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adj-Diazuliporphyrins, a New Family of Dicarbaporphyrinoids with Unprecedented Mesoionic Characteristics[†]

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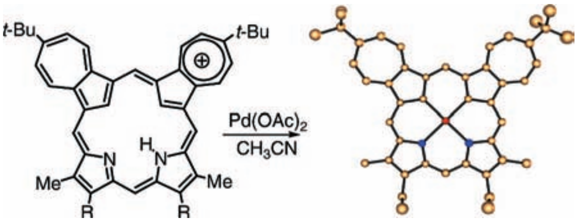
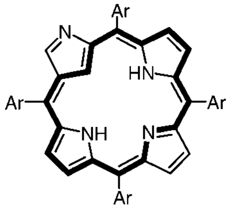
ABSTRACT

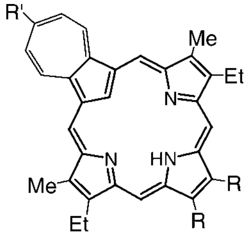


A diazulenylmethane dialdehyde reacted with dipyrrylmethanes in the presence of HCl or HBr, followed by oxidation with $FeCl_3$, to give aromatic *adj*-diazuliporphyrins. The free base structures must exist as mesoionic species, although these porphyrinoids were isolated as salts of the monoprotonated macrocycles. Reaction with $Pd(OAc)_2$ gave an unprecedented zwitterionic palladium(II) complex that was characterized by X-ray crystallography.

N-Confused porphyrins (NCPs; **1**)[1] and related carbaporphyrinoid systems such as the azuliporphyrins **2**[2] have attracted considerable interest due to their unusual reactivity and spectroscopic properties,[3] as well as their potential utility in medicinal applications.[4] These analogues also provide insights into the nature of porphyrinoid aromaticity[5] and have been shown to generate organometallic derivatives under mild conditions.[6,7] Two examples of doubly N-confused porphyrins (N_2CPs) have been reported that introduce a second carbon atom into the porphyrinoid core, but these retain the ability to form organometallic derivatives with metals in higher oxidation states such as Ag(III).[8] In our previous investigations, several examples of dicarbaporphy-



1 N-confused porphyrins



2 Azuliporphyrins

[†] Conjugated Macrocycles Related to the Porphyrins. 49. For part 48, see: Lash, T. D.; Young, A. M.; Von Ruden, A. L.; Ferrence, G. M. *Chem. Commun.* **2008**, DOI: 10.1039/b816057k.

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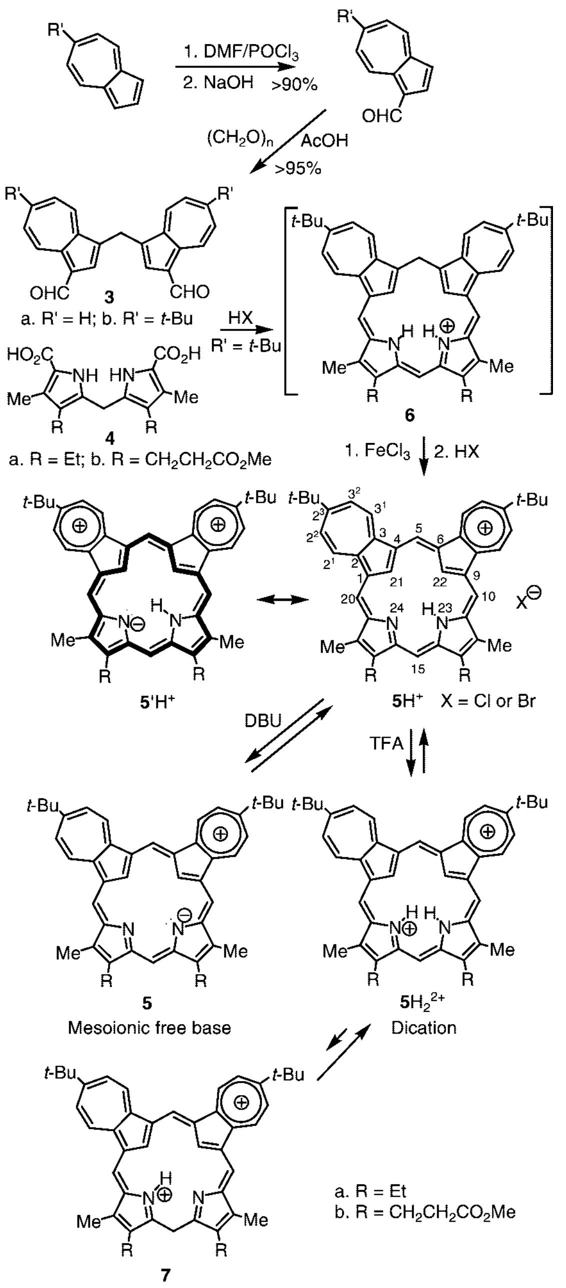
10.1021/ol802406f CCC: $40.75

rinoids with either two indene subunits[9a] or an azulene and indene moiety have been described,[9b,c] and these results have provided further insights into the nature of porphyrinoid aromaticity. In this paper, the synthesis of a remarkable new family of dicarbaporphyrinoids with two adjacent azulene subunits is described.[10] To the best of our knowledge, these diazuliporphyrins are the first examples of mesoionic porphyrinoid systems.

