DOI: 10.1002/chem.200901187

Tetraaryl Tetradecahydroporphyrazins: Novel Porphyrin Derivatives Featuring a Cyclic Benzene-Ring Tetramer

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Abstract: Treatment of tetramethylsuccinonitrile **1** with aryl lithium compounds and subsequent quenching with chlorotrimethylsilane yields 5-aryl-3,3,4,4-tetramethyl-*N*-(trimethylsilyl)-3,4-dihydropyrrol-2-imines **2a–c** in 49–71% yield. Attempts to crystallise **2a–c** in the presence of wet air yielded the tetraaryl tetradecahydroporphyrazins **3a–c** in yields of 4–84% as single diastereomers. X-ray diffraction studies of **3b** and **c** showed that only the isomer with four aryl substituents pointing in the same direction was formed. The resulting four-bladed pinwheel-like structures were characterised by four intramolecular aromatic interactions, in which each phenyl ring points with its edge towards the centre of a neighbouring phenyl moiety, resembling the arrangement of benzene molecules in T-shaped dimers. Temperature-dependent NMR spectra give insight into the dynamic properties of the aryl substituents. Quantum chemical calculations that included dispersion corrections indicated the importance of aryl–aryl interactions for the diastereoselectivity of the reaction and for the structural properties of the single isomers observed.

Keywords: aromaticity · density functional calculations · imines · porphyrins · tetramerisation

Introduction

Hydroporphyrins, partly saturated derivatives of the macrocyclic tetrapyrrol derived porphins, are interesting for a variety of technical and analytical applications. They are conformationally more flexible than their aromatic counterparts, which affects not only their electronic properties but also their ability to form coordination compounds with metals and other guest ions.[1] This makes them applicable for anion binding and recognition, for example.[2] However, the synthesis of hydroporphyrin derivatives is usually not trivial, comprising either the (often not very selective) modification of porphyrins by reduction,[3] addition of substituents,[1a] or by a multistep total syntheses.[4]

Inter- and intramolecular non-bonding aromatic interactions play an important role in various fields of chemistry and materials science. This relatively weak form of interaction has a significant influence on the three-dimensional structure of both small molecules and macromolecules of biological and non-biological origin, and of supramolecular systems. Furthermore, they affect the packing structure in crystals of aromatic compounds.[5a] As a result, they have been the focus of a multitude of theoretical[5] and experimental[6] studies. Although examples of two interacting aromatic groups in larger systems are experimentally abundant,[6a–b,7] data on higher clusters consisting of more such moieties are far more rare. Only recently, one of those rare results was published by H. Furuta and co-workers. They reported a supramolecular system, the formation of which was modulated by the interaction of three phenyl substituents.[8] Examples of structures with four mutually interacting aryl groups are, to the best of our knowledge, unknown to date.

Herein, we report a new facile synthesis for hydroporphyrin derivatives of an unprecedented degree of saturation and substitution, containing, in addition, a four-bladed pinwheel-shaped arrangement[9] of interacting phenyl moieties as one of their most striking structural features.

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.200901187.

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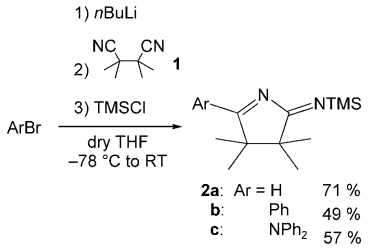
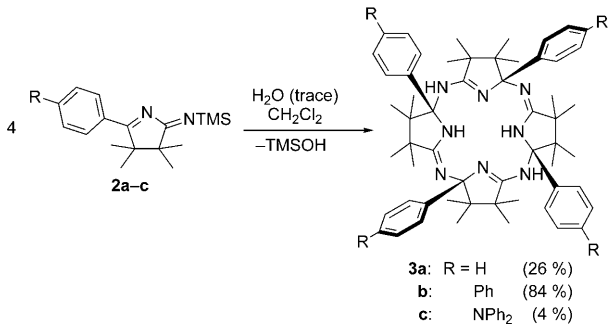
Results and Discussion

Part of our ongoing research on oligonitriles[10] was the synthesis of 5-aryl-3,3,4,4-tetramethyl-*N*-(trimethylsilyl)-3,4-dihydropyrrol-2-imines **2**[11] by treating an aryl lithium species with tetramethylsuccinonitrile (**1**) and subsequently quenching the reaction with chlorotrimethylsilane (Scheme 1).



