Adaptation of the Rothemund Reaction for Carbaporphyrin Synthesis: Preparation of *meso*-Tetraphenylazuliporphyrin and Related Benzocarbaporphyrins**

Denise A. Colby and Timothy D. Lash*[a]

Abstract: Electrophilic substitution of azulene has recently been shown to provide the means by which carbon–carbon bonds can be generated to form novel macrocyclic systems such as calixazulenes. These studies inspired us to develop a "one-pot" Rothemund-type synthesis of *meso*-tetraphenylazuliporphyrin. Azuliporphyrins, a group of cross-conjugated carbaporphyrinoids that exhibit intriguing chemistry and metallation properties, have previously only been available by multistep syntheses. In this work, azulene, pyrrole and benzaldehyde were shown to react in a 1:3:4 ratio in the presence of boron trifluoride etherate to give *meso*-tetraphenylazuliporphyrin **7a**. The free base shows only a minor diatropic ring current, but addition of TFA generates the related dication which shows greatly enhanced diatropicity where the internal CH shifts from $\delta = +3.35$ to -0.5 ppm. Addition of pyrrolidine to **7a** gave rise to a carbaporphyrin adduct which showed a porphyrin-like UV/Vis spectrum and the internal CH shifted further upfield to give a resonance near $\delta = -5.7$ ppm. Treatment of **7a** with *tert*-butyl hydroperoxide in the presence of potassium hydroxide afforded a mixture of benzocarbaporphyrins **9a–c**. These tetraphenylcarbaporphyrins were fully aromatic by NMR spectroscopy and gave typical porphyrin-type UV/Vis spectra with a strong Soret band near 446 nm. This new methodology makes these important porphyrin analogues readily available for further study.

Keywords: azulenes · azuliporphyrins · carbaporphyrins · porphyrinoids · Rothemund reaction

Introduction

Carbaporphyrinoids (e.g. benzocarbaporphyrins **1**),[1] porphyrin-like molecules with carbon rings in place of one or more of the usual pyrrole units, have considerable potential in the synthesis of organometallic derivatives[2–4] and the stabilization of unusual oxidation levels.[2–5] Furthermore, these porphyrin analogues exhibit unusual reactivity[6] and commonly show strong absorptions above 700 nm that make them potentially useful as photosensitizers for photodynamic therapy applications.[1, 6] The related N-confused porphyrins **2** are easily prepared by using modified Rothemund-type reaction conditions,[7] but macrocycles with carbocyclic rings have to this point only been available by stepwise routes and for this reason are not as easily accessible.[1, 8] In Rothemund chemistry,[9] pyrrole is condensed with an aldehyde, most commonly an aromatic aldehyde, to afford *meso*-tetrasubstituted porphyrins **3**. In perhaps the most versatile version of this chemistry, developed by Lindsey and co-workers, equimolar quantities of pyrrole and the aldehyde are reacted at room temperature in the presence of the Lewis acid $BF_3 \cdot Et_2O$ to generate a hexahydroporphyrin or porphyrinogen, and subsequent dehydrogenation with DDQ or chloranil affords the porphyrin **3**.[10] The chemistry is remarkable in that four pyrrole units and four aldehyde moieties are selectively combined to generate the porphyrin macrocycle. This involves the formation of a total of eight carbon–carbon bonds by selective electrophilic substitution at the α positions of the individual pyrrole rings. If one of the linkages occurs at a β position while the other seven connections are α, the resulting product would be the N-confused porphyrin system **2**. In the course of our studies on the synthesis of carbaporphyrinoid systems, we have examined the application of azulene in the synthesis of novel macrocyclic systems.[11–13] Azulene favors electrophilic substitution at the 1- and 3-positions, which are structurally equivalent to the α positions in pyrrole (Scheme 1), and we speculated that this system could be utilized in the formation of porphyrin-like ring systems. Recently, we demonstrated that azulene reacts with paraformaldehyde in the presence of florisil to give calix[4]azulene **4** in excellent yields.[11] This result indicates that azulene's reactivity may allow it to be a suitable component for Rothemund-type condensations. Azuliporphyrin **5** has pre-

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[**] Conjugated macrocycles related to the porphyrins, Part 23; for Part 22 see ref. [2].

