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# Synthesis and crystal structure of a *meso*-trialkynyl-[28]hexaphyrin †

**Alexander Krivokapic and Harry L. Anderson** *
*Department of Chemistry, University of Oxford, Dyson Perrins Laboratory, South Parks Road, Oxford, UK OX1 3QY. E-mail: harry.anderson@chem.ox.ac.uk; Fax: 44 1865 275674; Tel: 44 1865 275704*

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**A 5,15,25-trialkynyl [28]hexaphyrin(1.1.1.1.1.1) is the main product of the boron trifluoride-catalysed condensation of *meso*-anthryl dipyrromethane and triisopropylsilylpropynal; it absorbs strongly in the near-infrared, out to 1093 nm.**

## Introduction

The acid catalysed condensation of dipyrromethanes with aldehydes is a well established route to 5,15-disubstituted porphyrins.[1–3] As part of a project on the synthesis of porphyrins for nonlinear optics,[4] we recently prepared porphyrin **1** by condensation of dipyrromethane **2** with triisopropylsilylpropynal **3** (Scheme 1). We were surprised to find that the main product of this reaction is the hexaphyrin **4**, isolated in 37% yield. ‡ This yield may seem modest, but exceeds that of all previously reported hexaphyrins.[5–9] § This is also the first time that a hexaphyrin has been prepared in which the substituents at the six *meso*-positions are not all identical. The expected porphyrin was also isolated from the reaction mixture in 22% yield. The chlorine substituent is not essential for this reaction, and the chlorine-free analogue of dipyrromethane **2** gives a similar ratio of porphyrin to hexaphyrin. However other dipyrromethanes do not give significant amounts of hexaphyrins under these conditions,[10] and dipyrromethane **2** does not form hexaphyrins when condensed with simple benzaldehydes such as 3,5-di-(*t*-butyl)benzaldehyde and 3,5-dimethoxybenzaldehyde. The formation of a hexaphyrin in this reaction may be partly due to the electron-deficient nature of triisopropylsilylpropynal **3**, because other electron-deficient aldehydes, such as pentafluorobenzaldehyde, also have a propensity for hexaphyrin formation.[7,8] We have not tested the condensation of pentafluorobenzaldehyde with dipyrromethane **2**.

Crystals of porphyrin **1** and hexaphyrin **4** were grown from toluene by addition of methanol, and analysed by X-ray diffraction.¶ The molecular structure of **4** is shown in Fig. 1. The structure of **1** does not have any unusual features so is not illustrated here. The four NH hydrogens of the hexaphyrin were located directly from the electron-density map, and their locations were confirmed by the wider N–C–N bond angles at these protonated nitrogens (108–111° *vs.* 105–106°). The macrocycle is essentially planar, with the anthracene units almost perpendicular to the main π-system. Trans-annular steric interactions between the inwardly pointing β-pyrrole hydrogens (at C2, C3, C17 and C18) result in a slight distortion away from

