Pergamon

Tetrahedron Letters, Vol. 36, No. 49, pp. 9061-9064, 1995
Elsevier Science Ltd
Printed in Great Britain
0040-4039/95 $9.50+0.00

0040-4039(95)01912-X

5,10,15,20-*meso*-Tetraarylethynylporphyrins.

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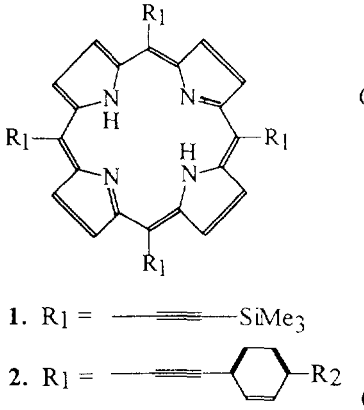
Abstract: examples of the title porphyrins are prepared via Lindsey's method from arylpropynals and pyrrole, and their spectroscopic properties reported. They are green with uv/visible spectra more extensively red-shifted than previously observed for alkynyl-substituted porphyrins.

Porphyrins substituted with one or two alkynyl groups are finding application, e.g., as precursors for novel conducting polymers,[1] non-linear optically-active (NLO) materials,[2] photosynthetic model compounds,[3] and enzyme mimics.[4] *Meso*-tetraalkynyl-substituted porphyrins would be a useful addition to this group of compounds, in their own right and as precursors for potential discotic liquid crystals and two-dimensional conjugated polymeric arrays.[5] As far as we know, however, there is only one report of such a compound, i.e., **1**.[6] Deprotection gives an intractable material on which no further studies can be performed.

Like trimethylsilylpropynal, arylpropynals, would be less susceptible to Michael addition,[6] and would provide arylethynyl *meso*-substituents with a (phenyl) platform on which to attach groups to solubilise the porphyrin. We report here for the first time, the synthesis and spectroscopic properties of some 5,10,15,20-*meso*-tetra(arylethynyl)porphyrins.

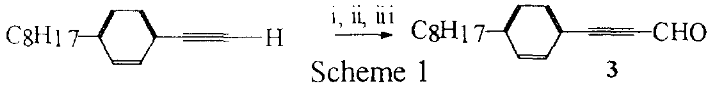


1. R_1 = —≡—$SiMe_3$

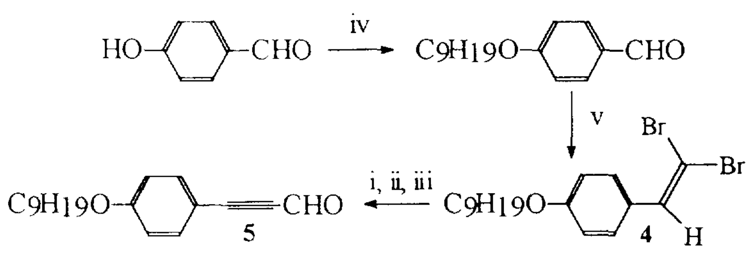
2. R_1 = —≡—C_6H_4—R_2

a: R_2 = H; **b:** R_2 = C_8H_{17};

c: R_2 = OC_9H_{19};



Scheme 1 **3**



5 **4**

Scheme 2 (See ref. 12 for key to reactions)

The first attempt at the title compounds involved Lindsey[7] porphyrin synthesis with pyrrole and phenylpropargyl aldehyde (obtained from Aldrich), using $BF_3.OEt_2$ as catalyst. This gave the porphyrin **2a** as a slightly soluble green solid which could not be separated from the DDQ used to oxidise porphyrinogen to the porphyrin.[7] Porphyrin **2a** was abandoned in favour of more soluble *meso*-tetraarylethynylporphyrins synthesised from substituted arylpropynals (Schemes 1 and 2).

Thus, 4-octylphenylpropynal **3** was prepared from 4-octylphenylacetylene by quenching the acetylide (formed by low-temperature reaction with BuLi)[8] with DMF, followed by acid hydrolysis. Lindsey porphyrin synthesis with pyrrole gave porphyrin **2b** in 8% yield and a small amount of a second porphyrin-like product that eluted more slowly from a silica column with dichloromethane (DCM).

