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Tetraphenyl-*p*-benziporphyrin: A Carbaporphyrinoid with Two Linked Carbon Atoms in the Coordination Core

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Carbaporphyrinoids are porphyrin analogues that possess at least one CH unit replacing a pyrrolic nitrogen in the coordination core. This "internal carbon" atom normally belongs to a carbo- or heterocyclic ring substituting one of the pyrroles.[1−6] It may participate in coordination of metal ions leading to stable organometallic complexes with often unusual properties.[4]

5,10,15,20-Tetraphenyl-*p*-benziporphyrin (**1a**) is a novel carbaporphyrinoid with a *p*-phenylene ring embedded in the tripyrrolic framework. **1** may be considered to have two adjacent CH units in the macrocyclic core. The coordinating properties of **1** are exemplified by a cadmium(II) complex.

1 is an aromatic isomer of the nonaromatic 6,11,16,21-tetraphenyl-*m*-benziporphyrin,[5] related to hexaalkyl-*m*-benziporphyrin and its modifications including aromatic oxybenziporphyrin.[6]

1 is obtained in a simple modification of the synthesis described for tetraphenyl-*m*-benziporphyrin (Scheme 1).[5] After chromatographic workup compound **1** was obtained in 1% yield.[7]

1b and the dication (**1a**-H_2)Cl_2 have been found to adopt similar conformations in the solid state (Figure 1). The macrocycle is planar (**1b**) or only slightly ruffled (**1a**-H_2^{2+}) except for the tilt of the *p*-phenylene moiety. The dihedral angle between the six-membered ring and the N_3 plane is almost invariant and equals 48° and 44° for the two independent molecules of **1b**, and 43° for **1a**-H_2^{2+}. The dication coordinates two chloride ions through hydrogen bonds. In the structures of **1b** and **1a**-H_2^{2+} the phenylene moiety displays a slight but statistically significant distortion from the idealized benzene geometry. The C(2)−C(3) and C(21)−C(22) bond lengths vary in the range 1.365(2)−1.390(2) Å and are systematically shorter than the remaining distances within the six-membered ring (1.394(2)−1.415(3) Å). Along with the lengths of C(1)−C(20) and C(4)−C(5) bonds (1.454(3)−1.464(2) Å), which are shorter than the respective distances in 22-acetoxy-*m*-benziporphyrin,[5] they indicate that the phenylene is partly conjugated with the tripyrrolic brace.

At 168 K the phenylene protons 2,3-H and 21,22-H have strongly differentiated chemical shifts (7.68 and 2.32 ppm, respectively). They are a clear manifestation of the diatropic ring current, which deshields the external and shields the internal protons. At higher temperatures the two signals coalesce into a singlet due to a dynamic process. The molecule switches rapidly between two equivalent conformations, which differ by a flip of the *p*-phenylene (Scheme 2).

Activation parameters of this process determined for **1c** are $\Delta H^{\ddagger} = 34.0(3)$ kJ/mol and $\Delta S^{\ddagger} = 9.6(1.3)$ J/(mol·K). Such conformational flexibility is not typical of regular porphyrins but was observed in certain porphyrin analogues.[8]

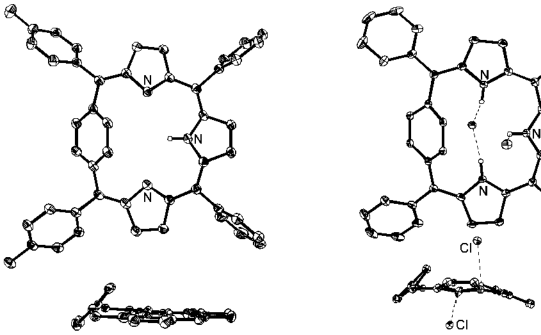
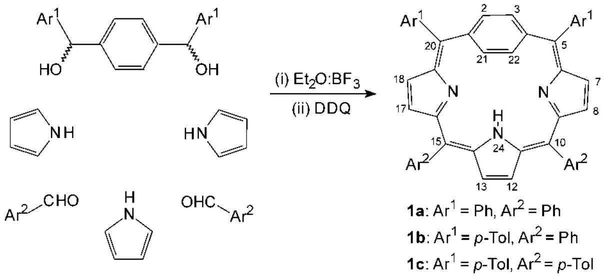


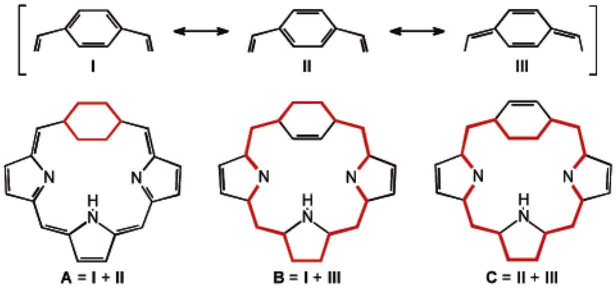
Figure 1. Crystal structures of **1b** and (**1a**-H_2)Cl_2·$2CH_2Cl_2$·H_2O (50% thermal ellipsoids, one of two symmetry-independent molecules shown for **1b**). Solvent molecules and hydrogen atoms (except for NH) are omitted for clarity.

