Tetrahedron Letters,Vol.30,No.9,pp 1129-1132,1989
Printed in Great Britain

0040-4039/89 $3.00 + .00
Pergamon Press plc

meso-TETRA(*meso*-TETRAPHENYLPORPHYRINYL)PORPHYRIN, A MACROCYCLE WITH FIVE COVALENTLY LINKED PORPHYRIN UNITS

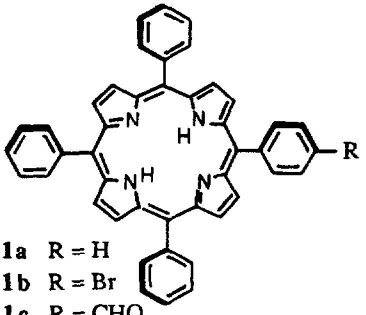
Olof Wennerström*[a], Harriet Ericsson[a], Ilona Raston[a], Susanne Svensson[a] and Weston Pimlott[b].

[a]Department of Organic Chemistry, Chalmers University of Technology, S-412 96 Göteborg,
[b]Department of Medical Biochemistry, University of Göteborg, P.O.Box 33031, S-400 33 Göteborg, Sweden

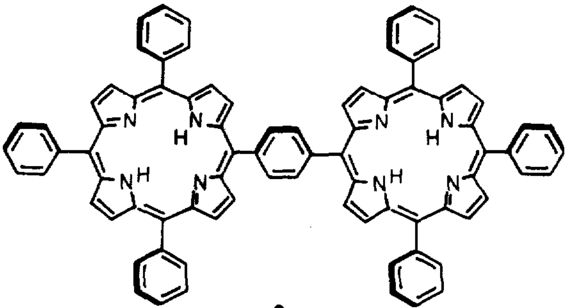
Abstract: A convenient synthesis of a *meso*-tetraphenylporphyrin monoaldehyde, **1c**, is reported. Condensation of this aldehyde with excess benzaldehyde and pyrrole gives the bis-porphyrin **2**. A low yield of the title compound, the penta-porphyrin **3** is obtained from **1c** and pyrrole in refluxing propionic acid.

Recent advances in the understanding of primary photosynthetic processes[1] have led to a need of model compounds with two or more closely bonded porphyrin units.[2] The rapid progress in molecular electronics and the increasing interest in materials for supermolecular chemistry[3] have also inspired us to make molecules in which more than one porphyrin unit is linked by various bridging groups. For this purpose we required a simple and reactive monofunctionalised porphyrin *e.g.* a *meso*-tetraphenylporphyrin monoaldehyde, **1c**. This aldehyde can conveniently be prepared from the corresponding monobromo-compound **1b**, which on treatment with six equiv. of butyllithium in ether at 0°C for 3h, addition of DMF and then hydrolysis after 1h with dilute HCl, gave **1c** which was purified by chromatography on silica gel [^{1}H NMR (400 MHz, $CDCl_3$): δ -2.8 (broad s, 2H), 7.77 (m, 9H), 8.22 (m, 6H), 8.29 (d, J=8.2 Hz, 2H), 8.41 (d, J=8.2 Hz, 2H), 8.78 (d, J=4.6 Hz, 2H), 8.86 (s, 4H), 8.88 (d, J=4.6 Hz, 2H), 10.39 (s, 1H); MS (70 eV): m/e 642 (M^+, 71%), 614 (19), 321 (M^{2+}, 48), 307 (100)]. The bromoporphyrin **1b** was prepared by the standard Adler procedure[4] from pyrrole, benzaldehyde and 4-bromobenzaldehyde in refluxing propionic acid in a 25% yield of the crude product. The aldehydes were used in a 3:1 ratio. Assuming that the reactivity of the benzaldehyde and the 4-bromobenzaldehyde are the same and thus a statistical distribution of 4-bromophenyl groups in the porphyrin, one arrives at a total yield of **1c** of 15% for the first two steps. The porphyrin aldehyde **1c** was used in Wittig reactions with different bis-ylids to be reported elsewhere[5], but was also used in new porphyrin-forming condensation reactions. Thus, **1c** was mixed with benzaldehyde (9 equiv.) and pyrrole (10 equiv.) in refluxing propionic acid to give a 10% yield of the bis-porphyrin **2** purified by chromatography on silica gel. The corresponding bis-porphyrin with a central 1,3-disubstituted benzene ring has been studied by Tabushi and co-workers.[6] Metal complexes of **2** (copper, zinc, nickel) were also prepared by standard methods.[7]

