Supporting information

The colorful Friedel-Crafts chemistry of *meso*-tetraarylporphyrins. An unexpected route to porphyrinic spiro dimers

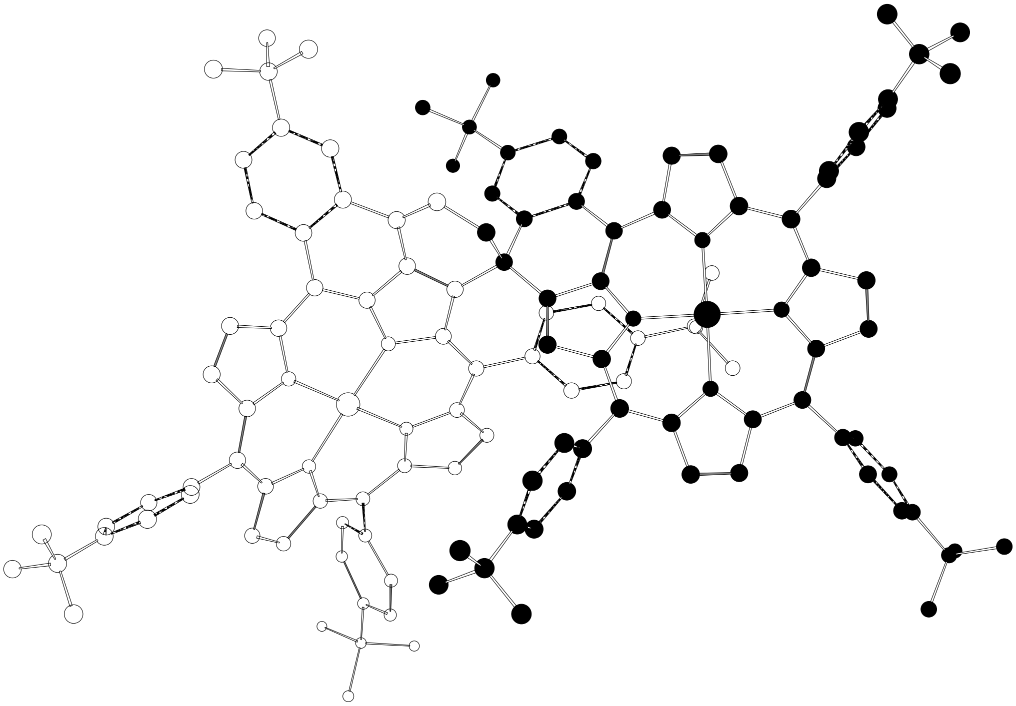
Christophe Jeandon, Romain Ruppert, Sébastien Richeter, and Henry J. Callot*

Faculté de Chimie, UMR 7123 CNRS, Université Louis Pasteur

1 rue Blaise Pascal, 67000 Strasbourg (France).

E-mail: callot@chimie.u-strasbg.fr

Crystal data for dimer 3 : $2C_{124}H_{118}N_8Ni_2 \cdot CH_2Cl_2 \cdot 4C_7H_8 \cdot H_2O$, M = 4163.11, triclinic, space group P-1 ; a = 19.6163(4), b = 19.6665(3), c = 20.5896(4) Å, α = 115.059(5)°, β = 108.474(5)°, γ = 92.893(5)°, V = 6665.1(5) Å^3, Z = 1, Dc = 1.04 gcm^{-3}. A total of 48615 ±h±k+l reflections was collected on a brown crystal of dimensions 0.08*0.08*0.06 mm^3, using a KappaCCD diffractometer, graphite monochromated MoKα, 2.5 < θ < 27.91, temperature 173 K. 11704 unique reflections having I > 3 σ(I) were used to determine and refine the structure. Final results : R = 0.109, Rw = 0.143, GOF = 1.301, largest peak in final difference = 1.485 eÅ^{-3}.

