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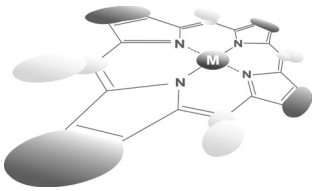

An alternative synthesis of benziporphyrins starting from isophthaloyl chloride

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ABSTRACT: An alternative route to benziporphyrins has been developed. Reaction of an α-unsubstituted pyrrole ethyl ester with isophthaloyl chloride in the presence of aluminum chloride afforded a diketone that underwent selective reduction with diborane to give a benzitripyrrane. Cleavage of the ethyl esters with sodium hydroxide in refluxing ethylene glycol, followed by acid catalyzed condensation with a pyrrole dialdehyde and oxidation with DDQ, generated the targeted benziporphyrin product. Spectrophotometric titration of the benziporphyrin with trifluoroacetic acid (TFA) demonstrated the sequential formation of mono- and dicationic species. At lower dilutions, the free base benziporphyrin showed unusually strong $^{5}J_{HH}$ coupling between two adjacent methyl substituents, indicating that the connecting unit has substantial olefinic characteristics.

KEYWORDS: carbaporphyrinoids, benziporphyrins, "3 + 1" syntheses, aromaticity, protonation.

INTRODUCTION

Carbaporphyrinoid systems [1, 2], including true carbaporphyrins (*e.g.* **1a** and **1b**) [3, 4], azuliporphyrins (*e.g.* **2**) [5], tropiporphyrins (*e.g.* **3**) [6] and benziporphyrins (*e.g.* **4**) [7], have been widely investigated over the last 20 years (Chart 1). Benziporphyrins **4** have emerged as an important class of porphyrin analogs with unique spectroscopic and chemical properties [7]. The benziporphyrin system essentially differs from regular porphyrins by having a benzene unit in place of one of the pyrrole moieties. This results in cross-conjugated structures that are devoid of macrocyclic aromatic properties [8]. However, electron-donating substituents such as methoxy groups introduce a degree of diatropic character [9] and protonated benziporphyrins also appear to possess significant diamagnetic ring currents [9–15]. Benziporphyrins act as dianionic organometallic ligands, forming stable derivatives with Ni(II), Pd(II), Pt(II), *etc.* [13–20]. In addition, *meso*-tetraarylbenziporphyrins undergo selective oxidation reactions with silver(I) acetate [12, 17], and rhodium(III) derivatives can undergo ring contraction reactions to afford metalated carbaporphyrins [21]. Furthermore, dihydrobenziporphyrins have been utilized as components of nanomolecular arrays [22] and have shown promise as fluorescent zinc cation detectors [23].

Several routes to benziporphyrins have been described. Acid catalyzed "3 + 1" MacDonald condensation of isophthalaldehyde with tripyrranes **5**, followed by oxidation with DDQ, affords *meso*-unsubstituted benziporphyrins **4** (Scheme 1) [10, 14]. Alternatively, benzene dicarbinols **6** react with 3 equivalents of pyrrole and 2 equivalents of an aromatic dialdehyde in the presence of boron trifluoride etherate to give *meso*-tetraarylbenziporphyrins **7** (Scheme 1) [11, 17]. These strategies have been adapted for the synthesis of heterobenziporphyrins [13,15], naphthiporphyrins [14] and fully aromatic oxybenziporphyrins [10, 14, 24, 25]. In order to further extend our inquiries into these types of porphyrinoid analogs, we have investigated the development of new synthetic routes to benziporphyrins and related systems. Herein, we report an alternative strategy for preparing benziporphyrins using isophthaloyl chloride as the key precursor.

◊ SPP Full member in good standing.

