

TWO DISTINCT DYNAMIC PROCESSES IN NON-PLANAR TETRABENZOPORPHYRIN

Ru-Jen Cheng*, Yu-Ren Chen, and Chun-Chang Chen

Department of Chemistry, National Chung-Hsing University,
Taichung, Taiwan 402, Republic of China

Abstract----- Two distinct dynamic processes including N-H tautomerism and porphyrin ring inversion have been established through variable-temperature ^1H nmr spectroscopy and isotope effect analysis in *meso*-tetraphenyltetrabenzoporphyrin consistent with the non-planar nature of the macrocycle from previous structural result.

Previous single crystal X-ray structure determination of a five-coordinate zinc tetrabenzoporphyrin, (tetrahydrofuran)(*meso*-tetraphenyltetrabenzoporphyrin)Zn(II) (TPTBPZn(THF)), has confirmed the molecule to be severely non-planar and assume saddle shape.¹ The consequences of saddle deformation on the properties of the non-planar tetrabenzoporphyrin are significant. As reported previously the cumulative effects of conformational changes and substituent addition are reflected in the red-shifted optical spectrum, diminished fluorescence, increased basicity² and ease of oxidation of the neutral compound, and in a shift of unpaired spin density from a_{1u} (TBPZn) to a_{2u} (TPTBPZn) character in the cation radical.³ Fajer believes that conformational variations provide an attractively simple mechanism for varying a wide range of chemical and physical properties of porphyrinic chromophores and prosthetic groups *in vitro* and *in vivo*.⁴ Our main interest about TPTBP system is the coordination chemistry in solution. It's a common practice to ask that whether the molecule remain the same conformation both in solution and in the crystals. Nmr is a sensitive technique to study the structure of molecules in solution⁵

^1H Nmr spectra of TPTBPZn, TPTBPH₂, and TPTBPH₄²⁺ are shown in Figure 1. Other than the shifts of the peaks due to phenyl protons, patterns of α , β -resonances are totally different between them. The spectra differences between TPTBPZn and TPTBPH₄²⁺ could be ascribed to the conformation difference. It has been noticed that as the result of the steric hindrance and possibly the electrostatic repulsion of the four hydrogen atoms at the center of the porphyrin ring, porphyrin diacids tend to be severely deformed into saddle shape.⁶

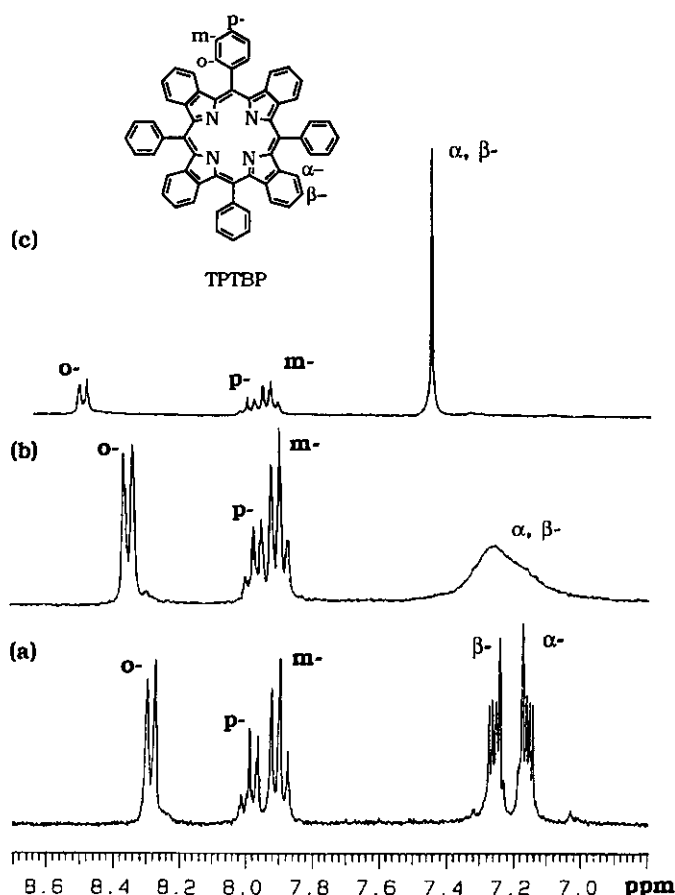


Figure 1. 300 MHz ^1H Nmr spectra of (a) TPTBPZn, (b) TPTBPH₂, and (c) TPTBPH₄²⁺ in CD_2Cl_2 .

This conformation difference will change the ring current effects both from tetrabenzoporphyrin macrocycle and the phenyl substituent experienced by α , β -protons, and makes the original AA'XX' pattern observed in TPTBPZn coalescence into one in TPTBPH₄²⁺. Because of the deshielding effect from the macrocycle and the shielding effect from the phenyl substituent, it is hard to predict whether α -H or β -H of TPTBPZn will absorb at higher field. But according to our NOE difference experiment, the high field multiplet obtained larger enhancement from saturation of the o-H and has been assigned as α -H. In the case of TPTBPH₂, α , β -

region shows a broad unsymmetric band. This must be related to the N-H tautomerism.