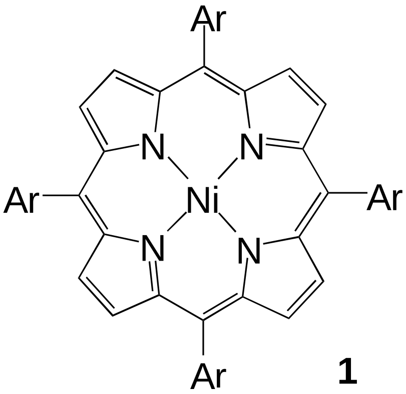


Scheme 1. X-ray structure of brown dimer **3** (hydrogen atoms omitted for clarity)

Preparation of nickel *meso*-tetra-(*p*-*t*-butylphenyl)porphyrin 1 (R = *p* -*t*-butylphenyl)

Several experiments using various batches of **1** (Ar = *p*-*t*-butylphenyl) showed that beneficial factors are a high initial concentration of **1** and a very fast dissolution of the porphyrin upon reaction. Accordingly, high cristallinity of the starting material resulted in the lowest conversion. Batches of **1** precipitated by addition of a saturated solution in chloroform to methanol in large excess or crushed in a mortar gave acceptable yields of **3** (up to 35 %), but only moderate conversion due to the slow dissolution of the starting material and the side reactions being faster than the dimer formation. Chloroform, although giving a homogeneous solution of **1** (Ar = *p*-*t*-butylphenyl) under the same conditions (50 mg in 10 mL), had a detrimental effect (lower conversion and multiple side-products). We found that the best yields (45-58 %) and conversion (100 %) were reproducibly obtained when samples of **1** were prepared according to the procedure described below.

A solution of pyrrole (1.7 mL) and 4-*t*-butylbenzaldehyde (4 mL) in propionic acid (120 mL) was refluxed for 1 h, and then evaporated to dryness. To the resulting black gum was added nickel acetylacetonate (2 g) and xylene (120 mL). The mixture was stirred and refluxed for 2h, then the solvent evaporated. Addition of methanol to the resulting black gum (150 mL; at once) gave a fine purple-brown powder which was filtered on a sintered glass, washed with methanol, and dried under vacuum (1.28 g; 23 %). The product was found to be ≥ 95 % pure according to the NMR data, and was used as such.



