

Synthesis and NMR Studies of Core-Modified, *N*-Confused Porphyrins Possessing Alkyl Groups at the Rim Nitrogen

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The '3+1' type condensation of 16-thiatripyrromethane with *N*-alkyl-2,4-bis[(α -hydroxy- α -phenyl)methyl]pyrrole in the presence of acid catalyst afforded core-modified, *N*-confused porphyrins bearing alkyl groups at the rim nitrogen. The proton NMR spectra indicate that the bulkiness of the *N*-alkyl substituents is somewhat related with the tiltedness of the inverted pyrrole ring. The changes in chemical shift of inner methine protons depending on the *N*-alkyl group and protonation site is discussed.

Introduction

The isolation of porphyrin isomer bearing an inverted pyrrole ring opened a new door for the porphyrin chemists and some unusual chemistry has been reported in the literature.¹⁻⁸ Modification of the basic framework of porphyrins while keeping aromaticity intact has resulted in altering the spectroscopic and electronic properties of the porphyrins. A typical example is the so-called '*N*-confused porphyrins'. The *N*-confused porphyrins show longer wavelength Q-bands than the normal porphyrins.^{2,3,9} Porphyrin-based model systems are usually designed by the principle of quantitative relationship between the structural modification and reactivity. Most of the model systems have been devoted to understand this principle and the systematic construction of such model systems requires precise tuning of energetics and electronic structures of the molecules. The achievement of such control could be accomplished by several different approaches. The simplest method would be replacing nitrogen in the core with some other heteroatoms such as oxygen, sulfur and selenium. This alteration results in change of symmetry and accordingly the transition energy among the molecular orbital changes.¹⁰ We have been interested in the development of new synthetic methods for unsymmetric porphyrins bearing different core ligands. As a part of these efforts, we have recently reported the synthesis of several core-modified porphyrins and their tautomeric behaviour.²⁻⁴ Having succeeded in the development of a synthetic method for core-modified porphyrins, we wished to investigate the influence of the substituents at rim nitrogen on the flexibility of porphyrins. A steric interaction between the substituents at rim nitrogen and *meso*-substituents also is influential on the degree of distortion of porphyrin plane. Anisotropic shielding of the inner methine proton in the *N*-confused, core-modified porphyrins must be correlated with the degree of tiltedness of the flipped pyrrole from the imaginary plane of the porphyrin. In this paper we report the synthesis of core-modified porphyrins bearing alkyl substituents on the rim nitrogen and change in chemical shift of inner methine proton depending on the substituents at rim nitrogen (Scheme 1). In addition to this, we have attempted to corre-

late the effect of substituents at the rim nitrogen on the chemical shifts of inner (or outer) methine protons. The conformational changes resulting from the protonation of porphyrins will be also discussed.

Experimental Section

¹H NMR spectra (400 MHz, Bruker IFS 48), IR spectra (JASCO IR 100), and absorption spectra (Kontron 941) were collected routinely. Mass spectra were obtained by FAB. Column chromatography was performed on silica (Merck, 230-400 mesh). Pyrrole was distilled at atmospheric pressure from CaH₂. CH₂Cl₂ (reagent grade) was distilled from K₂CO₃. All other reagents were obtained from Aldrich.

***N*-Methyl-2,4-dibenzoylpyrrole (2b).** Typical procedure: To a mixture of 2,4-dibenzoyl pyrrole (0.50 g, 1.82 mmol) and K₂CO₃ (2.5 g, powdered, 18.08 mmol) dissolved in DMF (10 mL) was added methyl iodide (28.9 g, 200 mmol). The mixture was stirred for 48 hr at room temperature. When no starting material was shown on TLC, the mixture was combined with water (50 mL). Then the mixture was extracted with methylene chloride (30 mL \times 3) and organic layer was dried (Na₂SO₄). The solvent was removed *in vacuo* and the remaining solid was pure enough to carry out the next step. Yield was quantitative. mp 135 °C; ¹H NMR (CDCl₃) δ 7.87-7.80 (m, 4H, Ar-H), 7.63-7.44 (m, 7H, Ar-H and pyrrole-H), 7.23 (d, 1H, pyrrole-H), 4.09 (s, 3H, *N*-methyl).

