Table II. Formation of *cis,cis*-1,3,5-Octatriene (2) from *cis,cis,cis*-2,4,6-Octatriene (1) at 111 °C

T ($\times 10^{-2}$), s	[2], mol %	T ($\times 10^{-2}$), s	[2], mol %
0	0.2[a]	7.8	1.92; 1.87
0.3	0.48	9.0	2.11; 2.28
0.6	0.75; 0.97[b]	10.2	1.80
0.9	1.18	12.0	2.15
1.2	1.01; 1.39	13.2	2.28
1.8	1.46; 1.48	15.0	1.9
3.0	1.61; 1.65	16.8	2.0
4.2	2.01; 2.03	18.0	2.14
5.4	1.92; 1.99	21.0	2.0
6.6	1.84; 1.92	27.0	1.97

[a] At time = 0, [1] = 93.9 mol %, [3] = 5.9 mol%. [b] Second value from independent run, here and below.

H, C2-H, C7-H), 5.83 (dd, 2 H, J = 6.5 Hz, C3-H, C6-H), 6.5 (m, 2 H, C4-H, C5-H): MS, m/z 108 (M^+).

Kinetic Measurements. Kinetics of thermolyses were measured by using sealed 0.5-mm capillary tubes and an oil bath maintained at 111 °C by a Bayley precision temperature controller (Model 253), and monitored by a Hewlett-Packard 2802A thermometer. While temperature at a fixed position in the bath was constant to ±0.1 °C, temperature across the entire bath was constant only to ±1 °C. Typically, 10 μL of a dilute solution of triene 1 or 3 in dodecane, with 2-methylpentane of comparable GC area percent magnitude as internal standard, was filled in each capillary tube, chilled in dry ice–acetone under argon, and sealed. The sample tubes were immersed in the kinetic bath, then withdrawn from the bath at appropriate time intervals, cooled briefly in liquid nitogen, allowed to reach room temperature, opened, and analyzed by capillary GC. Trienes 1–4 have distinctive retention times on the fused silica capillary columns employed.[8] Kinetic data are summarized in Tables I and II.

Calculations of theoretical values for [2] formed from triene 1 as a function of time, initial concentrations of 1–3, and six rate constants (Scheme I) were performed, first, with the aid of a Hewlett-Packard 11C calculator and, later, with a Pascal program; the two theoretical curves in Figure 1 utilized output from the latter and an HP 7470A plotter. The analytical expression for [2(t)] was taken from Szabó (p 31, eq 2).[11]

Tautomerism in 2-Hydroxy-5,10,15,20-tetraphenylporphyrin: An Equilibrium between Enol, Keto, and Aromatic Hydroxyl Tautomers

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Tautomerism in free-base and metallo derivatives of 2-hydroxy-5,10,15,20-tetraphenylporphyrin (**2**) has been investigated. In the case of the free-base porphyrin **2**, ^{1}H NMR experiments show the existence of three tautomeric forms, **2a–c**, in solution. Each of these species maintains aromaticity in the macrocycle by an 18-atom 18-π-electron (i.e., [18]diazaannulene) "inner–outer–inner–outer" delocalization pathway. Two of the forms, **2a** and **2b**, result from proton transfer processes on the inner periphery and retain the hydroxyl group, while the third form, **2c**, results from tautomerism directly involving the substituent. This is the first observation of prototropic tautomerism at a porphyrin β-pyrrolic position. Other possible species, e.g., **2d** and **2e**, in which aromaticity is maintained by a 17-atom 18-π-electron delocalization pathway were not detected. The position of the tautomeric equilibrium in **2** is solvent dependent, with the hydroxyl forms, **2a** and **2b**, predominating in dimethyl sulfoxide and the keto form, **2c**, the main species in less polar solvents. Infrared spectral studies on **2** show the presence of keto and hydroxyl tautomers in the solid state, as well as in solution. By comparison, 2-amino-5,10,15,20-tetraphenylporphyrin (**4**) exists in solution as a mixture of the two tautomers that retain the amino group; i.e., corresponding imino tautomers were not detected. The possibility that metalloporphyrins, like the free-base compounds, exist as a mixture of tautomeric species with 18-atom 18-π-electron delocalization pathways was probed by monitoring the extent of (the secondary) keto–enol tautomerism shown by the substituent. The zinc(II) and copper(II) 2-hydroxy-5,10,15,20-tetraphenylporphyrins, **5** and **6** respectively, exist almost entirely in hydroxyl forms in both solution and the solid state. However, in the zinc porphyrin **5**, the β-pyrrolic hydrogen adjacent to the hydroxyl substituent undergoes base-catalyzed exchange showing the presence of low equilibrium concentrations of metalated species which have a keto chlorin structure.

