5,10,15-Triphenylcorrole: a product from a modified Rothemund reaction

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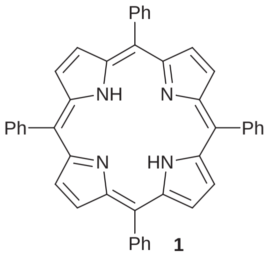
One-pot synthesis of 5,10,15-triphenylcorrole has been achieved by reaction of benzaldehyde with an excess of pyrrole; the triphenylphosphinocobalt complex of 5,10,15-triphenylcorrole has been structurally characterized using X-ray crystallography.

5,10,15,20-Tetraphenylporphyrin **1** is probably the most ubiquitous synthetic porphyrin and it has often been utilized to study biomimetic and/or catalytic systems.[1,2] Its success in these roles is probably due to the relatively easy synthetic approach to **1**, which is obtained by condensation of pyrrole and benzaldehyde.[3] Since the first synthetic approach reported by Rothemund,[4] a huge number of studies related to the synthetic aspects of **1** have been reported in the literature.[3] Different reaction conditions have been utilized and the reaction mechanism has been minutely discussed, but until recently[5–9] the possibility that other macrocycles might be generated from this reaction had been ignored. This aspect has now been investigated and different macrocycles have been isolated and characterized from the Rothemund reaction; these include the 'N-confused'-porphyrin **2** (NC-TPP)[5,6] and 5,10,15,20-tetraphenylsapphyrin **3** (TPS)[7] from the standard pyrrole/benzaldehyde condensation, and a *meso*-hexa(pentafluorophenyl)hexaphyrin, in low yield, from a related reaction.[8] While a study by Lindsey and Geier established the scope of the formation of NC-TPP and TPS, additional pigments were observed but in very low yield and therefore were not characterized.[9]



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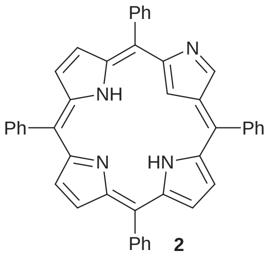

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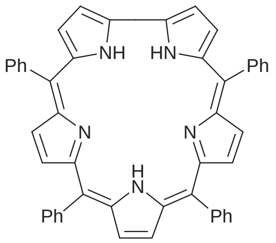

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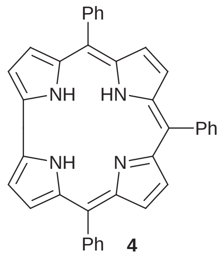

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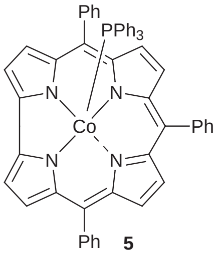

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During our studies on the chemistry of corrole, we reported the formation of a *meso*-phenyl-β-substituted corrole from the cobalt catalyzed cyclization of a hydroxybenzylpyrrole,[10] the first intermediate in the condensation of pyrrole and benzaldehyde. This result, and knowledge that the ring-expanded sapphyrin system was also isolated,[7] caused us to suspect that 5,10,15-triphenylcorrole **4** might also be another, albeit diminutive, product of the Rothemund reaction. Two examples of *meso*-substituted corroles have since been reported in the literature;[11,12] these corroles were obtained as by-products of the expected porphyrins in the reaction of pyrrole and aldehydes. These examples further supported our hypothesis that corroles might be obtained from the condensation of pyrrole and aldehydes, but because of the low yields and the particular aldehydes used, these results cannot be generalized. Here we report that, under certain defined conditions, triphenylcorrole **4** is formed in reasonable yield from the Rothemund reaction;† cobalt was easily inserted into **4** and the corresponding triphenylphosphino complex **5** was structurally characterized.

Pyrrole and benzaldehyde (3 : 1 molar ratio) were reacted in refluxing AcOH for 4 h with spectrophotometric monitoring. Following work-up and chromatographic separation on alumina, triphenylcorrole **4** was obtained in 6% yield (unoptimized) as red–green crystals. The expected tetraphenylporphyrin **1** was also obtained from this reaction in yields comparable with those of **4**, indicating that under these modified conditions the ring closure to corrole is competitive with the formation of the larger porphyrin macrocycle; trace amounts of NC-TPP were also observed. [5,6] When the reaction was carried out in propionic acid[14] (for 2 h) the yields of corrole were slightly lower. The choice of reaction conditions is critical for the formation of useful amounts of **4**.

The ^{1}H NMR spectrum of **4** shows broad AB patterns for the β-pyrrolic protons because of the reduced symmetry of the corrole ring. Spectrophotometry of **4** provided the optical spectrum shown in Fig 1. The Soret band appears at 416 nm (ε 101 000), without significant shift with respect to that of **1**; three

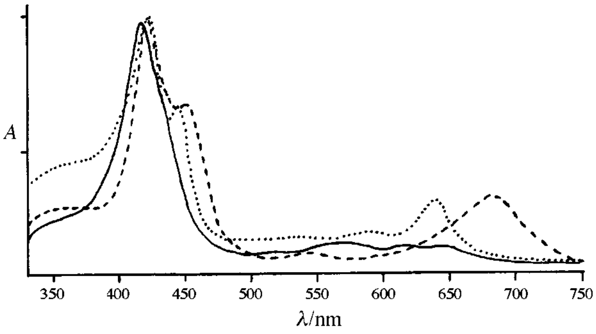

Fig. 1 Optical spectra of **4** in CH_2Cl_2 (solid line), in DMF (dotted line) and in AcOH (dashed line). Absorbances are normalized to their maxima.

