Characterisation of new 26,28-diheterosapphyrins: 5,10,15,20-tetraphenyl-26,28-dioxasapphyrin and 5,10,15,20-tetraphenyl-26,28-dithiasapphyrin

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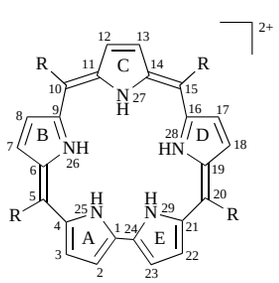
5,10,15,20-Tetraphenyl-26,28-dioxasapphyrin (O_2TPSH) and 5,10,15,20-tetraphenyl-26,28-dithiasapphyrin (S_2TPSH), heteroanalogues of 5,10,15,20-tetraphenylsapphyrin ($TPSH_3$) have been synthesised by condensation of the respective precursors, namely 2,5-bis(arylhydroxymethyl)furan or bis(arylhydroxymethyl)thiophene and pyrrole. 26,28-Dioxasapphyrin presents an unusual skeleton with an inverted pyrrole ring lying opposite to the bipyrrolic unit at each protonation stage. In contrast, the planar arrangement of the macrocycle has been determined for 26,28-dithiasapphyrin.

The tautomeric equilibrium of S_2TPSH which involves the exchange of a proton between N-25 and N-29 has been found to be slow on the ^{1}H NMR timescale below 213 K. Activation parameters of tautomerization were determined by the line shape analysis: $\Delta H^{\ddagger} = 47.2 \pm 1.1$ kJ mol^{-1}, $\Delta S^{\ddagger} = 19.9 \pm 5.5$ J K^{-1} ($\Delta H^{\ddagger} = 10.9 \pm 0.3$ kcal mol^{-1}, $\Delta S^{\ddagger} = 4.6 \pm 1.4$ cal K^{-1}).

Introduction

A logical formal extension in the self assembling of pyrrole and aldehyde into a cyclic structure simply involves the insertion of one pyrrole ring between the *meso*- and α-carbons of the porphyrin macrocycle. Such a hypothetical addition leads to the simplest larger aromatic pyrrole-containing system, namely sapphyrin.[1–3]



Sapphyrin

The sapphyrin is the simplest member of the expanded porphyrin class. The molecule possesses an overall aromatic 22 π-electron annulene framework.[1–6] Decaalkyl-substituted sapphyrin was serendipitously discovered by Woodward and co-workers in their effort to synthesise vitamin B_{12}.[1,3] The synthetic procedures, subsequently developed by Brodhurst *et al.*,[2] Bauer *et al.*[3] and Sessler *et al.*,[4a] require preorganised substrates and involve a MacDonald-type [3 + 2] condensation between a functionalised bipyrrole and a dicarboxyl-substituted dipyrrane. A reaction between functionalised bipyrrole, pyrrole and benzaldehyde was also used.[4b]

We have previously established that the routine condensation of the pyrrole and benzaldehyde yields, apart from tetraphenylporphyrin and inverted tetraphenylporphyrin, a pentapyrrolic macrocyclic molecule with an aromatic sapphyrin nucleus, namely 5,10,15,20-tetraphenylsapphyrin.[7] This discovery of 5,10,15,20-tetraphenylsapphyrin has proved the validity of the expectation that the pentapyrrolic products are allowed by a mechanism of the Rothemund synthesis.[8]

Core modification of 5,10,15,20-tetraphenylsapphyrin by the replacement of nitrogen atoms with various heteroatoms will permit the preparation of a series of new heterocycles that may be interesting in terms of their aromatic properties and their ability to bind metal ions. They may have potential as potent anion chelating reagents and particularly as likely photosensitisers in photodynamic therapy. The series of heteroatom-containing sapphyrins constitute a group in which the extent and localisation of substitution can be systematically varied. From the monoheterosubstituted skeleton the following isomers can be constructed: 25-, 26- and 27-heterosubstituted sapphyrins. The hypothetical disubstitution creates six isomers, specifically 25,29-, 25,26-, 25,27-, 25,28-, 26,27- and 26,28-diheterosubstituted sapphyrins. Until now only the 27-monoheterosubstituted, 25,29-diheterosubstituted and 25,27,29-triheterosubstituted sapphyrins have been characterised.[2,9] Thus, the following pyrrole-alkylated expanded porphyrin derivatives with one or two pyrrolic fragments replaced by furan were investigated: 27-oxasapphyrin,[2,9] 25,29-dioxasapphyrin,[2] dioxasmaragdyrin,[2] ozaphyrin (isomeric analogue of oxasapphyrin)[10] and oxobronzaphyrin (isomeric analogue of rubyrin).[11] The following extended porphyrins containing thiophene(s) instead of pyrrole(s) were synthesised: 27-thiasapphyrin,[2,9] 25,29-dioxa-27-thiasapphyrin,[9a] oxobronzaphyrin,[11] bronzaphyrin[12] and thioozaphyrin (isomeric analogues of thiophen-containing sapphyrins),[12] decaethylpentathiaphyrin dication related to pentaphyrin[13] and hexathiahomoporphycene dication with a bronzaphyrin-like skeleton.[14]

