

# <sup>1</sup>H-NMR spectroscopic studies of paramagnetic superstructured iron(III) porphyrins†‡

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The electronic properties of several superstructured iron(III) porphyrins, in which the two faces of the porphyrin are protected by two chains linked at the opposite phenyl rings, have been investigated. The paramagnetic <sup>1</sup>H NMR spectra of three iron(III) “basket-handle” porphyrins such as Fe<sup>III</sup>[e-BHP(C<sub>12</sub>)<sub>2</sub>], Fe<sup>III</sup>[a-BHP(C<sub>12</sub>)<sub>2</sub>] and Fe<sup>III</sup>[e-BHP(C<sub>12</sub>)(ImC<sub>11</sub>)] in organic solvent have been assigned. The <sup>1</sup>H T<sub>1</sub> values of the signals were measured and resonance assignments made based on NOESY and COSY experiments. The electronic structure of the iron(III) is discussed on the basis of the temperature dependence of the isotropic shifts and relaxation times. The hyperfine-shifted resonances in these spectra are compared with those of unhindered iron(III) porphyrins.

Over the last decades, considerable effort in the modelization of metalloporphyrins has been carried out in order to study the role of different metalloproteins such as peroxidases, cytochrome P-450, hemoglobin, myoglobin and cytochrome c oxidase.<sup>1–3</sup> In this context, superstructured porphyrins with different types of protection around the metallic center are of interest. One example is the superstructured “two-face” hindered porphyrins, such as “basket-handle” porphyrins<sup>4</sup> derived from 5,10,15,20-tetraphenylporphyrin, in which the opposing phenyl rings are linked by two identical or different chains.

Application of paramagnetic <sup>1</sup>H NMR techniques to iron(III) porphyrins has proved to be useful to evaluate the metal ion coordination and electronic properties in solution.<sup>5–7</sup> The magnitude of electronic relaxation times of high-spin d<sup>5</sup> iron(III) porphyrins (S = 5/2) allow the observation of isotropically shifted signals narrow enough to be observed in the <sup>1</sup>H NMR spectra. The paramagnetic <sup>1</sup>H NMR properties of unprotected high-spin iron(III) porphyrins have been thoroughly investigated in the last decade.<sup>8–12a</sup> Nonetheless, few examples of superstructured iron(III) porphyrins soluble in organic solvents have been reported up to now.<sup>12b</sup>

Previously, we reported the electronic properties of two water-soluble iron(III) porphyrins with different environments around the metallic center.<sup>13</sup> In this work, we study the electronic properties of three iron(III) “two-face” hindered porphyrins, Fe<sup>III</sup>P–OH, where P is e-BHP(C<sub>12</sub>)<sub>2</sub><sup>2–</sup>, α,5,15-β10,20-bis[2,2'-(dodecamethyleneoxy)diphenyl] porphyrinato dianion, a-BHP(C<sub>12</sub>)<sub>2</sub><sup>2–</sup>, α,5,15:β10,20-bis[2,2'-(dodecanediamido)diphenyl] porphyrinato dianion or e-BHP(C<sub>12</sub>)(ImC<sub>11</sub>)<sup>2–</sup>, α,5,15-[2,2'-(dodecamethyleneoxy)diphenyl]:β10,20-[2,2'-(6-imidazol-1-ylundecyleneoxy)diphenyl] porphyrinato

dianion; with different environments of the metallic center. We have recorded the <sup>1</sup>H NMR spectra, measured the <sup>1</sup>H longitudinal relaxation times, T<sub>1</sub>, and analyzed the temperature dependence of the chemical shifts.

## Experimental

### Materials

The “basket-handle” porphyrins, [e-BHP(C<sub>12</sub>)<sub>2</sub>] (1), [a-BHP(C<sub>12</sub>)<sub>2</sub>] (2) and [e-BHP(C<sub>12</sub>)(ImC<sub>11</sub>)] (3) were prepared as reported in the literature.<sup>14–16</sup> Anaerobic insertion of iron into the free base porphyrins was carried out by using iron(II) chloride in dimethylformamide under reflux in the presence of 2,6-dimethylpyridine.<sup>14</sup> Pure Fe<sup>III</sup>P–OH complexes were obtained by shaking a toluene solution of chloroiron(III) porphyrins with a saturated aqueous potassium carbonate solution for 12 h.<sup>14,17</sup> All the other reagents were analytical grade chemicals, purchased from Aldrich and Merck. CDCl<sub>3</sub> (99.9%) was obtained from SDS Chemical. The concentrations of samples for 1D and 2D <sup>1</sup>H NMR was 6 to 8 mM in metalloporphyrin.

### Physical techniques

<sup>1</sup>H NMR experiments were performed on a Varian Unity 400 spectrometer operating at 400 MHz. One-dimensional spectra were recorded in CDCl<sub>3</sub> solvent with presaturation of the CHCl<sub>3</sub> signal during part of the relaxation delay. Presaturation times of 50–100 ms, acquisition times of 20–100 ms, 10–100 kHz spectral widths and relaxation delay times of 50–100 ms were used. 1D spectra were processed using exponential line-broadening weighting functions with values of 20–40 Hz. Chemical shifts were referenced to residual solvent protons of CDCl<sub>3</sub> resonating at 7.25 ppm relative to TMS. A variety of NMR parameters were utilized to overcome the problems of artifacts in the variable-temperature <sup>1</sup>H NMR spectra.

† This article is dedicated to the memory of Professor Michel Momenteau of Institut Curie.

‡ Abbreviations. 1D and 2D: one-dimensional and two-dimensional; COSY: correlated spectroscopy; NOESY: nuclear Overhauser effect spectroscopy; TPP: 5,10,15,20-tetraphenylporphyrinate dianion.