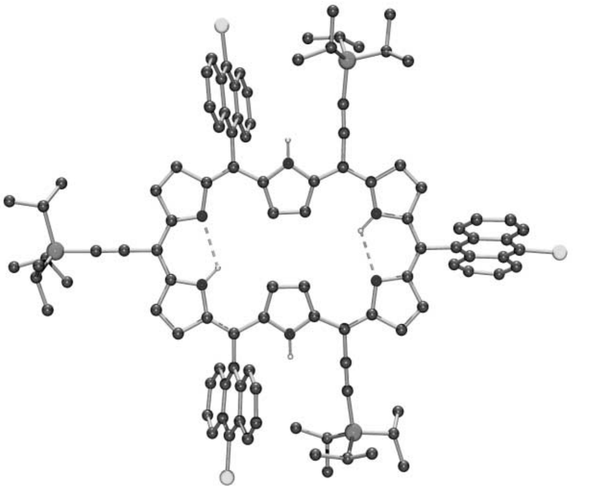
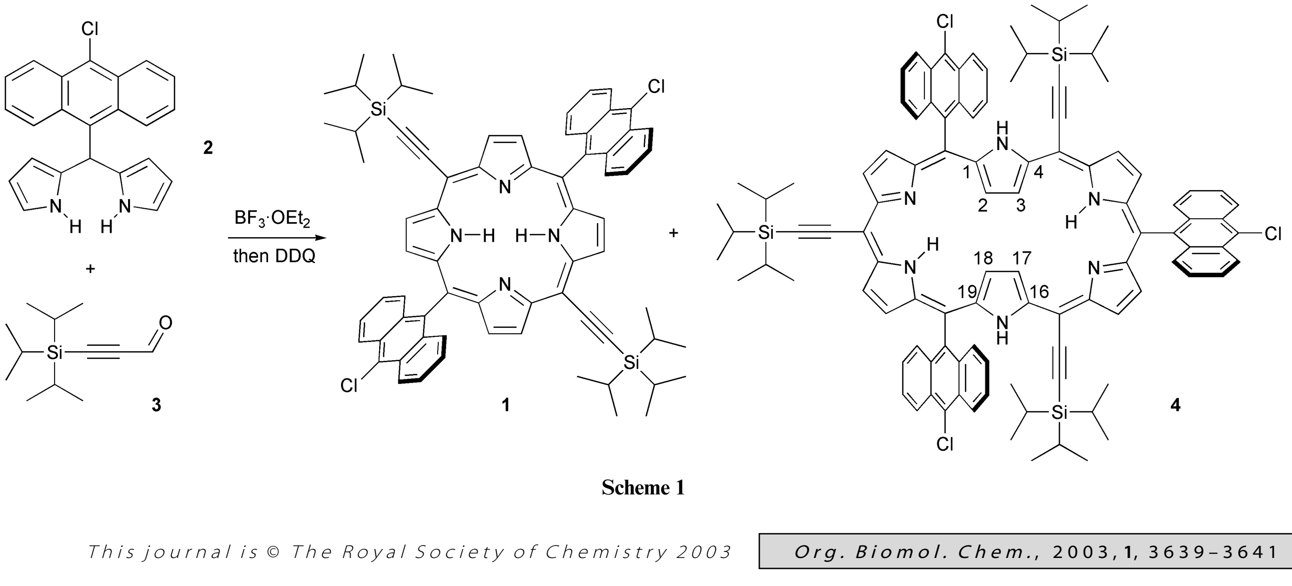


**Fig. 1** Structure of hexaphyrin **4**. (H atoms are omitted except on N.)



**Scheme 1**

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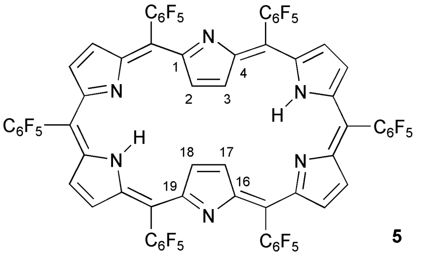
† This is one of a number of contributions from the current members of the Dyson Perrins Laboratory to mark the end of almost 90 years of organic chemistry research in that building, as all its current academic staff move across South Parks Road to a new purpose-built laboratory.

planarity at the centre of the hexaphyrin. There are only two previously reported crystal structures of hexaphyrins.§ The bis-inverted conformation of **4** is similar to that of the *meso*-pentafluorophenyl [26]hexaphyrin **5** reported by Neves *et al.*[7] and contrasts with the highly nonplanar dodecaethyl *meso*-alkynyl [28]hexaphyrin which we reported recently.[9] A detailed comparison of the bond lengths and bond angles in the structures of [28]hexaphyrin **4** and [26]hexaphyrin **5** reveals several differences in geometry due to the difference in oxidation state. The C–NH–C bond angles (111°) at the external nitrogens in **4** are wider than the external C=N–C bond angles (107°) in **5**. The Cα–Cβ bond lengths in these central pyrrole rings (C1–C2, C3–C4, C16–C17 and C18–C19) are longer in **5** (mean 1.459 Å) than in **4** (mean 1.392 Å) reflecting the difference in formal bond order (1.0 in **5** and 1.5 in **4**).