We have already noted that tetraphenylsapphyrin has a similar relationship to decaalkylsapphyrins as tetraphenylporphyrin does to octaethylporphyrin, due to the identical substituents at the *meso*- and β-pyrrole positions.[7] By analogy to core modified 5,10,15,20-tetraarylporphyrins,[15–17] we wish to extend the class of 5,10,15,20-tetraphenylsapphyrin by the addition of a core modified 5,10,15,20-tetraphenylsapphyrin, formed by the replacement of 26-N and 28-N nitrogen atoms by oxygen or sulfur respectively, yielding 5,10,15,20-tetraphenyl-26,28-dioxasapphyrin (O_2TPSH) and 5,10,15,20-tetraphenyl-26,28-dithiasapphyrin (S_2TPSH). Considering the unorthodox, inverted, geometry determined for 5,10,15,20-tetraphenylsapphyrin,[7] the impact of the replacement of nitrogens by heteroatoms on the macrocycle structure is particularly interesting.

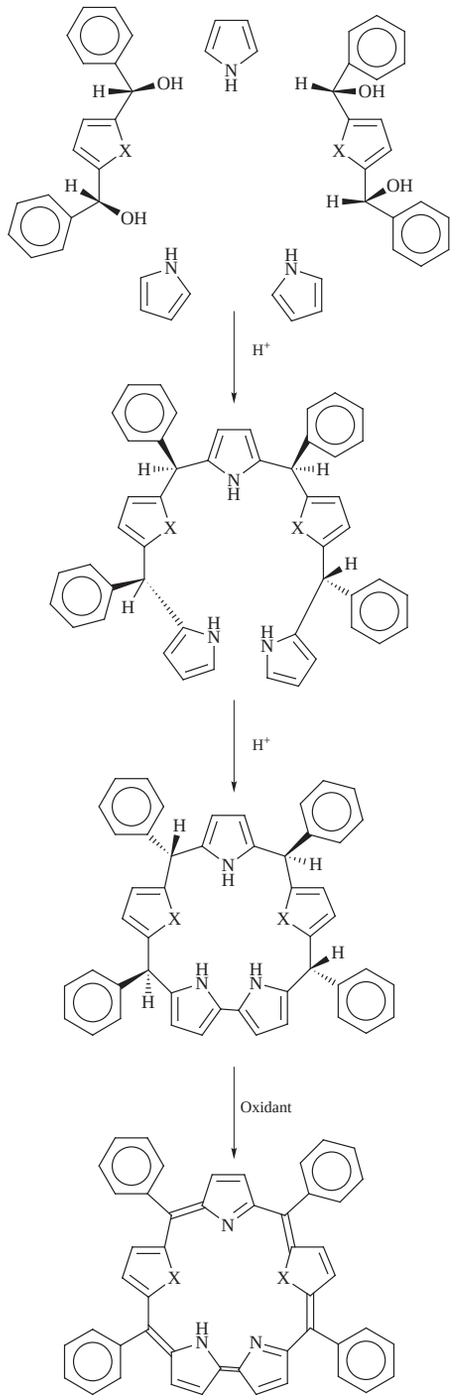
Results and discussion

Synthesis and characterisation

A key step in the synthesis of 26,28-diheterosapphyrins is the construction of condensation precursors which allows the insertion of a furan or a thiophene ring into the macrocyclic structure. 2,5-Bis(arylhydroxymethyl)furan or 2,5-bis(arylhydroxymethyl)thiophene, which were previously used successfully to obtain the corresponding core modified tetraarylporphyrins,[15–17] have been found to be suitable substrates for heterosapphyrin synthesis. 5,10,15,20-Tetraphenyl-26,28-dioxasapphyrin (O_2TPSH) and 5,10,15,20-tetraphenyl-26,28-dithiasapphyrin (S_2TPSH) could be obtained by a procedure analogous to that described previously for 5,10,15,20-tetraphenyl-21,23-dioxaporphyrin (O_2TPP) and 5,10,15,20-tetraphenyl-21,23-diathiaporphyrin (S_2TPP) taking into account the mechanistic considerations related to the synthesis of 5,10,15,20-tetraphenylsapphyrin. The resulting schematic synthetic route is presented in Scheme 1.

The synthesis involves the one-pot reaction of 2,5-bis(arylhydroxymethyl)furan [2,5-bis(arylhydroxymethyl)thiophene] with pyrrole in excess (2:3 molar ratio), carried out in dichloromethane, catalysed by $BF_3{\cdot}Et_2O$, *i.e.* in conditions perturbed in comparison to the optimised synthesis of diheteroporphyrin.[16,17] The process produces, in addition to the expected 5,10,15,20-tetraphenyl-21,23-dioxaporphyrin (5,10,15,20-tetraphenyl-21,23-dithiaporphyrin), the expanded porphyrin, *i.e.* 5,10,15,20-tetraphenyl-26,28-dioxasapphyrin (5,10,15,20-tetraphenyl-26,28-dithiasapphyrin). The rather small yields of 26,28-diheterosapphyrins were still sufficient for detailed spectroscopic characterisation. [$^2H_6$]-5,10,15,20-Tetraphenyl-26,28-dioxasapphyrin ([$^2H_6$]O_2TPSH), specifically deuterated at the pyrrolic positions was obtained, using [$^2H_5$]-pyrrole for condensation.

