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Meso-Alkynyl Porphyrins

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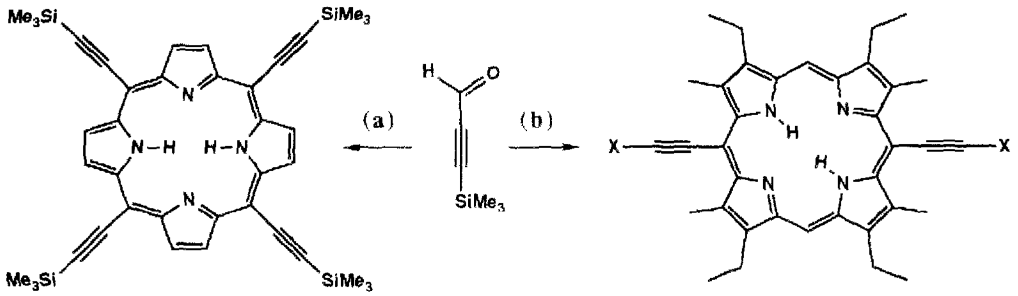
Abstract: *Porphyrins with meso-alkynyl substituents have been synthesised from trimethylsilyl propynal. Their red-shifted UV spectra and unusual reactivity towards nucleophiles indicate that there is good overlap between the porphyrin π-systems and the triple bonds.*

As part of a project aimed towards the development of highly conjugated porphyrin polymers and nets, we have recently developed the chemistry of porphyrins with *meso*-acetylene substituents. When aryl groups are attached to the *meso*-position of a porphyrin, they twist out of conjugation, but with acetylene groups this is impossible, so we reasoned that the electronic interaction between the substituent and the porphyrin would be much greater. The results presented here support this prediction. These molecules are of interest both in their own right and as precursors to extended conjugated arrays.

Propynal reacts with nucleophiles predominantly at the 3-position,[1] so we chose to synthesise our porphyrins from trimethylsilylpropynal,[2] which is less susceptible to Michael addition. The synthesis of porphyrins from aryl and alkyl aldehydes has been much studied,[3,4,5] but very few porphyrins have been synthesised from other aldehydes.[6] Our synthesis is summarised in Scheme 1. H_2**1** was readily prepared in 14% yield using Lindsey's porphyrin synthesis conditions[3] provided that $BF_3{\cdot}OEt_2$ was used as the catalyst; the yield dropped to 0.5% with trifluoroacetic acid (TFA).[9] Use of Gunter's conditions[4] enabled H_2**2a** to be obtained in 72% yield. The ester functionalised version, H_2**3a**, was synthesised analogously in 19% yield

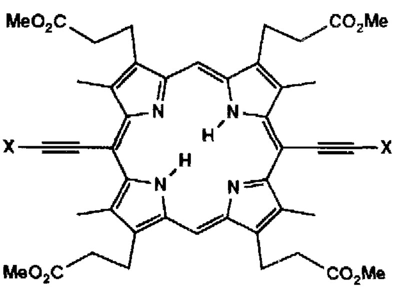


H_2**1**

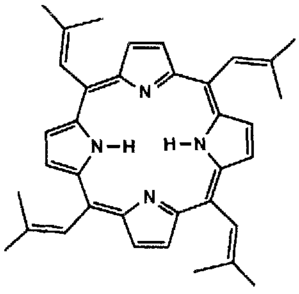
H_2**2a** (X = $SiMe_3$)

Scheme 1 (a) TMSC≡CCHO, pyrrole, $BF_3{\cdot}OEt_2$. 14% Yield; (b) TMSC≡CCHO, dipyrrylmethane, $TsOH{\cdot}H_2O$. 72% Yield.

using our published modification of Gunter's procedure, which involves deprotecting the dipyrrylmethane immediately before use.[10] Treatment of H_2**2a** and H_2**3a** with tetrabutylammonium fluoride cleanly removed the TMS groups to give H_2**2b** (X = H) and H_2**3b**. The desilylated forms of H_2**1** and Zn**1** are insoluble and have not been studied; the other porphyrins dissolve readily in chlorinated solvents to give green solutions.