4-Nonyloxyphenylpropynal **5** was prepared in a three-step synthesis from 4-hydroxybenzaldehyde. Alkylation of the phenolic -OH with 1-bromononane, was followed by a Corey and Fuchs reaction with CBr_4, triphenylphosphine, and zinc,[9] to give the ß,ß-dibromostyryl derivative **4**. Low temperature reaction of **4** with two and a half equivalents of BuLi, followed by quenching of the acetylide with DMF and acid hydrolysis, yielded **5**. Care was taken not to allow the acidity of this reaction to drop below pH 6-7 otherwise no arylpropynal was produced.[10] Lindsey porphyrin synthesis with pyrrole and **4**, using $BF_3.OEt_2$ as catalyst, afforded porphyrin **2c** in 3% yield. A second porphyrin-like product was separated as the major product via column chromatography on silica gel, eluting with DCM.

Alkynyl *meso*-substituents significantly red-shift the porphyrin B and Q bands.[6] Thus, compared to *meso*tetraphenylporphyrin (TPP), the B band of porphyrin **1** is red-shifted by about 34 nm. Replacing the trimethylsilyl group of **1** with an aryl group increases the B and Q band red shifts even further (46 {**2a**}, 54 {**2b**}, and 57 {**2c**} nm for the B band). In addition, there is a marked increase in the main Q band absorption relative to that of the B band, and two of the Q bands appear as smaller shoulders either side of the main Q band absorption. This illustrates that the ethynyl groups mediate communication between the porphyrin and aryl pi-systems more effectively than when the aryl group is connected directly to the porphyrin macrocycle.

Porphyrin[a,b,c]	λ_{max}/nm (ε)[d]						
H_2TPP	419(470)	515(18.7)	548(8.1)	592(5.3)	647(3.4)		
H_4TPP^{2+}	439(411)		556(4.1)	604(11.0)	655(53.2)		
H_2**1**	451(371)		567(20.9)	606(57.5)	646(12.0)	710(14.1)	
H_2**2a**	463			621		717	
H_4**2a**$^{2+}$	485						726
H_2**2b**	466(351)			599(sh)	642(67.2)	675(sh)	737(28.8)
H_4**2b**$^{2+}$	488(311)						762(94.9)
H_2**2c**	472(297)			600(sh)	653(89.1)		744(55.9)
H_4**2c**$^{2+}$	496(189)					712(sh)	795(90.7)

[a]see ref. 11a for H_2TPP: [b]see ref. 11b for H_4TPP^{2+}: [c]see ref. 6 for H_2**1**: [d]Decadic extinction coefficient.

Table. Uv/visible Absorption Spectra of Porphyrins in DCM.

Because solid samples and DCM solutions of the neutral porphyrins **2b** and **2c** are green, we suggest the trivial name "chlorphyrin" as a short-hand nomenclature for *meso*-tetraalkynyl-substituted porphyrins. Acidification (with several drops of TFA) turns solutions of **2b** mustard yellow and solutions of **2c** pink.

Finally, we have as yet to completely identify the second porphyrin-like compounds obtained as by-products (in the case of **2c**, it is the major component) from these reactions. However, preliminary spectroscopic data, e.g., FAB mass spectroscopy (which gives molecular ions with the same $^m/_e$ values as porphyrins **2b** and **2c**), and ^{1}H-nmr (which shows separate doublets for each of the β-protons - a pattern **not** consistent with one or two different *meso*-susbtituents[13] - and separated peaks at higher field than TMS, i.e., two different protons inside the macrocycle) suggest that these porphyrin-like by-products may be isomers of **2b** and **2c**, containing the novel 2-aza-21-carbaporphyrin macrocycle.[14] We shall be reporting more fully on this at a later date.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the assistance of the EPSRC Mass Spectrometry Service at Swansea for all FAB and accurate-mass spectra, financial support from the EPSRC and DRA, and the technical assistance of Mr S. Bury of Hewlett-Packard.

