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Corrole Chemistry

Hemiporphycene from the Expansion of a Corrole Ring[**]

Roberto Paolesse, Sara Nardis, Manuela Stefanelli, Frank R. Fronczek, and Maria Graça H. Vicente*

Porphyrins are extensively studied macrocycles as their unique properties allow multiple and diverse applications in various fields ranging from medicine to the material sciences.[1] Interest in this type of compound has been further expanded by the discovery of porphyrin analogues,[2] that is, macrocycles which have a modified skeleton relative to that of porphyrin. Porphyrin analogues are interesting from both the theoretical and application points of view, as they are amenable to investigation of structure–property relationships as well as the rational modification of the macrocycle to suit a specific application. This approach mimics what happens in

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[*] Prof. Dr. R. Paolesse
Dipartimento di Scienze e Tecnologie Chimiche
Università di Roma "Tor Vergata" and CNR-IMM
00133 Roma (Italy)
Fax: (+39) 067-259-4328
E-mail: roberto.paolesse@uniroma2.it

Dr. S. Nardis, M. Stefanelli
Dipartimento di Scienze e Tecnologie Chimiche
Università di Roma "Tor Vergata"
00133 Roma (Italy)

Prof. Dr. F. R. Fronczek, Prof. Dr. M. G. H. Vicente
Department of Chemistry
Lousiana State University
Baton Rouge, LA 70803 (USA)

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natural systems, where iron porphyrins are used for oxygen transport and activation, while magnesium chlorins are exploited in photosynthetic systems.[3]

Among the large number of porphyrin analogues reported, corrole has received increased attention in recent years, although it was one of the first known members of this family of compounds with Johnson and Kay's studies on the synthesis of vitamin B_{12}.[4] Such renewed interest is in large part due to the peculiar behavior of this macrocycle, which is able to stabilize formal high oxidation states of coordinated metals,[5] thus opening interesting applications for metallocorrolates in catalysis.[6] The coordination chemistry of corrole is made even more intriguing by its non-innocent character as a ligand.[7]

The tumultuous increase of corrole-related papers in the last few years has been based on the definition of simple synthetic routes for the preparation of this macrocycle from commercially available precursors.[8] The synthesis of 5,10,15-triarylcorroles has opened the way to the study of the peripheral functionalization of the macrocycle,[9] which is a topic far less studied than its coordination chemistry.

We contributed to this field by studying the Vilsmeier formylation of free-base corroles. The reactivity of both the β-alkyl and *meso*-triaryl derivatives showed a peculiar and intriguing behavior.[10,11] In particular, 5,10,15-triphenylcorrole (**1**) afforded an unexpected and unprecedented *N*-ethane-bridged inner-core derivative as the major product in the presence of excess DMF (*N*,*N*-dimethylformamide). This compound is particularly intriguing and for this reason we decided to further study the reaction of 5,10,15-triphenylcorrole **1** with CI_4 to investigate whether a one-carbon-unit-bridged inner-core derivative could be similarly obtained. The reaction was carried out under conditions similar to those used for the Vilsmeier reaction, by heating in CH_2Cl_2/DMF at reflux.[12] Chromatography on silica gel afforded two green fractions: the first band, obtained in trace amount, was characterized as 5-iodo-10,15,20-triphenylporphyrin; the second fraction represented the major product of the reaction and was obtained in a yield of 30%.

The spectral characterization of this second compound showed the presence of a macrocycle, although its properties were different from those of corroles. For example, the UV/Vis absorption spectrum of the major product was porphyrin-like, with the presence of four Q bands, while the ^{1}H NMR spectrum showed the presence of different doublets for protons of the pyrrolic units which indicates that the product has a lower symmetry than **1**.[12] Solid-state X-ray analysis of a single crystal of the product[13] showed the presence of a two-carbon *meso* bridge, with the new carbon unit close to pyrrole B, and allowed us to identify the isomer as the 5-iodo-6,11,16-triphenylhemiporphycene (**2**; Figure 1). A similar triphenylhemiporphycene was reported by Callot et al. in 1995 as the serendipitous product obtained by a demetalation–metalation sequence carried out on a homoporphyrin.[14] Note, in that case the hemiporphycene was obtained from ring contraction of a homoporphyrin, whereas in the present case it results from the ring expansion of a corrole ring. Such a ring-expansion reaction is interesting from a synthetic point of view as it is possible to obtain the hemiporphycene from a triphenylcorrole precursor in a single step, whereas the rational synthesis developed by the groups of Vogel and Sessler requires a multistep approach.[15]

