Bis-vinylogous Corrole: The First Expanded Corrole[**]

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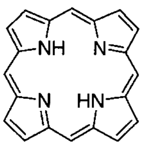
In memory of Tristano Boschi

The porphyrin system **1** is ubiquitous in natural systems, where it plays essential functions in life processes.[1] The sheer richness of porphyrin properties has interested researchers in the chemistry of their analogues, that is, macrocycles that have been characterized as contracted, expanded, or isomeric porphyrins.[2] The original aim of studies with analogues was to explore structure–aromaticity relationships.[3] These investigations showed contracted, expanded, and isomeric porphyrins have often unprecedented properties compared with the corresponding porphyrins.[2, 3] A typical example of an expanded porphyrin is represented by bis-vinylogous porphyrin **2**. Franck and co-workers[4] reported such macrocycles and used them to study the aromaticity of expanded annulenes; these macrocyles have been also exploited as new photosensitizers in photodynamic therapy.[4–6]



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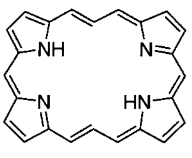

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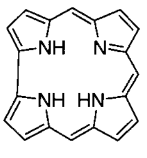
We have been interested for some time[7] in the chemistry of corrole (**3**), the prototypical norporphyrin in which one of the *meso* carbon bridges is missing. Corrole has recently experienced renewed interest because of some of its unexpected properties with regard to corresponding porphyrins.[8] The relationship between porphyrin and corrole led us to explore the existence of a bis-vinylogous system **4** similar to **2**. Our target macrocycle **5**, according to the nomenclature suggested by Franck,[6, 9] would be called [22]porphyrin(3.1.3.0). Herein we describe the synthesis and characterization of **5**, a bis-vinylogous corrole.



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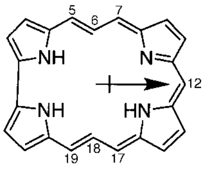

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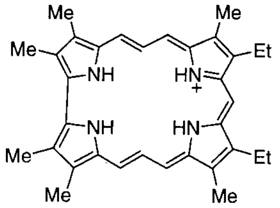

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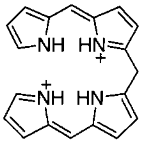

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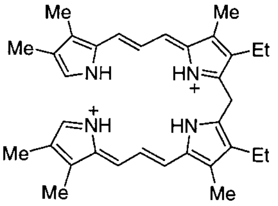
The method of choice to synthesize corroles is the base-catalyzed oxidative cyclization of an *a*,*c*-biladiene (**6**).[10] Acidic condensation of such an extended *a*,*c*-biladiene with aldehydes, in fact, was one of the synthetic approaches used to obtain bis-vinylogous porphyrins **2**.[4]

Compound **7** was used as precursor to **5**; it was obtained in 75% yield by acid-catalyzed condensation of two equivalents of **8** with **9**. The cyclization reaction of **7** was carried out at room temperature in ethanol, using $NaHCO_3$ or sodium acetate as base and chloranil as oxidizing agent. The progress of the reaction was spectrophotometrically monitored; when the absorbances of the starting material disappeared, N_2H_4 was used to quench the excess chloranil. Column chromatography afforded a green polar compound as the major product (54% yield) together with a small amount of the corresponding bis-vinylogous porphyrin, probably due to cleavage and recombination reactions of **7**.



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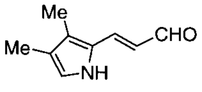

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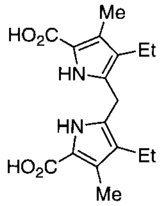

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The spectroscopic characterization of **5** yielded unexpected data.[11] For example the FAB mass spectrum showed an apparent molecular ion at m/z 491, but a peak was also present at m/z 1019 which could not simply be attributed to a dimer of **5**. The electronic absorption spectrum of **5** is shown in Figure 1. Strong absorptions, possessing a significant red shift with respect to those of the corresponding porphyrins, indicated an expanded aromatic system. The Soret-like band is split into two different absorptions of almost equal intensity.

The aromaticity of **5** was confirmed by ^1H NMR spectroscopy, wherein a diatropic ring current effect is notable (not shown); the protons inside the macrocycle ring (H-6, H-18) resonate at $\delta = -9.20$, whereas the signals for the "external" protons (H-5,19, H-7,17) appear at $\delta \approx 11$. The resulting $\Delta\delta$ in the chemical shifts of about 20 ppm is similar to that for **2**.[4]

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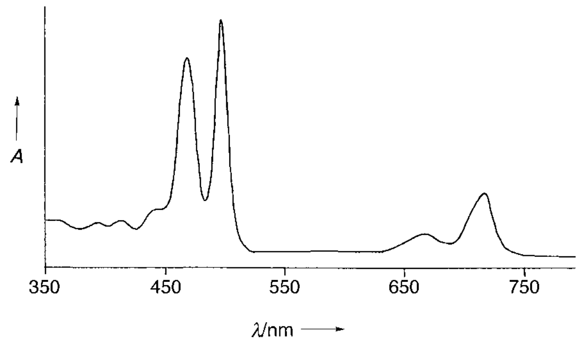

Figure 1. Electronic absorption spectrum of **5** in CH_2Cl_2.