Data for non-selective longitudinal relaxation times were determined using the inversion recovery pulse sequence<sup>18</sup> ( $d_1 - 180^\circ - \tau - 90^\circ - \text{Acq}$ ), 23 values of  $\tau$  were selected, ( $d_1 + \text{Acq}$ ) values were at least five times that of the longest expected  $T_1$ , and the number of scans was 256. The  $T_1$  values were calculated from the inversion-recovery equation.

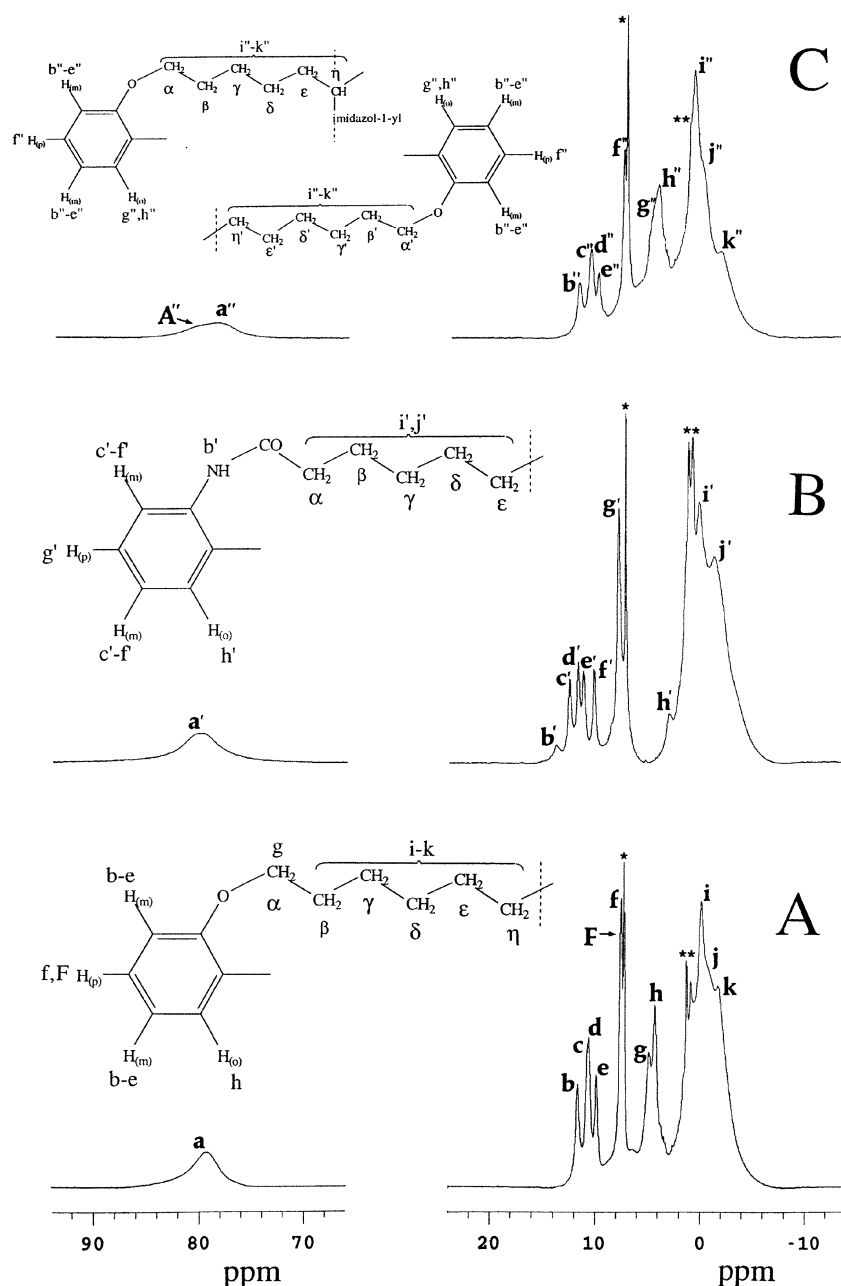
COSY spectra were the conventional n-type (MCOSY).<sup>19</sup> NOESY experiments were performed in the hypercomplex (States–Haberhorn) mode.<sup>20</sup> Because the  $^1\text{H}$  relaxation times were diverse, 2D spectra were recorded using a wide range of conditions: 256–512  $t_1$  increments, 256–1024 scans, 512–2048 points in the  $t_2$  dimension, 10–50 kHz spectral widths in both dimensions, acquisition times of 20–100 ms and relaxation delays of 40–120 ms. Mixing times for NOESY ranged over 2–10 ms. Additionally, different processing conditions were also used. NOESY spectra were Fourier-transformed using square sine bell weighting functions shifted  $45^\circ$ ,  $60^\circ$  or  $75^\circ$ , depending on the paramagnetic character of the observed signals. The number of points used for processing was 512,

1024 or 2048 in both dimensions. NOESY spectra were baseline corrected. COSY spectra were transformed using unshifted sine-squared window functions and zero-filled to  $1\text{K} \times 1\text{K}$  points. NMR data were processed on a SUN Sparc 5 station using the VNMRX 4.3B program.

