4.33 and 7.8 eV (Figure 4 and ref 38).

It is often possible to assign electron transmission resonances in terms of virtual orbitals obtained from ab initio calculations and sometimes trends in virtual orbital energies within a series of closely related molecules match well against trends in experimental resonance energies. The calculations of ref 5 indicate that the two unoccupied π^* orbitals ($2e''$ and $2a_2''$ in borazine) are the lowest energy unoccupied orbitals for both benzene and borazine and support our assignment of the electron transmission resonances to occupation of those orbitals. However, our calculation with a larger GTO basis set predicts two σ^* MOs (a_1' and e') to lie between the two π^* MOs of borazine. A parallel calculation on benzene places four such σ^* MOs between the π^* MOs. While we do believe that the resonances reported here involve occupation of the π^* MOs, it is likely that resonances to σ^* MOs will be found at intermediate energies in both borazine and benzene. The calculated difference of the two π^* orbital energies is about 60% too large for benzene and 20% too small for borazine. This suggests that the relaxation and correlation effects which influence the occupied π orbital ionization potentials also influence the electron transmission resonance energies in these molecules.

It is interesting to note that the π^* splitting in benzene as deduced from the electron transmission resonances (3.76 eV) is very close to that deduced from the inner-shell excitation energies to π^* MOs (3.7 eV). Turning to borazine, the π^* splitting amounts to 3.72 eV in the electron transmission spectrum, whereas the B 1s spectrum yields 4.43 (5) eV and the N 1s spectrum yields 3.35 (8) eV for this splitting. As argued in the discussion of the inner-shell spectra, this increase of the π^* splitting in the B 1s spectrum and decrease in the N 1s spectrum relative to the π^* splittings in the benzene and borazine negative ions is due to the strong polarization of the π^* manifold by the $(1s)^{-1}$ holes in borazine.

The electron transmission resonances of cyclohexane (Figure 4) can be given a tentative interpretation. Temporary negative ions can be formed at high energies by the induction of a free-molecule Rydberg excitation and the subsequent two-electron occupation of the Rydberg orbital by the excited electron and the impacting electron. Called a Feshbach resonance, such negative-ion states occur at ca. 0.5 eV below the corresponding free-molecule Rydberg transition.[21] With the lowest Rydberg excitation in cyclohexane ($4e_g \rightarrow 3s$) at 7.04 eV,[39] the lowest possible Feshbach resonance in this molecule will involve the $^2(4e_g, 3s^2)$ configuration and will fall at 6.5 eV. Consequently, the resonance observed at 4.33 eV in cyclohexane cannot be a Feshbach resonance and so must involve the one-electron occupation of one of the lower σ^* MOs. A likely candidate is the $\sigma^*(5a_{1g})$ MO invoked above in our discussion of the inner-shell spectrum of cyclohexane. The 7.8-eV resonance of cyclohexane fits energetically as the $^2(4e_g, 3p^2)$ Feshbach resonance as measured with respect to the upper Jahn-Teller component of the $(4e_g)^{-1}$ ionization at 10.93 eV; however, it is considerably broader than Feshbach resonances normally appear in electron transmission spectra.

Conclusions

Though the earlier claims for a nonbenzenoid electronic spectrum for borazine in the near ultraviolet are confirmed here, the extended spectrum of borazine nonetheless is clearly that of an unsaturated system on the basis of its ordering of valence and Rydberg transitions. The earlier assignment of the 7.6-eV band of borazine as corresponding to the π-electron transition at 7.0 eV in benzene terminating at degenerate π^* MOs is confirmed by the *A*-term signatures of both in the MCD spectra and the near equality of their upper-state magnetic moments. As with the photoelectron spectra, the electron transmission spectra of benzene and borazine show a close relationship, indicating comparable π-MO splittings in the two systems. The B 1s and N 1s core excitation spectra of borazine are remarkably similar to the C 1s spectrum of benzene and the C 1s and N 1s spectra of pyridine, again illustrating the similarities of the π-electron systems in borazine and benzene. We note however, that the splitting of the π^* MOs in borazine varies between 3.3 and 4.45 eV, depending upon the charge distribution of the core which is polarizing the π^* MOs. Overall, we conclude that the spectral characteristics of borazine are much more like those of benzene than previously thought.

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Registry No. Borazine, 6569-51-3; cyclohexane, 110-82-7; benzene, 71-43-2.

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Tautomerism in 2-Substituted 5,10,15,20-Tetraphenylporphyrins

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Abstract: β-Substitution of 5,10,15,20-tetraphenylporphyrin alters the position of the tautomeric equilibrium **2a** $\rightleftarrows$ **2b**, which can be observed by high-field variable-temperature NMR spectroscopy. When R = NO_2, CHO, Cl, Br, OMe, CN, NHCOMe, SPh, OCOPh, or OH the dominant tautomer is **2a**, where R lies on the isolated double bond, while when R = $CH{=}CH_2$, CH_2OH, NH_2, Me, $CH(Me)_2$, or $(CH_2)_3Me$ the major tautomer is **2b**, where R lies on the aromatic delocalization pathway. These substituent effects do not follow a known scale.

