Organic & Biomolecular Chemistry

Cite this: *Org. Biomol. Chem.*, 2012, **10**, 3463

www.rsc.org/obc

PAPER

Core-modified hexaphyrin: synthesis and characterization of 31,34-disilahexaphyrinoid†

Janusz Skonieczny, Lechosław Latos-Grażyński* and Ludmiła Szterenberg

Received 19th December 2011, Accepted 29th February 2012
DOI: 10.1039/c2ob07134g

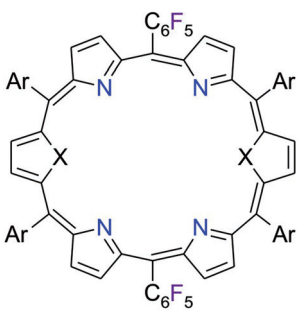
Condensation of 16-silatripyrrane with pentafluorobenzaldehyde under catalytic conditions followed by DDQ oxidation leads to 31,34-disilahexaphyrinoid – a four times reduced derivative of 31,34-disilahexaphyrin which contains two built-in silole units flanked by four tetrahedrally hybridized *meso* carbons. In the preferred folded macrocyclic conformation the silole rings remain perpendicular to each other. The steric hindrance of bulky substituents at silicon atoms and β-positions of siloles prevented aromatization. Only one meso diastereomer (5*S*, 15*S*, 20*R*, 30*R*) has been isolated and subsequently identified by 1D and 2D NMR techniques. The density functional theory (DFT) has been applied to model the molecular structure of 31,34-disilahexaphyrinoid consistent with constraints imposed by NOE experiments. The total energies calculated at the B3LYP/6-31G**//B3LYP/6-31G** level for four feasible meso diastereomers clearly demonstrated the energetic preference for the meso diastereomer (5*S*, 15*S*, 20*R*, 30*R*).

Introduction

Porphyrinoids can be derived from the regular porphyrin using contraction, isomerisation, expansion or/and core modification concepts.[1–10] In the group of expanded porphyrins, hexaphyrins are macrocycles containing six heterocyclic units connected by *meso*-carbon bridges. Apart from regular hexaphyrins (1.1.1.1.1.1)[11,12] some non-regular systems have been also synthesized bearing their own common names: amethyrin (1.0.0.1.0.0),[13] rosarin(1.0.1.0.1.0),[14] rubyrin(1.1.0.1.1.0)[15] or cyclo[6]pyrrole.[16]

Geometry of the hexaphyrin(1.1.1.1.1.1) **1**-NH (Chart 1) skeleton highly depends on *meso*-aryl substituents, both in the solution and in the solid state.[17–19] Organometallic complexes of **1**-NH (Hg(II), Ni(II), Pd(II), Pt(II), Ag(III), Au(III), Cu(III) and Rh(III)) reveal mono and bimetallic, homo and heteronuclear modes of coordination.[20–24] Owing to the conformational flexibility hexaphyrins are able to form two types of binuclear complexes of substantially different geometry: almost flat (*e.g.* bis-gold(III) complex with inverted pyrroles)[20] and gable structured (*e.g.* complex where bis-copper(II) ions are coordinated by six nitrogens without inversion of pyrroles).[25] Calix[3]dipyrrin,[26] which is the three times *meso* reduced form of regular hexaphyrin, simultaneously accommodates three metal ions such as Ni(II) or Cu(II) in a hexagonal M_3O_3 manner.[27] Coordination of phosphorus(V) favours a formation of [4*n*]π Möbius aromatic and [4*n* + 2]π Möbius antiaromatic systems.[28] On the other hand insertion of boron(III) induced a skeletal rearrangement of hexaphyrin(1.1.1.1.1.1) to bis-boron hexaphyrin(2.1.1.0.1.1).[29] Rearrangements of porphyrinoids, especially contractions, triggered by boron(III), phosphorus(V) and silicon(IV) ions were previously examined by our group.[30–32]

In construction of a nontrivial macrocyclic environment for organometallic chemistry, the heteroatom confusion (X-confusion) concept, originally exemplified by a porphyrin – 2-aza-21-carbaporphyrin couple,[33,34] has been applied.[2,6] The analogous approach namely interchanging of nitrogen atoms in hexaphyrin frame with a β-methine group transforms the regular hexaphyrin into the singly or doubly N-confused isomers.[35,36]



1-X, X = NH, O, S, Se, $SiMe_2$

Chart 1 Hexaphyrin and 31,34-diheterohexaphyrin.

Department of Chemistry, University of Wrocław, 14 F. Joliot-Curie St., Wrocław 50 383, Poland. E-mail: lechoslaw.latos-grazynski@chem.uni.wroc.pl

†Electronic supplementary information (ESI) available. See DOI: 10.1039/c2ob07134g

Interestingly, confusion also occurs during the metalation reaction of regular hexaphyrin with copper(II) chloride in pyridine.[37]

Diheterohexaphyrins **1**-X (Chart 1) are formally related to regular hexaphyrin by a replacement of NH fragments by heteroatoms (X), typically from 16 group of the periodic table. A common synthetic route leading to modified expanded porphyrin involves an acid catalysed condensation of 16-heterotripyrrane.[38,39] The MacDonald type synthesis of converted heterotripyrranes (furan-, thiophene-, or selenophene-analogues) with TSA and arylaldehyde in dichloromethane using chloranil as an oxidant leads to appropriate diheterohexaphyrins.[40,41] The conformations of these diheterohexaphyrins are critically dependent on the nature of *meso* substituents and the state of protonation. For instance di-*p*-benzihexaphyrin undergoes three-level topological interconversions (planar Hückel, Möbius and figure-eight Hückel) triggered by solvent, temperature and acid–base control.[42,43] Finally calix[2]metallocenyl[4]phyrin, where metallocene is (ferrocene or ruthenocene) replaces the pyrrole ring, belongs to carbahexaphyrin[44] demonstrating the structural analogy to both calix[6]phyrin[45] and the expanded heterohexaphyrins.[46]

Diheterosapphyrins were one of the first synthesized *meso*-aryl expanded heteroporphyrins, where two pyrrole rings are converted to furan, thiophene or selenophene respectively.[47,48] The recent report by Matano *et al.* on the synthesis of phosphadithiasapphyrin presented the replacement of nitrogen by phosphorous for the very first time in an expanded porphyrin environment.[49] This remarkable step in the field of core modified porphyrin provides a stimulus to search for expanded porphyrinoids which contain a built-in non-trivial heteroatom.