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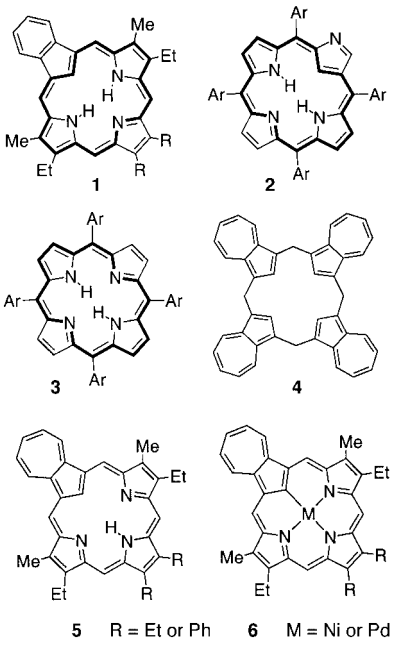
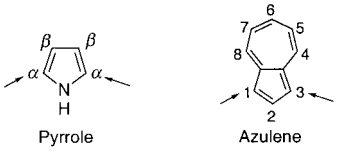


viously been synthesized by the "[3+1]" methodology[12, 13] and this cross-conjugated porphyrinoid shows unique chemistry,[14] including the ability to form organometallic complexes **6**.[3] The possibility of forming azuliporphyrins under Rothemund conditions was appealing, as this would make this system readily available for further study. We now report the realization of this concept.[15]

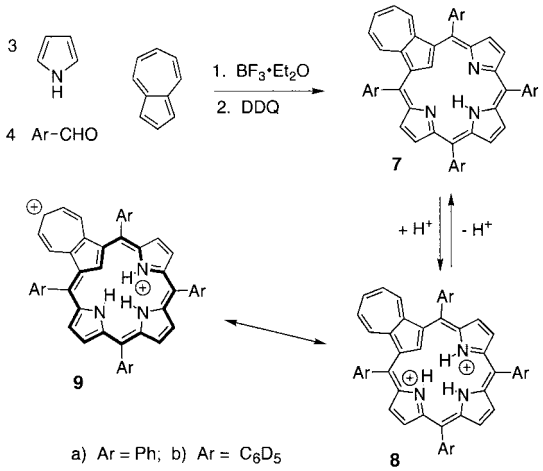


Scheme 1. Preferred sites for electrophilic substitution in pyrrole and azulene.

Results and Discussion

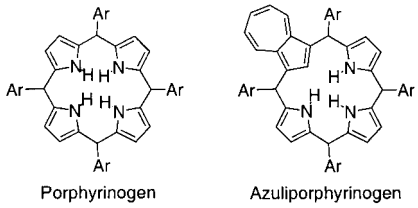
Azulene (0.29 mmol), pyrrole, and benzaldehyde were combined in a molar ratio of 1:3:4 in chloroform (120 mL) and condensed in the presence of boron trifluoride etherate at room temperature under nitrogen for 16 hours (Scheme 2). Following oxidation with DDQ and extraction, the crude products were purified by chromatography on Grade III basic alumina eluting with dichloromethane. Initially a fraction corresponding to tetraphenylporphyrin eluted, followed by trace amounts of carbaporphyrin by-products, and then a brown fraction corresponding to *meso*-tetraphenylazuliporphyrin **7a** was collected (Scheme 2).

Recrystallization from chloroform/methanol gave lustrous green flaky crystals of the desired macrocycle in 10–11% yield. The yield was raised to 13% under more dilute conditions in 480 mL of chloroform. It is noteworthy that the blue azulene color persisted for several hours in the early stages on this reaction sequence. Under these types of



Scheme 2. Rothemund synthesis of *meso*-tetraphenylazuliporphyrin.

conditions, optimal tetraphenylporphyrin formation is known to occur after only one hour,[16] but this is clearly not the case in the present chemistry. These observations suggest that porphyrinogen formation (the precursor to porphyrin) occurs more rapidly than azuliporphyrinogen formation (the precursor to **7a**), but that under equilibrium conditions a substantial amount of the latter product accumulates (Scheme 3). Therefore, prior to DDQ oxidation, the formation of the azulene containing macrocycle appears to be under thermodynamic rather than kinetic control.



Scheme 3. Structures of hexahydroporphyrinoid intermediates.

Tetraphenylazuliporphyrin **7a** differs somewhat from its *meso*-unsubstituted counterparts,[13] although many of the same spectroscopic and chemical trends are evident. The UV/Vis spectrum for tetraphenylazuliporphyrin shows broad, ill-defined bands between 350 and 550 nm and weaker broad absorptions through the remainder of the visible region (Figure 1). However, addition of TFA generated a far more porphyrin-like spectrum, with a strong Soret-like band at 519 nm (Figure 1). This is attributed to the formation of the dication **8a** which favors resonance contributors such as **9a** with tropylium and carbaporphyrin characteristics.

