Synthesis and ^1H, ^{19}F NMR Spectroscopic Characterization of (Pentafluorophenyl)$_{3-n}$ (Pyrazol-1-yl-tetrafluorophenyl)$_{n=1,2}$ Porphyrins

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Three new porphyrins bearing in the *meso* positions 4-(pyrazol-1-yl)-2,3,5,6-tetrafluorophenyl substituents have been prepared and characterized by nmr spectroscopy.

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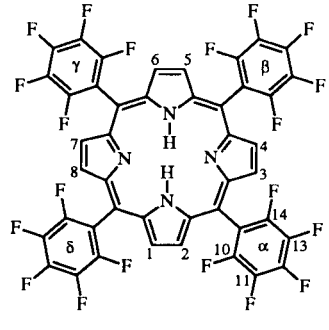
In previous papers we described the substitution of fluorine atoms of hexafluorobenzene, tris(pentafluorophenyl)phosphine and tetrafluorophthalonitrile by pyrazolate anions [1-3] as well as the synthesis of porphyrins bearing four pyrazolyl residues at the *meso* positions [4,5]. We report here the preparation and characterization of the mono(pyrazol-1-yl)tetrafluorophenyltris(pentafluorophenyl)porphyrin **2** and the two disubstituted isomers **3** and **4** obtained from tetra(pentafluorophenyl)porphyrin **1**. The structural determination has been done by combined use of mass spectometry, ^1H and ^{19}F nmr spectroscopy.

Results and Discussion.

Treatment of pyrazole with sodium hydride affords the pyrazolate anion which is able to substitute the fluorine atoms of tetra(pentafluorophenyl)porphyrin **1**. Using 4 molar equivalents of pyrazole for 1 molar equivalent of porphyrin **1**, a mixture of three substituted porphyrins **2, 3**, and **4** has been obtained in a 6/1/3 ratio. The separation of these porphyrins has been performed by column chromatography on silica gel. The mass spectra of **2**, **3**, and **4**, registered using the DCI technique, are in agreement with the proposed molecular formula. These porphyrins have been identified by ^1H and ^{19}F nmr spectroscopy.

The ^{19}F nmr spectra of these compounds are very similar (see Table 1). They show five complex signals at 26.4, 25.9, 14.4, 11.2 and 1.1 ppm. Their relative intensities are respectively 2:6:2:3:6 for porphyrin **2** and 2:2:2:1:2 for porphyrins **3** and **4**. This indicates that the former is sub-

Scheme 1



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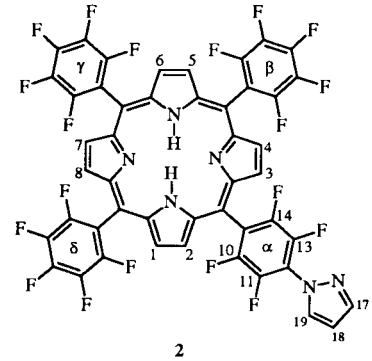

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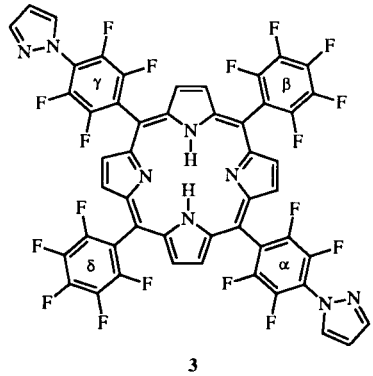

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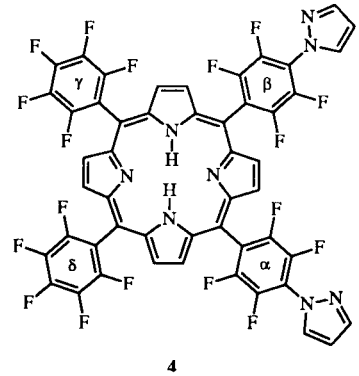

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Table 1

^{19}F NMR Spectroscopy of Compounds **2-4** (in deuteriochloroform: δ, ppm, J, Hz)