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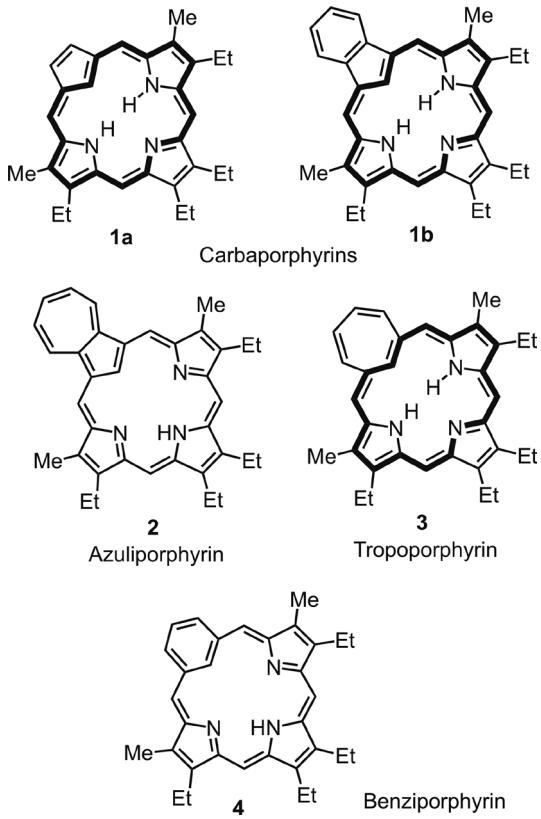
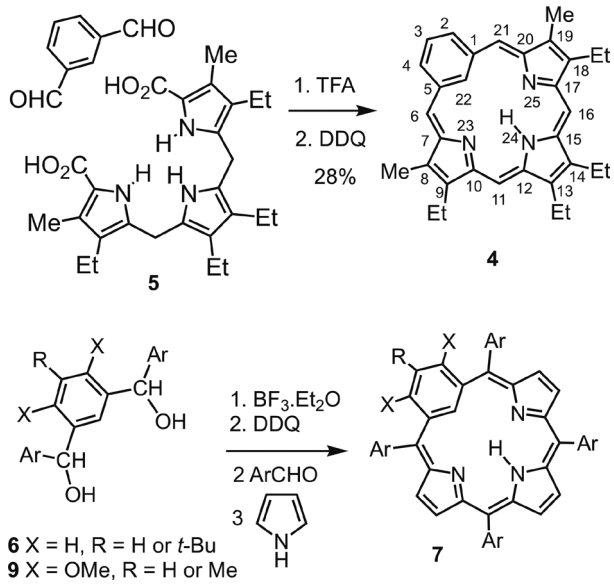


Chart 1. Selected carbaporphyrinoid structures



Scheme 1. Earlier syntheses of benziporphyrins

EXPERIMENTAL

Melting points are uncorrected. NMR spectra were recorded using a 500 MHz NMR spectrometer and were run at 300 K unless otherwise indicated. ^{1}H NMR values are reported as chemical shifts δ, relative integral, multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad peak) and coupling constant (*J*). Chemical shifts are reported in parts per million (ppm) relative to $CDCl_3$ (^{1}H residual $CHCl_3$ δ 7.26, ^{13}C $CDCl_3$ triplet δ 77.23) and coupling constants were taken directly from the spectra. NMR assignments were made with the aid of ^{1}H–^{1}H COSY, HSQC, DEPT-135 and nOe difference proton NMR spectroscopy. 2D experiments were performed by using standard software. High-resolution mass spectra (HRMS) were carried out by using a double focusing magnetic sector instrument.

1,3-Bis(5-ethoxycarbonyl-3,4-dimethyl-2-pyrroloyl) benzene (16). Aluminum chloride (3.00 g, 22.5 mmol) was added to a solution of ethyl 3,4-dimethylpyrrole-2-carboxylate (1.50 g, 8.97 mmol) and isophthaloyl chloride (1.00 g, 4.93 mmol) in carbon disulfide (50 mL) and the resulting mixture was stirred under reflux overnight. The solvent was removed under reduced pressure, water (100 mL) was cautiously added, and the mixture was allowed to stand overnight. The mixture was extracted with dichloromethane and washed sequentially with water, 10% hydrochloric acid, 10% sodium bicarbonate solution, and brine. The organic layer was dried over sodium sulfate and the solvent removed under reduced pressure. The residue was purified by column chromatography on silica gel eluting with dichloromethane and then recrystallized from 95% ethanol to give the diketone (1.05 g, 2.26 mmol, 50%) as a yellow crystalline solid, mp 146–147 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ_H, ppm 1.38 (6H, t, J = 7.2 Hz, 2 × CH_2CH_3), 1.99 (6H, s, 2 × pyrrole 3-Me), 2.28 (6H, s, 2 × pyrrole 4-Me), 4.36 (4H, q, J = 7.2 Hz, 2 × OCH_2), 7.62 (1H, t, J = 7.7 Hz, 5-H), 7.88 (2H, dd, J = 1.7, 7.7 Hz, 4,6-H), 8.01 (1H, t, J = 1.7 Hz, 2-H), 9.42 (2H, br s, 2 × NH). ^{13}C NMR (125 MHz, $CDCl_3$): δ_C, ppm 10.2 (2 × pyrrole 3-Me), 11.6 (2 × pyrrole 4-Me), 14.6 (2 × CH_2CH_3), 61.0 (2 × OCH_2), 123.7, 127.91, 127.94, 129.08 (5-CH), 129.15 (2-CH), 129.6, 132.0 (4,6-CH), 139.6, 161.2 (2 × ester C=O), 186.4 (2 × bridge C=O). HR-MS (EI) *m/z* 464.19445 (calcd. for $C_{26}H_{28}N_2O_6$ $[M]^+$ 464.19474).

1,3-Bis(5-ethoxycarbonyl-3,4-dimethyl-2-pyrrolylmethyl)benzene (17). Boron trifluoride etherate (3.5 mL) in THF (8 mL) was added dropwise to a stirred solution of diketone **16** (500 mg, 1.08 mmol) and sodium borohydride (409 mg, 10.8 mmol) in THF (11 mL) under a nitrogen atmosphere. After the mixture was stirred for 1.5 h at room temperature, the solvent was removed under reduced pressure, methanol was added and the resulting mixture stirred under reflux for 1 h. The methanol was removed on a rotary evaporator and the residue dispersed between ether and water. The ether layer was separated and washed with 10% sodium bicarbonate solution and then with water. The ether solution was dried over magnesium sulfate and the solvent removed under reduced pressure. The residue was purified on a silica column eluting with dichloromethane. The product fraction was evaporated under reduced pressure to give the benzitripyrrane

(240 mg, 0.55 mmol, 51%) as a pale reddish solid, mp 184–185 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ_H, ppm 1.32 (6H, t, J = 7.1 Hz), 1.94 (6H, s, 2 × pyrrole 3-Me), 2.27 (6H, s, 2 × pyrrole 4-Me), 3.87 (2 × bridge-CH_2), 4.26 (4H, q, J = 7.1 Hz, 2 × OCH_2), 6.92 (1H, br, 2-H), 6.9 (2H, br dd, J = 1.6, 7.6 Hz, 4,6-H), 7.22 (1H, t, J = 7.6 Hz, 5-H), 8.38 (2H, br s, 2 × NH). ^{13}C NMR (125 MHz, $CDCl_3$): δ_C, ppm 9.1 (2 × pyrrole 3-Me), 10.8 (2 × pyrrole 4-Me), 14.8 (2 × CH_2CH_3), 32.5 (2 × bridge-CH_2), 59.9 (2 × OCH_2), 117.7, 117.8, 126.9 (4,6-CH), 127.6, 128.8 (2-CH), 129.4 (5-CH), 131.7, 139.2, 161.9 (2 × ester C=O). HR-MS (EI) *m/z* 436.23534 (calcd. for $C_{26}H_{32}N_2O_4$ $[M]^+$ 436.23621).

1,3-Dihydroxymethylbenzene dimethylsulfonate (12) [26]. Methanesulfonyl chloride (1.7 mL, 22 mmol) was added dropwise over a period of 5 min to a stirred mixture of 1,3-benzenedimethanol (1.38 g, 10.0 mmol) and triethylamine (2.8 mL, 20 mmol) in dichloromethane (40 mL) while maintaining the temperature below 5 °C with the aid of a salt-ice bath. The resulting mixture was stirred at room temperature for 1 h. The solution was sequentially washed with water, 2 M hydrochloric acid and brine, and then dried over sodium sulfate. The solvent was removed on a rotary evaporator and the residue treated with ether, suction filtered and then washed with additional ether to give the dimesylate (2.218 g, 7.54 mmol, 75%) as a white solid, mp 91–92 °C. The product was used in the next step without further purification. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H, ppm 2.98 (6H, s), 5.25 (4H, s), 7.45–7.48 (4H, m). ^{13}C NMR (125 MHz, $CDCl_3$): δ_C, ppm 38.5, 70.8, 129.0, 129.7, 134.6. ^{13}C NMR (125 MHz, d_6-DMSO): δ_C, ppm 37.2, 71.2, 128.8, 129.20, 129.26, 134.8. HR-MS (EI) *m/z* 294.0233 (calcd. for $C_{10}H_{14}O_6S_2$ $[M]^+$ 294.0232).

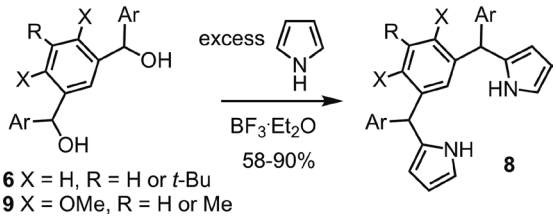
1,3-Bis(2-pyrrolylmethyl)benzene (11). Dimesylate **12** (612 mg, 2.08 mmol) was dissolved in a mixture of pyrrole (10 mL) and dichloromethane (20 mL) and the mixture stirred at room temperature under nitrogen overnight. The solvent was removed on a rotary evaporator, initially using a water aspirator and then a vacuum pump. The residue was purified on a silica gel column eluting with a mixture of dichloromethane, hexanes and triethylamine in a ratio of 60:40:1. The product fraction consisted of a mixture of benzitripyrranes. Further column chromatography enabled the separation of the desired isomer and following removal of the solvent under reduced pressure the benzitripyrrane (20.7 mg, 0.088 mmol, 4.2%) was isolated as an off-white solid, mp 74–76 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ_H, ppm 3.94 (4H, s, 2 × bridge-CH_2), 5.98–6.00 (2H, m, 2 × pyrrole 3-H), 6.14–6.16 (4H, m, 2 × pyrrole 4-H), 6.65–6.67 (2H, m, 2 × pyrrole 5-H), 7.06–7.09 (3H, m, 2,4,6-H), 7.23–7.26 (1H, m, 5-H), 7.79 (2H, br s, 2 × NH). ^{13}C NMR (500 MHz, $CDCl_3$): δ_C, ppm 34.2 (2 × bridge-CH_2), 106.7 (2 × pyrrole 3-CH), 108.6 (2 × pyrrole 4-CH), 117.2 (2 × pyrrole 5-CH), 127.0 (2-CH or 4,6-CH), 129.1 (5-CH), 129.2 (2-CH or 4,6-CH), 130.8, 140.1. HR-MS (EI) *m/z* 236.1313 (calcd. for $C_{16}H_{14}N_2$ $[M]^+$ 236.1315).

