7**, indeed, materialized when tris(triphenylphosphine)rhodium(I) chloride (50° C) was employed as the catalyst. The dibenzohomopyracylene thus obtained solely exists, both in solution and in the crystalline state, as the tautomer **7** containing a cyclopropane ring.[5] This assignment of structure unequivocally follows from the ^{13}C NMR data (CH_2: $J_{^{13}C,H}$ = 169 Hz) and from an X-ray study (C-CH_2-C angle: 62°; transannular C···C distance: 1.555 Å) of the compound, respectively. The interesting question whether **7**, when forming part of the surface of $C_{60}CH_2$, will retain its tautomeric preference or will be forced by steric and/or electronic factors to become 1,6-methano[10]annulene-type remains to be settled. Taking into account that the equilibrium **1**⇌**2** is strongly influenced by substituent effects, $C_{60}CH_2$ need not conform structurally to the CX_2-adducts to C_{60} presently known.



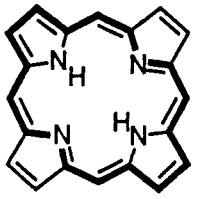
8 **9** **10**

A pivotal role in linking bridged annulenes to yet another area of chemistry, i.e., to porphyrin chemistry, is played by 1,6-imino[10]annulene (**8**)[1] and its 14π-homologue *syn*-1,6:8,13-diimino[14]annulene (**9**).[6] As we already pointed out at the time of their synthesis, these imino bridged [4n+2]annulenes favorably compare with porphyrin (**10**) in ^1H NMR spectroscopic terms, especially with respect to ring current effects. This analogy made us receptive to the [18]annulene model of porphyrin which, emphasizing the presence of an 18π main conjugation pathway in the molecule, invites the application of Hückel's 4n+2 rule to the tetrapyrrolic macrocycle. Although the ramifications of this model had been demonstrated by the landmark syntheses of sapphyrins by R. B. Woodward[7] and of corroles by A. W. Johnson[8] as early as 1965-70, the cornucopia of novel porphyrinoid chromophores it entails became fully apparent only in recent years. Guided by our experience in annulene chemistry, we set out in the mid-eighties on a systematic exploration of potentially aromatic porphyrin structural variants that could be anticipated to generate interdisciplinary interest. As a result, the porphycenes/metalloporphycenes and the tetraoxa-, tetrathia- and tetraselenaporphyrin dications were discovered.[9] In this account our contributions to the field since ISNA-6 will be delineated.

PORPHYRIN HOMOLOGUES

The concept to relate porphyrin (**10**) to [18]annulene, supported by a recent AM1 theoretical study[10], implies the possible existence of aromatic porphyrin homologues, i.e., [22]porphyrin-(2.2.2.2) (**11** and configurational isomers), [26]porphyrin-(3.3.3.3) (**12**) etc., featuring (4n+2)π main conjugation pathways.

Although quite a number of expanded porphyrins[11] have been brought to light lately, the neutral porphyrin homologues with free NH groups have remained elusive. In pursuing the synthesis of such molecules it must be kept in mind that the transition from porphyrin to its homologues is accompanied by the occurrence of configurational isomerism. Evidently, an essentially strain-free porphyrin-like geometry exhibiting D_{2h} symmetry can only be attained by homologues in which the number (n) of the carbon atoms of the $(CH)_n$ segments connecting the pyrrole rings is odd.



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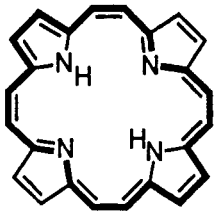

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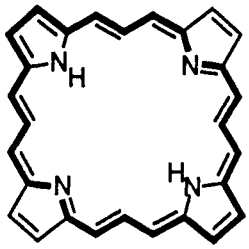
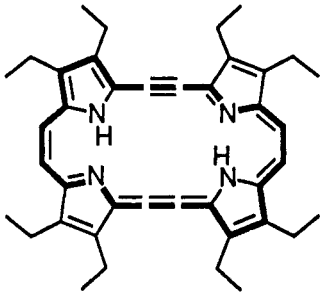


12

The primary target of our studies was [22]porphyrin-(2.2.2.2), the next higher homologue of porphyrin, for which, besides the isomer **11** containing four *cis*-CH=CH bonds, isomers with *trans*-CH=CH bonds must be considered. As concluded from force-field calculations, **11** is too highly strained to be planar whereas the *cis,trans,cis,trans*-isomer (corresponding to **14**), found to be the energetically favored isomer, can adopt a planar conformation with only slight skeletal strain and might even profit from the presence of strong N-H···N hydrogen bonds tending to support planarity.