Scheme 1. Synthesis of 5-aryl-3,3,4,4-tetramethyl-*N*-(trimethylsilyl)-3,4-dihydropyrrol-2-imines **2**.

The resulting compounds were solids in most cases, depending on the aryl substituent, but not always crystalline. The question arose of whether it is possible to obtain suitable crystals for an X-ray analysis. To achieve this, a sample of compound **2c** was dissolved in dichloromethane. The solution was subsequently slowly concentrated by gradual evaporation of the solvent, and after a few days, cubic, colourless crystals were acquired. However, these crystals unexpectedly consisted of tetraaryl tetradecahydroporphyrazin **3c** as a result of a tetramerisation of the starting material, clearly after hydrolytic cleavage of the trimethylsilyl moiety (Scheme 2). We could confirm that this method is reproducible and applicable to other derivatives, so that we were able to obtain also compounds **3a** and **b**, which differ in the size and nature of the aryl substituents.



Scheme 2. Synthesis of tetraaryl tetradecahydroporphyrazins **3**.

In all three cases, only a single isomer has been isolated in racemic form and unambiguously identified. For derivative **3c**, an attempt was made to isolate other substances from the oily residue of the synthesis. Apart from unchanged starting material, several other compounds were found, although only in very small amounts of less than 10 wt%. From NMR spectroscopy and mass spectrometry, it appears that these by-products are also oligo- or even polymers of the dihydropyrrol-2-imine, but their exact composition and structure could not be elucidated.

It was possible to afford suitable crystals for X-ray crystal-structure analysis from compounds **3b** and **c**.[12] Both compounds have many principal structural characteristics in common. The most striking feature is the arrangement of the four aryl substituents that are all pointing in the same direction from the central heterocyclic system, regardless of the partly significant structural bulk. Furthermore, the phenyl groups proximal to the tetradecahydroporphyrazin ring itself form a four-bladed pinwheel-like structure, in which each phenyl ring points with its edge towards the centre of a neighbouring phenyl moiety (Figure 1b). This bears resemblance to the arrangement of benzene molecules in T-shaped dimers. The observation of such an arrangement of four benzene units has never been reported, and is distinctly different from the packing structure in crystalline benzene II at high pressure.[13]

The crystal structure of tetradecahydroporphyrazin **3b** contains two independent molecules A and B in the asymmetric unit, each showing opposite stereodescriptors (Figure 1a). The centre to centre distances of the proximal phenyl groups (inner phenyl groups of the biphenyl substituent) vary from 4.885 to 5.368 Å, averaging at 5.122 Å. The planes of those phenyl groups are almost perpendicular to each other, with angles averaging at 85.23° (Figure 1b). The distal phenyl moieties (outer phenyl groups of the biphenyl substituent) on the other hand are much farther apart, with distances ranging from 6.0 to 7.2 Å (Figure 1c). Taking the apparently irregular arrangement of the planes of those rings relative to each other additionally into account, it appears that no substantial direct interaction between these distal phenyl groups exists.

A dichloromethane molecule is enclosed in a cavity formed by the distal substituents. In the case of host molecule A, it is significantly shifted away from the central axis and is almost situated between two of the phenyl moieties (Figure 1d and e).

The crystal structure of **3c** is highly symmetric, so that the proximal phenyl groups form a perfect square with distances of 5.03 Å measured from ring centre to ring centre and angles of 88.6° between the planes of the rings (Figure 2b).

