values being $A_{iso}(^1H)$ = 127.2 G and g_{iso} = 2.0042. Since these results are very similar to those calculated from the neon data, namely, $A_{iso}(^1H)$ = 128.6 G and g_{iso} = 2.0038, it is reasonable to conclude that these parameters are characteristic of the uncomplexed cation irrespective of the nature of the matrix. Consequently, the significantly different parameters observed for the cation above 120 K in the CFCl$_3$ matrix (Table III) now become anomalous for a dissociated cation. On the other hand, these 120 K parameters are just what would be expected if the complex persists and the loss of fine structure results simply from a motional averaging of the ^{35}Cl hyperfine tensor components.

Except for a recent investigation of the cubane radical cation $(C_8H_8^+)$,[39] the acetaldehyde ion is the largest cation studied to date by the neon matrix ESR method. Given the high resolution that can be achieved in neon and the chance of preferential orientation, it seems that much larger molecular ions could be analyzed in detail in this host material which has been used primarily for diatomic and triatomic radical ions.[1] A wide range of ion generation and deposition techniques allows neon to be used for nonvolatile inorganic ions[40] including the trapping of ion

intermediates produced under reactive laser sputtering[21] and other high-energy conditions.[41] The use of the neon ESR matrix technique for studying ion products formed in ion–neutral reactions has also been demonstrated for the following reactions which are important in stratospheric chemistry: $CO + CO^+ \rightarrow C_2O_2^+$,[42] $N_2 + N_2^+ \rightarrow N_4^+$,[43] $N_2 + CO^+ \rightarrow N_2CO^+$,[1] and $O_2 + O_2^+ \rightarrow O_4^+$.[44]

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High-Resolution Solid-State 13C NMR Spectra of Porphine and 5,10,15,20-Tetraalkylporphyrins: Implications for the N–H Tautomerization Process

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Abstract: The solid-state high-resolution 13C nuclear magnetic resonance spectra of porphine and of 5,10,15,20-tetraalkylporphyrins were recorded with use of the CP/MAS technique. The solution kinetics of the hydrogen migration between the two tautomers of porphine, *meso*-tetrapropyl- and *meso*-tetrahexylporphyrins, were also studied, and the activation parameters were found to be similar to those reported in the literature for tetraarylporphyrins. Porphine showed the same dynamical behavior in the solid state as in solution, while in the solid state the tetraalkylporphyrins showed doubling of the pyrrole carbon resonances at room temperature. The results obtained with the tetraalkylporphyrins can be explained assuming either a proton-transfer reaction slow on the NMR time scale or a fast exchange between two unequally populated tautomers. Three hypotheses are discussed with regard to the kinetic solid-state effects involved: (a) a quenching of the tunneling contribution to the proton-migration process; (b) a fixed geometry adopted by the four nitrogen atoms in the crystal that controls the migration; (c) a coupling between the proton-exchange process and the deformation of the porphyrin skeleton, the latter being hindered by neighboring molecules.

Porphyrins and porphyrin derivatives have attracted considerable attention due to the biological relevance of these naturally occurring compounds. In addition, these molecules have an intrinsic significance in chemistry because of their unique electronic structure, the large number of synthetic structures available for study, and the many phenomena that they exhibit.[1–3]

Free-base porphyrins have two protons in the inner part of the skeleton. Early information about the localization of these hydrogens in the framework of the four nitrogen atoms came from

X-ray crystallographic studies.[4–6] However, most of the experimental observations of interest regarding the migration of these two hydrogens among the four nitrogens have been obtained from solution NMR spectroscopy.[7–12]

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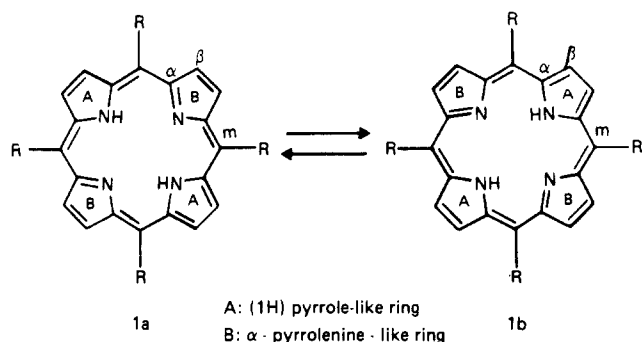(6) Webb, L. E.; Fleischer, E. B. J. Chem. Phys. **1965**, 43, 3100.

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Porphyrin N-H Tautomerization

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Scheme I

A: (1H) pyrrole-like ring

B: α - pyrrolenine - like ring

1a   1b

The rate of the proton transfer process between the two tautomers **1a** ⇌ **1b** (Scheme I) has been extensively studied in 5,10,15,20-tetraaryl systems and has been found to be fast on the NMR time scale at room temperature. Activation parameters have been obtained by fitting reaction rate data as a function of temperature to the Arrhenius equation,[8,10-13] as well as from kinetic isotope effects upon replacement of the central protons by deuterons.[7,8,10,12,13] Various explanations have been advanced in order to account for the observed data: an asynchronous 1,5 sigmatropic rearrangement,[8] a simultaneous movement of the two hydrogens through a symmetrical transition state,[10] a synchronous tunneling through a double-minimum potential,[14,15] an incoherent migration coupled to in-plane skeletal vibrations,[16,17] and a migration of the hydrogens in a four-minima potential energy surface coupled to out-of-plane distortions of the macrocycle.[18]

Since crystal-packing forces occurring in the solid state may significantly alter the dynamical processes taking place in the liquid state, high-resolution solid-state NMR spectroscopy is a useful technique for the study of dynamical processes in solids. This method, involving cross polarization (CP),[19] high-power decoupling,[20] and magic-angle spinning[21] (MAS) offers a useful complement to information available for X-ray analysis.[22,23] It has been recently applied to the study of chlorophyll and chlorophyll derivatives[24] as well as to the analysis of the tautomeric process in tetraarylporphyrins and in phthalocyanine.[25,26] TTP[27] and