Significant line broadening was also observed for these resonances and for those of the inner NH protons (which were difficult to locate). The signals attributed to the β-alkyl substituents did not suffer any line broadening.

X-ray analysis was performed on a single crystal of **5**-Cl and allowed its unambiguous characterization.[12] Compound **5**-Cl (Figure 2) exists as a fairly planar molecule with one pyrrole ring slightly out of the plane; a similar deviation from planarity of one pyrrole ring was also observed in the case of **3**,[14] and the corresponding corrole monocation showed significant deviations from planarity.[15] This behavior was attributed to steric repulsion between the inner core hydrogen atoms; it is reasonable to attribute to a similar effect the deviation observed in the case of **5**. A chloride counterion is located 1.519(3) Å above the plane of the molecule with six inner hydrogen atoms bound to it. The hydrogen atoms located on the nitrogen centers form H ⋯ Cl bonds with lengths ranging between 2.24(4) and 2.35(4) Å. Two other H ⋯ Cl bonds are formed by the inner CH hydrogen atoms with lengths of 2.62(3) and 2.71(3) Å. A dimeric species is formed by an additional H ⋯ Cl bond from a CH unit of another molecule with a length of 2.72(4) Å. The N–Cl distances are between 3.11 and 3.25 Å, which is consistent with strong hydrogen bonding.[16] These dimeric species have a head-to-tail arrangement with a vertical interplanar distance between the macrocycles of 3.51 Å (Figure 3), and there is no evidence of π stacking.

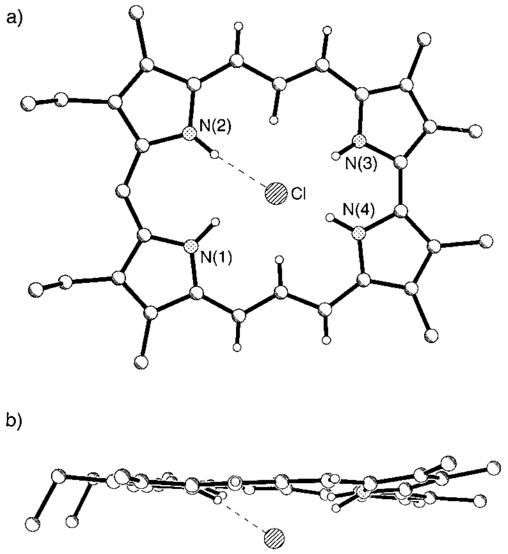

Figure 2. Molecular structure of the monomer of **5**-Cl: a) top view; b) side view. Hydrogen atoms have been omitted for clarity.

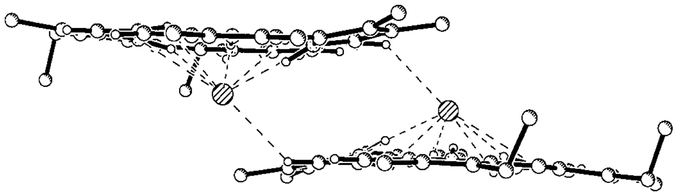

Figure 3. Side view of molecular structure of the aggregated dimer of **5**-Cl.

The presence of such a dimeric species in the solid state indicated interesting chloride binding properties. For this reason it was of value to establish the presence of this dimer in solution to explain some of the unusual spectroscopic features observed. For example, the parent peak in the FAB mass spectrum corresponds to the dimeric species with the loss of one chloride ion. Solution-state structural information was obtained by NMR spectroscopy; Franck and Nonn observed line broadening for high-and low-field protons, similar to that seen with **5**, in the ^1H NMR spectrum of the octavinylogous[34]porphyrin and attributed it to aggregation phenomena.[6] In contradistinction, the spectrum of **5** did not change upon dilution, and no deviations from the Lambert–Beer law were observed spectrophotometrically in the range of concentrations examined (10^{-6}–10^{-8} M). Both of these observations rule out further aggregation of the dimeric species. On the other hand, variable-temperature ^1H NMR spectra ($CDCl_3$, −50 to 50 °C) showed significant changes; at higher temperature there was a sharpening of the resonances and the theoretically expected spectrum of **5** was obtained. A completely resolved spectrum (not shown) was obtained in C_6D_6 at 70 °C; the line broadening affected only the protons involved in the interactions with the chloride ion. Strong hydrogen bonding can induce the broadening observed, while at higher temperature the H ⋯ Cl coupling was probably less effective and allowed the spectrum to be well-resolved. Upon lowering the temperature it was possible to detect the formation of additional downfield signals, and a complex pattern was observed for the β-alkyl substituents. These results suggest the presence of π–π aggregation phenomena between the dimeric macrocycles.

