Tetrahedron Letters No. 44, pp 4225 - 4228.
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0040-4039/78/1029-4225$02.00/0

THE SYNTHESIS OF A 22π-ELECTRON TETRAPYRROLIC MACROCYCLE, [1,3,1,3] PLATYRIN

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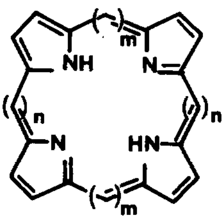
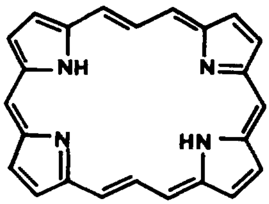
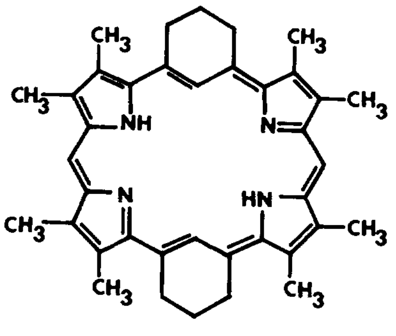
Expansion of the porphyrin macrocycle by formally inserting odd numbers of carbon alternately between the pyrrolic rings, 1, gives rise to a family of coplanar porphyrin vinylogs, the platyrins.[1] Like the porphyrins,[m,n,m,n]platyrins (m and n = odd numbers) are conjugated tetraazaannulenes containing 4n + 2 π-electrons. Thus,they might be expected to be "aromatic"(diatropic).[2] The synthesis of the first member of this new system 3 was accomplished using the following sequence of reactions.



