Porphyrinoids

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Room-Temperature Autoconversion of Free-Base Corrole into Free-Base Porphyrin**

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Corrole chemistry has attracted a renewed interest as a result of recently reported synthetic procedures for the preparation of various *meso*- and β-substituted monocorroles as well as of cofacial biscorrole systems.[1–10] Moreover, metal complexes of corroles can serve as catalysts for the reduction of dioxygen[11] and epoxidation,[12] as well as gas sensors.[13,14]

Corrole macrocycles are generally less stable in solution than their porphyrin analogues. Indeed, a photocatalyzed ring opening of the corrole usually occurs in the presence of dioxygen, leading to the corresponding biliverdin species when the free-base corrole is substituted at the 10-*meso* position by an aryl group (e.g. phenyl).[15,16] It was suggested that the cleavage of the direct C–C bond occurs via the formation of a dioxetan intermediate.[15,16] Metalation provides a way to stabilize the corrole ring,[9,17] but it has been shown that insertion of nickel into a face-to-face biscorrole or porphyrin-corrole dyads leads to the formation of an oxocorrole by insertion of an oxo group at one of the *meso* positions.[18]

Free-base corroles are photosensitive, and investigation into their photochemistry, for example, may be problematic. Therefore, great care must be taken to obtain reproducible spectra.[16,19,20] Free-base *meso*-triaryl corroles (e.g. phenyl, *p*-nitrophenyl) showed a diminished and broadened Soret band when left in solution in methylene chloride and exposed to air and light during a few hours.[4,19] On the other hand, perfluorophenylcorrole is thermally more stable than regular corroles as a result of the presence of electron-withdrawing groups; nevertheless, this system decomposes after a few hours of light exposure.[4,19] Many instabilities have been observed, but until now no decomposition product has been

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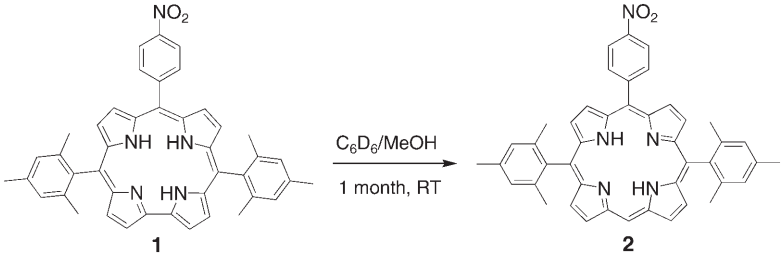
identified and fully characterized; the only exception was an open-chain tetrapyrrole structure reported by some of us[15] and by Paolesse et al.[16]

We report here the first example of an autoconversion of a free-base A_2B-corrole into its AB_2C-porphyrin analogue at room temperature. The 5,15-dimesityl-10-nitrophenylcorrole free base (**1**) was prepared according to a published procedure.[21] To our surprise, a solution of **1** in benzene/methanol slowly converted at room temperature in the presence of air into the corresponding *trans*-AB_2C-porphyrin **2** (Scheme 1).



1 2

Scheme 1. Autoconversion at room temperature of the free-base corrole **1** into the free-base porphyrin **2**.

The formation of the porphyrin analogue **2** was observed by mass spectrometry (MALDI-TOF), which showed a molecular pattern centered at *m*/*z* 667.8 (compared to *m*/*z* 655.3 for the monocorrole), and confirmed by X-ray crystallography (Figure 1).[22] Compounds **1** and **2** cocrystallize, occupying the same unit-cell regions and showing site-occupation factors of 0.50:0.50. Owing to the direct C_{pyr}–C_{pyr} bond between two pyrrolic groups in **1**, their orientation in the macrocyclic moiety is different to those in **2**. The rest of the atoms of both compounds share the same positions in the crystal structure (Figure 1). Further structural features related to the different orientations of the two pyrrolic groups concern the dissimilar attractive NH···N and repulsive H···H interactions that take place in the macrocyclic cavities of **1** and **2** as a result of the extra hydrogen atom $H(N_{pyr})$, which points to this region in the free-base corrole.

