[22]Porphyrin-(3.1.1.3), a New Vinylogous Expanded Porphyrin System[†]
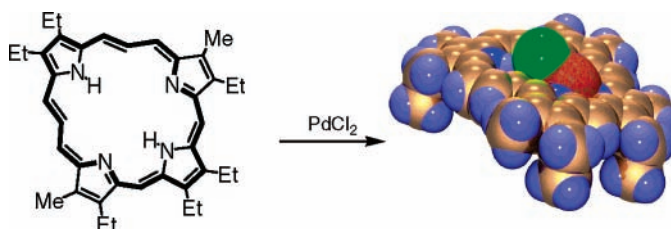
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ABSTRACT

Acid-catalyzed condensation of a pyrrole bisacrylaldehyde with a tripyrrane, followed by oxidation with ferric chloride, gave a [22]porphyrin-(3.1.1.3). This stretched macrocycle shows a strong diamagnetic ring current by ^{1}H NMR spectroscopy and gives red-shifted porphyrin-like UV–vis spectra; coordination with palladium(II) induces an EZ isomerization to accommodate the metal cation while retaining highly diatropic characteristics.

The aromatic character of the porphyrin ring system is dependent upon the presence of a closed 18π-electron substructure within the macrocycle.[1] Porphyrins consist of four pyrrole rings linked by 4 single carbon bridges, but the same type of aromatic characteristics can be obtained by varying the number of bridging atoms or constituent subunits.[2] A series of porphyrin isomers have been investigated where the four bridging carbon atoms are rearranged to give structures such as porphycene (Figure 1) that still possess the [18]annulene substructure.[2–4] Expanded porphyrins with five or more pyrrolic subunits,[5] and contracted structures such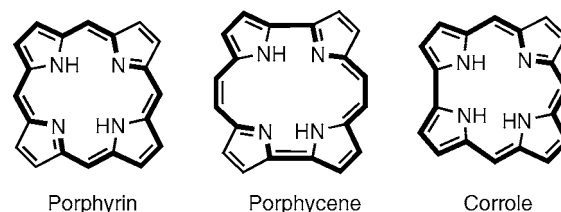 as corroles (Figure 1), have also been shown to possess this type of aromatic character.[6] In fact, variations on the porphyrin system have produced intriguing new macrocycles that often combine their own unique characteristics with

Figure 1. Examples of conjugated tetrapyrroles with [18]annulene substructures.

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[†] Part 39 in the series Conjugated Macrocycles Related to the Porphyrins. For Part 38, see: Lash, T. D.; Colby, D. A.; Graham, S. R.; Chaney, S. T. *J. Org. Chem.* **2004**, *69*, 8851-8864.

(1) Vogel, E. *J. Heterocycl. Chem.* **1996**, *33*, 1461.

(2) (a) Vogel, E.; Köcher, M.; Schmickler, H.; Lex, J. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 257. (b) Vogel, E.; Balci, M.; Pramod, K.; Koch, P.; Lex, J.; Ermer, O. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 928. (c) Sessler, J. L.; Gebauer, A.; Vogel, E. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Academic Press: San Diego, CA, 2000; Vol. 2, pp 1−54.

(3) (a) Sessler, J. L.; Brucker, E. A.; Weghorn, S. J.; Kisters, M.; Shäfer, M.; Lex, J.; Vogel, E. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2308. (b) Aukauloo, M. A.; Guilard, R. *New J. Chem.* **1994**, *18*, 1205.

(4) (a) Callot, H. J.; Rohrer, A.; Tschamber, T. *New J. Chem.* **1995**, *19*, 155. (b) Vogel, E.; Bröring, M.; Scholz, P.; Deponte, R.; Lex, J.; Schmickler, H.; Schaffner, K.; Braslavsky, S. E.; Müller, M.; Pörting, S.; Weghorn, S. J.; Fowler, C. J.; Sessler, J. L. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1651.

(5) Sessler, J. L.; Seidel, D. *Angew. Chem., Int. Ed.* **2003**, *42*, 5134.