Tautomerism in 5,10,15,20-tetraphenylporphyrin and several other free base porphyrins has been established unequivocally by NMR spectroscopy.[1-7] In each tautomer the aromatic delocalization pathway is defined by an 18-annulene system, with two

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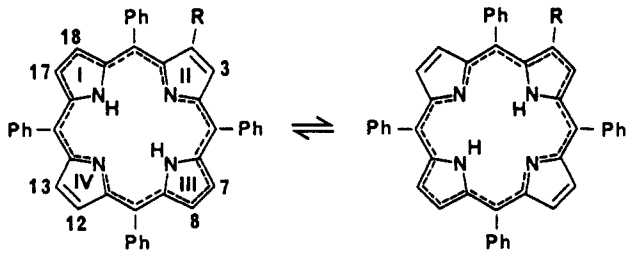

R = H 1a 1b
R = X 2a 2b

Figure 1. Tautomerism in tetraarylporphyrins.

isolated double bonds on the porphyrin periphery[8] (Figure 1). Exchange between the two equally populated tautomers **1a** ⇄ **1b** leads to uniform electron density at each of the β-pyrrolic and at each of the meso positions in the ring over a time scale of ca. 6000 s^{-1} at 293 K.[9]

The nature and mechanism of this tautomerism in both free base porphyrins and chlorins has been widely studied in its relation to the reactivity and hence biological function of naturally occurring porphyrins and metalloporphyrins[5-7] as well as theoretically, where the porphyrin unit provides an excellent model for the study of two-proton exchange.[9-18]

In solution, the two tautomeric forms of 5,10,15,20-tetraphenylporphyrin, **1a** and **1b**, exchange rapidly. This process has been monitored by ^1H,[1,2,6,9] ^{13}C,[3,4] and ^{15}N[5,7] variable-temperature NMR. Activation parameters for the process as well as kinetic isotope effects have been reported and interpreted by several groups.[2,4,6,9] Studies on para-substituted tetraphenylporphyrins indicate that the rate of exchange is independent of phenyl ring substituents.[6]

The mechanism of the proton transfer has evoked much discussion.[9-18] The reaction has been interpreted in terms of transition-state theory[1-4] as a proton transfer between adjacent nitrogens. Migration via proton tunneling as the dominant exchange process has also been proposed,[9-16] but ^{13}C spin saturation transfer experiments are at variance with this result.[17,18]

A recent ^{15}N CPMAS NMR study has shown that this tautomerism also occurs in the solid state and that an unequal population of tautomers can result from crystal packing forces.[19] Rate constants and isotope effects in the solid state were found to be identical with or different from solution data depending on substitution in the aryl ring, and these results have aided in the interpretation of X-ray crystal data.[20-24]

With one exception,[25] all previous studies[1-8] of tautomerism in the porphyrin macrocycle in solution have involved porphyrins with at least D_2h symmetry in which the tautomers are degenerate and so equally populated. In the one report[25] of work on asymmetric porphyrins, which used [$^{15}N_4$]protoporphyrin IX dimethyl ester and [$^{15}N_4$]coproporphyrin III tetramethyl ester, no perturbation of tautomeric equilibria from a 1:1 mixture was noted.

We report here the effect of β-substitution on the tautomeric equilibrium of 5,10,15,20-tetraphenylporphyrin. The asymmetry induced by this substitution gives rise to nondegenerate tautomers and provides a more informative system for the investigation of tautomerism in porphyrins. Electron density at the various pyrrolic positions of the ring is also modified by this substitution.

Experimental Section

NMR Spectra. Proton NMR spectra were recorded on a Bruker WM 400-MHz spectrometer locked on solvent deuterium. Samples were prepared as ca. 0.02 M solutions and were degassed. All low-temperature spectra were recorded in dideuteriodichloromethane and referenced to the solvent peak. Temperature was calibrated by comparison to the shift difference in methanol.[26] Assignments are based on the numbering scheme of Figure 1.

Materials. Porphyrins **3–15** were prepared by literature methods. Porphyrins **16**, **17**, and **18** were prepared in the course of other work in our laboratories by the use of novel nucleophilic substitution reactions on (2-nitro-5,10,15,20-tetraphenylporphinato)copper(II), followed by demetallation with sulfuric acid, details of which will be reported elsewhere.

The following are NMR spectra at 298 K.

2-Cyano-5,10,15,20-tetraphenylporphyrin (3):[27] ($CDCl_3$) −2.68 (bs, NH), 7.71–7.84 (m, $H_{m,p}$), 8.18 (m, H_o), 8.74 (s, $H_{12,13}$), 8.90 and 8.92, 8.93 and 8.97 (2 AB q, J_{AB} = 4.81, 4.87 Hz, $H_{7,8}$ and $H_{17,18}$), 9.37 (s, H_3).

2-Nitro-5,10,15,20-tetraphenylporphyrin (4):[28] ($CDCl_3$) −2.61 (bs, NH), 7.67–7.80 (m, $H_{m,p}$), 8.16–8.21 (m, H_o at $C_{5,10,15}$), 8.26 (m, H_o at C_{20}), 8.70 and 8.72 (AB q, J_{AB} = 4.72 Hz, $H_{12,13}$), 8.89 and 9.02 (AB q, J_{AB} = 5.02 Hz, $H_{17,18}$), 8.90 and 8.94 (AB q, J_{AB} = 5.03 Hz, $H_{7,8}$), 9.06 (s, H_3).