The proton NMR spectrum of **7a** shows only a small diatropic ring current (Figure 2). The internal CH appears at $\delta = 3.35$ ppm, compared with $\delta = 1.3$ ppm for **5**,[12] while the NH resonance is observed near 5 ppm. The decrease in the macrocyclic ring current is attributable to the presumed decrease in planarity for **7a** due to crowding around the azulene unit from the flanking phenyl substituents. The downfield region of the spectrum is moderately complex due to the presence of two types of phenyl units. In order to simplify the spectrum, azulene and pyrrole were treated with

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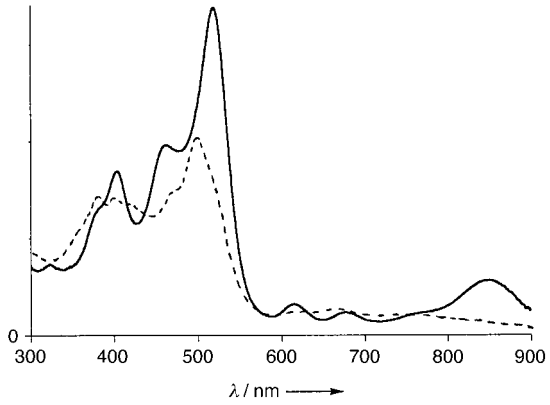
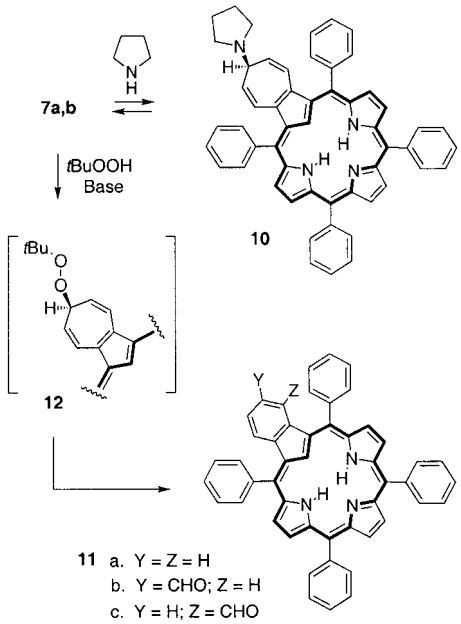


Figure 1. UV/Vis spectra of azuliporphyrin **7a** in chloroform (•••• free base) and 1% TFA/$CHCl_3$ (—— dication).

perdeuterobenzaldehyde to give **7b**. This sample allowed the azulene and pyrrole protons of the macrocycle to be clearly observed (Figure 2). The central pyrrole ring gave a 2H singlet at $\delta = 7.61$ ppm, while the remaining pyrrole units produced two 2H doublets ($J = 4.8$ Hz) at 7.32 and 7.96 ppm. The external azulene protons gave rise to a 2H triplet at 6.93 ppm, a 1H triplet at 7.26 ppm and doublet at 7.64 ppm ($J = 10$ Hz). These values are all consistent with a much reduced diatropic ring current in **7a** than was observed in the alkyl substituted azuliporphyrins **5**.[12] The ^{13}C NMR spectrum in $CDCl_3$ confirms that the macrocycle has a plane of symmetry and the expected 22 carbon resonances were observed between 115 and 166 ppm. Addition of TFA to **7a** gave rise to dication **8a** and as expected this showed a dramatic increase in the macrocyclic ring current as evidenced by the proton NMR spectrum. The inner CH shifted upfield to $\delta = -0.5$ ppm, while the NH protons resonated at $\delta = +2.5$ and $+1.1$ ppm. However, these upfield shifts were again significantly smaller than those noted for the dication derived from **5**.[13] The downfield region shows significant broadening to some of the phenyl resonances due to conformational restrictions, although these sharpen up as the temperature is increased from 20 °C to 55 °C. The ^{13}C NMR spectrum for the dication also gave rise to 22 resonances, although some broadening was observed for two of these peaks at room temperature.

Addition of pyrrolidine to solutions of **7a** in $CDCl_3$ gave rise to the pyrrolidine adduct **10** (Scheme 4), as had previously been observed for azuliporphyrins **5**.[14] This adduct allows the



Scheme 4. Oxidative ring contraction of azuliporphyrin **7a** to afford *meso*-tetraphenylbenzocarbaporphyrins **11**.