In our synthetic approach to [22]porphyrin-(2.2.2.2)[12], for reasons of solubility as its octaethyl derivative, we took advantage of the availability of the 22π acetylene-cumulene porphyrinoid **13**, a novel type of tetrapyrrolic macrocycle developed during the last few years (see section on porphycenes).[13] This compound offered the chance to get to octaethyl-all-*cis*-[22]porphyrin-(2.2.2.2) since its partial catalytic hydrogenation by means of Lindlar-catalyst could be expected to occur by *cis*-addition of hydrogen. As it turned out, however, hydrogenation of **13** afforded the *cis,trans,cis,trans*-[22]porphyrin-(2.2.2.2) **14** as the sole [22]porphyrin. That **14** must be the favored isomer is also evident from the remarkable finding that it was formed, albeit in poor yield (2 %), as the only low molecular weight product of the reductive carbonyl coupling of 3,4-diethyl-2,5-pyrrole dialdehyde (**15**). Analogously, parent *cis,trans,cis,trans*-[22]porphyrin-(2.2.2.2) is obtained when the coupling reaction is performed on 2,5-pyrrole dialdehyde.[12]



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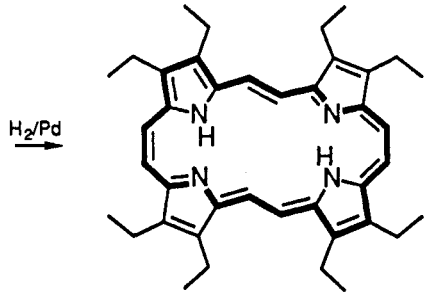

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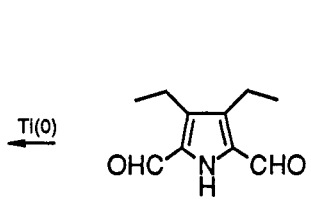

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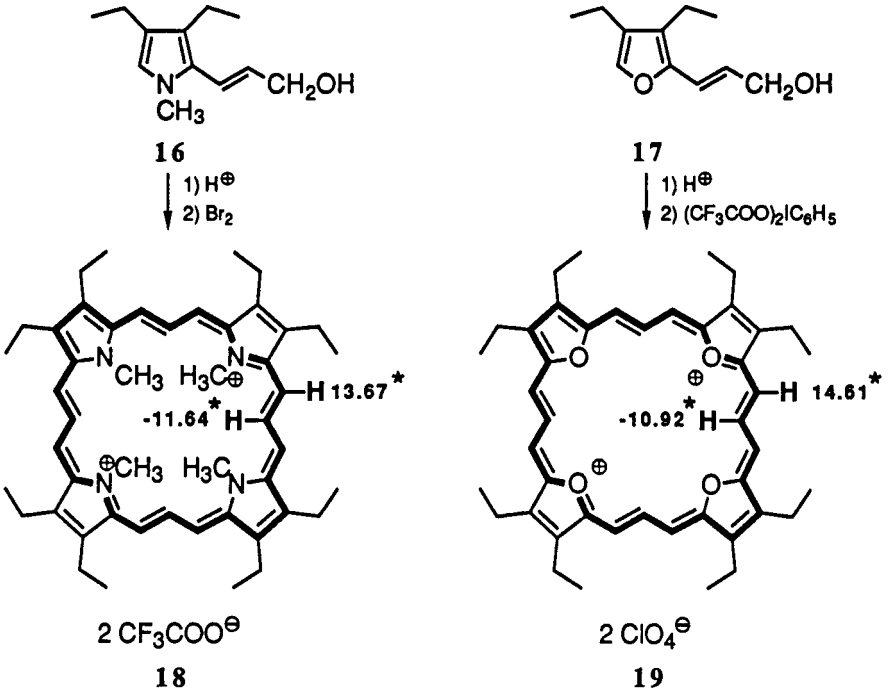
The ^{1}H NMR spectrum of **14** is consistent with the anticipated *cis,trans,cis,trans*-configuration of the compound. The extreme low- and high-field positions of the resonances of the outside and inside perimeter protons, respectively, convincingly demonstrate the aromatic porphyrinoid nature of **14**, whereas the resonance of the NH protons at relatively low field (presence of strong N-H···N hydrogen bonds) clearly reveals its structural relationship to porphycene **26**. From the changes in the spectrum observed above 70° C it is apparent that [22]porphyrin-(2.2.2.2), in *cis,trans,cis,trans*-configuration, undergoes an isodynamic transformation involving rotation around the *trans*-CH=CH bonds - tantamount to a transition from C_{2h} to effective D_{2h} molecular symmetry. The UV/VIS spectrum of **14**, containing a strong Soret band as well as Q bands, is that of a porphyrinoid. Due to the shape and position of the bands, it might be looked upon as a porphycene spectrum (more so than that of a porphyrin) shifted to longer wavelengths. Failure of the IR spectrum to show an NH stretching vibration provides additional evidence that the compound, like porphycene, features strong N-H···N hydrogen bonds. An X-ray crystallographic analyis of **14** confirms the *cis,trans,cis,trans*-configuration of the molecule and the supposed planarity of the ring framework.