1

Preparation of dimers 2 and 3

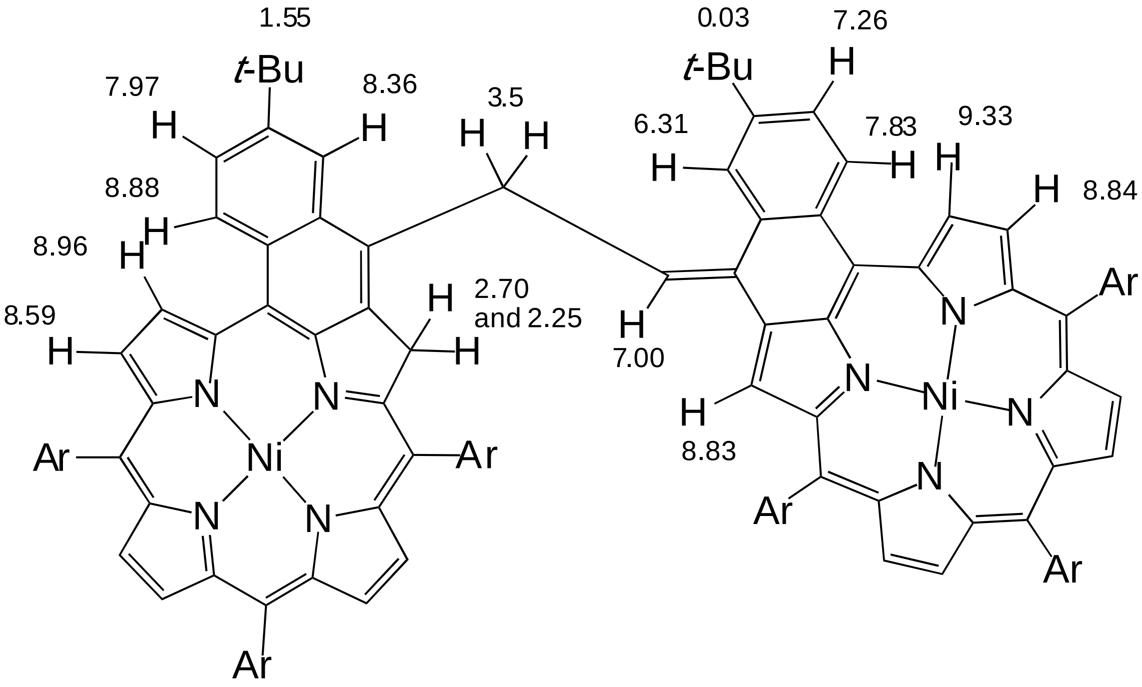
To a stirred suspension of nickel-*meso*-tetra-*p*-*t*-butylphenylporphyrin **1** (Ar = *p*-*t*-butylphenyl) (50 mg; prepared according to the procedure described above) in CH_2Cl_2 (10 mL) was added acetic anhydride (0.2 mL) and $SnCl_4$ (0.1 mL). The solution turned rapidly chocolate brown and homogeneous. After 5 min, TLC showed the absence of starting material and the reaction mixture was poured into a large excess saturated aqueous $NaHCO_3$ (100 mL) and stirred vigorously for 15 min. The organic phase was washed with H_2O (3x 200 mL), and dried over Na_2SO_4. Evaporation and crystallization of the residue from CH_2Cl_2-MeOH gave crude dimer **2** as a green powder. Chromatography on silica gel (eluent CH_2Cl_2+ hexane 2 : 8) gave pure **2** (19 %; crystallized from CH_2Cl_2-MeOH). The slow decomposition of **2** in solution accounts for the moderate yield obtained.

When kept in solution, this compound slowly transformed into brown dimer **3**, which could be crystallized from CH_2Cl_2-MeOH as a dark brown powder. The transformation of **2** into **3** is strongly accelerated in pyridine. The simplest procedure for obtaining **3** consists in dissolving the crude residue from the first step in pyridine (5 mL) and stir the green solution in air. The color turns rapidly from green to olive-brown (*ca* 15 min). Evaporation and filtration on a short silica gel column (elution with CCl_4) gave **3** as the least polar fraction (23-30 mg; crystallized from CH_2Cl_2-MeOH; 45-58 % from **1**). Crystals suitable for the X-ray study were obtained by slow diffusion of MeOH in a CH_2Cl_2 + toluene solution of **3** at room temperature.

Green dimer 2

^{1}H NMR ($CDCl_3$) (see also Scheme below): 9.33 (1 H, d, J = 5 Hz, pyrrole), 8.96 (1 H, d, J = 5 Hz, pyrrole), 8.88 (1 H, J = 8 Hz, phenyl), 8.84 (1 H, d, J = 5 Hz, pyrrole), 8.83 (1 H, s, pyrrole), 8.70 (1+1 H , 2 d, J = 5 Hz, pyrrole), 8.64 (1 H, d, J = 5 Hz, pyrrole), 8.60 (1 H, d, J = 5 Hz, pyrrole), 8.59 (1 H, d, J = 5 Hz, pyrrole), 8.36 (1 H, J = 1.8 Hz, phenyl), 8.07 (2 H, s, pyrrole), 7.97 (1 H, dd, J = 8 and 1.8 Hz, phenyl), 7.83 (1 H, d, J = 8 Hz, phenyl), 8.1-7.5 (22 H, m, 21 phenyl + 1 pyrrole), 7.53 (2 H, d, J = 8 Hz, phenyl), 7.26 (1 H, d, J = 8 Hz, phenyl), 7.07 (1 H, d, J = 5 Hz, pyrrole), 7.00 (1 H, broad s, bridge olefinic H), 6.31 (1 H, broad s, phenyl), 3.5 (2 H, broad s, bridge CH_2), 2.70 and 2.25 (1+1 H, 2 broad d, J = 11 Hz, chlorinic H), 1.57, 1.45, 1.44, 0.03, -0.80 (3+3+3+3+3 H, 5 s, *t*-butyl; the remaining *t*-butyl signals are at *ca* 1.55 and obscured by the water signal).