A study of two tautomeric processes working in concert, one involving tautomerism in the porphyrin macrocycle and the other involving a β-pyrrolic substituent on the porphyrin periphery, is reported. In solution, simple tetraarylporphyrins exist in two tautomeric forms, each containing an 18-π-electron aromatic delocalization pathway with two isolated double bonds on the porphyrin periphery (Figure 1).[1] We have recently shown by high-field dynamic NMR studies that β-pyrrolic substituents alter the position of the tautomeric equilibrium **1a** ⇄ **1b**,[2] and we have examined the kinetics of the process.[3] Thus, 2-nitro- and 2-cyano-5,10,15,20-tetraphenylporphyrin exist in solution almost exclusively (>96%) in the form **1a**, where the substituent resides on the carbon of an isolated double bond. In contrast, the tautomeric equilibrium in 2-isopropyl-5,10,15,20-tetraphenylporphyrin lies substantially in the direction of **1b**, in which the substituent resides on a carbon in the aromatic delocalization pathway. Porphyrins, therefore, differ from simpler arenes in that additional tautomeric forms which directly involve the substituent are possible, e.g., arising from tautomer **1a**,

(1) Storm, C. B.; Teklu, Y. *J. Am. Chem. Soc.* **1972**, *94*, 1745.
(2) Crossley, M. J.; Harding, M. M.; Sternhell, S. *J. Am. Chem. Soc.* **1986**, *108*, 3608.
(3) Crossley, M. J.; Field, L. D.; Harding, M. M.; Sternhell, S. *J. Am. Chem. Soc.* **1987**, *109*, 2335.

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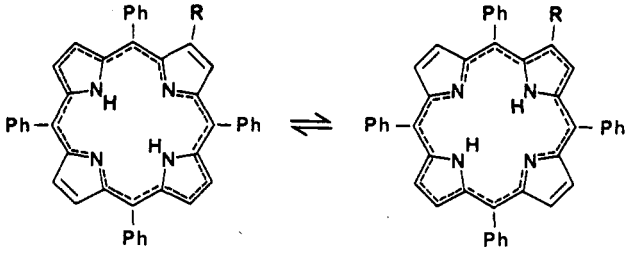

1a 1b

Figure 1. Tautomerism in tetraphenylporphyrins.

without loss of aromaticity in the macrocycle. While there are no previous reports of the detection of such tautomeric forms, they are possible when the β-pyrrolic substituent is hydroxyl, an amino, or a thiol group, provided that there is an unsubstituted adjacent β-pyrrolic position. The existence of such additional prototropic tautomerism on the porphyrin periphery might also provide a means of monitoring the extent of double-bond localization between β–β-pyrrolic positions of metalloporphyrins.

In this work, valence-bond tautomerism in 2-hydroxy-5,10,15,20-tetraphenylporphyrin (**2**) and the corresponding 2-aminoporphyrin **4** has been investigated. The effect of metal complexation on the solution and the solid-state structure of 2-hydroxy-5,10,15,20-tetraphenylporphyrin has also been examined.

Results and Discussion

Materials. 2-Hydroxy-5,10,15,20-tetraphenylporphyrin (**2**) was prepared by base hydrolysis of 2-(benzoyloxy)-5,10,15,20-tetraphenylporphyrin (**3**). The ester **3** was obtained by treatment of a solution of 5,10,15,20-tetraphenylporphyrin in chlorobenzene at 110 °C with benzoyl peroxide for 2 h following the literature procedure[4] for the preparation of the zinc(II) complex. The hydroxyporphyrin **2** has previously been reported to be very unstable.[4] In our hands, however, the porphyrin **2** was quite stable in the solid state although it was prone to photooxidation when adsorbed on silica gel. It was purified by flash chromatography on silica gel in the absence of light.

2-Amino-5,10,15,20-tetraphenylporphyrin (**4**), was prepared from 2-nitro-5,10,15,20-tetraphenylporphyrin by reduction of the nitro group with sodium borohydride and methanol in the presence of palladium on charcoal.[5] The product is also susceptible to photooxidation,[6] but it could be readily purified by flash chromatography on silica gel, provided light was rigorously excluded. 2-Hydroxy-5,10,15,20-tetraphenylporphyrin (**2**), was converted to its zinc(II) and copper(II) complexes, **5** and **6** respectively, by treatment with the appropriate metal(II) acetates under standard conditions.[7]

Tautomerism in the 2-Hydroxyporphyrin 2. The β-pyrrolic region of the room temperature ^{1}H NMR spectrum of 2-hydroxy-5,10,15,20-tetraphenylporphyrin (**2**) in toluene-d_8 is shown in Figure 2, and the NH region of the spectrum is shown in Figure 3a; a sharp singlet at δ 4.62 was also present. The multiplicity of resonances clearly indicates that several species are present in solution.

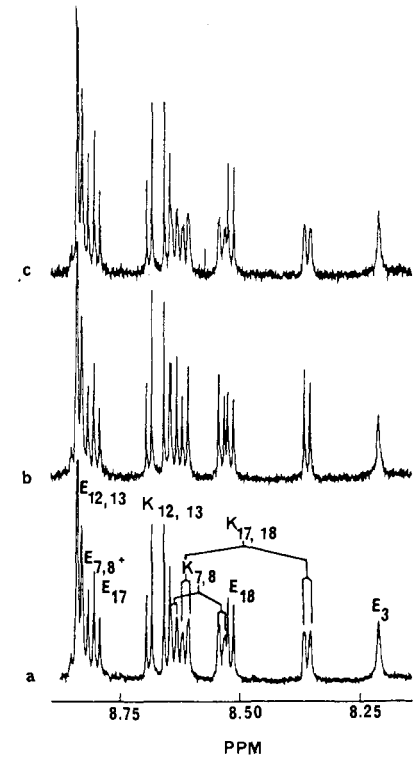

Figure 2. β-Pyrrolic region of ^{1}H NMR spectrum of 2-hydroxy-5,10,15,20-tetraphenylporphyrin (**2**) in toluene-d_8, at 298 K: (a) normal spectrum, (b) spectrum with irradiation of N–H protons at δ −1.75, (c) spectrum with irradiation of N–H protons at δ −2.3. K_x denotes keto protons, and E_x denotes enol protons.