The electronic spectrum of O_2TPSH shows the Soret-like band at 474 nm which is indicative of polypyrrolic aromatic macrocycles, accompanied by *Q* bands at 586, 630, 735 and 837 nm (Fig. 1). A similar pattern has been observed for S_2TPSH (Fig. 2) although a shift in some of the electronic bands has been noticed. The spectra resemble those of all-nitrogen $TPSH_3$.[7,18] The aromaticity of O_2TPSH and S_2TPSH molecules has been confirmed by ^{1}H NMR data because all outer pyrrole and *meso*-phenyl resonances are strongly shifted downfield due to the ring current effect (Fig. 3, Table 1). To account for the ^{1}H NMR spectra of O_2TPSH and its protonation products we have considered an inverted skeleton, introduced previously for 5,10,15,20-tetraphenylsapphyrin.[7,18] The structural data for neutral polyalkylated sapphyrins are not available but the protonated forms typically demonstrated a roughly planar arrangement with the pyrrole nitrogens pointed towards the centre of the macrocycle.[5,6] Ozaphyrin, an isomeric analogue of furan-containing sapphyrin, is planar and contains all pyrrolic nitrogen and furan oxygen inside the macrocycle as established by X-ray crystallography.[10] Such geometry is preserved in solution for ozaphyrin and thioazaphyrin (isomeric analogues of thiophene-containing sapphyrins) as confirmed by ^{1}H NMR spectroscopy.[11,12] The ^{1}H NMR spectrum of O_2TPSH exhibits an AB pattern at the 9.79 and 8.91 ppm positions which is readily assigned to the bipyrrolic unit by comparison to the spectrum of [$^2H_6$]O_2TPSH where the intensity of the pyrrolic resonances diminished because of deuteration. The considerable difference of the 2-H and 3-H chemical shifts reflects the upfield ring current contribution of the 5-phenyl ring available for the 3-H but not for the 2-H proton. The inner 12,13-H protons gave a very characteristic upfield singlet at −0.85 ppm. The furan unit shows the AB pattern predicted by symmetry considerations at 9.54 and 9.17 ppm. The ^{1}H NMR spectrum of S_2TPPH reveals features fully accounted for by a planar macrocyclic structure with the 12,13-H protons situated at the 26,28-dithiasapphyrin periphery (Fig. 4, Table 1). Accordingly the 12,13-H resonance has been identified as a singlet at the typical porphyrin pyrrolic position, 8.80 ppm.



Scheme 1

Protonation and tautomeric equilibria

A ^{1}H NMR titration of O_2TPSH with trifluoroacetic acid (TFAH) dissolved in [$^2H_2$]dichloromethane results in the gradual formation of a monocationic form, $O_2TPSH_2^+$, followed by a dicationic form (Fig. 3). The upfield locations of the 12,13-H pyrrolic resonances confirmed the inverted 26,28-dioxasapphyrin structure at any protonation stage. Additionally the downfield position of the 27-NH resonance determined for $O_2TPSH_2^+$ at 13.5 and at 14.95 ppm (203 K) for $O_2TPSH_3^{2+}$ provides a convincing structural verification.

S_2TPSH and its diprotonated form $S_2TPSH_3^{2+}$ demonstrate completely different ^{1}H NMR behaviour (Fig. 4) in comparison to $TPSH_3$ or O_2TPSH, respectively.[7,18] Here, the structurally informative 12,13-H resonances are located at 8.80 ppm for the

Table 1 Selected ^{1}H NMR data for O_2TPSH, S_2TPSH and their protonated forms in CD_2Cl_2 solution[a]

Proton assignment	O_2TPSH **I**0 (rt)	O_2TPSH **I**0 (203 K)	$O_2TPSH_3^{2+}$ **I**2 (203 K)	S_2TPSH **P**0 (rt)	S_2TPSH **P**0 (183 K)	$S_2TPSH_3^{2+}$ **P**2 (TFA) (192 K)
2, 23 (pyrr)	9.79	9.91	10.56	10.00	10.26	10.32
3, 22 (pyrr)	8.91	9.00	10.17	9.30	9.36	9.72
7, 18[b]	9.54	9.70	10.24	10.10	10.16	10.32
8, 17[b]	9.17	9.34	9.65	9.96	10.00	10.15
12, 13 (pyrr)	−0.85	−1.27	−2.20	8.80	8.80	9.02
25-NH, 29-NH		3.36 (183 K)	−2.63		−4.99	−2.50
27-NH	—	—	14.90	—	—	−2.61

[a] Chemical shifts relative to TMS; TFA = trifluoroacetic acid. [b] Furan or thiophene protons.

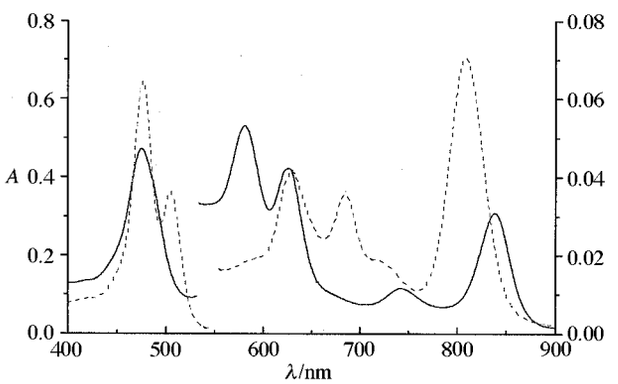


Fig. 1 Electronic spectra of O_2TPSH (——) and $O_2TPSH_3^{2+}$ (– – –) in dichloromethane. $O_2TPSH_3^{2+}$ has been obtained by addition of TFAH.