## Results and discussion

### $^1\text{H}$ NMR spectra of iron(III) porphyrins 1, 2, 3

The 1D  $^1\text{H}$  NMR spectrum of the iron(III) porphyrin **1** is shown in Fig. 1(A). The proton NMR chemical shifts and  $T_1$  values are reported in Table 1. In the downfield region, it displays eight well resolved isotropically shifted signals (a–h) and three other signals (i–k) shifted upfield. The signals a–k display relatively short  $T_1$  values from  $<0.1$  ms, in the case of signal a, to 8.7 ms for signal f. The peaks show linewidths, measured at half-height, of around  $\sim 200$  Hz, excepting signal



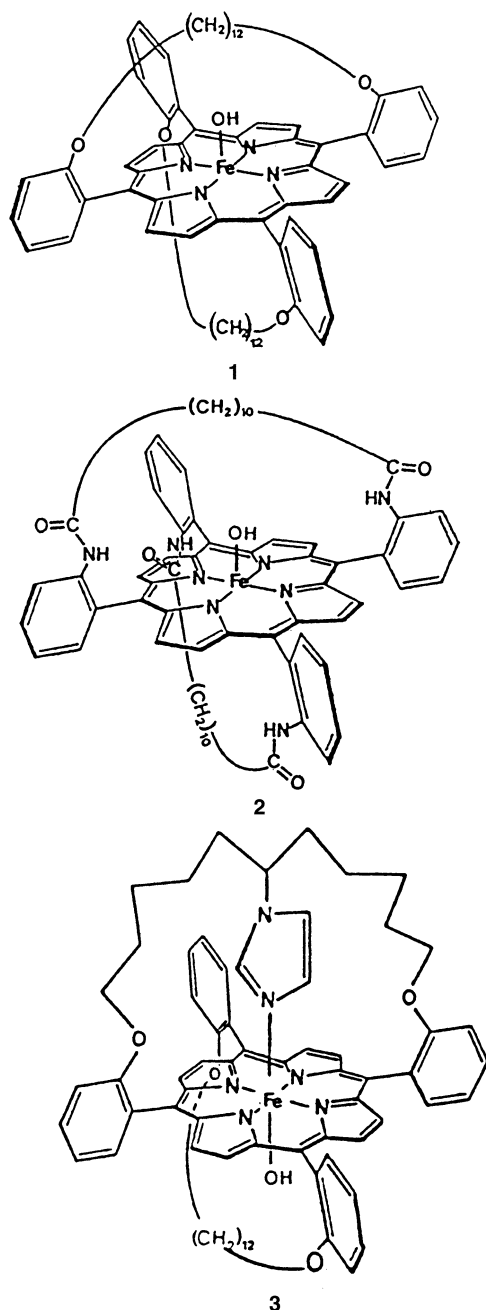
**Fig. 1**  $^1\text{H}$  NMR (400 MHz) spectra of three iron(III) porphyrins in  $\text{CDCl}_3$  at 298 K: (A)  $\text{Fe}[\text{e-BHP}(\text{C}_{12})_2](\text{OH})$  (**1**), (B)  $\text{Fe}[\text{a-BHP}(\text{C}_{12})_2](\text{OH})$  (**2**), (C)  $\text{Fe}[\text{e-BHP}(\text{C}_{12})(\text{ImC}_{11})](\text{OH})$  (**3**). The asterisks mark the residual solvent and impurity signals (\*,  $\text{CHCl}_3$ ; \*\*, HOD).

**Table 1** Paramagnetic  $^1\text{H}$  NMR resonances of the iron(III) porphyrin **1** in  $\text{CDCl}_3$  at 298 K

Signal	$\delta$	Assigned protons	Number of protons	$T_1/\text{ms}$	$\Delta\nu_{1/2}/\text{Hz}$	$T_2/\text{ms}^a$
a	79.2	$\text{H}_{\text{pyr}}$	8	$<0.1$	1158	0.3
b	11.6	$m\text{-Ph}$	8	4.3	124	2.6
c	11.0 <sup>b</sup>			— <sup>c</sup>	— <sup>c</sup>	— <sup>c</sup>
d	10.6			4.3	— <sup>c</sup>	— <sup>c</sup>
e	9.9			4.3	108	2.9
F	7.7 <sup>d</sup>	$p\text{-Ph}$	— <sup>c</sup>	— <sup>c</sup>	— <sup>c</sup>	— <sup>c</sup>
f	7.5			8.7	— <sup>c</sup>	— <sup>c</sup>
g	4.8	$\alpha\text{-CH}_2$	12	1.4	— <sup>c</sup>	— <sup>c</sup>
h	4.2	$o\text{-Ph}$		2.9	— <sup>c</sup>	— <sup>c</sup>
i	—0.12	$(\beta\text{-}\eta)\text{-CH}_2$	$\sim 40$	1.4	— <sup>c</sup>	— <sup>c</sup>
j	— <sup>c</sup>			— <sup>c</sup>	— <sup>c</sup>	— <sup>c</sup>
k	—1.7			1.2	— <sup>c</sup>	— <sup>c</sup>

<sup>a</sup> Measured from the linewidth at half-height. <sup>b</sup> Measured at 283 K.

<sup>c</sup> Overlap prevents measurement of this value. <sup>d</sup> Measured at 273 K.

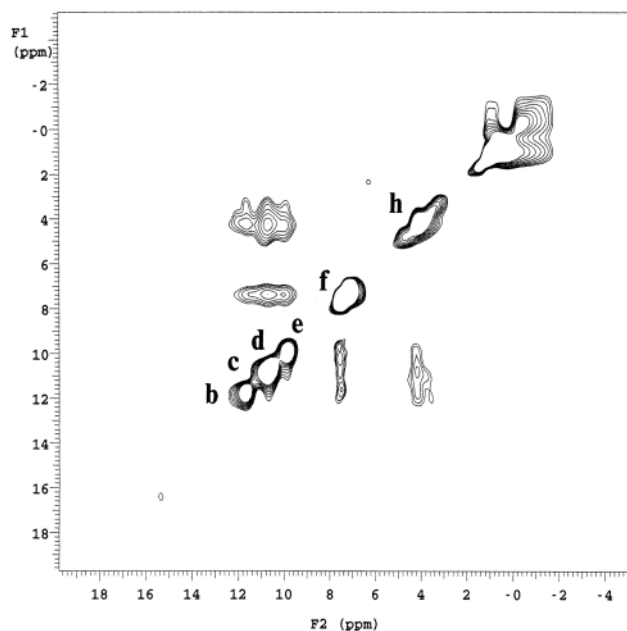


Scheme 1

a with an average linewidth of 1158 Hz. The signal a at 79.2 ppm that integrates eight protons was assigned on the basis of the large isotropic shift and the short  $T_1$  value as the pyrrole protons. As already described in a previous paper,<sup>13</sup> high-spin iron(III) porphyrin pyrrole protons have similar large shifts, short  $T_1$  values and broad linewidths.

