# A remarkable side-product from the synthesis of an octaalkylphthalocyanine: formation of a tetrabenzotriazaporphyrin

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1,4,8,11,15,18,22,25-Octahexyl-29$H$,31$H$-tetrabenzo[$b$,$g$,$l$,$q$]-[5,10,15]triazaporphyrin has been isolated as the main side product in the preparation of 1,4,8,11,15,18,22,25-octahexylphthalocyanine *via* a lithium pentyloxide induced cyclotetramerisation of 3,6-dihexylphthalonitrile.

Linstead and co-workers described several routes to phthalocyanine of which the lithium alkoxide induced cyclotetramerisation of phthalonitrile is one.[1] The reaction gives initially the lithium metallated macrocycle but work-up with dilute acid replaces the lithium ions in the central cavity with protons. The procedure, in various guises, has been applied extensively and successfully for the syntheses of numerous substituted metal-free phthalocyanines from appropriately substituted phthalonitriles.[2] These can be converted into the corresponding metallated macrocycles by reaction with a metal salt. In our laboratories this protocol has provided access, for example, to liquid crystalline derivatives,[3] compounds for photodynamic therapy,[4] and derivatives appropriate for deposition as thin films.[5] In our experience, the cyclotetramerisation reaction gives yields of 20–35% of the substituted metal-free phthalocyanine. Side products are presumed to be non-cyclised material but on occasions we have noted the formation of traces of other blue-green material.

We have now discovered that subtle changes to the experimental protocol of the lithium pentyloxide induced conversion of 3,6-dihexylphthalonitrile into 1,4,8,11,15,18,22,25-octahexylphthalocyanine **1** can suppress or enhance the formation of one particular coloured side product. Much appears to depend upon the sequence through which the reagents and substrate are added, and more particularly the lithium to phthalonitrile ratio and concentration. Thus addition of phthalonitrile to a solution of preformed lithium pentyloxide in pentanol, procedure A, either at reflux or at room temperature followed by heating to reflux, affords **1** with no trace of other coloured products. However, when lithium pentyloxide is generated by addition of freshly cut lithium to a solution of the phthalonitrile in pentanol, procedure B, a coloured side product appears. Both procedures are undertaken under $N_2$ and in the dark. In a typical experiment using procedure B, 2.1 equivalents of lithium were added to a solution of 3,6-dihexylphthalonitrile (100 mg) in pentanol (1 ml) and heated to reflux for 6 h. This produced a 95 : 5 ratio of **1** and a second product **2** separable by column chromatography (cyclohexane as eluent) with the former eluted first. On increasing the number of equivalents of lithium to 19, the proportion of **2** increased to a ratio of **1** : **2** = 77 : 23

(Scheme 1). When the same reaction was performed in refluxing octanol with excess lithium the ratio became 53 : 47.

Compound **2** was identified as 1,4,8,11,15,18,22,25-octahexyl-29$H$,31$H$-tetrabenzo[$b$,$g$,$l$,$q$][5,10,15]triazaporphyrin, initially on the basis of the ^{1}H- and ^{13}C-NMR spectra which are more complex than those of **1**. Fast exchange of the central protons of the latter (on the NMR timescale) renders the symmetry to be effectively $D_{4h}$. In contrast, **2** has effectively $C_{2v}$ symmetry. Thus the aromatic protons which appear as a singlet in the spectrum of **1** give rise to two AB patterns in the spectrum of **2**. The latter also shows four types of benzylic methylene groups but the most characteristic signal is a singlet at 10.8 ppm ($CDCl_3$) assigned to the methine proton on the central core. The ^{13}C-NMR spectrum includes four separate aromatic C–(H) signals *ca.* 128–131 ppm and the methine carbon at 104.6 ppm. MALDI-tof spectra show a cluster centred at 1187 D for **2** compared to 1188 D for **1**.

The single crystal X-ray structure of **2**,† Fig. 1, confirmed the assignment. The locations of the hexyl groups and the molecular packing of the molecules are closely similar to those already reported for **1** itself[6] and, as expected, the challenge was to establish that a bridging CH had indeed replaced the bridging N of **1**. Thus towards the end of the refinement, difference peaks close to atom (20), denoted by an asterisk (*) in Fig. 1, and N(1) were taken to represent H atoms and were included with occupancies of 0.5 and 1.0 respectively: the $U_{iso}$ values were refined freely and satisfactorily. The atom (20) is disordered, half as nitrogen, half as carbon (with the H atom), so that overall there is one bridging CH group per molecule. (See also the legend to Fig. 1).