Like all-*cis*-[22]porphyrin-(2.2.2.2) (**11**), the homologous [26]porphyrin-(3.3.3.3) (**12**) corresponding to **10** in geometry, has so far escaped all efforts at its synthesis. However, an elegant pathway to the dicationic *N,N',N'',N'''*-tetramethyl[26]porphyrin-(3.3.3.3) as its octaethyl derivative **18**, patterned after the biosynthesis of porphyrin, has been opened up in recent years by pioneering work of B. Franck.[14] As shown by this author, the *N*-methyl-pyrrylpropenol **16** is capable of undergoing an acid-catalyzed biomimetic cyclotetracondensation to give the respective expanded porphyrinogen which on oxidation affords **18**. The ^{1}H NMR spectrum of **18**, apart from being in agreement with a porphyrin-like geometry of the molecule, exhibits extreme chemical shifts arising from the added effects of a pronounced diamagnetic ring current and the positive charges.



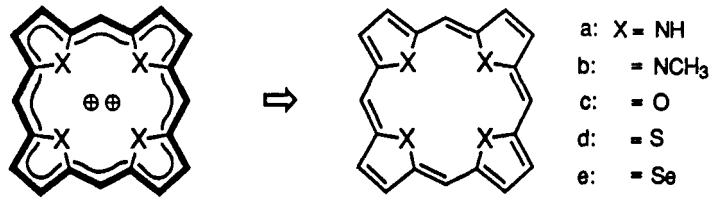
* Chemical shift values (δ); ^{1}H NMR spectra (300 MHz) of **18** in $CDCl_3$ and of **19** in CD_2Cl_2.

After having demonstrated that the scheme of porphyrin biosynthesis, when modified appropriately, also provides access to the tetraoxaporphyrin dication (**20c**) (see next section) starting out from furfuryl alcohol, we speculated as to whether the tetraoxa[26]porphyrin-(3.3.3.3) dication **19** might be synthesized analogously from the alcohol **17**. Treatment of **17** in nitromethane with citric acid, indeed, brings about cyclotetracondensation with formation of the corresponding porphyrinogen (yield 3 %), and this on oxidation with bis(trifluoroacetoxy)iodobenzene followed by addition of 70 % perchloric acid furnished the desired dication **19** (as its perchlorate), isolated as bluish-green crystals of metallic luster (orange coloured solutions).[15] The close structural and electronic relationship of **19** to Franck's dication **18** is borne out most strikingly by a spectroscopic comparison of the two compounds. In the ^{1}H NMR spectra, the dications **19** and **18** 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 **19** and **18** furthermore extends to their UV/VIS spectra as well as to other spectral properties, as will be outlined in a forthcoming publication. That the 26π-dication **19** is a homologue of the 18π-dication **20c** convincingly follows from the systematic spectral changes observed as one goes from **20c** to **19**.

DICATIONIC PORPHYRINS - ISOPHLORINS

Dicationic porphyrins, represented by formula **20**, are 18π-electron systems (when main conjugation pathways are considered) that formally derive from diprotonated porphyrin (**20a**) as the prototype. Evidently, these species are to be regarded as resonance hybrids to which canonical structures with the positive charges residing in the C_{20}-perimeter (used in this section) are assumed to make a major contribution. Apart from diverse diprotonated porphyrins, dicationic porphyrins, such as **20b-20e** have remained a "white spot" on the colorful porphyrin landscape, presumably because evidence that would suggest their involvement in biological processes has as yet not been forthcoming.

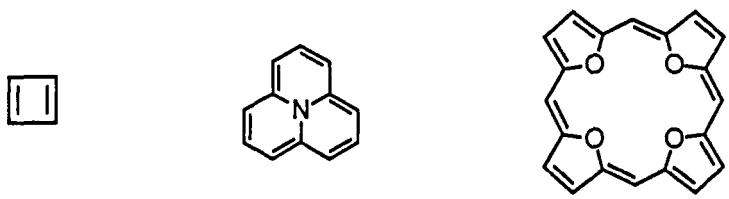
An inroad into this area of porphyrin chemistry has been made in recent years by B. Franck's biomimetic synthesis of alkyl derivatives of the *N,N',N'',N'''*-tetramethylporphyrin dication (**20b**) (as bromides and perchlorates)[16] and by the discovery in our laboratory that the acid-catalyzed condensation of furfuryl alcohol affords among other products the crown ether tetraoxaporphyrinogen which, employing conventional methods, could be converted into the tetraoxa-, tetrathia- and tetraselenaporphyrin dications [**20c**, **20d** (as perchlorates) and **20e** (only in solution), respectively]. Among these dicationic porphyrins, the tetraoxaporphyrin dication (**20c**) is a particularly attractive canditate for further development since it is a planar, stable aromatic molecule to be looked upon as a fundamental porphyrin structural variant.