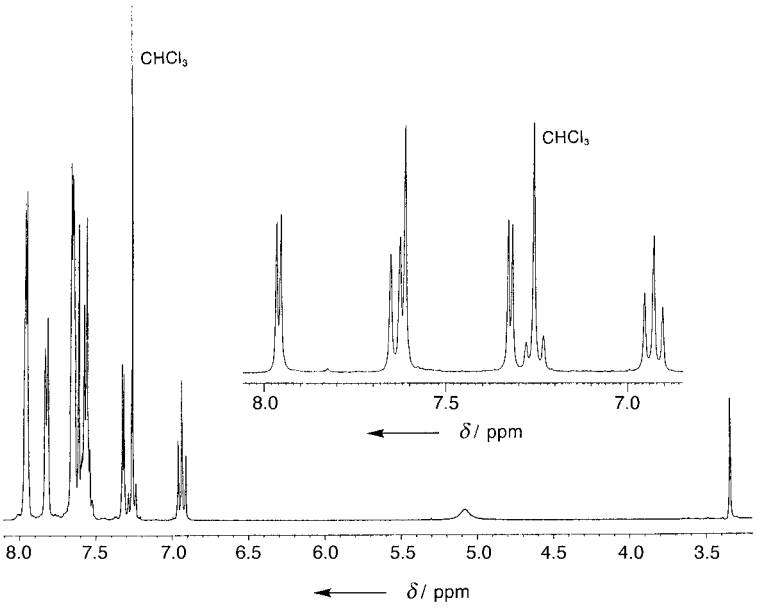


Figure 2. 400 MHz proton NMR spectrum of *meso*-tetraphenyl-azuliporphyrin **7a** in deuteriochloroform at 21 °C. Inset: downfield region for the corresponding deuterated azuliporphyrin **7b** showing only the external azulene and pyrrole resonances. The 1H triplet at 7.26 ppm coincides exactly with the chloroform peak in these spectra. This triplet shifts slightly upfield to 7.25 ppm at 45 °C.

molecule to take on the characteristics of a fully aromatic carbaporphyrin. The proton NMR spectrum for **7a** (Figure 3) in the presence of pyrrolidine shows the internal CH upfield at $\delta = -5.69$ ppm, while the pyrrolic protons resonate downfield between 8.4 and 8.8 ppm.

The UV/Vis spectrum of **7a** in the presence of pyrrolidine (Figure 4a) also confirmed the production of a porphyrin-like species showing the appearance of a strong Soret band at 438 nm, followed by series of Q bands through the remainder of the visible region. Previously, we have shown that the susceptibility of azuliporphyrins to nucleophilic substitution can be utilized in their conversion to true carbaporphyrins.[14]

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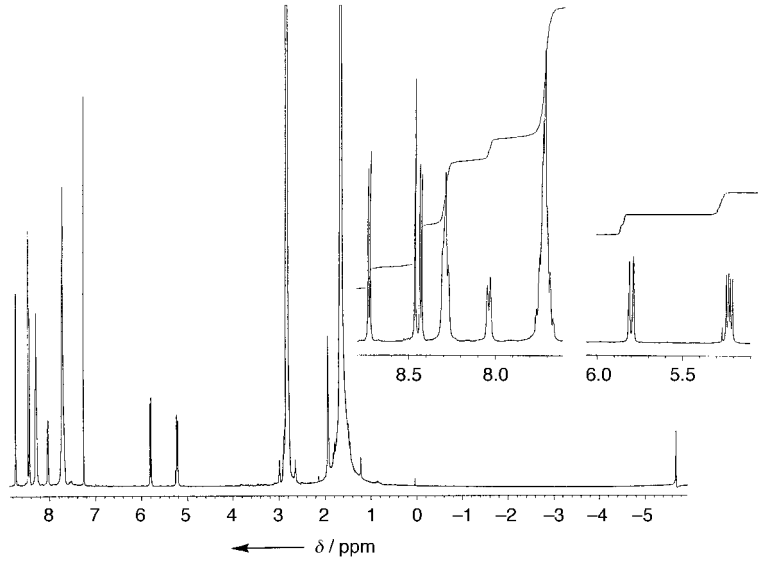

Figure 3. 400 MHz proton NMR spectrum of **7a** in the presence of pyrrolidine showing the formation of the carbaporphyrin adduct **10**. Inset (right): details of downfield region.

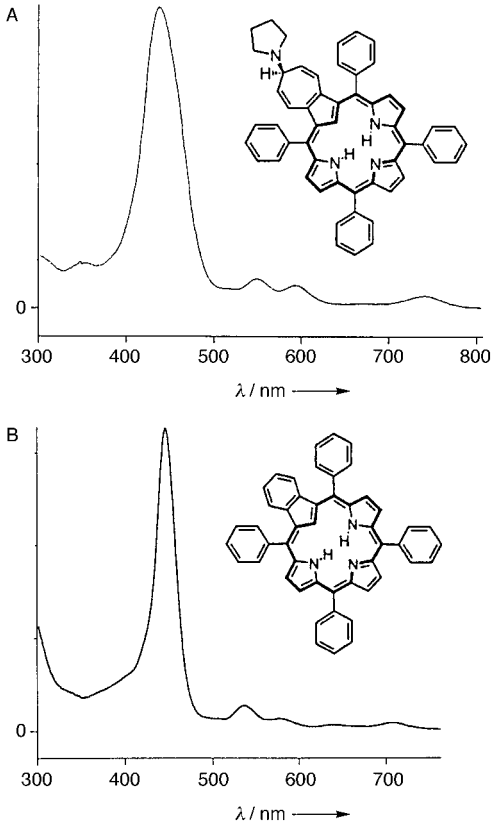

Figure 4. A) UV/Vis spectrum of azuliporphyrin **7a** in 1% pyrrolidine/chloroform showing the carbaporphyrin-type absorptions for adduct **10**. B) UV/Vis spectrum of tetraphenylbenzocarbaporphyrin **11a** in chloroform.