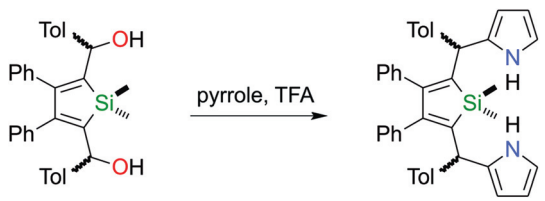
Herein, we report the synthesis and characterization of 31,34-disilahexaphyrinoid which contains two built-in silole units.

Results and discussion

Synthesis of 7,8-diphenyl-16,16-dimethyl-5,10-bis(*p*-tolyl)-16-silatripyrrane

A key step in the synthesis of 31,34-disilahexaphyrinoid is the construction of the 16-silatripyrrane which is a suitable synthon for introducing the silole ring into a hexaphyrin-like skeleton. The one-pot silole cyclization method has been applied to obtain 2,5-dilithiosilole,[50–52] which can be easily modified at the 2,5 positions leading to 1,1-dimethyl-3,4-diphenyl-2,5-bis(*p*-tolylhydroxymethyl)silole **2**. We have previously described this synthetic procedure.[53] Compound **2** reacts with an excess of pyrrole in the presence of trifluoroacetic acid as shown in Scheme 1.

Acid neutralisation and removing of pyrrole afforded 7,8-diphenyl-16,16-dimethyl-5,10-bis(*p*-tolyl)-16-silatripyrrane **3** as a mixture of diastereomers (**3**-*RR*, **3**-*SS* and meso form **3**-*SR*), which could not be separated by chromatography. The diastereomers have been readily identified by NMR spectroscopy because of the apparent difference in the molecular symmetry (**3**-*RR*, C_2; **3**-*SR*, C_s).



2 **3**

Scheme 1 Synthesis of 16-silatripyrrane.

Accordingly a single silicon bound methyl resonance (−0.40 ppm) has been detected for **3**-*RR* (*SS*) but two (0.00 and −0.85 ppm) were detected for **3**-*SR*. The $^{1}H–^{29}Si$ scalar coupling detected by HMBC experiment confirmed the assignment (see ESI, Fig. S1†). The impressive chemical shift difference reflects the mutual orientation of the MeSi, *p*-tolyl and 2-pyrrolyl groups as shown in Fig. 1. In the extreme case of **3**-*SR* the upfield shifted resonance corresponds to the methyl located in the shielding zone of two adjacent aryls where its counterpart positioned on the other side of the silole ring stays away from this influence. Consistently, the **3**-*RR* (*SS*) spectrum reveals the shielding due to a single *meso*-aryl yielding the intermediary chemical shift. An analogous situation was observed in the case of 1,1-dimethyl-3,4-diphenyl-2,5-bis(*p*-tolylhydroxymethyl)silole **2**.[53]

Synthesis and characterization of 31,34-disilahexaphyrinoid

The synthetic route leading to 31,34-disilahexaphyrinoid is summarized in Scheme 2.

The synthesis involves the one-pot reaction of 16-silatripyrrane **3** with pentafluorobenzaldehyde (1 : 1 molar ratio), carried out in dichloromethane in low temperature, catalysed by methanesulfonic acid, which is followed by oxidation with DDQ. The procedure follows the slightly modified methodology previously utilized for the synthesis of *meso*-aryl expanded porphyrins[54] and the intended product was aromatic 31,34-disilahexaphyrin (**1**-$SiMe_2$). Instead of the expected 31,34-disilahexaphyrin, a non-aromatic macrocyclic product was isolated with 1% yield after chromatographic workup: 31,34-disilahexaphyrinoid **4a**.

The preference for reduced 31,34-disilahexaphyrin formation is consistent with the reported chemistry of hexaphyrinogens.[55] Hexaphyrinogens are reduced hexaphyrin derivatives which

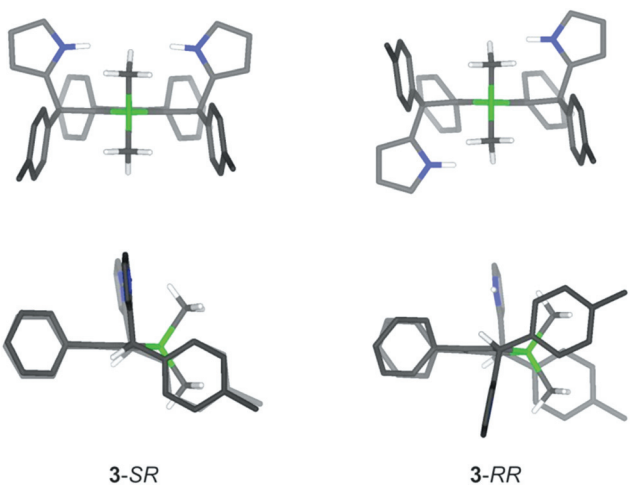
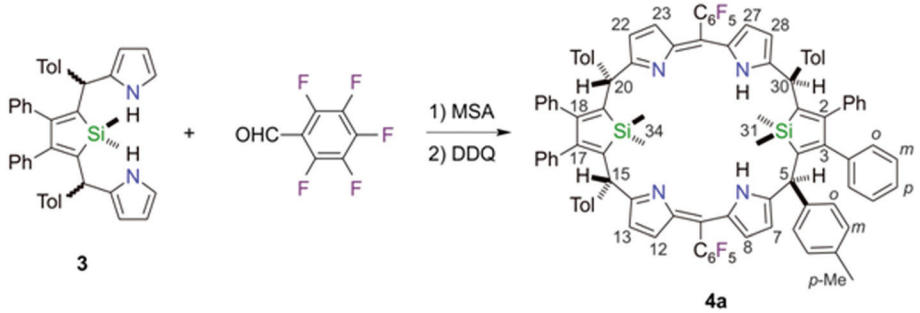