The distances between the diphenylamino nitrogen atoms are 5.99 Å (Figure 2c), signifying that the large pendant groups at the tetradecahydroporphyrazins are slanted outwards relative to the central molecule axis, giving the molecule are slightly tapered appearance. Of the two phenyl rings of the diphenylamine subunit, the phenyl rings I (Figure 2c) are again arranged in a pinwheel-like fashion. With distances of 5.90 Å, they are much farther apart than the proximal phenyl groups. The planes of the phenyl rings I form an angle of 87.6°. The phenyl rings I and II of neighbouring diphenylamino groups are in close vicinity to each other with distances of 4.98 Å in a similar interaction range as the proximal phenyl groups. The angle between the ring

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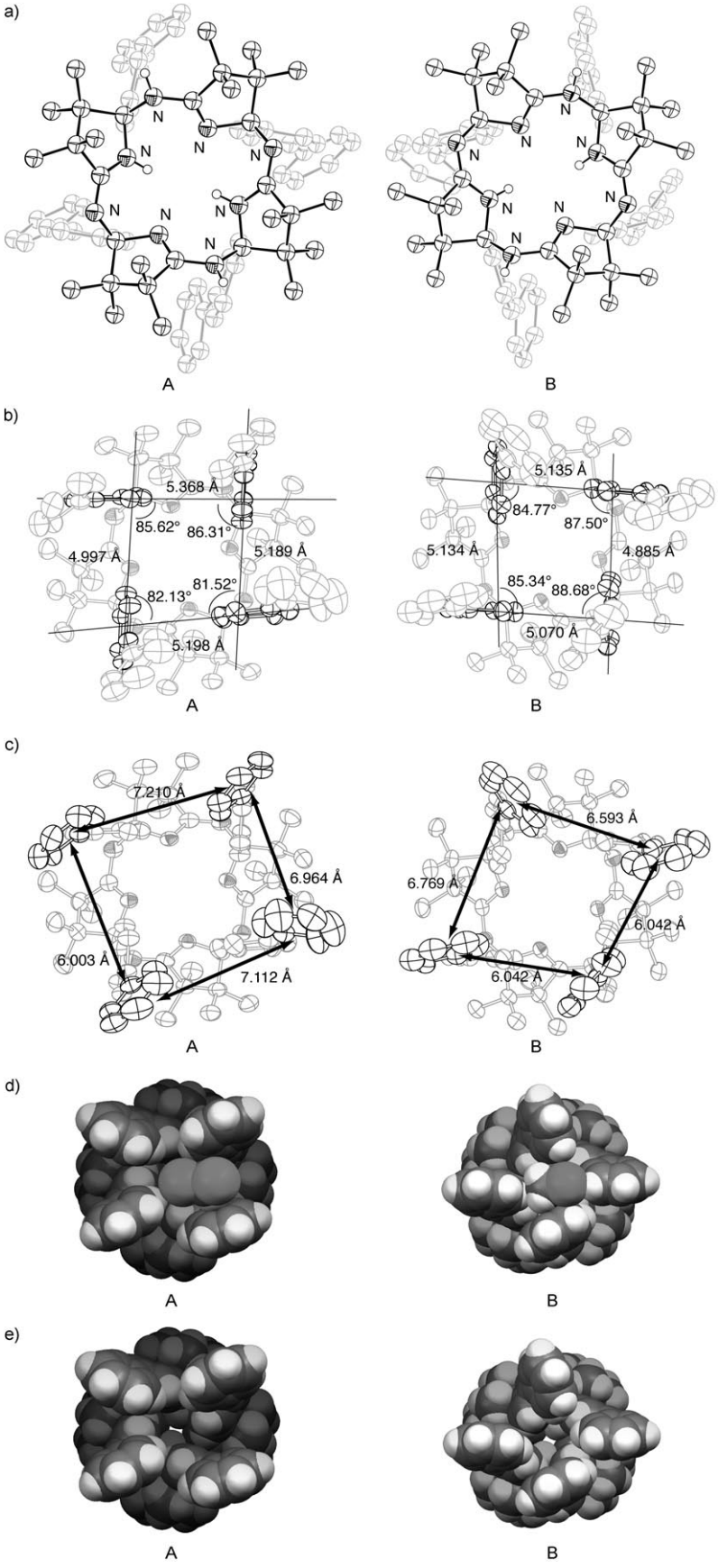

Figure 1. X-ray crystal structure of **3b** of both independent molecules A and B. a) Central tetradecahydroporphyrazin ring, b) centre-to-centre distances and angles between the planes of the proximal phenyl groups of the biphenyl substituents, c) centre-to-centre distances between the distal phenyl moieties of the biphenyl substituents. (ORTEP plots with thermal ellipsoids at 50% probability level, hydrogen atoms omitted for clarity), d) inclusion of dichloromethane in the cavity formed by the distal substituents, e) cavity with the CH_2Cl_2 molecule omitted.

planes is 58.3°, which is much more acute than the angle between the proximal phenyl groups.

