

Variable-Temperature Solid-State ^{13}C - and ^{15}N -CPMAS NMR Analyses of Alkyl-Substituted Porphycenes

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The tautomeric exchange of the inner hydrogens of free base alkylporphycenes was examined with the help of ^{13}C -CPMAS and ^{15}N -CPMAS NMR recorded at variable temperatures. The porphycenes used were octaethylporphycene **2**, 2,7,12,17-tetrapropylporphycene **3**, and 9,10,19,20-tetrapropylporphycene **4**. The CPMAS spectra revealed that the interconversion of NH tautomers in **2–4** is so fast that even in the solid state it was not possible to determine rate constants for the migration of the central hydrogens by simulating the experimental data. However, using ^{15}N -CPMAS spectra recorded at natural abundance and variable temperature, it was possible to calculate the equilibrium constant (K) of NH tautomerism for each of the alkylporphycenes **2–4**. By measuring variations in the T_1 relaxation times as a function of temperature, it was possible to detect rotations in the alkyl side chains of **2–4**.

Introduction

Porphyrinoids (summary expression for the porphyrins and their structural variants) are of fundamental importance in organic chemistry.¹ Commanding interdisciplinary interest, porphyrinoids have been subjected over the years to virtually all pertinent methods of physical and chemical investigation available to the organic chemist.² Porphycene **1** (Figure 1), a tetrapyrrole macrocycle with effective D_{2h} symmetry, is the most simple structural variant of porphyrin.³ Convincing evidence as to the aromaticity of **1** is provided by its ^1H NMR, its double-charged molecular ion reminiscent of that of porphyrins, and its X-ray analysis that shows that **1** is a planar molecule. Although its central cavity is smaller than that of a porphyrin, it nevertheless allows the obtention of metalloporphycene derivatives.⁴ While in porphyrins the central hole is a square with side lengths of 2.89 Å, in porphycene (Pc) it forms a rectangle the sides of which are 2.83 Å ($\text{N}_{(1)}\text{--}\text{N}_{(2)}$ distance) and 2.63 Å ($\text{N}_{(1)}\text{--}\text{N}_{(2)}$ distance).

In free-base porphyrins the two inner hydrogens can migrate between the four central nitrogens, giving rise to two possible tautomers and therefore to a hydrogen migration process that has been extensively studied by means of solution^{5–8} and solid-state NMR.^{9–13} The latter

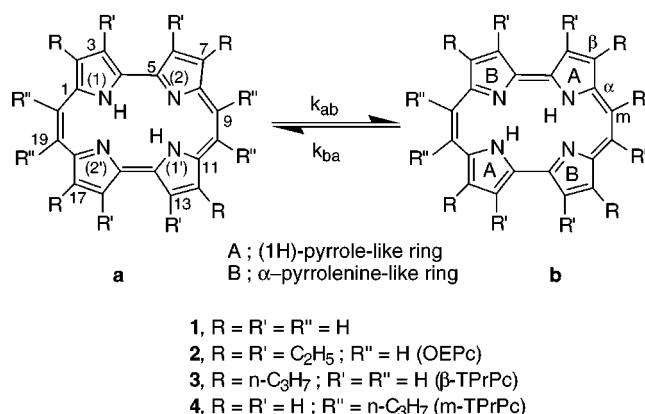


Figure 1. N–H tautomerism in octaethylporphycene (OEPc), β -tetrapropylporphycene (β -TPrPc), and m-tetrapropylporphycene (m-TPrPc) showing the atoms labeling.

studies revealed the presence of dynamic processes for structures that X-ray diffraction studies presented as motionless solids, a fact that can be attributed in part to the difficulties that X-ray diffraction has for localizing hydrogens.¹⁴ In porphycene **1** the porphyrinoid structure can also give rise to two tautomeric structures since it allows the presence of the NH exchange process **1a** \rightleftharpoons **1b** (Figure 1). Although the ^1H variable-temperature solution NMR spectra of porphycene did not allow detection of the presence of each of the tautomers, an ^{15}N -CPMAS NMR study of porphycene¹⁵ showed that al-

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Table 1. Distance between the Nitrogen Atoms in Symmetrically Substituted Porphycenes^a

atoms	Pc 1 (Å)	β -TPrPc 3 (Å)	OEPC 2 (Å)	m-TPrPc 4 (Å)
N ₁ -N ₂	2.83	2.811	2.74	2.898
N ₁ -N _{2'}	2.63	2.615	2.80	2.528

^a From refs 17–19.

though the hydrogen migration process was too fast to be quantified by the changes introduced in the spectral line shapes, the potential energy profile of the reaction in the solid possessed two minima. Moreover, as also happens to be the case for porphyrins,^{9–12} it was found that the symmetry of the double-minimum potential that can be expected in the cases of symmetrically substituted porphycenes was broken when the molecules go from solution to the solid phase. An explanation for the abnormally high rate of proton migration in porphycenes as compared to porphyrins can be obtained from the X-ray crystal structure of porphycene,³ according to which in **1** the presence of a short N₍₁₎-N₍₂₎ distance strongly favors the N₍₁₎-H \cdots N₍₂₎ interaction. In addition, whereas in **1** all the N-H bonds point toward the center of the macrocycle, the N₍₁₎-H \cdots N₍₂₎ atoms in porphycene are almost in a linear arrangement that allows exceptionally strong N-H \cdots N hydrogen bridges to be formed.