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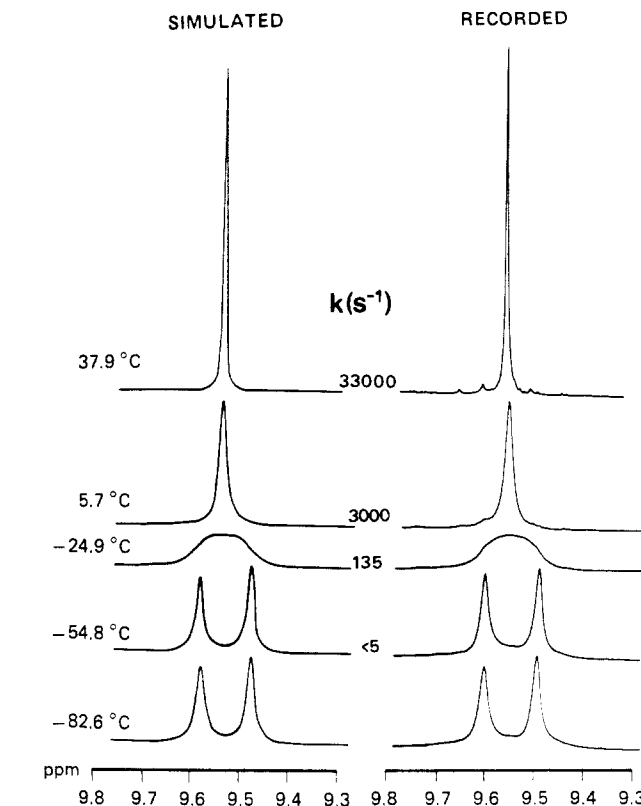
Figure 1. Experimental and calculated line shapes of the ¹H NMR (500-MHz) resonances of the β-hydrogens in TPrP at different temperatures. The spectra were recorded of a saturated solution in CD₂Cl₂. Spectral parameters used: number of scans, 64; SW, 6500 Hz; flip angle, 60°; acquisition time, 5.043 s. The simulated spectra were obtained by fitting the observed spectra to the standard equation for a two-sites exchange problem with a nonlinear regression analysis. At very low temperature the downfield signal contains an additional static broadening of ca. 3 Hz due to an unresolved coupling with the central hydrogens. For the nonexchanging chemical shifts a weak linear dependence with the temperature was taken into account.

phthalocyanine showed in the solid state activation parameters similar to those found in solution, whereas in TPP the solid-state effects modified the rate constants, shifting the equilibrium toward one of the tautomers.[25] A high-resolution ¹³C NMR study has also been performed on OEP and its Zn(II) and Ni(II) complexes.[28] The free base showed a doubling of the α- and the β-carbon signals (see Scheme I) that was attributed to the quenching of the N–H tautomerism. Available X-ray data for this case also seemed to lend support to the idea of hydrogen localization in the solid.[29]

In this report the process of the N–H tautomerism was analyzed for a series of 5,10,15,20-tetraalkylporphyrins, as well as for the unsubstituted parent compound H₂P (Scheme I). Activation parameters were measured in solution for TPrP, THeP, and H₂P by applying a line shape analysis to the coalescing signals of the β-hydrogens. A solid-state ¹³C NMR study was also carried out on several alkyl-substituted porphyrins, and H₂P was studied at several temperatures. Possible kinetic solid-state effects (KSSE) are discussed, as well as the implications of these results regarding the mechanism of the proton-transfer reaction.

Experimental Section

The CP/MAS ¹³C NMR spectra at room temperature were obtained on a Bruker CXP-200 NMR spectrometer at 50 MHz with a home-built probe. A single-contact Hartmann–Hahn cross polarization, CP, was used with a contact time of 3 ms, and ¹H and ¹³C rf fields matched at approximately 87 kHz. A spin–temperature inversion sequence using phase alternation of the initial π/2 proton pulse and of the receiver phase was employed to reduce base-line distortions. A π/2 proton flip-back

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Table I. Relevant Parameters of the Solution Proton Transfer

porphyrin	nonexchanging frequencies[a]	$\Delta G^{\ddagger}_{298}$, kcal·mol^{-1}	E_a, kcal·mol^{-1}
H$_2$P	9.71, 9.48	11.4	8.3
TPrP	9.60, 9.48	12.0	10.0
THeP	9.55, 9.44	12.7	8.2

[a] Downfield (ppm) from Me$_4$Si. CD$_2$Cl$_2$ used as solvent.

pulse was applied at the end of the acquisition in order to recover the remaining ^{1}H magnetization and to shorten the repetition time to 3 s. A boron nitride rotor was used with a spinning frequency of about 6 kHz.

The solid-state variable-temperature spectra of H$_2$P were run on a Bruker CXP-100 NMR spectrometer at 25 MHz for ^{13}C. Temperature was regulated with a home-manufactured temperature controller and probe. The spinning rate varied between 3.0 and 3.3 kHz. The single-contact CP pulse sequence used was similar to that used for the CXP-200.

Solution NMR spectra were obtained on a Varian VXR-500 spectrometer. The temperature was monitored against the chemical shifts of CH$_3$OH. The concentration of solute used was about 10^{-3} mol·L^{-1} in methylene-d_2 chloride.

The tetraalkylporphyrins used were synthesized according to methods previously described in the literature[30] by condensation of pyrrole with the appropriate aldehyde in xylene containing 0.1 M trifluoroacetic acid. H$_2$P was prepared[31] by heating 2-(hydroxymethyl)pyrrole in xylene at 110–115 °C in the presence of 0.7 M acetic acid.