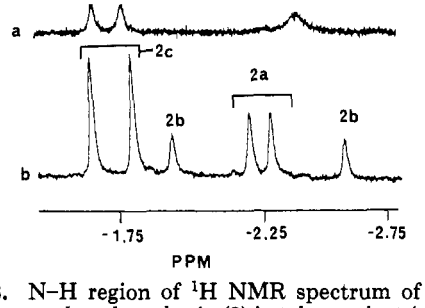

Figure 3. N–H region of ^{1}H NMR spectrum of 2-hydroxy-5,10,15,20-tetraphenylporphyrin (**2**) in toluene-d_8 at (a) 298 K and (b) 200 K.

Our recent study[3] of the kinetics of the tautomeric exchange involving inner hydrogen migration in a range of 2-substituted 5,10,15,20-tetraphenylporphyrins showed that the exchange mechanism involves net synchronous two-proton transfer between tautomers in which the two hydrogens reside on diagonally opposite nitrogens, i.e., **1a** ⇄ **1b**. Tautomers in which the inner hydrogens reside on adjacent nitrogens would be sterically congested and were not detected either directly[2,3] or indirectly.[3] In all the porphyrins that have been investigated previously, the tautomeric exchange **1a** ⇄ **1b** is fast on the NMR time scale at 298 K and leads to a time-averaged spectrum.[2] The present case is clearly more complicated.

Allowing for additional keto–enol tautomerism involving the substituent, there are three possible tautomers, **2a–c**, of 2-hydroxy-5,10,15,20-tetraphenylporphyrin in which substantial aromaticity is retained in the macrocycle (Figure 4), and the ^{1}H NMR spectrum of **2** can be fully assigned as arising from a tautomeric equilibrium involving

(4) Callot, H. J. *Bull. Soc. Chim. Fr.* **1974**, 1492. A more convenient and highly efficient method for the synthesis of hydroxyporphyrins, involving nucleophilic displacement of a nitro group, has recently been reported (Crossley, M. J.; King, L. G.; Pyke, S. M. *Tetrahedron* **1987**, *43*, 4569).

(5) Baldwin, J. E.; Crossley, M. J.; DeBernardis, J. F. *Tetrahedron* **1982**, *38*, 685.

(6) Crossley, M. J.; King, L. G. *J. Chem. Soc., Chem. Commun.* **1984**, 921.

(7) Fuhrhop, J.-H.; Smith, K. M. In *Porphyrins and Metalloporphyrins*; Smith, K. M., Ed.; Elsevier: Amsterdam, 1975; p 757.

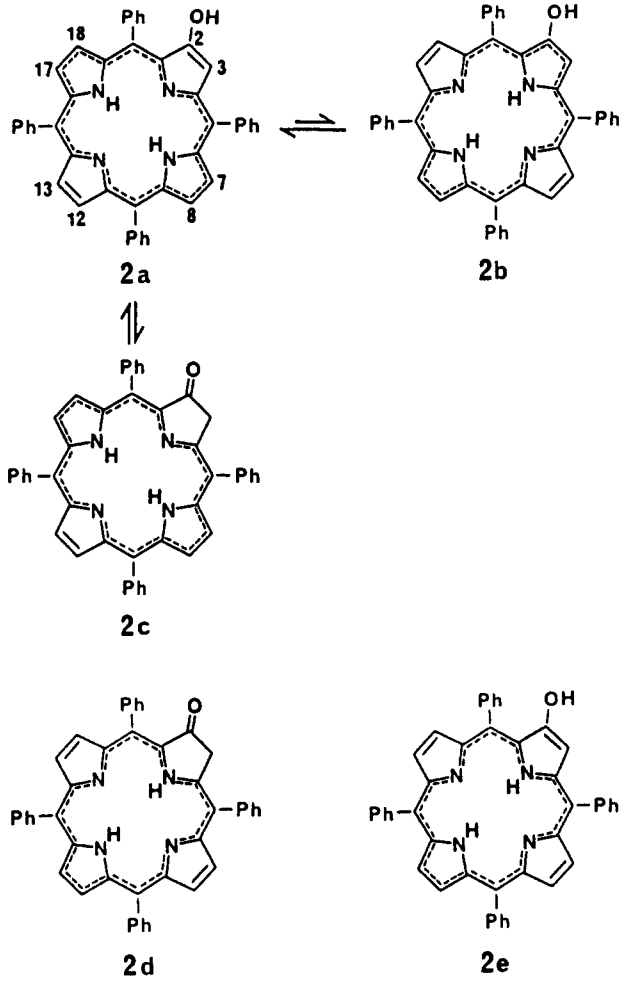

Figure 4. Tautomerism in 2-hydroxy-5,10,15,20-tetraphenylporphyrin (2).