**5**

The identification of **4** as a nonaromatic [28]hexaphyrin, with four NH hydrogens, rather than an aromatic [26]hexaphyrin, with two NHs, is supported by mass spectrometry and NMR. Its FAB+ MS shows a cluster of isotope peaks centred at 1639.2 Da and fits the calculated pattern for the $C_{105}H_{103}Cl_3N_6Si_3$ molecular ion. The $^1H$ NMR spectrum has no signals upfield of TMS, showing the absence of an aromatic ring current, in contrast to the $^1H$ NMR of **5** which has a CH resonance at −2.43 ppm and an NH resonance at −1.98 ppm.[7] The $^1H$ NMR spectrum of **4** in $CDCl_3$ is broad and poorly resolved with many overlapping signals in the region 7.0–7.7 ppm, and we have been unable to identify the NH signals, however the spectrum shows two TIPS environments (21H multiplet at 1.04 ppm, 42H multiplet at 0.58 ppm), and two anthracene environments (*e.g.* 2H doublet at 8.49 ppm and 4H doublet at 8.32 ppm, both 8.8 Hz) as expected for the symmetry of the conformation adopted in the crystal. These environments remain in slow-exchange on the NMR timescale even at 110 °C in $C_2D_2Cl_4$.

The absorption spectra of porphyrin **1** and hexaphyrin **4** are compared in Fig. 2. Both compounds show the expected $S_0$–$S_3$ and $S_0$–$S_1$ anthracene bands at 260 and 390 nm, although in the case of the porphyrin, the second of these bands is largely obscured by the Soret band. The hexaphyrin spectrum is like a very red-shifted porphyrin free-base spectrum, with an intense Soret-like band at 638 nm ($\varepsilon_{max}$ 1.9 × $10^5$ $M^{-1}$ $cm^{-1}$) and four Q-like bands at 803, 898, 952 and 1093 nm. The absorption spectrum of **4** is more red-shifted than that of the [28]hexaphyrin analogue of **5**, due to the *meso*-alkyne substituents. Porphyrins can be useful reverse-saturable absorbers in the low-absorption window between the Soret and Q bands (typically 500–600 nm),[4,11] implying that hexaphyrins might be useful reverse-saturable absorbers in the near-IR (*ca.* 700–900 nm) if a way can be found to reduce the ground-state absorption in this region. With this in mind, we attempted, unsuccessfully, to prepare metal complexes of **4** with a range of metal cations ($Mg^{2+}$, $Ni^{2+}$, $Cu^{2+}$, $Zn^{2+}$, $Pb^{2+}$, $Pd^{2+}$, $Th^{4+}$ and $UO_2^{2+}$).[5,12]

