Pergamon

Tetrahedron Letters 40 (1999) 8457–8460

TETRAHEDRON LETTERS

A Tetraphenylthiaporphyrin with an Inverted Thiophene Ring

Natasza Sprutta and Lechosław Latos-Grażyński*

Department of Chemistry, University of Wrocław, 14 Joliot-Curie St., 50 383 Wrocław, Poland

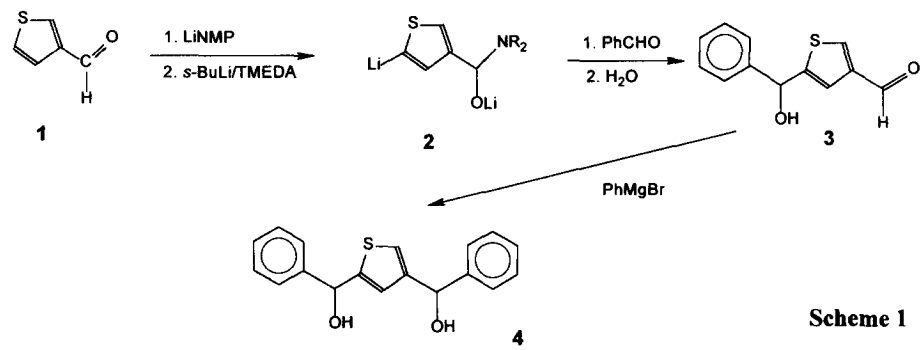
e-mail llg@wchuwr.chem.uni.wroc.pl

Received 21 June 1999; accepted 14 September 1999

Abstract. A novel isomer of 5,10,15,20-tetraphenyl-21-thiaporphyrin with an inverted thiophene ring, i.e. 2-thia-5,10,15,20-tetraphenyl-21-carbaporphyrin (SCTPPH) has been produced by condensation of 2,4-bis(phenylhydroxymethyl)thiophene with pyrrole and benzaldehyde *via* a one pot, two-step reaction or by the [3 + 1] condensation of the thiophene precursor and 5,10-diphenyltripyrrin.

Inverted porphyrins,[1] carbaporphyrinoids with one pyrrole ring replaced by an all-carbon ring,[2] and isomers of 21-oxaporphyrin and 21-thiaporphyrin with an inverted pyrrole ring[3] belong to the newly emerging class of porphyrin-related macrocycles identified by the presence of a common CH motif in the inner macrocyclic perimeter.

Here we report on the synthesis and spectroscopic properties of a novel isomer of 5,10,15,20-tetraphenyl-21-thiaporphyrin (STPPH) which can be formally constructed by the exchange of a thiophene sulfur atom and a pyrrolic β-methine group to create the porphyrin-like skeleton of 2-thia-5,10,15,20-tetraaryl-21-carbaporphyrin, i.e., an inverted thiaporphyrin.



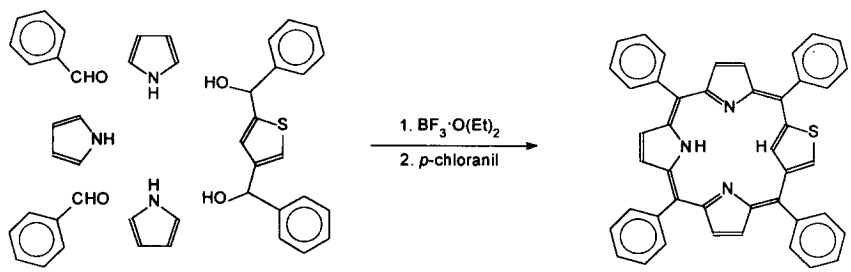
Scheme 1

A key stage in the synthesis of 2-thia-5,10,15,20-tetraphenyl-21-carbaporphyrin is the construction of a condensation precursor 2,4-bis(phenylhydroxymethyl)thiophene **4** (Scheme 1). Lithiation of the α-amino alkoxide derived from 3-thiophenecarboxaldehyde **1** and the "blocking" amine – *N*-methylpiperazine (NMP) using *sec*-buthyllithium/TMEDA, is directed to the remote α-site of the thiophene ring.[4] The formed 2-thienyllithium derivative **2**, when reacted with benzaldehyde, yielded 2-(phenylhydroxymethyl)-4-thiophenecarboxaldehyde **3**.