only these species. Thus, the two tautomers **2a** and **2b** give rise to a time-averaged spectrum of three AB quartets for $H_{7,8}$, $H_{12,13}$, and $H_{17,18}$ and an upfield singlet for H_3 (signals designated E in Figure 2a). The remaining resonances designated K, were assigned to the ketone **2c**, which displayed a singlet at 4.62 ppm (methylene at C-3), a sharp AB quartet for $H_{12,13}$, and two broad AB quartets for $H_{7,8}$ and $H_{17,18}$ both of which contained additonal ^4J coupling to the inner N–H protons. Decoupling experiments confirmed these assignments (Figure 2b,c).

Poor signal dispersion and broadness due to N–H coupling made interpretation of the aromatic region of the low-temperature spectrum of **2** difficult. However, the spectrum of the N,N-dideuteriated derivative was considerably simplified as this labeling removed the ^4J coupling between the β-pyrrolic and N–H protons. Due to the large isotope effect observed in the N–H exchange in tetraarylporphyrins,[1,3] deuteriation also allowed spectral analysis at a much higher temperature where the resolution was considerably improved due to the decrease in solvent viscosity (Figure 5). The assignments were supported by appropriate decoupling experiments of the undeuteriated compound and by accurate integration of the individual resonances. The ratio of the β-pyrrolic proton resonances of the individual species in the spectrum of the N,N-dideuteriated sample at 220 K was **2a**:**2b**:**2c** = 3:2:5.

It is informative to consider the nature of the species involved in this tautomeric equilibrium. The two porphyrin N–H tautomers, **2a** and **2b**, contain the hydroxyl group situated on the aromatic delocalization pathway and on the isolated double bond, respectively, and are analogous to the tautomers **1a** and **1b** that have been observed in a wide range of 2-substituted 5,10,15,20-tetraphenylporphyrins. Both these species maintain aromaticity in the macrocycle by an 18-atom 18-π-electron (i.e., [18]diazaannulene) "inner–outer–inner–outer" delocalization pathway. The hydroxyl group is thus enolic in **2a** and "phenolic" in **2b**. Tautomers that have the inner hydrogens on adjacent nitrogens have never been detected. Tautomerism involving the hydroxyl substituent and the adjacent β-pyrrolic position in the enolic form **2a** gives rise to the keto tautomer **2c**, in which the [18]diazaannulene aromatic delocalization pathway is maintained. The alternate keto–enol tautomerism, which involves the adjacent α-pyrrolic position and other tautomerism, which involves proton shifts to remote sites, necessarily involve

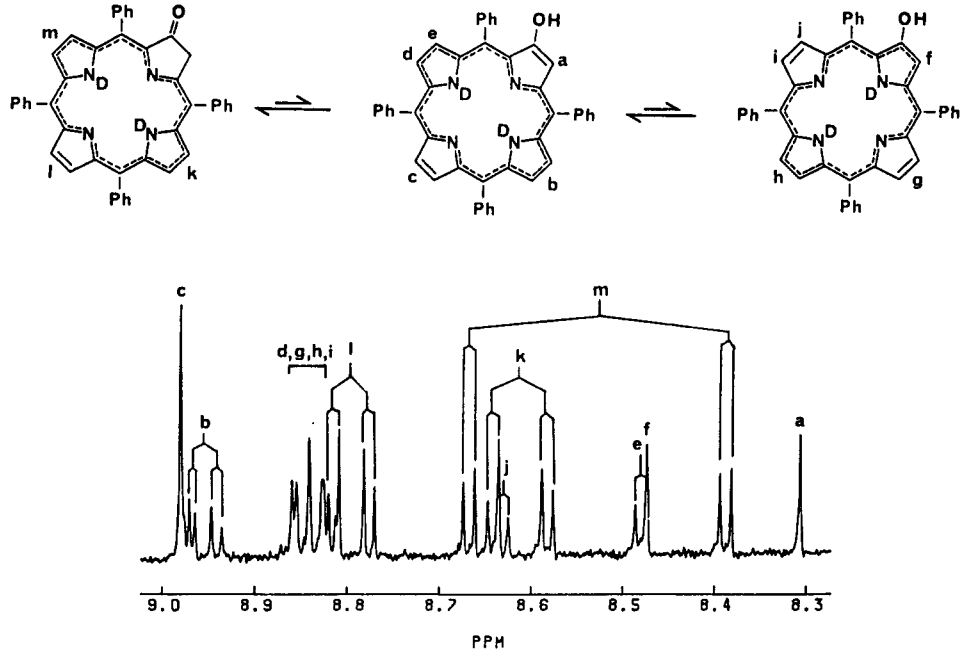

Figure 5. β-Pyrrolic region of ^1H NMR spectrum of N,N-dideuteriated 2-hydroxy-5,10,15,20-tetraphenylporphyrin, in toluene-d_8 at 220 K.