Results

In order to evaluate the possible KSSE, solution NMR variable-temperature analyses were performed on H$_2$P, TPrP, and THeP in concert with the solid-state NMR studies.[32] Room-temperature chemical shifts (ppm) from Me$_4$Si for these porphyrins in CD$_2$Cl$_2$: H$_2$P (pyrrole H) 9.60, (meso H) 10.43; TPrP (pyrrole H) 9.53, (CH$_2$, t, J = 8 Hz) 4.92, (CH$_2$, h, J = 8 Hz) 2.54, (CH$_3$, t, J = 8 Hz) 1.32; THeP (pyrrole H) 9.51, (CH$_2$, t, J = 7.5 Hz) 4.94, (CH$_2$ q, J = 7.5 Hz) 2.53, (CH$_2$, q, J = 7.5 Hz) 1.84, (CH$_2$, q, J = 7.5 Hz) 1.55, (CH$_2$, h, J = 7.5 Hz) 1.45, (CH$_3$, t, J = 7.5 Hz) 0.92. Chemical shifts were measured relative to CHDCl$_2$ and converted to the TMS scale. Tautomerism was studied for these three compounds over the full temperature range from slow to fast-exchange regimes.

In Figure 1 a set of pyrrole proton spectra of TPrP undergoing tautomerization is shown. In the spectra recorded at −55 and −83 °C the pyrrole protons are split into two peaks at 9.60 and 9.48 ppm. The areas under the two peaks are the same, but the peak at 9.60 ppm is broader. As already reported for tetraaryl-porphyrins,[7] the splitting can be ascribed to the proton exchange (slow on the NMR time scale) between tautomers **1a** and **1b**. As has been suggested for TPP,[33] the broader peak (which in TPrP appears at 9.60 ppm; see Figure 1 at −83 °C) may be assigned to the protons in the pyrrole rings that bear the N–H hydrogens. The broadening can be attributed to the known w-type J^4 coupling between the central and the β-protons.[7,34] Since the proton migration has been found to be intramolecular,[35,36] the β-hydrogens on the $1H$-pyrrole-like rings and the central hydrogens behave as an AX system when $k \ll J$ and as an AX$_2$ system when $k \gg J$. Therefore, a triplet is expected for these β-hydrogens at tem-

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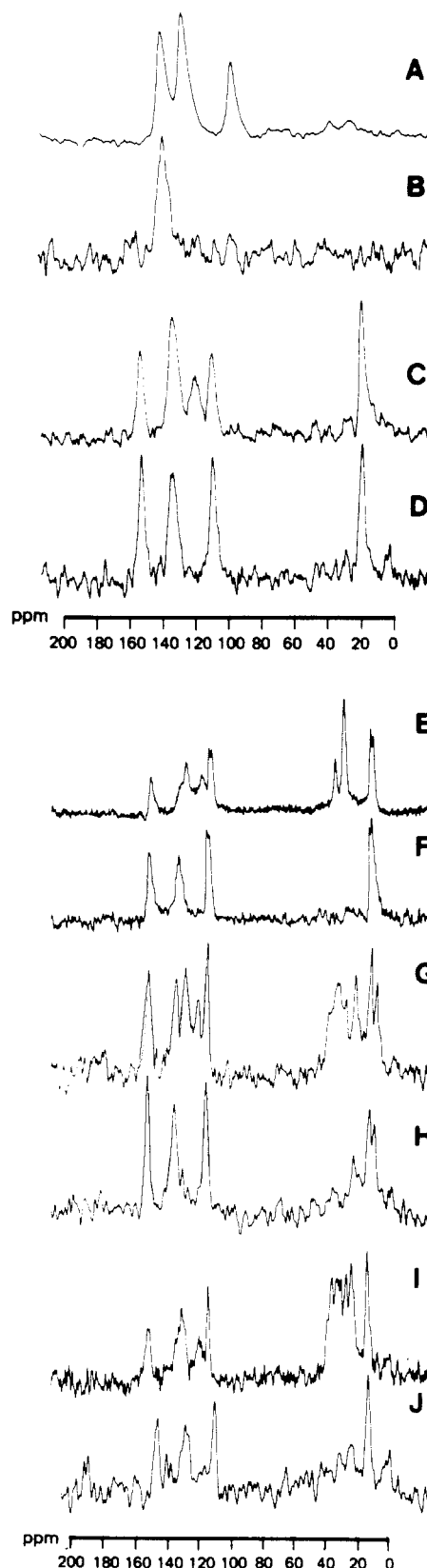

Figure 2. Solid-state ^{13}C CP/MAS NMR spectra: (A) H$_2$P; (C) TMeP; (E) TPrP; (G) TBuP; (I) THeP; (B, D, F, H, J) dipolar dephased spectra of H$_2$P, TMeP, TPrP, TBuP, and THeP, respectively. All spectra were run at room temperature at 50.3 MHz. Other parameters: LB, 0 Hz; SW, 11905 Hz; repetition time, 3 s; average number of scans, 5000. Spectra were Fourier transformed using 1024 points. Spectra were recorded of 50 mg of sample. The dipolar dephased spectra, using a dephasing time of 50 µs, only show methyl and quaternary carbons.

peratures below coalescence (in this case −25 °C; see Figure 1); and though this fine structure is obscured by exchange and relaxation effects, the coupling is preserved as a differential broadening between the two observed resonances.

Qualitatively similar results were obtained for H_2P and THeP. The rates of exchange were determined by comparison between the observed and calculated spectra, and an approximate error of 10% was estimated, except in the slow- and fast-exchange regimes where a larger error should be expected. Activation parameters for each porphyrin were obtained from Arrhenius and Eyring equations over a range of 110 °C for each porphyrin. The relevant parameters involved in the line-shape calculations are summarized in Table I.

