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STERICALLY BULKY PORPHYRINS: THE ATROPISOMERS OF TETRAKIS(3,5-DI-TERT-BUTYL-2-NITROPHENYL)PORPHYRIN AND THEIR IRON(III) COMPLEXES

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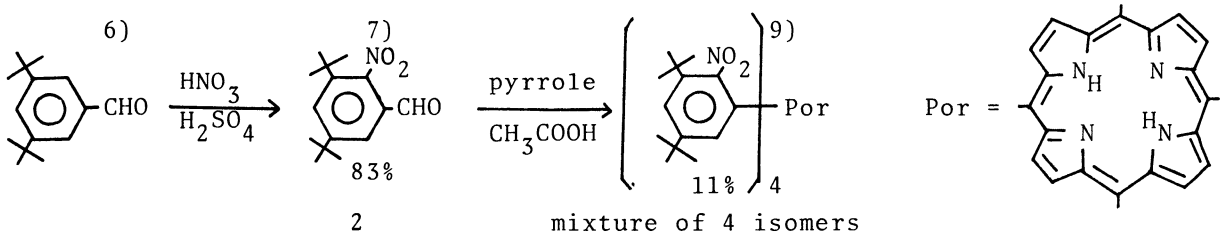
A new "bis pocket" porphyrin has been prepared and characterized. Its four geometric isomers (atropisomers) have been separated by chromatography. Each isomer has relatively high conformational stability to light and prolonged heating. Practical utility of this ligand system to iron(III) chemistry has been demonstrated.

A variety of the protected porphyrins have so far provided much information relating to dioxygen reactivity.[1] Collman's "picket-fence"[2] and Baldwin's "capped"[3] porphyrins have proved very useful for reversible oxygenation studies. The use of "bis pocket" porphyrins such as meso-tetramesitylporphyrin or meso-tetrakis(2,4,6-trimethoxyphenyl)porphyrin has also led to the successful isolation of the reactive ferryl cation radical[4] or to prohibition of oxo, peroxo-bridged dimer formation.[5] For a more complete understanding of the structure-function relationship of hemoproteins, syntheses of another protected porphyrins will be obviously required. Among others, "bis-pocket-type" porphyrins will be most promising candidate for the possible unsymmetrical protection to both sides of a porphyrin plane. We wish to report here the synthesis and characterization of a new "bis pocket" porphyrin; meso-tetrakis(3,5-di-tert-butyl-2-nitrophenyl)porphyrin.

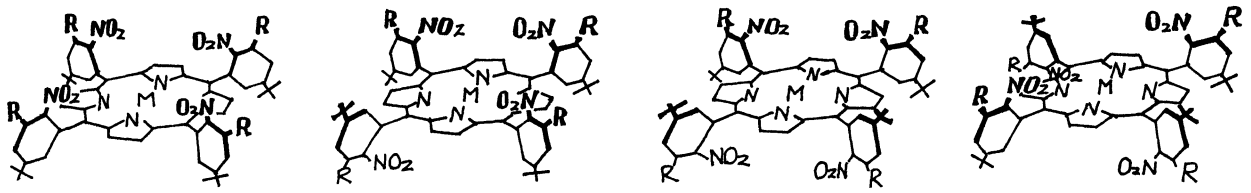
The porphyrin 1 has been prepared by condensation[8] of pyrrole with a nitrobenzaldehyde derivative 2[7] as shown in Scheme 1. The resulting solid 1[9] are the mixture of four atropisomers(Fig. 1). Their separation and purification have been effected by alumina column or silica gel thin layer chromatography.[10] All isomers 1a-1d show identical electronic absorption spectra,[11] but their proton NMR patterns are substantially different from each other. (See Table 1)



2 mixture of 4 isomers

1 (Abbr. TBNPP-H_2)

Scheme 1.



	αααα	ααβ	ααββ	αβαβ
R = t-bu, M = H_2	1a	1b	1c	1d
R = Me, M = H_2	3a	3b	3c	3d
R = t-bu, M = FeCl	4a	4b	4c	4d
R = t-bu, M = FeOH	5a	5b	5c	5d

Fig. 1. Atropisomers.

