Extended π Systems

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Annularly Fused Hexapyrrolohexaazacoronenes: An Extended π System with Multiple Interior Nitrogen Atoms Displays Stable Oxidation States**

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There is a considerable demand for the synthesis of large two-dimensional molecules with extended π systems such as polycyclic aromatic hydrocarbons (PAHs), in part because of their technological applications.[1] Nitrogen-containing PAHs are of particular interest since such heteroatoms influence the electronic nature without modifying the structure. For instance, all-carbon triphenylenes are p-type and hexaazatriphenylenes n-type semiconductors.[2,3] In contrast, nitrogen atoms in pyrrole derivatives make the π systems electron rich, and oligo- and polypyrroles are conductive in their oxidized forms.[4] Their polycyclic analogues—fused oligopyrroles—have remained elusive, and only the fusion of two pyrrole rings has been reported.[5,6]

While the products resulting from the oxidation of hexapyrrolylbenzene **1** have been analyzed by MALDI-TOF mass spectrometry,[7] the isolation and spectroscopic properties of ring-fused analogues have not yet been reported. Herein, we describe the synthesis, X-ray crystal structure, and spectroscopic properties of annularly fused hexapyrrolohexaazacoronenes **2** (HPHAC)[8] and their corresponding dications $\mathbf{2}^{2+}$. In HPHAC **2**, the nitrogen atoms fully contribute to the stabilization of higher oxidation states of the HPHAC core, and this is the first example with multiple interior nitrogen atoms within the extended disk-type π system.

Hexapyrrolylbenzene **1** was synthesized by nucleophilic aromatic substitution of hexafluorobenzene with pyrrolyl sodium salts (Scheme 1).[7,9] In a first attempt to synthesize HPHAC **2**, hexapyrrolylbenzene **1a** was oxidized with iron(III) trichloride and subsequently neutralized with hydrazine. MALDI-TOF mass spectrometry (solid-state analyte prepared in a 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ) matrix[10]) of the resulting black powder showed a complex mixture in which the parent molecular ion of HPHAC **2a** was the main component. To isolate **2** in the neutral form, more electron-deficient pyrroles, namely, β-dibromopyrrole and β-di(4-trifluoromethylphenyl)pyrrole were chosen as building blocks leading to **1b** and **1c**, respectively. Whereas cyclodehydrogenation of **1c** successfully afforded HPHAC **2c** as an orange solid in 53% yield, **2b** was obtained from **1c** as a mixture with mono- and didebrominated compounds in 81% yield (for full characterization see the Supporting Information). HPHAC **2b** showed remarkable thermal stability up to 535 °C in thermogravimetric analysis (TGA) under N_2-flow conditions.

The ^{1}H NMR spectrum of HPHAC **2c** in CD_2Cl_2 indicates a completely fused structure.[11] Signals for the α protons of **1c** ($\delta = 6.72$ ppm) are absent, and doublets due to the peripheral 4-trifluoromethylphenyl groups appear at $\delta = 6.81$ and 6.57 ppm with upfield shifts of $\Delta\delta = 0.71$ and 0.64 ppm, respectively, relative to the signals of **1c** (see the Supporting Information). This reflects the ring-current effect of the nearby phenyl groups associated with the ring fusion of pyrroles. In the UV/Vis absorption spectrum of **2c** the absorption maxima at 313, 373, 485, and 520 nm (Figure 1) are hypsochromically shifted compared to those of corresponding all-benzenoid hydrocarbons such as hexa-*peri*-hexabenzocoronene (HBC).[12] Surprisingly enough, **2c** exhibits a bathochromically shifted red fluorescence at 570, 617, and 673 nm (Figure 1), whereas HBC fluoresces at much shorter wavelengths ($\lambda_{max} = 465, 484, 492, 517$, and 528 nm).[12] Such a bathochromically shifted fluorescence could be useful for scintillators, solar collectors, and biological fluorescence probes.[13]

The molecular structure of HPHAC **2c** was confirmed by single-crystal X-ray diffraction (Figure 2a).[14a] In contrast to the expected bowl-shaped structure arising from the annually fused five-membered rings, which was predicted by DFT calculations of parent HPHAC **2a** (see the Supporting Information), a nearly coplanar conformation was detected. The distance between two phenyl groups of neighboring pyrroles is less than that between the two phenyl groups attached to the same pyrrole. Furthermore, the centers of gravity of the twelve peripheral phenyl groups are not in the same plane but above and below the plane forming a wavelike pattern; this possibly plays a crucial role in the planarity of the HPHAC core. In the packing structure, **2c** is arranged as slipped parallel sheets, and the π planes are approximately 4.9 Å apart (see the Supporting Information).