The other group of signals (b–k) can be assigned on the basis of integrated protons and of the longitudinal relaxation times of the hyperfine-shifted resonances. The  $T_1$  values were related with the metal-proton distance according to the Solomon equation.<sup>21</sup> Signals i–k, which integrate forty protons and exhibit very short  $T_1$  values (1.2 and 1.4 ms) can be assigned to the two chain protons,  $(\beta\text{-}\eta)\text{-CH}_2$ , linked at the opposite phenyl rings (see Scheme 1). The signal g, partially overlapped with signal h, has the same relaxation time as that of the other signals (i–k) assigned above and can be assigned to the rest of the aliphatic protons of the chains ( $\alpha\text{-CH}_2$ ). The other group of signals (b–f) was assigned by exclusion to the phenyl group protons. The first four signals (b–e) have the same  $T_1$  values (4.3 ms) and integrate eight protons. Signals F (non-resolved), f and h present  $T_1$  values of 8.7 and 2.9 ms, respectively. On the basis of the  $T_1$  measurements, the specific assignment of the phenyl proton resonances is given in Table 1. In the COSY spectrum, one intense cross peak was observed between the group of signals b–e and the signal f (data not shown). In addition, the existence of dipolar connectivities between the group of signals b–e and the signals f and h (see Fig. 2) confirms their vicinal origin and the assignment to *meta*, *para* and *ortho* phenyl protons, respectively.

The 1D  $^1\text{H}$  NMR spectra for the iron(III) porphyrins **2** and **3** are shown in Fig. 1(B) and 1(C), and the hyperfine-shifted resonances, linewidths at half-height and  $T_1$  values are reported in Tables 2 and 3, respectively. The spectra show a similar pattern of chemical shifts as the spectrum of the iron(III) porphyrin **1** [see Fig. 1(A)]. The assignment of the isotropically shifted signals by means of the integration of signals, the longitudinal relaxation times of the paramagnetic signals and NOESY spectra (data not shown) is in close agreement with the  $^1\text{H}$  NMR assignment of **1** discussed above (see the assignments for **2** and **3** in Tables 2 and 3). Nevertheless, some differences between them can be shown. In the  $^1\text{H}$  NMR spectrum of **2** a relatively broad signal b' at 13.8 ppm can be found, and we



**Fig. 2** Portion of the 400 MHz NOESY map of iron(III) porphyrin **1** in  $\text{CDCl}_3$  solvent at 298 K. Conditions are given in the text.

**Table 2** Paramagnetic  $^1\text{H}$  NMR resonances of the iron(III) porphyrin **2** in  $\text{CDCl}_3$  at 298 K

Signal	$\delta$	Assigned protons	Number of protons	$T_1/\text{ms}$	$\Delta\nu_{1/2}/\text{Hz}$	$T_2/\text{ms}^a$
a'	79.8	$\text{H}_{\text{pyr}}$	8	<0.1	1605	0.2
b'	13.8	NH-a	— <sup>b</sup>	2.8	209	1.5
c'	12.5	m-Ph <sup>c</sup>	8	4.3	126	2.5
d'	11.7			4.2	— <sup>b</sup>	— <sup>b</sup>
e'	11.2			4.3	— <sup>b</sup>	— <sup>b</sup>
f'	10.2			4.1	105	3.0
g'	7.8	p-Ph	— <sup>b</sup>	7.2	138	2.3
h'	3.1	o-Ph <sup>c</sup>	~4	2.7	— <sup>b</sup>	— <sup>b</sup>
i'	0.24	$(\alpha-\epsilon)\text{-CH}_2$	~40	1.1	— <sup>b</sup>	— <sup>b</sup>
j'	-1.2			0.6	— <sup>b</sup>	— <sup>b</sup>

<sup>a</sup> Measured from the linewidth at half-height. <sup>b</sup> Overlap prevents measurement of this value. <sup>c</sup> Confirmed by means of NOESY spectra.

**Table 3** Paramagnetic  $^1\text{H}$  NMR resonances of the iron(III) porphyrin **3** in  $\text{CDCl}_3$  at 298 K

Signal	$\delta$	Assigned protons	Number of protons	$T_1/\text{ms}$	$\Delta\nu_{1/2}/\text{Hz}$	$T_2/\text{ms}^a$
a''	78.9	$\text{H}_{\text{pyr}}$	8	<0.1	2126	0.15
b''	11.7	m-Ph <sup>d</sup>	8	3.9	210	1.5
c''	10.6			3.9	— <sup>b</sup>	— <sup>b</sup>
d''	11.5 <sup>c</sup>			— <sup>b</sup>	— <sup>b</sup>	— <sup>b</sup>
e''	9.9			3.9	149	2.1
f''	7.5	p-Phe <sup>d</sup>	— <sup>b</sup>	8.4	— <sup>b</sup>	— <sup>b</sup>
g''	4.6 <sup>e</sup>	o-Ph <sup>d</sup>	4	— <sup>b</sup>	— <sup>b</sup>	— <sup>b</sup>
h''	4.1			1.7	— <sup>b</sup>	— <sup>b</sup>
i''	0.82	$(\alpha-\epsilon)\text{-CH}_2$ , $\eta\text{-CH}$ , $(\alpha'-\eta')\text{-CH}_2$	~45	1.5	— <sup>b</sup>	— <sup>b</sup>
j''	0.11 <sup>e</sup>			— <sup>b</sup>	— <sup>b</sup>	— <sup>b</sup>
k''	-1.7			0.6	— <sup>b</sup>	— <sup>b</sup>