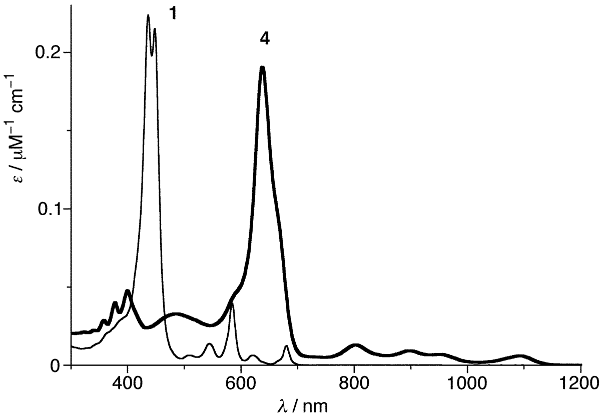


**Fig. 2** Absorption spectra of **1** and **4** in $CH_2Cl_2$.

It seems surprising that hexaphyrin **4** is most stable in its non-aromatic 28-electron oxidation state, but we have been unable to isolate the aromatic 26-electron analogue. Treatment of **4** with DDQ in dichloromethane in a UV cuvette results in formation of a new compound with a broader blue-shifted absorption band ($\lambda_{max}$ 611 nm; $\varepsilon_{max}$ 1.5 × $10^5$ $M^{-1}$ $cm^{-1}$), which is probably the [26]hexaphyrin, but this compound proved too unstable to isolate. Cyclic voltammetry reveals that **4** is easily oxidised; it exhibits two reversible oxidation waves ($E_1^{Ox}$ 0.57 V; $E_2^{Ox}$ 0.76 V) whereas the first oxidation of porphyrin **1** occurs at a substantially higher potential ($E_1^{Ox}$ 1.74 V *vs.* Ag) and is irreversible.||

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## Notes and references

‡ Brief experimental procedure: $BF_3 \cdot OEt_2$ (24 μL, 190 μmol) was added to a solution of **2** (200 mg, 561 μmol) and **3** (134 μL, 561 μmol) in $CH_2Cl_2$ (60 mL) under $N_2$. After 80 min, $Et_3N$ (1 mL) was added, followed by DDQ (446 mg, 2.05 mmol). Chromatography ($SiO_2$; 3 : 7 toluene–pet. ether) yielded **1** (70 mg, 22%) and **4** (114 mg, 37%).

§ Here we use the term "hexaphyrin" to mean hexaphyrin(1.1.1.1.1.1), with a single carbon atom at each pyrrole–pyrrole link. Other hexaphyrins with different pyrrole–pyrrole links are also known.[13]

¶ *Crystal data* for porphyrin **1**: $C_{70}H_{68}Cl_2N_4Si_2 \cdot 4C_7H_8$, $M$ = 1430.91, monoclinic, space group $P2_1/c$, $a$ = 13.7851(3), $b$ = 17.4951(4), $c$ = 17.3777(4) Å, $\beta$ = 102.9007(15)°; $V$ = 4085.22(16) $Å^3$, $Z$ = 2, $\mu$ = 0.157 $mm^{-1}$, $R$ = 0.0634, $Rw$ = 0.0749, $I_o$ = 6298 observed [$I > 3.5\sigma(I)$] reflections out of $N$ = 9262 unique, GOF = 1.1072.

*Crystal data* for hexaphyrin **4**: $C_{105}H_{103}Cl_3N_6Si_3 \cdot C_7H_8$, $M$ = 1731.77, monoclinic, space group $P2_1/a$, $a$ = 32.9322(14), $b$ = 8.6290(4), $c$ = 36.665(2) Å, $\beta$ = 99.019(2)°; $V$ = 10290.4(9) $Å^3$, $Z$ = 4, $\mu$ = 0.173 $mm^{-1}$, $R$ = 0.1833, $Rw$ = 0.1611, $I_o$ = 6858 observed [$I > 1.0\ \sigma(I)$] reflections out of $N$ = 8605 unique, GOF = 0.9523.

Both data sets were collected on an Enraf Nonius Kappa CCD diffractometer ($T$ = 150 K, $\lambda$(Mo-Kα) = 0.71073 Å) and refined on $F$. All non H-atoms were refined anisotropically except for a disordered TIPS group in the hexaphyrin which was refined isotropically. Hydrogen atoms were included in the refinement in geometrical positions with $U_{iso} = 1.2U_{eq}$ of the parent atom. CCDC reference numbers 212654–212655. See http://www.rsc.org/suppdata/ob/b3/b306725b/ for crystallographic data in .cif or other electronic format.

|| Redox potentials were measured by cyclic voltammetry (0.1 V $s^{-1}$) in $CH_2Cl_2$ with 0.1 M $Bu_4NBF_4$ and a Pt working electrode, and calibrated with internal ferrocene ($E_1^{Ox}$ 0.78 V *vs.* Ag).

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