Table I. Relative Populations (±5%) of Enol 2a, Aromatic Hydroxyl 2, and Keto 2c Tautomers in Different Solvents at 298 K

solvent	species (relative population) 2a	2b	2c
toluene-d_8[a]	29	18	53
CD_2Cl_2[a]	13	9	78
$CDCl_3$	30[b]		70
$(CD_3)_2SO$	100[b]		0

[a] Determined by integration of low-temperature spectra; values extrapolated to 298 K assuming a Boltzmann variation of populations with temperature; see ref 2. [b] Sum of **2a** and **2b**.

loss of the macrocyclic aromaticity. Proton transfer on the inner periphery of the keto tautomer **2c** would lead to the keto tautomer **2d**. In this case the [18]diazaannulene aromaticity is lost but aromaticity could be maintained in the macrocycle by using the nitrogen lone pair of the substituted ring, i.e., by invoking a 17-atom 18-π-electron delocalization pathway. The keto tautomer **2d** could also arise from **2b** in two steps via the tautomer **2e**, which also has an aromatic 17-atom 18-π-electron delocalization pathway. There would be a considerable energy penalty associated with the formation of **2d** or **2e** although an analogous species is implicated as a high-energy intermediate in proton exchange in chlorins.[1] The NMR spectrum of **2d**, if present, would contain two sharp AB quartets, one AB quartet with additional coupling to the N–H protons, and an upfield two-proton resonance due to the methylene group and showing additional ^4J coupling. This pattern of signals was not detected. Similarly, no evidence was found for the existence of **2e** (or related species) as a separate entity.

It is evident that the keto–enol tautomerism **2a** ⇄ **2c** is slow on the NMR time scale at room temperature under neutral conditions. Integration of the N–H protons in the NMR spectrum of **2** (Figure 3a) indicated that the relative populations of keto:enol in toluene-d_8 at room temperature were 44:56. At low temperature the exchange **2a** ⇄ **2b** was also slow on the NMR time scale, and integration of the N–H protons showed the populations **2a**:**2b**:**2c** = 29:18:53 (Figure 3b). The proton exchange on the inner nitrogens, i.e., **2a** ⇄ **2b**, is an intramolecular process.[3] The relatively slower rate of the keto–enol tautomerism is expected on the basis that, in the absence of acid or base catalysis, intramolecular proton transfer from carbon to oxygen involves a very high energy barrier,[8] while transfer involving a bimolecular process will be sterically impeded by the adjacent phenyl substituents which are orthogonal to the plane of the reacting groups in **2**.

As expected, the ratio of keto:enol in **2** was solvent dependent. Polar solvents such as dimethyl sulfoxide-d_6 stabilized the enol, and no ketone was detected. Approximately equal amounts of keto to enol were present in toluene-d_8 while the ketone was the predominant species in both $CDCl_3$ and CD_2Cl_2 (Table I).

Absorptions due to carbonyl and hydroxyl stretching were observed in the FT infrared spectra of **2**, both in CH_2Cl_2 solution and in the solid state (KBr), showing the coexistence of keto and hydroxyl forms of **2** (Table II).

The results found in this study of a β-hydroxyporphyrin contrast with those found in the case of *meso*-hydroxyporphyrins. The position of the tautomeric equilibrium in metal-free *meso*-hydroxyporphyrins lies, apparently, exclusively on the keto (oxophlorin) side, in which a high degree of conjugation is maintained presumably due to

(8) Toullec, J. *Adv. Phys. Org. Chem.* **1982**, *18*, 1.

Table II. Infrared Frequencies in the Carbonyl and Hydroxyl Regions of Hydroxyporphyrins in Solution and the Solid State

compound	medium	λ_{max}, cm^{-1}[a]
2	CH_2Cl_2	1720 (s), 3676 (sh), 3690 (br m)
2	KBr	1724 (s), 3503 (br m)
5	CH_2Cl_2	3502 (br m), 3609 (br s), 3676 (sh), 3690 (br m)
5	KBr	3449 (br m), 3507 (br m)
6	CH_2Cl_2	3502 (br m), 3603 (br w), 3690 (br s)
6	KBr	3485 (m), 3510 (m)

[a] Strong, s; medium, m; weak, w; broad, br; shoulder, sh.

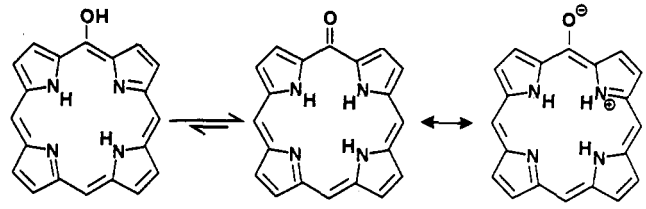

Figure 6. Tautomerism in *meso*-hydroxyporphyrins. The β-pyrrolic substituents are omitted for clarity.

contributions from valence bond dipolar forms shown in Figure 6.[9] Complexes with trivalent metal ions also have an oxophlorin structure.[9] However, pure *meso*-hydroxy compounds can be obtained in neutral solution with divalent metal complexes of oxyphlorins or when a peri keto group stabilizes the hydroxyl group by intramolecular hydrogen bonding.[10]