H_2**3** (**a**: X = $SiMe_3$, **b**: X = H)



H_2TVP

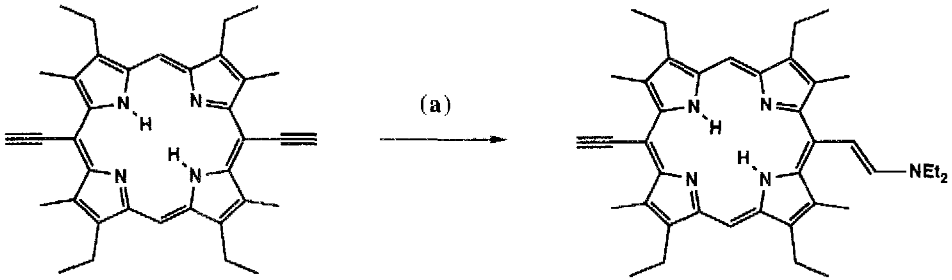
The UV absorption properties of the free-base and zinc porphyrins are compared with those of octaethylporphyrin (OEP), *meso*-tetra(*p*-tolyl)porphyrin (TTP)[11] and *meso*-tetra(2-methyl-propenyl)porphyrin (TVP)[8] in Table 1. Alkynyl substituents red-shift all the bands by about three times as much as aryl groups, and by about twice as much as vinyl groups. Interestingly a TMS-acetylene group causes a significantly larger shift than an unprotected acetylene substituent, illustrating the good communication between the π-systems of the porphyrin and the triple bond.

Table 1 UV - Visible Absorption Spectra of Porphyrins in CH_2Cl_2.

Porphyrin	λ_{max}/nm (log ε) for main absorptions				
H_2**1**	451 (5.57)	567 (4.32)	606 (4.76)	646 (4.08)	710 (4.15)
H_2**2a**	425 (5.40)	533 (4.00)	573 (4.51)	605 (3.85)	661 (4.04)
H_2**2b**	417 (5.26)	525 (4.00)	565 (4.26)	598 (3.74)	655 (3.89)
H_2**3a**	427 (5.38)	534 (4.01)	574 (4.49)	606 (3.85)	662 (4.04)
H_2**3b**	420 (5.30)	526 (4.04)	566 (4.30)	599 (3.79)	656 (3.90)
H_2**4**	461 (5.04)		615 (4.18)		
$H_2OEP^†$	397 (5.24)	500 (4.08)	535 (4.00)	569 (3.86)	622 (3.61)
$H_2TPP^†$	417 (5.62)	515 (4.22)	552 (3.95)	594 (3.70)	650 (3.60)
$H_2TVP^‡$	423 (5.43)	523 (4.03)	561 (3.99)	600 (3.56)	661 (3.46)
Zn**1**	460 (5.75)		604 (4.23)	652 (4.36)	
Zn**2a**	432 (5.63)		572 (4.11)	601 (4.29)	
Zn**2b**	425 (5.53)		565 (4.04)	609 (4.15)	
Zn**3a**	434 (5.66)		572 (4.15)	608 (4.32)	
Zn**3b**	427 (5.56)		567 (4.04)	610 (4.15)	
$ZnOEP^†$	400 (5.51)		530 (4.15)	570 (4.31)	
$ZnTPP^†$	419 (5.74)		548 (4.34)	589 (3.72)	

(† data from Ref 11, ‡ data from Ref 8, in C_6H_6)

Conjugation to the porphyrin also has a dramatic effect on the reactivity of the acetylene groups, making them more susceptible to nucleophilic attack. For example H$_2$**2b** reacts cleanly with diethylamine to give the mono-enamine H$_2$**4** (> 90% yield by NMR, 70% yield after recrystallisation[9]) as shown in Scheme 2. Phenylacetylene does not react with diethylamine under these conditions. The electron-donating effect of the enamine group apparently prevents attack at the second triple bond; no bis-enamine was detected in the product. The ^{1}H and ^{13}C NMR spectra of H$_2$**4** indicate that the electron density in the porphyrin is severely unsymmetrical; for example the two N<u>H</u> signals are separated by 0.25 ppm. The ^{1}H NMR spectrum shows two 14 Hz doublets at 7.76 ppm and 5.83 ppm which are characteristic of the *trans*-enamine geometry. The porphyrin chromophore in H$_2$**4** is also drastically perturbed; the Soret band is red-shifted by 44 nm relative to H$_2$**2b** and the four Q bands coalesce to a single maximum at 615 nm.



H$_2$**2b** H$_2$**4**

Scheme 2 (a) Et$_2$NH, reflux 12 hr. 70% Yield.