The possibility of synthesizing tetraarylcarbaporphyrins in this fashion is particularly appealing. Reaction of **7a** with *tert*-butyl hydroperoxide in the presence of potassium hydroxide gave a mixture of three benzocarbaporphyrins **11a–c** in a combined yield of approximately 50% (Scheme 4). The chemistry presumably involves initial attack by the *tert*-butyl hydroperoxide anion to give the addition product **12**, and subsequent Cope rearrangement and elimination of *tert*-butyl alcohol produces the observed products.[14] Carbaporphyrins **11a** and **11b** are the major products and are isolated in roughly equal quantities after separation by flash chromatography. The minor product **11c** presumably results from nucleophilic attack at a different position on the seven-membered ring.

The new carbaporphyrins show strong ring currents, although once again these are not quite as large as those observed for the *meso*-unsubstituted series.[8c,g] In the 400 MHz proton NMR spectrum of **11a** (Figures 5 and 6), the internal CH is observed at $\delta = -5.3$ ppm, while the external pyrrolic protons resonate between 8.5 and 8.8 ppm. The NMR spectrum also shows that **11a** retains a plane of symmetry. The NH protons give rise to a very broad resonance near -3 ppm. The broadening of the NH varied

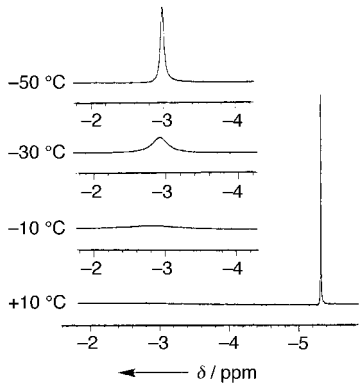

Figure 5. Upfield region for the 400 MHz NMR spectrum of **11a** in $CDCl_3$ at $+10\,^{\circ}C$, $-10\,^{\circ}C$, $-30\,^{\circ}C$, and $-50\,^{\circ}C$.

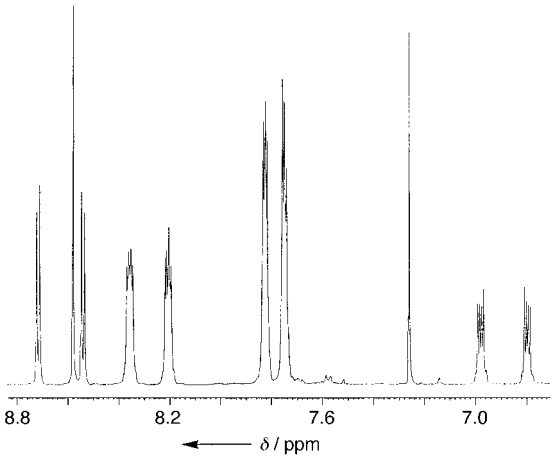

Figure 6. Downfield region for the 400 MHz NMR spectrum of **11a** at $20\,^{\circ}C$ in $CDCl_3$.

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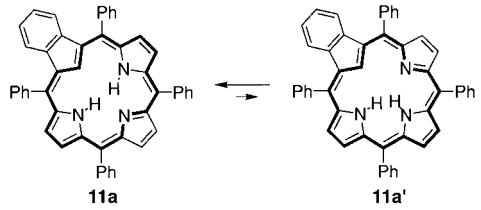
somewhat with concentration, but also sharpened up as the temperature of the NMR solution was lowered to −50 °C (Figure 5). Unlike *meso*-unsubstituted benzocarbaporphyrins,[8c,g] the chemical shift for the internal CH resonance was not affected by concentration or temperature, possibly because the *meso*-substituents inhibit aggregation in solution. In addition, no other changes are observed in the NMR spectrum for **11a** at lower temperatures. These data are consistent with **11a** favoring the specific tautomer shown in Scheme 5 where the two pyrrole hydrogens flank a central



Scheme 5. Tautomers of benzocarbaporphyrin **11a**.

pyrrolene nitrogen rather than the alternate species **11a′**. This tautomeric preference has also been noted for carbaporphyrins **1**.[8c,g] The plane of symmetry for **11a** was confirmed by ^{13}C NMR spectroscopy. The internal carbon resonated at $\delta =$ 107.3 ppm, while the remaining 20 types of sp^2 carbon atoms gave rise to 19 resonances over the range of $\delta = 118-$ 156 ppm. The UV/Vis spectrum for **11a** (Figure 4a) shows a Soret band at 446 nm and a series of four Q bands that extend beyond 700 nm. As had previously been reported for *meso*-unsubstituted carbaporphyrins **1**,[8c,g] addition of TFA to solutions of **11a** leads to the formation of monocations and at higher acid concentrations C-protonated dications are generated. The major formyl carbaporphyrin product **11b** gave similar spectroscopic properties, although the proton NMR spectrum was far more complex due to the lack of symmetry in this structure (Figure 7). The benzo unit gave rise

