

# Monodeprotonated Free Base Porphyrin

Torgil Vangberg and Abhik Ghosh\*

Department of Chemistry, Institute of Mathematical and Physical Sciences (IMR), University of Tromsø, N-9037 Tromsø, Norway

Received: October 31, 1996; In Final Form: December 16, 1996<sup>®</sup>

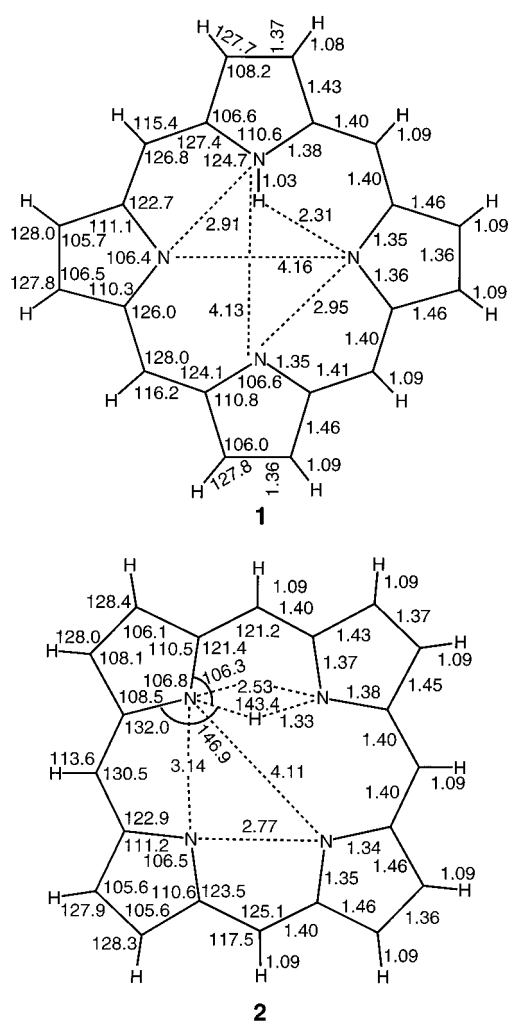
Using nonlocal density functional theory and extended basis sets, full geometry optimizations have been performed on two stationary points on the potential energy surface of monodeprotonated porphine, viz. the ground state and the transition state for NH tautomerism. The transition state is calculated to be approximately 11.84 kcal/mol above the ground state. The porphyrin framework deforms considerably along the reaction pathway of the proton transfer, with the internal angles of the central C<sub>12</sub>N<sub>4</sub> macrocycle undergoing the maximum changes.

Many investigations have aimed at achieving a better understanding of the dynamics of NH tautomerism in free base porphyrins.<sup>1</sup> This process has long served as a prototype for double proton transfer reactions. A detailed understanding of this process is also a prerequisite for understanding the mechanism of metal insertion into the porphyrin macrocycle. To complement the efforts of experimentalists, we have started to explore this area with modern first-principles quantum chemical methods. This has proven to be a fruitful endeavor, with theory furnishing unique and detailed information that may be difficult or impossible to obtain from experiment.<sup>2</sup>

Recently, monodeprotonated porphine (PH<sup>−</sup>) has been prepared and spectroscopically and kinetically characterized.<sup>3</sup> At ca. 152 K, the proton NMR spectrum of PH<sup>−</sup> is consistent with a maximum molecular symmetry of C<sub>2v</sub> indicating a central proton which is static or migrating slowly on the NMR time scale.<sup>3</sup> Fast proton transfer sets in at ca. 200 K, and the NMR spectrum is consistent with time-averaged D<sub>4h</sub> symmetry.<sup>3</sup> PH<sup>−</sup> is of interest not only as a new system exhibiting degenerate proton transfer but also for its potential relevance to other areas of porphyrin chemistry and biochemistry. We present here the results of an initial theoretical exploration of this system.

Using gradient-corrected or nonlocal density functional theory (NLDFT), we have performed full geometry optimizations of the ground state (**1**) and the proton transfer transition state (**2**) of PH<sup>−</sup> (Figure 1). All calculations were performed with the ADF program<sup>4</sup> using the Vosko–Wilk–Nusair (VWN)<sup>5</sup> local exchange–correlation functional, either Perdew–Wang 1991 (PW91)<sup>6</sup> or Becke<sup>7</sup>–Perdew<sup>8</sup> (BP) nonlocal functionals, Slater-type triple- $\zeta$  plus double polarization (TZDP) basis sets,<sup>4</sup> and a fine mesh for numerical integrations. Both **1** and **2** have C<sub>2v</sub> symmetry. This considerably simplified the task of geometry optimization of the transition state **2**, since this could be performed with the usual procedure for locating a minimum and a symmetry constraint that forces the migrating proton to maintain equal distances to the two nitrogens to which it is partially bonded. Accordingly, we used C<sub>2v</sub> symmetry constraints in optimizations of both **1** and **2**. All calculations were frozen-core and spin-restricted.