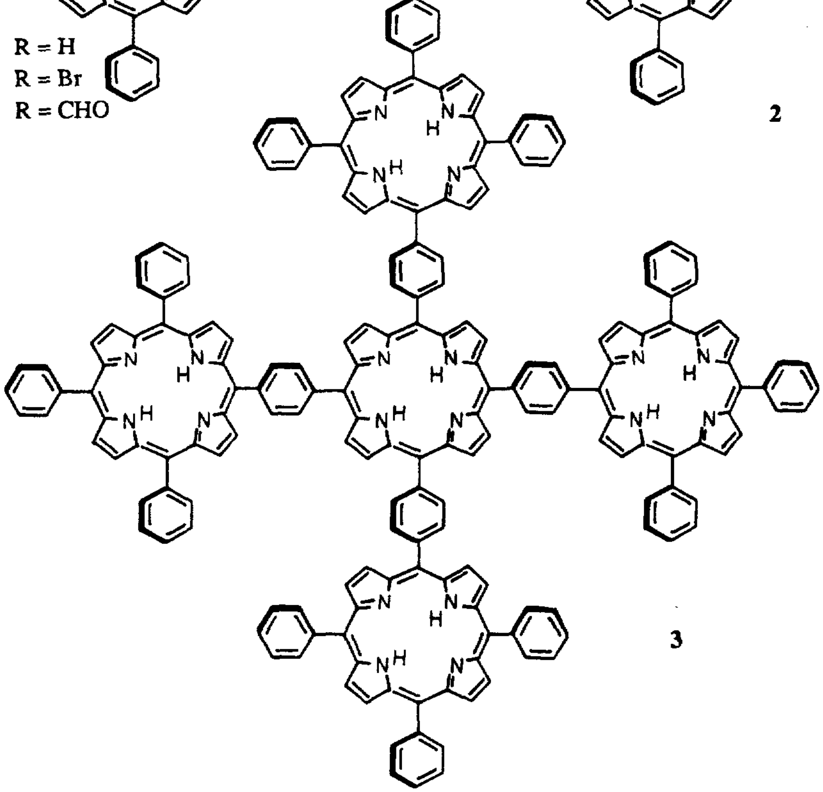
Having a good supply of **1c** and knowing that this aldehyde does react with pyrrole (compare the reaction above), we could not resist the temptation to try its reaction with pyrrole in the absence of other aldehydes. A crystalline precipitate was collected from the reaction in refluxing propionic acid after cooling. After several unsuccessful attempts to separate and purify the desired penta-porphyrin **3**, we were finally able to remove polymeric impurities by absorbing the crude precipitate onto Sephadex® (LH-20) and to wash out the impurities with 1% HAc in DMF and to extract the product from the top of the column with $CHCl_3$. Alternatively, the product **3** can be purified by flash-chromatography on silica gel with $CHCl_3$ as eluant to give a low yield[8] of an almost insoluble crystalline material which we belive is the title compound, *meso*-tetra(*meso*-tetraphenylporphyrinyl) porphyrin, **3**, based on an analysis of its MS, ^1H NMR and UV/visible spectral data. The synthesis of **3** from pyrrole and benzaldehyde requires the formation off 44 new C-C bonds and the closure of 5 macrocycles. It can be achieved in three steps with a total yield of *ca.* 1%.



1a R = H
1b R = Br
1c R = CHO



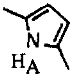
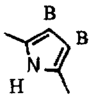
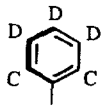
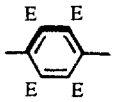
2



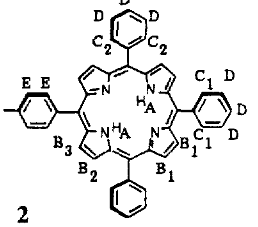
3

The visible absorption spectra of **2** and **3** both show a split Soret band [416 (ε=2.9x10^5), 425 (3.4x10^5) and 418 (8.5x10^5), 431 nm (6.0x10^5) respectively]. The weak bands at longer wavelenghts are only slightly red-shifted as compared to the bands of **1a**. The MS of **2** (60 eV) showed the parent peak at m/e 1150 (M^+, 100%) and main peaks at 797 (18), 575 (M^{2+},17) and 207 (35). After several attempts to obtain a MS of **3**, we finally succeded in observing a cluster of peaks centred at m/e 2763 (M^++2) with positive FAB [3-nitrobenzylalcohol and trifluoroacetic acid (TFA), calibrated against CsI].[9] Smaller peaks at m/e 2777 and 2877 (2763+TFA) were also observed. A MS of the zinc complex of **3** by the same method gave a series of peaks centred at m/e 3075. Further support for the suggested structures **2** and **3** came from an ^{1}H NMR investigation. The spectra from **2** and **3** can readily be assigned in consistency with the suggested structures. Table 1 shows the chemical shifts and assignments of the ^{1}H NMR spectra of **1a**, **2**, and **3** (400 MHz, $CDCl_3$) as well as the induced shifts on addition of excess TFA-*d*. The dominant effect in the spectra of all three compounds is the induced ring current effects from the different porphyrin rings. A detailed analysis shows that the long range effects are almost additive in **2** and **3**. The shifts induced by addition of TFA have the same sign and size within the series.