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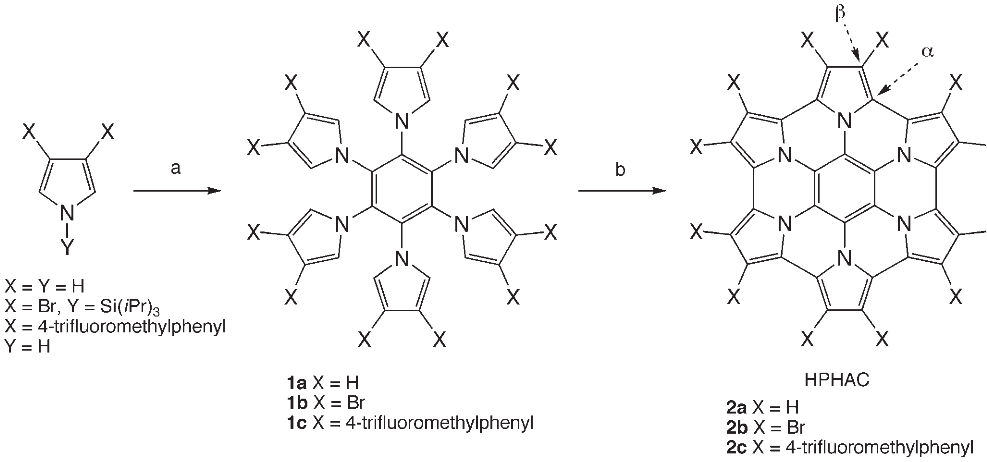

Scheme 1. Synthesis of annularly fused hexapyrrolohexaazacoronenes **2** (HPHAC). Reagents and conditions: a) NaH or NaOMe, DMF; then hexafluorobenzene; b) $FeCl_3$, CH_3NO_2/CH_2Cl_2; then hydrazine.

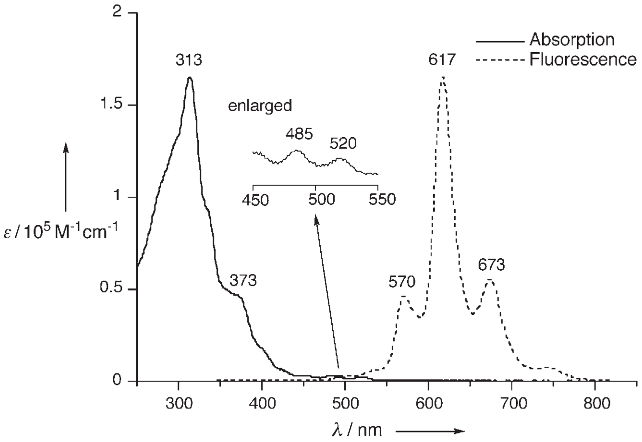

Figure 1. UV/Vis absorption and fluorescence ($\lambda_{ex}=313$ nm) spectra of **2c** in CH_2Cl_2. The insert shows an enlargement of the absorption spectrum between 450 and 550 nm.

The electrochemical properties of HPHAC **2c** were studied by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) (CH_3CN, RT, Ag/Ag^+), revealing four reversible one-electron oxidation steps with the following half-wave potentials: $E_{ox1}=0.355$ V, $E_{ox2}=0.520$ V, $E_{ox3}=1.52$ V, $E_{ox4}=$ ca. 1.88 V (see the Supporting Information).

Since the interior nitrogen atoms of **2** can thus be considered to stabilize higher oxidation states, **2c** was oxidized with antimony pentachloride ($SbCl_5$) in CH_2Cl_2 at room temperature. Incremental addition of $SbCl_5$ under anaerobic conditions afforded the green-colored monocation $\mathbf{2c}^{+\bullet}$ (absorption maxima at 845 and 965 nm together with a broad band centered at 1450 nm) and then the dark green-colored dication $\mathbf{2c}^{2+}$ (absorption maxima at 676 and 739 nm together with a broad band centered at 1150 nm; see the Supporting Information). The oxidation could be reversed by addition of tetrabutylammonium iodide (Bu_4NI), which reduced the dication $\mathbf{2c}^{2+}$ back to the starting **2c** quantitatively. While the ESR spectrum of the monocation $\mathbf{2c}^{+\bullet}$ exhibits a sharp single-line signal ($g=2.0023$), indicating that the spin density is localized within the HPHAC core, treatment of **2c** with an excess amount of $NOSbCl_6$ (10 equiv) in CD_2Cl_2 at room temperature gave the ESR-silent dication $\mathbf{2c}^{2+}$ (see the Supporting Information). The ^1H NMR resonances of peripheral 4-trifluoromethylphenyl groups are shifted downfield ($\Delta\delta=1.45$ and 0.80 ppm), while the ^{13}C NMR resonances of the three sp^2 carbons of the HPHAC core appear with considerable downfield shifts into the region of common polycyclic aromatic nitrogen heterocycles such as quinoline, acridine, and phenazine ($\delta=141.01$, 124.95, and 122.78 ppm).[15] This is due to the decrease in electron density of the HPHAC core.[15,16a]

Slow evaporation of the CD_2Cl_2 solution gave single crystals of dication $\mathbf{2c}^{2+}$ ($\mathbf{2c}^{2+}[SbCl_6^-]_2$). No decomposition of the dication crystal was observed when it was stored at room temperature under air for several days.[16] The molecular structure of $\mathbf{2c}^{2+}$ was determined by X-ray diffraction for the first time as a dication of fused pyrroles (Figure 2 b).[14b] The two hexachloroantimonate counter anions are located above and below opposite nitrogen atoms, and no intermolecular π-stacking between the HPHAC cores was observed as in the case of the neutral form.