Scheme 1



Dialdehydes **3** are easily prepared in virtually quantitative yields by reacting the corresponding azulene monoaldehydes[11,12] with paraformaldehyde in acetic acid.[11] In principle, dialdehyde structures of this type can be used in MacDonald "2 + 2" condensations[13] with dipyrrylmethanes **4** to form porphyrinoid macrocycles (Scheme 1). Initially, reactions of **3a** and **3b** with **4a** were attempted in TFA$-$CH$_2$Cl$_2$, but no porphyrinoid products could be isolated. However, when these condensations were conducted in acetic acid with catalytic HCl or HBr, followed by oxidation with FeCl$_3$,[14] the novel *adj*-diazuliporphyrins **5** were generated. Although poor results were obtained for reactions using **3a**, excellent yields (43−56%) of diazuliporphyrins **5a**·HCl or **5a**·HBr could be isolated using bis-*tert*-butyl dialdehyde **3b**. Prior to the oxidation step, a diazuliphlorin **6a** or a related dihydroporphyrinoid would be produced, and it was not immediately clear how this framework could allow conjugation between the two azulene units. However, following the oxidation step and treatment with HCl or HBr, the fully conjugated dications **5**H$_2^{2+}$ were indeed generated, and after column chromatography on silica the monoprotonated hydrochloride or hydrobromide salts could be isolated. A related diester **5b**·HBr was also synthesized from **3b** and **4b**. The UV−vis spectra of the nondescript gray-purple solutions of **5**·HCl and **5**·HBr were similar, showing broad absorptions at 379 and 566 nm (Figure 1). Addition of TFA produced violet solutions of the dications **5**H$_2^{2+}$ with a strong absorption at 571 nm. However, in 1% DBU−chloroform, green solutions of the free base species **5** were generated. The neutral system can

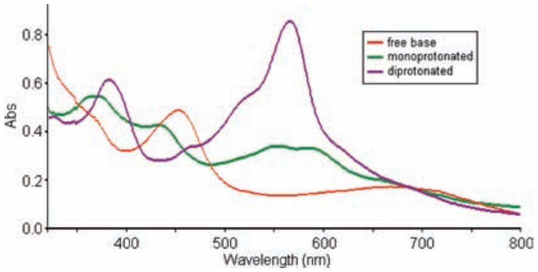


Figure 1. UV−vis absorption spectra for **5b**·HBr in CHCl$_3$ (monocation; green line), 1% TFA−CHCl$_3$ (dication; purple line), and 1% DBU−CHCl$_3$ (mesoionic free base; red line) showing the formation of three different species.

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only be written as a series of dipolar resonance contributors and for this reason may be considered to be a very unusual example of a mesoionic system. The isolated monoprotonated species must also take on unconventional tropylium type contributors such as $5H^+$ and $5'H^+$, and the dications $5H_2^{2+}$ are also best represented in this way. Hydrochloride salt **5a**·HCl was somewhat insoluble in organic solvents, but proton NMR data was obtainable in $CDCl_3$ and these showed that **5a**H^+ has a significant diatropic ring current as the internal 21,22-CH resonance shows up as a broad upfield singlet at 0.9 ppm. Better resolved spectra could be obtained for the more soluble hydrobromide salts **5a**·HBr and diester **5b**·HBr. The 21,22-CH resonance for **5a**·HBr in $CDCl_3$ was shifted upfield to −0.05 ppm, while the *meso*-protons gave rise to three singlets at 7.3 (1H), 8.1 (2H), and 10.6 ppm (1H) (Figure 2). Apart from confirming that this highly modified porphyrin analogue system retains a high degree of diatropic character, the proton NMR spectra confirm that the macrocycle possesses the plane of symmetry that is expected for the fully delocalized aromatic species. This symmetry is also evident in the carbon-13 NMR spectra for **5a** and **5b**. Addition of a drop of TFA to the NMR tube gave the dications $5H_2^{2+}$, and these also showed diatropic ring currents with the 21,22-CH resonance at 0.8 ppm. The NH resonance could also be identified near 2.5 ppm while the external *meso*-protons shifted further downfield giving resonances at 8.4 (1H), 9.2 (2H), and 10.7 ppm (1H). When TFA-*d* was added to the NMR solution of **5a**·HBr in $CDCl_3$, slow exchange of the 15-CH resonance occurred over several hours at room temperature and this result indicates that a C-protonated dication **7**, or a related tricationic species, must be present in equilibrium with $5H_2^{2+}$. X-ray crystallographic data were also obtained for **5b**·HBr, and this confirms that the porphyrinoid macrocycle contains two azulene and two pyrrole moieties. However, the quality of these results were only sufficient to confirm the connectivity and conformation of the carbon framework and could not identify the internal protons or the location of the bromide ion (Figure 3; see also the Supporting Information). The weakly diffracting crystal refined to only a relatively high *R* value, although prior to any refinement, all of the non-hydrogen atoms present in the four crystallographically independent $[C_{50}H_{53}N_2O_4]^+$ residues were immediately identified from the SHELXS-97 solution. As all four diazuliporphyrins show essentially the same macrocyclic conformation, the crystal structure adequately proves the non-hydrogen content of the main residues.

