Conformational Flexibility of 1,4-Naphthiporphyrin Promotes a Palladium Mediated Contraction of Naphthalene toIsoindene

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Supporting Information

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Experimental section

Synthesis.

Scheme S1. Synthesis and reactivity of 11; i – benzene, aluminium chloride, 1,2-dichloroethane, 48 hours; ii – lithium aluminium hydride, tetrahydrofuran, 24 hours.

Synthetic procedures and analytical data.

1,4-dibenzoylnaphthalene (10). In a small beaker protected from moisture, naphthalene-1,4-dicarboxylic acid dichloride (9.1 g, 36 mmol) and anhydrous aluminium chloride (11.7 g, 88 mmol) were stirred in ethylene dichloride (20 mL) until a homogeneous suspension was obtained. The suspension was slowly added to benzene (10 mL, 0.12 mol) placed in a 250 mL round-bottomed flask with continuous stirring following addition of second portion of ethylene dichloride (150 mL). The reaction mixture was then refluxed for 48 hours. The reaction mixture was quenched by addition to 200 mL of brine and extracted with dichloromethane (4×100 mL). The organic extracts were dried over anhydrous magnesium sulfate, filtered and evaporated to dryness. The product was sufficiently pure to be used in the next step. Yield 9.7 g (80 %).

\[1H\text{ NMR (500 MHz, chloroform-}d, 298K) \delta 8.03 (\text{AA'BB' spin system, 2H}), 7.88 (d, 4H, }^{3}J=7.8 \text{ Hz}), 7.61 (t, 2H, }^{3}J=7.4 \text{ Hz}), 7.58 (s, 2H), 7.50 \text{ AA'BB' spin system, 2H), 7.47 (t, 4H, }^{3}J=7.7 \text{ Hz).}\]

\[13C\text{ NMR (126 MHz, chloroform-}d, 298K) \delta 197.61, 139.23, 137.67, 133.74, 131.13, 130.44, 128.65, 127.63, 126.08, 125.30.\]

1,4-Bis(phenylhydroxymethyl)naphthalene (11). In a 500 mL round-bottomed flask equipped with a magnetic stirring bar and immersed in an oil bath, 1,4-dibenzoylnaphthalene 10 (9.7 g, 29 mmol) was dissolved in THF (700 mL) under a protective atmosphere. Solid lithium aluminum hydride (2.7 g, 2.5 equiv.) was then added in small portions, so as to avoid excessive gas evolution. The reaction mixture was then refluxed for 24 hours. After reaching the ambient temperature, the reaction was quenched by cautious addition of water (10 mL) followed by 2 M aqueous NaOH (5 mL). The reaction mixture was filtered and stripped of solvent on a rotary evaporator, affording a white solid. Yield 8.7 g (90 %).

\[1H\text{ NMR (500 MHz, chloroform-}d, 298K, mixture of isomers): }\delta 8.07 \text{ and 8.05 (2x AA'BB' spin system, 2H), 7.65 and 7.61 (2xs, 2H), 7.41 – 7.37 (m, 6H), 7.32 (t, 4H, }^{3}J=7.3 \text{ Hz), 7.26 (t, 2H, }^{3}J=7.3 \text{ Hz), 6.53 and 6.52 (2xd, 2H, }^{3}J=4.1 \text{ Hz), 2.34 and 2.33 (2xd, 2H, }^{3}J=4.1 \text{ Hz).}\]

\[13C\text{ NMR (126 MHz, chloroform-}d, 298K, mixture of isomers) }\delta 143.02, 139.03 \text{ and 138.96, 131.22, 128.60 and 128.57, 127.79 and 127.73, 127.12 and 127.04, 125.87, 124.78 and 124.66, 124.30 and 124.14, 73.80 and 73.64.}\]
### Table S1. Crystal data and structure refinement for compound 1, 2, 4 and 6.

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**Unit cell dimensions**

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Figure S1. $^1$H NMR spectra of 1,4-naphthiporphyrin in chloroform-$d$ at 220 K: (A) spectrum of 1-i alone NH (1H), 2.86 ppm; (B) spectrum after addition of 40 μL of chloroform-$d$ saturated with water (NH 2.27 ppm (1H), H$_2$O ppm (0.84 H)); (C) spectrum after addition of 60 μL of chloroform-$d$ saturated with water (NH 1.94 ppm (1H), H$_2$O –1.87 ppm (1.34 H)); (D) spectrum of 1-i in chloroform-$d$ saturated with water (NH 2.00 ppm (1H), H$_2$O –0.16 ppm (1.91 H)). The specific resonance assignments, if given, follow the systematic numbering of 1-i, * not identified impurities.

Figure S2. Part of NOESY spectrum of 1-i(H$_2$O) recorded in chloroform-$d$, 220K.
Figure S3. Parts of $^1$H NMR spectra of 1-i recorded in chloroform-$d$ in 300K – 220K temperature range.
Figure S4. $^1$H NMR of 10 (500 MHz, chloroform-$d$, 298 K).

Figure S5. $^1$H NMR of 11 (500 MHz, chloroform-$d$, 298 K).
Figure S6. $^1$H NMR of 3 (500 MHz, chloroform-$d$, 298 K).

Figure S7. $^{13}$C NMR spectrum of 10 (126 MHz, chloroform-$d$, 298 K).
Figure S8. $^{13}$C NMR spectrum of 11 (126 MHz, chloroform-$d$, 298K).

Figure S9. $^{13}$C NMR spectrum of 3 (126 MHz, chloroform-$d$, 298K).
Figure S10. $^{13}$C NMR spectrum of 1 (126 MHz, chloroform-$d$, 298K).

Figure S11. $^{13}$C NMR spectrum of 2 (151 MHz, chloroform-$d$, 298K).
Figure S12. $^{13}$C NMR spectrum of 4 (151MHz, chloroform-$d$, 220K).

Figure S13. $^{13}$C NMR spectrum of 6 (151MHz, chloroform-$d$, 298K).
Figure S14. $^{13}$C NMR spectrum of 7 (151MHz, chloroform-$d$, 298K).
**Figure S15.** HR-MS spectrum of 3 (ESI+, TOF).

**Figure S16.** HR-MS spectrum of 1 (ESI+, FT-MS).

**Figure S17.** HR-MS spectrum of 2 (ESI+, TOF).
Figure S18. HR-MS spectrum of 4 (ESI+, TOF).

Figure S19. HR-MS spectrum of 6 (ESI+, TOF).

Figure S20. HR-MS spectrum of 7 (ESI+, TOF).
Figure S21. The electronic absorption spectrum (dichloromethane, 298K) of 1.

Figure S22. The electronic absorption spectrum (dichloromethane, 298K) of 1·2H⁺
Figure S23. The electronic absorption spectra recorded during titration of 1 with trifluoroacetic acid (1 – green line, 1·H⁺ – orange line, 1·2H⁺ – red line, dichloromethane, 298K).

Figure S24. The electronic absorption spectrum (dichloromethane, 298K) of 2.
Figure S25. The electronic absorption spectrum (dichloromethane, 298K) of 2·2H⁺.

Figure S26. The electronic absorption spectrum (dichloromethane, 298K) of 4.
**Figure S27.** The electronic absorption spectrum (dichloromethane, 298K) of 6.

**Figure S28.** The electronic absorption spectrum (dichloromethane, 298K) of 7.
References:
