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^{1}H NMR Study on the Molecular Dynamics of Solid Porphine-d_2

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^{1}H pulsed NMR techniques were used to investigate the solid-state dynamics of porphine molecules in which the central protons have been replaced by deuterons. Changes observed in the line width of the ^{1}H NMR signal suggest that, as happened to be the case with the fully protonated derivative, molecules of deuterated porphine rotate in the crystal. Variable-temperature measurements of the proton relaxation times in the rotating frame provided the activation parameters for this motion, which were found to be slightly higher than those observed for the nondeuterated compound. This effect can be related to a combined motion that has been proposed for reconciling the CPMAS NMR and the X-ray results available for porphine, according to which the solid-state tautomerism of the central hydrogens might produce a reorientation of the molecules in the crystals about their main molecular axes. Upon replacement of the central protons by deuterons this model predicts that kinetic isotope effects known to characterize the N–H tautomerism of porphyrins will slow the rates of macrocycle reorientations in the crystal, a dynamic behavior which is reflected in the experimental results.

Introduction

Free-base porphyrins possess two central hydrogens that may bind to any of the four inner nitrogens in the molecule. Exchange among the different possible hydrogen arrangements results in a tautomeric process (Figure 1) which has been extensively studied by variable-temperature solution NMR.[1-8] According to these studies, exchange in symmetrically substituted porphyrins takes place in an effective double-minimum potential between two equally populated tautomers, at rates that are highly sensitive to the substitution of the inner protons by deuterons. High-resolution NMR studies on the tautomeric behavior of porphyrins have also been recently carried out in the solid state.[9-13] These analyses showed that crystal packing forces may perturb the equilibrium constant of the tautomerism, yielding exchange processes between nondegenerate states even in the case of symmetrically substituted molecules. It is possible to understand this difference between the solution and the solid-state behavior of N–H tautomerisms in terms of intermolecular packing interactions, which may stabilize one tautomeric structure of an exchanging porphyrin with respect to the other. In the case of two compounds however, porphine (**1**) and *meso*-tetratolylporphyrin, the hydrogen tautomerism was found to proceed between two equally populated states both in solution as well as in the solid state.[10-12] Whereas for the latter molecule solid-state NMR results agree with its reported crystal structure,[14] the X-ray analysis of **1** displays the central hydrogens localized on opposite pairs of pyrrolic rings and the macrocycle distorted towards the D_{2h}-like configuration that can be expected for a nonexchanging system.[15] These conflictive pictures that X-ray and NMR afford for **1** could be reconciled if the central hydrogens migration were coupled to 90° rotations of the molecules about their main symmetry axes (Figure 2). Similar cases involving coupled exchange and rotational processes have been observed in carboxylic acids[16] and were proposed to reconcile diffraction and NMR results in other exchanging solids such as tropolone[17] and bullvalene.[18] In the case of porphine, macrocycle rotations could be driven by crystal packing forces arising as a result of molecular distortions induced by the tautomerism. Whereas for most symmetric solid porphyrins these exchange-related differences in packing energies lead to the phenomenon of unequally populated tautomers, in **1** they would originate 90° rotations whose net effect is to restore the translational symmetry of the crystals observed in the X-ray analysis.

We have recently explored the presence of this combined exchange-rotational process in porphine **1a** using ^{1}H wide line and ^{13}C CPMAS variable-temperature NMR techniques.[19] According to the results obtained by these two methods, **1a** molecules rotate in the crystals with activation parameters that closely resemble those measured for the N–H tautomerism. If this rotation would be a consequence of distortions introduced by the hydrogen-exchange process, it can be expected that the kinetic isotope effect (KIE) that is known to affect the tautomerism of porphyrins[1-5] will also affect the rates of macrocycle rotations. In the present study, we discuss the presence of these effects in the N-deuterated porphine derivative **1b**. Solid-state ^{1}H NMR line widths of **1b** were measured at different temperatures, and the observed changes provided evidence for the presence of molecular rotations in the crystals. The dynamics of this process were characterized from the relaxation behavior observed for the proton NMR signal; its significance when compared with the results observed in **1a** is briefly discussed.

Experimental Section

NMR spectra were recorded at 100.06 MHz on a spectrometer based on a Varian V-7704 electromagnet (2.35 T) and Tecmag Inc. rf and data acquisition systems. The observation probe was a home-built system in which special precautions were taken to remove interferences from stray ^{1}H NMR signals. Temperatures were monitored using a thermocouple placed at the base of the irradiation coil and were controlled using a home-manufactured system possessing an accuracy of ±2 °C.

Porphine was synthesized following methods described in the literature.[20] Although deuteration of the central hydrogens was initially assayed by refluxing porphine in perdeuterated methanol, the solid product that could be isolated showed only a ca. 60% deuterium enrichment. Replacement of the central protons was finally accomplished by dissolving batches of **1a** in a mixture of $CDCl_3$–CD_3OD and heating them during 1 week at 100 °C in a sealed flask. Usually three runs were enough for achieving a (92 ± 3)% isotopic enrichment of the labile hydrogens in the sample, as judged by comparing the IR spectra of **1a** and **1b**. Although this degree of enrichment renders negligible the amount of porphine-H_2 present in the deuterated sample, it predicts the presence of ca. 16% of the HD derivative. Nevertheless, the relevance of this contaminant on the results discussed in the present study can be neglected in view of its small concentration and of the very similar rates that for the range of studied temperatures characterizes the tautomerism of the HD and of the D_2 derivatives.[5]

Results and Discussion

Figure 3 presents the changes observed in the line width of the **1b** ^{1}H NMR signal as a function of temperature. The behavior displayed by the ^{1}H resonance of this derivative is qualitatively similar to that observed in **1a**,[19] although in the deuterated compound the absence of central protons removes one of the main contributions to the overall signal broadening. In principle, the line width observed for deuterated porphine in the low-temperature limit could be estimated from the crystal structure of the com-

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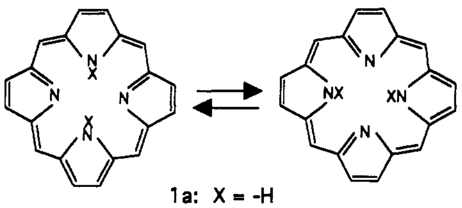

1a: X = -H
1b: X = -D

Figure 1. Scheme of the central hydrogen tautomerism in porphine.

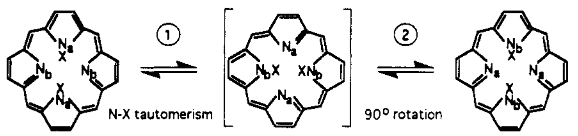

Figure 2. Possible rearrangements of porphine molecules in the crystal. The different pictures that X-ray and CPMAS NMR present for porphine can be reconciled if the hydrogen tautomerism (process 1) were coupled to 90° rotations of the molecules (process 2) that restore the initial arrangement of molecules in the crystal. Pairs of opposite nitrogens were labeled (a, b) in order to help visualize the net effects of the rearrangement.

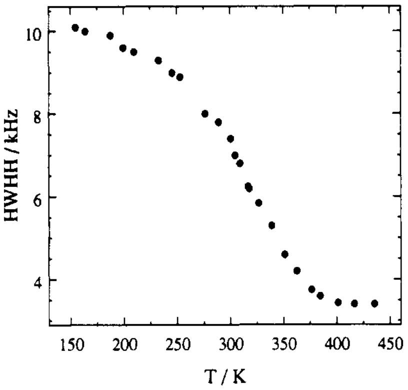

Figure 3. Variations observed in the half-width at half-height (hwhh) of the **1b** ^{1}H NMR resonance as a function of temperature. Each point was obtained by acquiring 32 phase-cycled scans on a vacuum-sealed sample.

pound using Van Vleck's equation for the second moment M_2 of the signal averaged over all possible orientations:[21]

$$M_2 = {}^3\!/_5\gamma_I{}^4h^2I(I+1)N_I{}^{-1}\sum_{\mathrm{II},\, i\neq j} r_{ij}{}^{-6} + {}^4\!/_{15}\gamma_I{}^2\gamma_S{}^2h^2S(S+1)N_S{}^{-1}\sum_{\mathrm{IS},\, i\neq j} r_{ij}{}^{-6} \quad (1)$$