(6) Paolesse, R. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Academic Press: San Diego, CA, 2000; Vol. 2, pp 201−232.

porphyrin-type properties. Stretched aromatic porphyrin systems with a total of >5 bridging carbon atoms linking the four pyrrole units were first investigated by Berger and LeGoff.[7] These authors coined the term "platyrin" from the Greek word for flat to describe the stretched macrocycle **1** (Figure 2), which has a 22π-electron substructure, and a
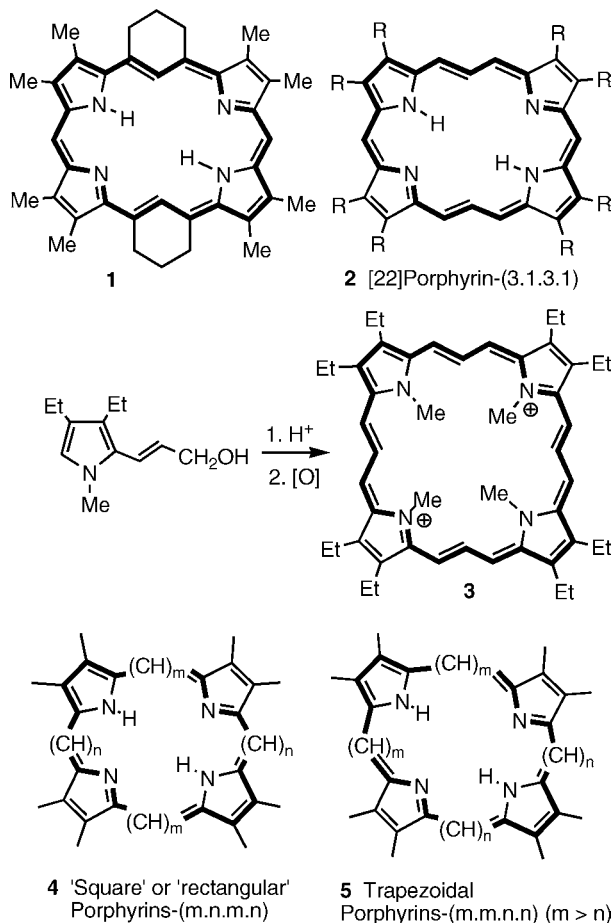

Figure 2. Vinylogous porphyrins.

related 26π e$^-$ conjugated structure.[7,8] More extensive studies were subsequently conducted by Franck on the synthesis of related macrocycles, e.g., **2**, and further expanded systems such as **3** (Figure 2).[9–11] Franck favored the use of an alternative nomenclature where all of these ring systems were designated as porphyrins with the electron count for the aromatic substructure given first in square brackets and the number of bridging carbon atoms between each pyrrole unit listed afterward. Hence, compound **2** is designated [22]-porphyrin-(3.1.3.1), while **3** would be [26]porphyrin-

(3.3.3.3). Impressively, further expanded porphyrins of this type were reported including [34]porphyrin-(5.5.5.5), [26]-porphyrin-(5.1.5.1), and [30]porphyrin-(7.1.7.1).[9–11] These systems have strongly red-shifted absorptions that have potential applications as photosensitizers in photodynamic therapy.[12] In addition, the modified porphyrinoid cores can give insights into porphyrin-type aromaticity[13] as well as providing elongated ligands for generating unusual metal-loderivatives.[14] Inspite of all these studies, all of the previous work in this area has dealt with "rectangular" or "square" shaped porphyrin-like systems of the (*m.n.m.n*) type **4**. No reports on more distorted vinylogous porphyrins-(*m.n.n.m*) **5** with two adjacent bridging units longer than the other two connecting bridges have been reported previously, even though these systems are likely to have rather different properties due to conformational factors. In this paper, we report the first example of a trapezoidal bis-vinylogous porphyrin system of this type and present preliminary results on the metalation of this unusual porphyrinoid structure.

The "3 + 1" variant of the MacDonald condensation provides an ideal methodology[15] for synthesizing the new macrocycle [22]porphyrin-(3.1.1.3) **6**. The necessary pyrrole bisacrylaldehyde intermediate **7** was prepared by using a vinylogous Vilsmeier−Haack reaction (Scheme 1). 3,4-

Scheme 1
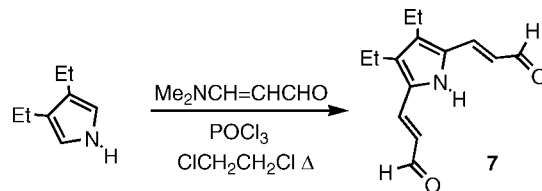
Diethylpyrrole[16] and 3-dimethylaminoacrolein were treated with POCl$_3$ in 1,2-dichloroethane, and the resulting mixture was refluxed for 90 min. Following hydrolysis with an aqueous sodium acetate solution, the highly insoluble dial-dehyde was isolated in >70% yield. The brown solid was essentially pure by NMR spectroscopy and could be used directly to prepare the stretched porphyrin system. Tripyrrane **8**[17] was treated with TFA then diluted with CH$_2$Cl$_2$, and then 1 equiv of the dialdehyde was added to the stirred solution (Scheme 2). After stirring for 16 h, the reaction mixture was washed with aqueous ferric chloride to oxidize the interme-

(7) Berger, R. A.; LeGoff, E. *Tetrahedron Lett.* **1978**, *19*, 4225.

