

N-H TAUTOMERISM IN PORPHYRINS: AN NMR STUDY

Raymond J. Abraham, * Geoffrey E. Hawkes, and Kevin M. Smith,

The Robert Robinson Laboratories, University of Liverpool,

P.O. Box 147, Liverpool L69 3BX

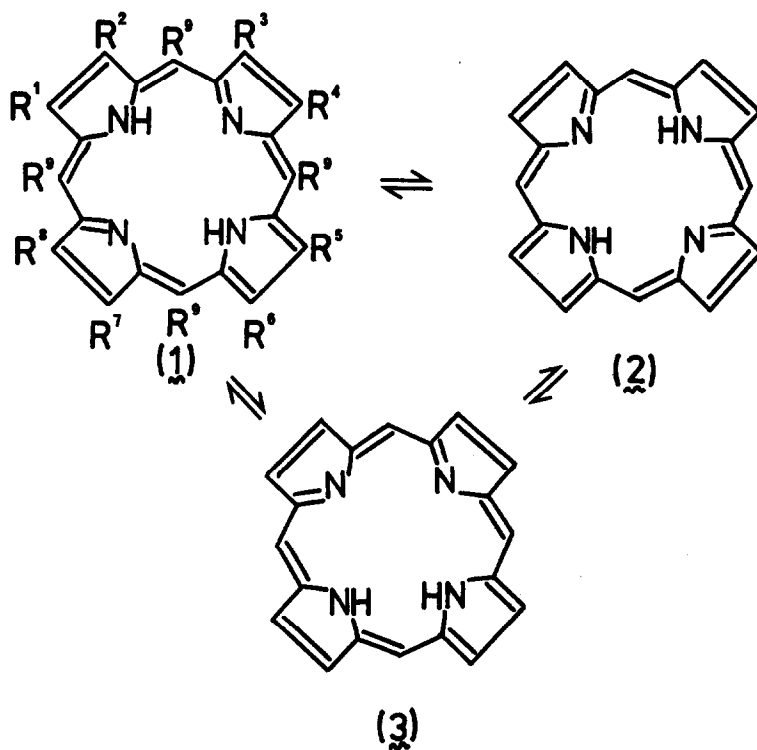
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A fundamental aspect of the chemistry of porphyrins is the tautomerism of the "inner" hydrogens. Recent studies^{1,2} have shown that this tautomerism may be observed by low temperature ¹H NMR spectroscopy. The kinetic isotope effect ($k_{\text{NH}}/k_{\text{ND}}$) obtained from these studies² was 67 for meso-tetraphenylporphyrin (TPP) and 8.9 for deuteroporphyrin-IX dimethyl ester (Deut-IX), and was claimed as evidence for direct interconversion of tautomers (1) and (2) for TPP by a simultaneous two-proton shift, but stepwise via tautomer (3) for Deut-IX. Tautomer (3) was postulated to be more favourable for Deut-IX owing to differential basicity of the "pyrrole" rings arising from different numbers of electron-releasing substituents on those rings.

We have followed this tautomerism by ¹³C and ¹H NMR spectroscopy for TPP, Deut-IX, and coproporphyrin-I tetramethyl ester (Copro-I) (Table). The low temperature ¹³C spectra of N,N'-dideuterio-TPP (TPP-d₂) and Copro-I-d₂ unambiguously confirm our earlier suggestion³ that the broadening of the "α-pyrrole" carbon signals is due to tautomeric exchange,⁴ and not ¹⁴N quadrupole effects. The number and relative positions of the ¹³C resonances at low temperature are consistent with the "H-opposite" tautomers (1) and (2), and not the "H-adjacent" tautomer (3).

The ¹³C spectrum of TPP at 35° shows (Table) that the "α-pyrrole" carbon signals are just above their coalescence temperature, while for TPP-d₂ at 35°, the "β-pyrrole" carbon signals are just above coalescence.⁵ By use of the equation for the fast exchange limit⁶ it is possible to estimate the rates of tautomerism k_{NH} , k_{ND} at the same temperature. This yields the isotope effect $k_{\text{NH}}/k_{\text{ND}}$ ca. 12.1, and ΔG_{308}^\ddagger

* Address correspondence to this author.



TPP	$R^{1-8} = H, R^9 = Ph$
Deut-IX	$R^{1,3,5,8} = Me, R^{2,4,9} = H, R^{6,7} = P$
Copro-I	$R^{1,3,5,7} = Me, R^{2,4,6,8} = P, R^9 = H$
Copro-II	$R^{1,4,5,8} = Me, R^{2,3,6,7} = P, R^9 = H$
	$P = CH_2 \cdot CH_2 \cdot CO_2Me$

ca. 12.3 and 13.9 kcal/mole for the protio and deuterio TPP respectively. From the coalescence temperatures in the ^1H spectra we find $\Delta G_{225}^{\ddagger}$ ca. 11.4 (100 MHz) and $\Delta G_{213}^{\ddagger}$ ca. 11.0 kcal/mole (60 MHz) for TPP and $\Delta G_{265}^{\ddagger}$ ca. 13.5 (100 MHz) and $\Delta G_{256}^{\ddagger}$ ca. 13.3 kcal/mole (60 MHz) for TPP- d_2 . This immediately gives $\Delta H_{\text{NH}}^{\ddagger}$ ca. 9.2, $\Delta H_{\text{ND}}^{\ddagger}$ ca. 10.8 kcal/mole and ΔS^{\ddagger} -10 (± 1) e.u. for both the protio and deuterio compounds. The

Deut-IX- d_2 (CH_2Cl_2)	^1H	-20°	8.93 8.95	<u>meso</u>		
	"	-40°	coalescence	9.81(2H)	9.88	9.84
	"	-65°		coalescence		
	"	-80°	8.72 8.82 8.90 9.00	9.51(2H)	9.73 9.80	9.69 9.77
TPP (CDCl_3)	^{13}C	35°	" α -pyrrole" 145.8 (25 Hz) ^c	" β -pyrrole" 130.6		
	^{13}C	35°		130.6 (50 Hz) ^c		
TPP- d_2^{b} (CDCl_3)	"	-60°	137.1 154.0	127.3 133.9		
	^{13}C	35°	143.5 (30 Hz) ^c	136.2 137.9		
Copro-I (CD_2Cl_2)	^{13}C	-75°	133.2 134.5 150.6 151.7	133.2 134.5 138.9 139.9		

TABLE : ^{13}C and ^1H NMR Chemical Shifts (δ)^a

Footnotes to Table

^a ^1H Spectra measured at 100 MHz and ^{13}C spectra at 25.2 MHz.

^b Due to the isotope effect upon the rate of tautomerism, replacement of the "inner" protons with deuterons raises the coalescence temperature, facilitating observation of the slow exchange spectra.

^c Approximate line widths at half height.

large isotope effect previously reported^{1,2} is thus due to the direct comparison of ΔG^\ddagger measured at two different temperatures and consequent neglect of the entropy of activation. The lower value for the isotope effect found in this study does not require the tautomeric exchange (1) \rightleftharpoons (2) to proceed via the simultaneous two-proton shift, but is consistent with tautomer (3) as an intermediate. Thus, the mechanism of this exchange for TPP is precisely the same as for Deut-IX and is independent of substituent electronegativity. Both the magnitude of the isotope effect and the sign of ΔS^\ddagger are consistent with values found for sigmatropic 1,5 hydrogen shifts in carbocyclic systems.⁷

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