Valuable information on the mechanism of the N-H tautomerism in **1** could be expected from a systematic analysis of substituted porphycenes. As has been revealed by solution ¹H NMR, the free energies involved in the N-H tautomerism in porphyrins is affected by the presence of substituents in the β -positions of the pyrrole rings.¹⁶ Since similar effects on the hydrogen migration process were observed when electron-donor or electron-acceptor groups were employed, the observed changes were assumed to reflect the effects that are introduced by bulky substituents in the geometry of the macrocycle. An analogous effect can be expected if bulky substituents are placed in the different positions of porphycene. Figure 1 shows the different kind of substitution patterns that can be obtained from symmetric porphycenes. The effects that the substituents exert on the N-N axes are summarized in Table 1. As can be seen, the dynamics of the hydrogen-migration process could be expected to range from an almost porphyrin-like double minimum potential in octaethylporphycene (OEPC, **2**) to an almost single-minimum potential profile in *meso*-tetrapropylporphycene (*m*-TPrPc, **4**). We report below on the solid-state CPMAS studies carried out to detect a possible influence of the geometry of the central cavity in substituted porphycenes on the tautomerism of the central hydrogens.

Results

Relaxation Behavior of the ¹H NMR Signals of 2–4. Solid state ¹H NMR line widths of **2–4** were measured at different temperatures. The observed changes provided evidence for the presence of molecular motions in the crystals, and a line-narrowing process was observed (data not shown). To calculate the activation energy (E_a) of the latter, ¹H spin-lattice relaxation times (T_1) were measured for **2–4** at different temperatures. This relaxation time is particularly useful for measuring

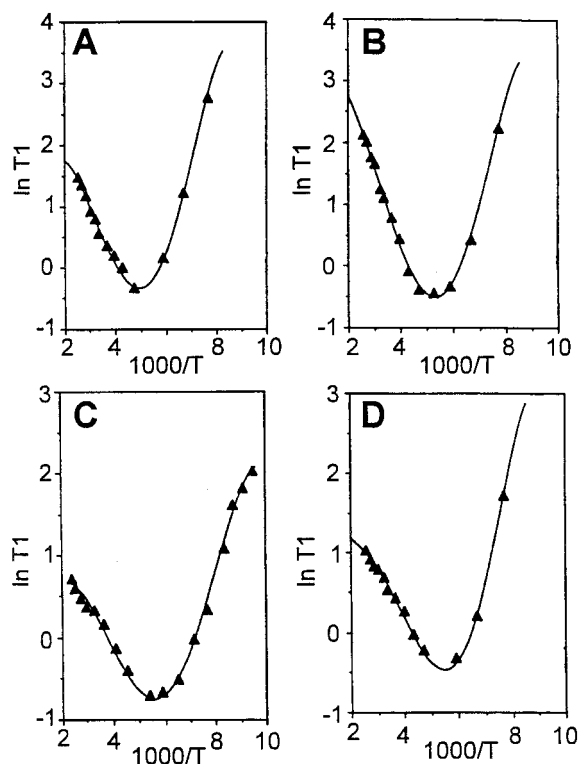
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Figure 2. Temperature dependence of the ¹H relaxation times T_1 in **2–4** for $\gamma H_1 = 50$ kHz. The lines represent the best fit of the experimental data and yield the Arrhenius equation for the correlation times $\delta = 2 \times 10^{-12} e^{6000/T}$.

slow motions such as those taking place in porphyrins, as its time scale is given by the frequencies associated to the H_1 fields applied to spin-lock the magnetization:²⁰

$$T_1^{-1} = C[\tau_c/1 + \omega_0^2 \tau_c^2 + 4\tau_c/1 + 4\omega_0^2 \tau_c^2]$$

where $\omega_0 = \gamma H_0$ is the Larmor frequency of the protons, τ_c is the correlation time of the reorientation at each temperature, and C is a constant. Figure 2 shows the inverse temperature dependence of $\ln T_1$ as function of $1/T$ for **2–4**. Assuming an Arrhenius-type behavior for the correlation times:

$$\tau_c = A \exp(E_a/RT)$$

a best fit of the experimental data allows us to obtain an activation energy $E_a = 2.0 \pm 0.5$ kcal/mol for each of the porphycenes. It is known^{11–13} that the range of E_a for the tautomeric processes in porphyrins is of 9–11 kcal/mol; hence, the dynamic process in **2–4** could be related to the movement of the alkyl side chains, very likely to the rotation of the methyl residues. We therefore measured the activation energy of Ni- β -tetrapropylporphycene since the chelate is devoid of central protons. Similar results of $\ln T_1$ vs $1/T$ (Figure 2D) to those measured with the free bases were obtained, strongly suggesting that the detected molecular movements originate in the side