Compound	10α (14α)	11α (13α)	10β (14β)	11β (13β)	12β	10γ (14γ)	11γ (13γ)	12γ
2 [a]	26.39	14.42 $^4J(10\alpha,14\alpha) = 2.3$	25.93 $^3J(10\alpha,11\alpha) = -23.7$	1.14	11.23 $^5J(10\alpha,13\alpha) = 11.3$	25.92	1.13 $^4J(11\alpha,13\alpha) = 3.7$	11.23
3 [b]	26.39	14.42 $^4J(10\alpha,14\alpha) = 2.3$ $^3J(11\beta,12\beta) = -21.0$	25.94 $^3J(10\alpha,11\alpha) = -23.7$ $^5J(10\beta,12\beta) = 1.7$	1.12	11.19 $^5J(10\alpha,13\alpha) = 11.3$	26.39	14.42 $^4J(11\alpha,13\alpha) = 3.7$	----
4 [c]	26.39	14.43 $^4J(10\alpha,14\alpha) = 2.4$ $^3J(11\gamma,12\gamma) = -21.0$	26.39 $^3J(10\alpha,11\alpha) = -23.6$ $^5J(10\gamma,12\gamma) = 1.7$	14.43	----- $^5J(10\alpha,13\alpha) = 11.3$	25.93	1.10 $^4J(11\alpha,13\alpha) = 2.4$	11.18

[a] $C_6F_5(\beta)$ identical to $C_6F_5(\delta)$. [b] $C_6F_5(\alpha)$ identical to $C_6F_5(\gamma)$, $C_6F_5(\beta)$ identical to $C_6F_5(\delta)$. [c] $C_6F_5(\alpha)$ identical to $C_6F_5(\beta)$, $C_6F_5(\delta)$ identical to $C_6F_5(\gamma)$

stituted with one pyrazole and the two other ones with two pyrazoles. Thereby fluorine spectra show that compounds **3** and **4** are both pyrazolyl-disubstituted derivatives but do not indicate the substitution positions. Study of the proton spectra of **3** and **4** allows us to conclude that **3** is substituted at 12α and 12γ positions while **4** is substituted at the 12α and 12β positions (see Table 2). Effectively, the pyrrole protons of the macrocycle **2**, with a C_{2h} symmetry structure, appeared as a single AB system while for porphyrin **4**, for which a C_{2v} symmetry is attributed, these pyrrole protons appeared as one AB and two A_2 systems.

When each signal is expanded, it is clear that, amongst the three compounds, **2** has the most complex ^{19}F spectrum, mainly because a small shift (about 0.01 ppm) exists between the signals of the γ C_6F_5 group and those of β and δ groups, superposed for symmetry reasons. For the two other isomeric compounds, **3** and **4**, signals of the five-spin system are more simple, but not enough transitions are well resolved to allow complete analyses of the corresponding AA'MM'X systems as we made in 1-pentafluorophenylpyrazole for example [6].

When fluorine spectra are recorded under proton broad-band decoupling, the AA'XX' spin system formed by fluorine atoms 10α, 11α, 13α, and 14α, can be easily analysed [6]. The two central transitions of each AA' and XX' moieties are narrow singlets. When protons are not irradiated, these central transitions became doublets for the moiety at 14.4 ppm and triplets for the moiety at 26.4 ppm. This proves that the signal at 14.4 ppm belongs to $F_{11\alpha}$ and $F_{13\alpha}$ which are coupled with the pyrazole proton $H_{19\alpha}$ (which appears in the ^1H spectrum as ddt-d with $H_{18\alpha}$, d with $H_{17\alpha}$, t with $F_{11\alpha}$ and $F_{13\alpha}$) and that the signal at 26.4 ppm belongs to $F_{10\alpha}$ and $F_{14\alpha}$ coupled to the porphyrin protons H_2 and H_3 (signal at 9.02 ppm in the proton spectrum). This last coupling has been confirmed by a CW irradiation of the proton signal at 9.02 ppm.

Table 2

^1H NMR Spectroscopy of Compounds **2-4** (in deuteriochloroform: δ, ppm, J, Hz)