0040-4039/99/$ - see front matter
PII: S0040-4039(99)01773-6

Reaction with a phenyl Grignard reagent converted **3** into a mixture of stereoisomers of the 2,4-bis(phenylhydroxymethyl)thiophene **4**.[5]

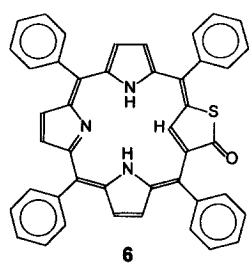
Condensation of the 2,4-bis(phenylhydroxymethyl)thiophene **4** with pyrrole and benzaldehyde *via* a one pot, two-step, room temperature reaction afforded green 2-thia-5,10,15,20-tetraphenyl-21-carbaporphyrin (SCTPPH) **5** in 4% yield (unoptimized) (Scheme 2).[6]



4 **5**

Scheme 2

Oxidation of **5** with DDQ or with an excess of *p*-chloranil produced a new yellow species (yield 30%, unoptimized) identified by ^{1}H NMR spectra and high resolution mass spectrometry as 2-thia-3-oxo-5,10,15,20-tetraphenyl-21-carbaporphyrin ($SCOTPPH_2$) **6**.[7]



6

Scheme 3

A [3 + 1] condensation of 5,10-diphenyltripyrrin, and 2,4-bis(phenylhydroxymethyl)-thiophene **4**, catalyzed by BF_3 and followed by oxidation with 3 equivalents of *p*-chloranil also gave SCTPPH (yield 2%, unoptimized).

The ^{1}H NMR spectrum of SCTPPH (Figure 1, Trace A) shows three AB patterns assigned to the three pyrrole rings. The inverted thiophene ring contributes with a 3-H doublet at 8.25 ppm, i.e., upfield relative to the position of the thiophene fragment of STPPH (9.78 ppm)[8] but downfield with respect to the unsubstituted thiophene resonances (7.18 ppm). The resonance of the 23-NH (the proton located on the inner macrocycle perimeter) gave a singlet at 5.81 ppm (293 K), i.e., upfield with respect to the unsubstituted NH pyrrole resonance. The unique inner 21-CH resonance of the inverted thiophene ring is located at 4.76 ppm, i.e., upfield with respect to the corresponding 3-H resonance of thiophene (6.99 ppm). The inner

21-CH and outer 3-H protons are scalar coupled ($^4J_{HH}$ = 1.1 Hz). The 23-NH proton of SCTPPH can be readily exchanged by D_2O leaving only the 21-CH resonance of SCTPPD at the 6 – 4.5 ppm region. The diagnostic shift difference of 3.49 ppm between the outer and inner thiophene resonances reflects their location in the deshielding (3-H) and shielding (21-H) zones of the macrocycle diatropic ring current. The downfield shifts of the regular pyrrole resonances and the upfield shifts of the 23-NH and 21-CH are less pronounced than the corresponding values found for $CTTPH_2$[1] or STPPH.[8] In contrast, the ^{1}H NMR spectrum of $SCOTPPH_2$ **6** demonstrated typical aromatic features with three AB patterns and 21-CH (not exchangeable with D_2O) and NH resonances located at -5.31, -3.37 and -2.93 ppm respectively (Figure 1, Trace B).

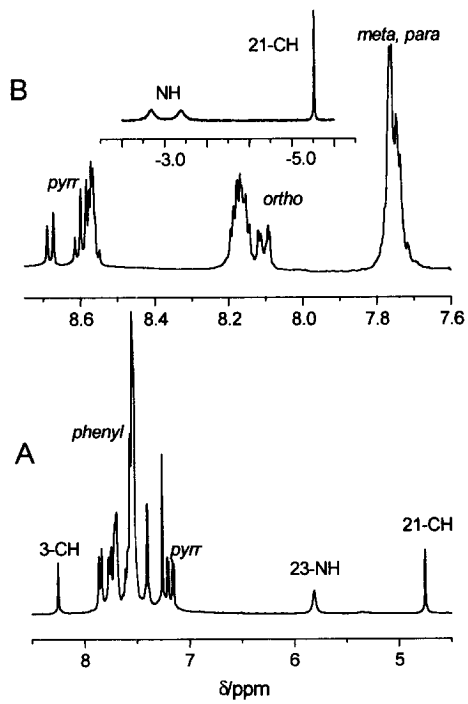


Figure 1. The ^{1}H NMR spectra of : A, SCTPPH **5** in $CDCl_3$ at 293 K; B, $SCOTPPH_2$ **6** in CD_2Cl_2 at 293 K. The inset in Trace B presents the upfield region measured at 213 K.