***N*-Ethyl-2,4-dibenzoylpyrrole (2c).** 2,4-Dibenzoyl pyrrole (0.10 g, 0.36 mmol), K₂CO₃ (50 mg, 0.36 mmol) and ethyl bromide (3.95 g, 36.3 mol) was treated identically as for the synthesis of *N*-Methyl-2,4-dibenzoyl pyrrole. Yield was quantitative. ¹H NMR (CDCl₃) δ 7.85-7.81 (m, 4H, Ar-H), 7.60-7.54 (m, 3H, Ar-H and pyrrole-H), 7.50-7.46 (m, 4H, Ar-H), 7.21 (d, 1H, pyrrole-H), 4.50 (q, 2H, methylene), 1.51 (t, 3H, methyl).

***N*-Isopropyl-2,4-dibenzoylpyrrole (2d).** 2,4-Dibenzoyl pyrrole (0.10 g, 0.36 mmol), K₂CO₃ (50 mg, 0.36 mmol) and isopropyl bromide (4.46 g, 36.3 mmol) was treated identically as for the synthesis of *N*-Methyl-2,4-dibenzoyl pyrrole. Column chromatography on silica (methylene chloride/

ethyl acetate, 9/1) afforded pure product. Yield 74 mg (64%); ^1H NMR (CDCl_3) δ 7.84-7.81 (m, 4H, Ar-H), 7.78 (d, 1H, pyrrole-H), 7.58-7.53 (m, 2H, Ar-H), 7.48-7.44 (m, 4H, Ar-H), 7.15 (d, 1H, pyrrole-H), 5.53 (septet, 1H, methine), 1.54 (d, 6H, methyl).

***N*-Benzyl-2,4-dibenzoylpyrrole (2e).** 2,4-Dibenzoyl pyrrole (0.10 g, 0.36 mmol), K_2CO_3 (50 mg, 0.36 mmol) and benzyl bromide (6.21 g, 36.4 mmol) was treated identically as for the synthesis of *N*-methyl-2,4-dibenzoyl pyrrole. Column chromatography on silica (methylene chloride/ethyl acetate, 9/1) afforded pure product. Yield 64 mg (47%); ^1H NMR (CDCl_3) δ 7.81-7.78 (m, 4H, Ar-H), 7.58 (d, 1H, pyrrole-H), 7.54-7.51 (m, 2H, Ar-H), 7.46-7.41 (m, 4H, Ar-H), 7.31-7.20 (m, 6H, pyrrole-H and Ar-H), 5.68 (s, 2H, methylene).

Reduction of *N*-alkyl-2,4-dibenzoylpyrrole. A suspension of LiAlH_4 (0.20 g, 5.45 mmol) in THF (15 mL) was added dropwise to the solution of *N*-alkyl-2,4-dibenzoyl pyrrole (0.36 mmol) dissolved in THF (50 mL). The progress of the reaction was carefully monitored by TLC (methylene chloride/ethyl acetate, 1/1). The reaction was quenched by adding water when no more starting material was observed on TLC (~1.5 hr). The mixture was combined with chloroform (25 mL) and washed with water twice. The organic layer was dried (Na_2SO_4) and the solvent was removed *in vacuo*. IR spectra clearly showed the disappearance of carbonyl stretching at 1640 cm^{-1} and the appearance of hydroxyl stretching at 3400 cm^{-1} . Due to limited stability of the reduced compound, they were used immediately to the next step without further purification.