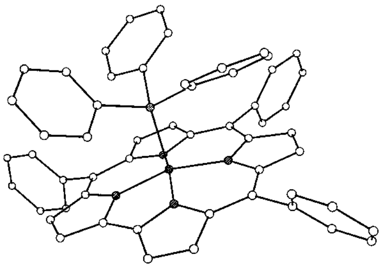

Fig. 2 Molecular structure of **5**; hydrogen atoms have been omitted for clarity.

broad Q bands are present in the 570–650 nm region. It is interesting to note that **4** is more acidic than the corresponding β-octaalkyl analogues[15] because DMF is sufficiently basic to give the corresponding monoanion derivative without addition of bases, as evidenced by the visible spectrum (Fig. 1) recorded in DMF. The same spectrum is obtained by addition of a few drops of base (NaOH 10% in water) to a methanolic solution of **4**. The monocation of **4** was formed in AcOH, as is also shown in Fig. 1. Addition of increasing amounts of H_2SO_4 to the AcOH solution of **4** led to further changes in the visible absorption spectrum; these indicated additional protonation processes which have not yet been characterized, but which do not involve disruption of the conjugated pathway (*i.e.* no removal of the Soret band). In the case of β-octaalkylcorroles[16,17] protonation at the 5-position in H_2SO_4 has been proposed on account of the disappearance of the Soret band in the electronic absorption spectrum.

The insertion of the cobalt(III) ion into **4** was performed by reaction of corrole and $Co(OAc)_2$ in refluxing MeOH in the presence of PPh_3 to give the corresponding complex **5** in 88% yield. The ^1H NMR spectrum of **5** is similar to that of **4**, but with more resolved resonances. The axial phosphine ligand shows three sets of resonances for the *ortho*, *meta* and *para* protons, in accord with observations in the corresponding β-octaalkylcorrole complexes,[10,18] indicating that the PPh_3 ligand does not suffer from steric interactions with the *meso*-phenyl groups.

The electronic spectrum of **5** shows a Soret band at 385 nm (ε 51 000) and a Q band centered at 561 nm (ε 11 500). Its EI mass spectrum shows an $[M - PPh_3]^+$ ion, while use of the FAB technique allowed observation of the molecular ion without loss of the axial ligand.

The structure of **5** was determined by X-ray crystallography.‡ Compound **5** was slightly non-planar with a 0.069 Å mean deviation of the macrocyclic atoms from the corrole mean plane. The conformation observed resembles the porphyrin-type dome conformation.[20] The central Co^{III} ion featured M–N bond lengths of 1.863(2), 1.891(2), 1.886(2) and 1.867(2) Å; the two shortest of these bonds involved the nitrogens adjacent to the C_α–C_α linkage. This is typical of metallocorroles and has been observed in the crystal structures of other corroles.[10,21] In **5**, the Co^{III} ion is displaced from the corrole mean plane by 0.389 Å and the Co–P bond length is 2.201(1) Å.

In conclusion, we have shown that the synthesis of **4**, even at only 6% yield, permits the corrole field to utilize and exploit a direct analogue of tetraphenylporphyrin; this should provide a starting point for further development of the comparative chemistry of this contracted macrocyclic system.

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Notes and references

† After the present paper had been submitted and reviewed, a report of the synthesis of 5,10,15-tris(pentafluorophenyl)corrole from pyrrole and pentafluorobenzaldehyde appeared (ref. 13). These authors showed that using their conditions with pyrrole and benzaldehyde does not afford 5,10,15-triphenylcorrole (**4**). We thank a reviewer for informing us of the imminent publication of this article.

‡ *Crystal data* for **5**: Crystals were grown by slow diffusion of MeOH into a CH_2Cl_2 solution of **5** ($C_{55}H_{38}N_4PCo$). The selected crystal (0.28 × 0.52 × 0.54 mm) had a triclinic unit cell, space group $P\bar{1}$ and cell dimensions a = 8.5269(8), b = 13.1028(13), c = 18.161(2) Å, α = 94.284(8), β = 92.308(8), γ = 97.677(8)°, V = 2002.6(3) Å^3 and Z = 2 (FW = 844.8). Data were collected on a Siemens R3 m/V diffractometer with a sealed tube source [λ(Mo-Kα) = 0.71073 Å] at 130(2) K in ω scan mode to $2\theta_{max}$ = 55.0°. Of 9795 reflections measured ($+h$, $\pm k$, $\pm l$) all were independent and 7351 had $I > 2\sigma$ (T_{min} = 0.78, T_{max} = 0.89, ρ_{calc} = 1.40 g cm^{-3}, μ = 0.515 μ^{-1}). The structure was solved by direct methods and refined (based on F^2 using all data except for three suppressed reflections) by full-matrix least-squares methods with 550 parameters (Siemens SHELXTL ver. 5.03). Hydrogen atom positions were generated by their idealized geometry and refined using a riding model. An empirical absorption correction was applied (ref. 19). Final R factors were $R1$ = 0.041 (observed data) and $wR2$ = 0.112 (all data). CCDC 182/1277.

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