Fig. 1 Drawing of the **3**-*SR* and **3**-*RR* structures (top: front projections, bottom: side projections) as obtained from the molecular mechanics calculations (MM+).



Scheme 2 Synthesis of disilahexaphyrinoid **4a**.

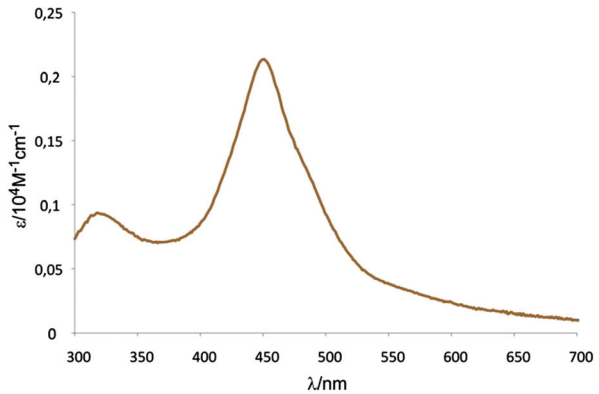


Fig. 2 The electronic spectrum of **4a** in dichloromethane.

contain six pyrroles bridged by six sp^3 *meso*-carbon atoms. In most cases they are treated just as unstable intermediates and readily oxidized to the targeted porphyrinoids without isolation. However, if an appropriate pyrrole with sufficiently bulky β-substituents *e.g.* mesityl, 2,6-$Cl_2C_6H_3$ or C_6F_5 groups is use for synthesis, hexaphyrinogens can be easily isolated. They are stable and resistant to oxidation with DDQ either under reflux in toluene or in the presence of an acid such as TSA and $BF_3{\cdot}OEt_2$.[56]

The UV-vis specturm of **4a** is shown in Fig. 2. 31,34-Disilahexaphyrinoid shows broad absorption peaks below 500 nm and less intensive above 300 nm. There are no bands in the regions typically assigned to the Soret-like and Q bands of aromatic hexaphyrin[57] or diheterohexaphyrin.[40] In fact the electronic spectrum is very similar to non-aromatic calixphyrin[58] which has a smaller chromophore but contains the same sp^3 *meso*-bridges and conjugated system of two pyrrole subunits.

The steric barrier which occurs in 31,34-disilahexaphyrinoid is primarily imposed by the substitution of 31,34-silicon atoms with methyls (*vide infra*). Two $SiMe_2$ groups cannot be simultaneously placed towards the hexaphyrin centre because the packing is too tight. Both of the silole units must remain perpendicular to each other. Furthermore, the steric hindrance also created by phenyl rings located at the β-silole positions is the reason for the parallel position of the conjugated dipyrrolic parts with the plane consisting of two silicon atoms and four MeSi carbon atoms getting in the way of planarization and consequently aromatization.

NMR investigations

The identities of **4a** have been confirmed by high-resolution mass spectrometry and NMR spectroscopy. Thus the assignments of the 31,34-disilahexaphyrinoid resonances, which are given above selected groups of peaks (Fig. 3) have been made on the basis of relative intensities and detailed two-dimensional NMR studies ($^1H,^1H$ (COSY, NOESY), $^{19}F,^{19}F$ (COSY), $^1H,^{13}C$ (HMQC, HMBC) and $^1H,^{29}Si$ (HMBC)) carried out at 240 K in dichloromethane-d_2.

The ^1H NMR spectrum of **4a** (240 K) exhibits two AB patterns and four methyl signals of two non-identical siloles. Two different sets of *meso*-*p*-tolyl ring resonances have been detected. This multiplets have been readily correlated *via* COSY and NOESY with particular methyl resonances. The fast rotation has been detected for 5,30- and 15,20-*p*-tolyls which are adjacent to the silole moieties as documented by a single doublet for the ortho and meta positions in each case. Actually the phenyl rings attached at β-silole positions revealed the different dynamic behavior. Namely the fast rotation has been detected for all β-phenyl resonances in the whole temperature range. Such sets of resonances reveals the specific symmetry of disilahexaphyrinoid molecule. The structural formula of **4a** shown in Scheme 2 demonstrated merely the projection facilitating a presentation. To account for the ^1H NMR characteristic of **4a** a non-planar structural scaffolds have been considered (Fig. 4 and 5).

In principle the different mutual orientations of dipyrromethene units of **4a** could generate three major macrocyclic conformers: two boats and one chair (Fig. 4). Dihedral angles between dipyrromethene planes are markedly different as determined from MM+ models (Fig. 4): 25–33° (31–35° for DFT, boat), 157–162° (chair) and 288–303° (boat-I conformers). Similar conformations have been adopted by calix[6]phyrin,[27] calix[2]metallocenyl[4]phyrin,[44] tetraazuliporphyrin tetracation,[59] tetraphenylmetacyclophanes[60,61] or squaraine rotaxanes.[62,63] In fact we have readily demonstrated that the NOE determined fundamental connectivity pattern excludes chair and boat-I geometries.