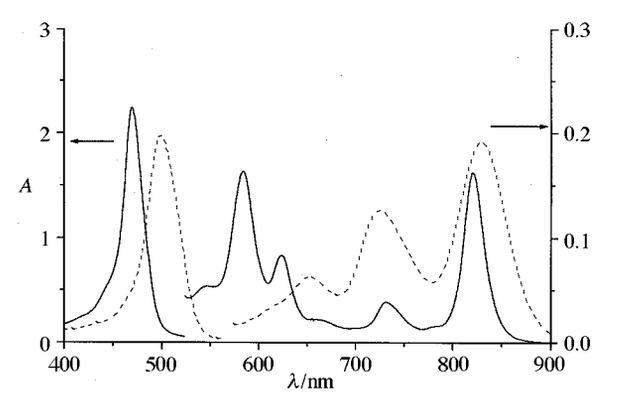


Fig. 2 Electronic spectra of S_2TPSH (——) and $S_2TPSH_3^{2+}$ (– – –) in dichloromethane. $S_2TPSH_3^{2+}$ has been obtained by addition of TFAH.

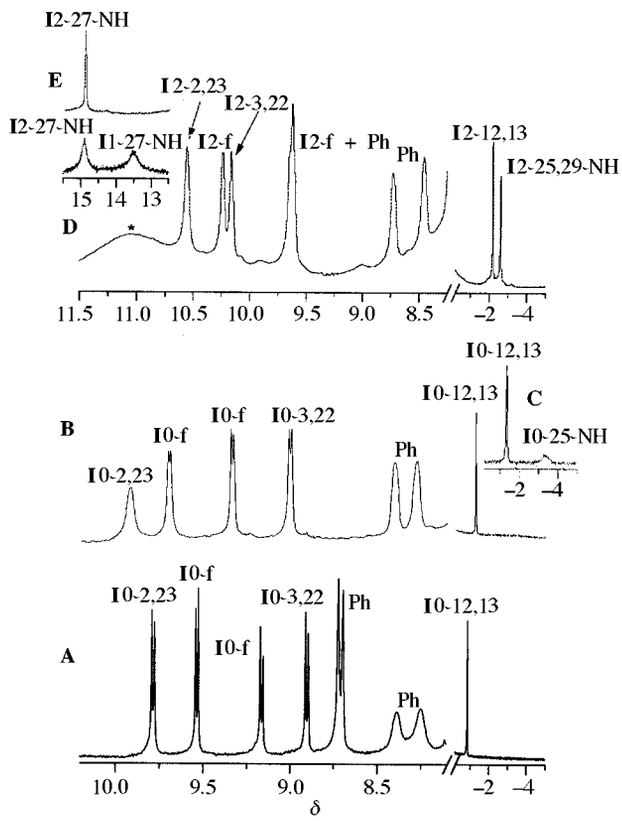


Fig. 3 ^{1}H NMR spectra (300 MHz) of (A) O_2TPSH (293 K); (B) O_2TPSH (203 K); (C) the 25-NH and 12,13-CH region of O_2TPSH (183 K); (D) $O_2TPSH_3^{2+}$ (203 K). Inset (E) the lower trace presents spectral fragments confirming the formation of the monocation (203 K), and the upper trace shows the 27-NH region of $O_2TPSH_3^{2+}$ (203 K). All spectra measured in CD_2Cl_2. Resonance assignments follow the systematic numbering of the sapphyrin skeleton, * the COO*H* resonance of TFAH.

neutral species and at 9.02 ppm (192 K) for the diprotonated species, respectively. Consequently 26,28-dithiasapphyrin prefers an extended skeleton at each protonation stage.

Such behaviour contrasts with the previously determined, peculiar flexibility of the 5,10,15,20-tetraphenylsapphyrin.[7,18] We have found that the protonation of $TPSH_3$ proceeds stepwise *via* a mono- and a variety of di-cationic forms. The monoprotonated species preserves the inverted skeleton. Two fundamental structures, inverted and planar, have been detected in the case of dications. The transformation of the macrocycle involves a reversible flip of a single pyrrole unit which relocates the 27-NH pyrrolic nitrogen between the periphery and the centre of the macrocycle. Such a rearrangement has been triggered by proton and/or anion addition and involves binding of anion(s) *via* a system of multiple NH–anion hydrogen bonds. Generally, the larger expanded porphyrins showed an analogous flexibility. The impressive rotations of the two pyrrole units of the hexaphyrin macrocycle were encountered in the course of palladium amine dichloride coordination.[19] Protonated forms of non-aromatic expanded porphyrins, *i.e.* hexapyrrolic rosarin and decapyrrolic turcasarin, demonstrated remarkably twisted conformations.[20] The conformational changes coupled to NH tautomerism were observed for octaphyrin.[21]

Thus the replacement of 26-N and 28-N nitrogens of sapphyrin by oxygen or sulfur atoms respectively imposes an exclusively inverted geometry for 26,28-dioxasapphyrin but a planar geometry for 26,28-dithiasapphyrin. Contrary to the regular tetraphenylsapphyrin the geometry is not controlled by protonation. Considering the established structural preferences the protonation and tautomeric equilibria are presented in Schemes 2 and 3, respectively.