No changes were observed in the electronic absorption spectrum upon addition of triethylamine to a solution of **5** in CH_2Cl_2, indicating the presence of the cationic species in basic solution; the same spectrum was also obtained in neat pyridine. The presence of the dimeric species can explain this strong resistance to deprotonation and to formation of the free base species. Addition of stronger bases, such as NaOH in DMF, induced decomposition of the material.

The unusual splitting of the Soret band in the visible spectrum can also be related to the presence of these dimeric species: Excitonic interactions between the two macrocycles in the dimeric species can explain the observed behavior. The excited states of both monomeric and dimeric species of **5**

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were computed using the INDO/SCI technique.[17–19] The simulation was performed with the MOCINDO[20] program, treating the dimer as a supermolecule.[21] The number of orbitals considered in the calculation was doubled to acknowledge the size, and the chloride ion was not included because it does not contribute to the $\pi \rightarrow \pi^*$ transitions.[22] The resulting absorption spectra (not shown) show a split Soret band for the dimeric species which compared well with the experimentally observed spectrum (Figure 1); the calculated spectrum of the corresponding monomer featured a single, unsplit Soret band. The relative calculated oscillator strength of the double Soret bands in the dimer was also in agreement with the experimental results. Localization of the eigenvectors on the basis of single monomer molecular orbitals allows one to distinguish between exciton or charge resonance terms;[21] the data confirm the excitonic origin (over 80%) of the split Soret band. Our theoretical calculations show that the observed double Soret band is not a function of the individual behavior of the monomer, but rather is due to excitonic splitting in the dimer mainly resulting from transition dipole coupling.

Finally, strong electrostatic effects are thought to be responsible for the slipped geometry of the dimer in the solid state and in solution; the monomer has a strong dipole moment of 5.2 D (PM3 calculation) in the direction shown by the arrow in structure **4**. The dimeric form, with C_i symmetry, has no ground-state dipole moment, the ground-state dipole direction coinciding with the slipping direction.

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[1] A. R. Battersby, C. J. R. Fookes, G. W. J. Matcham, E. McDonald, *Nature* **1980**, *285*, 17.

[2] Review: “Expanded, Contracted and Isomeric Porphyrins”: J. L. Sessler, S. J. Weghorn, *Tetrahedron* **1997**, *15* (Tetrahedron Org. Chem. Series).

[3] E. Vogel, *J. Heterocycl. Chem.* **1996**, *33*, 1461.

[4] H. König, C. Eickmeier, M. Möller, U. Rodewald, B. Franck, *Angew. Chem.* **1990**, *102*, 1437; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 1393; S. Beckmann, T. Wessel, B. Franck, W. Hönle, H. Borrmann, H.-G. von Schnering, *Angew. Chem.* **1990**, *102*, 1439; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 1395.

[5] G. Knübel, B. Franck, *Angew. Chem.* **1988**, *100*, 1203; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 1170.

[6] B. Franck, A. Nonn, *Angew. Chem.* **1995**, *107*, 1941; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1795.

[7] S. Licoccia, R. Paolesse, *Struct. Bonding (Berlin)* **1995**, *84*, 71; R. Paolesse, R. K. Pandey, T. P. Forsyth, L. Jaquinod, K. R. Gerzevske, D. J. Nurco, M. O. Senge, S. Licoccia, T. Boschi, K. M. Smith, *J. Am. Chem. Soc.* **1996**, *118*, 3869.

[8] R. Paolesse, S. Licoccia, G. Bandoli, A. Dolmella, T. Boschi, *Inorg. Chem.* **1994**, *33*, 1171; S. Will, J. Lex, E. Vogel, H. Schmickler, J.-P. Gisselbrecht, C. Haubtmann, M. Bernard, M. Gross, *Angew. Chem.* **1997**, *109*, 367; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 357; E. Vogel, S. Will, A. Schulze Tilling, L. Neumann, J. Lex, E. Bill, A. X. Trautwein, K. Wieghart, *Angew. Chem.* **1994**, *106*, 771; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 731.

[9] M. Gosmann, B. Franck, *Angew. Chem.* **1986**, *98*, 1107; *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 1100.

