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Phthalocyanines bearing bulky cycloalkylmethyl substituents on non-peripheral sites

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ABSTRACT

Octasubstituted phthalocyanines bearing bulky (cyclopentyl)methyl- and (cyclohexyl)methyl-substituents in non-peripheral positions are prepared and characterised. The synthesis of the precursor phthalonitriles is achieved through nickel-catalysed cross-coupling employing alkylzinc reagents. In the case of the (cyclopentyl)methyl derivative the formal precursor is 5-hexenyl bromide which yields the cyclised material exclusively on formation of the zinc reagent and subsequent cross-coupling.

Phthalocyanines are important molecular materials because of the potential for such molecules to form the functional component of optoelectronic devices.[1,2] Their use in such applications typically requires a combination of molecular (optical absorption/band gap, redox, etc.) and bulk (solubility, processability, self-assembly, mesophase formation, etc.) properties. For this reason, a large number of phthalocyanine derivatives have been prepared. Such modifications can focus on a combination of variation of the (organic) core structure (e.g. introduction of substituents to change absorption and/or solubility properties) and the central metal ion (more than 70 elements can be introduced) Figure 1.

One drawback to using phthalocyanines in cheap, mass production devices is the difficulty in applying them through conventional solution phase processes such as inkjet or screen printing. Simple phthalocyanines have poor solubility and tend to be applied through high-vacuum evaporation techniques. The solubility issue has been overcome through preparation of substituted derivatives and high solubilities can be achieved.[3] We have paid particular attention to phthalocyanines substituted in the so-called non-peripheral positions[4] and introduction of eight alkyl groups renders the phthalocyanines, and their metallated derivatives, freely soluble in most organic solvents. However, at moderate-high concentrations the macrocycles self-assemble into higher aggregates.[5] A potential strategy to overcome this (face-to-face) aggregation is to increase the steric bulk of the substituent close to the phthalocyanine core. Such perturbation also has the potential to distort the phthalocyanine nucleus from planarity and induce useful spectral changes.[6] In this Letter we report two such derivatives where (cycloalkyl)methyl substituents are introduced onto the non-peripheral sites of the phthalocyanine core.

Our two target molecules are shown in Figure 2 and bear, respectively, eight (cyclopentyl)methyl- and (cyclohexyl)methyl substituents. As with most phthalocyanine syntheses the main challenge rests with the preparation of appropriate phthalonitrile precursors. 3,6-Dialkylphthalonitriles are prepared routinely in our laboratories and a number of synthetic routes are available.[7] Our preferred route (Scheme 1) employs Negishi coupling between phthalonitrile ditriflate **3** and an alkylzinc halide, and we reasoned that this procedure could be modified to achieve the synthesis of (cyclohexyl)methyl-derivative **1**.

(Cyclohexyl)methyl bromide is readily available but, in our hands, its conversion into the corresponding alkylzinc reagent (using activated zinc dust) proved inefficient and capricious. Conversion into the corresponding iodide (Finkelstein reaction using sodium iodide) avoided this problem and permitted smooth forma-

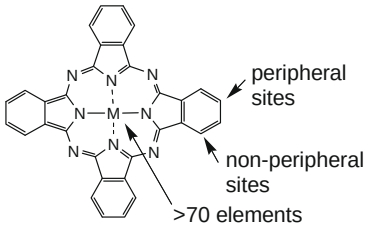

Figure 1. Phthalocyanine and simple sites for modification.

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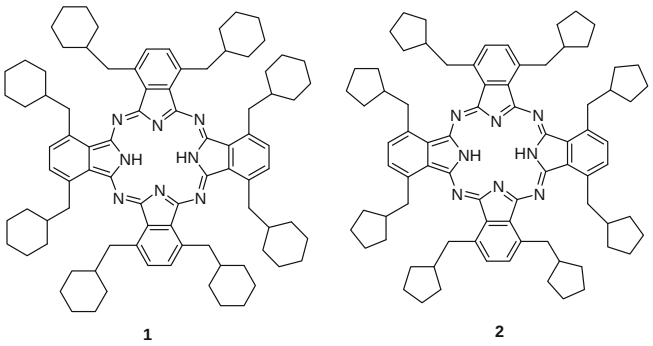
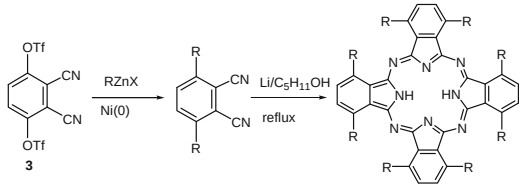


Figure 2. Target phthalocyanines.