8,9,13,14,18,19-Hexamethylbenziporphyrin (20). Benzitripyrrane diethyl ester **17** (100 mg, 0.215 mmol) was refluxed with sodium hydroxide (40 mg) in ethylene glycol under nitrogen for 1 h. The mixture was cooled to room temperature, diluted with water, and extracted with hexanes. The hexane solution was washed with water, dried over sodium sulfate and the solvent removed under reduced pressure. The resulting intermediate was used immediately for the next step in the synthesis.

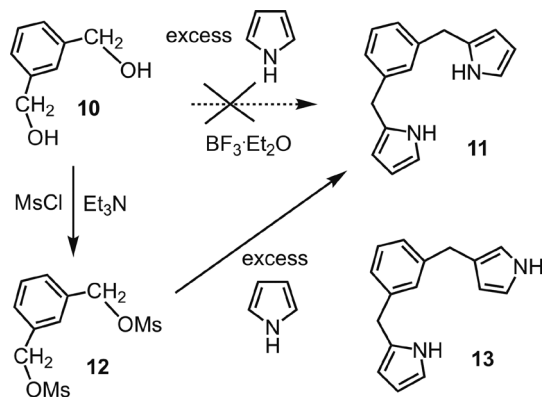
The deprotected benzitripyrrane was dissolved in dichloromethane, 3,4-dimethylpyrrole-2,5-dicarbaldehyde [27, 28] (36.6 mg, 0.229 mmol) was added, and nitrogen was bubbled through the mixture for 5 min. TFA (1 mL) was added and the resulting solution was stirred for 2 h in the dark. DDQ (51 mg, 0.22 mmol) was then added and the mixture stirred for a further 1 h. The solution was washed with 5% sodium bicarbonate solution and water, and then dried over sodium sulfate. The solvent was removed under reduced pressure and the residue purified by column chromatography on grade 3 alumina eluting with dichloromethane. Recrystallization from chloroform-methanol gave the benziporphyrin (21 mg, 0.052 mmol, 24%) as dark blue crystals, mp >300 °C. UV-vis (1% Et_3N-CH_2Cl_2, free base): λ_{max}, nm (log ε) 309 (4.71), 379 (4.80), 610 (sh, 3.69), 658 (3.79), 714 (3.63). UV-vis (5 equivalents TFA-CH_2Cl_2, monocation **20**H$^+$): λ_{max}, nm (log ε) 395 (4.84), 486 (3.29), 522 (3.59), 562 (3.70), 684 (sh, 3.45), 756 (3.93), 837 (4.22). UV-vis (1% TFA-CH_2Cl_2, dication **20**H_2^{2+}): λ_{max}, nm (log ε) 308 (4.56), 398 (4.84), 529 (3.36), 571 (3.34), 723 (3.86), 779 (3.87). ^{1}H NMR (500 MHz, $CDCl_3$): δ_H, ppm 2.32 (6H, q, J = 1.0 Hz, 9,18-CH_3), 2.39 (6H, s, 13,14-CH_3), 2.41 (6H, q, J = 1.0 Hz, 8,19-CH_3), 6.52 (6H, s, 11,16-H), 7.25 (2H, s, 6,21-H), 7.74 (1H, t, J = 7.6 Hz, 3-H), 7.90 (1H, br t, 22-H), 7.96 (2H, dd, J = 1.6, 7.6 Hz, 2,4-H), 8.93 (1H, br s, 2 × NH). ^{1}H NMR (500 MHz, TFA-$CDCl_3$, dication **20**H_2^{2+}): δ_H, ppm 2.476 (6H, br s, 9,18-CH_3), 2.485 (6H, s, 13,14-CH_3), 2.63 (6H, br s, 8,19-CH_3), 5.22 (1H, br s, 22-H), 6.98 (6H, s, 11,16-H), 7.95 (1H, t, J = 7.7 Hz, 3-H), 8.00 (2H, s, 6,21-H), 8.24 (2H, dd, J = 1.2, 7.7 Hz, 2,4-H), 9.52 (1H, br s, 2 × NH). ^{13}C NMR (125 MHz, $CDCl_3$): δ_C, ppm 10.2 (2 × CH_3), 10.5 (2 × CH_3), 10.7 (2 × CH_3), 92.8 (11,16-CH), 122.4 (6,21-CH), 125.0 (22-CH), 128.9 (3-CH), 134.2, 134.90, 134.96, 137.4 (2,4-CH), 141.9, 149.0, 157.2, 169.7. ^{13}C NMR (125 MHz, TFA-$CDCl_3$, dication **20**H_2^{2+}): δ_C, ppm 9.5 (2 × CH_3), 10.0 (2 × CH_3), 10.6 (8,19-CH_3), 94.2 (11,16-CH), 109.8 (22-CH), 127.6 (6,21-CH), 131.7, 133.5 (3-CH), 135.9, 139.8 (2,4-CH), 141.5, 143.4, 148.7, 155.2, 163.0. HR-MS (EI) *m/z* 405.22113 (calcd. for $C_{28}H_{27}N_3$ $[M]^+$ 405.22050).