The distal substituents again form a cavity that is big enough to incorporate a dichloromethane molecule in the crystal structure, which is disordered with regard to its orientation relative to the symmetry axis (Figure 3).

The NMR spectra of all three tetradecahydroporphyrazins **3** share most characteristics, so it can be concluded that compound **3a**, of which no X-ray structure was obtained, has comparable structural features. Especially the proton NMR spectra show that the tetradecahydroporphyrazins assume a C_2 symmetric structure in solution, since eight equally sized singlets for a total of sixteen methyl groups can be found. Two signals corresponding to two amino protons are visible, one at approximately 5.3 ppm, the other one at roughly 7.6 ppm. This signifies that of the four NH protons, two are bound to the dihydropyrrol nitrogen atoms, whereas the other two are situated at the porphyrin meso nitrogen atoms.

The interactions between the proximal phenyl moieties are also evident in the proton NMR spectra, because the protons in the 2-position, which are pointing towards the neighbouring phenyl ring, are experiencing additional shielding by the aromatic ring current of these groups. In all three cases, one multiplet stands out that can be assigned to these *ortho* protons. Variable-temperature NMR experiments (see below) reveal that this signal actually consists of two signals with equal intensity but somewhat different chemical shifts, each corresponding to two protons. Thus, we conclude that the proximal phenyl moieties in tetradecahydroporphyrazins are not equally far apart, but that two slightly differently distant types of pairs exist, so that the proximal phenyl groups do not form a perfect square but a parallelogram-like shape.

On heating, the two signals exhibit a slightly different dynamic behaviour (Figure 4). Whereas the more low-field-shifted signal broadens from 298 K onwards, the high-field

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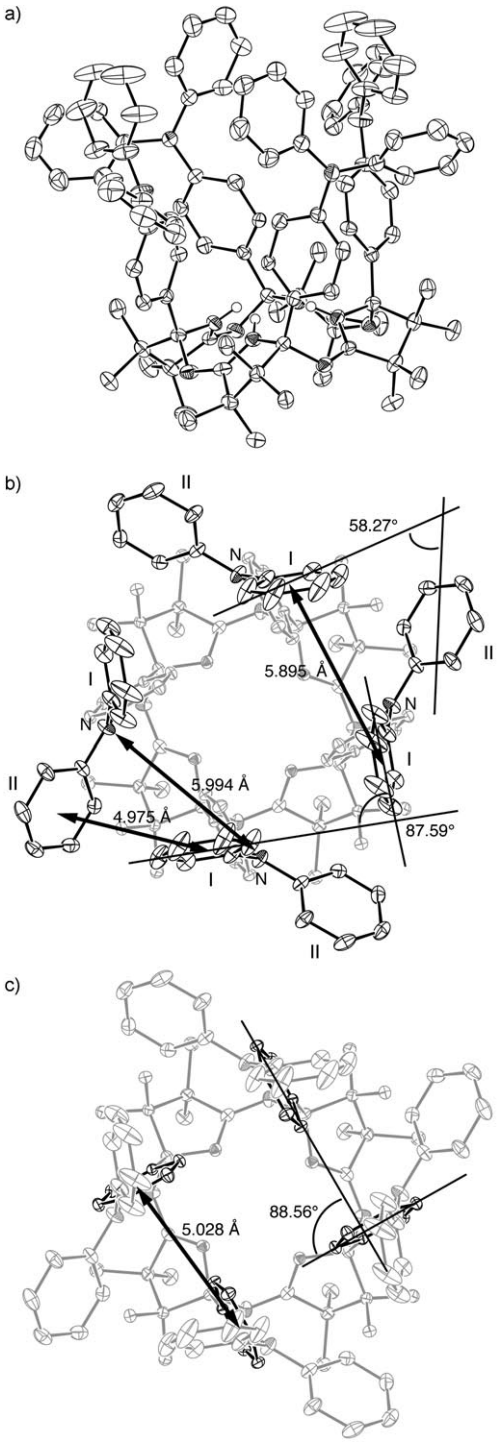