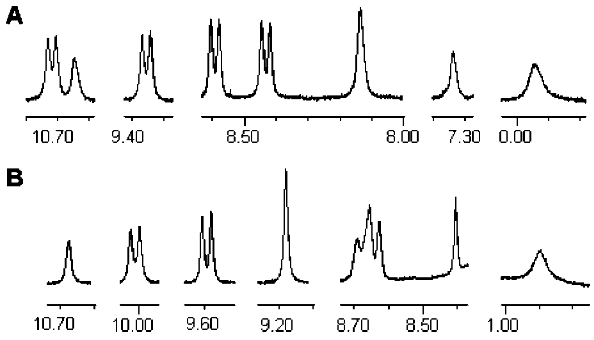


Figure 2. Partial 400 MHz proton NMR spectra of **5a**·HBr showing details of the upfield and downfield regions. (A) **5a**·HBr in $CDCl_3$. (B) Dication $5H_2^{2+}$ in TFA−$CDCl_3$. The broad upfield resonance for the internal CHs shifts upfield by nearly 1 ppm on addition of TFA.

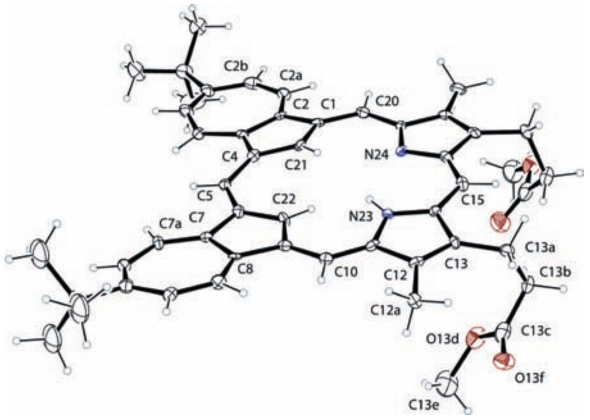
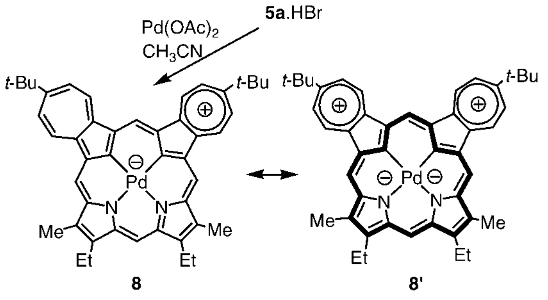


Figure 3. ORTEP-3 drawing (50% probability level, hydrogen atoms drawn arbitrarily small, one of four crystallographically independent molecules, bromide counterion not shown) of diazuliporphyrin hydrobromide **5b**·HBr.

Scheme 2



8 **8'**

Mesoionic palladium complex

The formation of the palladium(II) complex of **5a** was also investigated (Scheme 2). The best results were obtained when **5a**·HBr was heated with a slight excess of $Pd(OAc)_2$ in acetonitrile, and following chromatography on silica gel, the polar metallo-derivative **8** was isolated in 26% yield. In addition to forming two carbon−palladium bonds under mild conditions, this species must exist as an unprecedented mesoionic structure in order to accommodate the palladium(II) cation. Again, this system must possess extensive tropylium character, as represented in canonical forms **8** and **8′**. Proton NMR data for **8** could only be obtained in DMSO-d_6 (Figure 4), but in this solvent the complex displayed a similar diatropic ring current to the parent system and the *meso*-protons gave rise to three downfield resonances at 7.9 (1H, s), 8.8 (2H, s), and 10.0 ppm (1H, s). The symmetry of this system is evident in the proton and carbon-13 NMR