RESULTS AND DISCUSSION

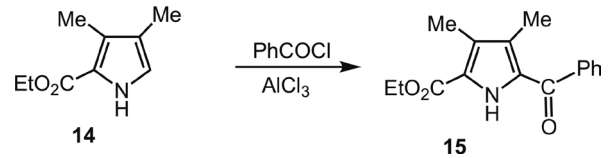
In an earlier study, good yields of benzitripyrranes **8** were prepared by reacting benzene dicarbinols **6** or **9** with pyrrole in the presence of a catalytic amount of



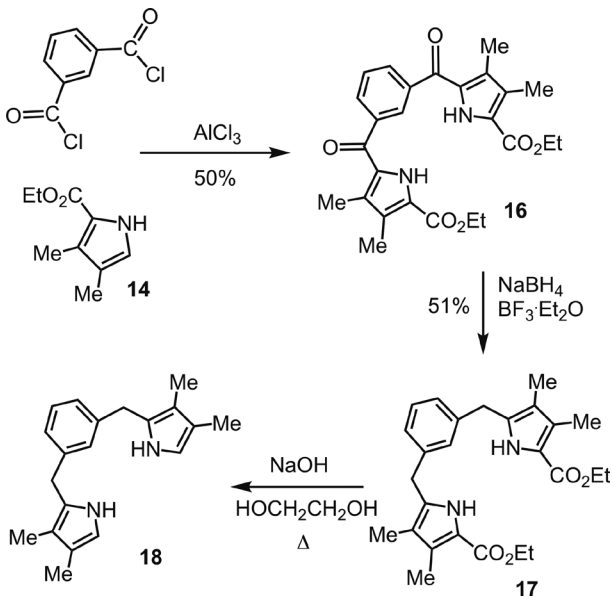
Scheme 2. Synthesis of aryl-substituted benzitripyrranes



Scheme 3. Synthesis of an unsubstituted benzitripyrrane



Scheme 4. Preparation of a 2-benzoylpyrrole

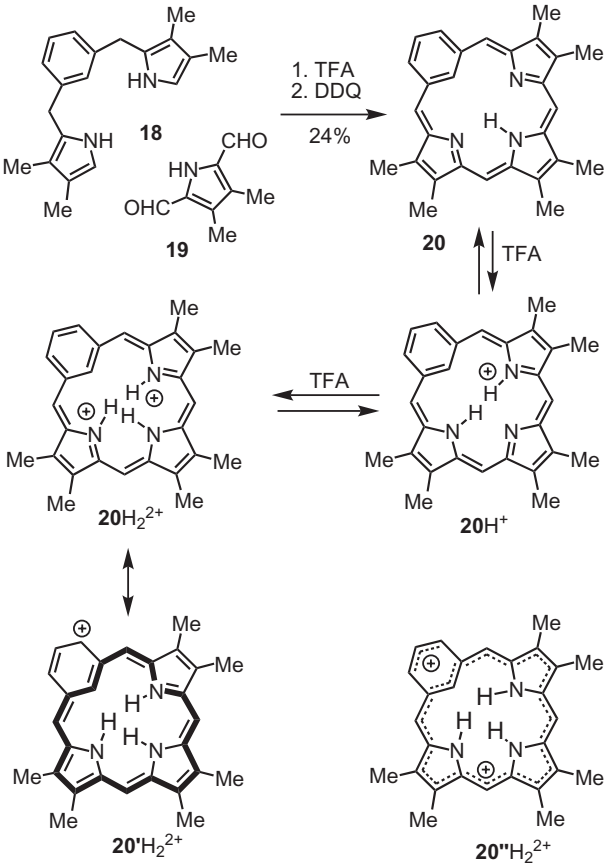


Scheme 5. Synthesis of a benzitripyrrane from isophthaloyl chloride

boron trifluoride etherate in refluxing 1,2-dichloroethane (Scheme 2). However, attempts to carry out similar condensations with 1,3-benzenedicarbinol **10** failed to give unsubstituted benzitripyrrane **11** (Scheme 3). In order to increase the reactivity of the benzene precursor, **10** was converted into the corresponding dimesylate **12**. Further condensation was carried out by reacting **12** with excess pyrrole in dichloromethane at room temperature overnight. This resulted in a mixture of products including the targeted benzitripyrrane **11** and an isomeric *N*-confused benzitripyrrane **13**. Separation of these mixtures could be achieved by column chromatography on silica gel. However, **11** was only isolated in 4.2% yield, in part due to the difficulties encountered in separating the benzitripyrrane from its isomer **13**. In principle, the formation of *N*-confused isomers could be prevented by using β-substituted pyrroles in place of pyrrole. However, a large excess of pyrrole is needed to circumvent further reaction to give oligomeric species and this makes such a strategy impractical.