UV-vis. (CH_2Cl_2) λ_{max} = 444 nm (ε = 412000), 450 (slight sh.), 560 (33700), 598 (36000), 674 (19500).



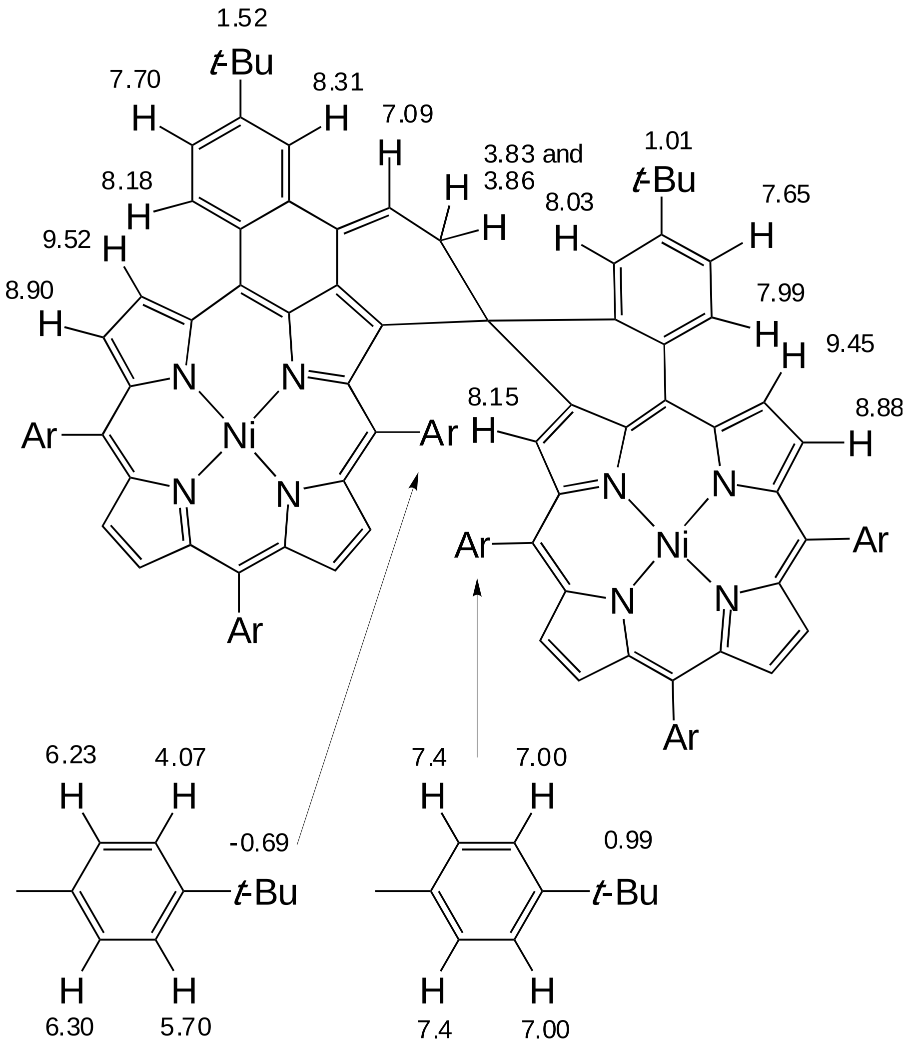
Scheme 2. NMR data for green dimer **2**. The molecule is shown unfolded for clarity. All signals appearing on schemes have been unequivocally assigned (COSY + ROESY).