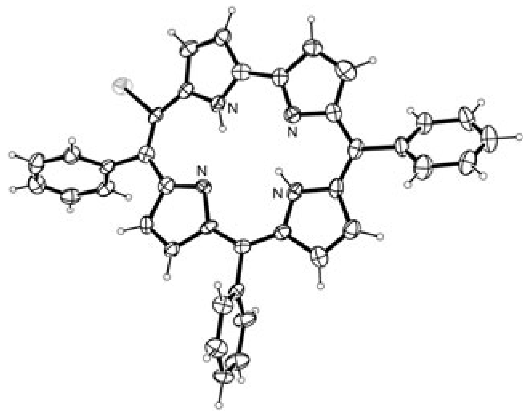
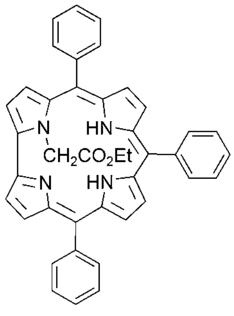


Figure 1. Crystal structure of **2** (N dark gray (labeled), I light gray, C black, H small circles).

Our unexpected result led us to further investigate the plausible reaction sequence that leads to hemiporphycene **2** from the corrole ring. To verify whether the expansion of the corrole was caused by the attack of a carbenic species, we treated the triphenylcorrole **1** with ethyldiazoacetate in bromobenzene. We obtained the corresponding *N*-21-substituted corrole **3** as the major product, as well as the hemiporphycene **4**,[14] although in very low yields, among other minor reaction products.



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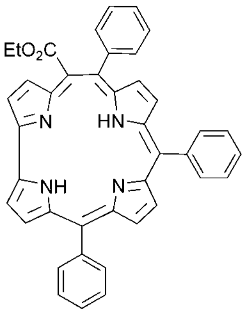

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Similar to the stepwise conversion of the *N*-substituted porphyrin into the corresponding homoporphyrin as reported by Callot and Tschamber in 1975,[16] the *N*-21 isomer obtained from the reaction of 5,10,15-triphenylcorrole and ethyl iodoacetate was heated at reflux in bromobenzene to afford the hemiporphycene in low yields. No hemiporphycene was obtained when the *N*-22 isomer was treated under the same conditions. These results led us to hypothesize a plausible reaction mechanism for the formation of the hemiporphycene, as shown in Figure 2.

The first step involves the formation of the *N*-substituted derivative, which can then rearrange as shown to finally give the hemiporphycene ring upon loss of HI. This novel reaction represents a facile route to the hemiporphycene ring. The