To simplify the description of the equilibria we will refer to the particular cationic species by defining their idealised geometry, *i.e.* **I***n* for inverted and **P***n* for approximately planar species, respectively, with an overall cationic charge equal to *n*+. The tautomers are numbered successively. Generally, three different tautomeric forms $\mathbf{I}0_1$, $\mathbf{I}0_2$, $\mathbf{I}0_3$ could be suggested for O_2TPSH (Scheme 2). The equivalence of two furan (B and D) and two pyrrole rings (A and E of the bipyrrolic fragment) as well as a single line for 12,13-H protons at 298 K have been readily explained by assuming that O_2TPSH, like $TPSH_3$ and

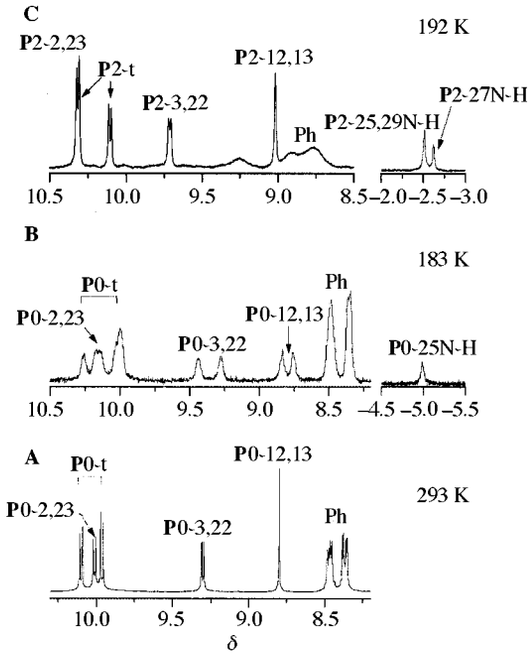
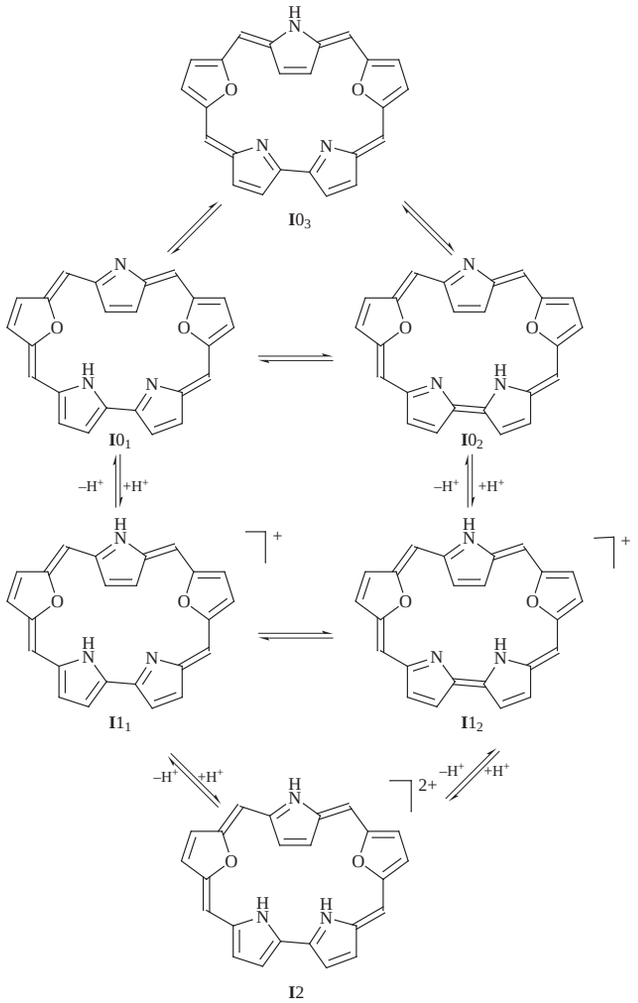


Fig. 4 ^{1}H NMR spectra (300 MHz) in CD_2Cl_2 of (A) S_2TPSH (293 K); (B) S_2TPSH (183 K); (C) $S_2TPSH_3^{2+}$ (192 K). Coupling between β-CH and NH protons has been observed for all pyrrolic protons. Resonance labelling follows that in Fig. 3.

many other porphyrins, is subject to a NH tautomerism that is rapid on the ^{1}H NMR timescale.[22–26] The presence of $\mathbf{I}0_3$ has been easily excluded as a single NH resonance at low temperature is observed in the upfield but not in the downfield region of the spectrum, revealing unambiguously its inner localisation. The peripheral NH proton is expected to be strongly shifted downfield due to the ring current effect.[7,18] The tautomeric equilibrium of O_2TPSH has been found to be slower on the ^{1}H NMR timescale at 183 K in CD_2Cl_2 but even in that case only the selective broadening of resonance has been observed. The broadening is more severe for the $\mathbf{I}1_1 \rightleftharpoons \mathbf{I}1_2$ equilibrium of monocationic species (trace E of Fig. 3). Apart from 27-NH and 12,13-H resonances other lines are practically beyond detection.