[10] N. S. Genokhova, T. A. Melent'eva, V. M. Berezowzskii, *Russ. Chem. Rev.* **1980**, *49*, 1056; T. A. Melent'eva, *Russ. Chem. Rev.* **1983**, *52*, 641.

[11] Spectroscopic data for **5**: ^{1}H NMR (400 MHz, C$_6$D$_6$, 70 °C): $\delta = -7.60$ (t, 2H, $J = 9.4$ Hz), -4.11 (s, 2H), -3.42 (s, 2H), 2.19 (t, 6H, $J = 7$ Hz), 3.87 (s, 6H), 3.92 (s, 6H), 4.03 (s, 6H), 4.50 (q, 4H, $J = 7$ Hz), 10.88 (s, 1H), 11.40 (d, 2H, $J = 9.4$ Hz), 11.42 (d, 2H, $J = 9.4$ Hz); UV/Vis (CH$_2$Cl$_2$): $\lambda_{\max}$ ($\varepsilon \times 10^{-4}$) = 442 (2.7), 468 (12.4), 496 (13.8), 666 (1.8), 714 (4.5); MS (FAB): m/z (%): 1019 (90), 491 (100).

[12] Crystal structure analysis: Single crystals of **5**-Cl ($C_{33}H_{39}N_4 \cdot Cl$) were grown from chloroform/methanol. The crystals were immersed in hydrocarbon oil, and a single crystal (dimensions $0.22 \times 0.08 \times 0.02$ mm) was selected, mounted on a glass fiber, and placed in a low-temperature N$_2$ stream generated by a LT-1 device. X-ray diffraction data were collected on a Siemens P3/R4 rotating anode with a normal-focus sealed tube ($\lambda(\mathrm{Cu}_{K\alpha}) = 1.54178$ Å) at 130(2) K in the $\theta/2\theta$ scan mode to $2\theta_{\max} = 113°$. $M_r = 527.13$, triclinic, space group $P\bar{1}$, $a = 9.953(3)$, $b = 10.534(2)$, $c = 14.081(3)$ Å, $\alpha = 79.11(2)$, $\beta = 96.05(2)$, $\gamma = 77.91(2)°$, $V = 1408.3(6)$ Å^3, $Z = 2$, $\rho_{\text{calcd}} = 1.409$ g mL^{-1}. Two standard reflections were measured every 198 reflections for a total of 3760 reflections, of which 3720 were unique ($R_{\text{int}} = 0.010$); number of parameters = 383. Final R factors were $R1 = 0.059$ (based on observed data ($I > 2\sigma(I)$)) and $wR2 = 0.154$ (based on all data). The intensities were corrected for Lorentz and polarization effects. An absorption correction was applied using XABS2;[13] extinction effects were disregarded. The structure of **5**-Cl was solved using direct methods and refined (based on F^2 using all independent data) by full-matrix least-squares methods (Siemens SHELXTL V. 5.02). Hydrogen atoms were included at calculated positions by using a riding model. Hydrogen atoms on the aliphatic carbon atoms were located on the difference map. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-114944. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[13] S. R. Parkin, B. Moezzi, H. Hope, *J. Appl. Crystallogr.* **1995**, *28*, 53.

[14] H. R. Harrison, O. J. R. Hodder, D. C. Hodgkin, *J. Chem. Soc. B* **1971**, 640.

[15] B. F. Anderson, T. J. Bartczak, D. C. Hodgkin, *J. Chem. Soc. Perkin Trans. 2* **1974**, 977.

[16] E. Cetinkaya, A. W. Johnson, M. F. Lappert, G. M. MacLaughlin, K. W. Muir, *J. Chem. Soc. Dalton Trans.* **1974**, 1236; J. L. Sessler, T. D. Mody, D. A. Ford, V. Lynch, *Angew. Chem.* **1992**, *104*, 461; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 452.

[17] J. E. Ridley, M. C. Zerner, *Theoret. Chim. Acta* **1973**, *32*, 111.

[18] J. E. Ridley, M. C. Zerner, *Theoret. Chim. Acta* **1976**, *42*, 223.

[19] M. C. Zerner, G. H. Loew, R. F. Kirchner, U. T. Mueller-Westerhoff, *J. Am. Chem. Soc.* **1980**, *102*, 589.

[20] F. Della Sala, A. Di Carlo, P. Lugli, in house developed INDO/S code based on QCPE no. 372.

[21] M. A. Thompson, M. C. Zerner, J. Fajer, *J. Phys. Chem.* **1990**, *94*, 3820.

[22] J. D. Petke, G. M. Maggiora, *J. Chem. Phys.* **1986**, *84*, 1640.