Scheme 1. Synthesis



Scheme 2

Scheme 3



To account for the structural and spectroscopic characteristics of **1**, it is necessary to include the quinoid canonical form **III** in the description of *p*-benziporphyrin (Scheme 3). In conjunction with the Kekulé structures **I** and **II** it defines two 18e macrocyclic π-delocalization pathways **B** and **C**, which may coexist with the [6]annulene aromaticity of the benzene ring (**A**). While **1** is the first porphyrinoid to exhibit the delocalization pattern shown in Scheme 3 it was shown earlier that *p*-phenylene moieties, when

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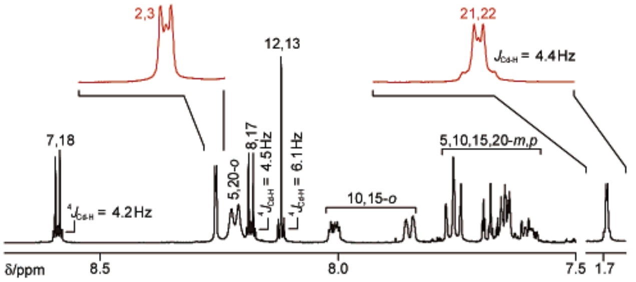

Figure 2. ^{1}H NMR spectrum of **2a** ($CDCl_3$, 298 K). Resonance assignments (obtained from COSY and NOESY maps) follow the numbering given in Scheme 1.

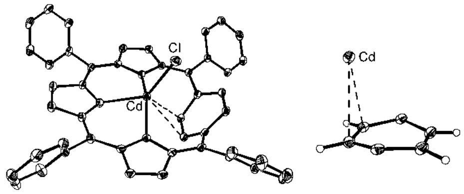

Figure 3. Structure of **2**·$2CDCl_3$ (50% thermal ellipsoids; solvent molecules and hydrogen atoms omitted for clarity). Inset presents the geometry of interaction between cadmium(II) and *p*-phenylene.

incorporated into an annulenoid structure, can likewise participate in the overall delocalization.[9] The simultaneous accessibility of local and macrocyclic aromaticity distinguishes **1** from the *m*-benziporphyrins with an isolated [6]annulene subsystem,[5,6a] and from oxybenziporphyrin,[6b] where macrocyclic aromaticity is achieved by transforming the benzene moiety into semiquinone.

1a reacts smoothly with $CdCl_2$ yielding chlorocadmium(II) tetraphenyl-*p*-benziporphyrin (**2a**), wherein the macrocycle acts as a monoanionic ligand. Complexation constrains the conformational dynamics of the macrocycle, and the ^{1}H NMR spectrum of **2a** taken at 298 K contains sharp *p*-phenylene signals ($\delta_{2,3} - \delta_{21,22} = 6.57$ ppm) with no signs of exchange (Figure 2). Coordination through the three nitrogen donors is confirmed by the presence of $^{111/113}$Cd satellites seen for all the β-pyrrolic signals. In addition a weak scalar coupling (4.4 Hz) is observed between $^{111/113}$Cd and protons 21,22-H, which results from spatial proximity between the cadmium ion and *p*-phenylene (the coupling is absent for 2,3-H).

The coordinating environment of Cd(II) forms a trigonal bipyramid, with the N(24) atom, chloride, and C(21)−C(22) bond occupying the equatorial positions. Cd(II) is displaced by 0.524(1) Å from the N_3 plane (Figure 3).

The separation between cadmium and C(21) or C(22) (2.748(2) and 2.762(2) Å, respectively) is smaller than the expected van der Waals contact (ca. 3.1 Å)[10] but still larger than normally observed Cd−C bond lengths (2.10−2.35 Å)[11] and belongs to the class of intermediate-range interactions,[12] whose existence was proved statistically for metal−arene complexes.[13] The projection of the cadmium(II) ion onto the C(2)C(3)C(21)C(22) plane (C_4 plane) lies close to the center of the C(21)−C(22) bond, so the metal ion interacts with the benzene ring in a η^2 fashion. To the best of our knowledge, this arrangement has no precedent in cadmium chemistry although is well-documented for Hg(II) and Ag(I) arene complexes.[14,15] The orientation of the phenylene ring in **2** is similar as in the free base (the tilt angle is 45°). However the six-membered ring shows a slight boatlike deformation (C(1) and C(4) are displaced from the C_4 plane by ca. 0.15 Å).

In conclusion, *p*-benziporphyrin, an isomer of *m*-benziporphyrin,[5,6] is a new aromatic porphyrinoid, which preserves the essential features of the [18]porphyrin(1.1.1.1) frame and can coordinate metal ions using the (C_n,N,N,N) coordination core. The *p*-phenylene ring may be able to participate in various metal−arene bonding modes ranging from η^2 to η.[6]

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Supporting Information Available: Synthetic procedures, UV−vis spectra, NMR data (including a ^{1}H−^{113}Cd 1D HMQC spectrum of **2a**) (PDF) and crystallographic data for **1b**, (**1a**-H_2)Cl_2, and **2** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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