Table 1. Proton NMR Data.[a)]

(chemical shifts in ppm relative to TMS, coupling constants J in Hz: solvent $CDCl_3$)

assignment	isomer 1a	isomer 1b	isomer 1c	isomer 1d
internal pyrrole H	-2.97(s,2H)	-2.98(s,2H)	-2.98(s,2H)	-2.99(s,2H)
5-t-butyl H	1.45(s,36H)	1.43(s,9H)	1.47(s,36H)	1.52(s,36H)
		1.48(s,18H)		
		1.52(s,9H)		
3-t-butyl H	1.60(s,36H)	1.55(s,9H)	1.60(s,36H)	1.57(s,36H)
		1.58(s,18H)		
		1.62(s,9H)		
ortho phenyl H	7.93(d,4H,J=2.1)	7.81(m,1H)	7.97(d,4H,J=0.5)	8.23(d,4H,J=1.8)
		8.06(m,2H)		
		8.17(m,1H)		
para phenyl H	7.99(d,4H,J=2.1)	7.99(m,4H)	7.99(d,4H,J=0.5)	7.99(d,4H,J=1.8)
β-pyrrole H	8.69(s,8H)	8.64(s,2H)	8.64(s,4H)	8.65(s,8H)
		8.66(s,2H)	8.68(s,4H)	
		8.68(s,2H)		
		8.69(s,2H)		

a) The assignment of observed proton NMR signals is ably assisted by the use of nuclear Overhauser method.

Atropisomerization of various ortho-substituted tetraphenylporphyrins has been the subject of considerable recent research.[12)] We therefore have carried out the thermal and photoinduced isomerization of new four porphyrins and the results are listed in Table 2. Each isomer is stable in refluxing in chloroform(61 °C), but gradually interconverts to others in refluxing toluene(111 °C). Strong UV irradiation with mercury lamp for 11 h gives no appreciable amount of other isomers.

For a comparative study,[13)] an analogous porphyrin, meso-tetrakis(5-tert-butyl-3-methyl-2-nitrophenyl)porphyrin 3 has been prepared[14)] and one of its atropisomers 3d has been separated.[15)] Heating in chloroform(61 °C) and photoirradiation in the toluene solution for 11 h result in easy isomerization of 3d with the conversion

percentage of 50 and 20 respectively. These data clearly indicate that the isomer 3a-3d has relatively low activation energy for restricted rotation about phenyl-porphyrin single bonds in comparison with 1a-1d. Thus it may be concluded that the high conformational stability of 1a-1d is due to the buttressing effect of the tertiary butyl adjacent to the nitro group.

Each isomer of the free base 1a-1d is converted to the corresponding iron(III) complex 4a-4d or 5a-5d with retention of the ligand conformation. The chloro complex, Fe(TBNPP)Cl 4a-4d , has been obtained by the reaction of 1a-1d with $FeCl_2 \cdot 4H_2O$ in the presence of pyridine and sodium acetate in a mixed solvent of chloroform/acetic acid (v/v = 1/7) at 70 °C.[16] The reaction of 4a-4d with sodium hydroxide simply gives hydroxy complex 5a-5d[17,18] in marked contrast to the formation of oxo dimer complexes in unprotected porphyrin-iron(III) systems.[19] All the isolated complexes 5a-5d are stable in chloroform under reflux for at least 8 h .

In this way, steric bulk of a new "bis pocket" porphyrin 1 leads to the stabilization of hydroxoiron(III) species. Further research to extract information from this new ligand system is in progress in our laboratory.

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Table 2. Thermal and Photoinduced Atropisomerization.