The melting behaviour of **1**, leading to a thermotropic columnar mesophase of disordered hexagonal symmetry in the range 161–171 °C,[3] is paralleled by the behaviour of **2**. The latter shows the same type of mesophase, as judged by the characteristic birefringence pattern observed by polarised light microscopy, between 151–172 °C. This broader temperature range may reflect the minor disordering arising from the two possible locations of the C–H unit. The compounds give different Q-band absorptions in the visible spectra: **1**, $\lambda_{max}$ 726 nm (Qx) and 696 (Qy); **2**, $\lambda_{max}$ 716 nm and 674 nm.

We subsequently showed that 3,6-dimethyl-, 3,6-dioctyl- and 3,6-didecylphthalonitriles gave corresponding mixtures of phthalocyanine and tetrabenzotriazaporphyrin. However, we detected no formation of a tetrabenzotriazaporphyrin derivative when the reaction was applied to 4-$t$-butylphthalonitrile or 4,5-dihexylphthalonitrile.

Tetrabenzotriazaporphyrins[7] have been prepared hitherto by reacting phthalonitriles with a Grignard reagent and indeed we subsequently prepared a further sample of **2** by reacting

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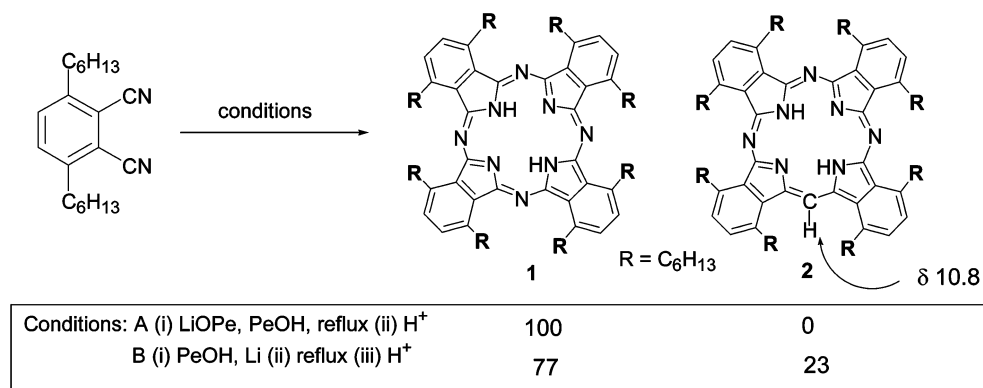
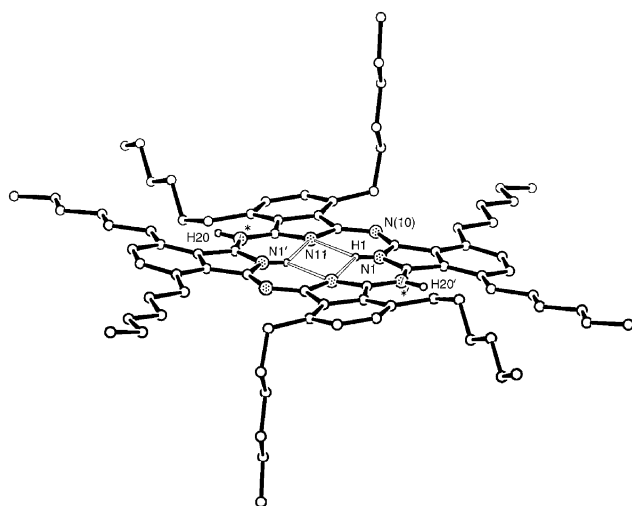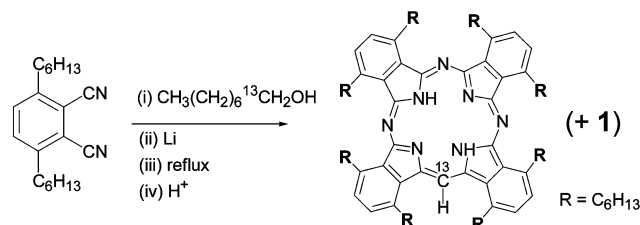Scheme 1 The unexpected formation of triazatetrabenzoporphyrin 2.



Fig. 1 Crystal structure of 2. The atom marked * is disordered and is either N(20) or C(20); correspondingly *' is C(20') or N(20').