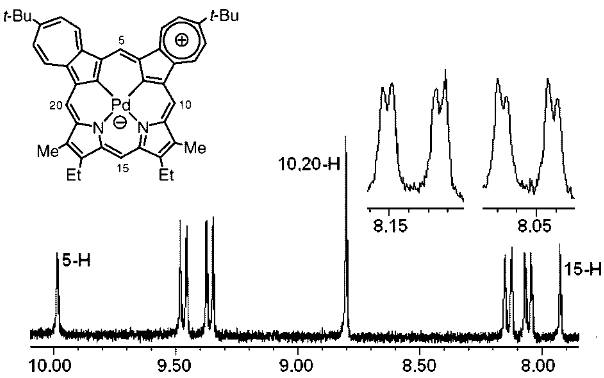


Figure 4. Partial 400 MHz proton NMR spectrum of **8** in DMSO-d_6 showing details of the aromatic region. The downfield shifts indicate that the palladium complex retains significant diatropic character.

spectra for **8**, and FAB MS confirmed the presence of a palladium atom. The structure of **8** was confirmed by single-crystal X-ray diffraction analysis of a partial chloroform solvate. Bond parameters for only one of the two crystallographically independent molecules are shown in Figure 5; however, there are no significant differences in the values obtained for these two molecules. The data for **8**·0.6CHCl$_3$ confirms a macrocycle containing two azulene moieties, each coordinated along with the two pyrrole moieties to a central palladium(II) ion. The distances (0.118 Å rms) at which skeletal atoms lie from the plane defined by PdL$_4$ classify the porphyrin skeleton as slightly saddled, although this is slightly less than the value (0.293 Å rms) observed for a related palladium(II) monoazuliporphyrin complex.[7a] As the framework bond distances are consistent with a somewhat localized π-bonding model, the planarity must primarily be dictated by constraints of metal atom binding, namely the Pd(II) size, square-planar coordination, and optimal Pd−N and Pd−C bond lengths.

In conclusion, unusual mesoionic diazuliporphyrins have been synthesized and the spectroscopic data demonstrate that this system possesses tropylium and porphyrin-like aromatic characteristics. In addition, the formation and structural characterization of a stable palladium(II) organometallic derivative has been accomplished.

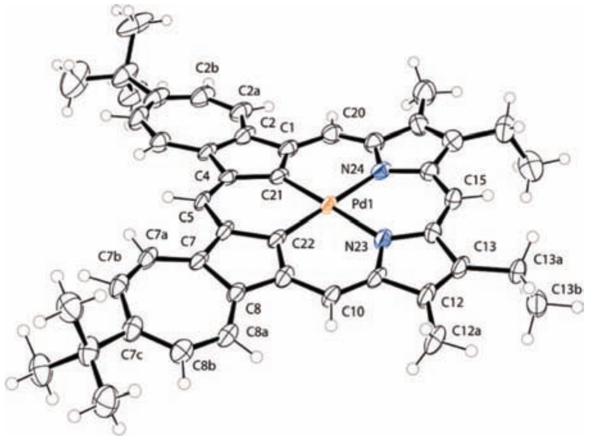


Figure 5. ORTEP-3 drawing (50% probability level, hydrogen atoms drawn arbitrarily small, one of two crystallographically independent molecules) of palladium complex **8**. Selected bond lengths (Å): Pd1−C21 1.960(4), Pd1−C22 1.969(5), Pd1−N24 2.058(4), Pd1−N23 2.075(4), C1−C2 1.451(6), C2−C3 1.427(7), C3−C4 1.445(6), C4−C21 1.432(6), C21−C1 1.438(7), C4−C5 1.395(6), C5−C6 1.398(6), C6−C7 1.434(7), C7−C8 1.452(6), C8−C9 1.445(6), C9−C22 1.425(6), C22−C6 1.438(6), C9−C10 1.415(6), C10−C11 1.360(6), C11−C12 1.470(6), C12−C13 1.331(7), C13−C14 1.471(6), C14−C15 1.380(7), C15−C16 1.388(7), C16−C17 1.457(7), C17−C18 1.364(7), C18−C19 1.456(7), C19−C20 1.373(7), C20−C1 1.415(7), C11−N23 1.386(6), N23−C14 1.365(6), C16−N24 1.371(6), N24−C19 1.385(6). Selected bond angles (deg): C21−Pd1−C22 89.1(2), C22−Pd1−N23 90.7(2), N23−Pd1−N24 88.9(2), N24−Pd1−C21 91.4(2).

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Supporting Information Available: Experimental procedures, selected UV−vis, ^{1}H NMR and ^{13}C NMR spectra, and crystallographic data for **5b**·HBr and **8** are provided. This material is available free of charge via the Internet at http://pubs.acs.org.

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