Brown dimer 3

^{1}H NMR ($CDCl_3$) (see also Scheme below): 9.52 (1 H, d, J = 5 Hz, pyrrole), 9.45 (1 H, d, J = 5 Hz, pyrrole), 8.90 (1 H, d, J = 5 Hz, pyrrole), 8.88 (1 H, d, J = 5 Hz, pyrrole), 8.70 (1 H, d, J = 5 Hz, pyrrole), 8.65 (1 H, d, J = 5 Hz, pyrrole), 8.63 (1 H, d, J = 5 Hz, pyrrole), 8.61 (1 H, d, J = 5 Hz, pyrrole), 8.58 (1 H, d, J = 5 Hz, pyrrole), 8.50 (1 H, d, J = 5 Hz, pyrrole), 8.31 (1 H, d, J = 1.8 Hz, phenyl), 8.23 (1 H, d, J = 5 Hz, pyrrole), 8.18 (1 H, d, J = 8 Hz, phenyl), 8.15 (1 H, s, pyrrole), 8.03 (1 H, d, J = 1.8 Hz, phenyl), 7.99 (1 H, d, J = 8 Hz, phenyl), 7.70 (1 H, d, J = 8 Hz, phenyl), 7.65 (1 H, dd, J = 8 and 1.8 Hz, phenyl), 8-7.7 (15 H, 3 m, phenyl + 1 pyrrole), 7.57 (2 H, d, J = 8 Hz, phenyl), 7.4 (2 H, broad signal, phenyl), 7.09 (1 H, dd, J = 3.6 and 4.5 Hz, 6-membered ring olefinic H), 7.00 (2 H, d, J = 8 Hz, phenyl), 6.30 (1 H, d, J = 8 Hz, phenyl), 6.23 (1 H, d, J = 8 Hz, phenyl), 5.70 (1 H, d, J = 8 Hz, phenyl), 4.07 (1 H, d, J = 8 Hz, phenyl), 3.86 (1 H, dd, J = 17 and 3.6 Hz, 6-membered ring CH_2), 3.83 (1 H, dd, J = 17 and 4.5 Hz, 6-membered ring CH_2), 1.59, 1.58, 1.55, 1.52, 1.47, 1.01, 0.99, and -0.69 (3+3+3+3+3+3+3+3 H, 8 s, *t*-butyl).

UV-vis. (CH_2Cl_2) λ_{max} = 442 nm (ε = 229000), 465 (sh.) (ca 175000), 562 (29200), 598 (24000), 635 (sh.) (ca 12000). ^{1}H NMR ($CDCl_3$), see Scheme below.

Elemental analysis calcd for $C_{124}H_{118}N_8Ni_2$: C 81.04, H 6.47, N 6.10; found : C 80.98, H 6.81, N 5.98.



Scheme 3. NMR data for brown dimer **3**. The molecule is shown unfolded for clarity. All signals appearing on schemes have been unequivocally assigned (COSY + ROESY).

Acylation of nickel *meso*-tetra-(3,5-di-*t*-butylphenyl)porphyrin 1 (Ar = 3,5-di-*t*-butylphenyl)

To a solution of porphyrin **1** (Ar = 3,5-di-*t*-butylphenyl) (200 mg) and acetic anhydride (1 mL) in CH_2Cl_2 (10 mL) was added $SnCl_4$ (0.2 mL). The solution turned rapidly green and, after being stirred for 4 min, was treated with saturated aqueous $NaHCO_3$ (100 mL), washed with water (3 x 100 mL), dried (Na_2SO_4) evaporated and chromatographed on silica gel (400 mL in toluene). Slow elution with toluene gave successively green **6** (Ar = 3,5-di-*t*-butylphenyl) (50 mg; 24 %), red **4** (Ar = 3,5-di-*t*-butylphenyl) (70 mg; 33 %), a minor green fraction, followed by a mixture of diacetylated starting material (26 mg; 12 %), identified as such by mass spectrometry and NMR (pyrrole H / acetyl methyl ratio) but not further studied. When the reaction mixture was kept for a longer time before hydrolysis, diene **6** formed at the expense of **4** and its yield could reach 63 %.