Consequently, DFT studies have been used to visualize the suggested structures of 31,34-disilahexaphyrinoid and to assess the degree of the macrocycle distortion (Fig. 5). The geometry of **4a** was optimized at the B3LYP/6-31G** level of theory. The optimized structure of **4a** highlights the fact that the silole rings are almost mutually perpendicular. Consequently the internal methyl group (31-*i*-MeSi) is wedged between methyl substituents of the opposite silole.

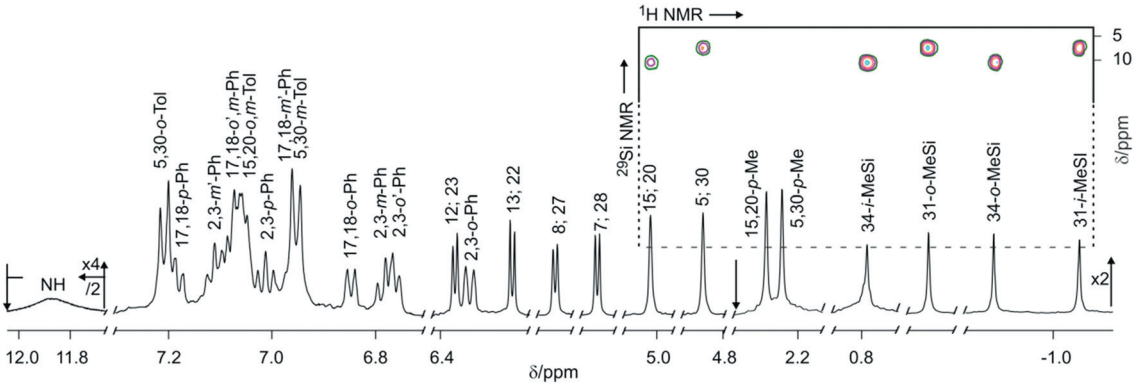


Fig. 3 ^{1}H NMR spectrum of **4a** (dichloromethane-d_2, 240 K). Inset: ^{1}H–^{29}Si NMR correlations.

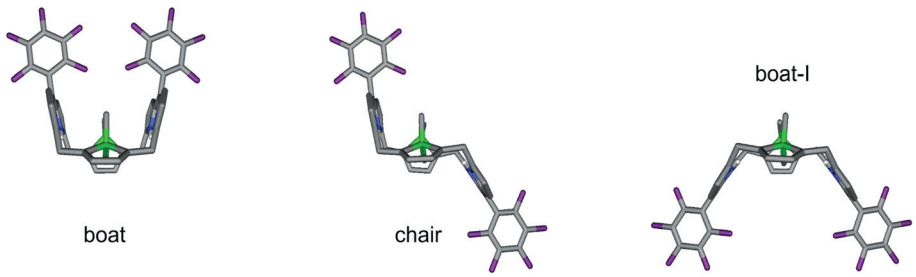


Fig. 4 The conformers of 31,34-disilahexaphyrinoid (*p*-tolyl, β-phenyl and hydrogen substituents omitted for clarity; geometries obtained from the molecular mechanics calculations (MM+)).

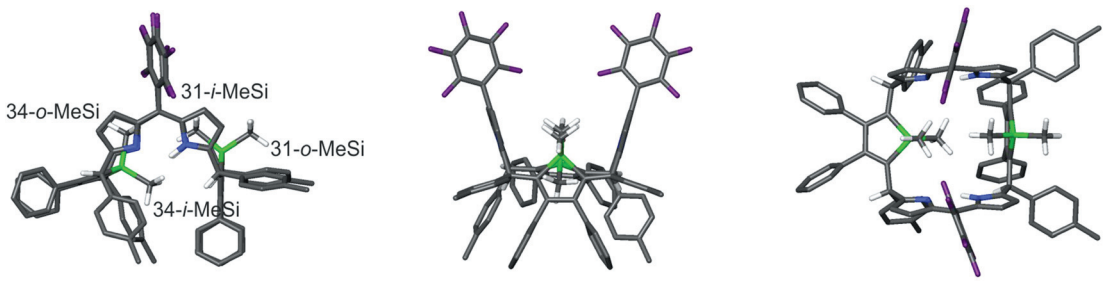


Fig. 5 The DFT optimized structure of **4a** (left: side views, middle: front views, right: perspective views with aromatic and *p*-Me hydrogens removed for clarity).

Additionally, one might consider a variety of different mutual spatial orientations of methyl siloles, but, consistent with the considered geometry, only one methyl group 31-*i*-MeSi is close enough to produce the detectable dipolar 31-*i*-MeSi ↔ 34-*o*-MeSi (2.64 Å) and 31-*i*-MeSi ↔ 34-*i*-MeSi (2.66 Å) couplings (the shortest H–H distances from DFT optimized geometry are given in parentheses). The distances to hydrogen atoms of 31-*o*-MeSi (>5.89 Å) are too large to allow any efficient dipolar coupling to 34-MeSi groups. These structural features have been reflected in the NOESY map by two well defined cross peaks (see ESI, Fig. S2†). The straightforward assignment of 31,34-MeSi and H(5,30 and 15,20) resonances *via* ^{1}H–^{29}Si scalar coupling (Fig. 3, inset) provided the initial step for the ^{1}H NMR analysis. Significantly the complementary HMQC experiment allowed the unambiguous identification of the unique C(5,30 and 15,20) resonances revealing their tetrahedral geometry consistent with the 46.7 and 47.9 ppm chemical shifts respectively. Subsequently the HMBC studies revealed the cross-correlation which involved *o*-H(5-Tol) ↔ C(5,30 and 15,20) and H(5,30 and 15,20) ↔ *o*-C(5,30-Tol and 15,20-Tol) couples. Once assigned this particular set of resonances has been used as a starting point for NOE studies.