Figure 2. X-ray crystal structure of **3c**. a) Overview. Centre-to-centre distances and angles between the planes of the b) proximal and c) distal phenyl substituents. (ORTEP plots with thermal ellipsoids at 50% probability level, hydrogen atoms omitted for clarity).

signal remains sharp for longer and only begins to show line broadening at temperatures higher than 323 K. This line broadening can be assumed to be caused by a breaking of the fairly rigid pairings of the phenyl groups, leading to a mobilisation of the aryl groups, which is somewhat limited

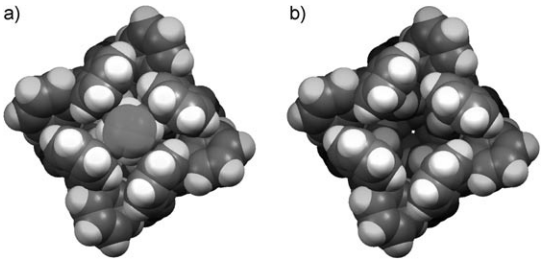

Figure 3. a) Inclusion of a four-fold disordered dichloromethane molecule in a cavity formed by the distal substituents of **3c**. b) Cavity with the CH_2Cl_2 molecule omitted.

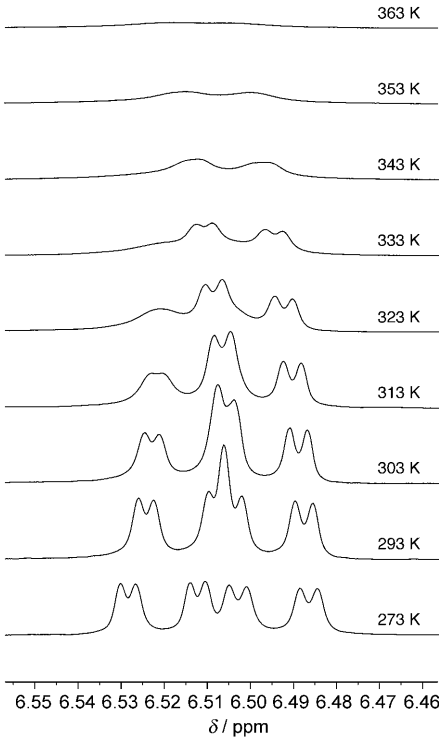

Figure 4. Temperature-dependent behaviour of the ^{1}H NMR signals of the *ortho* protons of the proximal phenyl groups in **3b**.

by steric hindrance. We quantified the kinetics of these dynamic processes by line-shape analysis for tetradecahydroporphyrazin **3b** in which the signals in question are best visible and resolved, and could thus determine the activation energy required breaking the pairs of phenyl groups. Corresponding to the observed differing behaviour, two different energy values were found, namely, $\Delta H_1 = 14.0$ kcal mol^{-1} for the low-field signal and $\Delta H_2 = 15.3$ kcal mol^{-1} for the high-field signal. This means that the pairs of phenyl rings with a shorter distance require about 1.3 kcal mol^{-1} more than the pairs with a longer distance to surmount the interaction and become mobile. However, note that the determined enthalpies not only contain the isolated interaction energy of the phenyl moieties, but also the required energy for geometry changes of the whole molecular framework. Furthermore, cooperative effects between the phenyl rings can also be as-

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sumed to play a role because it appears to be plausible that the breaking up of one pair of interacting phenyl groups affects the whole molecular geometry in its vicinity.

To validate our experimental observations and to find a plausible explanation for the prevalence of a single observed isomer of the tetradecahydroporphyrazins, we used quantum chemical calculations. Because traditional methods such as the popular B3LYP density functional either tend to estimate the strength of weak dispersion interactions incorrectly or require unaffordable amounts of calculation time and resources, we employed the recently developed B97-D density functional that includes a long-range dispersion correction.[14] The relatively small phenyl-substituted tetradecahydroporphyrazin **3a** has been chosen as model compound for the calculations, which have been performed with TURBOMOLE.[15]

The formation reaction of the tetradecahydroporphyrazins, starting from the dihydropyrrol-2-imine (after hydrolytic desilylation of **2a**), is very exothermic with a reaction enthalpy of $-67.6\ \mathrm{kcal\,mol^{-1}}$ calculated on the B97-D/TZVP level, thus explaining why these macrocycles form under such mild conditions.