(8) LeGoff, E.; Weaver, O. G. *J. Org. Chem.* **1987**, *52*, 710.

(9) Franck, B.; Nonn, A. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1795.

(10) König, H.; Eickmeier, C.; Möller, M.; Rodewald, U.; Franck, B. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1393.

(11) (a) Gosmann, M.; Franck, B. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 1100. (b) Knübel, G.; Franck, B. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1170. (c) Eickmeier, C.; Franck, B. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2213.

(12) (a) Beckmann, S.; Wessel, T.; Franck, B.; Hönle, W.; Borrmann, H.; von Schnering, H.-G. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1395. (b) Bonnett, R. *Chem. Soc. Rev.* **1995**, *24*, 19. (c) Pandey, R. K.; Zheng, G. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Academic Press: San Diego, CA, 2000; Vol. 6, pp 157−230.

(13) Lash, T. D. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Academic Press: San Diego, CA, 2000; Vol. 2, pp 125−199.

(14) Sessler, J. L.; Gebauer, A.; Weghorn, S. J. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Academic Press: San Diego, CA, 2000; Vol. 2, pp 55−124.

(15) Lash, T. D. *Chem. Eur. J.* **1996**, *2*, 1197.

(16) Sessler, J. L.; Mozaffari, A.; Johnson, M. R. *Org. Synth.* **1991**, *70*, 68.

(17) (a) Sessler, J. L.; Johnson, M. R.; Lynch, V. *J. Org. Chem.* **1987**, *52*, 4394. (b) Lash, T. D. *J. Porphyrins Phthalocyanines* **1997**, *1*, 29.

Scheme 2
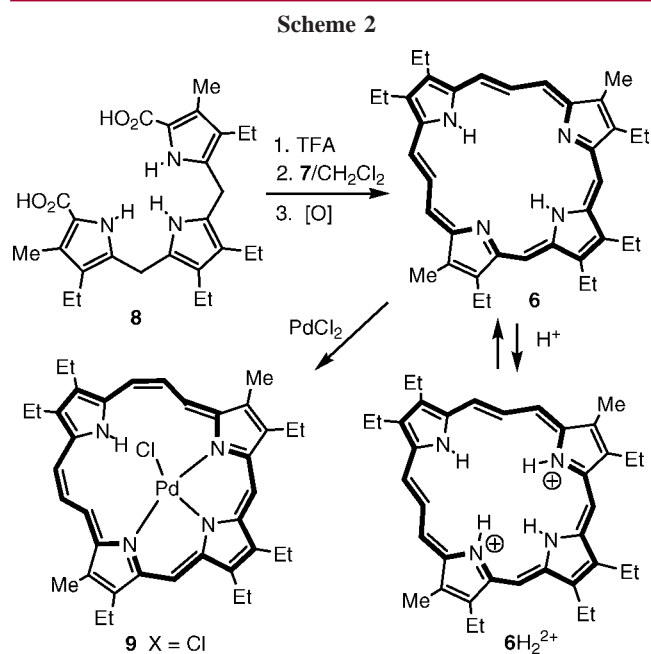
diate,[18] and the macrocyclic product was purified by column chromatography on grade 3 alumina. A major green fraction was collected, and following recrystallization from chloroform−hexanes, the new porphyrin analogue was isolated in 32% yield.

The presence of two adjacent three-carbon bridges could potentially lead to so much distortion that the system would not be able to maintain continuous conjugation over the macrocycle. However, the proton NMR spectrum of **6** in TFA-CDCl$_3$ showed that this macrocycle has a very large diatropic ring current where the expanse from upfield to downfield for the proton resonances ($\Delta\delta$) is almost 23 ppm (Figure 3). The proposed geometry of the three-carbon
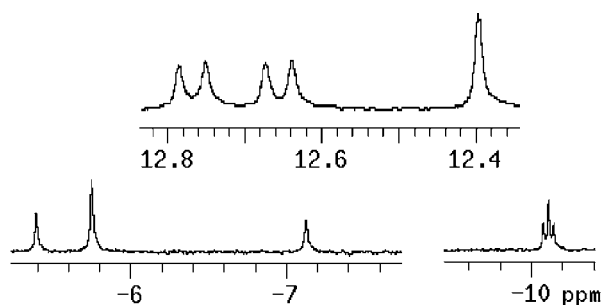