<sup>a</sup> Measured from the linewidth at half-height. <sup>b</sup> Overlap prevents measurement of this value. <sup>c</sup> Measured at 243 K. <sup>d</sup> Confirmed by means of NOESY spectra. <sup>e</sup> Measured at 318 K.

can assign this signal to the amide protons. Additionally, the  $T_1$  value of this signal is in accordance with this assignment. On the other hand, in the  $^1\text{H}$  NMR spectrum of **3** the signals of the ring protons of imidazole were not observed, probably because of the short distance to the metallic center.<sup>22</sup>

In general, the longitudinal relaxation times and broad linewidth at half-height of these three iron(III) “basket-handle” porphyrins are characteristic of a hexa- or pentacoordinated high-spin iron(III) porphyrin with an  $S=5/2$  ground state.<sup>23,24</sup> The pyrrole protons experience a large paramagnetic chemical shift in the downfield region ( $\sim 79$  ppm). This observation is consistent with those from other similar high-spin iron(III) porphyrins reported earlier (see Table 4 and references therein), and is due to the  $\sigma$ -spin electronic delocalization in the iron(III) ion  $d_{x^2-y^2}$  orbital.<sup>23,25</sup> In addition, for the eight *meta* phenyl protons we can observe four resonances. The chemical shifts of these protons in the three superstructured iron(III) porphyrins appear in the ranges 11.6 to 9.9 ppm for **1**, 12.5 to 10.2 ppm for **2** and 11.7 to 9.9 ppm for **3** (see Fig. 1 and Tables 1, 2 and 3). This behavior can be interpreted as being due to the unpaired electron spin density at the C–H bond, but also to the electron-withdrawing characteristics corresponding to nearby substituents.<sup>23,26–28</sup> In this sense, the amide group ( $-\text{NH}-\text{CO}-$ ) of **2** is more electron-donating than the corresponding ether ( $-\text{O}-$ ) linkage in **1** and **3**. Consequently, the signals c'–f' have larger chemical shifts. Thus, these differences in the downfield isotropic shifts are due to a larger unpaired electron spin density.

Finally, for the superstructured iron(III) porphyrins **1** and **3** we have observed a partial multiplet structure for resonances of the pyrrole protons at different temperatures. This behavior was shown in previous papers<sup>13,29a</sup> for other high-spin iron(III) porphyrins and appears to be due to the inequivalence of the pyrrole positions through the distortion of the porphyrin ring in solution. In the case of **1**, with an ether “basket-handle”, where the iron presents axial coordination,  $\text{solv-Fe-OH}$ , we have observed the multiplet structure solely at 223 K, whereas for **3** with axial coordination to iron,  $\text{imidazole-Fe-OH}$ , we have detected the multiplet structure in the range from 298 [see Fig. 1(C), signals A'' and a''] to 223 K. The axial ligation mode