12-Aza-23-carba-10,15-diphenyl-5,20-dimesityl-12-methyl-21-thiaporphyrin (4). To a mixture of *N*-Methyl-2,4-bis-[(α -hydroxy- α -phenyl)methyl]pyrrole (0.15 g, 0.5 mmol) and 5,10-dimesityl-16-thiatripyromethane (0.24 g, 0.5 mmol) dissolved in chloroform (60 mL) was added $\text{BF}_3\cdot\text{OEt}_2$ (0.12 μL , 1.0 mmol). The mixture was stirred for 20 min then combined with DDQ (0.45 g, 2 mmol) and stirring continued for additional 30 min. Solvent was removed *in vacuo*. Remaining black solid was loaded on silica column and eluted with methylene chloride/ethyl acetate (9/1). Yield 0.11 g (30%); ^1H NMR (CDCl_3) δ 7.91-7.87 (m, 6H, thiophene and Ar-H), 7.73 (d, 1H, $J = 4.5$ Hz, pyrrole-H), 7.66 (d, 1H, $J = 4.5$ Hz, pyrrole-H), 7.62-7.58 (m, 6H, Ar-H), 7.24 (m, 2H, pyrrole-H), 7.11 (s, 4H, Ar (mesityl)-H), 7.38 (d, 1H, pyrrole-H), 3.36 (s, 3H, *N*-methyl), 2.48 (s, 6H, Ar-methyl), 2.36 (d, 1H, inner C-H), 2.0 (m, 12H, Ar-methyl). ^1H NMR (CDCl_3 + excess TFA-d) δ 8.61, 8.60 (two doublets, 2H, $J = 10.85$ Hz, thiophene-H), 8.47, 7.94 (two doublets, 2H, $J = 4.84$ Hz, pyrrole-H), 8.28, 7.93 (two doublets, 2H, $J = 4.63$ Hz, pyrrole-H), 8.25-8.18 (m, 4H, Ar-H), 8.06-7.96 (m, 6H, Ar-H), 7.41 (s, 1H, pyrrole-H), 7.28 (s, 4H, mesityl-H), 3.58 (s, 3H, *N*-methyl), 2.56 (s, 6H, Ar-methyl), 2.00 (d, 12H, $J = 3.54$ Hz, Ar-methyl), -0.79 (d, 1H, $J = 1.16$ Hz, inner C-H). HRMS calcd for $\text{C}_{51}\text{H}_{43}\text{N}_3\text{S}$ 729.3178, found 729.3191.

12-Aza-23-carba-10,15-diphenyl-5,20-dimesityl-12-ethyl-21-thiaporphyrin (5). ^1H NMR (CDCl_3) δ 7.91-7.85 (6H,

m, thiophene and Ar-H), 7.72 (1H, d, pyrrole-H, $J = 4.48$ Hz), 7.66 (1H, d, pyrrole-H, $J = 4.53$ Hz), 7.60-7.57 (6H, m, Ar-H), 7.45 (1H, d, pyrrole-H, $J = 1.59$ Hz), 7.25 (1H, d, pyrrole-H, $J = 2.43$ Hz), 7.10 (4H, s, mesityl-H), 6.98 (1H, s, pyrrole-H), 3.66 (2H, q, *N*- CH_2 -, $J = 1.17$ Hz), 2.47 (6H, s, Ar-methyl), 2.27 (1H, s, inner C-H), 2.00 (12H, d, mesityl- CH_3), 1.00 (3H, t, *N*-methyl- CH_3 , $J = 7.32$). ^1H NMR (CDCl_3 - TFA-d) δ 8.61 and 8.58 (two doublets, 2H, $J = 5.2$ Hz, thiophene-H), 8.46 and 7.90 (two doublets, 2H, $J = 4.5$ Hz, pyrrole-H), 8.25 and 7.93 (two doublets, 2H, $J = 5.2$ Hz, pyrrole-H), 8.28 and 8.19 (two doublets, 4H, $J = 6.8$ Hz, Ar-H), 8.08-7.98 (m, 6H, Ar-H), 7.53 (s, 1H, pyrrole-H), 7.28 (s, 4H, Ar (mesityl)-H), 3.92 (q, 2H, $J = 7.0$ Hz, *N*- CH_2 -), 2.56 (d, 6H, $J = 1.01$ Hz, Ar (mesityl)- CH_3), 1.99 (d, 12H, $J = 3.15$ Hz, Ar (mesityl)- CH_3), 0.93 (t, 3H, $J = 7.0$ Hz, *N*-ethyl), -0.80 (s, 1H, inner C-H). FAB MS calcd for $\text{C}_{52}\text{H}_{45}\text{N}_3\text{S}$ 743.33 Found 743.74.