In the case of S_2TPSH the equivalence of two thiophene and two pyrrole rings (bipyrrolic fragment) at 293 K is readily explained assuming that the NH tautomerism of S_2TPSH is rapid on the ^{1}H NMR timescale (Scheme 3). The tautomeric equilibrium of S_2TPSH has been found to be slow on the ^{1}H NMR timescale below 213 K. Two sets of equal intensity resonances have been clearly identified at the thiophene and pyrrole regions at 183 K (Fig. 4, trace B). Thus, we have proven that the tautomerisation involves an exchange between two degenerated asymmetric tautomers ($\mathbf{P}0_1 \rightleftharpoons \mathbf{P}0_2$) (Scheme 3). The third feasible tautomer, $\mathbf{P}0_3$ is symmetric with respect to the mirror symmetry plane, passing through 27-N and the middle of the C^1–C^{24} bond. Accordingly, the low temperature ^{1}H NMR spectrum of this form should resemble the symmetric pattern seen for the fast exchange limit at 293 K.

The lineshape analysis of the 12,13-H regions of the ^{1}H NMR spectra of S_2TPSH has been carried out using the iterative computer program, yielding the appropriate rate constants (Fig. 5). An approach assuming an exchange between two equally populated, scalar coupled sites has been applied.[27] The spectra were analysed according to the process defined in Scheme 3 in the 194–213 K temperature range with one rate constant k. The proton transfer was restricted to the exchange N-25⇌N-29. Activation parameters were obtained from the least square fits of the rate constants to the Arrhenius and Eyring equations. They are $E_a = 48.8 \pm 1.1$ kJ mol^{-1} (11.2 ± 0.3 kcal mol^{-1}) (frequency factor $10^{14.2 \pm 0.3}$); $\Delta H^{\ddagger} = 47.2 \pm 1.1$ kJ mol^{-1} $\Delta S^{\ddagger} = 19.9 \pm 5.5$ J K^{-1} ($\Delta H^{\ddagger} = 10.9 \pm 0.3$ kcal mol^{-1} $\Delta S^{\ddagger} = 4.6 \pm 1.4$ cal K^{-1}). They are in the range found for the tautomeric equilibria of regular porphyrins[22–26,28] where Limbach and co-workers have found $\Delta H^{\ddagger}$ equals 12.9 kcal mol^{-1} with no significant activation entropy.[26] This value is in agreement with a calculated activation energy using *ab initio* MP2 limited geometry optimisation.[28] Reimers *et al.*[28] considered that the two inner-hydrogen migration of porphyrin proceeds using an ansychronous pathway *via* a transition state from a *trans* to a *cis* tautomer. This distinct step of tautomerisation requires a single NH proton transfer.