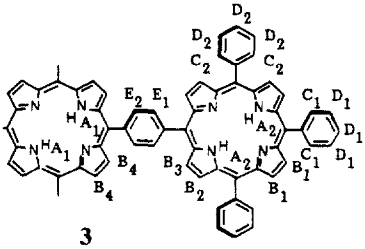
Table 1. ^{1}H NMR data (400 MHz, $CDCl_3$) of *meso*-tetraphenylporphyrin **1a**, *meso*-(*meso*-tetraphenylporphyrinyl)triphenylporphyrin **2**, and *meso*-tetra(*meso*-tetraphenylporphyrinyl)porphyrin **3**. The numbers in brackets refer to the induced shift on addition of excess of TFA-*d*.

			C	 D	
1a	-2.78 s	8.84 (-0.13) s	8.22 (+0.39)[b]	7.7-7.8 (+0.3) m	
2	-2.60 s	8.90 (-0.07) m B_1 9.05 (-0.09)[a] B_2 9.31 (-0.15)[a] B_3	8.26 (+0.41)[b] C_1 8.31 (+0.39)[b] C_2	7.7-7.9 (+0.3) m	8.64 (+0.71) s
3	-2.17 s A_1 -2.56 s A_2	8.94 (-0.13) m B_1 9.13 (-0.17)[a] B_2 9.44 (-0.19)[a] B_3 9.64 (-0.20) s B_4	8.29 (+0.39) m C_1 8.36 (+0.36) m C_2	7.82 (+0.3) m D_1 7.87 (+0.3) m D_2	8.78 (+0.71)[b] E_1 8.86 (+0.71)[b] E_2

[a]doublet J=4 Hz; [b]doublet J=8 Hz



2



3

In *meso*-tetraphenylporphyrin, **1a**, the planes of the benzene rings are twisted more than 60° relative to the plane of the macrocycle.[10] Thus, it seems resonable to assume that the porphyrin rings in **2** and **3**, respectively, are roughly coplanar. This is consistent with the observed long range ring current effects on the ^1H NMR shifts as well as the splitting of the Soret bands in the visible absorption spectra of **2** and **3**. The dimensions of the pentaporphyrin **3** can be estimated from the structure of **1a**[10] to be *ca.* 4.3 x 4.3 x 0.42 nm a truly disc-like molecule (assuming coplanar porphyrin rings). The symmetry of **3** (allowing for a rapid migration of the central hydrogens in each porphyrin ring) is D_{4h} and the rigid and presumably planar structure is also aesthetically quite attractive.

Acknowledgements. We thank prof. K. Müllen, Mainz, for valuable discussions and the Swedish Natural Science Research Council and Board of Technical Development for financial support.

References and notes

1. J. Deisenhofer, O. Epp, K. Miki, R. Huber and H. Michel, *J. Mol. Biol.* **1984**, *180*, 385.
2. J.L. Sessler and M.R. Johnsson, *Angew. Chem.* **1987**, *99*, 679; D. Gust, T.A. Moore, A.L. Moore, L.R. Makings, T.T. Trier, D.K. Luttrull and X.C. Ma, *XII IUPAC Symposium on Photochemistry*, Bologna, **1988**, abstr. p. 85.
3. T.A. Arrhenius, M. Blanchard-Desce, M. Dvolaitzky, J.-M. Lehn and J. Malthete, *Proc. Natl. Acad. Sci. USA*, **1986**, *83*, 5355.
4. A.D. Adler, F.R. Longo, J.D. Finarelli, J. Goldmacher, J. Assour and L. Korsakoff, *J. Org. Chem.* **1967**, *32*, 476.
5. O. Wennerström, H. Ericsson, I. Raston, to be published.
6. I. Tabushi and T. Sasaki, *Tetrahedron Lett.* **1982**, 1913; I. Tabushi, S. Kugimiya, M.G. Kinnaird and T. Sasaki, *J. Am. Chem. Soc.* **1985**, *107*, 4192; I. Tabushi, S. Kugimiya and T. Sasaki, *J. Am. Chem. Soc.* **1985**, *107*, 5159.
7. see *e.g.* J.W. Buchler, "The Porphyrins", ed. D. Dolphin, vol 1, Academic Press, New York 1978, p. 389 and references therein.
8. Our best yield of **3** is 5%, collected from a Sephadex® column. The compound slowly decomposes on silica gel (prep. TLC and columns).
9. M. Barber, R.S. Bordoli, R.D. Sedgwick and A.N. Tyler, *J. Chem. Soc. Chem. Commun.* **1981**, 325; W. Alerth, K.M. Straub and A.L. Burlingame, *Anal. Chem.* **1982**, *52*, 2029; C.N. McEwen, *Anal. Chem.* **1983**, *55*, 967.
10. M.J. Hamor, T.A. Hamor and J.L. Hoard, *J. Am. Chem. Soc.* **1964**, *86*, 1938; S.J. Silvers and A. Tulinsky, *J. Am. Chem. Soc.* **1967**, *89*, 3331.

(Received in UK 16 January 1989)