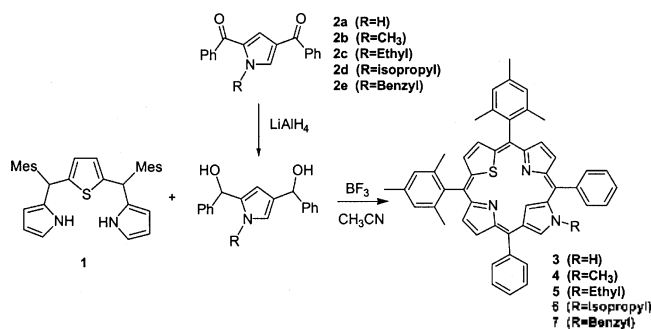
12-Aza-23-carba-10,15-diphenyl-5,20-dimesityl-12-iso-propyl-21-thiaporphyrin (6). ^1H NMR (CDCl_3) δ 7.90-7.84 (m, 6H, thiophene-H and phenyl-H), 7.72 and 7.24 (two doublets, 2H, $J = 4.5$ Hz, pyrrole-H), 7.67 and 7.23 (two doublets, 2H, $J = 4.5$ Hz, pyrrole-H), 7.61-7.58 (m, 6H, phenyl-H), 7.57 (d, 1H, $J = 1.6$ Hz, pyrrole-H), 7.10 (s, mesityl-H), 4.19 (septet, 1H, $J = 6.6$ Hz, *iso*-propyl-CH), 2.47 (s, 6H, Ar(mesityl)- CH_3), 2.36 (d, 1H, $J = 1.6$ Hz, pyrrole-H), 2.00 (d, 12H, $J = 1.33$ Hz, Ar(mesityl)- CH_3), 1.14 (d, 6H, $J = 6.6$ Hz, *iso*-propyl- CH_3). ^1H NMR (CDCl_3 - TFA-d) δ 8.67-8.64 (two doublets, 2H, $J = 5.4$ Hz, thiophene-H), 8.50, 7.93 (two doublets, 2H, $J = 4.7$ Hz, pyrrole-H), 8.27, 7.97 (td, 2H, $J = 4.8$ Hz, pyrrole-H), 8.3-8.26, 8.20-8.16 (2m, 4H, phenyl-*o*-H), 8.12-8.02 (m, 6H, phenyl-*m,p*-H), 7.69 (s, 1H, pyrrole-H), 7.26 (s, 4H, mesityl-*m*-H), 4.34 (m, 1H, *i*-propyl-CH), 2.57 (s, 6H, mesityl-*p*- CH_3), 2.00 (d, 12H, $J = 4.8$ Hz, mesityl-*o*- CH_3), 1.13 (bs, 1H, *i*-propyl- CH_3), -0.86 (s, 1H, pyrrole-H). FAB MS calcd for $\text{C}_{53}\text{H}_{47}\text{N}_3\text{S}$ 757.35, found 758.21.