The structure resulting from a geometry optimisation is in accordance with the one deduced from the spectroscopic data with two types of phenyl pairs at distances that differ by 0.33 Å (Figure 5).

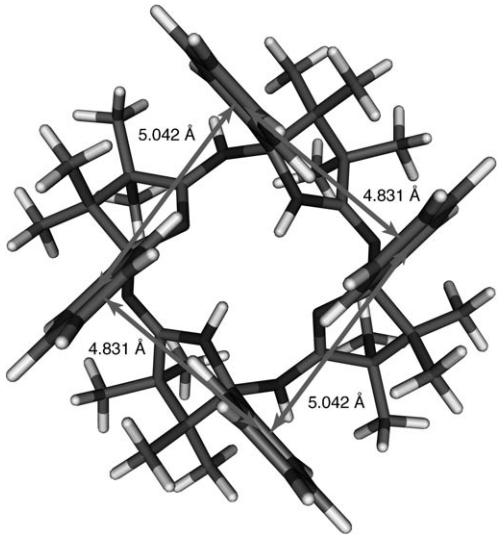
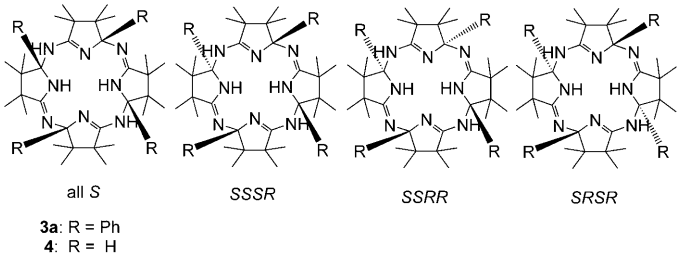


Figure 5. Structure of **3a** optimised on the B97-D/TZVP level of theory.[14]

Comparison with the optimised structures of the other three hypothetically diastereomers of the tetradecahydroporphyrazins in which the aryl substituents are differently aligned (Scheme 3) reveals that the observed diastereomer with all four substituents pointing in the same direction is in fact the energetically most favourable one (Table 1). Thus, it is safe to assume that under thermodynamic control (which



Scheme 3. Potential diastereomers of compound **3a** and hypothetical model compound **4**.

Table 1. Relative energies of the potential diastereomers of compounds **3a** and **4** (B97-D/TVZP) [$\mathrm{kcal\,mol^{-1}}$].

Compound	all *S*	*SSSR*	*SSRR*	*SRSR*
3a	0.0	13.9	16.7	15.3
4	0.0	4.5	5.2	1.3

appears to be the case, considering the long reaction time and conditions) only the single observed diastereomer forms.

To obtain information about the contribution of the aromatic interactions to the stability of the tetraaryl-tetradecahydroporphyrazins, the single-point energy of a benzene tetramer with the individual molecules arranged exactly like the proximal phenyl groups in the optimised structure of compound **3a** has been calculated. On the B97-D/TZVP level of theory, such a cyclic benzene tetramer is favoured by $11.8\ \mathrm{kcal\,mol^{-1}}$ in comparison with four single benzene molecules, thus amounting to approximately $3\ \mathrm{kcal\,mol^{-1}}$ per interaction.[5,14b,16] On the other hand, the macrocyclic system itself only slightly favours the all *S* diastereomer, indicated from calculations without the phenyl substituents (Table 1, model compound **4**).[16] Based on these results, it is clear that the interactions between the aryl moieties essentially contribute to the formation and stabilisation of the whole macrocylic structure.

Conclusion

In summary, we have discovered a simple method to synthesise highly saturated and substituted porphyrazin derivatives with excellent diastereoselectivity. The structures of the obtained compounds have been elucidated in solid phase and solution by X-ray crystallography and NMR spectroscopy, respectively, and have been found to contain four aryl moieties in close contact, arranged in a cyclic fashion. In solution, the tetradecahydroporphyrazins prefer a slightly oblong C_2 symmetric structure with two types of pairs of phenyl groups at different distances and of different interaction strengths. Quantum chemical calculations employing the new B97-D density functional with dispersion correction[14] are in good agreement with the experimentally deter-

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mined structure and confirm the preference of the found diastereomer.