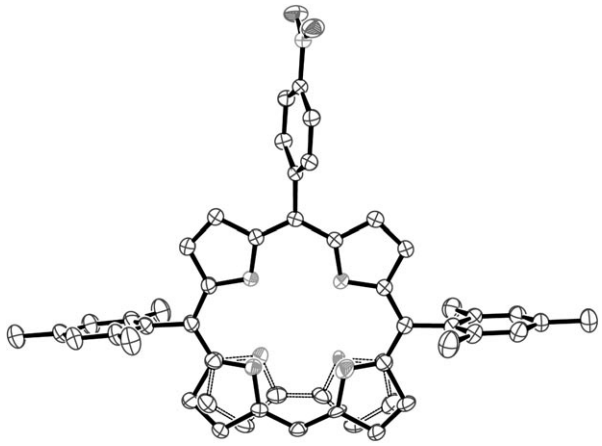


Figure 1. ORTEP view showing the molecular structure of the cocrystallized corrole **1** (background) and porphyrin **2** (foreground). Ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. N pale gray; O dark gray; C white.

Note that separation of **1** and **2** by column chromatography on silica gel or alumina was impossible because of their similar elution characteristics. However, porphyrin **2** was successfully isolated in 19% yield by irradiating (400-W visible light) a solution of **1** (40 mg) in benzene/methanol (5:1) at room temperature during 48 h. The conversion reaction was monitored by UV/Vis and ^{1}H NMR spectroscopy as well as MALDI-TOF mass spectrometry by following the total disappearance of the corrole molecular ion peak at *m*/*z* 655.4 and the appearance of the porphyrin molecular ion peak at *m*/*z* 667.8 (see Supporting Information). The ^{1}H NMR spectrum of **2** (C_6D_6) shows the characteristic patterns of a porphyrin macrocycle (see Table 1) with a singlet for a *meso* hydrogen atom at $\delta = 9.78$ ppm, while the electronic absorption spectrum (CH_3CN) displays a Soret band at $\lambda_{max} = 412$ nm ($\varepsilon = 176\,000$ cm M^{-1}) and four Q bands at 508 ($\varepsilon = 11\,000$), 541 (2700), 583 (3700), and 638 nm (1400 cm M^{-1}).

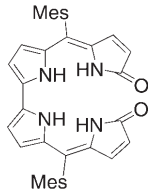
Table 1: ^{1}H NMR data for compounds **2** and **3**.

2: ^{1}H NMR (500 MHz, C_6D_6): $\delta = 9.78$ (s, 1H, *meso*), 8.96 (d, 2H, β-H), 8.93 (d, 2H, β-H), 8.88 (d, 2H, β-H), 8.58 (d, 2H, β-H), 8.04 (d, 2H, H_o-nitro-Ph), 7.61 (d, 2H, H_m-nitro-Ph), 7.26 (s, 4H, H-Mes), 2.51 (s, 6H, CH_3-Mes), 1.96 (s, 12H, CH_3-Mes), −2.28 ppm (s, 2H, NH).

3: ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 11.25$ (s, 2H, NH pyr), 11.15 (s, 2H, NH pyr), 6.80 (s, 4H, H-Mes), 6.38 (d, 4H, β-H), 5.98 (d, 2H, β-H), 5.70 (d, 2H, β-H), 2.25 (s, 6H, CH_3-Mes), 2.01 ppm (s, 12H, CH_3-Mes).

Our first thought was that the 5-*meso*-carbon atom originated from a methanol molecule (one of the two crystallization solvents). To further confirm this hypothesis, four parallel experiments were carried out in benzene solutions with $^{13}CH_3OH$, CD_3OD, CH_3OD, and CH_3OH, respectively, as cosolvents. In all cases, a molecular ion peak at *m*/*z* 667.8 was observed, showing clearly that the *meso*-carbon atom at the 5-position of porphyrin **2** did not originate from a methanol molecule. Furthermore, no signal for the ^{13}C-*meso*-carbon atom was observed in the ^{13}C NMR spectrum of the isolated porphyrin **2** (obtained from benzene/$^{13}CH_3OH$ solution).

