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# Synthesis, Crystal Structure, and Electronic Structure of a 5,15-Dialkylideneporphyrin: A TCNQ/Porphyrin Hybrid

Iain M. Blake,[†] Harry L. Anderson,*,[†] David Beljonne,[‡]
Jean-Luc Brédas,[‡] and William Clegg[§]

*Department of Chemistry, University of Oxford*
*Dyson Perrins Laboratory, South Parks Road*
*Oxford, U.K. OX1 3QY*
*Service de Chimie des Matériaux Nouveaux*
*Centre de Recherche en Electronique*
*et Photonique Moléculaires, Université de Mons-Hainaut 20*
*Place du Parc, B-7000, Mons, Belgium*
*Department of Chemistry, University of Newcastle*
*Newcastle-upon-Tyne, U.K. NE1 7RU*
*CCLRC Daresbury Laboratory*
*Warrington, U.K. WA4 4AD*

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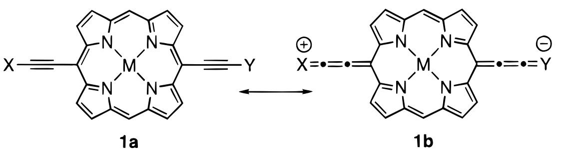
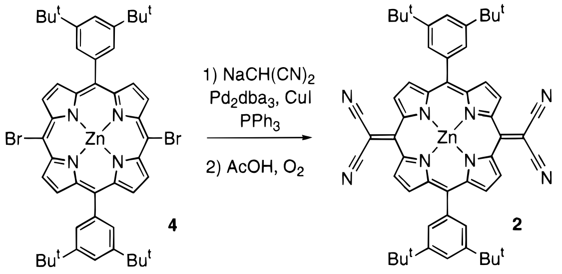
The strong nonlinear optical behavior of 5,15-dialkynylporphyrins, of general structure **1a**/**b**, can be attributed to the contribution of quinoidal/cumulenic resonance forms of type **1b** (Scheme 1), particularly in the excited state.[1] This has inspired us to explore the chemistry of 5,15-dialkylideneporphyrins, in which the macrocycle is locked in its quinoidal resonance form. Here we report the synthesis of the first structurally characterized compound of this type, 5,15-bis(dicyanomethylene)-10,20-bis-(3,5-di-*tert*-butylphenyl)porphyrin **2**, together with a theoretical analysis of its unusual absorption spectrum.

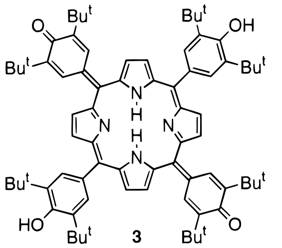
**Scheme 1**



**Scheme 2**

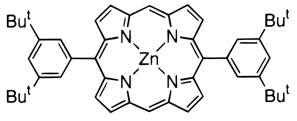


Earlier attempts to prepare 5,15-dialkylideneporphyrins by reacting 5,15-dioxoporphyrins (sometimes called dioxoporphodimethenes) with carbanions failed;[2] however, Otto and Breitmaier have synthesized a tetraalkylideneporphyrin by treating a tetraoxoporphyrin (xanthoporphyrinogen) with methyllithium.[3] The only 5,15-dialkylideneporphyrins to have been reported are the oxidation products of 4-hydroxyphenyl-substituted porphyrins, such as **3**.[4] The structures of these compounds are uncertain because they exist as a variety of tautomers and **3** adopts a porphyrinogen-type structure in the solid state. We found that **2** can be prepared in 53% yield from the 5,15-dibromoporphyrin **4**[5] by palladium/copper catalyzed Takahashi coupling[6] with the malononitrile anion, followed by aerobic oxidation (Scheme 2);[7] both palladium and copper catalysts proved to be essential.



**3**

$^{1}$H and $^{13}$C NMR support the structure of **2** and show that it has no aromatic ring-current; for example, the NH protons of the free-base of **2** (from treatment of **2** with acid) give a sharp singlet at 13.89 ppm in CDCl$_3$, whereas those of the free-base of **5** resonate at −3.00 ppm. The molecular structure of the pyridine complex of **2**, obtained from a small single crystal by synchrotron X-ray diffraction at 120 K, is shown in Figure 1.[8] Steric repulsion between the $\beta$-hydrogens and the nitriles results in a severely nonplanar, saddle-shaped conformation; the $\beta$-hydrogen-to-nitrile carbon distances (2.50 and 2.63 Å) are approximately the sum of the van der Waals radii. A similar situation arises in tetracyanoanthraquinodimethane.[9] Selected bond lengths are shown in Figure 2 together with the displacements from the mean plane of the four central nitrogens (the molecule has a crystallographic $C_2$ symmetry). The bond lengths in the macrocycle are similar to those in a normal zinc porphyrin (with ±0.03 Å) except for the *meso*-to-α C−C bonds next to the dicyanomethylene substituents, which are 0.07 Å longer than normal because these bonds have a formal bond order of 1.0 rather than 1.5 (a similar distortion is observed in 5,15-dioxoporphyrins[10]). The zinc−pyridine



**5**

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[†] University of Oxford.