The solid-state ^{13}C CP/MAS NMR spectra of H_2P and four tetraalkylporphyrins are shown in Figure 2. The assignments of the peaks were based on a comparison with solution NMR data[37] and on dipolar dephased data recorded with the pulse sequence devised by Opella and co-workers.[38] This routine allows one to obtain spectra only showing resonances from quaternary carbons and methyl groups. Signals due to carbons having stronger dipolar coupling to protons (e.g., CH, CH_2), decay during a delay time introduced prior to the acquisition.

In general, the porphyrin carbons show the expected resonances, although in some cases additional signals appear. Since the site symmetry in porphyrin crystals has been generally found to be lower than the molecular symmetry, it is conceivable that chemically equivalent nuclei in the isolated molecule will not be equivalent in the lattice. These inequivalences may have different origins. Side chains frozen in different conformations may render otherwise equivalent alkyl carbons inequivalent, an effect that has been well characterized in ^{13}C NMR studies in solution.[39] On the other hand, splittings in the α-, β-, or *meso*-carbons that are equivalent in the isolated molecule could also arise from deformations of the porphyrin macrocycle, as has been detected in the ^{13}C CP/MAS NMR spectra of some metallophthallocyanines.[40] Intermolecular ring current shifts can also produce splittings in the solid-state NMR resonances.[28] These shifts, although very useful in solution ^{1}H NMR studies,[41] have seldom been invoked to account for splittings or shifts appearing in solution ^{13}C NMR spectra. However, the high aromaticity of the porphyrin macrocycle and the small intermolecular distances observed for porphyrins in the solid state (ca. 3–4 Å) are factors that may collaborate in producing appreciable shifts in the ^{13}C CP/MAS NMR signals. Since it has been found that in general porphyrin molecules do not have fourfold symmetry in the lattice, these shifts may in principle be different for nuclei that are chemically equivalent in solution. This effect could account for some of the splittings observed in the ^{13}C CP/MAS NMR spectra of porphyrins.[42] Other general features found in all the spectra (Figure 2) include the large line widths of the peaks (ca. 4 ppm), which can be associated with unresolved cases of the splitting mechanisms mentioned above, as well as with effects induced by the anisotropic magnetic susceptibility of the porphyrin crystals.[43,44]

Although the tetraalkylporphyrins showed more resonances in the pyrrole region than expected, the dipolar dephasing sequence permitted the assignment of all the peaks. Since in this sequence no β-carbons should appear, the remaining signals occurring in the 130–160 ppm zone are only due to the α-carbons. Subtraction of the dipolar dephased spectra from the normal spectra identify the β-carbon resonances. For the α-carbons the downfield signals
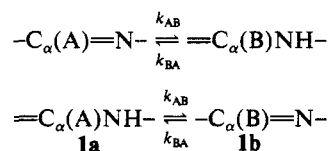
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Table II. ^{13}C CP/MAS NMR Chemical Shift Values for the Carbons in the Aromatic Region and Splittings Observed in the α- and β-Carbons of H_2P and Four Tetraalkylporphyrins[a]

porphyrin	*meso*-carbon	β-carbon (S)[b]	α-carbon (S)
H_2P	98.6	127.5	140.3
TMeP	110.4	120.8, 134.0 (13.2)	134.0, 153.5 (19.5)
TPrP	115.0, 116.7	121.0, 130.8 (9.8)	134.1, 152.3 (18.2)
TBuP	116.3	122.4, 130.6 (8.2)	136.4, 153.3 (16.9)
THeP	114.5	120.0, 130.7 (10.7)	134.1, 152.1 (18.0)

[a] From TMS (ppm) using the CH_3 resonance of hexamethylbenzene as an external reference. [b] S = splitting.

were assigned to the α-pyrrolenine-like ring (see Scheme I) on the basis of the difference in the shifts of the α-carbons bonded to nitrogens in C=CN and CC=N in model heterocyclic compounds (e.g. α-carbons in pyridine are at 150.6 ppm, while in pyrrole they appear at 118.5 ppm[45]). The chemical shift values and the assignment of the aromatic carbons, as well as the magnitude of the splittings observed in the resonances of the α- and β-carbons are summarized in Table II.

If it is assumed that the main factor controlling the line shape of the 120–155 ppm zone is the chemical exchange process 1a ⇌ 1b in the solid state, there are two hypotheses that can explain the doublings observed in the pyrrole carbon resonances in the solid state. The first one is the quenching of the rapid N–H tautomerism. In this case, the proton-transfer reaction would be slow on the NMR time scale, and the spectra would consist of four pyrrole signals, two from the α-carbons and two from the β-carbons. A second possibility could be the existence of a proton-transfer reaction taking place in the fast-exchange limit but occurring between two unequally populated tautomers. Although differences in the populations of 1a and 1b are very unlikely (or even impossible) in solution due to symmetry considerations, crystal-packing forces may lift this degeneracy, thereby favoring one of the tautomeric structures over the other. If this were the case, the spectra would reflect a superposition of two intramolecular proton-exchange processes taking place between two unequally populated sites. For example, these events may be represented for the α-carbons as

$$-C_\alpha(A){=}N- \underset{k_{BA}}{\overset{k_{AB}}{\rightleftharpoons}} {=}C_\alpha(B)NH-$$

$$\underset{\textbf{1a}}{{=}C_\alpha(A)NH-} \underset{k_{BA}}{\overset{k_{AB}}{\rightleftharpoons}} \underset{\textbf{1b}}{-C_\alpha(B){=}N-}$$

If the assumption is made that the chemical shifts of $-C_\alpha{=}N-$ and $=C_\alpha NH-$ in 1a and 1b are equal, then in the fast-exchange regime two lines will appear centered at

$$\delta_1 = p_A \delta_{C_\alpha=N-} + p_B \delta_{C_\alpha NH-}$$

$$\delta_2 = p_A \delta_{C_\alpha NH-} + p_B \delta_{C_\alpha=N-}$$

where p_A and p_B are the populations of the two tautomers 1a and 1b. In solution, $p_A = p_B = 1/2$ and only one line is observed. In the solid state, a difference in the populations p_A and p_B would be expressed as a splitting $\delta_1 - \delta_2 = \Delta_0(p_A - p_B)$, where Δ_0 is the chemical shift difference $\delta_{C_\alpha=N-} - \delta_{C_\alpha NH-}$.