Temperature dependence ^1H nmr spectra of TPTBPH₂/ CD_2Cl_2 with addition of CH_3OH ⁷ between 35°C--90°C are shown in Figure 2(a). Upon cooling, the broad band finally separated into four sets of peaks at -90°C, corresponding to α , β -protons of isoindole rings with and without a proton on the nitrogen. This peak growing process actually can be divided into two stages. First is the separation of the right and left bands at --10°C (the right band grows as two separate peaks). Second is the splitting of the left two peaks at --40°C. Similar two-stage temperature dependence spectroscopic change is even more pronounced in the solvent system of THF-d₈ as shown in Figure 2(c). These two stages seem to suggest that there may be another dynamic process involved other than N-H tautomerism in the temperature range we studied.

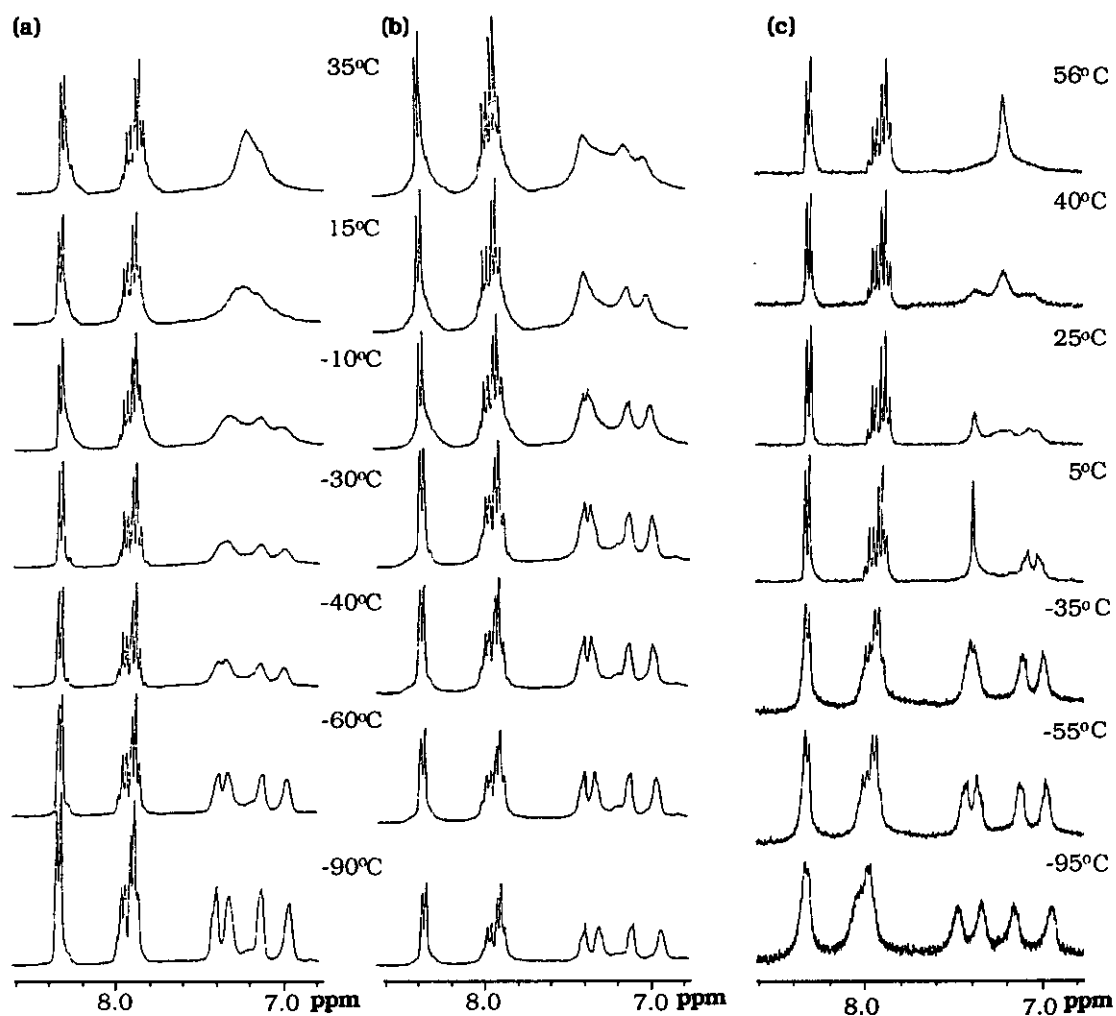


Figure 2. 300 MHz ^1H Nmr variable temperature spectra of TPTBPH₂ (a) in $\text{CD}_2\text{Cl}_2/\text{CH}_3\text{OH}$, (b) in $\text{CD}_2\text{Cl}_2/\text{CD}_3\text{OD}$, and (c) in THF-d_8 .