$2\ ClO_4^{\ominus}$

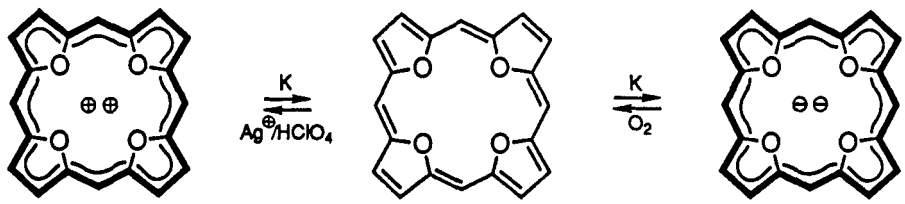
20 **21**

One of the more interesting chemical aspects of dicationic porphyrins, to be addressed here, is their possible two-electron reduction to give isophlorins **21**, yet another class of structurally simple, hitherto unknown porphyrin derivatives. As far as we are aware of, the only reference to isophlorins in the chemical literature is by R. B. Woodward[17] who, in the course of his ingenious synthesis of chlorophyll, pointed out that **21a** is a true non-Hückel [20]annulene, anticipated to be very prone to oxidation to porphyrin. For us, isophlorins hold special fascination since their discovery would demonstrate in a most telling way how intricately porphyrin and annulene chemistry can be intertwined.



22 **23** **21c**

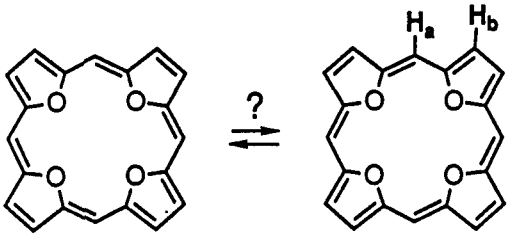
The primary target of our synthetic efforts in the domain of isophlorins was tetraoxaisophlorin (**21c**), a [20]annulene commanding considerable theoretical interest. It is a structural virtue of **21c** that it is planar without being strained and that it possesses high symmetry, D_{4h} or D_{2h} depending on whether the π-bonds are delocalized or not. In the light of such properties, tetraoxaisophlorin - which according to simple Hückel theory might be a diradical - qualifies, like cyclobutadiene (**22**) and cycl[3.3.3]azine (**23**), as a [4n]annulene model compound.



$2\ ClO_4^{\ominus}$ $2\ K^{\oplus}$

20c **21c** **24**

The direct synthesis of tetraoxaisophlorin (**21c**) from **20c** by two-electron reduction utilizing potassium in THF met with only partial success because the reaction could not be arrested at the stage of **21c** (actually traced) but proceeded further to give the 22π tetraoxaporphyrin dianion (**24**). This result prompted attempts to prepare the supposedly highly reactive **21c** by partial oxidation of **24**. The method of choice in bringing about oxidation of **24** to **21c** proved to be, strange to say, molecular oxygen applied at low temperature. Tetraoxaisophlorin (**21c**) thus produced is isolated as air-sensitive black crystals (can be stored at -78° C) forming green solutions.



21c

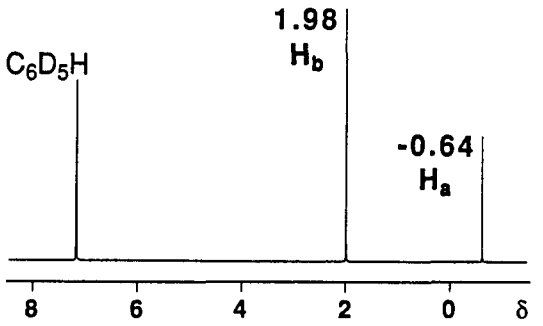
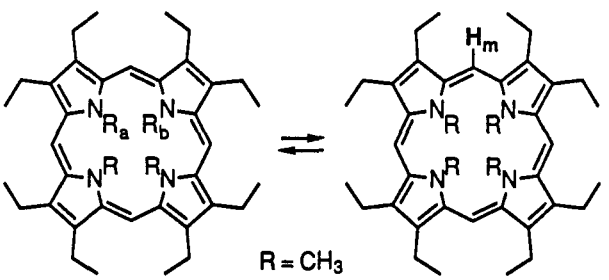


Fig. 1. ^1H NMR spectrum (300 MHz) of **21c** (C_6D_6).