To decide which of the two hypotheses best explains the actual process taking place in the solid at room temperature and leading to the doubling of the pyrrole carbon signals, a variable-temperature analysis can be used. If tautomerism is quenched (the reaction is slow on the NMR time scale), the isotropic values of the α peaks will remain relatively unchanged as the temperature is increased, to the point where tautomerism becomes important and coalescence is observed. Above the coalescence temperature, the α-carbon resonances will consist of one or two lines, depending on whether or not the populations of tautomers above this temperature are equal. Conversely, if the spectrum results from a superposition of two independent two-site processes that are fast

(45) See: Reference 41, Chapter 7.

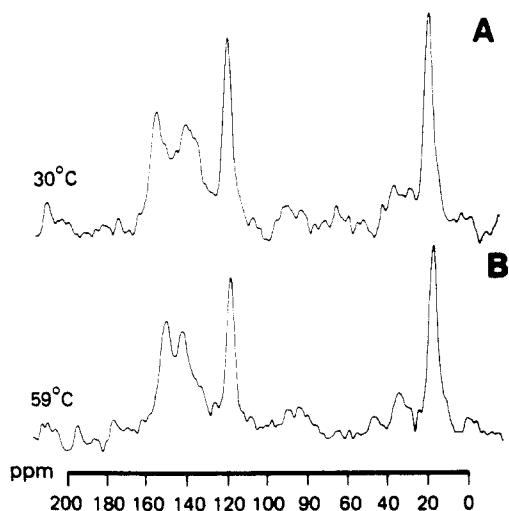340 *J. Am. Chem. Soc., Vol. 110, No. 2, 1988*

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Figure 3. Solid-state ^{13}C CP/MAS NMR spectra of TPrP: (a) room temperature (30 °C); (b) 60 °C. Only the dipolar dephased spectra are shown, since as they only show the α-carbon signals, they are easier to interpret than the normal ones. All spectra were run at 25.2 MHz. Other parameters: LB, 0 Hz; SW, 5000 Hz; repetition time, 3 s; dipolar dephasing time, 50 μs; average number of scans, 2000. All spectra were recorded of 100 mg of sample. The difference between the two signals in the 60 °C spectrum is 8 ppm less than at room temperature.

on the NMR time scale, the observed doubling for the α-carbons (δ_1 and δ_2) will change with the temperature as the equilibrium constant $K = p_B/p_A$ varies with temperature. Hence, as the temperature is raised, the splitting will continually decrease but without showing exchange broadening. Similar results are expected to take place with the β-carbon resonances.

Preliminary results obtained by recording the dipolar dephased spectra of TPrP revealed that the signals due to the α-carbons are shifted from 152.3 and 134.1 ppm, respectively, at room temperature (30 °C) and to 148.3 and 138.1 ppm at 60 °C (Figure 3). This implies that the dynamical process taking place in the solid at this temperature better fits the hypothesis of a proton exchange in the fast regime proceeding between two unequally populated tautomers. Otherwise, if tautomerism were quenched, no shift in the isotropic value of the resonances could be observed until coalescence were reached.[46] A similar explanation was used to interpret the data obtained in the ^{15}N CP/MAS NMR spectra carried out in the solid state on [^{15}N$_4$]TPP at different temperatures.[25]

Among all the solid-state spectra obtained, the H$_2$P spectrum is outstanding in that no doubling of the pyrrole carbon signals was observed at room temperature. The resonances appearing at 98.6, 127.5, and 140.3 ppm were tentatively assigned to the methine bridges and the β- and the α- carbons, respectively, by comparison with solution ^{13}C NMR literature values.[3,37] When the spectrum was recorded with use of the dipolar dephasing pulse sequence mentioned above with a delay time of 50 μs, only one signal remained at 140.3 ppm, corresponding to the pyrrole α-carbons. This confirms that at room temperature the eight α-carbons become indistinguishable in the NMR experiment, indicating either a fast-exchange process of a symmetrical placement of the hydrogens midway between two adjacent pairs of nitrogens.

In order to analyze the role of tautomerism in the equivalence of both the α- and of the β-resonances at room temperature observed in the solid-state spectrum of H$_2$P, the dipolar dephased spectra of this compound were run over a temperature range from fast to slow exchange (Figure 4). The changes observed can be explained assuming a two-proton exchange reaction between two equally populated tautomers. Between −20 and −50 °C exchange broadening is observed, whereas below −70 °C the slow-exchange
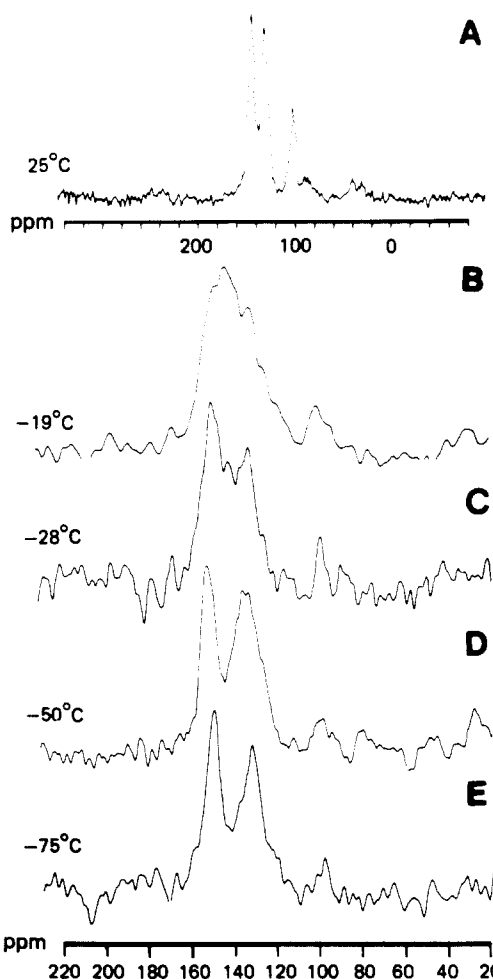