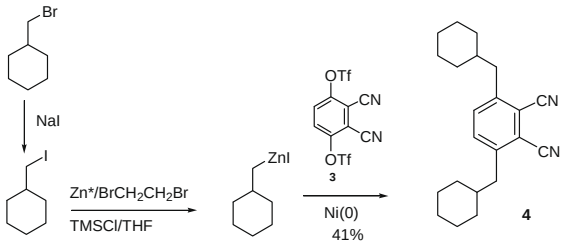


Scheme 1. Synthesis of non-peripherally substituted octaalkyl phthalocyanines.

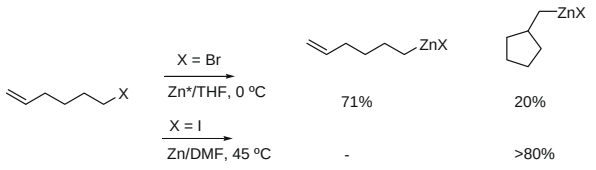
tion of (cyclohexyl)methylzinc iodide. The zinc reagent coupled smoothly with ditriflate **3**, despite its steric demand, to give the dialkylphthalonitrile **4**[8] (Scheme 2).

Synthesis of (cyclopentyl)methyl derivative **6** by a similar route was less straightforward because the corresponding iodide/bromide was not readily available. However, a survey of the literature revealed that formation of the zinc reagent from 5-hexenyl iodide/bromide leads to ring closure to form varying proportions of the required (cyclopentyl)methylzinc halide. Reports are, however, inconsistent. In the case of 5-hexenyl bromide (activated zinc, THF) Rieke[9] reports cyclisation of only ca. 20% and suggests that the cyclisation occurs during formation of the zinc reagent. In contrast, Marek and Normant[10] reported exclusive cyclisation when the zinc reagent was prepared from 5-hexenyl iodide using zinc in DMF at 45 °C (Scheme 3).

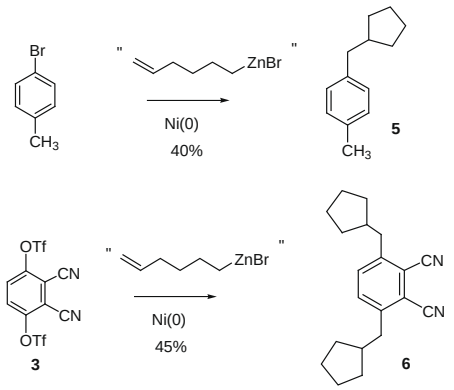
For our synthesis, where two couplings were required, exclusive formation of (cyclopentyl)methylzinc halide was clearly required to prevent formation of a complex mixture of products. A model coupling reaction was therefore performed between 4-bromotoluene and commercial[11] 5-hexenylzinc bromide under the conditions employed in our typical phthalonitrile syntheses (Scheme 4). Somewhat surprisingly, analysis of the crude product revealed that the only cross-coupled product was the (cyclopentyl)methyl derivative **5** (it shows a distinctive doublet at δ 2.60). Use of the same commercial reagent led therefore to smooth formation of 3,6-bis(cyclopentyl)methylphthalonitrile **6**[8] without the need for further refinement of reaction conditions or protocol.



Scheme 2. Synthesis of 3,6-bis[(cyclohexyl)methyl]phthalonitrile **4**.