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Table 2. ^{13}C NMR Chemical Shifts of 2–4 in the Solution and Solid-State Spectra

atom	chemical shift m-TPrPc 4		chemical shift β -TPrPc 3		chemical shift OEPc 2	
	solution ^a (20 °C)	solid ^b (30 °C)	solution ^c (20 °C)	solid ^b (30 °C)	solution ^d (20 °C)	solid ^b (30 °C)
C _{α} (C-1,8,11,18)	146.32	140.3–144.9	144.67	140.8	143.27	141.1
C _{α} (C-4,5,14,15)	134.22	130.0–133.2	134.05	131.7	137.23	135.2
C _{β} (C-2,7,2,17)	127.70	125.9–128.3	143.44	140.8	142.02	144.7
C _{β} (C-3,6,13,16)	125.48	121.5	122.59	124.8	136.72	137.7
meso (C-9,10,19,20)	129.66	126.0	110.33	106.3	109.82	109.3
CH _{2α}		34.2		26.0–31.8		20.3
CH _{2β}		26.9		20.2–26.0		
CH ₃		14.5–16.5		12.8–15.1		14.4–17.3

^a In ppm downfield from TMS (taken from ref 19). ^b In ppm downfield from TMS using the CH₃ resonance of hexamethylbenzene as external reference. Spectra recorded with parameters given in Experimental Section. ^c In ppm downfield from TMS (taken from ref 18). ^d In ppm downfield from TMS (taken from ref 17).

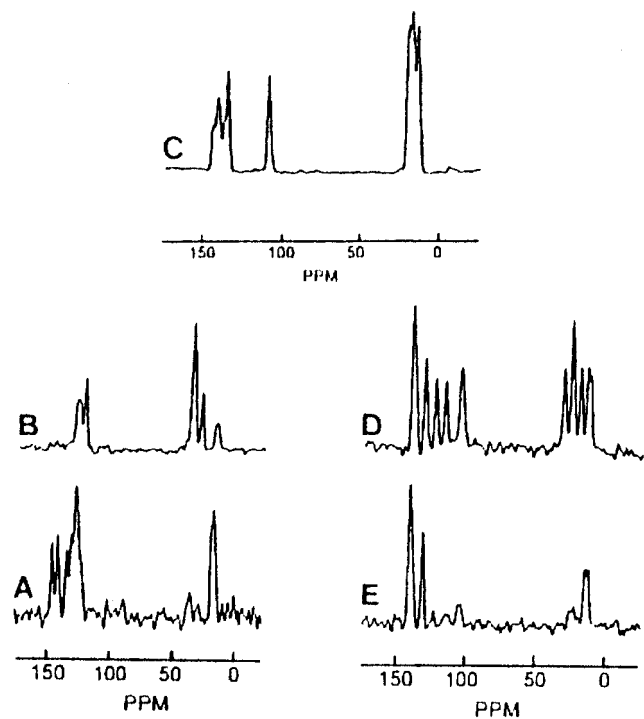


Figure 3. High-resolution solid-state 75.47 MHz ^{13}C NMR spectra of OEPc 2, β -TPrPc 3, and m-TPrPc 4 recorded at room temperature. (A) Spectrum of 4 introducing a 50 μs delay prior to acquisition; (B) spectrum of 4 using a contact time of 40 μs ; (C) full spectrum of 2; (D) full spectrum of 3; (E) spectrum of 3 introducing a 50 μs delay prior to acquisition. Number of scans = 512; repetition time = 2s; rotor speed = 2.5 kHz.

chains rather than in the tautomerism of the central protons. An analysis of the molecular motions in the solids by ^{13}C -CPMAS was therefore performed.

^{13}C -CPMAS Analysis of 2–4. The room-temperature high-resolution solid-state spectra of 2–4 are shown in Figure 3. To assist in the assignment of the solid-state data, the spectra were also recorded employing the pulse sequence devised by Opella and Frey.²¹ This routine allows us to obtain spectra that only show resonances of quaternary or methyl carbons by introducing a short delay (ca. 50 μs) prior to the acquisition, during which the signals with stronger dipolar couplings to protons decay. The ^{13}C NMR solution spectra of 2–4 were also of help with the peak assignments. The ^{13}C -CPMAS spectrum of 4 recorded under dipolar dephasing conditions is shown in Figure 3A where only signals of quaternary