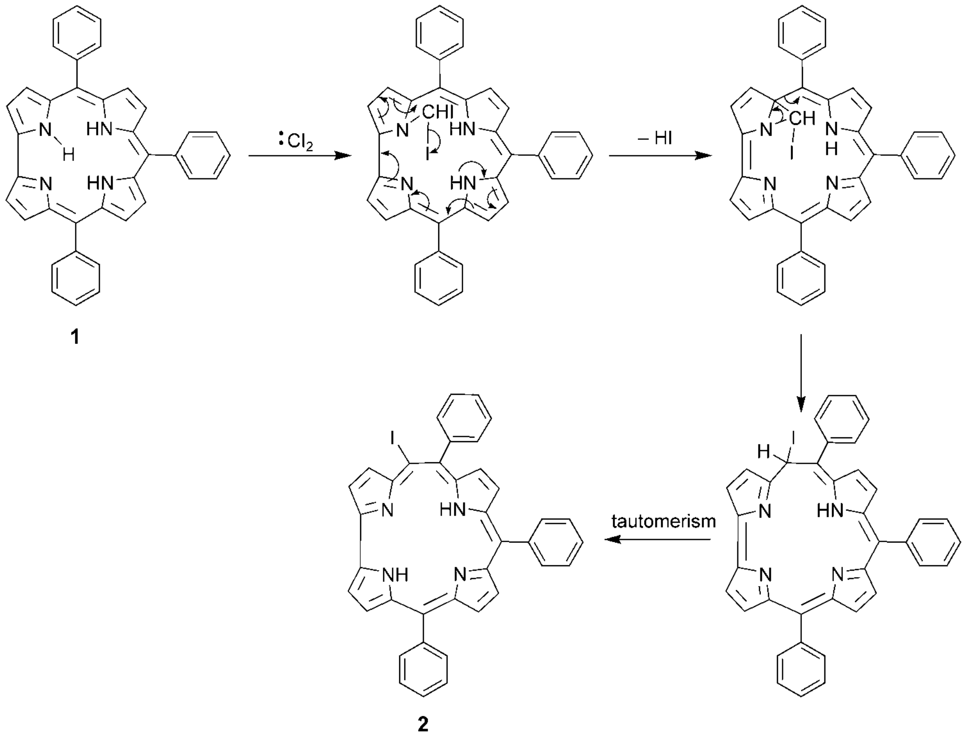

Figure 2. Proposed reaction and mechanistic pathway from **1** to **2**.

presence of an iodine atom at the vinylogous bridge offers the opportunity for further modification at this site and for exploitation of the hemiporphycene macrocycle to build more-complex molecular architectures with interesting properties for new applications.

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[12] A solution of 5,10,15-triphenylcorrole **1** (45 mg, 0.085 mmol), carbon tetraiodide (45 mg, 0.087 mmol), and DMF (0.9 mL, 11.6 mmol) in CH_2Cl_2 (50 mL) was heated at reflux for 1 h. The progress of the reaction was monitored by UV/Vis spectroscopy and by TLC. After disappearance of the starting material, the crude mixture was washed with water and a solution of $NaHCO_3$, and the solvent was evaporated under vacuum. Chromatography on silica gel using CH_2Cl_2 as the eluent afforded a green band as the major product, which, after crystallization from CH_2Cl_2/hexane, gave red–violet crystals of **2** (17 mg, 30%). UV/Vis (CH_2Cl_2): λ_{max} (log ε): 419 (5.28), 522 (3.8), 563 (4.15), 591 (4.02), 637 nm (4.03); ^1H NMR (400 MHz, $CDCl_3$, J [Hz]): $\delta = 9.37$ (d, 1H, $J = 4.4$, β-pyrrolic), 9.14 (d, 1H, $J = 4.4$, β-pyrrolic), 9.05 (d, 1H, $J = 4.5$, β-pyrrolic), 8.75 (d, 1H, $J = 4.5$, β-pyrrolic), 8.50 (d, 1H, $J = 4.4$, β-pyrrolic), 8.20 (d, 3H, $J = 6.6$, phenyl), 8.09 (d, 1H, $J = 4.4$, β-pyrrolic), 8.03 (d, 2H, $J = 7.1$, β-pyrrolic), 7.77(m, 7H, phenyl), 7.65 ppm (m, 5H, phenyl); MS (FAB): m/z (%): 664 (100), 538 (60).

[13] Single crystals of **2**, $C_{38}H_{25}N_4I$, were obtained by slow diffusion of hexane into a solution of **2** in CH_2Cl_2. The unit cell was

monoclinic, space group $P2_1/c$, $a = 24.637(5)$, $b = 10.172(3)$, $c = 24.663(6)$ Å, $\beta = 112.186(8)°$, $V = 5723(2)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.542$ g cm^{-3}, $\mu_{Mo} = 1.155$ mm^{-1}, $R = 0.079$ (8718 data with $F^2 > 2\sigma F^2$), $R_w = 0.192$ (all 13574 unique data), and 775 refined parameters. A total of 39732 data were collected at $T = 100$ K to $\theta = 28.3°$ with $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å) on a Nonius KappaCCD diffractometer using a green blade crystal of dimensions $0.37 \times 0.12 \times 0.05$ mm^3. Absorption corrections were carried out by a multiscan method using HKL Scalepack, with transmission coefficients 0.714–0.943. Refinement was by full-matrix least squares using SHELXL, with hydrogen atoms in idealized positions. There are two independent molecules in the asymmetric unit. CCDC-258645 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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