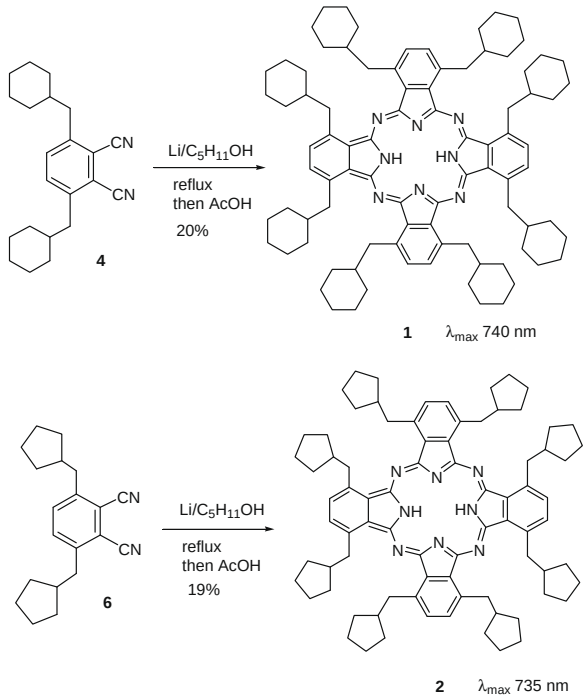


Scheme 3. Reaction of 5-hexenyl halides with zinc.



Scheme 4. Synthesis of 3,6-bis[(cyclopentyl)methyl]phthalonitrile **6** from commercial '5-hexenylzinc bromide'.

The phthalonitriles were cyclised to the corresponding phthalocyanines using the standard conditions of lithium/refluxing pentanol (Scheme 5). Work-up with acetic acid afforded the metal-free phthalocyanines which were purified by column chromatography.[8] Isolated yields of pure material were consistently around 20%, and typical for such phthalocyanine syntheses in our experience and independent of scale, indicating that the steric demand had only limited impact on the cyclisation reaction efficiency. UV–vis spectra showed no evidence of broadening due to aggregation but were



Scheme 5. Synthesis of phthalocyanines **1** and **2**.

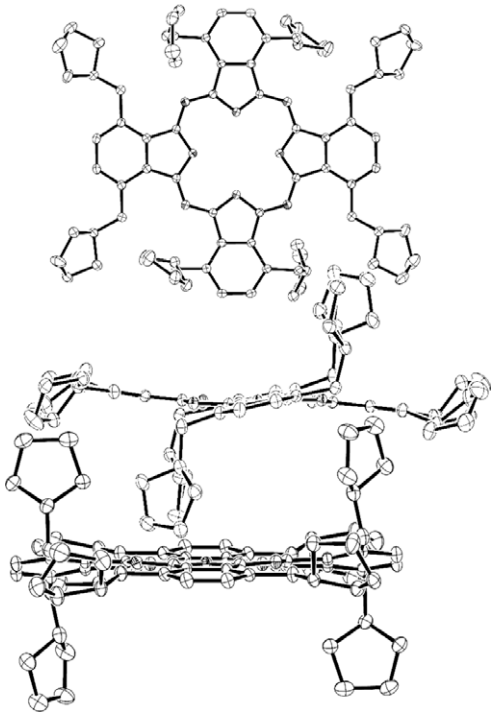


Figure 3. X-ray crystal structure of **2**.

red-shifted compared to straight-chain octaalkylphthalocyanines (λ_{max} **2** = 735 nm, **1** = 740 nm). Such spectral shifts are characteristic of twisting in the phthalocyanine core.[6] Crystals suitable for X-ray structure determination were obtained for **2** (Fig. 3) and deviation from planarity (a twist of ca. 12°) was clearly observed in the solid state.[12]

In conclusion, we have reported the synthesis of non-peripherally substituted phthalocyanines bearing eight (cyclopentyl)-methyl- and (cyclohexyl)methyl-substituents. The phthalonitrile precursors were prepared from the corresponding zinc reagent although, in the case of (cyclopentyl)methylzinc bromide, the reagent was formally accessed from 5-cyclohexenyl bromide via cyclisation. The phthalocyanines show red-shifted spectra indicating that the steric demand of the substituents causes a twist in the phthalocyanine core. The X-ray crystal structure of **2** clearly shows this twist in the solid state. UV–vis and ^{1}H NMR spectra show sharp peaks characteristic of non-aggregated species.

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Supplementary data

Supplementary data (experimental and X-ray crystallography details) associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2009.07.016.