carbons, i.e., pyrrole α -carbons and meso-carbons, as well as methyl groups were recorded. Figure 3B shows the spectrum of 4 recorded under the Opella and Frey conditions so that only carbons with strong dipolar couplings to protons (CH, CH₂) are allowed to cross-polarize. By overlapping both spectra, and taking into account the solution spectra, a tentative assignment of the ^{13}C peaks of 4 in the solid-state spectrum could be made (Table 2). The difference in the relative areas of the CH₂ peaks (Figure 3B) could be due to a splitting of the CH₂ peak at the higher field where one of the signals overlaps with the methylene peak resonating at the lower field. Figure 3C shows the ^{13}C -CPMAS spectrum of 2 at 25 °C. The complete assignment of peaks is more cumbersome than in the case of 4 since all the pyrrole carbons are quaternary, and the dipolar dephasing sequence does not simplify the spectrum. Assistance in the assignments could be found in the solution spectrum (Table 2). The broad peak in the aliphatic region is due to an overlapping of the CH₂ and CH₃ peaks, the peak at 109 ppm was assigned to the meso (C-9, C-10, C-19, C-20) carbons, and the quadriplet-like signal at 135–145 ppm was assigned to the pyrrole carbons. The CPMAS spectra of 3 is shown in Figures 3D and 3E. The spectrum in 3D has been recorded under normal conditions, and the one in 3E was recorded using dipolar dephasing. The peak at 106.3 ppm (Table 2) corresponds to the meso-carbons; the peaks corresponding to the pyrrole α -carbons can be assigned to the chemical shifts at 140.8 and 131.7 ppm. The higher relative area under the peak at 140.8 ppm suggests an overlapping of one of the α -carbons and the substituted β -carbon. The peak at 124.8 ppm was therefore assigned to the unsubstituted β -carbon on the pyrroles.

To understand the N–H tautomerization process of the substituted porphycenes, we performed a variable-temperature solid-state NMR analysis. Since the strong overlapping of the pyrrole region of the full spectra complicated the analysis, spectra of 2–4 were recorded, when possible, by using the dipolar dephasing sequence or short contact times. Thus, Figure 4 shows the CPMAS spectra of 4 at variable temperature using either short contact times (Figures 4A, 4B, and 4C) or the dipolar dephasing sequence (Figures 4D, 4E, and 4F). Both types of spectra show that the increase in temperature led to a displacement of the chemical shifts of the α - and β -carbons of the pyrrole rings. However, although the signals shifted toward each other, there was no evidence of exchange broadening due to a tautomeric process. The observed shifts are very likely due to effects of crystal packing on the NH tautomerism (see below). The CPMAS

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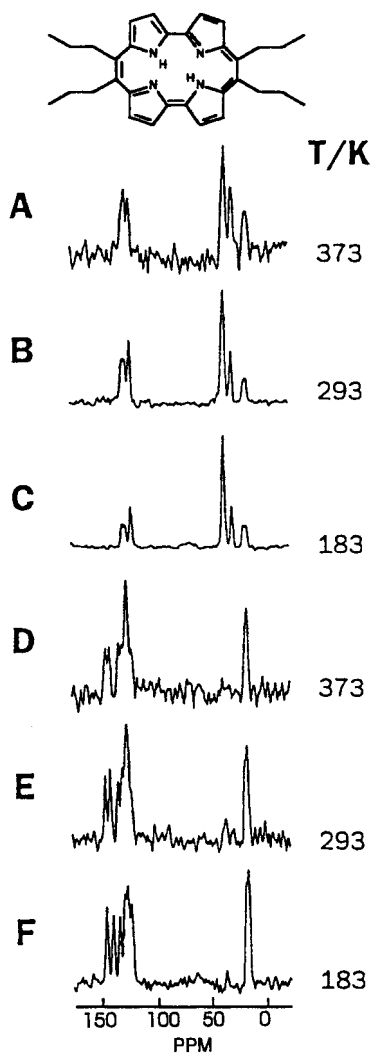


Figure 4. ^{13}C -CPMAS NMR spectra of **4** recorded at 75.47 MHz and variable temperature. A–C were recorded using short contact times (40 μs); D–F were recorded under dipolar dephasing conditions (50 μs delay prior to acquisition). Spectral parameters were as given in Experimental Section.

spectra of **3** at variable temperatures can be seen in Figure 5 where 5A, 5B, and 5C are the full spectra and 5D, 5E, and 5F are the spectra recorded under dipolar dephasing conditions. The CPMAS spectra of **2** at variable temperatures can be seen in Figure 6. In neither case was it possible to detect broadening of signals due to chemical exchange among NH tautomers. The most simple explanation for the absence of exchange broadening with temperature is that in substituted porphycenes, at variance with what happens with substituted porphyrins,^{11,12} exchange is still fast in the solid state with respect to the NMR time scale even at 183 °K. In other words, the tautomerism rate is faster than the time scale of ^{13}C NMR. However, several factors could affect the ^{13}C -CPMAS spectra in porphyrinoids and influence the spectra, as was the case with porphyrins.^{11,12} These are the ring current effects due to effective crystal packing, and the presence of ^{14}N nuclei where the eigenstates of the nuclei are not in general eigenstates of the Zeeman Hamiltonian and therefore preclude the averaging of the dipolar coupling between neighboring ^{13}C – ^{14}N nuclei by MAS. This residual coupling may affect the shape of the α -carbon resonances.¹¹ These factors are not always easy