In this equation the first term represents the contribution of the proton–proton dipolar couplings, the second term is the contribution of the proton–nitrogen and proton–deuteron dipolar couplings, and the sums run over all the relevant nuclei. Although the crystal structure necessary for evaluating this expression is to our knowledge not available, an estimation of the **1b** line width at low temperatures can be made from the reported X-ray structure of **1a**.[15] When applied to a hypothetical arrangement in which the central protons of this structure have been replaced by deuterons, eq 1 predicts a signal whose half-width at half-height (hwhh) is 12.4 kHz, close to the observed value of 10.2 kHz. The fact that the line width of the **1b** signal decreases as temperatures increase indicates the presence of a dynamic process in the crystal. Since in the labeled sample the central hydrogens contribution to the total line width is negligible the significant narrowing observed in the **1b** resonance can be ascribed only to the presence of an overall molecular motion, most likely a 90° jump of the molecules about their main axes of symmetry. In this case, an average over the motion of eq 1[22] and the molecular structure reported for **1a** predicts for the ^{1}H NMR resonance of the deuterated derivative at high temperatures a hwhh of 4.3 kHz, in good agreement with the observed value of 3.4 kHz.

To obtain the activation energy of the motion involved in the line-narrowing process shown in Figure 3, ^{1}H spin-lattice relaxation times in the rotating frame ($T_{1\rho}$) were measured for **1b** at different temperatures. This relaxation time is particularly useful for measuring slow motions like those taking place in porphine, as its time scale is given by the frequencies associated to the H_1 fields applied to spin-lock the magnetization:[23]

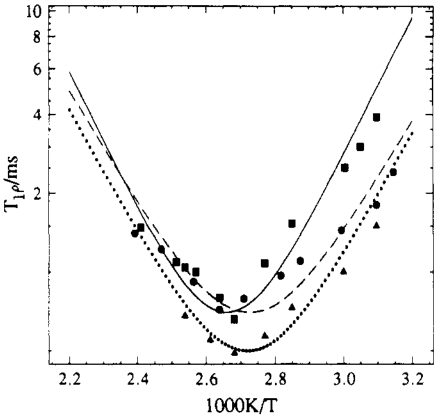

Figure 4. Temperature dependence of the ^{1}H relaxation times $T_{1\rho}$ in **1b** for γH_1 = 50 (■), 40 (●), and 35 kHz (▲). The lines represent the best fit of the experimental data and yield the Arrhenius equation for the correlation times τ (—) = $2 \times 10^{-12}e^{6000/T}$, τ (- -) = $1 \times 10^{-11}e^{5000/T}$, and τ (···) = $5 \times 10^{-12}e^{5400/T}$ (in descending order of γH_1 strength). Relaxation times were measured acquiring eight phase-cycled scans on a sealed **1b** sample using a 60-s repetition delay; 9 W of rf power were used for performing the γH_1 = 50 kHz experiment.

$$T_{1\rho}{}^{-1} = C[{}^5\!/_2\tau_c/(1+\omega_0{}^2\tau_c{}^2) + \tau_c/(1+4\omega_0{}^2\tau_c{}^2) + {}^3\!/_2\tau_c/(1+4\omega_1{}^2\tau_c{}^2)] \quad (2)$$

where $\omega_0 = \gamma H_0$ is the Larmor frequency of the protons $\omega_1 = \gamma H_1$, and τ_c is the correlation time of the reorientation at each temperature. Figure 4 presents the inverse temperature dependence of $T_{1\rho}$ times in deuterated porphine, measured for different H_1 fields. Assuming an Arrhenius-type behavior for the correlation times, a best fit of the experimental data allows one to obtain a preexponential factor $\tau_0 = (6 \pm 4) \times 10^{-12}$ s and an activation energy $E_a = 11.0 \pm 1$ kcal/mol characterizing the rotational process of porphine **1b** molecules.

When comparing these results with those obtained for the **1a** derivative,[19] it can be observed that upon replacing the central protons of porphine by deuterons there is an increase of ca. 2 kcal/mol in the activation energy and an overall decrease in the rates of the macrocycle motion. Although the origins of this kinetic effect cannot yet be unambiguously ascertained, it is possible to correlate them with similar KIE observed for the hydrogen tautomerism of porphyrins. For the best known of these systems, the substituted tetraphenylporphyrins, solution NMR analyses have shown that upon deuteration the activation energies of the tautomerism increase between 1.4 and 3.5 kcal/mol.[3,5] CPMAS NMR studied also revealed a nearly identical isotope effect in the degenerate case of solid tetratolylporphyrin.[10] Since it is very likely that in solid porphine the KIE of the N–H tautomerism will be very similar, the different rates of molecular rotations observed for the H_2 and for the D_2 derivatives of **1** strongly favor the presence of a coupled exchange-rotational dynamic process similar to that sketched in Figure 2.