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8. Synthesis of phthalonitrile **6**. Bis(triphenylphosphine)nickel dichloride (0.154 g, 10 mol%) and triphenylphosphine (0.124 g, 20 mol%) were dissolved in dry THF (10 ml) under argon. *n*-Butyllithium (0.2 ml, 20 mol%, 2.5 M in hexane) was added to afford a blood-red solution. 3,6-Bis(trifluoromethanesulfonyloxy)-phthalonitrile (1 g, 2.36 mmol) and lithium chloride (0.3 g, 7.1 mmol) were added at once to the reaction mixture under a fast stream of argon. The resulting brown solution was cooled to −78 °C. 5-Hexenylzinc bromide in THF (7.58 mmol, 15.15 ml of a 0.5 M solution) was added dropwise over 15 min. The solution was then left to warm to rt and stirring was continued overnight. A 5% aq solution of HCl (20 ml) was carefully added and the mixture was extracted with ethyl acetate (2 × 30 ml). The combined organic layers were successively washed with a 5% aq solution of HCl (20 ml), a 5% aq solution of NaOH (20 ml) and brine (20 ml), then dried ($MgSO_4$), filtered and the solvents removed under reduced pressure. The resulting brown oily residue was purified by column chromatography on silica gel [eluent: petroleum ether (bp 40–60 °C)-dichloromethane, 1:1] to give **6** (0.31 g, 45%). δ_H (400 MHz, acetone-d_6) 7.74 (2H, s), 2.90 (4H, d, *J* 7.6), 2.26–2.11 (m, 2H), 1.73–1.64 (8H, m), 1.58–1.51 (4H, m), 1.30–1.24 (m, 4H); δ_C (100 MHz, acetone-d_6) 145.8, 134.5, 115.9, 115.7, 41.6, 39.8, 32.1, 24.6; mp 119–121 °C; R_f 0.5 [1:1 petroleum ether (bp 40–60 °C)/dichloromethane]; HRMS (ES+) calcd 310.2278, obtained 310.2280 ($[M^+NH_4]^+$, 100%); ν_{max} (Nujol) 2221 (CN) cm^{-1}. Phthalonitrile **4** was similarly prepared (41%). δ_H (400 MHz, $CDCl_3$) 7.41 (2H, s), 2.74 (4H, d, *J* 6.8), 1.73–1.61 (m, 12H), 1.23–1.15 (6H, m), 1.09–1.03 (4H, m); δ_C (100 MHz, $CDCl_3$) 145.0, 134.1, 116.3, 115.7, 42.4, 39.7, 33.1, 26.4, 26.3; mp 125–126 °C; 0.41 [1:1 petroleum ether (bp 40–60 °C)/dichloromethane]; HRMS (ES+) calcd 338.2591, obtained 338.2592 ($[M^+NH_4]^+$, 100%); ν_{max} (Nujol) 2218 (CN) cm^{-1}. Synthesis of phthalocyanine **2**. 3,6-Bis(cyclopentylmethyl)phthalonitrile **6** (100 mg, 0.342 mmol) was dissolved in hot pentan-1-ol (5 ml). Lithium metal (9.49 mg, 4 equiv) was added in portions to the refluxing mixture. The solution was refluxed for 6 h. The resulting green mixture was allowed to cool slightly and acetic acid (5 ml) was added. This was stirred for 30 min until rt was achieved. Excess methanol (15 ml) was added subsequently and the flask was placed in a fridge overnight. The resulting green precipitate was filtered and washed with methanol. The solid was purified by column chromatography over silica gel [eluent: petroleum ether (bp 40–60 °C)]. The main green fraction afforded **2** which was recrystallised from THF–methanol (19 mg, 19%). δ_H (400 MHz, C_6D_6) 7.79 (8H, s), 4.67 (16H, d, *J* 7.2), 2.86–2.65 (m, 8H), 1.90–1.30 (64H, m), −0.15 (2H, br s); mp > 300 °C; MALDI-MS isotopic cluster at *m/z* 1171.8 [M$^+$, 100%]; λ_{max} (THF, log ε/M^{-1} cm^{-1}) 735 (5.3), 706 (5.2), 360 nm; ν_{max} (neat) 3301 (NH) cm^{-1}. Phthalocyanine **1** was similarly prepared (20% on reaction scales 100 mg and 370 mg). δ_H (400 MHz, C_6D_6) 7.82 (8H, s), 4.68 (16H, d, *J* 7.2), 2.32–2.15 (m, 8H), 2.10–1.09 (80H, m), −0.09 (2H, br s); mp > 300 °C; MALDI-MS isotopic cluster at *m/z* 1283.9 [M$^+$, 100%]; λ_{max} (toluene, log ε/M^{-1} cm^{-1}) 740 (5.4), 709 (5.4), 363 nm; ν_{max} (neat) 3297 (NH) cm^{-1}.
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