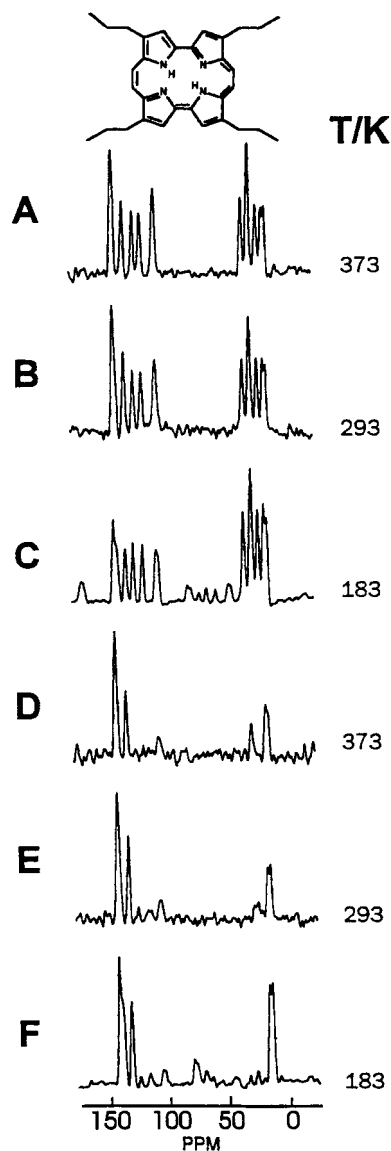


Figure 5. ^{13}C -CPMAS NMR spectra of **3** recorded at 75.47 MHz and variable temperature. A–C are the full spectra; D–F were recorded under dipolar dephasing conditions. Spectral parameters were as given in Experimental Section.

to isolate. We therefore decided to examine the presence of a possible chemical exchange between NH tautomers taking place above 173 °K by using the ^{15}N -CPMAS NMR technique under conditions of natural abundance.

^{15}N -CPMAS NMR of Porphycenes 2–4. The ^{15}N -CPMAS NMR spectra of **2–4** recorded at 25 °C showed that the *m*-tetrapropylporphycene **4** had two nitrogen peaks, one for the NH residue (154.8 ppm) and one for the $-\text{N}=\text{}$ residue (178.1 ppm). This was also the case for the β -tetrapropylporphycene **3** (NH: 161.5 ppm; $-\text{N}=\text{}$: 173.2 ppm), while octaethylporphycene **2** showed only one peak for both types of nitrogen atoms (164.7 ppm). A variable temperature analysis of **4** and **3** was therefore possible that should provide evidence for a chemical exchange process among both tautomers. Figures 7–9 show the variable temperature ^{15}N -CPMAS NMR spectra in the solid state of **2–4**. It can be seen that in the case of **4** and **3** the nitrogen peaks approach with increasing temperature and come further apart at lower temperatures, but without showing any line widening attributable to exchange broadening. The single resonance of **2**

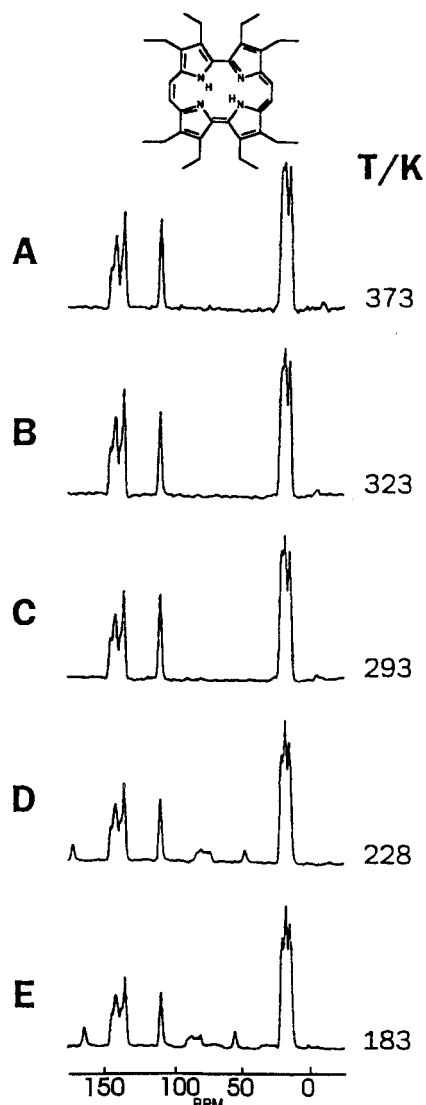


Figure 6. ¹³C-CPMAS NMR full spectra of **2** recorded at 75.47 MHz and variable temperature. Spectral parameters were as given in Experimental Section.

remains unaltered with temperature change (Figure 9). NH tautomerism in porphycene in the solid state is therefore a process that undoubtedly takes place above the coalescence temperature. The duplication of nitrogen resonances observed in **3** and **4** must be attributed to the presence in the solid of two unequally populated tautomers (see Discussion).