**Table 4**  $^1\text{H}$  NMR resonances of some high-spin iron(III) porphyrins in different solvents at 298 K

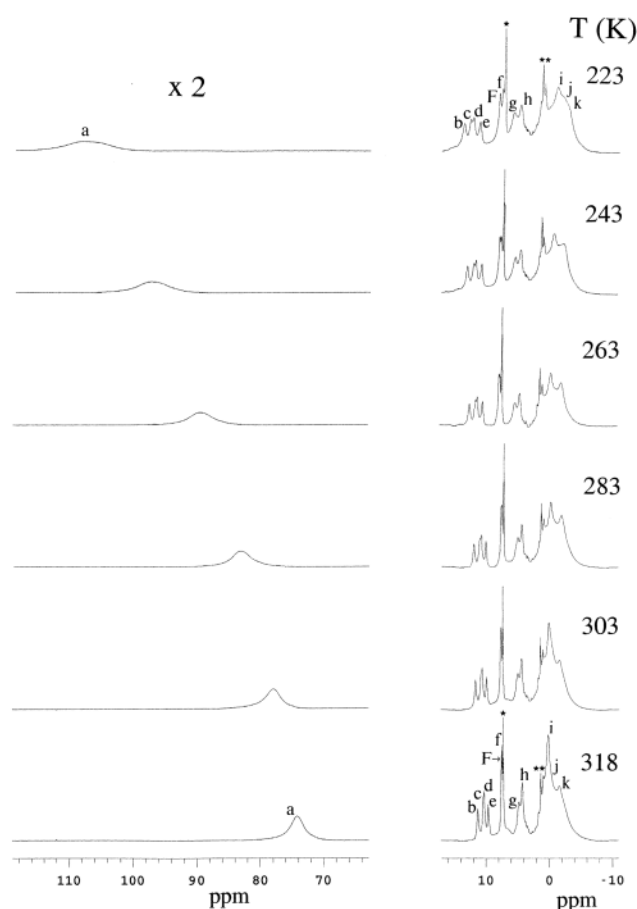
Compound	Solvent	$\delta$				Ref.
		$\text{H}_{\text{pyr}}$	o-Ph	m-Ph	p-Ph	
$\text{Fe}^{\text{III}}[\text{e-BHP}(\text{C}_{12})_2]\text{-OH}$	$\text{CDCl}_3$	79.2	4.2	11.6–9.9	7.7 <sup>a</sup> , 7.5	This work
$\text{Fe}^{\text{III}}[\text{a-BHP}(\text{C}_{12})_2]\text{-OH}$	$\text{CDCl}_3$	79.8	3.1	12.5–10.2	7.8	This work
$\text{Fe}^{\text{III}}[\text{e-BHP}(\text{C}_{12})(\text{ImC}_{11})]\text{-OH}$	$\text{CDCl}_3$	78.9	4.6 <sup>b</sup> , 4.1	11.7–9.9	7.5	This work
$\text{Fe}^{\text{III}}(2\text{-OH-TPP})\text{Cl}^{\text{c,d}}$	$\text{CDCl}_3$	85.0–76.4	8.5, 5.5	13.6–11.8	7.8, 6.7, 6.5	9
$\text{Fe}^{\text{III}}(2\text{-OH-TPP})\text{Br}^{\text{c,d}}$	$\text{CDCl}_3$	86.1–76.7	10.0, 6.0	14.6–12.5	8.3, 7.5, 6.8	9
$[\text{Fe}^{\text{III}}(\beta\text{-py-TPP})\text{Cl}_2]^{\text{d,e}}$	$\text{CDCl}_3$	103.7–77.4	—	12.9, 12.6	6.4	8
$\text{Fe}^{\text{III}}(\text{TMC})\text{Cl}^{\text{f,g}}$	$\text{CD}_2\text{Cl}_2$	86.4–67.6	—	17.4–13.6	—	10, 11
$\text{Fe}^{\text{III}}(\text{TPC})\text{Cl}^{\text{h,i}}$	$\text{CDCl}_3$	82–64	2–3	12.5–10	6.0	12a
$\text{Fe}^{\text{III}}(\text{TPP})\text{Cl}^{\text{j}}$	$\text{CDCl}_3$	80.0	4	13, 12	6.0	35
$\text{Fe}^{\text{III}}(\text{Me}_8\text{TPP})\text{-OH}^{\text{k}}$	$\text{CD}_2\text{Cl}_2$	81.1	2.8	12.1, 11.3	8.0	31
$\text{Fe}^{\text{III}}(\text{Me}_8\text{TPP})\text{Cl}^{\text{k}}$	$\text{CD}_2\text{Cl}_2$	80.0	6.6, 3.8	15.8, 14.2	8.2	31
$\text{Fe}^{\text{III}}(2\text{-CN-TPP})\text{Cl}^{\text{d,l}}$	$\text{CDCl}_3$	93.3–79.8	5–8	13.6–12.1	5–8	32
$\text{Fe}^{\text{III}}[(\text{C}_3\text{F}_7)_4\text{P}]\text{Cl}^{\text{m}}$	$\text{CDCl}_3$	101.5, 86.4	—	—	—	33
$\text{Fe}^{\text{III}}(\text{TrPP})\text{Cl}^{\text{a,n}}$	$\text{CDCl}_3$	81.9–78.5	8.2, 5.1	13.5–12.1	6.5, 6.4	34
$(\text{H}_3\text{O})_3\text{Fe}^{\text{III}}\text{TPPS}^{\text{o}}$	$\text{H}_2\text{O}/\text{D}_2\text{O}$	51.2, 49.8	14.0	10.1	—	13
$\text{Na}_3\text{Fe}^{\text{III}}[\text{e-HSP}(\text{C}_{12})]^{\text{p}}$	$\text{H}_2\text{O}/\text{D}_2\text{O}$	58.8	13.8	9.5	10.4	13

<sup>a</sup> Measured at 273 K. <sup>b</sup> Measured at 318 K. <sup>c</sup> 2-OH-TPP, dianion of 2-hydroxy-5,10,15,20-tetraphenylporphyrin. <sup>d</sup> Measured at 293 K. <sup>e</sup>  $\beta$ -py-TPP, anion of  $\beta$ -pyridiniumyltetraphenylporphyrin. <sup>f</sup> TMC, 7,8-dihydro-2,4,6-trimethylphenylporphyrin (tetramesitylchlorine). <sup>g</sup> Measured at 296 K. <sup>h</sup> TPC, tetraphenylchlorinate dianion. <sup>i</sup> Measured at 315 K. <sup>j</sup> Measured at 299 K. <sup>k</sup>  $\text{Me}_8\text{TPP}$ , dianion of 5,10,15,20-tetrakis(2,6-dimethylphenyl)porphyrin. <sup>l</sup> 2-CN-TPP, dianion of 2-cyano-5,10,15,20-tetraphenylporphyrin. <sup>m</sup>  $(\text{C}_3\text{F}_7)_4\text{P}$ , dianion of 5,10,15,20-tetrakis(heptafluoropropyl)porphyrin. <sup>n</sup> TrPP, dianion of 5,10,15-triphenylporphyrin. <sup>o</sup> TPPS, 5,10,15,20-tetrakis(*p*-sulfonatophenyl)porphyrinato anion. <sup>p</sup> e-HSP( $\text{C}_{12}$ ),  $\alpha,5,15$ -[2,2'-(dodecamethyleneoxy), (5-sulfonato)diphenyl]-10,20-bis(2-hydroxy,5-sulfonatophenyl)porphyrinato anion.

