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5-{4-Nitro-3-[1-(toluene-4-sulphonyl)-hexyl]-phenyl}-10,15,20-triphenylporphyrin Zinc(II)

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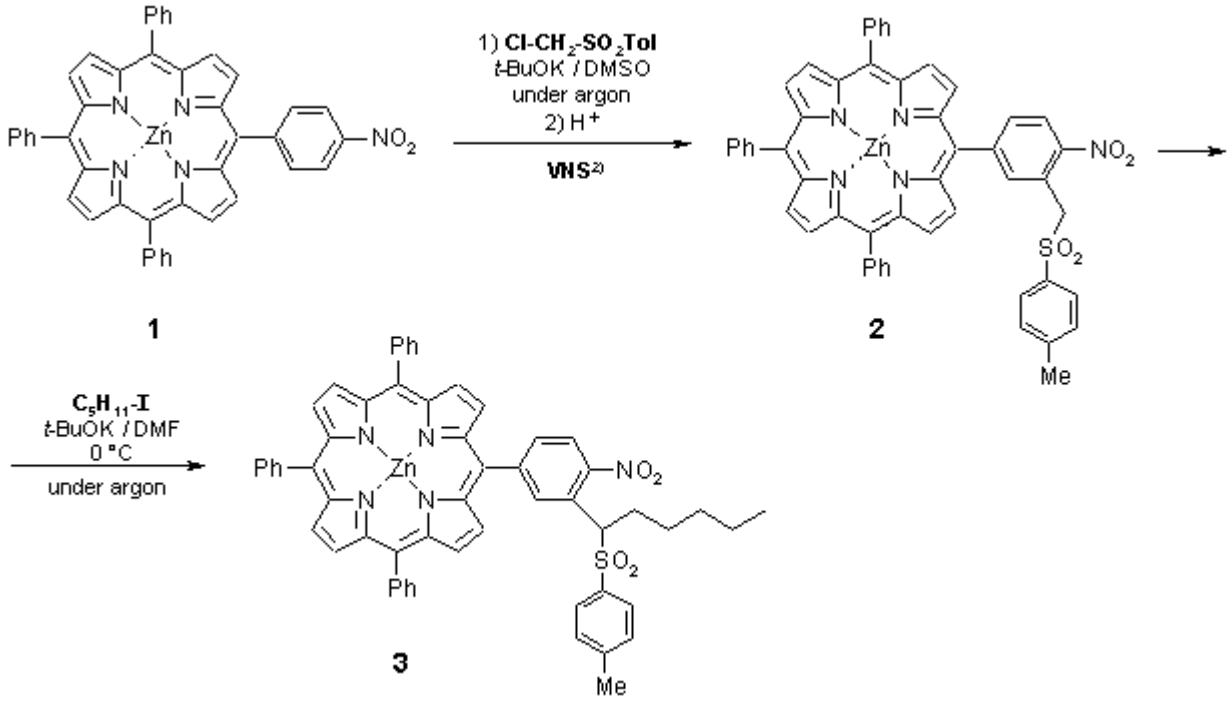
As part of ongoing research programme we synthesised the title *meso*-tetraarylporphyrin derivative possessing a high degree of complexity in one phenyl ring. This compound is valuable potential intermediate for reactions, leading to biologically active porphyrins, such as PDT agents.[1] We used for this purpose the Vicarious Nucleophilic Substitution of Hydrogen reaction (VNS)[2] and subsequent alkylation of the intermediate **2** by n-pentyl iodide.



To a stirred solution of *t*-BuOK (87 mg, 0.78 mmol) in anhydrous DMSO (2.5 ml, under argon) a solution of 5-(4-nitrophenyl)-10,15,20-triphenylporphyrin zinc(II)[3] (**1**; 79 mg, 0.11 mmol) and chloromethyl *para*-tolyl sulphone (45 mg, 0.22 mmol) in DMSO (1.5 ml) was added dropwise *via* syringe at room temp. during *ca* 5 min. After additional 30 min of stirring the mixture was poured into 3% HCl containing ice (30 ml). The precipitate was filtered, washed with water, and then dissolved in $CHCl_3$. After drying with anhydrous Na_2SO_4 and evaporation of the solvent the 5-[4-nitro-3-(toluene-4-sulphonylmethyl)-phenyl]-10,15,20-triphenylporphyrin zinc(II) (**2**; described in earlier literature[3]) was isolated by column chromatography (silica gel 200-300 mesh, Merck AG; eluent: $CHCl_3$/n-hexane - 3:1); yield - 86 mg, 88%.

In a round-bottom flask (10 ml), the solution of 5-[4-nitro-3-(toluene-4-sulphonylmethyl)-phenyl]-10,15,20-triphenylporphyrin zinc(II) (**2**; 86 mg, 0.096 mmol) in DMF (2.5 ml) was cooled to 0°C. Then, *t*-BuOK (45 mg, 0.40 mmol) was added in a one portion and the mixture was stirred for 15 min under argon. To this mixture, 1-iodopentane (79 mg, 0.40 mmol) in DMF (1 ml) was added at 0°C. The reaction was continued at this temp. for *ca* 3 h until completion (TLC monitoring; $CHCl_3$/n-hexane - 3:1). The mixture was poured onto water with ice (40 ml), the product was extracted with $CHCl_3$ (3 x 10 ml), and the organic layer was washed with H_2O (2 x 20 ml). After drying over $MgSO_4$ and evaporation of the solvent, the crude product was purified by column chromatography (silica gel 200-300 mesh, Merck AG) using CH_2Cl_2/n-hexane mixture (1:1) as eluent. Yield of pure deep-purple solid 5-{4-nitro-3-[1-(toluene-4-sulphonyl)-hexyl]-phenyl}-10,15,20-triphenylporphyrin zinc(II) (**3**) - 77 mg (83%).