Discussion

The duplication of nitrogen resonances that appear in the ¹⁵N-CPMAS NMR spectra of **3** and **4** could be attributed to a tautomerism process that has been quenched in the solid or that takes place at a slower rate than the NMR experiment. If this were the case, then as the temperature of the solid increases, a point will be reached where NH tautomerism lead to a coalescence of both signals. It is evident that in the case of **2** (Figure 9), the NMR experiment was already conducted above the coalescence temperature. Since two signals were observed in the case of **3** and **4** (Figures 7 and 8), a second explanation for the observed duplication in the nitrogen peaks is needed. The duplication of nitrogen signals

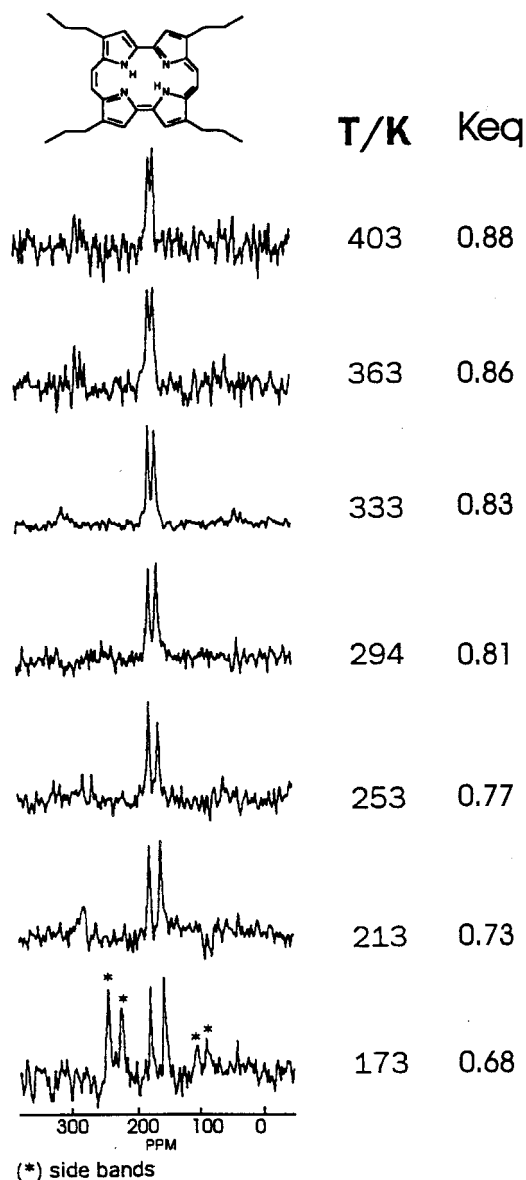


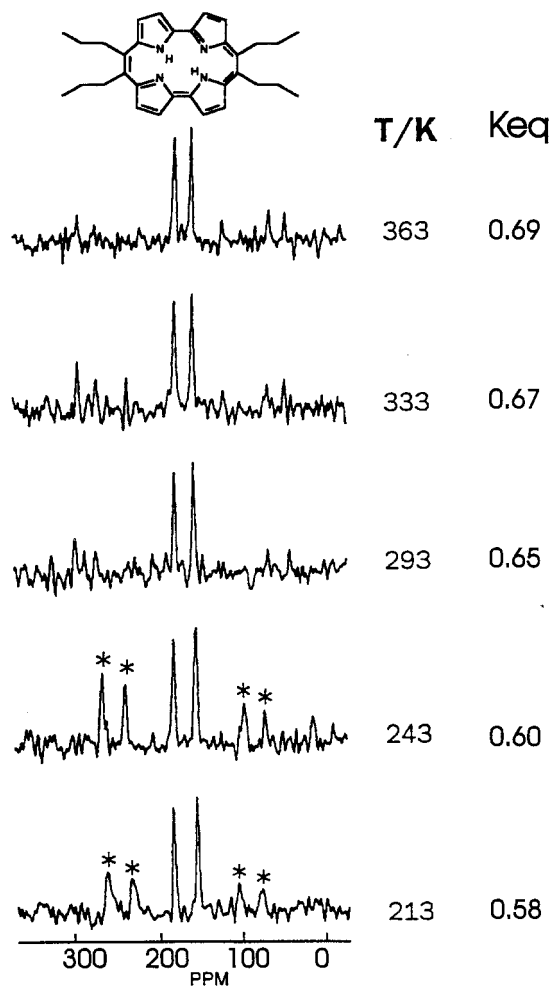
Figure 7. ¹⁵N-CPMAS NMR spectra of **3** recorded at 30.42 MHz and variable temperature. (*) Spinning sidebands. Spectral parameters were as given in Experimental Section.

should reflect an overlapping of two processes of intramolecular exchange between two unequally populated sites. We discussed this possibility at length in our analysis of NH tautomerism in substituted porphyrins in the solid state,^{11,12} and it is also relevant to the present case of the substituted porphycenes. Although in solution there are equal populations of **1a** and **1b**, in the solid the asymmetric packing forces lift the degeneracy and in the equilibrium **1a** ⇌ **1b** one tautomer should be more populated than the other. Each of the tautomers is a two-site system (N₁H···N₂; N₂···HN₁). A tautomeric process taking place under fast exchange conditions will produce two signals centered at the weighed averages of the frequencies:

$$\delta_1 = p_a \cdot \delta_{=N-} + p_b \cdot \delta_{-NH-}$$

$$\delta_2 = p_a \cdot \delta_{-NH-} + p_b \cdot \delta_{=N-}$$

where *p_a* and *p_b* are the relative populations of both tautomers. In solution where *p_a* = *p_b* = 1/2 only one line