4

^{1}H NMR ($CDCl_3$) : δ = 8.88 (1 H, s, pyrrole), 8.77 and 8.75 (1+1 H, 2 d, J = 5 Hz, pyrrole), 8.72 (3 H, m, pyrrole), 8.57 (1 H, d, J = 5 Hz, pyrrole), 784 (6 H, m, Ar-H_{ortho}), 7.79 (2 H, d, J = 1.8, Ar-H_{ortho} next to acetyl), 7.73 (1 H, dd, J = 1.8 Hz, Ar-H_{para} next to acetyl), 7.70 (3 H, m, Ar-H_{para}), 1.72 (3 H, s, methyl), 1.45 (72 H, broad s, *t*-butyl).

UV-vis. (CH_2Cl_2) λ_{max} = 424 nm (ε = 203000), 536 (17300).

Elemental analysis calcd for $C_{78}H_{94}N_4ONi$: C 80.60, H 8.15, N 4.82; found : C 80.62, H 8.31, N 4.70.

6

^{1}H NMR ($CDCl_3$) : δ = 9.39 and 8.81 (1+1 H, 2 d, J = 5 Hz, pyrrole next to cyclized aryl), 8.71 (1 H, s, pyrrole), 8.64 (2 H, s, pyrrole), 8.63 and 8.61 (1+1 H, 2 d, J = 5 Hz, pyrrole), 7.7-7.9 (6 H, very broad signal, Ar-H), 7.80 and 7.61 (1+1 H, 2 d, J = 1.8 Hz, Ar-H_{ortho}), 7.72, 7.68, and 7.67 (1+1+1 H, 3 dd, J = 1.8 Hz, Ar-H_{para}), 6.15 and 6.06 (1+1 H, 2 d, J = 1.2 Hz, =CH_2), 1.73 (3 H, s, *t*-butyl), 1.49, 1.47, 1.45, and 1.43 (18+18+18+9 H, 4 s, *t*-butyl).

UV-vis. (CH_2Cl_2) λ_{max} = 450 nm (ε = 171000), 570 (14200), 616 (12500).

Elemental analysis calcd for $C_{78}H_{92}N_4Ni$. CH_2Cl_2 : C 77.19, H 7.71, N 4.56; found : C 77.55, H 8.07, N 4.78.

When reacted with pivaloyl anhydride under identical conditions - except that the reaction time was 1 h - porphyrin **1** (Ar = *p*-*t*-butylphenyl) gave **7** (15 %) and **8** (5 %), in addition to recovered starting material (13 %).

7

^{1}H NMR ($CDCl_3$) : δ = 9.48 and 8.82 (1+1 H, 2 d, J = 5 Hz, pyrrole next to the cyclized phenyl), 8.77 (1 H, s, pyrrole), 8.63 and 8.59 (1+1 H, 2 d, J = 5 Hz, pyrrole), 8.61 (2H, s, pyrrole), 8.24 (1 H, d, J = 1.8 Hz, cyclized phenyl), 7.5-7.9 (14 H, m, phenyl), 2.61 (1 H, s, OH), 1.57, 1.55, 1.54, and 1.47 (9+9+9+9 H, 4 s, phenyl-*t*-butyl), 1.09 (9 H, s, *t*-butyl).

UV-vis. (CH_2Cl_2) λ_{max} = 442 nm (ε = 179000), 558 (15400), 598 (11500).

Elemental analysis calcd for $C_{65}H_{68}N_4ONi$: C 79.67, H 6.99, N 5.72; found : C 79.02, H 7.02, N 5.68.