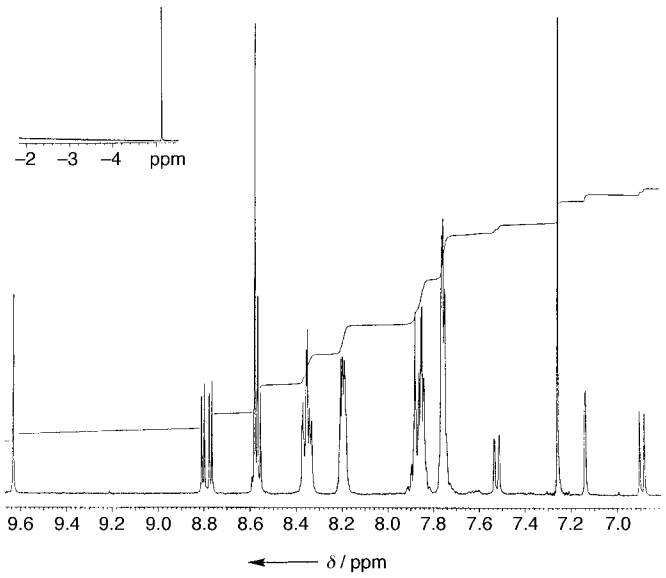


Figure 7. Downfield region for the 400 MHz NMR spectrum of **11b** at 20 °C in $CDCl_3$. Inset (left): Upfield region showing the characteristic internal CH resonance at $\delta = -5.1$ ppm.

to three diagnostic 1 H resonances at $\delta = 6.90$ (d, $J = 8.4$ Hz), 7.14 (d, $J = 1.2$ Hz) and 7.52 (dd, $J = 8.4$, 1.2 Hz), while the aldehyde appeared as a singlet at $\delta = 9.63$ ppm. The minor aldehyde by-product **11c** was also spectroscopically characterized and gave data that were consistent with the proposed structure.

Conclusion

The synthesis of *meso*-tetraphenylazuliporphyrin directly from azulene makes this organometallic ligand readily available for the first time.[17] In addition, the straightforward conversion of azuliporphyrin **7a** to benzocarbaporphyrins **11a–c** also makes the equally important carbaporphyrin system easily accessible. Furthermore, efficient syntheses of other porphyrinoid systems such as corroles and expanded porphyrins under modified Rothemund conditions have been reported recently,[18] and it may be possible to prepare analogous azulene-containing macrocycles using our approach. In any case, the results from our work are likely to herald an explosion of activity in the field of carbaporphyrinoid research.[19, 20]

Experimental Section

Azulene was prepared by a modification of the procedure reported by Hafner and Meinhardt.[21] *tert*-Butyl hydroperoxide (5–6 M in decane) and [D_6]benzaldehyde were purchased from Aldrich. UV spectra were obtained on a Varian Cary 1 Bio UV-Visible spectrophotometer. NMR spectra were recorded on a Varian Gemini-400 NMR spectrometer. Mass spectral data were obtained from the Mass Spectral Laboratory, School of Chemical Sciences, University of Illinois at Urbana-Champaign, supported in part by a grant from the National Institute of General Medical Sciences (GM27029). Elemental analyses were obtained from the School of Chemical Sciences Microanalysis Laboratory at the University of Illinois.