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 (**21c**), like cyclobutadiene (**22**) and cycl[3.3.3]-azine (**23**), exists in the singlet ground state. However, the HOMO-LUMO energy gap in **21c** must be very small since the ^1H NMR spectrum of this molecule (Fig. 1), 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 **21c** remain sharp down to -135°C, the lowest temperature reached so far, indicating that the degenerate π-bond shift assumed to take place in **21c** must be extremely fast. Bearing in mind that the free energy of activation ($\Delta G^{\ddagger}$) of the π-bond shift in some bridged [12]annulenes, which noticeably deviate from planarity, is of the order of only 4-5 kcal/mol, $\Delta G^{\ddagger}$ for this dynamic process in **21c** is presumably too small to be accessible by NMR spectroscopic methods. The UV/VIS spectrum of **21c** shows, in addition to relatively intense bands at 310-350 nm, very weak and broad long-wave absorption (600-900 nm) that is characteristic of 4nπ-electron systems in which such a transition involves alternating compression and expansion of adjacent bonds. An X-ray crystallographic analysis of **21c** 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 **21c** mainly rests upon MO theoretical arguments.



25

While the parent isophlorin **21a** is still shrowded in mystery, a partial breakthrough into the direction of this molecule has recently been accomplished by the synthesis of *N,N',N'',N'''*-tetramethylisophlorin as its octaethyl derivative **25**.[18] It was gratifying to find that the aromatic octaethyl-*N,N',N'',N'''*-tetramethylporphyrin dication smoothly undergoes two-electron reduction employing anthracene-sodium in THF to yield the fairly stable **25** (75%) as the sole product observed (no overreduction!). An X-ray crystallographic analysis of **25** established that the compound, like its dicationic precursor, possesses a saddle-shaped perimeter with *syn,anti,syn,anti*-conformation of the *N*-methyl groups. However, whereas the heterocyclic five-membered rings in the dication are equivalent, those in **25** are alternately pyrrole- and pyrroline-type identifying **25** as an isophlorin with localized π-bonds (reduction of molecular symmetry from D_{2d} to C_{2v}). The possibility that **25** is subject to a degenerate conformational inversion of the *N*-methyl groups is ruled out for steric reasons.

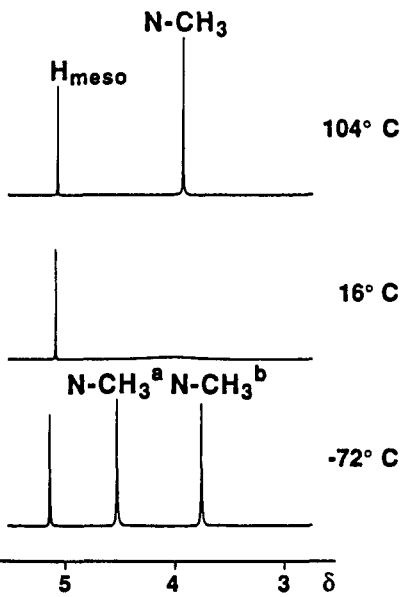
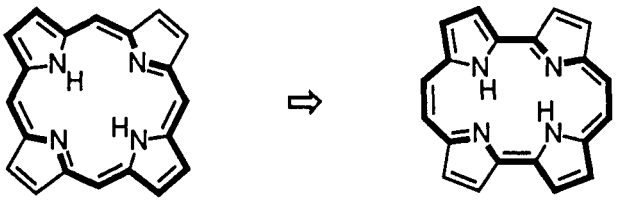


Fig. 2. ^1H NMR spectrum (300 MHz) of **25** (toluene-d_8) at -72° C (region of slow exchange), 16° C (coalescence range), and 104° C (region of fast exchange).

An interesting consequence to be expected from the non-planarity of the isophlorin-type [20]annulene **25** is a substantial increase of the activation barrier of the anticipated π-bond shift as compared to the conditions in **21c**. Accordingly, the ^{1}H NMR spectrum of **25**, in contrast to that of **21c**, exhibits temperature dependent changes in line shape that unequivocally can be attributed to the occurrence of a rapid degenerate π-bond shift at room temperature (Fig. 2). The dynamic process is sufficiently slow at -72° C so that the spectrum recorded corresponds to compound **25** with localized π-bonds (main feature: two *N*-CH_3 signals). As the temperature is raised, the signal of the *meso* protons remains unchanged, whereas the three pairs of signals for the protons involved in the exchange process (*N*-CH_3; CH_3; CH_2) each coalesce after initial line broadening (16° C for *N*-CH_3). Raising the temperature still further (to 104° C) results in the simple spectrum predicted for **25** in the range of rapid exchange. In order to derive the activation parameters of the π-bond shift the rate constants were determined by line shape analysis of the *N*-CH_3 signals between -72° C and 104° C using DNMR5. Evaluation of the kinetic data on the basis of the Eyring equation afforded the following parameters for the dynamic process: $\Delta H^{\ddagger}$ = 11.2 ± 0.2 kcal mol^{-1} and $\Delta S^{\ddagger}$ = -6.6 ± 0.6 cal K^{-1} mol^{-1}, and thus $\Delta G^{\ddagger}_{298}$ = 13.2 kcal mol^{-1}. It seems noteworthy that the activation energy of the π-bond shift in **25** is of the order of magnitude of that for other non-planar [4n]annulenes, particularly that of cyclooctatetraene.