5-[4-Nitro-3-(toluene-4-sulphonylmethyl)-phenyl]-10,15,20-triphenylporphyrin Zinc(II) (2):

M.p. > 300°C.

^{1}H NMR ($CDCl_3$, 200 MHz): 9.02 (d, J = 4.8 Hz, 2 H, H^b-pyrrole), 8.98 (s, 4 H, H^b-pyrrole), 8.83 (d, J = 4.8 Hz, 2 H, H^b-pyrrole), 8.37 (s, 1 H, H-Ar(NO_2)), 8.30-8.17 (m, 8 H, 2 H of H-Ar(NO_2) and 6 H of H-Ph), 7.84-7.68 (m, 9 H, H-Ph), 7.66 (apparent d, J = 8.5 Hz, 2 H, H-Tol), 7.38 (apparent d, J = 8.5 Hz, 2 H, H-Tol), 5.08 (s, 2 H, CH_2), 2.29 (s, 3 H, CH_3).

UV-VIS (CH_2Cl_2), l_{max} (log e): 590 (3.62), 549 (4.02), 420 (5.19, Soret), 348 nm (3.90).

MS (EI), m/z (% rel. int.): 893 (21), 891 (27), 889 (34) [isotopic $M^{+\cdot}$], 739 (3), 737 (5), 735 (9), 723 (6), 721 (10), 719 (15), 691 (9), 613 (5), 306 (4), 299 (4), 173 (14), 156 (14), 139 (10), 106 (15), 92 (52), 91 (100), 77 (10), 65 (27), 64 (53).

HR-MS (EI) Calcd for $C_{52}H_{35}N_5O_4SZn$: 889.1701; Found: 889.1699.

5-{4-Nitro-3-[1-(toluene-4-sulphonyl)-hexyl]-phenyl}-10,15,20-triphenylporphyrin Zinc(II) (3):

M.p. > 300°C.

IR (neat, cm^{-1}): 3103, 3055 & 3021 ($CH_{aromat.}$); 2956, 2921 & 2850 (CH_3, CH_2); 1597; 1524 & 1340 (NO_2); 1320 & 1147 (SO_2).

^{1}H NMR ($CDCl_3$, 200 MHz): 9.11 (d, J = 4.8 Hz, 1 H, H^b-pyrrole), 9.02-8.95 (m, 3 lines, 6 H, H^b-pyrrole), 8.77 (d, J = 4.6 Hz, 1 H, H^b-pyrrole), 8.66 (d, J = 1.7 Hz, 1 H, H-Ar(NO_2)), 8.30 (part of AB coupled with another proton, J = 8.3, 1.7 Hz, 1 H, H-Ar(NO_2)), 8.28-8.19 (m, 6 H, H-Ph), 8.18 (part of AB, J = 8.3 Hz, 1 H, H-Ar(NO_2)), 7.83-7.73 (m, 9 H, H-Ph), 7.70 (apparent d, J = 8.2 Hz, 2 H, H-Tol), 7.33 (apparent d, J = 8.2 Hz, 2 H, H-Tol), 5.69 (dd, J = 10.8, 4.2 Hz, 1 H, CH(SO_2Tol)), 2.50-2.38 (m, 2 H, CH_2), 2.41 (s, 3 H, CH_3-Tol), 1.37-1.22 (m, 6 H, 3xCH_2), 0.85 (t, J = 6.9 Hz, 3 H, CH_3).

UV-VIS ($CHCl_3$), l_{max} (log e): 596.5 (3.56), 556 (4.09), 518 (3.38), 423.5 (5.39, Soret), 356 (3.90), 333 nm (4.10).

LSIMS(+), m/z (% rel. int.): 961 (2), 960 (3, M+H), 959 (3), 958 (3), 803 (2), 601 (2), 523 (3), 395 (7), 369 (3), 307 (12), 154 (100).

Elemental analysis calcd. for $C_{57}H_{45}N_5SO_4Zn$ (961.46): C - 71.21, H - 4.72, N - 7.28. Found: C - 70.75, H - 5.26, N - 6.32.

References

1. Hsi, R.A.; Rosenthal, D.I.; Glatstein, E. *Drugs* **1999**, *57*, 725.
2. a) Makosza, M.; Wojciechowski, K. *Liebigs Ann. / Recueil* **1997**, 1805.
b) Ostrowski, S.; Shim, Y.K. *Bull. Korean Chem. Soc.* **2001**, *22*, 9.
3. Ostrowski, S.; Mikus, A.; Shim, Y.K.; Lee, J.-Ch.; Seo, E.-Y.; Lee, K.-I.; Olejnik, M. *Heterocycles* **2002**, *57*, 1615.