Figure 3. Partial 400 MHz proton NMR spectrum of vinylogous porphyrin **6**H$_2$$^{2+}$ in TFA-CDCl$_3$ showing the upfield and downfield regions.

bridges places the central CH inside the macrocyclic cavity

(18) (a) Lash, T. D.; Richter, D. T.; Shiner, C. M. *J. Org. Chem.* **1999**, *64*, 7973. (b) Richter, D. T.; Lash, T. D. *J. Org. Chem.* **2004**, *69*, 8842.

and this gives a 2H triplet at −10.2 ppm. The stretched porphyrin is in its diprotonated or dicationic form **6**H$_2$$^{2+}$ under these conditions, and the four NHs are observed at −7.2 (2H), −5.8 (1H), and −5.4 ppm (1H). The external protons for the bridging carbons gave two doublets for 2H each at 12.7 and 12.8 ppm, and a 2H singlet at 12.4 ppm. This system is evidently highly diatropic, in part due to the [22]annulene substructure, and even the methyl resonances are deshielded to almost 4.5 ppm. The presence of a plane of symmetry is also clear from both the proton NMR data and the carbon-13 NMR spectrum. The UV−vis spectrum for the dication in 1% TFA-chloroform gave two very strong Soret bands at 465 and 478 nm, with Q bands at 537, 667, and 709 nm (Figure 4). In chloroform, **6** gave a similar UV−
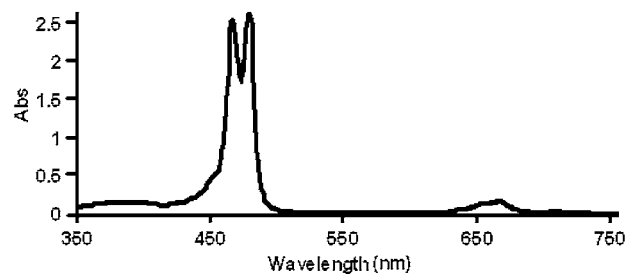

Figure 4. UV−vis spectrum of [22]porphyrin-(3.3.1.1) **6** in 1% TFA-chloroform.

vis spectrum, but in 5% Et$_3$N-chloroform the free base spectrum could be observed. This showed a weaker Soret band at 426 nm, and a series of smaller absorptions at 512, 545, 600, 656, and 719 nm.

The distorted cavity for the [22]porphyrin-(3.1.1.3) is likely to prevent coordination of a single metal cation to all four nitrogen atoms. However, the formation of a palladium(II) complex **9** was accomplished (Scheme 2). Stretched porphyrin **6** was heated with palladium(II) acetate or palladium-(II) chloride in chloroform−methanol. Following chromatography on deactivated silica, a fraction corresponding to the palladium complex could be isolated. Although the same type of product was observed in both cases, only the product derived from the palladium(II) chloride reaction was fully characterized. A green fraction eluted with ethyl acetate−dichloromethane and following recrystallization from chloroform−hexanes, the palladium complex was isolated in 22% yield. Although the UV−vis spectrum was considerably altered, the presence of a strong Soret band at 499 nm and two Q bands at 632 and 692 nm indicated that the complex retained porphyrin-type characteristics. The proton NMR spectrum was far more surprising and showed that the macrocyclic framework had been reorganized to accommodate the palladium ion (Figure 5). The internal CH was no longer a 2H triplet but instead showed up as a 2H doublet at −7.66 ppm. A single NH was present at −4.75 ppm, while the external CHs gave a 2H singlet at 10.4 ppm, an overlapping 2H doublet at 10.4 ppm, and a 2H doublet of doublets at 11.6 ppm. The methyl resonance for the complex
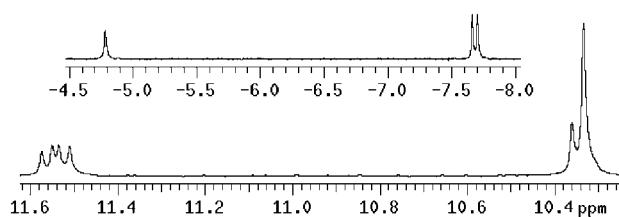
Figure 5. Partial 400 MHz proton NMR spectrum of palladium-(II) complex **9** in CDCl₃ showing the upfield and downfield regions.

gave a 6H singlet at 4.3 ppm. These data indicate that the ring current is slightly reduced in the metal complex, but more importantly show that the palladium complex has the rearranged structure **9**. The retention of a plane of symmetry is confirmed by the simplicity of the proton NMR spectrum as well as from the carbon-13 NMR spectrum. The latter shows the expected 7 carbon resonances for the alkyl substituents between 16 and 21 ppm, while the 12 types of sp² carbons gave the correct number of signals in the range of 98 to 154 ppm.