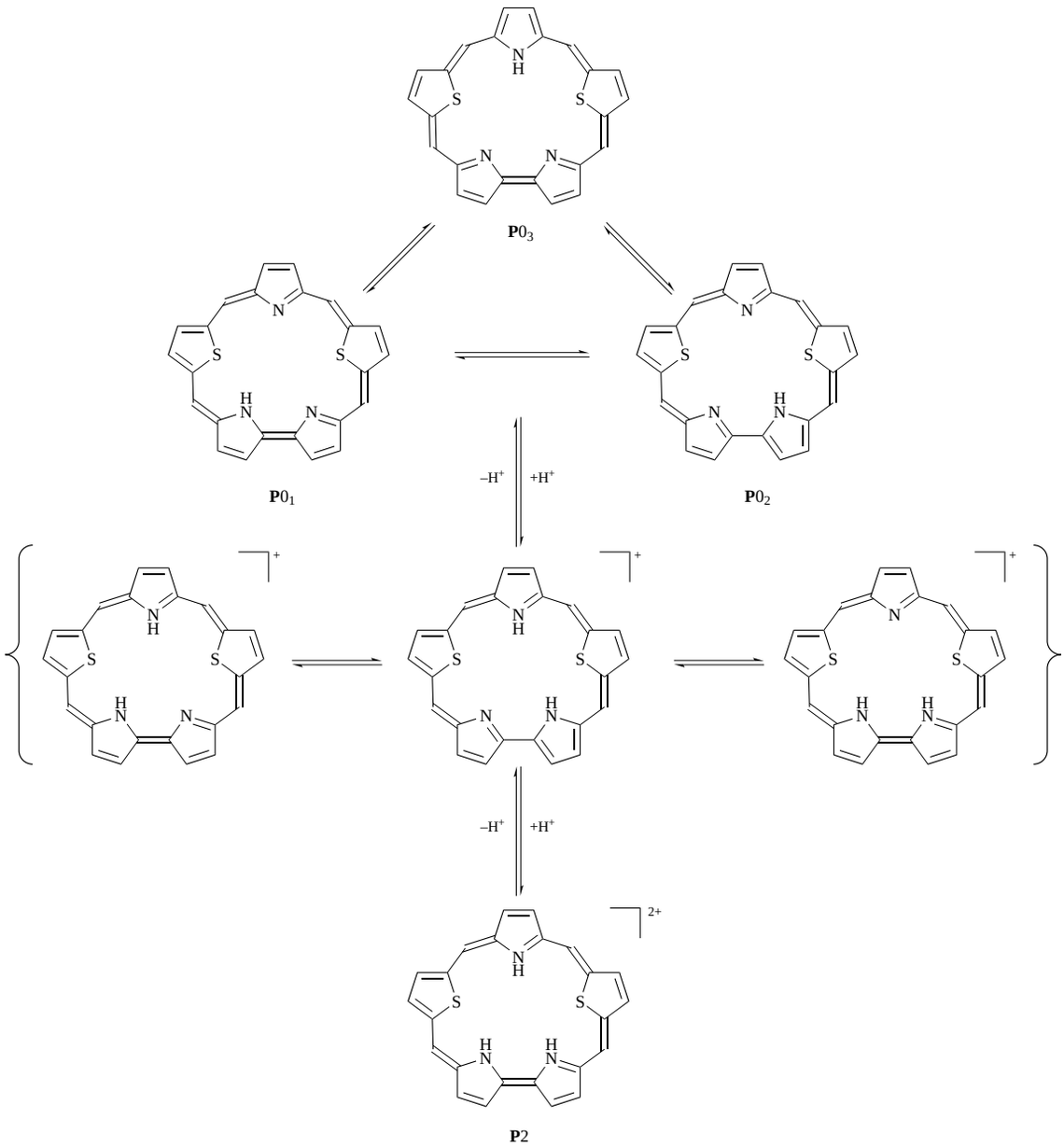


Scheme 2

The *trans–cis* transition in porphyrin and the tautomeric equilibrium of S_2TPSH have some similarities (Scheme 4). In both cases the process involves the transfer of a single NH proton between two neighbouring pyrrole nitrogens. Obviously this comparison has some limitations considering the structural differences of the crucial molecular moieties. In addition, our experimental approach sets some thermodynamic limits on the NH proton transfer in porphyrinic systems.

Conclusions

The formation of dioxasapphyrin and dithiasapphyrin sheds some additional light on the mechanism of the Rothemund-type condensation as the furan or thiophene building blocks provide a fixed localisation of the benzaldehyde related fragments. As for $TPSH_3$,[7,18] we suggest that an excess of pyrrole attacks the heteroanalog of hexahydrobilin, which preserves the preferred helical conformation of tetrapyrrolomethane,[29,30] to create a helical structure which includes two furan (thiophene)



Scheme 3

and three pyrrolic rings. The preliminary binding of the phenylmethanol fragment to the furan (thiophene) moiety has been essential to locate two pyrrolic units at the two ends of the open structure. The helical geometry of the open precursor provides the orientation required for the macrocyclic ring closure, through a classic acid α–α pyrrole coupling[31] to afford a diheterosapphyrinogen molecule which subsequently oxidises to 26,28-diheterosapphyrin.

We have noticed that the nature of the heteroatoms seems to be instrumental in stabilisation of the inverted and extended structures. Accordingly the smaller size of oxygen and nitrogens seems to favour the inverted structures. The large sulfur promotes the planar arrangement. We therefore note that, at least in the case of $TPSH_5^{2+}$, the geometry of the sapphyrin skeleton could be controlled by protonation and chelation of anions by the network of hydrogen bonds.[18] Accordingly the difference in stability between extended and inverted skeletons of sapphyrin and 26,28-dioxasapphyrin, at least in the tetraphenyl series, is relatively small.

Finally, the simple mechanism of the proton transfer has allowed for the direct estimation of its kinetic parameters for a single step for the bipyrrolic unit. This may be important for the study of other systems containing this unit (porphycene, sapphyrin).

Experimental

All solvents were purified by standard procedures.

Preparation of precursors

2,5-Bis(phenylhydroxymethyl)furan[17b] and 2,5-bis(phenylhydroxymethyl)thiophene[15] were obtained as described previously.

O_2TPSH

The condensation of 4 mmol of 2,5-bis(phenylhydroxymethyl)-furan and 6 mmol of pyrrole in dichloromethane (0.8 l) catalysed by BF_3 etherate (3 mmol), carried out over 1 h under nitrogen at room temperature, followed by oxidation with *p*-chloranil (2 g) under reflux for 1 h, produces a mixture of O_2TPP and O_2TPSH. The solution was evaporated to dryness. The solid material was subjected to chromatography on basic alumina to remove tar products. The crude porphyrin products were eluted with dichloromethane. A small amount of basic