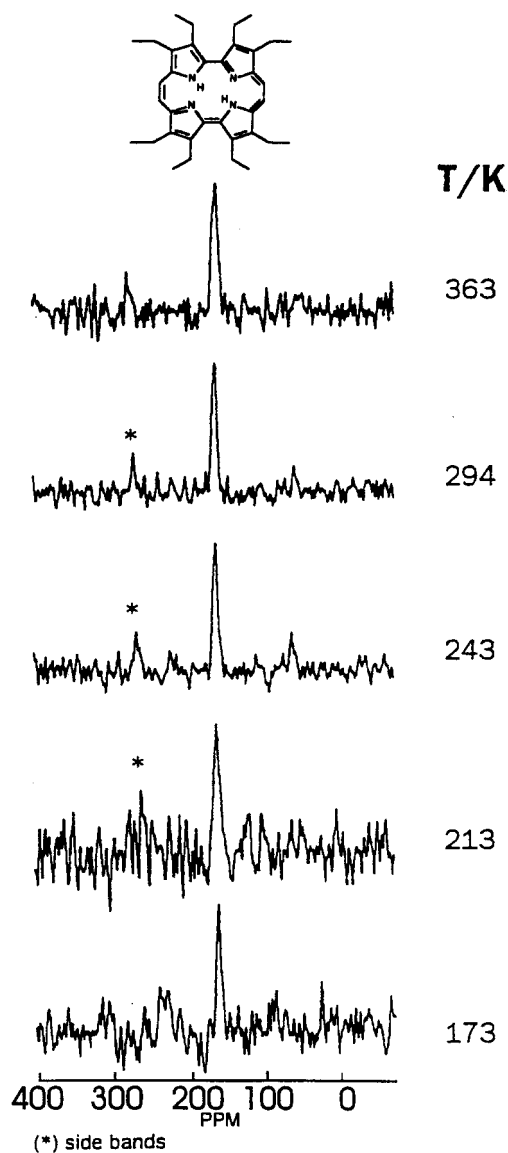
(*) side bands

Figure 8. ^{15}N -CPMAS NMR spectra of **4** recorded at 30.42 MHz and variable temperature. (*) Spinning sidebands. Spectral parameters were as given in Experimental Section.

is observed. In the solid-state each site has its own T_2 and its own Larmor frequency. Instead of using two kinetic constants (k_{ab} and k_{ba} , see Figure 1) to interpret the spectra, it is also possible to use one kinetic constant and the equilibrium constant $K = k_{ab}/k_{ba}$. The latter method is more convenient since in the fast exchange limit, K can be directly extracted from the spectra. Therefore, since $p_a = 1/(1 + K)$ and $p_b = K/(1 + K)$, the difference $\delta_1 - \delta_2$ can be written as

$$\Delta = \delta_1 - \delta_2 = \Delta_0(1 - K)/(1 + K)$$

where $\Delta_0 = \delta_{\text{N-}} - \delta_{\text{NH-}}$ is the chemical shift difference in the solution low-temperature spectrum. This allows us to obtain K from the high-temperature spectra, a value that was later extrapolated to the slow exchange region assuming that K has an exponential temperature dependence $K = A \exp(-E_a/RT)$. The process $\mathbf{1a} \rightleftharpoons \mathbf{1b}$ can then be analyzed by varying only the rate constant k_{ba} . In the case of porphyrines **2–4** the interconversion among tautomers is so fast that it was not possible to measure rate constants for hydrogen migration from simulations of the obtained spectra. It was possible, however, to calculate the values of the equilibrium constant K for the $\mathbf{1a} \rightleftharpoons \mathbf{1b}$ tautomerism as a function of temperature for



(*) side bands

Figure 9. ^{15}N -CPMAS NMR spectra of **2** recorded at 30.42 MHz and variable temperature. (*) Spinning sidebands. Spectral parameters were as given in Experimental Section.

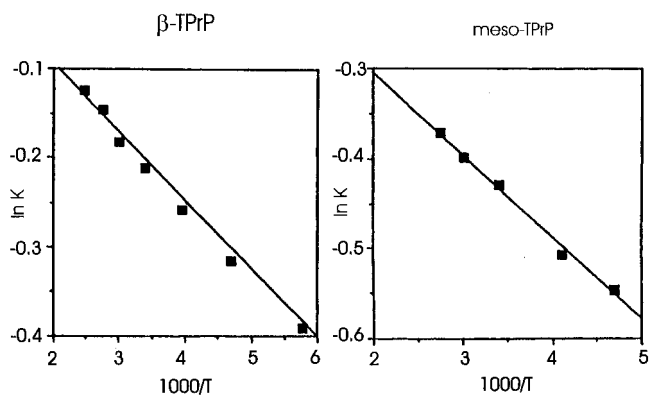


Figure 10. Temperature dependence of the logarithm of the NH tautomeric equilibrium constant (K) of **3** and **4**. The lines are the best fit of the experimental data.

the *meso*-tetrapropylporphyrine **4** and the β -tetrapropylporphyrine **3** (Figures 7, 8, and 10) as well as the energetic parameters involved in the solid-phase reactions (Table 3).