REFERENCES

1. See, for example, a; Wagner, R.W., and Lindsey, J.S., *J. Am. Chem. Soc.*, 1994, **116**, 9759: b; Anderson, H.L., *Inorg. Chem.*, 1994, **33**, 972: c; Arnold, D.P., and Nitschinsk, L.J., *Tetrahedron*, 1992, **48**, 8781.
2. See, for example, a; Anderson, H.L., Martin, S.J., and Bradley, D.D.C., *Angew. Chem. Int. Ed. Engl.*, 1994, **33**, 655: b; Arnold, D.P., and Heath, G.A., *J. Am. Chem. Soc.*, 1993, **115**, 12197.
3. See, for example, a; Wagner, R.W., Johnson, T.E., Li, F., and Lindsey, J.S., *J. Org. Chem.*, 1995, **60**, 5266: b; Lin, V.S.-Y., DiMagno, S.G., Therien, M.J., *Science*, 1994, **264**, 1105.
4. See, for example, a; Anderson, H.L., and Sanders, J.K.M., *Angew. Chem. Int. Ed. Engl.*, 1990, **29**, 1400: b; Anderson, H.L., and Sanders, J.K.M., *J. Chem. Soc., Chem. Commun.*, 1992, 946: c; Mackay, L.G., Anderson, H.L., and Sanders, J.K.M., *J. Chem. Soc., Chem. Commun.*, 1992, 43.
5. For an example of a non-acetylenic two-D array of porphyrins, see Drain, C.M., and Lehn, J-M., *J. Chem. Soc., Chem. Commun.*, 1994, 2313.
6. Anderson, H.L., *Tetrahedron Lett.*, 1992, **33**, 1101.
7. Lindsey, J.S., Schrieman, I.C., Hsu, H.C., Kearney, P.C., and Marguerettaz, A.M., *J. Org. Chem.*, 1987, **52**, 827.
8. See Brandsma, L., in *"Preparative Acetylenic Chemistry"* 2nd Edn., Studies in Organic Chemistry 34, Elsevier Science Publishers (Amsterdam) 1988, Ch. 2., p13.
9. Corey, E.J., and Fuchs, P.L., *Tetrahedron Lett.*, 1972, 3769.
10. See reference 8, Ch. 4, p102.
11. a; See Falk, J.E., *"Porphyrins and Metalloporphyrins"*, Elsevier, Amsterdam 1975: b; Dalton, J., Milgrom, L.R., and Pemberton, S.M., *J. Chem. Soc. Perkin Trans. 2.*, 1980, 370.
12. Key to reactions outlined in Schemes 1 and 2: i; BuLi/THF/-78^{o}C: ii; DMF/r.t.: iii; H^+/H_2O: iv; $C_9H_{19}Br/K_2CO_3$/DMF/70-80^{o}C: v; Zn/$(C_6H_5)_3P/CBr_4$/DCM. All new compounds gave satisfactory elemental analyses.

4-Octylphenylpropanal **3**: see Scheme 1 for synthesis from 4-octylphenylacetylene. Yield = 0.85g (84%). IR (neat thin-film); 2200 (-C≡C- stretch), 1660 (unsaturated -CH=O stretch) cm^{-1}: Mass spec. $^{m}/_{e}$; required M^{+} = 242; found M^{+} = 242; [M-CO]$^{+}$ = 214; [M-C$_4$H$_9$]$^{+}$ = 185; [M-CO-C$_4$H$_9$] = 157. ^{1}Hnmr, $_H$(CDCl$_3$): 9.41 (s, 1H, -C$\underline{H}$O), 7.37(q, 4H, centre of aryl AB spin-system, J_{AB} = 7.9 Hz), 2.64 (t, 2H, -CH$_2$- next to aryl ring), 1.61 (m, 2H, -CH$_2$- flanked by two others in octyl chain), 1.26 (m, 12H, rest of octyl chain), 0.88 (t, -CH$_3$, terminal methyl in octyl chain) ppm.

4-Nonyloxyphenylpropanal **5**: see Scheme 2 for 3-step synthesis. Yield of **4** = 4.9 gm (78% in two steps from from 4-hydroxybenzaldehyde). Mass spec. $^{m}/_{e}$; required M^{+} = 404; found M^{+} = 404; [M-C$_9$H$_{18}$]$^{+}$ = 278; ^{1}Hnmr, $_H$(CDCl$_3$): 7.40 (s, 1H, -C$\underline{H}$=CBr$_2$), 7.13(q, 4H, centre of aryl AB spin-system, J_{AB} = 8.5 Hz), 3.96 (t, 2H, -CH$_2$- next to oxygen on aryl ring), 1.78 (p, 2H, -CH$_2$- flanked by two others in nonyl chain near oxygen), 1.45 (p, 2H, -CH$_2$- flanked by two others in nonyl chain near terminal carbon), 1.28 (m, 10H, rest of nonyl chain), 0.88 (t, -CH$_3$, terminal methyl in nonyl chain) ppm.