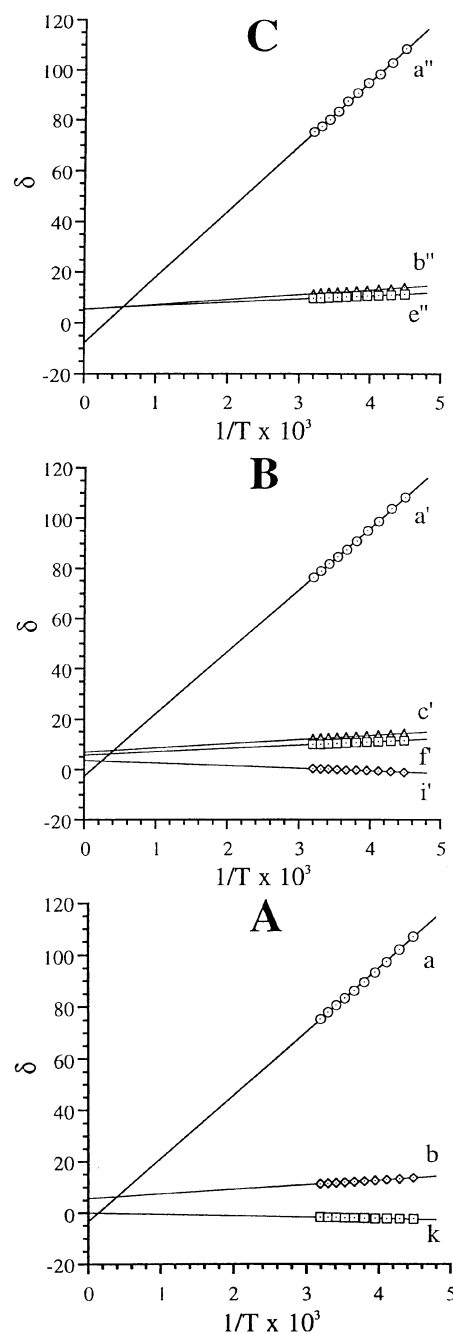
O-Fe-N ( $\text{OH}^-$  and imidazole) has been described in the similar compound  $\text{Fe}[\text{a-BHP}(\text{C}_{12})(\text{ImC}_{11})](\text{OH})$  by Schaeffer *et al.*<sup>29b</sup> Curiously, for the iron(III) porphyrin **2**, with an amide “basket-handle”, the multiplet structure was not observed in the range of temperatures studied. The order of increasing multiplet structure for the superstructured iron(III) porphyrins is thus  $2 < 1 < 3$ . Comparison of the results for the three iron porphyrins shows that the coordinated imidazole linked to the methylene carbon of the handle has a significant effect on the deformation of the porphyrin ring in solution.

#### Temperature dependence of the hyperfine-shifted resonances

Variable-temperature  $^1\text{H}$  NMR spectra of **1**, **2** and **3** were registered from 223 to 318 K (see Fig. 3 for **1**). In Fig. 4, the observed isotropically shifted resonances of the pyrrole, some phenyl protons and some aliphatic protons of the chains are plotted as a function of  $T^{-1}$ . All the signals of the three iron(III) porphyrins follow a Curie-like behavior, that is the positions of the paramagnetically shifted signals in the down-field region shift to higher field with increasing temperature. The isotropic shifts of resonances a, a' and a'', corresponding to the pyrrole protons, are temperature dependent (see Fig. 4), whereas the rest of the resonances are practically independent of temperature. In this case, plots of the paramagnetically shifted signals  $\delta$  vs.  $T^{-1}$  (see Fig. 4) appear linear and deviations due to a small  $T^{-2}$  component were not observed, in spite of the wide range of temperatures studied. As previously described,<sup>13</sup> the ordinary procedure for establishing a  $T^{-2}$  dependence of the isotropic shifts is to extrapolate the plot to  $1/T=0$ . Doing so, the intercept values at infinite temperature



**Fig. 3** 400 MHz proton NMR spectra of  $\text{Fe}[\text{e-BHP}(\text{C}_{12})_2](\text{OH})$  (**1**) in  $\text{CDCl}_3$  from 318 to 223 K. The intensity in the downfield region of the spectra is multiplied by two. The asterisks mark the residual solvent and impurity signals (\*,  $\text{CHCl}_3$ ; \*\*, HOD).



**Fig. 4** Temperature dependence of the  $^1\text{H}$  NMR hyperfine-shifted resonances: (A) **1**, (B) **2**, (C) **3**. Interval of temperature *ca.* 223–318 K.

were found to lie within or close to the diamagnetic region. Furthermore, the results are indicative of a small dipolar contribution to the hyperfine-shifted resonances in **1**, **2** and **3**, although it is more important for the iron(III) porphyrin **3**. Only signals a, a' and a'' show an appreciable deviation from the zero extrapolation at  $-3.3$ ,  $-2.4$  and  $-7.8$  ppm respectively. The order of increasing dipolar contribution to the shifts of the pyrrole protons is  $2 < 1 < 3$ . This dipolar contribution of the pyrrole protons is due to the presence of a small zero-field splitting and consequently of some magnetic anisotropy. This effect is more important in the case of **3** in which the iron(III) ion is coordinated to the N-atom of imidazole linked to the methylene carbon of the handle. It is important to note that these results agree with the existence of a multiplet structure of the pyrrole proton resonances, and also with the deformation of the porphyrin ring in solution described above. In general, the three iron(III) porphyrins

studied show isotropic shifts due to essentially a contact contribution, as expected for hexa- or pentacoordinated high-spin  $d^5$  iron(III) complexes with  $S=5/2$  spin state and an  ${}^6A_1$  ground state.<sup>23,30</sup>