2-(Benzoyloxy)-5,10,15,20-tetraphenylporphyrin (5):[27] ($CDCl_3$) −2.8 (bs, NH), 7.43 and 7.61 (2 m, OCOPh), 7.71–7.81 (m, $H_{m,p}$), 8.10 (m, H_o at C_{20}), 8.18–8.26 (m, H_o at $C_{5,10,15}$), 8.61 and 8.81 (AB q, J_{AB} = 4.73 Hz, $H_{17,18}$), 8.66 (s, H_3), 8.77 and 8.78 (AB q, $H_{12,13}$), 8.87 and 8.90 (AB q, J_{AB} = 4.89 Hz, $H_{7,8}$).

2-Chloro-5,10,15,20-tetraphenylporphyrin (6):[29] ($CDCl_3$) −2.85 (bs, NH), 7.62–7.80 (m, $H_{m,p}$), 8.08 (m, H_o at C_{20}), 8.16–8.21 (m, H_o at $C_{5,10,15}$), 8.70 (s, H_3), 8.75 and 8.78 (AB q, J_{Ab} = 4.88 Hz, $H_{12,13}$), 8.79 and 8.85 (AB q, J_{AB} = 4.95 Hz, $H_{17,18}$), 8.87 and 8.90 (AB q, J_{AB} = 4.92 Hz, $H_{7,8}$).

2-Bromo-5,10,15,20-tetraphenylporphyrin (7):[27] (CD_2Cl_2) −2.45 (bs, NH), 7.71–7.84 (m, $H_{m,p}$), 8.09 (m, H_o at C_{20}), 8.21 (m, H_o at $C_{5,10,15}$), 8.77 and 8.79 (AB q, J_{AB} = 4.70 Hz, $H_{12,13}$), 8.83 and 8.88 (AB q, J_{AB} = 4.95 Hz, $H_{17,18}$), 8.89 (s, H_3), 8.91 and 8.94 (AB q, J_{AB} = 4.93 Hz, $H_{7,8}$).

2-Formyl-5,10,15,20-tetraphenylporphyrin (8):[30] ($CDCl_3$) −2.54 (bs, NH), 7.71–7.97 (m, $H_{m,p}$), 8.18–8.25 (m, H_o), 8.76 and 8.78 (AB q, J_{AB} = 4.74 Hz, $H_{12,13}$), 8.85 and 8.89, 8.86 and 8.92 (2 AB q, J_{AB} = 4.86 and 4.86 Hz, $H_{7,8}$ and $H_{17,18}$), 9.23 (s, H_3), 9.41 (s, CHO).

2-Methoxy-5,10,15,20-tetraphenylporphyrin (9):[31] ($CDCl_3$) −2.81 (bs, NH), 3.98 (s, OMe), 7.68 (s, H_3), 7.63–7.77 (m, $H_{m,p}$), 8.02 (m, H_o at C_{20}), 8.17–8.22 (m, H_o at $C_{5,10,15}$), 8.69 and 8.81 (AB q, J_{AB} = 4.81 Hz,

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Table I. Relative Populations (±2%) of **2a** and **2b** at 200 K in CD_2Cl_2

	R	2a	2b
3	CN	>99	
4	NO_2	97	3
5	OCOPh	94	6
6	Cl	94	6
7	Br	91	9
8	CHO	84	16
9	OMe	82	18
10	SPh	81	19
11	NHCOMe	73	27
12	OH	61	39
13	CH_2OH	38	62
14	$CH{=}CH_2$	33	67
15	NH_2	22	78
16	$(CH_2)_3Me$	21	79
17	Me	19	81
18	$CHMe_2$	9	91

$H_{17,18}$), 8.75 and 8.76 (AB q, J_{AB} = 4.76 Hz, $H_{12,13}$), 8.76 and 8.85 (AB q, J_{AB} = 4.89 Hz, $H_{7,8}$).

2-(Phenylthio)-5,10,15,20-tetraphenylporphyrin (10):[32] (CD_2Cl_2) −2.77 (bs, NH), 7.32, 7.49 (2m, SPh), 7.58–7.85 (m, $H_{m,p}$), 8.06 (m, H_o and H_3), 8.21 (m, H_o), 8.71 and 8.84 (AB q, J_{AB} = 4.89 Hz, $H_{17,18}$), 8.79 (s, $H_{12,13}$), 8.84 and 8.87 (AB q, J_{AB} = 4.90 Hz, $H_{7,8}$).

2-Acetamido-5,10,15,20-tetraphenylporphyrin (11):[32] (CD_2Cl_2) −2.88 (bs, NH), 1.84 (s, Me), 7.72–7.98 (m, $H_{m,p}$ and H_3), 8.19–8.25 (m, H_o), 8.67 and 8.86 (AB q, J_{AB} = 4.85 Hz, $H_{17,18}$), 8.81 (s, $H_{12,13}$), 8.82 and 8.88 (AB q, J_{AB} = 4.77 Hz, $H_{7,8}$), 9.21 (bs, NHCOMe).