The bond-length alternation in molecules with extended π systems is important for discussing the nature of the π system. Table 1 shows selected bond lengths for pyrrole units of neutral **2c** and dication $\mathbf{2c}^{2+}$. The neutral **2c** exhibits bond-length alternations in the pyrrole units[17] with bond lengths comparable to those in the nonfused hexapyrrolylbenzene **1a**,[9] and the "new" bonds, C_α–C_α of neighboring pyrroles in **2c** are rather long. On the other hand, in the case of dication $\mathbf{2c}^{2+}$, the averaged C_α–C_β bonds are elongated and the averaged C_β–C_β and C_α–C_α bonds are shortened compared to those of **2c**. The tentative conclusion that the dication of parent HPHAC $\mathbf{2a}^{2+}$ possesses overall aromaticity is supported by a calculation of three-dimensional nucleus-independent chemical shifts (see the Supporting Information).[18,19]

In brief, we have reported the synthesis and isolation of annularly fused hexapyrrolohexaazacoronenes by cyclodehydrogenation of hexapyrrolylbenzene and subsequent neutralization. Electrochemical oxidation of HPHAC **2c** revealed that interior nitrogen atoms play an important role in stabilizing higher oxidation states of HPHAC. Thus it was possible to record spectroscopic properties of **2c** and isolate its dication under ambient conditions. This reversible redox behavior makes the present π system of potential interest as an electrochromic molecule and a charge-carrier material in organic electronics. In line with this, studies on the synthesis

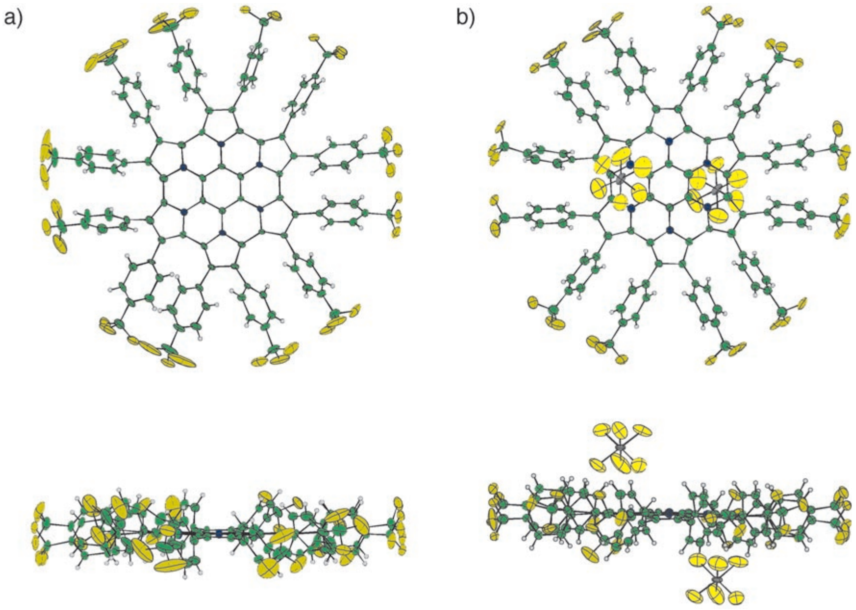

Figure 2. Molecular structures (top and side views) of a) HPHAC **2c** and b) $\mathbf{2c}^{2+}[SbCl_6^-]_2$. Solvent molecules are omitted for clarify. (50% probability for thermal ellipsoids).

Table 1: Selected bond lengths in the crystal structures [Å][a] of a) neutral form **2c** and b) the dication salt, $\mathbf{2c}^{2+}[SbCl_6^-]_2$.

Bond	**2c**	$\mathbf{2c}^{2+}[SbCl_6^-]_2$
$N-C_\alpha$	1.40±0.006	1.39±0.03
$C_\alpha-C_\beta$	1.39±0.007	1.42±0.03
$C_\beta-C_\beta$	1.44±0.01	1.40±0.05
$C_\alpha-C_\alpha$	1.48±0.009	1.45±0.04

[a] Averaged values are shown with standard deviations calculated by the following equation: $\{\Sigma(x_i-<x>)^2/(n-1)\}^{1/2}$.

of larger and/or bowl-shaped π systems with the same or different number of interior nitrogen atoms are currently underway.

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21 526 unique reflections, $R_{merge} = 0.0732$, 16 127 observed reflections ($I > 2.0\sigma(I)$); structure solution by direct methods (Shelxs), refinement by full matrix least squares on F with anisotropic temperature factors for the non-H atoms. Final $R = 0.0535$, $R_w = 0.0483$, GOF = 0.951. CCDC 642625 (**2c**) and CCDC 642626 (**2c**$^{2+}$) 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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