Figure 4. 25-MHz solid-state ^{13}C CP/MAS NMR spectra of H$_2$P recorded at different temperatures: (a) normal spectrum at 25 °C; (b–e) dipolar dephased spectra at −19, −28, −50, and −75 °C, respectively. SW: (a) 10 000 Hz; (b–c) 5000 Hz. Other spectral parameters used are the same as those in Figure 3. Small peaks appearing at about 99 and 128 ppm in spectra b and c may be due to incompletely suppressed meso- and β-carbons.

limit and above 25 °C the fast-exchange limit are reached. From the two nonexchanging frequencies and the coalescence temperature a $\Delta G^{\ddagger}_{260} = 11.4$ kcal·mol^{-1} can be estimated. A similar value ($\Delta G^{\ddagger}_{260} = 10.8$ kcal.mol^{-1}) was calculated with the data obtained from the solution NMR spectra of H$_2$P. This result, together with the general similarity between the solution- and the solid-state behavior of H$_2$P as revealed by the NMR spectra, suggests that the mechanisms of the proton-transfer process occurring in both phases are similar. Therefore, as has been previously described for tetraarylporphyrins in solution, the NMR spectrum of H$_2$P in the solid state at room temperature reflects a process analogous to that shown in Scheme I occurring in the fast-exchange limit, rather than a structure in which the two hydrogens are equally shared by two pairs of nitrogens.[47] It should be noticed that the solid-state NMR results appear to be in agreement with the first X-ray diffraction analysis performed on H$_2$P,[6] but not with the most recent one that showed a static picture of two localized hydrogen atoms in one pair of opposite pyrrole rings.[48]

(46) There is always the possibility that a temperature-dependent frequency shift occurs. However, data from solution ^{13}C NMR indicate that this temperature dependence can be neglected. See: Reference 3, Vol. 3, Chapter 1.

(47) A paper describing ^{15}N CP/MAS experiments on solid porphine is in press which supports the solid-state results obtained in this study: Wehrle, B.; Limbach, H. H.; Kocher, M.; Ermer, O.; Vogel, E. *Angew. Chem.* We are grateful to the authors for a preprint of their work.

(48) (a) Chen, B. M. L.; Tulinsky, A. *J. Am. Chem. Soc.* **1972**, *94*, 4144. (b) It should be noted that the H$_2$P sample used belonged to the same stock as that used by Dr. Tulinsky to make his analysis. Therefore, there is no reason to assume that the sample has quelated any metal, as was the case in ref 6. Although 15 years has elapsed since the synthesis of the sample, the ^{1}H NMR spectrum at 500 MHz did not show any sign of apparent decomposition of the porphine.

Porphyrin N-H Tautomerization

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Noteworthy, the two α-carbons in the spectra of H_2P run at -50 and -75 °C have different line widths (Figure 4D,E). The downfield signal is narrower ($\Delta\nu_{1/2}$ = 150 Hz) than the upfield one ($\Delta\nu_{1/2}$ = 250 Hz). This can be understood in terms of the dipolar coupling $^{13}C,^{14}N$. It has been shown that in the MAS experiment this coupling is not completely averaged to zero, and the residual interaction produces a splitting in the resonance of the ^{13}C bonded to the ^{14}N.[49] Recently, it was also shown[50] that a main contribution to the magnitude of this splitting has a (3 $\cos^2 \beta$ - 1) angular dependence, where β is the angle between the C-N internuclear vector and the z axis of the principal axis system of the ^{14}N electric field gradient (EFG) tensor. Some insight about the direction of the main axis of the EFG can be achieved by considering the electronic distribution at the ^{14}N nucleus. Since the ^{14}N s electrons are spherically symmetric, the quadrupole interaction will depend mainly on the lack of spherical distribution of p electrons.[51] This lack of symmetry is characterized by the ^{14}N lone pair of electrons, its direction coinciding with the main axis of the EFG tensor. While in the (1H) pyrrole-like rings the ^{14}N lone pair of electrons is perpendicular to the $C_\alpha NHC_\alpha$ plane (β = 90°); in the α-pyrrolenine-like rings they point toward the center of the macrocycle bisecting the $C_\alpha=NC_\alpha$ angle (β = 126°).[48a] Taking this into account, the residual splitting of the α-carbon in the former rings is expected to be larger than in the latter. This can be clearly seen in parts D and E of Figure 4 where although the splitting is masked by low resolution, it is preserved as a broadening in the C_α resonances. These arguments further confirm the proposed assignment of the downfield signal to the α-carbon of the α-pyrrolenine-like ring. The α-carbons signal in the 25-MHz spectrum of H_2P at room temperature does not exhibit this effect, presumably because in the fast-exchange limit the widths of the two coalesced lines are averaged and any residual dipolar coupling with ^{14}N becomes obscured by the natural line width of the H_2P resonances. The effects of the residual $^{13}C,^{14}N$ dipolar coupling are also absent in the 50-MHz solid-state spectra of the tetraalkylporphyrins (Figure 2) due to the inverse dependence of the splitting with the applied field.[50]

The ^{13}C CP/MAS NMR technique applied to porphyrins shows that the tautomeric behavior of H_2P is similar to that observed for symmetrically substituted porphyrins in solution. On the other hand, TMeP, TPrP, TBuP, and THeP show splittings in the pyrrole carbons that can be discussed in terms of the effects produced by crystal-packing forces on the kinetics of the N-H tautomerization process. Therefore, the usefulness of this technique for analyzing the dynamics of the hydrogen migration in porphyrin crystals is evident.