### Comparison of the hyperfine-shifted resonances of **1**, **2**, **3** with those of unhindered iron(III) porphyrins

In the last two decades, a number of paramagnetic  ${}^1H$  NMR studies have been reported on different iron(III) porphyrins.<sup>10–13,31–34</sup> The  ${}^1H$  NMR spectra of **1**, **2** and **3** are similar to those of high-spin iron(III) porphyrins previously studied,<sup>13,31–34</sup> but certain differences in isotropic shifts and longitudinal relaxation times of the signals were observed. The larger isotropic shifts observed for the pyrrole protons in the iron(III) porphyrins of this work suggest a strong  $\sigma$ -spin delocalization in the iron(III)  $d_{x^2-y^2}$  orbital compared, for instance, with the unhindered iron(III) sulfonato porphyrin,  $(H_3O)_3Fe^{III}(TPPS)$ , and “one-face”-hindered iron(III) sulfonato porphyrin,  $Na_3Fe^{III}[e-HSP(C_{12})]$ , in water.<sup>13</sup> In these compounds, the signals of the pyrrole protons appear at 51.2 and 58.8 ppm, respectively. Thus, the decrease in the isotropic shift of the pyrrole protons in the water-soluble iron(III) porphyrins (by about 25 ppm, see Table 4) may also be indicative of the polarizing and different distribution of charge density created by the different axial substituents on the iron(III), OH anion for the iron(III) porphyrin of this work and water molecules for the iron(III) sulfonato porphyrin. In other high-spin iron(III) unhindered porphyrins such as  $Fe^{III}(2-X-TPP)$ ,<sup>32</sup> depending of the X substituents we can find different isotropic shifts for the pyrrole proton 3-H, from 33.4 ppm for  $X=O^-$  up to 104 ppm for  $X=NO_2$ . This behavior can be related with the electron-donating or-withdrawing capacity of the  $\beta$ -substituents<sup>32</sup> and these modification studies suggest that the isotropic shifts for the pyrrole protons experience mainly a contact contribution. The chemical shifts of the phenyl protons for the three iron(III) porphyrins **1**, **2** and **3** appear in a similar, almost diamagnetic, region between 3 and 12.5 ppm, as those of other high-spin iron(III) porphyrins (see for this Table 4). Nevertheless, we can compare the *ortho* phenyl proton resonances of this work (approximately 3–4 ppm) with those of water-soluble paramagnetic iron(III) porphyrins mentioned above<sup>13</sup> (14 ppm). These larger observed shifts could be due to the modification of the unpaired electron spin density that the sulfonic groups produce in the aromatic ring. As we have pointed out the contact contribution to the isotropic shifts is sensitive to changes in the electron-donating and -withdrawing characteristics of the substituents.

Finally, we have compared the longitudinal relaxation times in the iron(III) porphyrins of this work and of two iron(III) sulfonato porphyrins.<sup>13</sup> The  $T_1$  values of the three superstructured iron(III) porphyrins (**1**, **2** and **3**) are smaller (for instance,  $\sim 4$  ms for the *meta* phenyl protons) in comparison with those of the water-soluble iron(III) porphyrins,  $(H_3O)_3Fe^{III}(TPPS)$  and  $Na_3Fe^{III}[e-HSP(C_{12})]$  ( $\sim 8$  ms for the *meta* phenyl protons).<sup>13</sup> Similar differences between these two groups of iron(III) porphyrins are observed for the *para* phenyl protons and the pyrrole protons. The observed differences in  $T_1$  values can be due to the different zero-field splitting (ZFS) and consequently the different magnetic anisotropy,<sup>27,35</sup> as we have deduced by means of the intercept values at infinite temperature in the study of the temperature dependence of the  ${}^1H$  NMR hyperfine-shifted resonances. The presence of ZFS is less important in the three iron(III) porphyrins **1**, **2** and **3** in comparison with those of the water-soluble iron(III) porphyrins<sup>13</sup> and comparatively the  $T_1$  values are significantly smaller in our case.

It has been reported that two  $H_2O$  or alcohol molecules as axial ligands (O–Fe–O type) in some iron(III) porphyrins such as  $[Fe(TPP)(H_2O)_2](ClO_4)$  or  $[Fe(TMCP)(EtOH)(H_2O)]-$

$(ClO_4)$ , where TMCP is tetramethylchioroporphyrin, allowed the intermediate spin state ( $S=3/2-S=5/2$ ).<sup>36,37</sup> In our case the sulfonato porphyrins (one or two  $H_2O$  molecules as axial ligands) are ground spin state  $S=5/2$  as can be demonstrated by EPR studies.<sup>13,38</sup> Moreover, the hydroxo species of the sulfonato porphyrin,  $Na_3Fe^{III}[e-HSP(C_{12})]$  has been studied by paramagnetic  ${}^1H$  NMR and the results of magnetic anisotropy and  ${}^1H$  relaxation times are similar to those of a aquo sulfonato iron(III) porphyrin.<sup>39</sup>

### Conclusions

The electronic properties of three paramagnetic iron(III) porphyrins,  $Fe^{III}[e-BHP(C_{12})_2]-OH$  (**1**),  $Fe^{III}[a-BHP(C_{12})_2]-OH$  (**2**) and  $Fe^{III}[e-BHP(C_{12})(ImC_{11})]-OH$  (**3**) have been studied. In these superstructured metalloporphyrins the two faces of the macrocycle ring are shielded by two different chains linked to the opposite phenyl groups and fixed by ether or amide groups. Moreover, two different axial ligands ( $-OH$  and  $-Im$ ) are coordinated to the metal center, the latter ligand is covalently attached to the chain linked to the macrocycle. The complete paramagnetic  ${}^1H$  NMR spectra of **1**, **2** and **3** have been assigned. These compounds not only present paramagnetic chemical shift patterns typical of a penta- or hexacoordinated high-spin iron(III) porphyrin with the ground spin state  $S=5/2$  ( ${}^6A_1$  ground state), but also characteristic longitudinal relaxation times. The above-mentioned electronic properties are manifested in the temperature dependence of the isotropic shifts and longitudinal relaxation times. In addition, the isotropic shifts show a Curie-like behavior. The magnitude of the small ZFS detected, as well as the magnetic anisotropy, follows the order  $2 < 1 < 3$ . This ordering is in accord with the deformation of the porphyrin ring in solution that implies the existence of a multiplet structure for the isotropic shift resonances of the pyrrole protons. Thus, our data clearly demonstrate that the coordination of the imidazole ligand covalently attached to the aliphatic chain increases the ZFS and also the degree of deformation of the porphyrin ring.

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