Yield of **5** = 1.54g (91%, from preceding **4**). IR (neat thin-film); 2190 (-C≡C- stretch), 1660 (unsaturated -CH=O stretch) cm^{-1}: Mass spec. $^{m}/_{e}$; required M^{+} = 272; found M^{+} = 272; [M-C$_9$H$_{18}$]$^{+}$ = 146; [M-C$_9$H$_{18}$-CO]$^{+}$ = 118; ^{1}Hnmr, $_H$(CDCl$_3$): 9.39 (s, 1H, -C$\underline{H}$O), 7.22(q, 4H, centre of aryl AB spin-system, J_{AB} = 8.5 Hz), 3.99 (t, 2H, -CH$_2$- next to oxygen on aryl ring), 1.79 (p, 2H, -CH$_2$- flanked by two others in nonyl chain near oxygen), 1.46 (p, 2H, -CH$_2$- flanked by two others in nonyl chain near terminal carbon), 1.28 (m, 10H, rest of nonyl chain), 0.88 (t, -CH$_3$, terminal methyl in nonyl chain) ppm.

5,10,15,20-Mesotetra(4-octylphenylethynyl)porphyrin **2b**: Boron trifluoride dietherate (40 μl, 0.33 mM) was added to a stirred, nitrogen-degassed solution of 4-octylphenylpropanal (0.61 g, 2.5 mM) and pyrrole (0.17 g, 2.5 mM) in dry, distilled DCM (250 ml) at -25°C. The reaction mixture was kept at this temperature during 4 h, then allowed to warm to room temperature overnight. DDQ (570 mg, 2.5 mM) was then added, resulting in the reaction solution turning green. The solvent was removed under vacuum, and the residue purified by column chromatography (silica gel; DCM) to give a dark green sticky solid. Trituration with methanol and filteration gave the desired porphyrin as a dark green powder 58 mg (8%), m.p. = 171-172°C (with decomposition): I.R. (nujol mull); 2196 cm^{-1} (weak: acetylenic triple bond) $_H$ (CDCl$_3$); 9.27 (s, 8H, ß-pyrrole-$\underline{H}$), 7.67 (q, 16H, centre of aryl AB spin-system, J_{AB} = 7.9 Hz), 2.78 (t, 8H, -C$\underline{H}_2$- next to aryl ring), 1.78 (p, 8H, -C$\underline{H}_2$- flanked by two methylene groups), 1.55 - 0.88 (m, 52H, rest of octyl chain). FABMS, [M^{+}] found 1158.7512 (5%); C$_{84}$H$_{94}$N$_4$ requires [M^{+}] = 1159.632. A second minor porphyrin-like fraction was isolated from the column as a green powder, yield = 5.2 mg.

5,10,15,20-Meso-tetra(4-nonyloxyphenylethynyl)porphyrin **2c**: the synthetic procedure for this porphyrin was the same as for **2b** using identical molar quantities of boron trifluoride etherate (40 μl, 0.33 mM), 4-nonyloxyphenylpropanal (0.68 g, 2.5 mM), pyrrole (0.17 g, 2.5 mM), DDQ (570 mg, 2.5 mM), and DCM (250 ml). Column chromatography (silica gel; DCM) of the product, followed by trituration with methanol of the dark green oil obtained, yielded **2c** as a green powder, yield = 19 gm (3%), m.p. = 147-148°C: I.R. (nujol mull); 2192 cm^{-1}(acetylenic triple bond): $_H$ (CDCl$_3$); 9.11 (s, 8H, ß-pyrrole-$\underline{H}$), 7.48 (q, 16H, centre of aryl AB spin-system, J_{AB} = 8.2 Hz), 4.08 (t, 8H, -C$\underline{H}_2$- next to aryl ring), 1.91 (p, 8H, -C$\underline{H}_2$- flanked by two methylene groups), 1.55 - 0.84 (m, 60H, rest of nonyl chain), -3.00 (s, 2H, N-$\underline{H}$). FABMS, found [M^{+}+2], 1280.2 (3%); [M^{+}+4], 1282.2 (3%). C$_{88}$H$_{102}$N$_4$O$_4$ requires [M^{+}] = 1278.92. A second major porphyrin-like fraction was isolated as a green powder, yield = 33 mg.

13. See, a; Milgrom, L.R., Mofidi, N., and Harriman, A., *Tetrahedron*, 1989, **45**, 7341: b; Milgrom, L.R., *J. Chem. Soc., Perkin Trans. 1.*, 1984, 1483.
14. Chmielewski, P.J., Lechoslaw, L-G., Rachlewicz, K., *Chem. Eur. J.*, 1995, **1**, 68.

(*Received in UK* 14 *September* 1995; *revised* 3 *October* 1995; *accepted* 6 *October* 1995)