12-Aza-23-carba-10,15-diphenyl-5,20-dimesityl-12-benzyl-21-thiaporphyrin (7). ^1H NMR (CDCl_3) δ 7.89, 7.87 (two doublets, 2H, $J = 5.6$ Hz, thiophene-H), 7.70, 7.25 (two doublets, 2H, $J = 4.5$ Hz, pyrrole-H), 7.49, 7.18 (two doublets, 2H, $J = 4.5$ Hz, pyrrole-H), 7.10 (d, 4H, $J = 5.9$ Hz, mesityl-*m*-H), 7.61-7.59 (m, 1H, pyrrole-H), 7.85-7.83, 7.61-7.59 (2m, 2H, phenyl-*o*-H), 7.55-7.51 (m, 4H, phenyl-*m*-H), 7.46-7.42 (m, 2H, phenyl-*p*-H), 6.58 (d, 2H, $J = 7.1$ Hz, Ar(benzyl)-H), 7.07-7.01 (m, 3H, Ar(benzyl)-H), 2.72 (d, 1H, $J = 1.64$ Hz, pyrrole-H), 2.47 (d, 6H, $J = 3.94$ Hz, mesityl-*p*- CH_3), 2.00 (d, 12H, $J = 10.2$ Hz, mesityl-*o*- CH_3), 4.94 (s, 2H, benzylic). ^1H NMR (CDCl_3 - TFA-d) δ 8.56, 8.54 (two doublets, 2H, $J = 5.47$ Hz, thiophene-H), 8.42, 7.89 (two doublets, 2H, $J = 4.7$ Hz, pyrrole-H), 8.15, 7.84 (two doublets, 2H, $J = 4.8$ Hz, pyrrole-H), 8.26 (d, 2H, $J = 6.66$ Hz, phenyl-*o*-H), 8.15 (d, 2H, $J = 7.22$ Hz, phenyl-*o*-H), 8.02-7.92 (m, 6H, phenyl-*m,p*-H), 7.37 (d, 1H, $J = 1.01$ Hz, pyrrole-H), 7.26 (s, 4H, mesityl-*m*-H), 7.08-7.04 (m, 1H, Ar(benzyl)-H), 6.96-6.93 (m, 2H, Ar(benzyl)-H), 6.53 (d, 2H, $J = 7.42$ Hz, Ar(benzyl)-H), 5.05 (s, 2H, benzylic), 2.55 (d, 6H, $J = 3.19$ Hz, mesityl-*p*- CH_3), 1.99 (d, 12H, $J =$

1.46 Hz, mesityl-*o*-CH₃), -0.64 (d, 1H, *J* = 1.36 Hz, pyrrole-H), FAB MS calcd for C₅₇H₄₇N₃S 805.35 found 805.37.

Results and Discussions

2,4-Diacylpyrroles (**2b-2e**) were synthesized by the reaction of pyrrole with excess acid chloride in the presence of AlCl₃. Pyrrole readily undergoes electrophilic substitution and introduction of first acyl group at 2-position deactivates 5-position.¹¹ Thus successive introduction of acyl group by electrophilic substitution usually gives 2,4-disubstitution. Introduction of *N*-alkyl substituents was possible by treating alkyl bromides with 2,4-diacylpyrrole in the presence of K₂CO₃. The reaction proceeded smoothly and gave quantitative yields of the desired *N*-alkylated products. The reduction of carbonyl group in *N*-alkyl-2,4-diacylpyrrole was performed with LiAlH₄ in THF at room temperature. The reaction gave quantitative yields of the corresponding diols. The progress of the reduction can be easily followed by observing disappearance of carbonyl stretching in IR spectroscopy. Condensation of (**1**) with *N*-alkyl-2,4-bis(α -hydroxy- α -phenylmethyl)pyrrole was carried out in chloroform in the presence of BF₃·O(Et)₂ (2.0 equiv) followed by oxidation with DDQ to afford the desired porphyrins. The porphyrins were isolated in 30% for (**4**), 19% for (**5**), 12% for (**6**) and 22% for (**7**) by usual column chromatography. Application of acetonitrile as a solvent at low temperature eliminated the scrambling of starting materials.¹² The reaction was clean and no other porphyrin-like components were isolated in these reactions. All the porphyrins were stable and soluble in chloroform.