Discussion

Porphyrins provide an excellent model for studying the case of a two-proton-transfer reaction taking place within a rigid framework. Much discussion has been given on the mechanism of this rearrangement of tetraarylporphyrins in solution, where the two tautomers were found to be degenerate.[7-12] Recently, the possibility of studying these transfer reactions by dynamic NMR spectroscopy in the solid state revived the interest in this problem.[25,26] This technique can be used in conjunction with X-ray diffraction analysis to study the role of symmetry and substituents in the proton-exchange process. Furthermore, since the rate constants in the solid state may be completely altered by KSSE,[52] the understanding of the role played by crystal-packing forces may shed light on the nature of the mechanism of the reaction.

The solution kinetics of the hydrogen migration in free-base porphyrins have been interpreted in terms of transition-state theory $(TST)^{7-11}$ or as tunneling through a double-minimum potential.[12,14,18,53,54] A quantum mechanical model has also been proposed incorporating the effects of skeletal vibrations[16,17] that were predicted to contribute a considerable part of the observed activation energy.

The symmetry of tetrasubstituted porphyrins in solution has been a matter of controversy due to its central role in the tunneling model. Slight distortions of the porphyrin macrocycle from D_{4h} symmetry would appreciably decrease the contribution of tunneling to the rate of tautomerization,[15,55] since the symmetry of the double-minimum potential in which the hydrogens move would be broken. Hence, this tunneling model predicts for porphyrins whose macrocycles depart from this geometry in the solid a lowering in the rate of the proton-transfer process.

Insight into the importance of symmetry on the N-H tautomerism can be obtained from the dynamics of this process in H_2P. As mentioned above (see Results) activation parameters in solid H_2P are similar to those found for porphyrins in solution, which implies that KSSE, if present, are very small. Nevertheless, the X-ray diffraction analyses carried out on H_2P showed that its skeleton was devoid of D_{4h} symmetry.[6,48a] A similar lack of correlation between symmetry and the existence of a solution-like hydrogen migration in the solid was found when the solid-state ^{15}N CP/MAS NMR spectrum of TTP was examined.[25] While the hydrogen exchange in monoclinic TTP was similar to that found in the solution spectra of tetraarylporphyrins, its X-ray diffraction analysis showed that it only had $\bar{1}$ symmetry.[56]

As revealed in the *Results* (see Figure 1) TPrP and THeP undergo in solution a tautomerization process with normal kinetic parameters; that is, at room temperature the reaction was found to proceed fast on the NMR time scale. However, in all the tetraalkylporphyrins investigated, the CP/MAS ^{13}C NMR indicated that there were perturbations of the tautomeric equilibrium in the solid state induced by the crystal structure (Figure 2). This was a rather unexpected result in view of the following considerations regarding the nature of the hydrogen migration process:

(a) Solution ^1H NMR analyses of ^{15}N-labeled TPP[35,36] have shown that the proton-transfer reaction in free-base porphyrins is intramolecular rather than intermolecular. Since intermolecular contacts in the porphyrin crystals are limited to the alkyl substituents and to the peripheral atoms of the skeleton, these remote interactions should not affect the kinetics of a reaction taking place at the center of the macrocycle.

(b) As mentioned above, the symmetry of the porphyrin skeleton does not appear to play a critical role in the case of tautomerism. Therefore, although X-ray crystallographic studies have shown that in general free-base porphyrins do not possess D_{4h} symmetry,[57] no firm correlations has been yet established between this feature and the presence of KSSE.

(c) Tautomerization has been found to be independent of solvent, as well as of the electron-donating or -withdrawing propertis of the meso substituents.[10]

Considering these characteristics of the reaction, the solid-state NMR study reveals that the crystal lattice plays a subtle but relevant role in the kinetics of the proton-exchange process, whose understanding may clarify some of the factors involved in the nature of the migration mechanism. In general, solid-state effects will mainly manifest themselves by preventing translational motions and by freezing molecules in the crystal in a specific conformation. The influence of the former effect on the solid state kinetics may be neglected in the case under study due to the intramolecular nature of the reaction. When the influence of conformational effects on tautomeric behavior of porphyrins in the solid is analyzed, two possibilities can be advanced, depending on whether or not the hydrogen migration is assumed to be coupled to a skeletal rearrangement; a matter that has recently awakened much discussion.[58]

(49) (a) Opella, S. J.; Frey, M. H.; Cross, T. A. *J. Am. Chem. Soc.* **1979**, *101*, 5856. (b) Groombridge, C. J.; Harris, R. K.; Packer, K. J.; Say, B. J.; Tunner, S. F. *J. Chem. Soc., Chem. Commun.* **1980**, 174.

(50) Olivieri, A. C.; Frydman, L.; Diaz, L. E. *J. Magn. Reson.* **1987**, *75*, 50.

(51) See: Reference 34, p 136.

(52) Byrn, S. R. *Solid State Chemistry of Drugs*; Academic: New York, 1982; references therein.

(53) Hennig, J.; Limbach, H. H. *J. Am. Chem. Soc.* **1984**, *106*, 292.

(54) Limbach, H. H.; Hennig, J.; Stulz, J. *J. Chem. Phys.* **1983**, *78*, 5432.

(55) (a) Brickmann, J.; Zimmermann, H. *J. Chem. Phys.* **1969**, *50*, 1608. (b) de la Vega, J. R. *Acc. Chem. Res.* **1982**, *15*, 185.