2-Hydroxy-5,10,15,20-tetraphenylporphyrin (12):[27] (CD_2Cl_2) enol −2.94 (bs, NH), 1.53 (bs, 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 (bs, $H_{12,13}$); keto −2.0, −2.06 (2 bs, NH), 4.62 (s, $-CH_2-$), 8.49 and 8.72 (b AB q, J_{AB} = 5.1 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).

2-(Hydroxymethyl)-5,10,15,20-tetraphenylporphyrin (13):[30] ($CDCl_3$) −2.75 (bs, NH), 1.95 (t, CH_2OH), 4.88 (d, CH_2OH), 7.66–7.78 (m, $H_{m,p}$), 8.06 (m, H_o at C_{20}), 8.16–8.21 (m, H_o at $C_{5,10,15}$), 8.59 and 8.77 (AB q, J_{AB} = 4.78 Hz, $H_{17,18}$), 8.79 and 8.83 (AB q, J_{AB} = 4.79 Hz $H_{7,8}$), 8.83 and 8.85 (AB q, J_{AB} = 4.83 Hz, $H_{12,13}$), 8.93 (bs, H_3).

2-Vinyl-5,10,15,20-tetraphenylporphyrin (14):[33] ($CDCl_3$) −2.68 (bs, NH), 5.15, 5.90, 6.42 (ABX system, J_{AB} = 1.84, J_{AX} = 17.2 J_{BX} = 10.78 Hz, vinyl side chain), 8.08 (m, H_o at C_{20}), 8.18–8.23 (m, H_o at $C_{5,10,15}$), 8.70 and 8.76 (AB q, J_{AB} = 4.89 Hz, $H_{17,18}$), 8.78 and 8.80 (AB q, J_{AB} = 4.90 Hz, $H_{7,8}$), 8.83 and 8.84 (AB q, J_{AB} = 4.98 Hz, $H_{12,13}$), 8.89 (bs, H_3).

2-Amino-5,10,15,20-tetraphenylporphyrin (15):[32] (CD_2Cl_2) −2.78 (bs, NH), 4.52 (bs, NH_2), 7.7–7.86 (m, $H_{m,p}$ and H_3), 8.11–8.22 (m, H_o), 8.52 and 8.74 (AB q, J_{AB} = 4.70 Hz, $H_{17,18}$), 8.69 and 8.78 (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-Butyl-5,10,15,20-tetraphenylporphyrin (16): ($CDCl_3$) −2.80 (bs, NH), 0.84 (t, J = 6 Hz, Me), 1.25 (m, $MeCH_2$), 1.75 (m, $MeCH_2CH_2$), 2.82 (m, $CH_2CH_2CH_2Me$), 7.65–7.78 (m, $H_{m,p}$), 8.08 (m, H_o at C_{20}), 8.17–8.22 (m, H_o at $C_{5,15,20}$), 8.59 and 8.71 (AB q, J_{AB} = 4.75 Hz, $H_{17,18}$), 8.62 (bs, H_3), 8.71 and 8.77 (AB q, J_{AB} = 4.76 Hz, $H_{7,8}$), 8.83 and 8.85 (AB q, J_{AB} = 4.95 Hz, $H_{12,13}$).

2-Methyl-5,10,15,20-tetraphenylporphyrin (17): ($CDCl_3$) −2.89 (bs, NH), 2.58 (d, J = 1.21 Hz, Me), 7.68–7.80 (m, $H_{m,p}$), 8.07 (m, H_o at C_{20}), 8.18–8.24 (m, H_o at $C_{5,10,15}$), 8.61 (q, H_3), 8.63 and 8.75 (AB q, J_{AB} = 4.76 Hz, $H_{17,18}$), 8.75 and 8.80 (AB q, J_{AB} = 4.75 Hz, $H_{7,8}$), 8.85 and 8.87 (AB q, J_{AB} = 4.91 Hz, $H_{12,13}$).

2-Isopropyl-5,10,15,20-tetraphenylporphyrin (18): (CD_2Cl_2) −2.90 (bs, NH), 1.37, 1.39 (2 s, 2 × Me), 3.11 (sept, J = 6.71 Hz, $CHMe_2$), 7.69–7.83 (m, $H_{m,p}$), 8.17 (m, H_o at C_{20}), 8.22 (m, H_o at $C_{5,10,15}$), 8.61 and 8.73 (AB q, J_{AB} = 4.72 Hz, $H_{17,18}$), 8.73 and 8.79 (AB q, J_{AB} = 4.73 Hz, $H_{7,8}$), 8.78 (s, H_3), 8.88 and 8.90 (AB q, J_{AB} = 4.64 Hz, $H_{12,13}$).

Results

The effect of the substituents listed in Table I on the tautomeric equilibrium **2a** ⇄ **2b** was determined by variable-temperature NMR and measurement of ^4J coupling between the N–H and β-pyrrolic protons.