The fundamental relays of NOE connectivities are shown in Fig. 6. The structural constraints determined by NOE have been built in the DFT optimized structure.

31,34-Disilahexaphyrinoid contains four sp^3 *meso*-carbon stereocentres which could potentially generate 16 stereoisomers. A molecule with an even number of chiral carbon atoms and a plane of symmetry can yield only 4 pairs of enantiomers and two meso forms. Eventually we have realized that the 31,34-disilahexaphyrinoid macrocycle is folded, acquiring the boat-like conformation (Fig. 4). The imposed lowering of symmetry increases the number of hypothetical stereoisomers twofold. Notably, the reduced number of macrocyclic frame signals and the

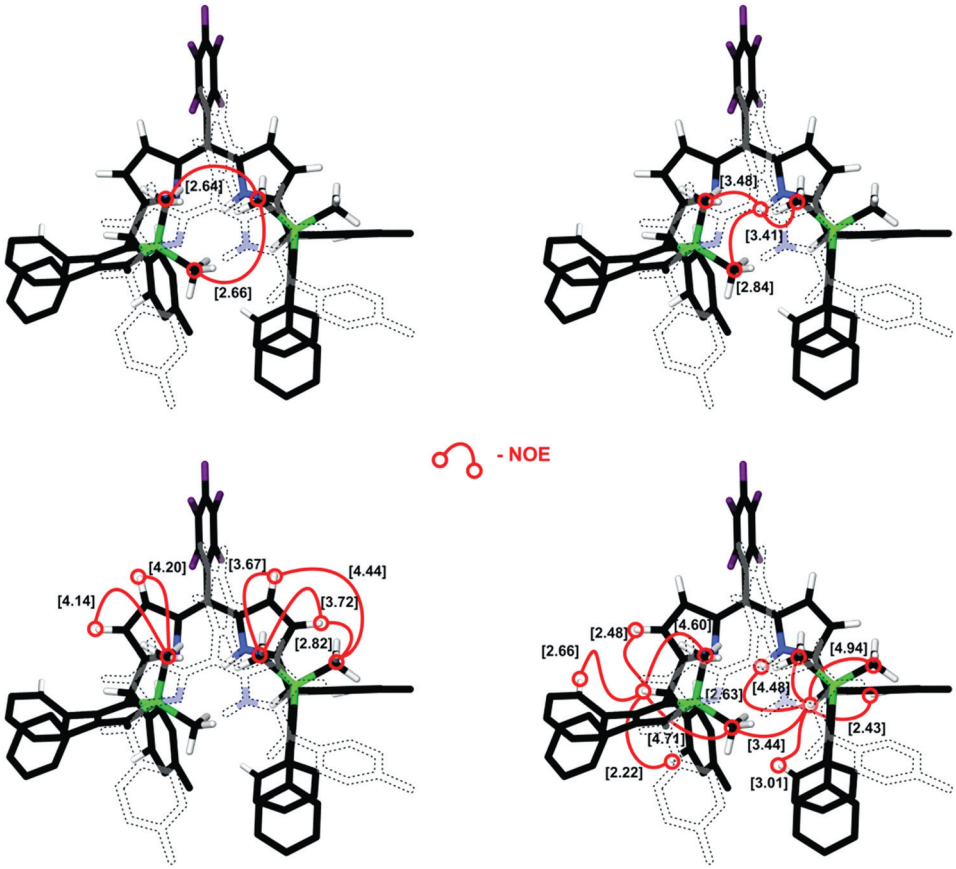


Fig. 6 The established NOE connectivities for **4a**. Only the analytically useful hydrogens are shown. For clarity, half of molecule has been plotted translucently. The spatial proximities (in Å) are in parentheses.

identification of four MeSi signals in ^{1}H NMR spectrum of **4a** have readily indicated the plane symmetry passing through two silicon atoms and four MeSi carbon atoms, preserving, however, the concurrent differentiation of two silole units. Consequently only four meso diastereomers of **4** have been further considered (Fig. 8). These meso forms share common structural motif of boat-like macrocyclic conformation where two conjugated dipyrrolic moieties take shape of a stem and a stern, and the C_4 plane (defined by the four *meso* carbon atoms) constructs a bottom.

Considering in detail the spatial proximity of the H(15,20) ↔ H(13,22), HN ↔ H(5,30) and H(31-*i*-MeSi) ↔ H(5,30) as found at the DFT optimized structure of four boat-like diastereomers, only the geometry of **4a** satisfactory reproduces quantitatively the constrains defined by NOE experiments. The relative intensities of NOE cross peaks follow the expected r^{-6} relation in the series H(15,20) ↔ H(13,22) (2.48 Å) > HN ↔ H(5,30) (2.63 Å) > H(34-*i*-MeSi) ↔ H(5,30) (3.44 Å) > H(31-*i*-MeSi) ↔ H(5,30) (4.48 Å) firmly confirming the structural analysis. The diagnostic spatial proximities determined for DFT optimized structures **4b**, **4c** and **4d** of 31,34-disilahexaphyrinoid meso diastereomers disclose the significant mismatch with the corresponding NOE data.

The five ^{19}F resonances: −140 (10,25-*o*-C_6F_5); −141 (10,25-*o*′-C_6F_5); −154 (10,25-*p*-C_6F_5); −162 (10,25-*m*′-C_6F_5) and −163 ppm (10,25-*m*-C_6F_5) serve as a fingerprint of the pentafluorophenyl moiety (see ESI, Fig. S3†). The detected differentiation of ortho and meta resonances seen for 10,25-pentafluorophenyl suggests that their rotation with respect to the

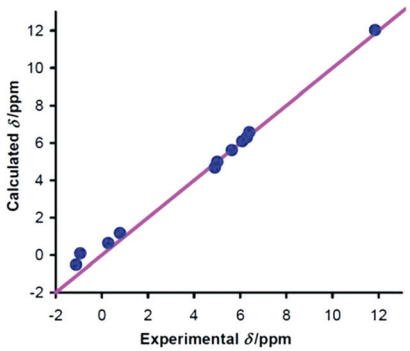


Fig. 7 Linear correlation between calculated and experimental values of chemical shifts for **4a**.