1

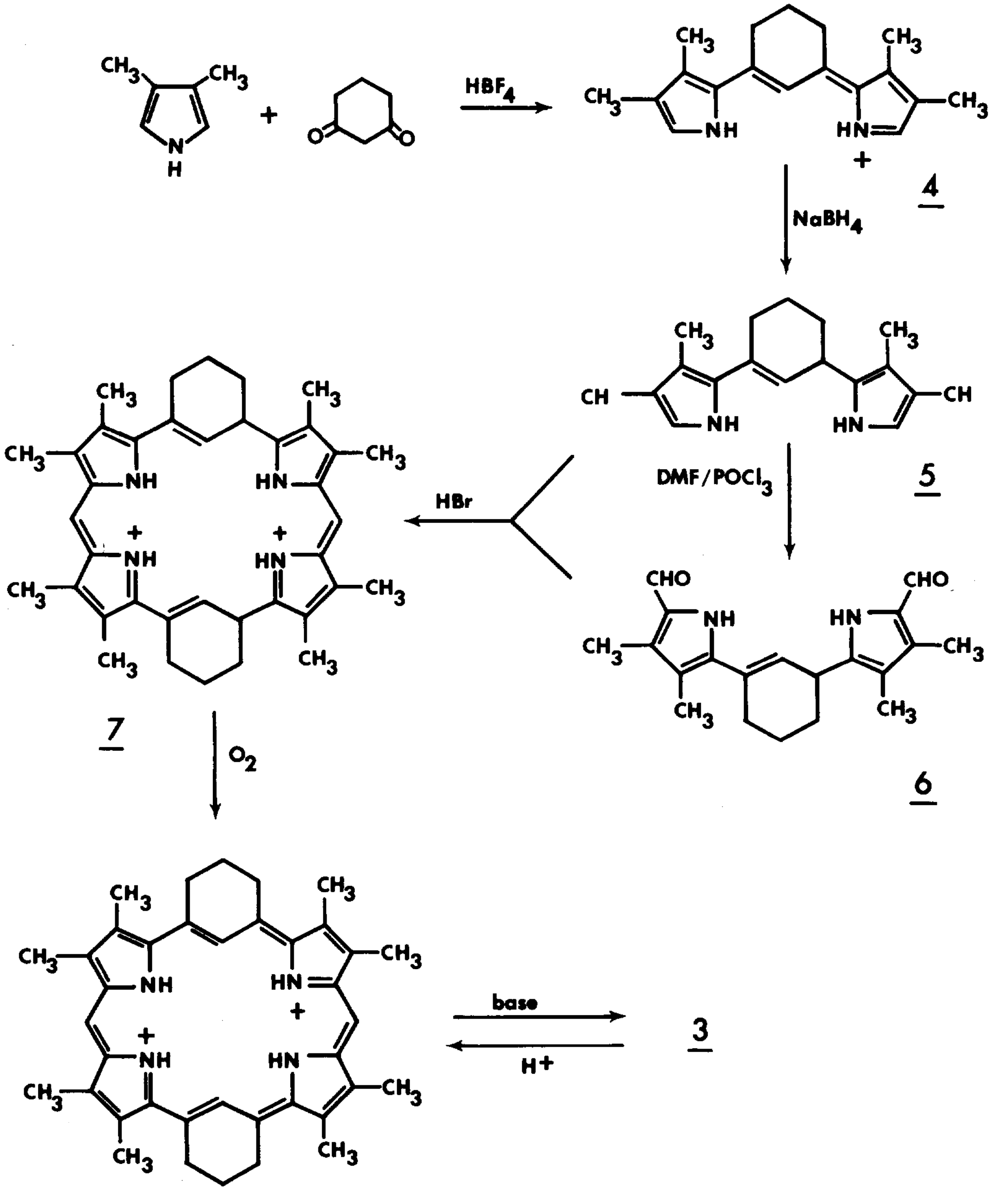


2



3

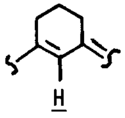
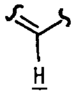
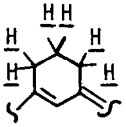
Acid-catalyzed (HBF_4) condensation of 3,4-dimethylpyrrole with 1,3-cyclohexanedione in ethanol gave in 35% yield the deep blue trimethine salt 4 [mp 245-6°; IR (Nujol): 3350 (NH), 1565 and 1535 cm^{-1} (C=C); Vis $\lambda_{max}^{CHCl_3}$ nm: 540 sh, 580; m/e = 226 (parent-HBF_4); PMR: Table I]. Partial reduction of 4 with $NaBH_4$ in CH_3CN afforded 5 as a pale yellow air-sensitive oil [IR (neat): 3380 cm^{-1} (NH), 1625 and 1580 cm^{-1} (C=C); PMR ($CDCl_3$): δ7.4 (2H, N$\underline{H}$), 6.24 (m, 2H, α-pyrrolic), 5.67 (m, 1H, C=C-$\underline{H}$), 3.60 (m, 1H, C$\underline{H}_2$-C=C), 2.4-1.5 (6H, C$\underline{H}_2$-C$\underline{H}_2$-C$\underline{H}_2$), 2.07 (s,3H, C$\underline{H}_3$), 1.98 (s, 9H, C$\underline{H}_3$)]. Bis-formylation of 5 with dimethylformamide and phosphorus oxychloride in dichloroethane gave in 80% overall yield from 4 the dialdehyde 6 [mp 174-6° (dec.);



8

IR (Nujol): 3250 (NH), 1630 cm^{-1} (CO): PMR (DMSO-d_6); δ9.40 (s, 1H, CHO), 9.35 (s,1H, CHO), 5.83 (m, 1H, C=C-H), 3.6 (m, 1H, CH_2-C=C), 2.22 (s, 6H, CH_3), 1.98 (s, 3H, CH_3), 1.93 (s, 3H, CH_3), 2.6-1.6 (m, 6H, CH_2-CH_2-CH_2); m/e = 326. Addition of a methanol/methylene chloride solution of 5 and 6 to a refluxing solution of hydrobromic acid in methanol while air was passed through the reaction mixture gave after chromatography (neutral alumina/1% MeOH in CH_2Cl_2) a 19% yield of the dark green macrocycle 3 [mp >300; m/e=552 (parent-2); UV-Vis $\lambda_{max}^{CH_2Cl_2}$ nm (ε): 230 (13,600), 265 (12,000), 276 (11,900), 298 (11,400), 326 (11,900), 390 sh (14,200), 453 (60,400), 477 (398,000), 607 (11,800), 649 (9340), 747 (2100), 767 sh (1520), 846 (1850)]. Acids diprotonate 3 forming the platyrin salt 8 [UV-Vis $\lambda_{max}^{CH_2Cl_2/CF_3CO_2H}$ nm (ε): 231 (19,900), 281 (9130), 290 (8920), 307 (7470), 375 (10,800), 408 (10,500) 453 sh (63,200), 477 (389,000), 625 sh (9030), 537 (10,700), 647 sh (9130), 672 (5190), 688 (6640), 705 (7990), 717 sh (6270), 734 sh (3630), 788 (6220)]; PMR: Table I. A comparison of the pmr of 8 with 4 shows 8 to be highly diatropic as expected of a 22π-electron system. The vinyl protons of 8 positioned within the cavity experience a 16.2 ppm shift to higher field while the outer methyl protons are shifted 2.1 ppm to lower field as a result of a substantial diamagnetic ring current.