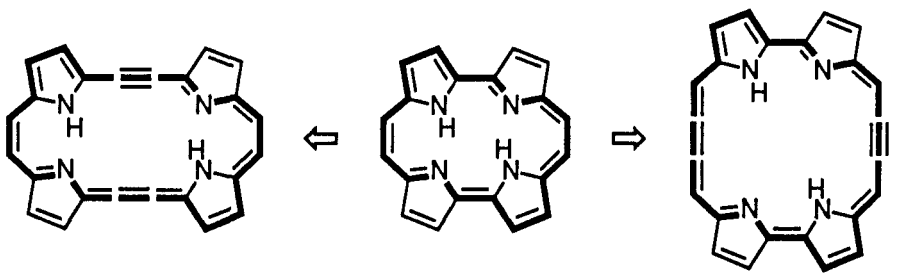
EXPANDED PORPHYCENES

Porphycene (**26**), an isomer of porphyrin (**10**) formally derived from the latter by a mere reshuffling of the pyrrole and methine moieties, is one of the more important novel porphyrinoids that emerged from structural variations of **10** with preservation of a (4n+2)π main conjugation pathway.[9]



[18]Porphyrin-(1.1.1.1) **10** [18]Porphyrin-(2.0.2.0) **26**

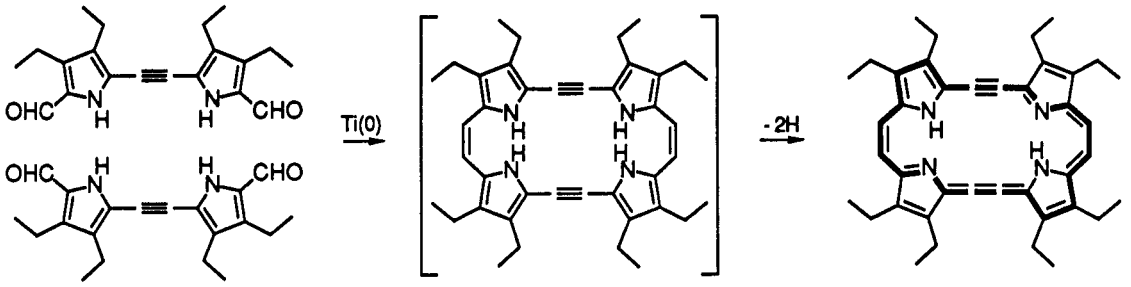
The growing interest in novel porphyrinoid chromophores both as free ligands and as receptors for metal ions and anions, reflected in the current drive to develop expanded porphyrins[11], were an incentive to us to devise porphycene-related tetrapyrrolic macrocycles harbouring extended (4n+2)π main conjugation pathways with n > 4. A clue as to how porphycenes might be translated into such variants - sort of counterparts to expanded porphyrins - is provided by consideration of the bonding in the intriguing acetylene-cumulene [4n+2]dehydroannulenes, a class of annulenes discovered by F. Sondheimer[19] and developed successfully by M. Nakagawa.[20] These annulenes possess one or more pairs of linear $C_{sp^2}(C_{sp}C_{sp})_nC_{sp^2}$ structural units and are best described by equivalent Kekulé resonance structures having acetylene and cumulene bonds.



27 **26** **28**

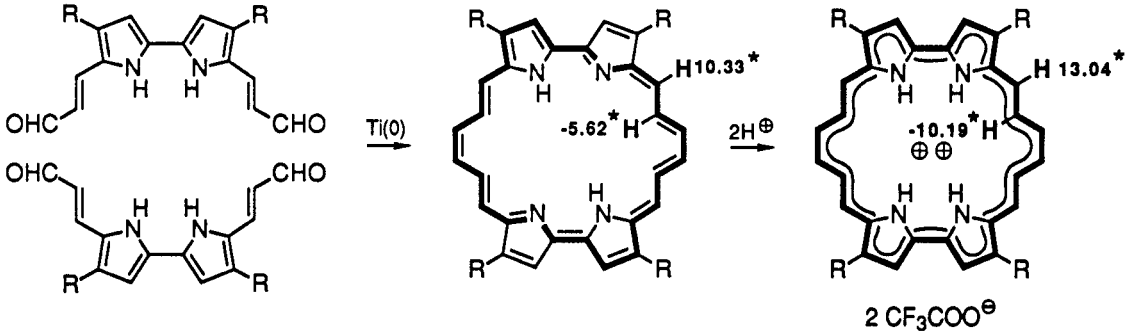
The most obvious porphycenes with extended (4n+2)π-electron systems featuring acetylene-cumulene units that come to mind are the laterally and vertically expanded variants **27** and **28**, respectively. Both compounds contain 22π main conjugation pathways embedded into planar ring skeletons. Interest in **27** and **28** primarily focuses on their physical and photophysical properties, since these macrocycles, due to the pronouncedly rectangular shapes of their coordination center, are not likely to form metal complexes in which the metal is bound to all of the four nitrogen atoms (other complexes are, of course, conceivable). In

the case of **28**, the as yet unsettled question to what extent porphycene derives its remarkable stability from the strong N-H···N hydrogen bonding is also addressed.