Starting isomer[a]	Solvent used	Temp °C	Time h	Conversion to other isomer (total %) [a]
1a	toluene	111	11	90
	chloroform	61	5	0
	toluene(hν)[b]	18	11	5
1b	toluene	111	11	30
1c	toluene	111	11	40
	chloroform	61	5	5
1d	toluene	111	11	20
	chloroform	61	11	0
	toluene(hν)[b]	18	11	0

a) Original isomer is converted to others. Total percentage represents amount of other isomers converted.

b) Photoirradiation with high pressure mercury lamp (400W, Riko UVL-400HA)

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6) M. S. Newman and L. F. Lee, J. Org. Chem., 37, 4468(1972).
7) Yellow crystals; mp 90-91 °C; bp 150-155 °C(0.1 mmHg); NMR (in $CDCl_3$) δ 1.3(s, 9H, 3-t-butyl H), 1.4(s, 9H, 5-t-butyl H), 7.7(m, 2H, phenyl H), 9.7(s, 1H, CHO); Mass Spectrum(70 eV): 262(intensity 33), 263(86), 264(47), 265(24); Found: C, 68.54; H, 8.07; N, 5.37%. Calcd for $C_{15}H_{21}NO_3$: C, 68.41; H, 8.04; N, 5.32%.
8) T. N. Sorrell, Inorg. Synth., 20, 161(1980).
9) Purple brown crystals. 1 is soluble in hydrocarbons such as toluene, benzene or chloroform. Found: C, 73.28; H, 7.46; N, 8.88%. Calcd for $C_{76}H_{90}N_8O_8$: C, 73.40; H, 7.29; N, 9.01%. The nitro groups show characteristic infrared absorptions: 760, 840, 1530 cm^{-1}.
10) The nomenclature of atropisomers are dependent on ref. 2. Toluene or chloroform is used as eluent. R_f values(silica gel TLC, toluene): 1a, 0.28; 1b, 0.65; 1c, 0.74; 1d, 0.88.
11) Electronic absorption data (in $CHCl_3$, 25 °C) λ nm (ε, $10^{13}M^{-1}cm^{-1}$): 421(352), 474(3.1), 512(21.6), 542(3.1), 586(6.9), 640(0.6).
12) R. A. Freitag, J. A. Mercer-Smith, and D. A. Whitten, J. Am. Chem. Soc., 103, 1226(1981) and references cited therein.
13) A known porphyrin, meso-tetrakis(2-nitrophenyl)porphyrin, is not suitable for the purpose intended, because of the extreme insolubility.
14) A similar method to Scheme 1 is used for the preparation. A starting material, 5-tert-butyl-3-methyl-nitrobenzaldehyde, has been prepared in a quantitative yield by nitration of 5-tert-butyl-3-methylbenzaldehyde. mp 58-59 °C; NMR (in $CDCl_3$) δ 1.4(s, 9H, 5-t-butyl H), 2.3(s, 3H, 3-methyl H), 7.5(d, 1H, J=2.1, ortho phenyl H), 7.7(d, 1H, J=2.1, para phenyl H), 9.9(s, 1H, CHO). The condensation of this aldehyde with pyrrole gives 3 in 4% yield. Electronic absorption data in $CHCl_3$ λ nm: 420, 480, 512, 588, 644.
15) The first eluate in use of alumina column chromatography is collected as 3d(eluent, toluene). NMR (in $CDCl_3$) δ -2.8(s, 2H, internal pyrrole H), 1.5(s, 36H, 5-t-butyl H), 2.6(s, 12H, 3-methyl H), 7.7(d, 4H, J=2, para phenyl H), 8.2 (d, 4H, J=2, ortho phenyl H), 8.7(s, 8H, β-pyrrole H).
16) Heating for 1 h is required. Each isomer 4a-4d shows satisfactory elemental analyses.
17) Bulky porphyrins, meso-tetramesitylporphyrin and meso-tetrakis(2,4,6-trimethoxyphenyl)porphyrin, also give the corresponding hydroxoiron(III) complexes. R. -J. Cheng, L. Latos-Grazynski, and A. L. Balch, Inorg. Chem., 21, 2412(1982).
18) A mixed solvent of toluene/water is used. The reaction goes to completion by 24 h . No chloride ion is detected in the obtained complexes 5a-5d(Beilstein's method). Electronic absorption data in toluene, λ nm: 416, 574. All isomers in toluene-d^8 show downfield β-pyrrole proton NMR signals (≈80 ppm), diagnostic of high spin five coordinate iron(III) complexes. See ref. 18.
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