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Registry No. 1-d_2, 57991-44-3.

References and Notes

(1) Storm, C. B.; Teklu, Y. J. *J. Am. Chem. Soc.* **1972**, *94*, 1745.
(2) Abraham, R. J.; Hawkes, G.; Smith, K. *Tetrahedron Lett.* **1974**, 1483.
(3) Eaton, S. S.; Eaton, G. R. *J. Am. Chem. Soc.* **1977**, *99*, 1601.
(4) Gust, D.; Roberts, J. D. *J. Am. Chem. Soc.* **1977**, *99*, 3637.

(5) Limbach, H.-H.; Hennig, J.; Gerritzen, D.; Rumpel, H. *Faraday Discuss. Chem. Soc.* **1982**, *74*, 229.
(6) Hennig, J.; Limbach, H.-H. *J. Am. Chem. Soc.* **1984**, *106*, 292.
(7) Stilbs, P. *J. Magn. Reson.* **1984**, *58*, 152.
(8) Crossley, M. J.; Field, L. D.; Harding, M. M.; Sternhell, S. J. *J. Am. Chem. Soc.* **1987**, *109*, 2335.
(9) Okazaki, M.; McDowell, C. A. *J. Am. Chem. Soc.* **1984**, *106*, 3185.
(10) Limbach, H.-H.; Hennig, J.; Kendrick, R.; Yannoni, C. S. *J. Am. Chem. Soc.* **1984**, *106*, 4059.
(11) Wehrle, B.; Limbach, H.-H.; Kocher, M.; Ermer, O.; Vogel, E. *Angew. Chem.* **1987**, *26*, 934.
(12) Frydman, L.; Olivieri, A. C.; Diaz, L. E.; Frydman, B.; Morin, F. G.; Mayne, C. L.; Grant, D. M.; Adler, A. D. *J. Am. Chem. Soc.* **1988**, *110*, 336.
(13) Frydman, L.; Olivieri, A. C.; Diaz, L. E.; Valasinas, A.; Frydman, B. *J. Am. Chem. Soc.* **1988**, *110*, 5651.
(14) Butcher, R. J.; Jameson, G. B.; Storm, C. B. *J. Am. Chem. Soc.* **1985**, *107*, 2978.
(15) Chen, B. M. L.; Tulinsky, A. *J. Am. Chem. Soc.* **1972**, *94*, 4144.
(16) Scheubel, W.; Zimmerman, H.; Haeberlen, U. *J. Magn. Reson.* **1988**, *80*, 401.
(17) Szeverenyi, N. M.; Bax, A.; Maciel, G. E. *J. Am. Chem. Soc.* **1983**, *105*, 2579.
(18) Meier, B. H.; Earl, W. L. *J. Am. Chem. Soc.* **1985**, *107*, 5553.
(19) Frydman, L.; Olivieri, A. C.; Diaz, L. E.; Frydman, B.; Kustanovich, I.; Vega, S. *J. Am. Chem. Soc.* **1989**, *111*, 7001.
(20) Beytchman, S. D. Ph.D. Dissertation, University of Pennsylvania, 1966.
(21) Van Vleck, J. H. *Phys. Rev.* **1948**, *74*, 1168.
(22) Gutowsky, H. S.; Pake, G. E. *J. Chem. Phys.* **1950**, *18*, 162.
(23) Cook, D. C., Lowe, I. J. *J. Chem. Phys.* **1966**, *44*, 2995.