One can consider the ^{1}H NMR shifts of the internally located CH proton and the peripheral pyrrole resonances as a convenient spectroscopic criterion of the aromaticity. The following porphyrinoids presented a relatively small degree of aromaticity: 2-*N*-methyl-5,10,15,20-tetraphenyl-21-carbaporphyrin (21-CH, 0.984 ppm; pyrrole, 7.48 – 7.96 ppm),[1d] 2-*N*-methyl-5,10,15,20-tetraphenyl-21-methyl-21-carbaporphyrin (pyrrole, 7.91-7.27 ppm),[1d] azuliporphyrin (internal CH, 1.5 ppm)[2f]. In the limiting case of benziporphyrin[2a] the strong

aromatic structure of benzene completely blocks a π delocalization pathway for the entire macrocycle (internal CH, 7.88 ppm). Thus, the SCTPPH can be classified as a border-line case demonstrating carbaporphyrinoid aromaticity. The thiophene subunit attenuates conjugative pathways in SCTPPH providing, however, the very efficient 18π delocalization path for STPPH,[8] which is due to the difference of orientation of the thiophene moiety in the macrocyclic structure.

Acknowledgment

Financial support from the State Committee for Scientific Research KBN of Poland (Grant 3 T09A 155 15) and the Foundation for Polish Science is kindly acknowledged.

References

1. (a) Chmielewski, P. J.; Latos-Grażyński, L.; Rachlewicz, K.; Głowiak, T. *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 779. (b) Furuta, H.; Asano, T.; Ogawa, T. *J. Am. Chem. Soc.* **1994**, *116*, 767. (c) Liu, B. Y.; Brückner, C.; Dolphin, D. *Chem. Comm.* **1996**, 2141. (d) Chmielewski, P. J.; Latos-Grażyński, L. *J. Chem. Soc. Perkin Trans. 2* **1995**, 503.(e) Chmielewski, P. J., Latos-Grażyński, L.; Głowiak, T. *J. Am. Chem. Soc.* **1996**, *118*, 5690.
2. (a) Berlin, K.; Breitmaier, E. *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1246. (b) Lash, T. *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2533. (c) Berlin, K.; Steinbeck, C.; Breitmaier, E. *Synthesis* **1996**, 336. (d) Lash, T. D.; Chaney, S. T. *Tetrahedron Lett.* **1996**, *37*, 8825. (e) Lash, T. D.; Hayes, M. J. *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 840. (f) Lash, T. D.; Chaney, S. T. *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 839. (g) Berlin, K. *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1820. (h) Hayes, M. J. ; Lash, T. D. *Chem. Eur. J.* **1998**, *4*, 508.
3. (a) Heo, P.-Y.; Shin, K.; Lee, C.-H. *Tetrahedron Lett.* **1995**, *37*, 197. (b) Lee, C.-H.; Kim, H.-J. *Tetrahedron Lett.* **1997**, *38*, 3935. (c) Lee, C-H.; Kim, H.-J.; Yoon, D.-W. *Bull. Korean Chem. Soc.* **1999**, *20*, 276.
4. Comins, D. L.; Killpack, M. O. *J. Org. Chem.* **1987**, *52*, 104.
5. Spectroscopic data for **4** (a mixture of stereoisomers) ^{1}H NMR (300 MHz, 293K, $CDCl_3$) δ = 7.35 (m, 20H), 6.99 (s,1H), 6.97 (s, 1H), 6.81(s, 1H), 6.79 (s, 1H), 5.87 (d, 2H), 5.68 (d, 2H), 2.86 (b, 2H), 2.62 (b, 2H)
6. Spectroscopic data for SCTPPH: ^{1}H NMR (300 MHz, 293K, $CDCl_3$) δ = 8.25 (3-CH), 7.16, 7.53 (J_{AB} = 4.8 Hz, pyrrole); 7.20, 7.54 (J_{AB} = 4.8 Hz, pyrrole); 7.40 (unresolved two protons, pyrrole), the unresolved multiplets at 7.8, 7.7, 7.55 assigned to phenyl resonances, 5.81 (23-NH), 4.76 (21-CH). UV/Vis λ_{max}/nm (log ε): 437(4.97), 705(sh), 763(sh); *m/z*=632; HR-MS: *m/z* = 632.21812 (found for $(M+1)^+$), 632.21606 (calc. for $C_{44}H_{30}N_3S$);
7. $SCOTPPH_2$: ^{1}H NMR (300 MHz, 293K, $CDCl_3$) δ = 8.68, 8.57 (J_{AB} = 4.8 Hz, pyrrole); 8.61, 8.58 (J_{AB} = 4.3 Hz, pyrrole); 8.58, 8.57 (J_{AB} = 4.8 Hz, pyrrole); the unresolved multiplets at 8.2, 8.1, 7.75 assigned to phenyl resonances, -5.34 (21-CH). UV/Vis λ_{max}/nm (log ε): 443(5.01), 533(4.09),575(3.90), 635(3.82), 696(3.78); *m/z* = 647; *HR-MS: m/z* = 647.19932 (found for M^+), 647.20313 (calc. for $C_{44}H_{29}ON_3S$).
8. Latos-Grażyński L.; Lisowski J.; Olmstead M.M.; Balch A. L. *J. Am. Chem. Soc.* **1987**, *109*, 4428.