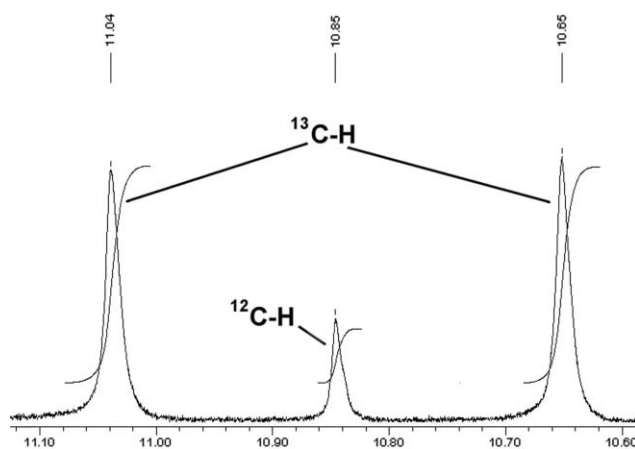Scheme 2 Labelling experiment to show the origin of methine carbon.



Fig. 2 Part of the ¹H-NMR spectrum of partially labelled 2 showing the methine singlet at 10.8 ppm and the corresponding doublet $J_{C-H}$ 155 Hz.

3,6-dihexylphthalonitrile with MeMgI. Whereas the origin of the bridging CH group is self evident in this procedure it is much less obvious under the new conditions described above. Repetition of the reaction with 3,6-dihexylphthalonitrile with lithium in pentanol as solvent but with addition of various one carbon atom species *i.e.* cyanide ion (from NaCN or tetra-*t*-butylammonium cyanide), $CO_2$ or CO failed to change the ratio of 1 : 2 in favour of 2.

There thus remained three possible but apparently unlikely sources of the bridging CH group: a benzylic chain from either the precursor or the phthalocyanine product, a CN of the phthalonitrile itself, or the solvent. We explored the last of these possibilities by running a small scale reaction of 3,6-dihexylphthalonitrile with lithium in labelled octanol (> 99% ¹³C at the 1-position) (Scheme 2). No ¹³C was incorporated into the phthalocyanine component of the product mixture as judged by ¹³C NMR; instead the ¹³C signal for the bridging CH position of 2 was much enhanced. The ¹H NMR signal for the CH proton is shown in Fig. 2. This clearly shows a doublet for the ¹³C coupled proton; however, there is also a singlet for a non-coupled proton. Integration of these signals shows that the ratio of ¹³C/¹²C at the bridging carbon is 87 : 13, *i.e.* 87% of this carbon is derived from the 1-position of octanol. At this time the source of the remaining 13% is unknown.

The reaction whereby the label is introduced into 2 evidently involves at some point the loss of seven carbon atoms from the octanol, or a product derived from it. Some insight into this has become available through one further experiment in which 3,6-dihexylphthalonitrile was reacted with decyl magnesium bromide. Rather than obtaining a derivative of 2 bearing a nonyl group at the bridging C atom, the product was 2 itself. Thus it appears that cleavage of an alkyl chain may be a feature of the synthesis of octaalkyltetrabenzotriazaporphyrins from 3,6-dialkylphthalonitrile precursors.

The mechanism of the reaction leading to 2 as a side product in phthalocyanine formation, and in particular the role of excess lithium, will be the subject of a future investigation.

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## Notes and references

† *Crystal data:* $C_{81}H_{115}N_7$, $M = 1186.8$. Dark blue, rectangular prism crystals. Triclinic, space group $P$-1 (no. 2), $a = 9.220(15)$, $b = 9.633(11)$, $c = 19.87(4)$ Å, $\alpha = 80.13(5)$, $\beta = 91.14(8)$, $\gamma = 84.48(6)°$, $V = 1729(5)$ Å$^3$. $Z = 1$, $F(000) = 650$, $T = 140(1)$ K, $\mu$(Mo-K$\alpha$) = 0.7 cm$^{-1}$, $\lambda$(Mo-K$\alpha$) = 0.71069 Å. Intensity data from Rigaku R-Axis IIc image-plate diffractometer with rotating anode X-ray source. From 6474 reflections to $\theta_{max} = 22.0°$, 3873 were unique ($R_{int} = 0.25$), 2384 'observed' with $I > 2\sigma_I$. Structure determined by direct methods in XS;[8] refinement by full-matrix least-squares methods, in XL[8] and SHELXL.[9] Non-hydrogen atoms refined anisotropically. Hydrogen atoms (except those discussed elsewhere) included in idealised positions with $U_{iso}$'s riding. At conclusion, $wR_2 = 0.198$ and $R_1 = 0.123$ for all 3873 reflections weighted $w = [\sigma^2(F_o^2) + (0.0990P)^2]^{-1}$ with $P = (F_o^2 + 2F_c^2)/3$; for the 'observed' data only, $R_1 = 0.074$. CCDC 252175. See http://www.rsc.org/suppdata/cc/b4/b414820g/ for crystallographic data in .cif or other electronic format.

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