Molecular Dynamics Simulations and Experimental Studies of the Formation of Endohedral Complexes of Buckminsterfullerene

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The formation of endohedral $C_{60}He^+$ complexes in mass spectrometric experiments in which C_{60}^+ collides with He at kiloelectronvolt energies has been modeled with molecular dynamics simulations. Experimental results have shown that the collision energy at which the greatest abundance of $C_{60}He^+$ is observed is 5000 eV, while molecular dynamics simulations predict that optimal complex formation should occur in 8000-eV collisions. When the effects of the experimentally observed unimolecular decomposition of the internally excited $C_{60}He^+$ complex are considered, however, there is relatively good agreement between the predictions of the simulations and the experimental results. The simulations provide a detailed picture of the trapping process and show that low-energy collisions with low impact parameters and high-energy collisions with high impact parameters are most likely to result in formation of $C_{60}He^+$. The molecular dynamics simulations also provide insight into inelastic scattering processes observed in the mass spectrometric experiments; the results are consistent with an impulsive collision in which momentum transfer occurs between He and an isolated portion of C_{60}^+, as predicted by the simulations.

Introduction

C_{60}, also known as buckminsterfullerene, has been the subject of numerous theoretical and experimental investigations from the time its structure was originally proposed.[1] With the development of a technique by which it can be synthesized in bulk quantities,[2] the number of investigations of C_{60} has increased significantly. Its truncated icosahedral structure and many of its properties have been elucidated with a variety of experimental techniques.[3-6] In addition, various theoretical methods, including molecular dynamics simulations, have been used to gain insight into the behavior of this molecule.[7-10] As a result, C_{60} presents an unusual case in which theoretical predictions and experimental observations have come almost simultaneously, with each guiding the other to some extent.

Among the physical techniques used to study C_{60}, mass spectrometry has been used in several investigations.[11-14] In addition to providing analytical information about the fullerenes, various mass spectrometric techniques have been used to characterize the stability and structures of the fullerenes and their derivatives. In early experiments, Smalley and co-workers[11] used mass spectrometric detection of the photodissociation products of C_{60} to determine that successive C_2 loss is the dominant fragmentation channel and that the activation energy for this process is high (>18 eV on the microsecond time scale). Additionally, high-energy collisions between C_{60} and target gases, combined with tandem mass spectrometry techniques, have been used to characterize the fragmentation behavior of the fullerenes.[13,14] More recently, attention has been focused on the mass spectrometric characterization of endohedral complexes of C_{60}. In 1986, Smalley and co-workers presented evidence for the existence of a gas-phase La@C_{60} endohedral complex (where the @ symbol indicates that the La atom is inside the cage).[15] Additionally, the synthesis of a La@C_{82} complex in milligram quantities has now been reported.[16] Recent theoretical studies have considered the structure, stability, and properties of endohedral complexes.[17-20]

Evidence that C_{60} can form endohedral complexes has also come from other sources. Recent studies by Schwarz and co-workers showed that C_nHe^+ fragments (n = 46, 48, 50, 52, 54, 56, 58) are formed by high-energy collisions (8 keV) between C_{60}^+ and He.[21] These investigators postulated that an endohedral complex (in which He was inside the fullerene cage) gave rise to these fragments, and they also noted that similar results were observed when Ne was used as a target gas. A subsequent study in our laboratory unambiguously demonstrated the formation of the HeC_{60}^+ complex.[22] Additionally, the $C_{60}He^+$ complex was formed and subsequently allowed to undergo 200-eV collisions with Xe (under multiple-collision conditions). Under these conditions the $C_{60}He^+$ complex remained intact, strongly supporting Schwarz's hypothesis that He was inside the fullerene (He@C_{60}).[22] Studies by Gross and co-workers have shown that $C_{60}D_2^+$, $C_{60}Ne^+$, and $C_{59}Ar^+$ complexes can be formed in high-energy collisions.[23] The Schwarz group has also shown that He and Ne are taken up in collisions with doubly- and triply-charged fullerenes.[24-26] A recent study by Gross and co-workers has considered the formation of endohedral complexes of fullerenes in detail; they have also observed that C_{70} can actually take up two He atoms under multiple-collision conditions.[27] These investigators also established that all of the major fragments (both He-containing and non-He-containing fragments) arose from a fullerene–He complex and showed that inelastic scattering of the target gas accounts for the appearance of a "foot" in the collision spectrum.[27]

The formation of complexes by which a target gas atom is taken up in a high-energy collision with a projectile is unprecedented in mass spectrometric experiments. Some details regarding the mechanism of this process can be inferred from the mass spectral data, but it is difficult to generate a detailed picture at the mo-