Isotope effect on N-H tautomerism has been studied previously for TPP system.⁸ Upon deuteration, the coalescence temperature is about 40°C higher for N-D tautomerism. We apply the same method to TPTBPH₂. By addition of CD_3OD instead of CH_3OH to CD_2Cl_2 solution, the variable-temperature spectra (Figure 2(b)) show clear differences. At 35°C, the right and left bands already separate and results in ~45°C isotope effect. The left two peaks split at ~-30°C, an isotope effect between 10~20°C is observed. Presumably, if the temperature dependence phenomenon is caused by a single dynamic process, the observed isotope effect

should parallel each other completely. This result is consistent with our previous expectation that there are two different dynamic processes involved. THF system did not offer any further information. Presumably, due to the hydrogen-bonding between CD₃OD and THF, addition of CD₃OD to THF solution of TPTBPH₂ did not show significant difference from Figure 2(c) upon cooling.

Based on the difference of the isotope effects, the first stage is assigned to N-H tautomerism with primary isotope influence, while the second stage is considered to be the conformation change or inversion of the saddle-shaped macrocycle with secondary isotope influence. Similar porphyrin ring inversion has been applied to explain the variable-temperature nmr results of Zn(II) octaethyltetraphenylporphyrinate⁹ and Ni(II) octaethylpyrrocorphinate¹⁰ both with saddle-shaped macrocycles.

Other than N-H tautomerism and ring inversion, there is one more dynamic process involved in TPTBPH₂ system. Free rotation of phenyl substituents is sterically prohibited,¹¹ but rocking between two extremes should still be feasible even at -90°C. Without this rocking motion, the ortho and meta phenyl protons should split into two doublets and two triplets, respectively, when N-H (or N-D) tautomerism and ring inversion are slow on the nmr time scale. This is not the case in Figure 2.

Although it's almost trivial to invoke ring inversion for a non-planar macrocycle, pattern of the temperature dependence spectroscopic changes observed here is novel. Most other related variable-temperature nmr phenomena are caused by the diastereotopic nature of the β-pyrrole substituents. At the first glance, the symmetry of TPTBPH₂ system seems to preclude similar conclusion. But the conformation-sensitive ring current effect experienced by α, β-protons (Figure 1) offers a unique probe for this system. Although the nature of the spectra prohibit further quantitative discussion at this stage, a preliminary account of these dynamic processes is noteworthy.

ACKNOWLEDGMENTS

This work was supported by National Science Council of Republic of China, Grant no. NSC78-0208-M005-15.

REFERENCES

1. R.-J. Cheng, Y.-R. Chen, S. L. Wang, and C. Y. Cheng, *Polyhedron*, 1993, 12, 1353.
2. R.-J. Cheng, Y.-R. Chen, and C.-E. Chuang, *Heterocycles*, 1992, 34, 1.
3. M. W. Renner, R.-J. Cheng, C. K. Chang, and J. Fajer, *J. Phys. Chem.*, 1990, 94, 8508.

4. (a) K. M. Barkigia, L. Chantranupong, K. M. Smith, and J. Fajer, J. Am. Chem. Soc., 1988, 110, 7566. (b) K. M. Barkigia, D. S. Gottfried, S. G. Boxer, and J. Fajer, J. Am. Chem. Soc., 1989, 111, 6444. (c) C & E NEWS, 1991, 69, 23.
5. (a) R. J. Abraham, G. E. Hawkes, and K. M. Smith, Tetrahedron Lett., 1974, 71. (b) C. J. Medforth, M. D. Berber, K. M. Smith, and J. A. Shelnutt, Tetrahedron Lett., 1990, 31, 3719. (c) C. J. Medforth and K. M. Smith, Tetrahedron Lett., 1990, 31, 5583. (d) J. A. Shelnutt, C. J. Medforth, M. D. Berber, K. M. Barkigia, and K. M. Smith, J. Am. Chem. Soc., 1991, 113, 4077.
6. A. B. Stone and E. B. Fleischer, J. Am. Chem. Soc., 1968, 90, 2735.
7. Just enough CH₃OH was added to make the disappearance of the N-H peak shown originally at -1.2 ppm
8. S. S. Eaton and G. R. Eaton, J. Am. Chem. Soc., 1977, 99, 1601.
9. K. M. Barkigia, M. D. Berber, J. Fajer, C. J. Medforth, M. W. Renner, and K. M. Smith, J. Am. Chem. Soc., 1990, 112, 8851.
10. R. Waditschatka, C. Kralky, B. Jaun, J. Heinzer, and A. Eschenmoser, J. Chem. Soc., Chem. Commun., 1985, 1604.
11. S. S. Eaton and G. R. Eaton, J. Chem. Soc., Chem. Commun., 1974, 576.

Received, 24th February, 1994