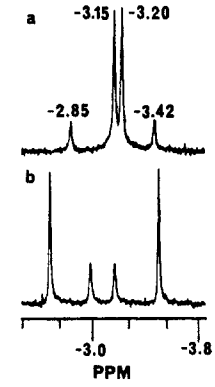

Figure 2. N–H region of 400 MHz ^1H NMR of (a) β-OMeTPP (**7**), and (b) β-NH_2TPP (**15**), in CD_2Cl_2 at 190 K.

The tautomerism **2a** ⇄ **2b** in 2-substituted 5,10,15,20-tetraphenylporphyrins may be monitored by dynamic NMR by analogy with 5,10,15,20-tetraphenylporphyrin.[1,2,9] At room temperature rapid tautomerism leads to one set of time-averaged resonances in the NMR spectrum. However, unlike in the case of 5,10,15,20-tetraphenylporphyrin, the presence of a substituent in the β-pyrrolic position removes the degeneracy of the two tautomers **2a** and **2b**. At sufficiently low temperature, where the tautomerism **2a** ⇄ **2b** is slow on the NMR time scale, two sets of peaks are observed, one set corresponding to each tautomer. Thus tautomer **2a**, with the R group on the isolated double bond, gives rise to two AB quartets for $H_{7,8}$ and $H_{17,18}$, both of which contain additional ^4J coupling to the N–H protons, a third AB quartet for $H_{12,13}$, and a resonance for H_3 of varying multiplicity depending on the nature of the R group. In contrast, the NMR spectrum of **2b** contains two sharp AB quartets for $H_{7,8}$ and $H_{17,18}$, while the resonances arising from $H_{12,13}$ (AB quartet) and H_3 display ^4J coupling to the N–H protons. Each tautomer gives rise to two signals for the N–H protons.

For all the porphyrins **3–18**, the tautomerism **2a** ⇄ **2b** was found to be slow on the NMR time scale at 200 K and the two sets of peaks were observed.[34] The relative populations of the tautomers **2a** and **2b** were in each case determined by integration of the N–H protons, as in general this region was well dispersed and all four singlets were observed (e.g., Figure 2). These estimates were confirmed in some instances by integration in other regions of the spectrum.

Assignment of the major tautomer as **2a** or **2b** was based on low-temperature spectra, i.e., under conditions of slow exchange. For porphyrins **3–9**, where R = CN, NO_2, OCOPh, Cl, Br, OMe, and CHO, the relative population of the major tautomer exceeded 85%. The major tautomer was identified as **2a** in each case, since two of the AB quartets corresponding to $H_{7,8}$ and $H_{17,18}$ exhibited coupling of ca. 1.5 Hz to the N–H protons, and this was confirmed by decoupling experiments (Figure 3). In the case of the porphyrins **10–16** the coupling to the N–H protons was not resolved and it was necessary to perform analogous decoupling experiments in order to assign the major tautomer.

While this method for assignment of the tautomers is unequivocal it is relevant to note that the difference in chemical shift of the N–H resonances in each tautomer allows independent determination of the major tautomer as **2a** or **2b**. In **2a** the chemical environment of the two interior protons is very similar. In contrast, tautomer **2b** contains an N–H on the pyrrole ring containing the substituent with the other N–H on the diagonally opposite pyrrole ring. Accordingly, a larger difference in chemical shift of the N–H protons in **2b** than **2a** would be expected and indeed was observed in all cases where the minor tautomer was of sufficient percent population to be detected, except for the formylporphyrin **8** in which the same small difference in chemical shifts was observed (Table II, Figure 2).

(32) Baldwin, J. E.; Crossley, M. J.; DeBernardis, J. F. *Tetrahedron* **1982**, *38*, 685.
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(34) These spectra were recorded in dideuteriodichloromethane due to its low viscosity and the good solubility of the porphyrins in this solvent at low temperatures.

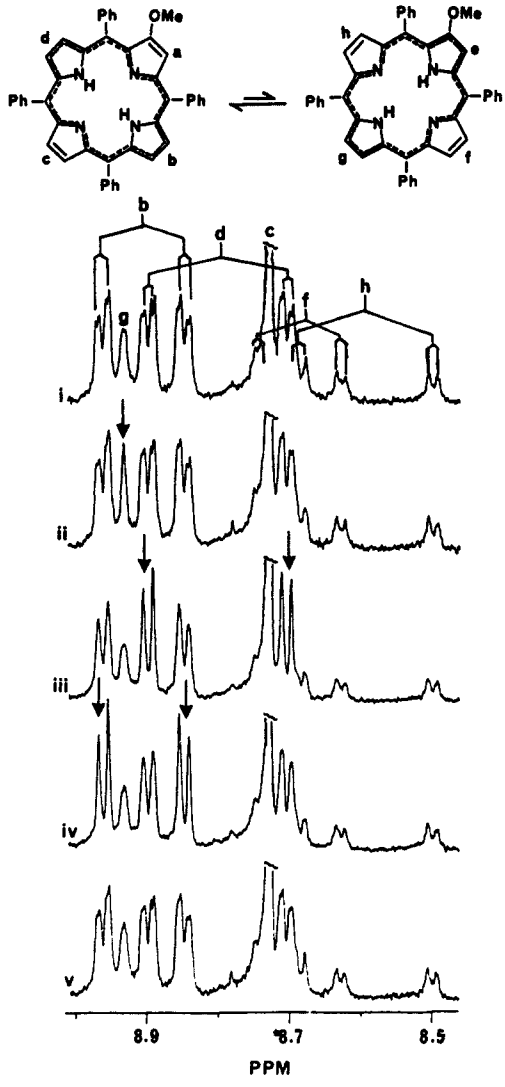


Figure 3. β-Pyrrolic region (the resonances of protons a and e are upfield with phenyl ring protons) of the 400-MHz ^{1}H NMR spectrum of β-OMeTPP (**7**) at 190 K in CD_2Cl_2: (i) normal spectrum; (ii) irradiation at −2.85 ppm; (iii) irradiation at −3.15 ppm; (iv) irradiation at −3.20 ppm; (v) irradiation at −3.42 ppm.