In order to overcome these difficulties and generate a benzitripyrrane intermediate, isophthaloyl chloride was utilized to generate key carbon–carbon linkages. It had previously been demonstrated that α-unsubstituted pyrrole ester **14** could be reacted with benzoyl chloride in the presence of aluminum chloride to form benzoylpyrrole **15** (Scheme 4) [29]. This approach was adapted for the reaction of isophthaloyl chloride with 2 equivalents of pyrrole ethyl ester **14a**. The reactants were refluxed with aluminum chloride in carbon disulfide to afford the dipyrrolyl diketone **16** in 50% yield (Scheme 5). In order to utilize this dipyrrolic derivative in the synthesis of benziporphyrins, it was necessary to selectively reduce the bridging carbonyl groups to methylene units while retaining the integrity of the terminal ester protective groups. This was achieved using diborane [30], which was generated *in situ* by reacting boron trifluoride etherate with sodium borohydride. The resulting benzitripyrrane **17** was isolated in 51% yield. Cleavage of the terminal ester groups with sodium hydroxide in refluxing ethylene glycol afforded the terminally unsubstituted tripyrrane analog **18** and this was immediately reacted with pyrrole dialdehyde **19** in the presence of trifluoroacetic acid (TFA) (Scheme 6). Following neutralization of the solution with triethylamine, the intermediates were oxidized with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ). Purification by column chromatography on grade 3 alumina and recrystallization from chloroform-methanol gave benziporphyrin **20** in 24% yield.

Benziporphyrin **20** produced blue colored solutions and the UV-vis spectrum gave a Soret-like band at 379 nm together with broad absorptions at higher wavelengths. Addition of TFA to solutions of **20** in dichloromethane showed the sequential formation of mono- and dicationic species $\mathbf{20}H^+$ and $\mathbf{20}H_2^{2+}$ (Scheme 6, Figs 1–3). Titration with TFA showed the formation of a species with a slightly intensified Soret-like band at 395 nm and weaker



Scheme 6. Synthesis and protonation of a hexamethylbenziporphyrin

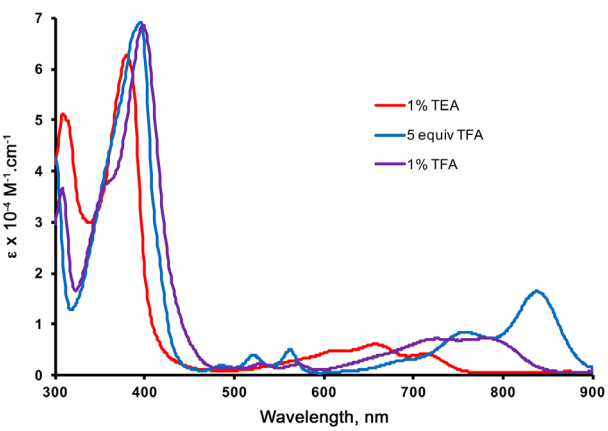


Fig. 1. UV-vis spectra of benziporphyrin **20** in 1% triethylamine (TEA)-dichloromethane (red line, free base), with 5 equivalents of TFA in dichloromethane (blue line, monocation **20**H^+) and in 1% TFA-dichloromethane (purple line, dication **20**H_2^{2+})

broad absorptions that extended well above 800 nm (Fig. 2). The formation of the monocation was complete after the addition of 3 equivalents of TFA and no further protonation was observed with 50 equivalents of TFA. However, at higher concentrations of acid a new species developed that was attributed to dication **20**H_2^{2+} (Fig. 3). This resulted in the loss of the absorption at 837 nm and

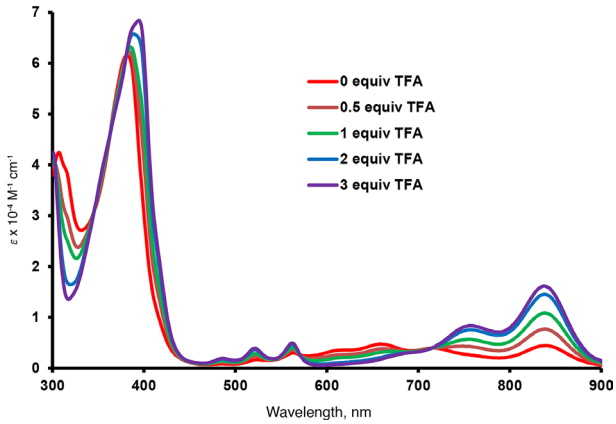


Fig. 2. Benziporphyrin **20** in dichloromethane with 0, 0.5, 1, 2 and 3 equivalents of TFA showing the formation of a monoprotonated species. Even though the dichloromethane was deacidified with basic alumina, some protonation is evident even before addition of TFA