The clear application of the porphyrazin macrocycle of these new compounds is its use as a valuable coordination ligand for metal complexation. Additionally, the hydrophobic cavity formed by the aryl substituents, which is expected to be variable in diameter, could be interesting for selective interactions with suitable molecules of appropriate size and polarity. Furthermore, the synthetic pathway discovered for this new class of compounds allows controlled functionalisation at the walls of the cavity as exemplified in compound **3c**, in which the diphenylamine substituent may serve as an example of Brønsted or Lewis base activity. Thus, we expect that this new class of compounds, owing to its unique structural and reactive properties, could serve as a basic framework for catalysts, supramolecular structures and container molecules.

Experimental Section

General procedure for the synthesis of 2: Aryl halide (10.0 mmol) was dissolved in anhydrous THF (10.0 mL) in a Schlenk flask that had been dried and flushed with argon. The solution was cooled to −78 °C and *n*-butyllithium (11.0 mmol; 6.9 mL of an 1.6 M solution in *n*-hexane) was added. After stirring for one hour at −78 °C, 2,2,3,3-tetramethylsuccinonitrile (11.0 mmol, 1.50 g) dissolved in anhydrous THF (10.0 mL) was slowly added. The reaction mixture was stirred at −78 °C for 30 min, warmed to 0 °C and stirred for additional 30 min. Then, the solution was cooled to −78 °C again and chlorotrimethylsilane (11.0 mmol, 1.20 g, 1.4 mL) was added. The reaction mixture was slowly warmed to room temperature and stirred for one hour. The crude product was obtained by removing the solvent under vacuum and was subsequently purified by Kugelrohr distillation.

Compound 2a: By using bromobenzene (1.57 g, 1.05 mL, 10.0 mmol) as the starting material, compound **2a** was synthesised by using the general procedure. The product was obtained after purification as a yellow solid in 71 % yield (2.02 g, 7.1 mmol). B.p. 122 °C (1.9×10^{-2} mbar); ^{1}H NMR (300.13 MHz, $CDCl_3$): $\delta=0.27$ (s, 9H; SiCH_3), 1.06 (s, 6H; CH_3), 1.27 (s, 6H; CH_3), 7.41–7.49 (m, 3H), 7.95–7.98 ppm (m, 2H; CH_{arom}); ^{13}C NMR (75.47 MHz, $CDCl_3$): $\delta=1.3$ (SiCH_3), 22.7 (CH_3), 23.3 (CH_3), 50.5 ($C_{quat.}$), 53.0 (C_{quat}), 128.5, 129.3, 131.3, (C_{arom}), 134.3 (C_{ipso}), 183.2, 191.3 ppm (*C*=N); IR: $\tilde{\nu}=3053$ (vw), 2997 (w), 2976 (w), 2965 (m), 2897 (w), 2868 (w), 2361 (w), 2336 (w), 1717 (w), 1682 (s), 1584 (w), 1545 (s), 1497 (w), 1474 (w), 1458 (w), 1447 (m), 1396 (m), 1377 (w), 1371 (w), 1362 (w), 1315 (m), 1298 (m), 1269 (m), 1238 (s), 1165 (w), 1144 (m), 1126 (w), 1103 (s), 1076 (m), 1034 (w), 1013 (w), 928 (w), 881 (vs), 843 (vs), 829 (vs), 785 (m), 770 (s), 758 (m), 743 (s), 702 (vs), 692 (s), 662 (m), 631 (m), 617 (w) cm^{-1} ; ESI-MS [*M*−TMS+H]: calcd: 215.1543; found: 215.1541.

General procedure for the synthesis of the tetraaryl tetradecahydroporphyrazins 3: The tetradecahydroporphyrazins were synthesised by dissolving *N*-silylated dihydropyrrol imine **2** (1.0 mmol) in dichloromethane (1 mL). This solution was slowly concentrated by evaporation of the solvent over the course of several days. To increase the yield, the residue was re-dissolved in dichloromethane and again slowly evaporated several times. The resulting crystals were collected, washed repeatedly with small amounts of pentane or hexane and dried under vacuum.