Table II. Chemical Shift Difference (Hz) at 400 MHz between N–H Protons in **2a** and **2b** at Slow Exchange

	R	2a	2b
3	CN	5	*a*
4	NO_2	33	*a*
5	OCOPh	0	56
6	Cl	20	86
7	Br	23	29
8	CHO	12	12
9	OMe	20	230
10	SPh	58	90
11	NHCOMe	39	201
12	OH[b]	31	259
13	CH_2OH	42	110
14	$CH{=}CH_2$	36	83
15	NH_2	67	309
16	$(CH_2)_3Me$	53	121
17	Me	48	117
18	$CHMe_2$	38	117

[a] Minor tautomer not detectable. [b] Keto form also present; details will be reported separately.

In certain instances, porphyrins **3–9** and **16–18**, the room temperature spectrum could also be used to ascertain the direction in which the position of the equilibrium had been shifted by inclusion of the β-pyrrolic substituent. As the temperature is raised, the relative populations of the tautomers **2a** and **2b** change according to a Boltzmann distribution, and, at room temperature, rapid tautomerism leads to a time-averaged spectrum. When each tautomer is equally populated the residence time of a hydrogen at each of the four interior nitrogens is equal and so an averaged coupling of the β-pyrrolic protons with the N–H protons results. Hence the line widths of the β-pyrrolic signals are, within experimental limits, the same. For porphyrins **3–9** the major tautomer was **2a**, where the R group is on the isolated double bond. The relative population of the major tautomer in each case was greater than 70% at room temperature and so the residence time of the interior hydrogens on NI and NIII was greater than NII and NIV. Hence the resonances resulting from $H_{7,8}$ and $H_{17,18}$ were considerably broader than those from H_3 and $H_{12,13}$ (Figure 4). This broadness was attributed to coupling of these protons to the N–H protons, and this assignment was confirmed by decoupling experiments. Similarly, for porphyrins **16–18** the dominant tautomer was **2b** and decoupling of the N–H protons resulted in $H_{12,13}$ and H_3 sharpening. This method of assignment of the major tautomer from room temperature spectra could only be accurately applied when the relative population of the major tautomer was at least 70% and signal dispersion was adequate.

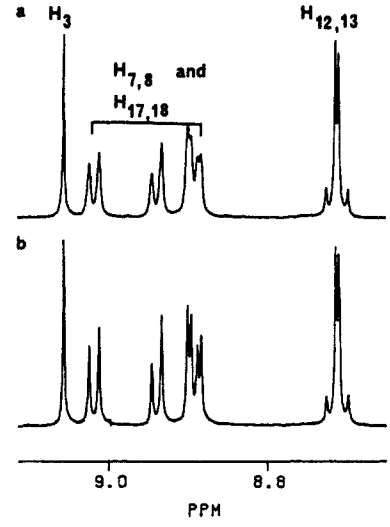


Figure 4. β-Pyrrolic region of the 400-MHz ^{1}H NMR spectrum of β-NO_2TPP (**4**) at 298 K in $CDCl_3$: (a) normal spectrum; (b) irradiation of NH protons, −2.61 ppm.

Table III. Relative Population (±2%) of **2a** in Different Solvents at 200 K

	R	CD_2Cl_2	toluene-d_8	acetone-d_6/DMF-d_7
4	NO_2	97	95	>98
9	OMe	84	85	81
13	CH_2OH	38	26	28
14	$CH{=}CH_2$	33	28	39
17	Me	19	13	insol

The equilibrium was found to be solvent dependent as expected. Thus spectra of porphyrins **4**, **9**, **13**, **14**, and **17** in CD_2Cl_2, toluene-d_8 and dimethylformamide-d_7/acetone-d_6 (1:1) afforded the results listed in Table III. The number of compounds tested was limited by their solubility in solvents suitable for low-temperature work. However, since no large variations in tautomeric populations were observed it is reasonable to assume that these results are representative for the range of compounds investigated.

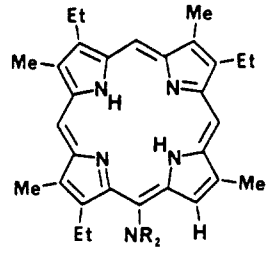
Discussion

The degeneracy of the tautomers, observed in previous studies[1-8,25] of porphyrins in solution, was overcome in the present study by the use of porphyrins with a single β-pyrrolic substituent. In all compounds investigated, porphyrins **3–18**, the tautomeric equilibrium **2a** $\rightleftarrows$ **2b** was shifted from equal populations of each tautomer (Table I), and thus indicated the presence of two energetically different tautomers whose stability is reflected in their relative populations.