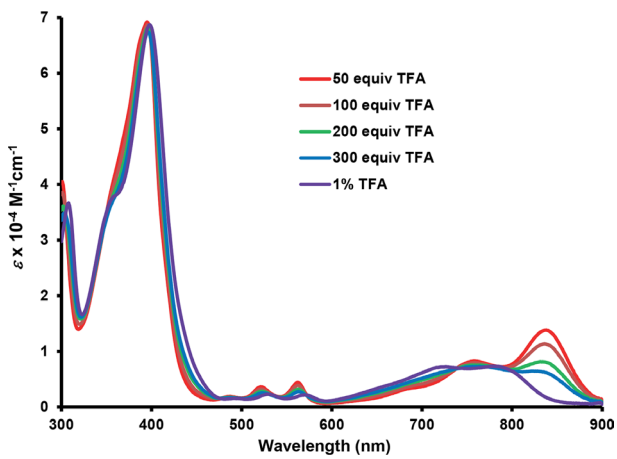


Fig. 3. Benziporphyrin **20** in dichloromethane with 50, 100, 200 and 300 equivalents of TFA and with 1% TFA in CH_2Cl_2 showing the formation of the diprotonated species **20**H_2^{2+}

the emergence of a new peak at 779 nm. The Soret-like band underwent a small bathochromic shift to 398 nm.

As expected, the proton NMR spectrum for **20** in $CDCl_3$ demonstrated the absence of any global aromatic characteristics. The precise chemical shifts for the arene protons varied slightly with concentration but the external and internal protons all showed up between 7.7 and 8.0 ppm (Fig. 4). The *meso*-protons gave rise to two 2H singlets at 6.52 and 7.25 ppm, while the NH appeared at 8.93 ppm, values that are consistent with the absence of a macrocyclic ring current. Unexpectedly, in relatively dilute solutions the 8,19- and 9,18-methyl substituents appeared as two weakly coupled quartets (Fig. 5). This is due to $^5J_{HH}$ or homoallylic coupling between the inequivalent methyl groups. The coupling constant of 1.0 Hz is relatively large for systems of this type and suggests that the 8,9- and 18,19-carbon–carbon bonds have substantial olefinic character. At higher