Conclusive proof for this unusual structure comes from X-ray crystallography (Figure 6). Black single-crystal plates
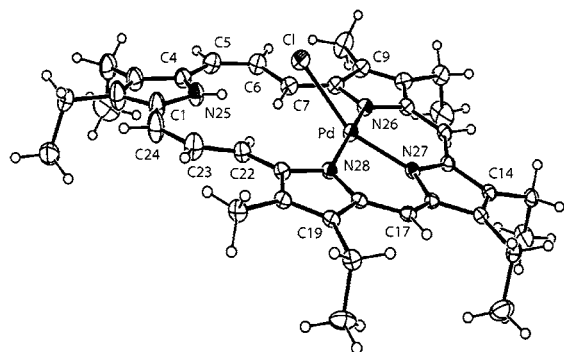

Figure 6. ORTEP III drawing (35% probability level, hydrogen atoms drawn arbitrarily small) of palladium complex **9**·CHCl₃. Selected bond lengths (Å): Pd−Cl 2.378(1), Pd−N(26) 2.033(4), Pd−N(27) 2.032(4), Pd−N(28) 2.010(4). Selected bond angles (deg): Cl−Pd−N(27) 153.6(1), N(26)−Pd−N(28) 170.1(2), N(26)−Pd−N(27) 90.2(2), N(27)−Pd−N(28) 90.2(2), Cl−Pd−N(26) 91.3-(1), Cl−Pd−N(28) 92.8(1).

of **9**·CHCl₃ were grown by vapor diffusion of hexane into a CHCl₃ solution followed by slow evaporation. The macro-cycle is remarkably planar given the steric crowding of the core atoms. The palladium(II) ion coordinates to the three

tripyrrene nitrogen atoms and is best described as having a distorted square planar coordination geometry. The nearly indistinguishable Pd−N bond lengths and the central N−Pd−N bond angles are similar to that observed for other divalent Pd(L)(N)₃ complexes. However, steric limitations prohibit the chloride ligand from completing an idealized square planar coordination. The chlorine atom is 1.9 Å, above the mean macrocyclic plane leading to a 153.6(1)° Cl−Pd−N(27) bond angle. The macrocycle is able to maintain planarity and the presence of internal hydrogen atoms on C7 and C22 due to the geometrical isomerization, and this contributes to the distortion of the metal coordination sphere. It is noteworthy that the coordination geometry in **9** is remarkably similar to that of halo(2,15-dimethyl-3,4,8,9,-13,14-hexaethyltripyrrinato)palladium(II) complexes.[19] In these tripyrrinato complexes, the methyl groups in the 2 and 15 positions provide sufficient steric hindrance to give this type of distorted structure, suggesting that for **9**, the most important factor in determining the coordination geometry is the fundamental sterics associated with having carbon atoms attached to the tripyrrinato ligand α-carbons.

The unprecedented double EZ isomerization of the three-carbon bridging units suggests that this vinylogous porphyrin system will exhibit unusual coordination chemistry, and further investigations are currently in progress. However, it is worth noting that the porphyrin isomer [18]porphyrin-(3.0.1.0) (isoporphycene) has been reported to undergo a similar EZ isomerization of its three-carbon bridge in both the palladium complex and the free base forms.[20] Neverthe-less, the relatively straightforward synthesis of [22]porphyrin-(3.1.1.3) makes this system far more accessible for further investigations.

Supporting Information Available: Experimental pro-cedures, X-ray characterization of **9**, and UV−vis, ¹H NMR, and ¹³C NMR spectra for selected compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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(19) Bröring, M.; Brandt, C. D. *J. Chem. Soc., Dalton Trans.* **2002**, 1391.
(20) (a) Vogel, E.; Bröring, M.; Erben, C.; Demuth, R.; Lex, J.; Nendel, M.; Houk, K. N. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 353. (b) Vogel, E.; Scholz, P.; Demuth, R.; Erben, C.; Bröring, M.; Schmickler, H.; Lex, J.; Hohlneicher, G.; Bremm, D.; Wu, Y.-D. *Angew. Chem., Int. Ed.* **1999**, *38*, 2919.