29 **30** **13**

As reported recently[13], the synthesis of **27** as its octaethyl derivative **13** could be accomplished in one step by reductive carbonyl coupling of the acetylenic dipyrrolic dialdehyde **29** with low valent titanium.[21] That the primary product of this reaction, the *N,N'*-dihydro compound **30**, would undergo spontaneous dehydrogenation yielding **13** seems noteworthy as there was no precedent for the formation of acetylene-cumulene bonds in this fashion. Compound **13** perfectly fits the description as a laterally stretched 22π-porphycene. The ^{1}H NMR spectrum of **13** is indicative of the presence of a pronounced diamagnetic ring current and of strong N-H···N hydrogen bonds whereas the UV/VIS spectrum bears a striking resemblance to that of octaethylporphycene but has shifted to longer wavelengths. Formulation of **13** as a resonance hybrid is supported by an X-ray crystallographic analysis according to which the $C_{sp^2}C_{sp}C_{sp}C_{sp^2}$ structural units on opposite sides are equivalent. The NH hydrogens in **13**, unlike those in **26**, are not disordered so that assignment to specific nitrogen atoms (due to symmetry, those at diagonal positions) is possible. A more detailed study of the spectral and photophysical properties of **13**, specifically with regard to potential applications of this porphyrinoid in photodynamic therapy, is currently in progress.

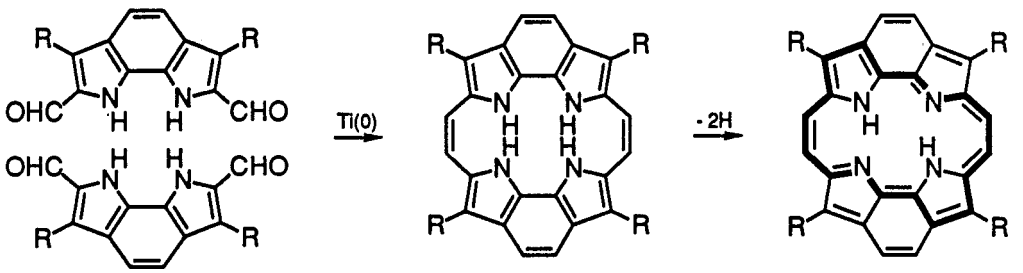


R = C_3H_7 **31** **32** **33**

* Chemical shift values (δ); ^{1}H NMR spectra (300 MHz) of **32** in $CDCl_3$ and **33** in $CDCl_3/CF_3COOD$

Apart from the still elusive acetylene-cumulene porphyrinoid **28**, 2,7,16,21-tetrapropyl[26]porphyrin-(6.0.6.0) (**32**) may be considered as an example of a vertically expanded porphycene which is devoid of strong N-H···N hydrogen bonding. Admittedly, **32** suffers from the disadvantage that it lacks the rigidity to be assumed for **28**. The approach to **32** followed the pattern of porphycene synthesis in that the dialdehyde **31**, readily obtained from 4,4'-dipropyl-2,2'-bipyrrole by reaction with 3-(dimethylamino)acrolein, was submitted to reductive carbonyl coupling mediated by low valent titanium. In striking parallel with the behavior of *N,N'*-dihydroporphycene, the primary product of this coupling, i.e., *N,N'*-dihydro-tetrapropyl[26]porphyrin-(6.0.6.0), experienced spontaneous dehydrogenation to give **32** isolated as the free base. Not too surprisingly, **32** turned out to be so mobile conformationally that the ^{1}H NMR spectrum of the compound (measured in the range from room temperature to -50° C in chloroform and other solvents) could not be interpreted due to excessive line broadening. However, when the spectrum was taken in chloroform containing a small amount of methanol, its resolution was sufficient to reveal that **32** sustains a marked diamagnetic ring current (for chemical shift values, see formula **32**), and hence qualifies as a porphyrinoid molecule. Methanol presumably coordinates to **32** and thus slows down conformational processes. Protonation of **32** with trifluoroacetic acid affords the dication **33** which shows a well-resolved ^{1}H NMR spectrum at room temperature due to the tendency of the positive charges to reduce the mobility of the ring system. As **33** exhibits a ring current effect comparable to that observed for Franck's dicationic *N,N',N'',N'''*-tetramethyl[26]porphyrins-(3.3.3.3) (see section on porphyrin homologues) it appears that

the charges in **33** are capable of arresting the molecule in a planar conformation rather efficiently. In the case of **32**, metal binding, though unlikely because of concomitant severe distortion of the ligand, cannot be dismissed outright.