The origin of the substituent effects observed in the present study is not straightforward since they do not parallel any known substituent scale, in particular they do not follow the Hammett scale, although some trends can be discerned such as the fact that alkyl substituents prefer to reside on aromatic bonds.

A significant feature of this system is the steric constraint imposed by the four phenyl rings at the meso positions. The extent of the steric interaction between the R group and the peri phenyl ring, which is determined by the size and orientation of the R group in solution, is related to the degree of conjugation attainable between the R group and the porphyrin ring, and indirectly affects the conformation of the porphyrin nucleus.

Conjugative vs. steric repulsion in porphyrins has been observed by Abraham et al.[35] Appreciable conjugation of the amino lone pair of electrons with the porphyrin π system occurs in *meso*-aminoporphyrins. Steric interaction with the adjacent ethyl group in the corresponding dialkylated porphyrins **19** and **20** predominated over the conjugative effect and the NR_2 group was rotated so that the lone pair was in an orthogonal position with respect to the porphyrin ring.



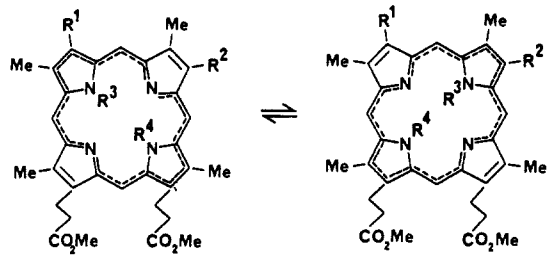
19 R = Me

20 R = Et

On the basis of these results, conclusive remarks as to the nature of the R group and the effect on the tautomeric equilibrium cannot be made, but clearly, a combination of steric and electronic factors need to be considered. While the energy differences involved here are only small (<6 kJ mol^{-1}), interpretation of chemical reactivity at room temperature must take into account the disturbed equilibrium. This has implications in the behavior of naturally occurring porphyrins which are highly functionalized.

The results from the study on [$^{15}N_4$]protoporphyrin IX dimethyl ester and [$^{15}N_4$]coproporphyrin III tetramethyl ester,[25] where, despite the overall asymmetry of these porphyrins, no perturbation of the tautomeric equilibrium from a 1:1 mixture was noted, are not surprising since in each case the two tautomers have identical β-pyrrolic substituents and almost identical steric interactions and would thus be expected to be of nearly equal energy.

We are currently looking at other β-substituted systems without meso substituents but where the electronic nature of the two tautomers is clearly different. Preliminary experiments on the 2- and 4-acetyldeuteroporphyrin IX dimethyl esters **21** and **22**



21 $R^1 = COCH_3$, $R^2 = R^3 = R^4 = H$

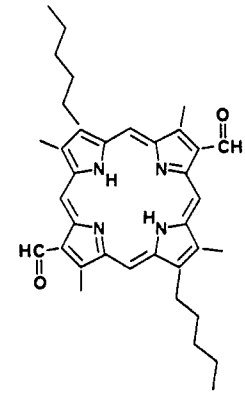
22 $R^2 = COCH_3$, $R^1 = R^3 = R^4 = H$

23 $R^1 = COCH_3$, $R^2 = H$, $R^3 = R^4 = D$

24 $R^2 = COCH_3$, $R^1 = H$, $R^3 = R^4 = D$

indicate the acetyl group does affect the electron distribution in the macrocycle. Studies on the deuterated derivatives **23** and **24** were undertaken since the tautomeric exchange **21a** $\rightleftarrows$ **21b** and **22a** $\rightleftarrows$ **22b** was still rapid on the NMR time scale at 175 K. The possibility that this exchange was due to catalytic intermolecular proton transfer is unlikely since saturation transfer experiments on 2-substituted 5,10,15,20-tetraphenylporphyrins indicate that intermolecular proton transfer is negligible at room temperature,[36] a result that has also been reported for 5,10,15,20-tetraphenylporphyrin.[5,9] Thus, results for the deuterated derivatives **23** and **24** under conditions of slow exchange ca. 220 K indicated that the major tautomer has the acetyl group on the isolated double bond. Magnetic circular dichroism studies[37,38] in a similarly substituted acetylporphyrin have detected two populations of conformers of the acetyl substituent, one in which the carbonyl moiety of the acetyl group achieves the maximum degree of coplanarity with the plane of the macrocycle allowed by steric interaction and the other in which it is much more out of plane. This conformer equilibrium is dependent on the tautomeric equilibrium. Interpretation of the results was complicated by lack of knowledge of tautomeric populations of substituted free base porphyrins in solution, which our results, in this instance, indicate is heavily to one side.

X-ray data of the diformylporphyrin **25** also support these



25

results in the solid state.[39] The inner nitrogen protons were found localized on the two opposite pyrrole rings not carrying the formyl groups, a result that would be predicted from this work.