Our choice of NLDFT was based on the following considerations. At the Hartree–Fock level, the minima of porphyrin potential energy surfaces correspond to frozen resonance forms with alternating single and double bonds.<sup>9</sup> Simple schemes of electron correlation such as second-order Møller–Plesset per-



**Figure 1.** NLDFT(PW91)/TZDP optimized internuclear distances and angles in **1** and **2**.

turbation theory (MP2) and density functional theories with local or nonlocal exchange–correlation functionals can correct this problem and lead to realistic delocalized structures.<sup>9</sup> However, optimizations using traditional *ab initio* correlated theories and a good basis set are somewhat impractical for molecules of this size. Also, local density functional (LDF) theory<sup>10</sup> is known to be generally unsuitable for calculations of transition states with stretched, semibroken, or semiformed bonds such as the

<sup>®</sup> Abstract published in *Advance ACS Abstracts*, February 1, 1997.

N–H bonds in **2**. Thus, NLDFT was the logical and pragmatic choice for this investigation.

At the VWN-PW91/TZDP and VWN-BP/TZDP levels, **2** is higher than **1** by 11.84 and 11.96 kcal/mol, respectively. From limited MP2/DZP optimizations, the analogous barrier for the *trans*-to-*cis* tautomerism of free base porphine (PH<sub>2</sub>) was estimated to be 16.7 kcal/mol.<sup>2b</sup> Assuming that both levels of theory yield comparable thermochemical data, one may conclude that the activation energy for proton transfer in PH<sup>−</sup> is significantly lower than that in PH<sub>2</sub>. Although an experimental activation energy is not yet available, our calculated results are in qualitative agreement with the experimental finding that proton transfer is significantly faster and occurs at lower temperatures in PH<sup>−</sup> than in PH<sub>2</sub>. However, so far, we have not calculated zero-point energy corrections nor taken proton tunneling into account. These will be addressed in a future paper on the subject. Overall, the high quality of the functionals and basis sets used and the excellent agreement between the energetics results calculated with the two functionals suggest that the calculated results should be reliable.

Aside from the activation energy, the principal interest in the present calculations lies in the insights they provide into the structural changes in the porphyrin skeleton that accompany proton migration. Figure 1 shows the optimized internuclear distances in **1** and **2**. The notable points about the structures are as follows.

To put the optimized structures in perspective, it is useful to first point out the features they have in common with typical free base porphyrins and metalloporphyrins. Thus, the order of bond lengths in the PH<sup>−</sup> molecule is essentially the same as in PH<sub>2</sub>.<sup>6</sup> The C<sub>α</sub>–C<sub>β</sub> bonds are the longest (1.43–1.46 Å), and these are followed by the sequence C<sub>α</sub>–C<sub>meso</sub> (1.40–1.41 Å) > C<sub>β</sub>–C<sub>β</sub> ≈ C<sub>α</sub>–N (1.35–1.38 Å). The C<sub>α</sub>–N–C<sub>α</sub> angle in the pyrrole ring with the protonated nitrogen (110.6°) in **1** is significantly larger than the corresponding angles in the other pyrrole rings which do not have protonated nitrogens. The N–C<sub>α</sub>–C<sub>β</sub> angles in the three N-unprotonated pyrrole rings of **1** (110.3–111.1°) are significantly larger than the corresponding angles in the N-protonated pyrrole ring. These too are characteristic features of free base porphyrin structures. Finally, the distances between opposite nitrogens in **1** are nearly equal at 4.13 and 4.16 Å. In this respect, the geometry of **1** is intermediate between D<sub>2h</sub> PH<sub>2</sub> and a D<sub>4h</sub> metalloporphyrin.

The structural peculiarities of **2** can be largely ascribed to the migrating proton. The partial N–H bonds in **2** are stretched to 1.33 Å, with the N–H–N angle being 143.4°. The two nitrogens bridged by the migrating proton are separated by only 2.53 Å. This may be compared to a distance of 2.77 Å between the other two nitrogens in **2**, a distance of 3.14 Å between one of the semiprotonated nitrogens and the nearest unprotonated nitrogen in **2**, and a distance of 2.91 Å between the protonated nitrogen and a neighboring unprotonated nitrogen in **1**.<sup>11</sup> These data imply that the N<sub>4</sub> core of **2** has a distinctly trapezoidal (or roughly rectangular) shape in contrast to the nearly square N<sub>4</sub> core of **1**. The molecular framework of **2** is compressed in a direction perpendicular to the C<sub>2</sub> axis and elongated along the C<sub>2</sub> axis. Additional manifestations of this effect are in various