C_{meso}–C_{ipso} bond is slow below 240 K and obviously the macrocycle is not planar. Remarkably, the ^{19}F chemical shifts of these fluorine atoms match those of typical *meso*-pentafluorophenyl porphodimethene (−138, −153 and −162 ppm).[64] Indirectly, the presence of fluorine atoms is suggested by a significant broadening of corresponding carbon signals (see ESI, Fig. S4†).

^{1}H NMR chemical shifts calculated for **4a** using the GIAO B3LYP/6-31G** method are given in ESI, Table S1.† There is a satisfactory qualitative agreement for the available set of theoretical and experimental data readily demonstrated by linear correlations between the calculated and experimental chemical shifts as shown for **4a** (Fig. 7).

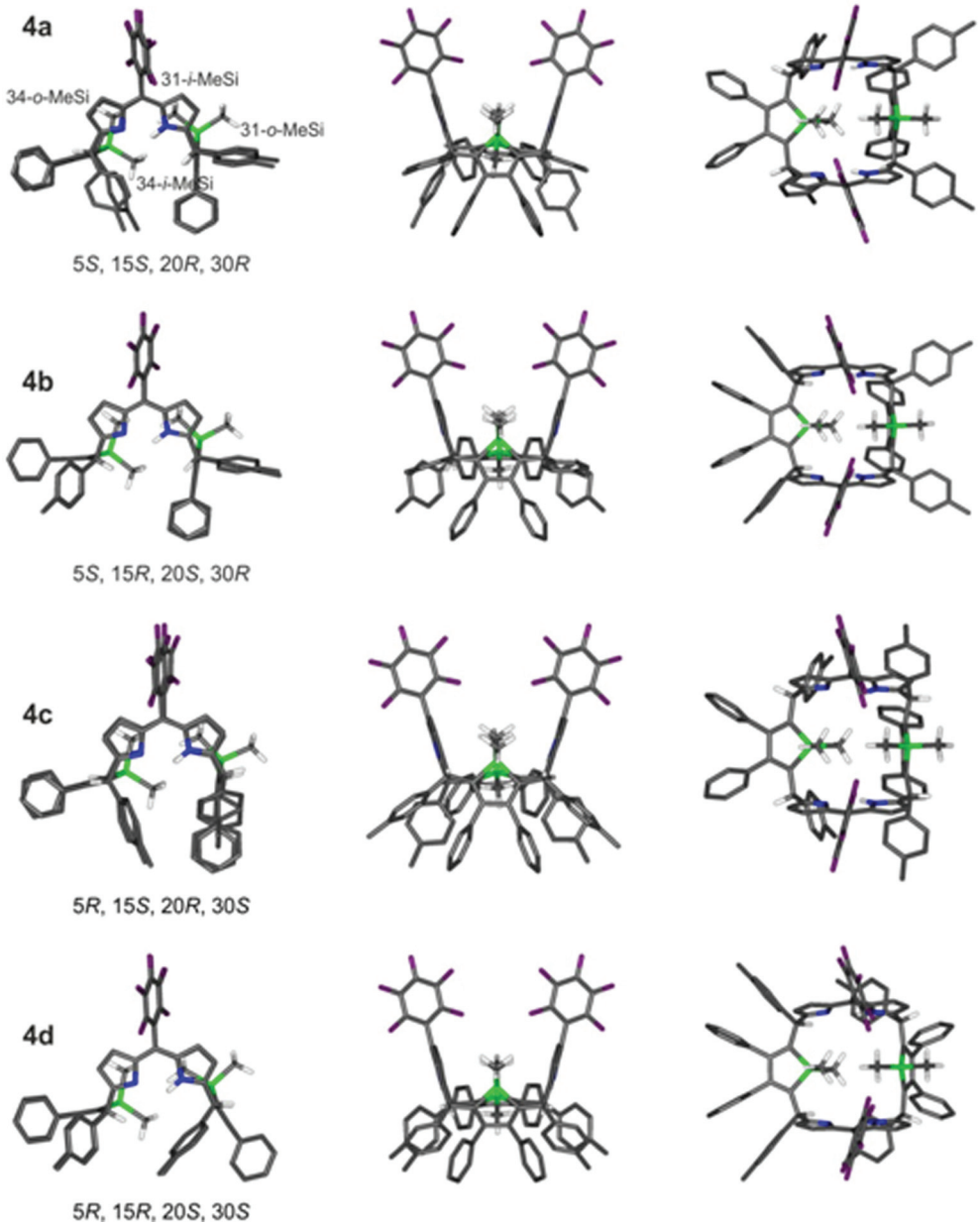


Fig. 8 The DFT optimized structures of **4a**, **4b**, **4c**, **4d** (left: side views, middle: front views, right: perspective views with aromatic and *p*-Me hydrogens removed for clarity). Right views preserve the orientation of structures and numbering of sp^3 *meso*-bridges in Chart 2.

DFT calculations

The condensation reaction leads to only one of four possible diastereomers of 31,34-disilahexaphyrinoid.