Compound	H (pyrrole)				H_{17} (pz)	H_{18} (pz)	H_{19} (pz)
2 [a]	8.95 (H_1,H_4) $^3J(H_1,H_2) = 4.6$	9.02 (H_2,H_3)	8.93 (H_5H_8)	8.93 (H_6,H_7) $^3J(H_{17},H_{18}) = 1.8$, $^3J(H_{18},H_{19}) = 2.5$, $^4J(H_{17},H_{19}) = 0.5$ $^6J(H_{19},F_{11},F_{13}) = 1.6$	8.05	6.74	8.10
3 [b]	8.94 (H_1,H_4,H_5,H_8) $^3J(H_1,H_2) = 4.6$		9.01 (H_2,H_3,H_6,H_7)	 $^3J(H_{17},H_{18}) = 1.9$, $^3J(H_{18},H_{19}) = 2.6$, $^4J(H_{17},H_{19}) = 0.5$ $^6J(H_{19},F_{11},F_{13}) = 1.5$	8.07	6.76	8.11
4 [c]	8.95 (H_1,H_6) $^3J(H_1,H_2) = 4.6$	9.02 (H_2,H_5)	9.04 (H_3,H_4)	8.93 (H_7,H_8) $^3J(H_{17},H_{18}) = 1.9$, $^3J(H_{18},H_{19}) = 2.6$, $^4J(H_{17},H_{19}) = 0.5$ $^6J(H_{19},F_{11},F_{13}) = 1.4$	8.07	6.76	8.11

[a] $H_1 = H_4$, $H_2 = H_3$, $H_5 = H_8$, $H_6 = H_7$. [b] $H_1 = H_4 = H_5 = H_8$, $H_2 = H_3 = H_6 = H_7$. [c] $H_1 = H_6$, $H_2 = H_5$, $H_3 = H_4$, $H_7 = H_8$.

A similar long-range F-H coupling has been detected between the fluorine atoms F_{10} and F_{14} of the C_6F_5 group and the corresponding pyrrole protons of the macrocycle. As these fluorine signals belong to a more complex system (AA'MM'X system), the central transitions of the F_{10}/F_{14} moiety at 25.9 ppm are not singlets. Thus the

long-range couplings induce a broadening of the signals and cannot be measured. This broadening disappears in proton decoupled spectra.

All these results are consistent with a picture of compounds **2-4** showing fast prototropic intramolecular proton exchange [7] and low rotational barriers about the C_{meso}-C_{ipso} bonds [8].

EXPERIMENTAL

Melting points (mp >300°) were determined with a Reichert Jung microscope apparatus and are uncorrected. The nmr spectra were recorded on a Bruker A-250 spectrometer operating at 250.13 and 235.32 MHz for ^1H and ^{19}F respectively. In all cases, the digital resolution was below 0.1 Hz (acquisitions of ^1H [^{19}F] spectra were performed with 64K [128K] points, spectral width of 3700 [9400] Hz and zero filling before Fourier transform). Reagent and solvents were purchased from common commercial suppliers [Tetra(pentafluorophenyl)porphyrin **1** from Aldrich] and were used without further purification.

Pyrazole (23 mg, 0.33 mmole) was dissolved in 5 ml of dry THF to which 13 mg of 60% sodium hydride in oil dispersion (0.54 mmole) was added. This mixture was stirred for 0.5 hours at room temperature. Then 80 mg of tetra(pentafluorophenyl)porphyrin **1** (0.082 mmole) dissolved in 10 ml of dry THF was added to the pyrazole solution. This reaction mixture was heated to reflux for 5 hours. After evaporation of the solvent, the residue was chromatographed on silica gel eluting with 10% hexane in dichloromethane. Three pyrazolyl substituted porphyrins were isolated.

Monosubstituted porphyrin **2** (24 mg, yield = 29%) was recovered; ms: DCI $[M]^{+\cdot}$ = 1022 (100%); uv-visible (dichloromethane): λ (nm)/(10^3 x M^{-1} cm^{-1}) 246 (20.1), 411 (209.3), 503 (18.2), 534 (1.9), 582 (5.8), 640 (0.8).

Disubstituted porphyrin **3** (4 mg, yield = 5%) was recovered; ms: DCI $[M]^{+\cdot}$ = 1070 (100%); uv-visible (dichloromethane): λ (nm)/(10^3 x M^{-1} cm^{-1}) 247 (22.3), 405 (245.8), 505 (15.5), 531 (2.1), 582 (4.6), 638 (0.4).

Disubstituted porphyrin **4** (13 mg, yield = 15%) was obtained; ms: DCI $[M]^{+\cdot}$ = 1070 (100%); uv-visible (dichloromethane): λ (nm)/(10^3 x M^{-1} cm^{-1}) 249 (26.9), 401 (250.2), 505 (17.9), 534 (2.1), 581 (5.6), 635 (0.4).

The overall reaction yield, taking into account the recovery of unreacted material, was 96%.

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