bond angles of the central C<sub>12</sub>N<sub>4</sub> ring of **2**. Thus, the C<sub>α</sub>–C<sub>meso</sub>–C<sub>α</sub> angles that are bisected by the C<sub>2</sub> axis of **2** (121.2 and 125.1°) are significantly smaller than the two other C<sub>α</sub>–C<sub>meso</sub>–C<sub>α</sub> angles (each 130.5°) in the molecule. Note also the wide variations in the N–C<sub>α</sub>–C<sub>meso</sub> angles. In these respects, the structure of transition state **2** is reminiscent of the structures of *cis*-porphyrin,<sup>2a</sup> the intermediate in the double proton migration in free base porphyrins, and *cis*-isobacteriochlorin,<sup>12</sup> both of which are C<sub>2v</sub>-symmetric species. Overall, the migrating proton affects the porphyrin framework structure chiefly by deforming the internal bond angles of the central C<sub>12</sub>N<sub>4</sub> macrocycle. The C<sub>α</sub>–C<sub>meso</sub> bond lengths are essentially unchanged between **1** and **2**.

A brief comment is warranted on the geometry of the pyrrole rings in **2**. In contrast to **1**, all the pyrrole rings in **2** are very similar in terms of their bond angles. The C<sub>α</sub>–N bonds (1.37–1.38 Å) adjacent to the partial N–H bonds in **2** are significantly longer than the other C<sub>α</sub>–N bonds (1.34–1.35 Å) in the molecule. This may be a consequence of structural strain brought about by the migrating proton.

In conclusion, using high-quality quantum chemical calculations we have structurally characterized the ground state and the proton transfer transition state structures of monodeprotonated free base porphine. The calculated activation energy of 11.8 kcal/mol is in qualitative accord with experimental results on PH<sup>−</sup> and PH<sub>2</sub>.<sup>1,3</sup> Future work will focus on providing a detailed description of the dynamics of the NH tautomerism.

## References and Notes

- (1) Braun, J.; Limbach, H. H.; Williams, P. G.; Morimoto, H.; Wemmer, D. E. *J. Am. Chem. Soc.* **1996**, *118*, 7231 and references therein.
- (2) (a) Ghosh, A.; Almlöf, J. *J. Phys. Chem.* **1995**, *99*, 1073. (b) Reimer, J. R.; Lü, T. X.; Crossley, M. J.; Hush, N. S. *J. Am. Chem. Soc.* **1995**, *117*, 2855.
- (3) Braun, J.; Hasenfratz, C.; Schwesinger, R.; Limbach, H. H. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2215.
- (4) The ADF program is sold by: Scientific Computing and Modelling, Department of Theoretical Chemistry, Vrije Universiteit, 1081 HV Amsterdam, The Netherlands. Details of the program, basis sets, and computational details are given in the ADF manual available from the above source.
- (5) Vosko, S. H.; Wilk, L.; Nusair, M. *Can. J. Phys.* **1980**, *58*, 1200.
- (6) Perdew, J. P.; Chevary, J. A.; Vosko, S. H.; Jackson, K. A.; Pederson, M. R.; Singh, D. J.; Fiolhais, C. *Phys. Rev. B* **1992**, *46*, 6671.
- (7) Becke's nonlocal exchange functional: Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098.
- (8) Perdew, J. P. *Phys. Rev. B* **1986**, *33*, 8822.
- (9) Almlöf, J.; Fischer, T. H.; Gassman, P. G.; Ghosh, A.; Häser, M. *J. Phys. Chem.* **1993**, *97*, 10964.
- (10) LDF theory has performed extremely well in a variety of other calculations on porphyrins that did not involve transition states: Ghosh, A.; Almlöf, J.; Que, L., Jr. *J. Phys. Chem.* **1994**, *98*, 5576. (b) Ghosh, A. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1028; *Angew. Chem.* **1995**, *107*, 1117. (c) Kalsbeck, W. A.; Ghosh, A.; Pandey, R. K.; Smith, K. M.; Bocian, D. F. *J. Am. Chem. Soc.* **1995**, *117*, 10959. (d) Ghosh, A.; Almlöf, J.; Que, L., Jr. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 770; *Angew. Chem.* **1996**, *108*, 846. (e) Ghosh, A.; Bocian, D. F. *J. Phys. Chem.* **1996**, *100*, 6363. (f) Ghosh, A. *J. Am. Chem. Soc.* **1995**, *117*, 4691. (g) Ghosh, A. *J. Mol. Struct.: THEOCHEM* **1996**, *388*, 359. (h) Ghosh, A.; Jynge, K. *Chem. Eur. J.*, in press.
- (11) For experimental evidence of analogous structural changes involving N–H...N hydrogen bonds have been observed for other tautomerizing systems: (a) Scherer, G.; Limbach, H. H. *J. Am. Chem. Soc.* **1994**, *116*, 1230. (b) Scherer, G.; Limbach, H. H. *Croat. Chem. Acta* **1994**, *67*, 431.
- (12) Ghosh, A. *J. Phys. Chem.*, in press.