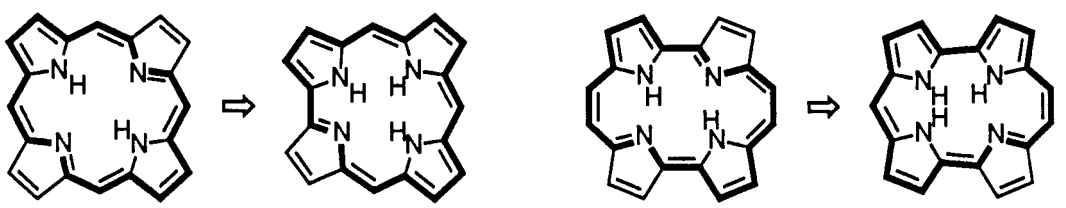
isolable

R = $C(CH_3)_3$ **34** **35** **36**

Among the porphycene variants with extended π-electron systems that can be envisaged, benzo derivatives are of particular interest since they should retain the capability to form metal complexes. The first representative of such porphycenes we came across is the macrocycle **36** (the *tert*-butyl groups serve as solubilizing substituents) formally arising from porphycene by linking the pyrrole rings of the bipyrrole units by CH=CH groups. In reality, the synthesis of **36** does not follow this line but is brought about by reductive carbonyl coupling of the dialdehyde **34** to give the corresponding *N,N'*-dihydroporphycene **35**, an isolable compound, and subsequent oxidation of the latter by means of DDQ. A discussion of **36** (the formula given does not represent the electronic nature of the compound adequately) must be deferred until completion of the still ongoing spectral and structural investigations.

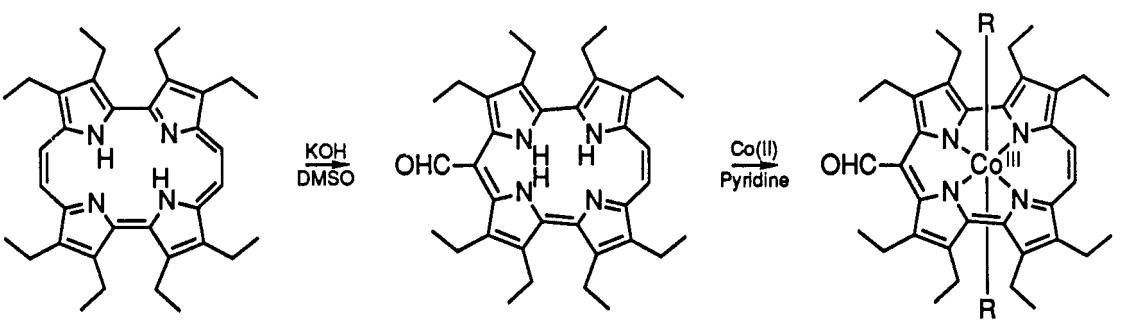
ISOCORROLES AND METALLOISOCORROLES - AN OUTLOOK

It would seem appropriate to conclude this account by addressing, albeit in brief, a structural variation of both porphyrin and porphycene that up to now has received only scant attention, i.e., contraction of the tetrapyrrolic ring system.



10 **37** **26** **38**

Porphyrin (**10**), on formal expulsion of a *meso* methine unit is converted into the already mentioned corrole (**37**), the aromatic basic structure of the ring framework of vitamin B_{12}. Like porphyrin, corrole features an 18π main conjugation pathway bestowing aromatic character on the molecule but, in contrast to the former, possesses three rather than two imino hydrogen atoms.



R = Pyridine

39 **40** **41**

It occurred to us that porphycene (**26**), being isomeric to porphyrin, might have a corrole counterpart, termed isocorrole (**38**), originating from **26** by extrusion of a methine unit from a non-pyrrolic CHCH moiety. This supposition, indeed, was found to be true. While the porphyrin-corrole conversion still awaits experimental verification, certain porphycenes can be induced - by mechanistic schemes that remain to be unraveled - to undergo contraction to give isocorroles.[22] Thus, 2,3,6,7,12,13,16,17-octaethylporphycene (**39**) on heating with conc. aqueous potassium hydroxide in dimethylsulfoxide/diglyme rearranges with formation of the octaethylisocorrole aldehyde **40**. In this regard, it should be noted that **40** is also encountered, though only as a minor product, in the synthesis of **39**.

Although the investigations on isocorroles are still in their early stage, there already is convincing spectral and X-ray crystallographic evidence to show that these latest porphyrin structural variants are aromatic - despite the presence of a non-planar ring skeleton. Undoubtedly, the main incentive to explore isocorroles is provided by their capability to form metalloisocorroles, such as the cobalt(III) complex **41** synthesized most recently, which invite comparative studies with the respective metallocorroles. Representing a new class of tetrapyrrolic macrocycles and ligands for metal complexation of great promise, isocorroles are to be regarded as yet another striking manifestation of the variability of the porphyrin structure that nature has devised so ingeniously in the course of evolution.

Acknowledgement

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