***meso*-Tetraphenylazuliporphyrin (7a)**: Azulene (150 mg, 1.172 mmol), benzaldehyde (480 mg), and pyrrole (240 mg) were dissolved in chloroform (480 mL), and the resulting solution was purged with nitrogen for 10 min. A 10 % solution of $BF_3 \cdot Et_2O$ in chloroform (1.2 mL) was then added, and the reaction stirred for 16 h under nitrogen in the dark. DDQ (800 mg) was added, and the solution was stirred for an additional 1 h. The mixture was washed with water and sat. $NaHCO_3$ solution, back extracting with chloroform at each stage, and the combined organic solutions were dried over sodium sulfate, filtered, and evaporated under reduced pressure. The residue was purified by column chromatography on Grade III basic alumina (10 % hexanes/CH_2Cl_2). Tetraphenylporphyrin eluted initially, followed by trace amounts of carbaporphyrins, and then a deep reddish-brown fraction corresponding to the azuliporphyrin product was collected. Recrystallization from chloroform/methanol afforded the tetraphenylporphyrinoid (77 mg, 10 %) as dark green crystals. M.p. 310–312 °C (decomp); UV/Vis (1 % $Et_3N/CHCl_3$): λ_{max} ($\log_{10}\varepsilon$) = 380 (4.64), 402 (4.65), 419 (4.62), 474 (sh, 4.66), 498 (4.80), 670 nm (3.94); UV/Vis (1 % TFA/$CHCl_3$): λ_{max} ($\log_{10}\varepsilon$) = 323 (4.35), 405 (4.71), 462 (4.77), 519 (5.01), 614 (3.99), 676 (3.86), 850 nm (4.23); UV/Vis (1 % pyrrolidine/$CHCl_3$): λ_{max} ($\log_{10}\varepsilon$) = 348 (4.34), 437 (5.15), 549 (4.14), 594 (4.03), 669 (3.58), 740 nm (3.76); ^1H NMR (400 MHz, $CDCl_3$, 45 °C): $\delta = 3.35$ (s, 1 H), 5.10 (br s, 1 H), 6.92 (t, 2 H, $J =$ 10 Hz), 7.25 (t, 1 H, $J = 9.8$ Hz), 7.32 (d, 2 H, $J = 4.4$ Hz), 7.52–7.60 (m, 6 H), 7.61 (s, 2 H), 7.63–7.68 (m, 8 H), 7.81–7.84 (m, 4 H), 7.95–7.97 (m, 6 H); ^1H NMR (400 MHz, TFA/$CDCl_3$, 55 °C, dication): $\delta = -0.33$[22] (s, 1 H), 1.27 (s, 1 H), 2.71 (s, 2 H), 7.64 (t, 2 H, $J = 10$ Hz), 7.77–7.87 (m, 7 H), 7.92–8.00 (m, 10 H), 8.14–8.16 (m, 4 H), 8.19 (s, 2 H), 8.32 (br m, 4 H), 8.43 (d, 2 H, $J = 4.8$ Hz); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 115.55$, 123.51, 127.03,

127.39, 127.56, 127.64, 128.32, 129.26, 130.28, 130.63, 133.80, 134.95, 135.17, 135.67, 138.99, 139.22, 139.63, 141.54, 142.81, 144.13, 155.66, 165.72; ^{13}C NMR (100 MHz, TFA/$CDCl_3$, 22 °C): δ = 114.42, 117.58, 127.69, 128.84, 129.49, 130.28, 130.31, 131.45, 132.00, 132.70, 136.29, 136.46, 137.5 (v br), 138.64, 138.77, 138.99, 141.07, 143.04, 143.88, 144.98, 146.80, 151.27; HRMS (FAB): calcd for $C_{50}H_{33}N_3$+H: *m/z*: 676.2753; found: 676.2756; elemental analysis calcd (%) for $C_{50}H_{33}N_3 \cdot \frac{1}{2}CHCl_3$: C 85.83, H 4.77, N 6.00; found: C 85.77, H 4.51, N 6.03.

[D_{20}]-*meso*-Tetraphenylazuliporphyrin (7b): Prepared under the foregoing conditions from azulene and [D_6]benzaldehyde. ^{1}H NMR ($CDCl_3$): δ = 3.36 (s, 1H), 5.10 (br s, 1H), 6.93 (t, 2H, *J* = 10 Hz), 7.26 (t, 1H, *J* = 10 Hz), 7.32 (d, 2H, *J* = 4.8 Hz), 7.61 (s, 2H), 7.64 (d, 2H, *J* = 10 Hz), 7.96 (d, 2H, *J* = 4.8 Hz). HRMS (FAB): calcd for $C_{50}H_{13}D_{20}N_3$+H: *m/z*: 696.4008; found: 696.4008.

Oxidative ring contraction of 7a: A solution of KOH (240 mg) in methanol (30 mL) was added to **7a** (28 mg) in dichloromethane (30 mL), followed by the addition of a solution of *tert*-butyl hydroperoxide (45 μL) in decane (5–6 M). The mixture was stirred at room temperature in the dark under nitrogen for 2 h. The mixture was diluted with chloroform, washed twice with water, dried over sodium sulfate, filtered and evaporated to dryness. The residue was loaded onto a silica gel flash chromatography column with CH_2Cl_2, and eluted with a gradient of CH_2Cl_2 and $CHCl_3$. Three carbaporphyrin fractions corresponding to **11a** (least polar), **11b** and **11c** (most polar) were collected. Each sample was recrystallized from chloroform/methanol to give pure **11a** (6.5 mg, 24%), **11b** (6.2 mg, 21.5%) and **11c** (0.2 mg, 0.5%).