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6. Porphyrins have previously been synthesised from EtO$_2$CCHO[7] and Me$_2$C=CHCHO.[8] Nickel porphyrins with vinyl and ethynyl *meso*-substituents have also been synthesised by electrophilic substitution of pre-formed porphyrins followed by functional group interconversion; see Gunter, M. J.; Robinson, B. C.; Gulbis, J. M.; Tiekink, E. R. T. *Tetrahedron* **1991**, *47*, 7853. Arnold, D. P.; Johnson, A. W.; Mahendran, M. *J. Chem. Soc. Perkin Trans. 1* **1978**, 366

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9. All new porphyrins gave satisfactory elemental analyses or mass spectra, and satisfactory ^{1}H and ^{13}C NMR spectra. IR spectra showed terminal acetylene and ester carbonyl signals in the normal regions (3302–3304 cm^{-1} and 1724–1732 cm^{-1}) where appropriate. Porphyrins were quantitatively converted into their zinc derivatives with zinc acetate in chloroform. Key synthetic procedures are outlined below:

   H_2**1**: Boron trifluoride etherate (40 μl, 325 μmol) was added to a solution of trimethylsilylpropynal[2] (370 μl, 2.5 mmol) and pyrrole (175 μl, 2.5 mmol) in dichloromethane (250 ml) under argon at −30°C. After 3 hr the mixture was allowed to warm to room temperature overnight. 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone, DDQ, (570 mg, 2.5 mmol) was added and the mixture was evaporated. The product was purified by flash-chromatography (SiO_2 / CH_2Cl_2) and recrystallised from dichloromethane / methanol. Yield 67 mg (14%) δ_H ($CDCl_3$): 9.39 (s, 8H), 0.66 (s, 36H), −2.62 (s, 2H). Zn**1** δ_H ($CDCl_3$): 9.57 (s, 8H), 0.62 (s, 36H); δ_C ($CDCl_3$ / C_5D_5N): 152.2, 131.6, 107.5, 102.1, 101.4, 0.3.

   H_2**2a**: Trimethylsilylpropynal (450 μl, 3.0 mmol) was added to a solution of 3,3'-diethyl-4,4'-dimethyl-2,2'-dipyrrylmethane (650 mg, 2.8 mmol) and *p*-toluenesulphonic acid monohydrate (130 mg, 0.7 mmol) in methanol (50 ml) under argon at −30°C. After 3 hr it was allowed to warm to room temperature and stirred with DDQ (1.25 g, 5.5 mmol) for 30 min. The mixture was neutralised with triethylamine (1 ml), evaporated and chromatographed (SiO_2 / CH_2Cl_2); the product came off as the first main band and was recrystallised from chloroform / methanol. Yield 683 mg (72%)
   δ_H ($CDCl_3$): 10.07 (s, 2H), 4.03 (q, 8H), 3.67 (s, 12H), 1.80 (t, 12H), 0.57 (s, 18H), −1.99 (s, 2H)
   Zn**2a** δ_H ($CDCl_3$): 9.91 (s, 2H), 3.99 (q, 8H), 3.69 (s, 12H), 1.78 (t, 12H), 0.57 (s, 18H);
   δ_C ($CDCl_3$ / C_5D_5N): 150.8, 145.5, 144.9, 137.5, 111.1, 110.6, 99.0, 97.8, 20.4, 18.3, 17.9, 0.8.

   H_2**2b**: Tetrabutylammonium fluoride (1 **M** in THF, 500 μl, 500 μmol) was added to a solution of H_2**2a** (300 mg, 447 μmol) in dichloromethane (50 ml). After 15 min the reaction was complete and methanol (50 ml) was added to crystallise the product. Yield 225 mg (95%)
   δ_H ($CDCl_3$): 10.09 (s, 2H), 4.47 (s, 2H), 4.04 (q, 8H), 3.67 (s, 12H), 1.80 (t, 12H), −2.05 (s, 2H).
   Zn**2b** δ_H ($CDCl_3$): 9.96 (s, 2H), 4.54 (s, 2H), 4.00 (q, 8H), 3.69 (s, 12H), 1.76 (t, 12H);
   δ_C ($CDCl_3$ / C_5D_5N): 150.0, 144.9, 143.8, 136.3, 98.0, 95.2, 93.1, 87.8, 19.2, 17.0, 16.3.

   H_2**4**: H_2**2b** (100 mg, 190 μmol) was refluxed with anhydrous diethylamine (50 ml) under argon for 12 hr. The solution was then evaporated to 10 ml and hexane (50 ml) was added to crystallise the product. Yield 80 mg (70%). δ_H ($CDCl_3$): 9.76 (s, 2H), 7.69 (d, 14 Hz, 1H), 5.83 (d, 14 Hz, 1H), 4.36 (s, 1H), 3.94 (m, 8H), 3.63 (s, 6H), 3.51 (q, 4H), 3.30 (s, 6H), 1.79 (t, 6H), 1.69 (t, 6H), 1.39 (t, 6H), −0.83 (s, 1H), −1.08 (s, 1H); δ_C ($CDCl_3$): 156.4, 149.9, 145.9, 145.2, 142.7, 140.5, 140.1, 135.1, 134.3, 124.0, 100.5, 98.4, 91.6, 87.9, 46.9, 20.5, 20.4, 18.1, 17.3, 16.5, 14.6.

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