This work has shown that the bond order in the porphyrin ring is modified by a β-pyrrolic substituent. For those porphyrins where **2a** is the dominant tautomer there is more double bond character in the pyrrolic rings II and IV. Hence positions 3, 12, and 13 should be more susceptible to electrophilic attack. Indeed we have observed this phenomenon in a number of cases involving electrophilic bromination reactions.[40]

The kinetics of the proton tautomerism in these systems is also under current investigation,[36] and these results will be reported shortly.

Conclusions

(i) Addition of a β-pyrrolic substituent removes the degeneracy of the tautomers of 5,10,15,20-tetraphenylporphyrin.

(ii) β-Pyrrolic substituents alter the position of the tautomeric equilibrium; this process can be observed by ^1H NMR at low temperatures.

(iii) In cases where the equilibrium lies predominantly to one side, the room temperature spectrum can be used to determine the structure of the major tautomer through coupling between

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the NH and β-pyrrolic hydrogens.

(iv) The observed substituent effects do not follow a known substituent scale, possibly due to steric interactions between the β-pyrrolic substituent and the peri phenyl ring.

(v) β-Substitution is predicted to modify chemical reactivities at the various pyrrolic positions; i.e., those involved in the major delocalization pathway should exhibit greater aromatic-type reactivity, while those on the localized double bond should be more susceptible to electrophilic attack.

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Structure of 1-Ethoxyhomotropylium Hexachloroantimonate: A Nonaromatic Homotropylium Cation[1]

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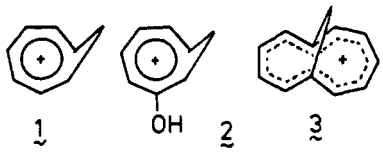
Abstract: Cycloocta-2,4,6-trienone, **4**, was reacted with $Et_3O^+SbCl_6^-$ to yield 1-ethoxyhomotropylium hexachloroantimonate, **5**. NMR spectra of solutions of this salt are consistent with the ion sustaining an induced ring current. Pale-yellow, near cubic crystals of **5** were obtained on recrystallization from CH_2Cl_2. The CPMAS ^{13}C NMR spectrum of the crystalline sample was very similar to its solution spectrum, indicating that there was no difference in the structure of the cation in the two phases. The crystal structure of **5** was determined by using X-ray diffraction. The cation has adopted an open conformation which was predicted by Haddon, with a large C_1, C_7 internuclear distance (2.284 (5) Å). A more detailed examination of the structure of **5** shows that the cation can best be regarded as a linear 1-ethoxyoctatrienyl cation and that on structural grounds this cation cannot be regarded as being homoaromatic. This conclusion is at odds with the NMR evidence and points to the need for caution in the use of the latter techniques as a criterion of homoaromaticity.

A major thrust of our current work has been the attempt to define more precisely the importance of homoaromaticity in medium ring cations such as the homotropylium ion, **1**.[2] To do



1 2 3

this we have used a combination of structure determinations using X-ray crystallography,[3] thermochemical measurements,[4] and both solution and solid-state NMR spectroscopy. In this latter area we have carried out a detailed analysis of the ring current criterion of homoaromaticity for some homotropylium cations and have shown that the large chemical shift difference of the exo and endo protons of the bridging methylene group of these ions is consistent with the presence of an induced ring current.[5] The conclusion reached from this multifaceted approach to a more rigorous definition of homaromaticity is that the original homoaromatic formulation of the structure of the 2-hydroxyhomotropylium cation, **2**, is correct.[6,2] The question arises as to how general is this conclusion.

Haddon, in a detailed theoretical investigation of the homotropylium cation, has concluded that there are two minima on the potential energy surface.[7] The lowest energy of these, which corresponds closely to the structure found experimentally for **2**,

Scheme I

has a calculated homoconjugate internuclear distance of 1.621 Å (MINDO-3). The second unsuspected energy minimum, which occurs along the pathway for the ring inversion process of the homotropylium cation,[8] was calculated to be some 6–10 kcal/mol less stable than the former conformation. The major distinguishing structural feature of this second conformation is the very long C_1,C_7 homoconjugate distance of 2.303 Å.

There are only two reported structure determinations of potential homotropylium cations. The first is **2**, mentioned above, and the second is the bridged annulene **3** reported by Simonetta et al.[9] This latter cation with a very long homoconjugate internuclear distance of 2.229 Å can formally be thought of as corresponding to the second, open conformation predicted by Haddon. However, this ion is also an annulenium cation with a 10 π-electron periphery and as such it is not clear how typical this structure is in terms of simpler homotropylium ions lacking the second carbon bridge.[10]

The relative energies of the two conformations of the homotropylium cation should depend on the position and nature of any substituents.[7] This is readily apparent from a consideration of the resonance structures of the homotropylium cation, Scheme I. Electron donor groups at C_1, C_3, C_5, and C_7 should favor the cyclooctatrienylium resonance structures as positive charge is maximized at these carbons in the open form of the cation. Conversely, donor substituents at C_2, C_4, and C_6 would be most effective in stabilizing the cation when it is in the closed bicyclo[5.1.0]octadienyl form. Substituents at C_8 might be expected

(1) This work was supported by grants from the Natural Sciences and Engineering Research Council of Canada, Imperial Oil Ltd., and the Science and Engineering Research Board at McMaster University.

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