Table 3. Relevant Parameters of the Solid State Tautomerism of β -TPrPc **3 and m-TPrPc **4****

parameter	β -TPrPc 3	m-TPrPc 4
ΔH (kcal/mol) ^a	0.16	0.18
ΔS (eu) ^a	0.14	0.24

^a From the equation $K = k_{ab}/k_{ba} = e^{\Delta S/R} e^{-\Delta H/RT}$.

In conclusion, we have shown that for alkylporphycenes in the solid state it was possible to detect rotations in the alkyl chains by measuring variations in the T_1 relaxation times as a function of temperature. The ¹³C-CPMAS NMR spectra of *meso*- and β -alkyl-substituted porphycenes and of octaalkylporphycene carried out at variable temperatures suggested the existence of a tautomeric process in alkylporphycenes analogous to that detected in alkylporphyrins.^{10–12} At variance with the latter process, the one taking place in porphycenes appeared as too fast to be measured in the NMR time scale employed. This was confirmed by measuring the ¹⁵N-CPMAS NMR spectra in the alkylporphycenes which revealed the existence in the solids of an NH tautomerism process that takes place above the coalescence temperature among two unequally populated tautomers. The parent porphycene **1** gave a four-line ¹⁵N spectrum that was interpreted as arising from four possible tautomers which become nondegenerate due to intermolecular interactions.¹⁵ The simpler ¹⁵N spectra shown by **3** and **4** must result from asymmetric crystal packing forces that favor one form over the other. The contribution of the crystal packing forces are very likely also reflected in the equilibrium constants. The shorter N₁–N_{2'} distances in **1** (Table 1) are expected to favor proton transfer among both rings. However, the reaction enthalpies (ΔH) reported for **1**¹⁵ are higher than those found for **3** and **4**. Since ΔH values reflect the energy needed for the proton transfer, it is evident that crystal packing forces are affecting the equilibrium constants of the tautomerism process. Also, when comparing the N₁–N_{2'} distances in **3** and **4** (Table 1), it could be expected that the shorter proton path in **4** will favor its transfer among both rings. Slightly higher ΔH values were, however, determined for **4** as compared to **3** (Table 3), again suggesting that crystal packing forces are influencing NH tautomerism.

A topological argument can be made that if proton transfer among the nitrogen atoms of porphycenes leads to a skeletal rearrangement similar to the one we suggested for porphyrin tautomerism,¹² then packing forces will affect more the core porphycene ring **1** than the propyl-substituted porphycenes **3** and **4** where the side chains keep the distance between the porphycene rings, hence the higher reaction enthalpies measured for **1** as compared to **3** and **4**. In any event, the energetic barrier among the tautomeric forms **a** and **b** (Figure 1) must be very small and results in a fast interconversion among them. It was therefore not possible to establish a correlation between the geometry of the central cavity and the dynamics of the tautomeric process in substituted porphycenes. An analysis of the problem using sterically hindered porphyrins will be published elsewhere.

Experimental Section

Syntheses of 2,3,6,7,12,13,16,17-octaethylporphycene **2** (OEPc),¹⁶ of 2,7,12,17-tetrapropylporphycene **3** (β -TPrPc),¹⁵ and of 9,10,19,20-tetrapropylporphycene **4** (m-TPrPc)¹⁹ were carried out as described elsewhere. The CPMAS NMR spectra were obtained on a Bruker MSL-300 equipped for variable temperature work. Rotors used were of 4 mm and 7 mm. ¹³C-CPMAS spectra were obtained at 75.47 MHz using 512 scans, pulse interval of 2s, contact time of 1.5 ms, rotor spinning speed of 2.5 kHz, spectral width of 25000 Hz, and Fourier number = 4096. ¹⁵N-CPMAS NMR spectra were obtained at 30.42 MHz over 4000 scans, pulse interval of 3s, contact time of 10 ms, rotor speed of 2.5 kHz, spectral width of 25000 Hz, Fourier number = 4096. Temperature dependence of the ¹H relaxation times T_1 in **2–4** for $\gamma H_1 = 50$ kHz were measured acquiring eight phase-cycled scans on a sealed sample using a 60 s repetition delay; rf power = 9W. Simulation of spectra was carried out using an EXCHANGE.C program for NMR spectra in a regime of chemical exchange. It allowed the calculation of chemical exchange between four isotropic resonances affected by two simultaneous reactions as found in a system of two unequally populated tautomers.

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