Compound 3a: Compound **3a** was synthesised from **2a** (247 mg, 0.86 mmol), following the general procedure and was obtained as colourless a crystalline solid in 26 % yield (47 mg, 0.06 mmol). M.p. 151 °C; ^{1}H NMR (300.13 MHz, $CDCl_3$): $\delta=-0.11$ (s, 6H), −0.02 (s, 6H), 0.99 (s, 6H), 1.01 (s, 6H), 1.05 (s, 6H), 1.18 (s, 6H), 1.30 (s, 6H), 1.31 (s, 6H, CH3), 5.27 (s, 2H; N*H*), 6.06 (d, 2H), 6.09 (d, 2H; *o*-CH_{arom}), 6.88–7.05 (m, 5H), 7.07–7.20 (m, 9H), 7.36 (d, $^3J=7.2$ Hz, 2H; CH_{arom}), 7.54 ppm (s, 2H; N*H*); ^{13}C NMR (75.47 MHz, $CDCl_3$): $\delta=16.3$, 18.2, 20.2, 21.1, 23.1, 24.7, 25.1, 26.2 (CH_3), 47.1, 48.1, 50.3, 51.1, 79.5, 90.6 ($C_{quat.}$), 124.5, 125.4, 125.8, 126.4, 126.6, 126.8, 127.3, 127.5, 127.8, 128.5, 128.6, 128.6, 128.7, 128.8, 130.5, 144.9, 148.1 (C_{arom}), 162.4, 169.0 ppm (*C*=N); IR: $\tilde{\nu}=$ 3372 (vw), 3061 (w), 2974 (w), 2938 (w), 2909 (w), 2870 (w), 2569 (vw), 2500 (vw), 1668 (s), 1628 (s), 1599 (w), 1582 (w), 1493 (w), 1464 (m), 1445 (m), 1404 (m), 1393 (m), 1375 (m), 1362 (m), 1342 (m), 1288 (w), 1261 (w), 1250 (w), 1225 (w), 1198 (w), 1173 (w), 1148 (m), 1124 (w), 1088 (m), 1061 (m), 1051 (m), 1032 (w), 1003 (w), 957 (m), 939 (w), 910 (m), 849 (w), 824 (vw), 756 (s), 733 (m), 704 (vs), 679 (w), 664 (m), 650 (w), 640 (w), 617 (w), 592 (w), 579 cm^{-1} (w); ESI-MS [*M*+H]: calcd: 857.5953; found: 857.5936; elemental analysis (for $C_{56}H_{72}N_8\cdot CDCl_3$): calcd: C 70.03 H 7.63 N 11.46; found: C 69.64 H 7.63 N 11.31.

Acknowledgements

This work was supported by the Deutsche Forschungsgemeinschaft (DFG, IRTG 1143 Münster–Nagoya, SFB 424) and the Fonds der Chemischen Industrie, Frankfurt. We thank Prof. Dr. S. Grimme, Münster, for helpful discussions.

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[12] Crystallographic data for **3b**: $C_{81.5}H_{91}Cl_3N_8$, $M_r=1288.97$; triclinic; space group $P\bar{1}$; $a=14.1518(4)$, $b=19.8854(5)$, $c=26.4582(8)$ Å; $\alpha=94.046(1)$, $\beta=90.867(1)$, $\gamma=101.212(2)°$; $V=7282.2(4)$ Å^3; $Z=4$; $\rho_{calcd}=1.176$ g cm^{-3}; $T=-50$ °C; 108369 reflections collected; 25673 unique reflections ($R_{int}=0.061$); $R=0.0796$; $R_W=0.1982$; GOF=1.022; Crystallographic data for **3c**: $C_{105}H_{110}Cl_2N_{12}$; $M_r=1610.95$; tetragonal; space group $P4/ncc$; $a=17.208(3)$, $b=17.208(3)$, $c=30.208(6)$ Å; $\alpha=90$, $\beta=90$, $\gamma=90°$; $V=8945(3)$ Å^3; $Z=4$, $\rho_{calcd}=1.196$ g cm^{-3}; $T=-150$ °C; 56073 reflections collected; 3953 unique reflections ($R_{int}=0.1043$); $R=0.1240$; $R_W=0.2343$; GOF=1.379. The quality of the measured data did not allow further refinement. CCDC 729167 (**3c**) and 729168 (**3b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

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Received: May 5, 2009
Published online: August 28, 2009

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