[‡] Université de Mons.

[§] University of Newcastle and Daresbury Laboratory.

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(8) Crystal data for **2**·C$_5$H$_5$N: C$_{59}$H$_{55}$N$_9$Zn, $M_r = 955.5$, $T = 120$ K, $\lambda = 0.4848$ Å, monoclinic, $a = 28.0614(10)$, $b = 8.4932(4)$, $c = 22.1477(10)$ Å, $\beta = 102.664(2)°$, $V = 5150.1(4)$ Å$^3$, space group $C2/c$, $Z = 4$, $\rho_{\text{calcd}} = 1.232$ g cm$^{-3}$; crystal size 0.15 × 0.15 × 0.04 mm. The final conventional $R$ value was 0.082 ($S = 1.054$). Data were collected at the Daresbury Synchrotron Radiation Source (U.K.).

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10.1021/ja9810078 CCC: $15.00

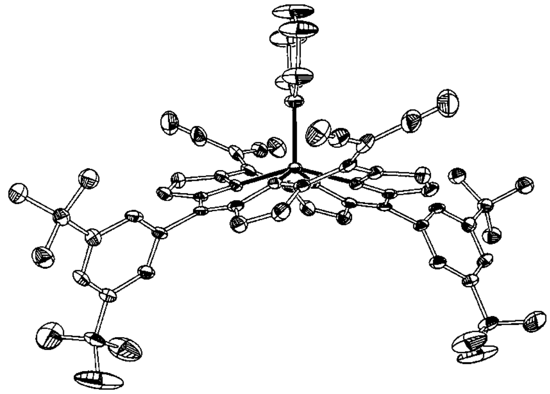

**Figure 1.** Structure of $2 \cdot C_5H_5N$ in the solid state, with 50% probability ellipsoids. H atoms are omitted for clarity.

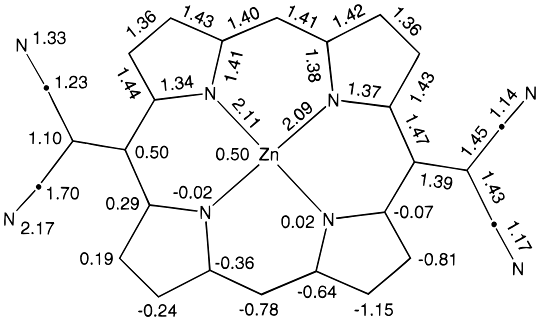

**Figure 2.** Structure of $2 \cdot C_5H_5N$ showing selected bond lengths (top right) and distances from the mean plane of the four central nitrogens (bottom left) in Å (note $C_2$ symmetry).

nitrogen distance is 2.084(6) Å which is shorter than in analogous complexes of simple porphyrins[11] (2.20−2.14 Å) and 5,15-dioxoporphyrins[10] (2.13−2.12 Å). This reflects the presence of an unusually strong zinc−pyridine interaction; the equilibrium constant for the formation of $2 \cdot C_5H_5N$ in $CD_2Cl_2$ is $(1.5 \pm 0.4) \times 10^6\ M^{-1}$ at 298 K, whereas the analogous binding constant of **5** is only $(5.6 \pm 0.3) \times 10^3\ M^{-1}$.[12] The greater affinity of **2** for pyridine can be attributed to the greater positive charge in the core of the porphyrin, as indicated by the charge distribution computed at the semiempirical INDO[13] level. Quantum-chemical calculations[14] predict a geometry for **2** which is very similar to the crystallographic geometry of $2 \cdot C_5H_5N$, suggesting that pyridine binding has little effect on the shape of the macrocycle, in keeping with our observation that the electronic spectrum of **2** does not change perceptibly when it binds pyridine.