This unexpected result led us to further investigate the plausible reaction sequences leading to porphyrin **2** from corrole **1**. Our attention was drawn by the systematic presence of a molecular peak at *m*/*z* 554.3 in MALDI-TOF mass spectra corresponding to a red-violet polar compound (see Supporting Information). The appearance of this peak as well as the increase in its intensity was shown to be concomitant with the formation of the porphyrin macrocycle (see Supporting Information). Spectral characterization allowed identification of this by-product as an open-chain biliverdin-type structure **3** (Mes =



3

mesityl). From accurate mass measurements carried out on the molecular ion, the molecular formula $C_{36}H_{34}N_4O$ was proposed (calculated for $C_{36}H_{34}N_4O$: 554.2682; found: 554.2684). Accordingly, this result demonstrates that the nitrophenyl substituent is the leaving group of the oxidation reaction. Compound **3** displays a ^{1}H NMR spectrum characteristic of a C_2-symmetric molecule (see Table 1). The electronic absorption spectrum shows a breakdown of the aromatic system and no Soret band (λ_{max} (CH_2Cl_2): 372 (100%), 540 (44%), 661 nm (43%)). A possible mechanism based on these data for the conversion of corrole into porphyrin and the parallel oxidation reaction is proposed in the Supporting Information. A 2π+2π cycloaddition of the corrole macrocycle is thought to occur to first give a spirocyclobutane intermediate, which is then split, after oxidation, into the porphyrin system **2** and the biliverdin derivative **3**.

Although there are a few examples of thermal splitting reactions of octaphyrins into porphyrin moieties during metalation reactions (at $T > 100\,^\circ$C),[23–25] no similar reaction was described before in corrole chemistry. In summary, we have reported the first example of room-temperature autoconversion of free-base A_2B-corrole to free-base AB_2C-porphyrin. As corroles become candidates for a wide variety of applications, their stability in solution has to be delineated. Further work is currently under progress on other free-base corrole derivatives that bear different electron-donating or electron-withdrawing substituents at the *meso*- or β-positions to fully identify the key intermediates of this conversion and to further confirm this mechanism.

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[22] Red-purple single crystals of the co-crystallized compounds **1** and **2** were obtained by slow diffusion of methanol into a solution of **1** in C_6D_6. A high-quality specimen of dimensions $0.50 \times 0.15 \times 0.10$ mm^3 was used for the X-ray diffraction experiment. Data were collected at $T = 115(2)$ K up to $\theta_{max} = 27.63°$ with graphite monochromatized $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å) on a Nonius KappaCCD diffractometer,[26] equipped with a nitrogen jet stream low-temperature system (Oxford Cryosystems). No significant decay of intensity was observed during the data collection. No diffractometer or temperature problems occurred during the experiment. Data reduction was performed by using the DENZO software.[27] No absorption corrections were applied. The structure was solved by direct methods (SIR97 program)[28] and refined by full-matrix least-squares on F^2 (SHELXL-97 program)[29] using the complete set of reflections. All non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms of **1** and **2**, except two H(N_{pyr}) hydrogen atoms of **1** and one H(N_{pyr}) atom of **2**, were located by Fourier synthesis and placed at calculated positions using a riding model. All deuterium atoms of the disordered solvent molecules were placed at calculated positions using a riding model, however only some of them were located in the Fourier synthesis. Two global isotropic thermal factors were refined, one for hydrogen atoms and the other for deuterium atoms. Compounds **1** and **2** co-crystallize with a C_6D_6 solvent molecule $0.5(Cor)\cdot 0.5(Por)\cdot C_6D_6$ in the triclinic system (space group $P\bar{1}$), $a = 8.1405(2)$ Å, $b = 15.7733(4)$ Å, $c = 15.8787(5)$ Å, $\alpha = 73.239(1)°$, $\beta = 81.074(1)°$, $\gamma = 82.885(1)°$, $V = 1921.85(9)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.279$ g cm^{-3}, $\mu(Mo_{K\alpha}) = 0.079$ mm^{-1}, 13902 collected reflections, 8842 independent reflections ($R_{int} = 0.0370$), and 612 refined parameters. At the convergence, the final agreement factors are $R(F) = 0.0634$ and 0.1078 and $R_w(F^2) =$

0.1521 and 0.1739, for $I > 2\sigma(I)$ and all data, respectively. The largest Fourier difference peak and hole are 0.311 and $-0.322\ e\ Å^{-3}$. Compounds **1** and **2** occupy the same unit cell regions, showing site-occupation factors of 0.50:0.50. Following this structural feature, the solvent molecule is also disordered over two close positions with equivalent site-occupation factors of 0.50:0.50. CCDC 603366 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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