1A reasonable hypothesis is that going to the smallest steric hindrance is the driving force leading to this preference. It seems that the weakest interaction between *meso* and β-silole aryls is for the diastereomer **4a**. In order to address this problem we have carried out DFT calculations. Density functional theory (DFT) has been successfully used to describe the properties of porphyrins and related systems, providing information on their energetics, conformational behavior, tautomerism, and aromaticity.[65] In particular, we were able to reproduce the experimental values of proton chemical shifts, conformations of the macrocycle ring and also the extent of π-conjugation for di-*p*-benzihexaphyrin.[43]

The optimized structures of **4a**, **4b**, **4c** and **4d** are shown in Fig. 8. The calculated total energies, using the B3LYP/6-31G**//B3LYP/6-31G** approach (Table 1), readily demonstrated that **4a** isomer of 31,34-disilahexaphyrinoid is the most stable. The relative energies of diastereomers increase in a series: **4a** < **4b** < **4c** < **4d**.

Conclusion

The acid-catalyzed condensation of 16-silatripyrrane with pentafluorobenzaldehyde yields the first 31,34-disilahexaphyrinoid. The macrocycle is related to reduced form derived from the [26]hexaphyrin(1.1.1.1.1.1) frame and contains two silole rings replacing the pyrroles. The DFT optimised geometry reflected all

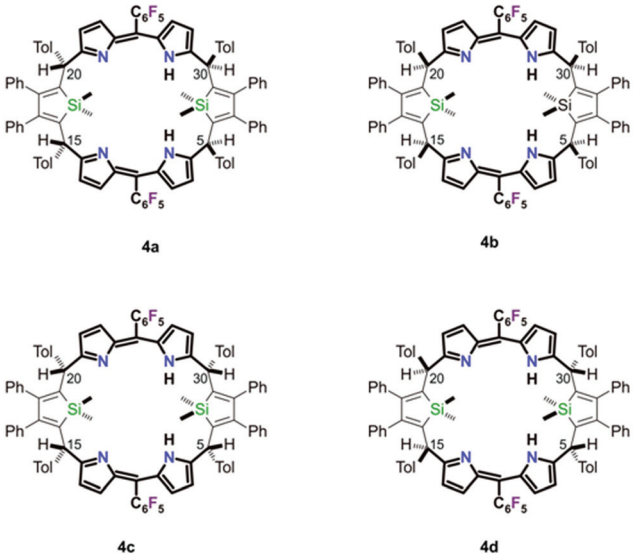


Chart 2 Four diastereomers of non-planar 31,34-disilahexaphyrinoid (see Fig. 8).

Table 1 The calculated total energies (B3LYP/6-31G**//B3LYP/6-31G**)

Diastereomers of 31,34-disilahexaphyrinoid	Energies (kcal mol^{-1}) *vs.* **4a**
4a	0.00
4b	9.41
4c	11.85
4d	17.59

structural constrains derived from 1D and 2D NMR experiments. The condensation reaction affords only one isolable product of four possible meso diastereomers of 31,34-disilahexaphyrinoid point for the smallest steric hindrance is the driving force of this preference.

Experimental section

Instrumentation

NMR spectra were recorded on a Bruker Avance 500 MHz spectrometer. The absorption spectrum was recorded on a Varian Cary 50 Bio spectrometer. The mass spectrum was recorded on a Bruker micrOTOF-Q spectrometer using the electrospray technique.

Computational chemistry

Density functional theory calculations were performed using Gaussian 03.[66] Geometry optimizations were carried out within unconstrained C_1 symmetry, with starting coordinates preoptimized using semiempirical methods. Becke's three-parameter exchange functional[67] with the gradient-corrected correlation formula of Lee, Yang, and Parr (B3LYP)[68] was used with the 6-31G** basis set. The chemical shift values were subsequently calculated relative to tetramethylsilane (TMS, absolute shielding: 31.75 ppm).

Materials

Dichloromethane and pyrrole were purified by standard procedures. Pentafluorobenzaldehyde, MSA and $BF_3{\cdot}OEt_2$ (Aldrich) were used as received.

1,1-Dimethyl-3,4-diphenyl-2,5-bis(*p*-tolylhydroxymethyl)-silole (2)

The synthetic procedure was previously described.[53]

7,8-Diphenyl-16,16-dimethyl-5,10-bis(*p*-tolyl)-16-silatripyrrane (3)

3,4-Diphenyl-1,1-dimethyl-2,5-bis(*p*-tolylhydroxymethyl)-silole **2** (0.5 g, 1.0 mmol) was dissolved in pyrrole (2.8 mL, 40.0 mmol) and the solution was purged with nitrogen for 20 min. Subsequently, $BF_3{\cdot}OEt_2$ (0.01 mL, 0.13 mmol) was added. Reaction was protected from light and stirred for 30 min in room temperature. Than dichloromethane (50 mL) was added and mixture was neutralized with 40% water solution of NaOH. Organic layer was separated and washed with water (2 × 25 mL) before dried with Na_2SO_4. Excess of pyrrole was removed under reduced pressure. 16-Silatripyrrane was obtained as a yellow dark oil. Yield (**3**) (mixture of diastereomers): 0.54 g (90%). ^{1}H NMR (500 MHz, CD_2Cl_2, 298 K) δ 7.76 (s, 4H, 15,17-NH); 7.14–6.99 (36H, 7,8-*o*,*m*,*p*-Ph, 5,10-*o*,*m*-Tol); 6.65, 6.62 (2m, 4H, 1,14); 6.15, 6.10 (2m, 4H, 2,13); 6.00, 5.92 (2m, 4H, 3,12); 4.96 (2s, 4H, 5,10); 2.35, 2.32 (2s, 12H, 5,10-*p*-Me); 0.00, −0.40, −0.85 (3s, 12H, MeSi). ^{29}Si NMR (99 MHz, CD_2Cl_2, 298 K) δ 6.45 (*SR*); 6.38 (*RR*(*SS*)).

31,34-Disilahexaphyrinoid (4a)

A 500 mL round-bottomed flask equipped with a stirring bar, topped with a tube filled with $CaCl_2$ and a nitrogen inlet, was charged with freshly distilled dichloromethane (400 mL).