**2** is bright green in solution.[15] Its absorption spectrum (Figure 3a) exhibits two bands of similar intensity, in contrast to normal porphyrins such as **5**. There is good agreement between these spectra and the simulated spectra (Figure 3b) obtained by combining the Hartree−Fock semiempirical INDO Hamiltonian to a configuration interaction (CI) scheme; the INDO one-electron energy diagram for the frontier levels is shown schematically in Figure 4. In **5** the $a_u$ and $b_{3g}$ levels are localized on the porphyrin macrocycle, with nodes on the 5,15-*meso*-positions, whereas the $b_{1u}$ and $b_{2g}$ levels have the correct symmetry to overlap with the dicyanomethylene substituents in **2**. Constructive interference between the close lying electronic transitions in **5** ($a_u$−$b_{3g}$ with $b_{1u}$−$b_{2g}$ and $a_u$−$b_{2g}$ with $b_{1u}$−$b_{3g}$) leads to the intense B band at 409 nm, while the weak Q-band at 537 nm results from destructive combinations of the same transitions. In contrast, the $a_u$−$b_{3g}$ and $b_{2g}$−$b_{1u}$ excitations have very different energies in **2**, due to $\pi$-delocalization over the dicyanomethylene substituents and the inductive effect of these electron-withdrawing moieties, and therefore lead to two separate bands with similar intensity at 458 and 637 nm; both of these transitions are polarized in the 5,15-direction.

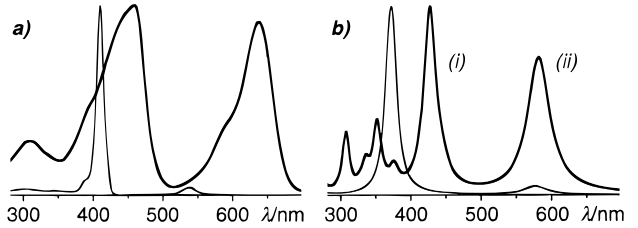

**Figure 3.** (a) Experimental (in $CH_2Cl_2$) and (b) simulated (on the basis of DFT geometries) INDO/CI normalized absorption spectra of **2** (bold) and **5** (plain).

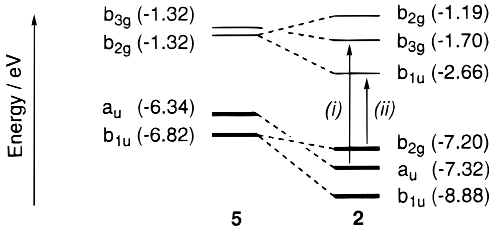

**Figure 4.** Frontier orbitals for **5** and **2** from INDO calculations, with occupied orbitals shown in bold. (Symmetry labels assume $D_{2h}$ symmetry for the macrocycle.)

The discovery of this new synthetic route to 5,15-dialkylideneporphyrins, with their strongly perturbed electronic structure and extended conjugation, opens the way for the synthesis of new chromophores for nonlinear optical applications. Work is underway toward exploring the electrochemistry and charge-transfer complexes of these TCNQ-analogues.[16,17]

**Acknowledgment.** This work was supported by the Engineering and Physical Sciences Research Council (EPSRC), the Defence Evaluation and Research Agency (DERA), the Council for the Central Laboratories of the Research Councils (CCLRC), the Belgian Federal Government “Inter University Attraction Pole on Supramolecular Chemistry and Catalysis”, FNRS-FRFC, and an IBM Academic Joint Study. We thank the EPSRC mass spectrometry service (Swansea) for FAB mass spectra. D.B. is a research fellow of the Belgian National Science Foundation (FNRS).

**Note Added in Proof.** Another 5,15-dialkylideneporphyrin has just been reported: Nelson, N. Y.; Medforth, C. J.; Khoury, R. G.; Nurco, D. J.; Smith, K. M. *Chem. Commun.* **1998**, 1687−1688.

**Supporting Information Available:** Experimental procedure for the synthesis of **2**, X-ray structural data for $2 \cdot C_5H_5N$, and computational details (10 pages, print/PDF). An X-ray crystallographic file, in CIF format, is available through the Web only. See any current masthead page for ordering information and Web access instructions.

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(12) The stability of the $2 \cdot C_5H_5N$ and $5 \cdot C_5H_5N$ complexes were determined by $^1H$ NMR and UV−vis titrations. **2** binds pyridine even more strongly than zinc dioxoporphyrins; McCallien, D. W. J.; Sanders, J. K. M. *J. Am. Chem. Soc.* **1995**, *117*, 6611−6612.

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(17) A preliminary cyclic voltammetry investigation by Dr. Jean-Paul Gisselbrecht (Université Louis Pasteur, Strasbourg, France) has shown that **2** is very easily reduced; it has reversible first oxidation and reduction potentials at +1.27 V and −0.31 V, respectively, whereas the analogous values for **5** are +0.79 V and −1.42 V, respectively (versus Ag/AgCl in $CH_2Cl_2$ containing 0.1 M $Bu_4NPF_6$, on a glassy carbon working electrode. Ferrocene used as an internal standard is oxidized at +0.40 V vs Ag/AgCl).