Previous NMR studies on 2-amino-5,10,15,20-tetraphenylporphyrin (**4**), in CD_2Cl_2 at 298 K, showed the presence of the two N–H tautomers (**1a**/**1b**, R = NH_2) in the ratio 22:78.[2] No imine tautomers were detected in a variety of solvents, and the region between δ −2 and 7 was free of any signal attributable to the methylene proton of C-2 in the hypothetical imine tautomer. This finding is in contrast to the case of *meso*-aminoporphyrins in which the imino tautomer is readily detected and is in some cases actually the predominant species in solution.[11]

The presence of keto–enol tautomerism in porphyrin **2** and the absence of detectable enamino–imine tautomerism in **4** is presumably a consequence of a number of factors, which include the greater basicity of the imino nitrogen compared to the carbonyl oxygen, as well as the total energies of the tautomeric structures. The results in this case parallel those found in a variety of simpler heterocyclic systems, a well-known example being the preference for 4-hydroxypyridine to exist in the tautomeric 4-pyridone form in relatively nonpolar solvents while the analogous amino compound exists predominantly in the 4-aminopyridine form.[12]

Effect of Metalation on the Tautomeric Process. The porphyrin N–H tautomerism has allowed the properties and electron distribution in free-base porphyrins to be monitored by NMR spectroscopy. However, the structure of metalloporphyrins is more difficult to define and to date has relied primarily on crystallographic data,

(9) Jackson, A. H.; Kenner, G. W.; Smith, K. M. *J. Chem. Soc. C.* **1969**, 302.

(10) Inhoffen, H. H.; Gossauer, A. *Justus Liebigs Ann. Chem.* **1969**, *723*, 135.

(11) Fuhrhop, J.-H. In *The Porphyrins*; Dolphin, D., Ed.; Academic: New York, 1978; Vol. II, p 131. Johnson, A. W.; Oldfield, D. *Tetrahedron Lett.* **1964**, 1549.

(12) For a review, see: Boulton, A. J.; McKillop, A. In *Comprehensive Heterocyclic Chemistry*, Boulton, A. J., McKillop, A., Eds.; Pergamon: Oxford, 1984; Vol. 2, pp 147–159.

supported by molecular orbital calculations which assume that the metalloporphyrin has square planar or D_{4h} symmetry.[13,14] With one exception,[15] the possibility that metalloporphyrins exist as a mixture of tautomeric valence bond forms in analogy to the free-base compounds does not appear to have been considered seriously. Such valence-bond tautomerism in a metalloporphyrin would involve relatively small movement of heavy atoms (skeletal carbons and nitrogens), and unlike the free-base-porphyrin case, there is no proton transfer step. Consequently, the energy barrier to tautomerism in a metalloporphyrin would be very low and not easily detectable. The presence of keto–enol tautomerism in the free-base hydroxyporphyrin **2** provides a probe that allowed this work to be extended to the study of metalloporphyrin structure. In particular, if the electron distribution in metalloporphyrins approximates the [18]diazaannulene delocalization pathway of the corresponding free-base porphyrin, then the formation of keto and enol forms of the metalloporphyrin would be expected.

The effect of metalation on the keto–enol tautomerism in 2-hydroxy-5,10,15,20-tetraphenylporphyrin (**2**) was investigated on the zinc(II) and copper(II) derivatives, **5** and **6** respectively. Infrared spectra, recorded in the solid state (potassium bromide disks) and solution (dichloromethane), showed hydroxyl stretches, but no significant signals in the carbonyl region of the spectrum (Table II). The variation in signal intensity and frequency is probably related to the structural differences in the porphyrins associated with the central metal ion. The NMR spectrum of the zinc(II) complex **5**, in CD_2Cl_2, was also consistent with this result. In particular, no signal due to methylene protons at C-3 of a keto form was present. However, treatment of a solution of the zinc(II) complex **5**, with deuteriated sodium methoxide in methanol-d_4, resulted in the slow disappearance of the resonance due to H-3 from the NMR spectrum. This result suggests that, while not detectable on the NMR time scale, there is an equilibrium between an enol and keto form of the metalloporphyrin which allows H-3 to exchange with deuterium. However, the difference in energy between the two species may be very high as is the case in the simple related aromatic compound, phenol. The ratio of enol to ketone in phenol is 10^{14}:1, but in the presence of base, the ortho and para hydrogens exchange with solvent deuterium.[16] The infrared spectrum of the zinc(II) complex **5** showed a very weak band (1724 cm^{-1}) that could be attributed to a keto species, but an analogous peak was not found in the spectrum of the copper(II) complex **6**.

Formation of the free-base ketone **2c** arises through the presence of substantial amounts of the aromatic enol **2a** in which the hydroxyl group is situated on the olefinic group. Examination of models indicates that steric interactions involving the hydroxyl (and oxo) substituent are very similar in the free-base case and metalloporphyrin cases. The absence of directly detectable amounts of ketone in the metallo complexes therefore suggests that the electron distribution is substantially different in the free-base and metalloporphyrins and that there is insufficient double bond character on the periphery of the metalloporphyrins to allow formation of a keto species.