Scheme 1

Each individual porphyrins (**3**)-(7) were identified by routine ¹H NMR and mass spectrometry. The proton NMR spectrum of free base form of porphyrin (**3**) was complex at room temperature due to the existence of different tautomeric forms. The two tautomers; the one where the proton resides on the inner nitrogen and the other where the proton resides on the outer nitrogen. But the two inner N-H tautomers were separately observed when temperature was adjusted to -50 °C. Diprotonation of porphyrin (**3**) on the other hand showed a single form of tautomer with a dramatic upfield shift of inner methine proton from 2.36 ppm to -1.05 ppm.¹³ The large ring anisotropic effect of inner methine proton observed in porphyrins (**3**) indicates that the inverted pyrrole unit is quite flexible. Alkylation of the rim nitrogen basically eliminate the existence of different tautomeric forms. Since the influence of magnetic anisotropy is directly proportional to relative distance from the core of the shielding area, the change in chemical shifts of inner and outer methine proton would be a good measure of distortion of the inverted pyrrole unit. The degree of tiltedness is also influenced by substituents at rim nitrogen. The Van der Waals radii of the sulfur atom in the core is larger than nitrogen and accordingly the repulsive force between inner methine proton and sulfur also affects the distortion. As shown in Table 1, the shift of the resonance lines of all the protons is very small in the free-base porphyrins. On the other hand, the shift of the resonance of the protonated porphyrin is appreciably large. The chemical shifts of the inner and outer methine protons attached to the inverted pyrrole unit are susceptible for varying degrees of influence depending on the nature of the *N*-substituents.

The Soret absorptions of the porphyrins (**3**)-(7) remained unchanged (447-450 nm) indicating that the macro-conjugation of π -system has not appreciably been altered by *N*-alkyl groups. The resonances of the inner methine proton in porphyrins (**4**)-(7) is slightly shifted to down field from 2.36 to 2.72 ppm. The value indicates that the methine proton is still under the influence of the anisotropic effect of the ring current but the effect is far less than those observed in *meso*-tetraphenylporphyrin (TPPH₂). On the other hand, the resonances of the inner methine proton of the protonated form were shifted to -1.05 ppm for (**4**) to -0.64 ppm for (**7**). Down-field shift of the inner methine proton with regard to different *N*-substituents indicates that there is a significant correlation

Table 1. Selected chemical shifts of porphyrins (**4**)-(7). a) Free base porphyrins (FB). b) Protonated porphyrins (FBH₂²⁺)

	Inner Methine		Thiophene		Pyrrole- α		Pyrrole- β (1)		Pyrrole- β (2)	
	^a FB	^b FBH ₂ ¹²	FB	FBH ₂ ¹²	FB	FBH ₂ ¹²	FB	FBH ₂ ¹²	FB	FBH ₂ ¹²
4	2.36	-0.79	7.91	8.62	7.37	7.41	7.73	8.48	7.66	8.28
			7.86	8.59			7.25	7.93	7.26	7.94
5	2.41	-0.80	7.91	8.61	7.45	7.53	7.72	8.46	7.67	8.25
			7.85	8.58			7.24	7.90	7.24	7.93
6	2.37	-0.86	7.90	8.67	7.57	7.69	7.72	8.50	7.72	8.27
			7.84	8.64			7.24	7.93	7.24	7.97
7	2.72	-0.64	7.89	8.56	7.60	7.37	7.70	8.42	7.70	8.15
			7.87	8.54			7.25	7.89	7.25	7.84