16-Silatripyrrane **3** (0.5 g, 0.83 mmol), and pentafluorobenzaldehyde (0.103 mL, 0.83 mmol) were added and the solution was purged with nitrogen for 20 min. The flask was placed in ice-water bath and protected from light. Subsequently, MSA (0.011 mL, 0.2 mmol) was added. After stirring at 0 °C for 2 h, a portion of DDQ (0.681 g, 3 mmol) was added and stirring was continued for a further 5 min. The solvent was removed by means of a vacuum rotary evaporator. The dark residue was dissolved in dichloromethane and subjected to preliminary chromatographic separation on a short basic alumina (grade II) column. The fast-moving fraction was collected and separated again by chromatography on a basic alumina (grade II) column using a mixture of dichloromethane–hexane (ratio 5 : 5 v/v) as the eluent. Compound **4a** eluted first as a brown-yellow. The crude product was further purified by column chromatography on a basic alumina (grade II, dichloromethane–hexane 4 : 6 v/v). Yield of **4a**: 6.6 mg (1%). ^{1}H MR (500 MHz, CD_2Cl_2, 240 K) δ 11.87 (s, 2H, NH); 7.18 (d, 4H, 5,30-*o*-Tol); 7.16 (d, 2H, 17,18-*p*-Ph); 7.08 (m, 2H, 5,3-*m*′-Ph); 7.05 (m, 4H, 17,18-*o*′-Ph, 17,18-*m*-Ph); 7.03 (2d, 8H, 15,20-*o*-Tol, 15,20-*m*-Tol); 6.99 (t, 2H, 2,3-*p*-Ph); 6.94 (m, 2H, 17,18-*m*′-Ph); 6.92 (d, 4H, 5,30-*m*-Tol); 6.81 (d, 2H, 17,18-*o*-Ph); 6.76 (m, 2H, 2,3-*m*-Ph); 6.73 (d, 2H, 2,3-*o*′-Ph); 6.37 (d, 2H, 12, 23); 6.34 (d, 2H, 2,3-*o*-Ph); 6.26 (d, 2H, 13, 22); 6.10 (d, 2H, 8, 27); 5.67 (d, 2H, 7, 28); 5.01 (s, 2H, 15, 20); 4.84 (s, 2H, 5, 30); 2.26 (s, 6H, 15,20-*p*-Me); 2.23 (s, 6H, 5,30-*p*-Me); 0.79 (s, 3H, 34-*i*-MeSi); 0.33 (s, 3H, 31-*o*-MeSi); −0.88 (s, 3H, 34-*o*-MeSi); −1.05 (s, 3H, 31-*i*-MeSi). ^{13}C NMR (126 MHz, CD_2Cl_2, 240 K): δ 166.6 (14, 21); 159.5 (6, 29); 156.4 (17, 18); 155.4 (2, 3); 145.0 (10,25-C_6F_5, $^{1}J_{(F,C)} \approx$ 250 Hz, $^{2}J_{(F,C)} \approx$ 20 Hz); 144.5 (10,25-C_6F_5, $^{1}J_{(F,C)} \approx$ 250 Hz, $^{2}J_{(F,C)} \approx$ 20 Hz); 142.3 (11, 24); 140.5 (1, 4); 139.8 (16, 19); 139.6 (C_1-15,20-Tol); 139.4 (10,25-C_6F_5, $^{1}J_{(F,C)} \approx$ 250 Hz); 138.7 (C_1-17,18-Ph); 138.4 (C_1-5,30-Tol); 138.3 (C_1-2,3-Ph); 137.4(2 × 10,25-C_6F_5, $^{1}J_{(F,C)} \approx$ 250 Hz); 136.5 (9, 26); 136.1 (C_4-15,20-Tol); 136.0 (C_4-5,30-Tol); 129.6 (12, 23); 129.2 (2,3-*o*-Ph); 129.1 (5,30-*m*-Tol); 129.0 (17,18-*o*-Ph); 128.9 (15,20-*o*-Tol, 15,20-*m*-Tol); 128.7 (2,3-*o*′-Ph); 128.6 (17,18-*m*′-Ph); 128.3 (5,30-*o*-Tol); 127.8 (17,18-*p*-Ph); 127.8 (2,3-*m*-Ph); 127.6 (17,18-*o*′-Ph); 127.0 (2,3-*m*-Ph); 126.6 (17,18-*m*-Ph); 126.1 (2,3-*p*-Ph); 125.3 (8, 27); 123.1 (13, 22); 121.5 (10, 25); 116.5 (7, 28); 111.3 (C_1-10,25-C_6F_5); 47.9 (15, 20); 46.7 (5, 30); 21.2 (5,30-*p*-Me); 21.0 (15,20-*p*-Me); −0.3 (34-*i*-MeSi); −2.4 (31-*o*-MeSi); −7.6 (34-*o*-MeSi); −8.1 (31-*i*-MeSi). ^{19}F NMR (470 MHz, CD_2Cl_2, 240 K) δ −140 (10,25-*o*-C_6F_5); −141 (10,25-*o*′-C_6F_5); −154 (10,25-*p*-C_6F_5); −162 (10,25-*m*′-C_6F_5); −163 (10,25-*m*-C_6F_5). ^{29}Si NMR (99 MHz, CD_2Cl_2, 298 K): δ 6.35 (34-Si); 5.39 (31-Si). UV-vis (CH_2Cl_2, 298 K): λ_{max} = 318, 450 nm. HRMS (ESI): *m*/*z* calcd for $C_{98}H_{75}N_4F_{10}Si^+$: 1553.5365, found: 1553.5275 $[M + H]^+$.

Acknowledgements

Financial support from the Ministry of Science and Higher Education (Grant N N204 021939) is kindly acknowledged. Quantum chemical calculations have been carried out at the Poznań Supercomputer Center (Poznań) and Wrocław Supercomputer Center (Wrocław).

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