Figure 7. Structure of magnesium(II) porphyrins proposed in ref 14.

Quantum mechanical calculations have suggested that the structure of a metalloporphyrin may vary with the nature of the central metal ion.[14,17] The structure of the parent magnesium(II) prophyrin complex, (porphinato)-magnesium(II), has been proposed to be best represented as a [16]tetraazaannulene dianion with two bonds to the dipositive central metal ion, the structure being of D_{4h} symmetry.[14] This [16]annulene dianion contains four localized double bonds between the β–β-pyrrolic positions of the porphyrin periphery (Figure 7). The absence of detectable amounts of keto form in the zinc(II) and copper(II) complexes, **5** and **6**, while by no means definitive, suggests the absence of the [16]annulene dianion delocalization pathway as a significant contributor to the structure of these metalloporphyrins as a high degree of bond order on the porphyrin periphery would be expected to favor ketone formation.

Conclusions

2-Hydroxy-5,10,15,20-tetraphenylporphyrin (**2**) in solution equilibrates between three tautomeric forms: an aromatic hydroxyl tautomer **2b**, an enol tautomer **2a**, and a keto tautomer **2c**. Keto and enol tautomers are also present in the solid state. In contrast, no imine tautomer of 2-amino-5,10,15,20-tetraphenylporphyrin (**4**) was detected in solution. The zinc(II) and copper(II) complexes of 2-hydroxy-5,10,15,20-tetraphenylporphyrin exist almost entirely as hydroxyporphyrins **5** and **6**. These data suggest that there is no significant localized double bond character between the β–β-pyrrolic positions of the metallophorphyrin periphery and, hence, that the [16]annulene dianion electron delocalization pathway is not an important contributor to the structure of zinc(II) and copper(II) porphyrins. The study of other such metallo complexes may provide further useful information on the structure of metalloporphyrins. Further studies on tautomerism and bond orders in porphyrin and related systems are under way in our laboratories.

Experimental Section

Deuteriated solvents used in the NMR studies were obtained from the Aldrich Chemical Co. Toluene-d_8 (99+ atom % D) and dimethyl sulfoxide-d_6 (99.9 atom % D) were used as received. Dichloromethane-d_2 (99.6 atom % D) and chloroform-d (99.8 atom % D) were passed through a short plug of anhydrous K_2CO_3 to remove acidic impurities immediately prior to use. Proton NMR spectra were recorded on a Bruker WM400 MHz spectrometer locked on solvent deuterium and referenced to residual solvent protons. Samples were ca. 0.02 M and were degassed. The spectrometer temperature was calibrated by the shift difference between the proton resonances in methanol.[18] Infrared spectra were recorded on a Digilab FTS 20/80 Fourier transform spectrometer. Ultraviolet spectra were recorded on a Hitachi 150-20 spectrometer in chloroform. Mass spectra were recorded on an A.E.I. MS 902 spectrometer at 70 eV. Column chromatography

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was performed on Merck silica gel 60 (type 9385). Petroleum ether refers to the fraction of bp 50–60 °C.

2-Hydroxy-5,10,15,20-tetraphenylporphyrin (2). 2-(Benzoyloxy)-5,10,15,20-tetraphenylporphyrin[4] (3) (240 mg, 0.33 mmol) was dissolved in tetrahydrofuran (6 mL) and ethanol (6 mL), protected from light, and heated to boiling. A saturated solution of sodium hydroxide in ethanol (2 mL) was added, and the solution was boiled under nitrogen for 45 min. The mixture was diluted with water and the product extracted into chloroform. The combined extracts were dried (Na_2SO_4), and the solvent was removed under reduced pressure to give a purple solid. Light was rigorously excluded in all workup procedures. Minor impurities were removed by flash chromatography on silica gel. The major band was eluted with CH_2Cl_2 and evaporated, and the product was washed successively with hot methanol and pentane to give **2** as purple crystals (170 mg, 83%): >300 °C; visible spectrum λ_{max} 419 (log ϵ 5.39), 517 (4.15), 556 (3.85), 592 (3.77), 648 nm (3.76); ^{1}H NMR (CD_2Cl_2) δ enol −2.94 (br s, NH), 1.53 (br s, OH), 8.62 and 8.85 (b AB q, J_{AB} = 5.03 Hz, $H_{17,18}$), 8.82 and 8.87 (b AB q, J_{AB} = 5.00 Hz, $H_{7,8}$), 8.83 (br s, $H_{12,13}$), keto −2.00, −2.06 (2 br s, NH), 4.62 (s, CH_2), 8.49 and 8.72 (b AB q, J_{AB} = 5.10 Hz, $H_{17,18}$), 8.53 and 8.78 (b AB q, J_{AB} = 5.10 Hz, $H_{7,8}$), 8.54 and 8.58 (AB q, J = 4.50 Hz, $H_{12,13}$), 7.65–7.80 (m, $H_{m,p}$), 7.87–8.25 (m, H_o); mass spectrum, m/z 630 (M^+, 100). The deuteriated derivative was prepared by three successive equilibrations of a solution of the porphyrin **2** in toluene-d_8 with D_2O. The solution was dried over Na_2SO_4 prior to NMR analysis.