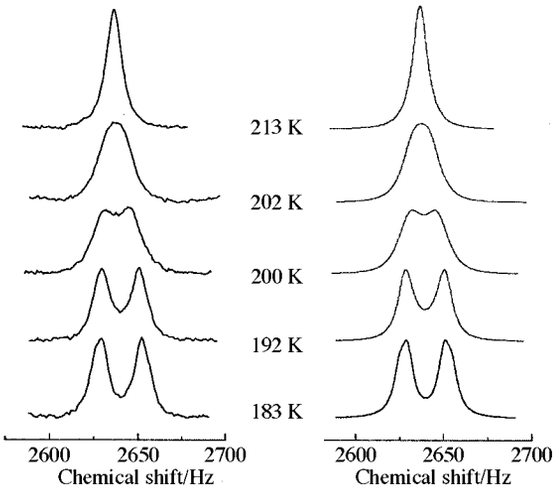
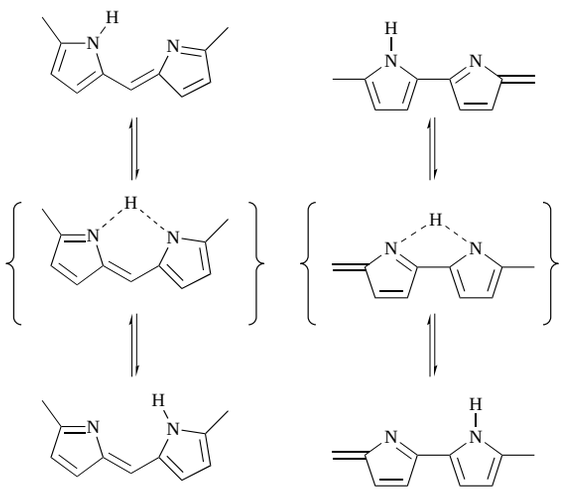


Fig. 5 ^{1}H NMR spectra (300 MHz) of the 12,13-H pyrrole region of S_2TPSH and matching theoretical curves at various temperatures



Scheme 4

alumina was added into the solution and was followed by removal of solvent by rotary evaporation. Solid material was deposited on the top of the column, packed with basic alumina and eluted with tetrachloromethane. The first eluted band contained O_2TPSH, and the second brown band containing O_2TPP was eluted with tetrachloromethane–dichloromethane (10:1 v/v). The pure fraction containing O_2TPSH was evaporated to give 14 mg of O_2TPSH (1% yield) as the brown powder. The product was converted into the dication by mixing dichloromethane solution with aqueous HCl (2%). The organic phase was then separated and a dark red–brown solid was obtained by precipitation with diethyl ether. The dication was filtered and dried. Calc. for $C_{53}H_{45}N_3O_3Cl_4$ [O_2TPSH·2HCl·CH_2Cl_2·$(C_2H_5)_2O$]: C, 69.66; H, 4.92; N, 4.60. Found: C, 69.2; H, 5.10; N, 4.66%. O_2TPSH: *m/z* (LSIMS) = 682, $(M + 1)^+$ (calc. for $C_{48}H_{31}N_3O_2$: 681.8). O_2TPSH: $\lambda_{max}(CH_2Cl_2)$/nm (log ε) 403 (sh), 474 (4.55, Soret), 586 (3.84), 630 (3.74), 735 (3.44), 837 (3.52). $O_2TPSH_3^{2+}$: $\lambda_{max}(CH_2Cl_2)$/nm (log ε) = 482 (4.40), 510 (4.19), 555 (sh), 633 (3.46), 682 (3.35), 7.24 (sh), 813 (3.45), 864 (sh).

S_2TPSH

The procedure followed that described for O_2TPSH using the 2,5-bis(phenylhydroxymethyl)thiophene precursor. However the order of elution of the fractions was reversed for the thia-analogs, the first fraction contained S_2TPP and the second S_2TPSH. The green band from the column chromatography carried out on basic alumina was collected and evaporated to dryness. The product was purified by crystallisation from a dichloromethane–diisopropyl ether mixture. The dark navy-blue crystals were dried *in vacuo*. Yield 21 mg of S_2TPSH·$2CH_2Cl_2$ (1.2%). Calc. for $C_{50}H_{35}N_3S_2Cl_4$ (S_2TPSH·$2CH_2Cl_2$): C, 67.95; H, 3.96; N, 4.75. Found: C, 67.67; H, 4.30; N, 4.68%. S_2TPSH: *m/z* 714, (HRMS) 714.203 802 $(M + 1)^+$ (calc. for $C_{48}H_{31}N_3S_2$: 714.203 767). S_2TPSH: $\lambda_{max}(CH_2Cl_2)$/nm (log ε) = 469 (5.44, Soret), 547 (sh), 584 (4.30), 624 (4.00), 666 (sh), 732 (3.67), 821 (4.30). $S_2TPSH_3^{2+}$: $\lambda_{max}(CH_2Cl_2)$/nm (log ε) = 498 (5.38, Soret), 620 (sh), 652 (3.89), 726 (4.19), 830 (4.37).

Sample preparation

The UV–VIS and ^{1}H NMR samples have to be prepared directly before measurements from the freshly deacidified solvents and carefully neutralised O_2TPSH or S_2TPSH. The neutralisation was carried out by stirring of dichloromethane solutions with 1 M aqueous NaOH. The organic layer was separated and evaporated to dryness in a vacuum and dissolved in an appropriate solvent that was freshly distilled and additionally passed through a basic alumina column before use.

Generation of dicationic forms

The solution of the trifluoroacetic acid in dichloromethane was added to the ^{1}H NMR tube or UV–VIS cell containing the solution of O_2TPSH or S_2TPSH by a syringe, and the progress of the reaction was followed by ^{1}H NMR or UV–VIS spectroscopy.

Instrumentation

NMR spectra were recorded on a Bruker AMX 300 spectrometer. Absorption spectra were recorded on a diode array Hewlett Packard 8453 spectrometer. Mass spectra were recorded on an AD-604 spectrometer using the electron impact and liquid matrix secondary ion mass spectrometry techniques.

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