(56) Butcher, R. J.; Jameson, G. B.; Storm, C. B. *J. Am. Chem. Soc.* **1985**, *107*, 2978.

(57) Tulinsky, A. *Ann. N.Y. Acad. Sci.* **1973**, *206*, 47.

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Table III. Cis and Trans Annular N–N Distances in the Solid State for the Porphyrins Analyzed by High-Resolution CP/MAS Techniques

	N–N dist, Å		soln-like
porphyrin	cis	trans	migration process
H_2P	2.89, 2.88[a] 2.89, 2.90	4.11, 4.06[a]	yes[b]
OEP	2.96, 2.92[c]	4.20, 4.05[c]	no[d]
triclinic TPP	2.92, 2.91[e]	4.20, 4.06[e]	no[f]
TTP	2.94, 2.89[g]	4.15, 4.08[g]	yes[f]
TPrP	2.92, 2.91[e]	4.16, 4.08[e]	no[b]

[a] Reference 48a. [b] Figure 2. [c] Reference 29. [d] Reference 28. [e] Reference 57. [f] Reference 26. [g] Reference 56.

If tautomerism requires a skeletal rearrangement, solid-state effects may be explained by assuming that the neighboring molecules in the lattice preclude the readjustment of the heavy atoms of the porphyrin. This hypothesis may be related to the quantum mechanical calculations performed by Sarai,[16,17] which showed that special attention should be given to the coupling between the proton-migration process and the conformational changes occurring in the porphyrin skeleton. According to a normal-mode analysis of TPP, a linear placement of the central hydrogens (hydrogens in opposite rings) reduces the symmetry of the macrocycle from D_{4h} to D_{2h} by a displacement along the B_{1g} normal coordinate. When the protons detach from one pair of nitrogens and attach to the other pair, the initial and final configurations become related by a 90° rotation about the main C_2-axis. When this model is applied to a molecule in the solid state, it is conceivable that intermolecular interactions stabilize one of these deformed structures over the other. It follows that unless the skeleton and the substituents have enough space to rearrange freely within the unit cell, the dynamics of the reaction will be affected. If tautomerism does not require a skeletal rearrangement, it can be assumed that even in solution where the porphyrin skeleton can freely rearrange, there is no coupling between proton migration and the vibrations of the heavy atoms. Hence, the freezing of the molecule in a special conformation upon crystallization may in principle allow the existence of a solution-like N–H tautomerization process. This was partially analyzed by Storm and co-workers[56] who suggested that the characteristics of the N–H tautomerism in the solid state are controlled by the fixed molecular conformation induced by crystal-packing forces. Attention was focused on the trans annular N–N separations, since in the solid a rhombic configuration of the nitrogen atoms may be brought about. Then, a short axis can arise in which the protons will fit only if this occurs without a corresponding increase in the H–H van der Waals repulsion energy. Also, cis annular N–N separations were proposed to be correlated to the presence or absence of the N–H tautomerism. In Table III cis and trans annular N–N distances are shown for all the porphyrins that have been analyzed by high-resolution solid-state NMR. In principle, no significant correlation is apparent between these data and the existence of a solution-like proton tautomerism in the solid state.

(58) (a) Sarai, A. *J. Chem. Phys.* **1984**, *80*, 5341. (b) Limbach, H. H. *J. Chem. Phys.* **1984**, *80*, 5343.

The separations of the nitrogen atoms are very similar in TPrP and TTP, even though they show different dynamical behavior. On the other hand, the arrangement of the four nitrogens is less symmetric in OEP than in H_2P, although the pyrrole carbons split in the former[28] (hindrance of the free hydrogen migration) but not in the latter.

Further theoretical and experimental work will be needed to ascertain which of these hypotheses best explains the nature of the molecular transformation in the porphyrin crystals.

Conclusion

The high-resolution solid-state ^{13}C NMR spectra of H_2P and of members of an homologous series of tetraalkylporphyrins (from tetramethyl to tetrahexyl) were obtained. All the tetraalkylporphyrins showed multiplicities in the signals from the pyrrole carbons. Although the possibility that the observed splittings arise from chemically equivalent nuclei in the isolated molecule that become crystallographically inequivalent in the lattice cannot be discarded, the magnitudes of the splittings suggest that their origin is related to perturbations of the tautomeric process **1a** ⇌ **1b** in the solid phase. If this is the case, the multiplicities can be explained on the basis of two different operating mechanisms. One involves the quenching of the N–H tautomerism while the other assumes an exchange process in the fast regime, which proceeds between two unequally populated tautomers. Both mechanisms reflect the existence of kinetic solid-state effects likely associated with crystal-packing forces. When the spectrum of H_2P was recorded at room temperature, it did not show any multiplicity in the pyrrole carbon signals. When recorded at lower temperatures, a coalescence process between two equally populated tautomers was observed, finally leading in the slow-exchange regime to two well-resolved resonances for the pyrrole α-carbons.

To elucidate the origins of the kinetic solid-state effects operating in the tetraalkylporphyrins, three different mechanisms are discussed. The first one suggests that as crystal forces break the D_{4h} macrocycle symmetry, the tunneling contribution to the migration process will be quenched. According to the second hypothesis, the existence of ordered or disordered protons can be related to the static geometry adopted by the four central nitrogens of the porphyrin. Finally, within the third model the explanation of the observed dynamical effects rests on the coupling between the proton migration and the skeletal deformations, which may be perturbed by neighboring molecules. In order to gain further information about the origin of the observed splittings, solution- and solid-state variable-temperature experiments coupled with theoretical calculations are currently being performed.

The results obtained in this paper with use of the solid-state CP/MAS technique for the analysis of the N–H tautomerism in porphyrins confirm the position that the data from this method offers a powerful complement to the information provided by X-ray crytallography on dynamical processes taking place in solids.