2-Amino-5,10,15,20-tetraphenylporphyrin (4). The crude aminoporphyrin **4** was prepared by the method of Baldwin et al.[5] Purification was effected by chromatography over silica gel (dichloromethane/petroleum ether, 1:1) with careful exclusion of light. The major brown band was collected and the solvent removed under reduced pressure. The residue was boiled in methanol and filtered to give **4** as shiny fine purple crystals (30 mg, 64%): mp >300 °C; ^{1}H NMR (CD_2Cl_2) δ −2.78 (br s, NH), 4.52 (br s, NH_2), 7.70–7.86 (m, $H_{m,p}$), 8.11–8.22 (m, H_o), 8.74 and 8.52 (AB q, J_{AB} = 4.70 Hz, $H_{17,18}$), 8.78 and 8.69 (AB q, J_{AB} = 4.79 Hz, $H_{7,8}$), 8.79 and 8.81 (AB q, J_{AB} = 4.60 Hz, $H_{12,13}$).

(2-Hydroxy-5,10,15,20-tetraphenylporphinato)zinc(II) (5). Treatment of **2** with zinc(II) acetate according to the method of Fuhrhop and Smith[7] gave the metalated porphyrin[4] **5** in quantitative yield: visible spectrum λ_{max} 424 (log ϵ 5.45), 552 (4.15), 588 (3.70), 618 nm (3.34); ^{1}H NMR ($CDCl_3$) δ 5.95 (s, OH), 7.69–7.92 (m, $H_{m,p}$), 8.09 (s, H_3), 8.15–8.25 (m, H_o), 8.65 and 8.90 (AB q, J_{AB} = 4.65 Hz, $H_{17,18}$), 8.88 and 8.94 (AB q, J_{AB} = 4.71 Hz, $H_{7,8}$), 8.91 and 8.92 (AB q, J_{AB} = 4.66 Hz, $H_{12,13}$); mass spectrum, m/z 692 (M^+, ^{64}Zn, 100), 694 (M^+, ^{66}Zn, 70), 696 (M^+, ^{68}Zn, 45).

(2-Hydroxy-5,10,15,20-tetraphenylporphinato)copper(II) (6). Porphyrin **2** (100 mg, 0.16 mmol) was treated with copper(II) acetate according to the method of Fuhrhop and Smith.[7] The crude metalated porphyrin was chromatographed on silica gel (dichloromethane/petroleum ether, 1:1). The major red band was collected, and the solvent was removed under reduced pressure. Recrystallization of the resultant product from dichloromethane/pentane afforded pure **6** as fine purple crystals (86 mg, 78%): mp >300 °C; visible spectrum λ_{max} 416 (log ϵ 5.62), 539 (4.28), 5.79 (3.83), 601 nm (3.37); mass spectrum, m/z 691 (M^+, 100), 675 (6).

Anal. Calcd for $C_{44}H_{28}N_4OCu$: C, 76.34; H, 4.08; N, 8.10. Found: C, 75.62; H, 4.00; N, 8.10.

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Polarizability Effects on the Aqueous Solution Basicity of Substituted Pyridines

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A quantitative dissection of polarizability (P), field (F) and resonance (R) substituent contributions to the relative gas-phase and aqueous solution basicities of 2-, 3-, and 4-substituted pyridines (XPy) is described in this work. The standard-free-energy changes for the reaction $XPyH^+ + Py \rightleftarrows XPy + PyH^+$ (eq 1) in the gas-phase ($\delta\Delta G°_g$) and in aqueous solution ($\delta\Delta G°_{(aq)}$) have been analyzed. $\delta\Delta G°_g$ has been found to be the sum of F, R, *and* P while $\delta\Delta G°_{aq}$ *only depends on* F *and* R. $\delta\Delta G°_g$ corrected for polarizability, ($\delta\Delta G°_g - P$) is a linear function of $\delta\Delta G°_{aq}$. This relationship holds for substituents in any of the three positions (ortho, meta, para), including 2-mono- and 2,6-disubstituted pyridines. These results show that the fundamental differences between gas-phase and solution basicities of pyridine are (i) the essentially complete disappearance of polarizability effects in solution and (ii) an attenuation (by a factor of ca. 2.3) of field and resonance contributions.

Studies of gas-phase acidities and basicities of organic compounds have led Taft and Topsom[1] to the quantitative dissection of substituent polarizability (σ_α), field-inductive (σ_F), and resonance (σ_R) effects. This scheme has successfully been applied to the analysis of structural effects on many kinds of proton-transfer reactions in the gas phase. A preliminary assessment also showed the applicability of this treatment to solution reactions wherein substituent solvation effects are absent or are corrected for.

Here, we wish to report that this formalism has also allowed the analysis of the main factor governing the basicity of 2-, 3-, and 4-substituted pyridines in aqueous solution.

Consider the proton-exchange reaction 1, where Py stands for pyridine itself and X–Py is a 2-, 3-, or 4-substituted pyridine. The standard free-energy changes for

$$X\text{–}PyH^+ + Py \rightleftarrows X\text{–}Py + PyH^+ \quad (1)$$

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