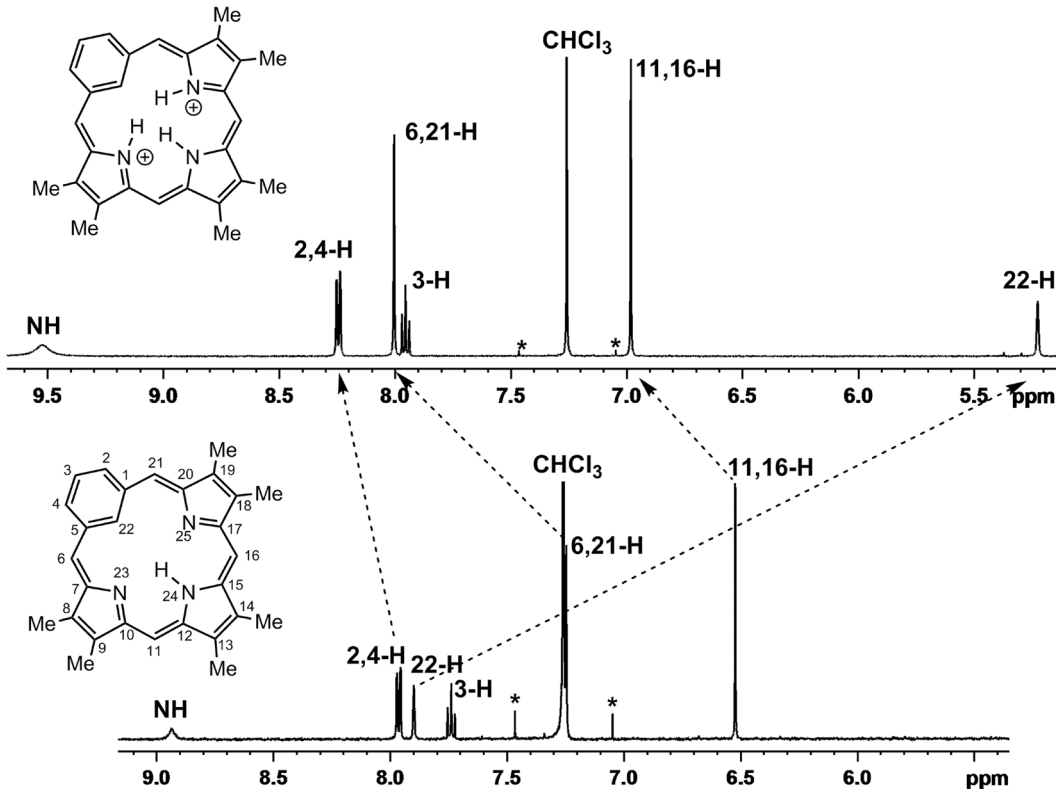


Fig. 4. Partial 500 MHz proton NMR spectra of benziporphyrin **20** and the related dication $\mathbf{20}H_2^{2+}$ in $CDCl_3$ and TFA-$CDCl_3$, respectively, showing the upfield shift to the internal CH proton and the downfield shifts of the external protons upon protonation. * = ^{13}C satellites for the $CHCl_3$ peak

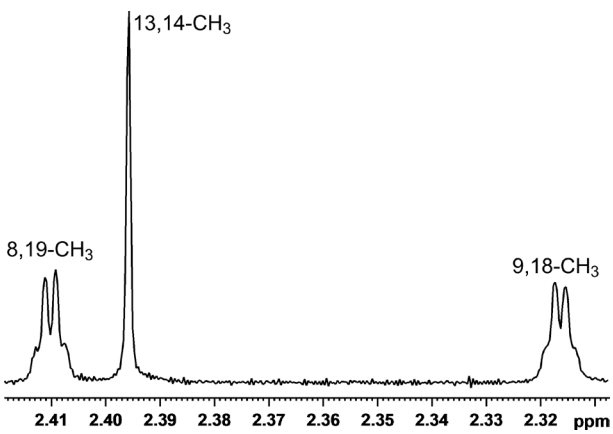


Fig. 5. Partial 500 MHz proton NMR spectrum of benziporphyrin **20** showing long range $^5J_{HH}$ coupling (1.0 Hz) between adjacent methyl substituents

concentrations the methyl resonances were broadened but did not fully resolve into quartets. The carbon-13 NMR spectrum of **20** confirmed the presence of a plane of symmetry. The internal CH was identified at 125.0 ppm, while the *meso*-protons appeared at 92.8 (11,16-CH) and 122.4 ppm (6,21-CH). The identity of **20** was confirmed by high resolution electron impact mass spectrometry. As had been noted previously [10], the mass spectrum shows abnormally large [M + 1] and [M + 2] peaks in addition to the molecular ion. Addition of TFA to **20** resulted in the formation of dication $\mathbf{20}H_2^{2+}$ and the proton NMR spectrum for this species showed the emergence of a diamagnetic ring current (Fig. 4). The internal 22-H shifted upfield from 7.90 ppm to 5.22 ppm, while the *meso*-protons were further deshielded to give 2H singlets at 6.98 and 8.00 ppm. Although the presence of positive charges could account for some of the downfield shift, the pronounced shielding for the internal CH must be due to the macrocycle taking on significant aromatic properties. This analysis has been confirmed by DFT calculations [31]. The aromatic properties of $\mathbf{20}H_2^{2+}$ can be rationalized by resonance contributors such as $\mathbf{20}'H_2^{2+}$ that introduce 18π electron delocalization pathways, although computational analysis is more consistent with contributions from the delocalized hybrid structure $\mathbf{20}''H_2^{2+}$ (Scheme 6) [31]. The signals for the methyl substituents are also shifted downfield by approximately 0.1–0.2 ppm. Two of the methyl resonances are broadened due to $^5J_{HH}$ coupling but in this case they do not resolve into quartets. In the carbon-13 NMR spectrum, the inner CH shifted upfield to 109.8 ppm, while the *meso*-protons appeared at 94.2 (11,16-CH) and 127.6 ppm (6,21-CH).

CONCLUSIONS

An alternative route to benziporphyrins has been developed. Reaction of an α-unsubstituted pyrrole ester with isophthaloyl chloride in the presence of aluminum chloride afforded a diketone and subsequent reduction with diborane gave a benzitripyrrane. Cleavage of the terminal ester functionalities with sodium hydroxide in refluxing ethylene glycol, followed by acid catalyzed condensation with a pyrrole dialdehyde and oxidation with DDQ gave a hexamethyl substituted benziporphyrin in 24% yield. Inequivalent methyl substituents exhibited relatively unusual homoallylic coupling, indicating that the pyrrole bonds have significant olefinic character. Addition of acid afforded a weakly diatropic dicationic species that showed the presence of a global aromatic ring current. The new synthetic strategy shows promise for applications in the synthesis of novel benziporphyrin analogs.

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Supporting information

Selected EI-MS, ^{1}H NMR, ^{1}H–^{1}H COSY, HSQC, DEPT-135, ^{13}C NMR, and UV-Vis spectra are provided as supplementary materials. This material is available free of change *via* the Internet at http://worldscinet.com/jpp/jpp.shtml.

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