Selected physical and spectroscopic data for *meso*-tetraphenylcarbaporphyrins: **11a**: m.p. 338 °C (decomp); UV/Vis (1% $Et_3N/CHCl_3$; free base): λ_{max} ($\log_{10}\varepsilon$) = 446 (5.27), 537 (4.20), 581 (3.94), 635 (3.68), 707 nm (3.71); UV/Vis (0.1% TFA/$CHCl_3$, monocation): λ_{max} ($\log_{10}\varepsilon$) = 342 (4.50), 466 (5.09), 654 (4.14), 720 nm (4.00); UV/Vis (50% TFA/$CHCl_3$, dication): λ_{max} ($\log_{10}\varepsilon$) = 458 (5.15), 560 (3.93), 614 (3.97), 677 nm (4.30); ^{1}H NMR (400 MHz, $CDCl_3$): δ = −5.31 (s, 1H), 6.78–6.82 (m, 2H), 6.96–7.00 (m, 2H), 7.73–7.77 (m, 6H), 7.81–7.84 (m, 6H), 8.18–8.22 (m, 4H), 8.33–8.37 (m, 4H), 8.53 (d, *J* = 5 Hz, 2H), 8.58 (s, 2H), 8.71 (d, *J* = 5 Hz, 2H); ^{1}H NMR (400 MHz, 50% TFA/$CDCl_3$, dication): δ = −2.22 (s, 2H), 3.1 (v br s, 1H), 3.20 (s, 2H), 7.25–8.04 (m, 24H), 8.30–8.36 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 107.81, 118.46, 122.45, 123.75, 125.42, 126.28, 126.85, 127.10, 127.84, 128.16, 128.50, 133.79, 134.99, 135.30, 138.28, 138.41, 138.57, 142.04, 142.27, 155.19; HRMS (EI): calcd for $C_{49}H_{33}N_3$: *m/z*: 663.2674; found: 663.2681.

Compound 11b: m.p. 310.5–311 °C (decomp); UV/Vis (1% $Et_3N/CHCl_3$; free base): λ_{max} ($\log_{10}\varepsilon$) = 455 (5.31), 540 (4.29), 580 (3.82), 647 (3.57), 712 nm (3.82); UV/Vis (50% TFA/$CHCl_3$): λ_{max} ($\log_{10}\varepsilon$) = 473 (5.15), 544 (4.16), 648 (4.12), 726 nm (4.03); ^{1}H NMR (400 MHz, $CDCl_3$): δ = −5.12 (s, 1H), −2.7 (v br, 2H), 6.90 (d, *J* = 8.4 Hz, 1H), 7.14 (d, *J* = 1.2 Hz, 1H), 7.52 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.75–7.77 (m, 6H), 7.84–7.89 (m, 6H), 8.18–8.22 (m, 4H), 8.33–8.38 (m, 4H), 8.55 (d, *J* = 5.2 Hz, 1H), 8.56–8.58 (overlapping s and d, 3H), 8.77 (d, *J* = 4.8 Hz, 1H), 8.81 (d, *J* = 4.8 Hz, 1H), 9.63 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 108.40, 118.60, 118.82, 123.17, 123.28, 123.84, 125.74, 125.84, 126.40, 126.87, 127.18, 127.42, 127.57, 127.98, 128.31, 128.84, 128.94, 132.53, 132.86, 134.11, 134.16, 134.22, 135.00, 135.41, 138.05, 138.16, 139.23, 139.37, 141.55, 141.64, 141.99, 142.02, 142.41, 155.75, 155.86, 192.78; FAB MS: *m/z*: 692.4 [M^++H]; HRMS (EI): calcd for $C_{50}H_{33}N_3O$: *m/z*: 691.2624; found: 691.2626.

Compound 11c: UV/Vis (1% $Et_3N/CHCl_3$; free base): λ_{max} ($\log_{10}\varepsilon$) = 457 (5.19), 548 (4.14), 592 (3.90), 658 (3.51), 723 nm (3.80); UV/Vis (50% TFA/$CHCl_3$): λ_{max} ($\log_{10}\varepsilon$) = 475 (5.02), 547 (3.96), 655 (4.13), 734 nm (4.01); ^{1}H NMR (400 MHz, $CDCl_3$): δ = −4.88 (s, 1H), −2.3 (v br, 2H), 7.01 (dd, ^3J = 8 Hz, ^4J = 1 Hz, 1H), 7.11 (t, *J* = 8 Hz, 1H), 7.48 (dd, ^3J = 8 Hz, ^4J = 1 Hz, 1H), 7.72 (t, *J* = 7.2 Hz, 1H), 7.74–7.83 (m, 8H), 7.87–7.90 (m, 3H), 8.14–8.17 (m, 2H), 8.21–8.24 (m, 2H), 8.37–8.41 (m, 5H), 8.42 (d, *J* = 4.8 Hz, 1H), 8.54 (d, *J* = 7.2 Hz, 2H), 8.67 (d, *J* = 4.8 Hz, 1H), 8.80 (d, *J* = 4.8 Hz, 1H), 9.78 (s, 1H); HRMS (FAB): calcd for $C_{50}H_{33}N_3O$ + H: *m/z*: 692.2702; found: 692.2700.

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