Table 1. PMR Spectra (δ)

	4	8	OMP[a]	DMS[b]
	7.18 (1H)	-8.97	—	—
	—	11.64 (2H)	10.98	11.80 11.71
-CH_3	2.32 2.00 (12H)	4.22 4.17 (24H)	3.76	4.22 4.19 4.08 4.04
	2.1-1.8(6H)	2.4-1.0(12H)	—	—
N-H	[c]	-5.6 (4H)	-4.82	-5.46 -5.00 -4.24

[a] octamethylporphyrin in trifluoroacetic acid
[b] decamethysapphyrin in trifluoroacetic acid (ref.3)
[c] the NH absorption is not visible; α-pyrrolic-H (doublet at δ7.5, J=3Hz)

The peripheral methyl protons, the external meso protons, and the internal N-H of platyrin 8 exhibit chemical shifts similar to those found in octamethylporphyrin and the 22π-electron macrocycle, decamethylsapphyrin[3].

Both playrin 3 and its diprotonated salt, 8, show an intense Soret-like absorption at 477 nm (ε398,000)[4] characteristic of a fully conjugated macrocycle. The value of ε represents a minimum since dissolution of samples of 3 or 8 in various solvents usually leave small amounts of highly insoluble residues.

Platyrin 3 forms highly insoluble metal complexes of as yet unknown structure with Ni^{+2} (λ_{max}: 545 and 522nm), Cu^{+2} (λ_{max}: 547 and 519 sh nm) and BF$_3$ (λ_{max}:538 and 517 nm). The metal ions are not strongly coordinated to the platyrin, however, since acetic acid can demetalate these complexes.

References and Notes

* To whom correspondence should be addressed.

1) The need for a generic name for this family of tetrapyrrolic macrocycles becomes apparent when one considers that the systematic name for 2 is: 25,26,27,28-tetraazapentacyclo[20.2.1.1^{3,6}.1^{10,13}.1^{15,18}]octacosa-1,3,5,7,9,11,13(27),14,16,18,20,22(25),23-tridecaene while the systematic name for 3 is even more cumbersome (see ref.5). To fill this need we have coined the word "platyrin" a word derived from the Greek "πλατύs" (platys) meaning "wide or broad" and the sufix "-rin" from the ending of porphyrin, hence a wide or broad porphyrin. A bracket indicating the number of methine carbons may be prefixed to the name, e.g., 2 is [1,3,1,3]platyrin. This system of nomenclature can be extended to any expanded tetrapyrrolic macrocycle, e.g. the homoporphyrins (Ref.6) become [1,1,1,2]platyrins.
2) F. Sondheimer, Accounts Chem.Res., **5**, 81 (1972).
3) M.M. King, Ph.D. Thesis, Harvard University,Cambridge,Mass., 1970.
4) Compare with the Soret bands in octamethylporphyrin (398nm; ε168,000) and decamethylsaphyrin (455nm; ε 329,000) [Ref.3].
5) E. LeGoff and R. A. Berger, Abstracts, 175th National Meeting of the American Chemical Society, Anaheim, Calif., March 1978, Orgn-132.
6) H. J. Callot and E. Schaeffer, J.Org.Chem., **42**,1567 (1977).

(Received in USA 15 May 1978)