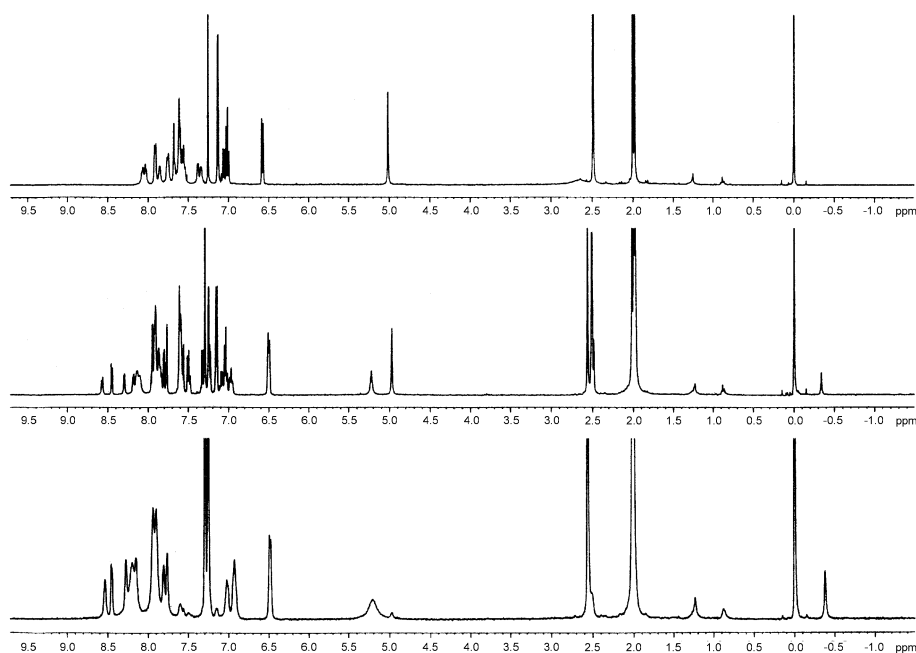
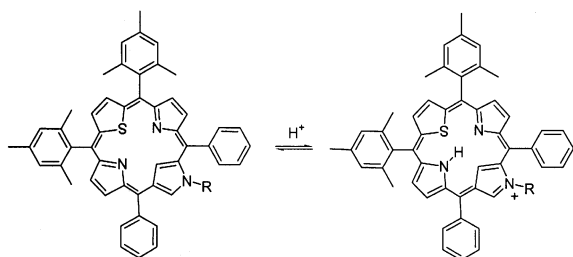


Figure 1. 400 MHz NMR spectra of porphyrins (7). Top trace is obtained after adding 0.31 equiv of TFA at 25 °C. Middle trace is obtained after adding 0.31 equiv of TFA at -30 °C showing the monoprotonated form as a minor fraction. The bottom trace is obtained after adding 0.91 equiv of TFA at -30 °C showing shift of the equilibrium. The benzylic protons and inner methine proton show large upfield shift of the resonance.



Scheme 2

between the *N*-substituents and the degree of distortion. The down field shift of the inner methine proton should be attributed to the bulkiness of the substituents on the rim nitrogen. As shown in Scheme 2, the positive charge by protonation is expected to cause downfield shift of all the protons. On the contrary, the inner methine proton is shifted upfield. The steric crowdedness in the core by protonation is expected to cause down field shift of the inner methine proton. But the azafulvene-type structure (8) lead to inward tilting of inverted pyrrole and consequently pushes both sulfur and proton outward from the imaginary plane. The repulsive interaction between *N*-alkyl and *ortho*-hydrogen in the *meso*-phenyl group must be less important. Net effect thus is upfield shift of the inner methine proton. The results obtained so far indicate that the steric crowdedness caused by substitution at the rim nitrogen seems to show correlation with chemical shifts. The protonated porphyrins also showed correlation with *N*-substituents. Figure 1 shows the spectroscopic changes observed depending on the amount acid added. The middle trace was obtained at -30 °C in the presence of 0.3 equivalent of acid. The benzylic protons originally shown at 4.94 ppm

(top trace) were shifted to 5.23 ppm after protonation. At the same time the inner methine proton observed at 2.49 ppm was shifted to -0.34 ppm. Increased amount of acid to 0.9 equivalent (bottom trace) shifted the equilibrium to the protonated form. Inner N-H proton could not be observed under these conditions. The results obtained so far was somewhat contrary with solid state structure reported by Furuta *et al.*¹

In conclusion, we have developed a typical route to the core-modified, *N*-confused porphyrins bearing various substituents at the rim nitrogen. The key step in the synthesis involves porphyrin formation by condensation of heteroatom substituted tripyromethanes with *N*-alkyl-2,4-(α -hydroxy- α -phenyl)methylpyrrole. The condensation gave single porphyrin product which was isolated cleanly by column chromatography. The synthetic method described in this paper enables the convenient preparation of porphyrins bearing various substituents at the rim nitrogen. The protonation occurred in the core nitrogen and the inverted pyrrole unit becomes flatter while other core-atoms such as sulfur and N-H proton move away from the plane of the porphyrin in order to compensate the steric crowdedness and macro-conjugation. The core-modified porphyrins will serve as a novel building blocks in many areas of porphyrin chemistry.

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