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GIAO Nuclear Magnetic Shielding Tensors in Free Base Porphyrin and in Magnesium and Zinc Metalloporphyrins

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The gauge including atomic orbital (GIAO) method at the self-consistent field (SCF) level of theory was used to calculate magnetic shielding tensors in free base porphyrin (H_2P) and in magnesium (MgP) and zinc (ZnP) metalloporphyrins, as well as in the $MgP(H_2O)$ and $MgP(H_2O)_2$ complexes. All principal components of the calculated shielding tensors are reported. We have recorded new solution NMR spectra for all three molecules under identical conditions, to ensure the reliability of small differences in their NMR shifts. The calculated isotropic values are compared with these values and with low-temperature solid-state shifts, which resolve the tautomerism in H_2P. Agreement with experiment is good. It is encouraging that the calculations correctly reproduce most of the the small differences in the chemical shifts. A comparison of the observed and calculated NMR shifts of MgP leads to the conclusion that the species observed in tetrahydrofuran solution is either $MgP(H_2O)_2$ or $MgP(THF)_2$. We have calculated the effect of the out-of-plane displacement of the metal ion in metalloporphyrins, with a view to using NMR as a probe of nonplanarity. Only the ^{15}N shifts show any sensitivity.

1. Introduction

There is considerable interest in porphyrins and metalloporphyrins because of their importance in biological, photochemical, and photophysical processes.[1,2] Nuclear magnetic resonance (NMR) spectroscopy is a powerful tool for investigating different aspects of porphyrin chemistry both in solution and in the solid state. For example, the tautomerization of free base porphyrin (H_2P), involving double proton transfer between four nitrogen atoms, has been extensively studied using ^1H, ^{13}C, and ^{15}N variable-temperature NMR measurements.[3−15] We may note in passing that there is still a contradiction between the latest X-ray results of Chen and Tulinsky,[16] which show localized hydrogens in the room-temperature crystal, and the ^{13}C cross polarization magic angle spinning (CPMAS-NMR) by Frydman et al.[13] The later show that H migration is quenched at low temperature (−90 °C), but between −30 and +30 °C, the tautomerically distinct peaks coalesce, indicating fast tautomerization on the NMR time scale. This is difficult to reconcile with the generally accepted X-ray structure,[16] which shows localized hydrogens at room temperature. To resolve the contradiction, these authors propose that the whole porphyrin ring executes facile 90° rotations in the solid state, coupled to the hydrogen tautomerization motion. In view of the tight packing of the porphyrin rings in the crystal, this explanation appears somewhat unlikely, and the contradiction between the NMR and X-ray data has not yet been resolved.[15] The NMR evidence agrees with the older X-ray data of Webb and Fleischer.[17] However, the purity of their sample was questioned.[13]

The tautomerization problem illustrates that NMR experiments can provide useful structural information complementary to the X-ray data. The first NMR spectra for porphyrins were published in 1959,[18] and several hundred references concerning experimental NMR studies exist in the literature. However, high quality ab initio calculations of the magnetic properties of porphyrins have not yet been carried out. For example, in the ^{13}C CPMAS-NMR study of Frydman et al.,[13] chemical shifts for porphyrin were only estimated from the chemical shift of benzene and pyrene. As our calculations show, these estimates are not very accurate, especially for the out-of-plane component, which is by far too low. The size of porphyrins has been a limiting factor in performing high-level ab initio calculations of the NMR parameters. However, recent advances in computer technology and software development have overcome this problem. In this study, the latest version of the TX90/GIAO program (TX95) has been used. The TX95 package is based on a fast two-electron integral program and can be used in non-, semi-, and fully-direct mode. Direct techniques can be applied to both the SCF and coupled perturbed Hartree−Fock (CPHF) equations. This allows us to perform calculations of NMR parameters for systems containing 100 atoms with 1000 basis functions on a single processor machine. We have recently completed a parallel implementation of this program, further extending its limits for large molecules.[19]

The primary aim of this paper is to provide theoretical NMR spectra of free base porphyrin (H_2P) and magnesium (MgP) and zinc (ZnP) metallporphyrins. H_2P can be considered as a basic

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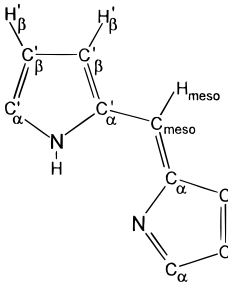

Figure 1. Atoms labeling in free base porphyrin. In the cases of MgP and ZnP, atoms with prime become equivalent to nonprimed atoms.

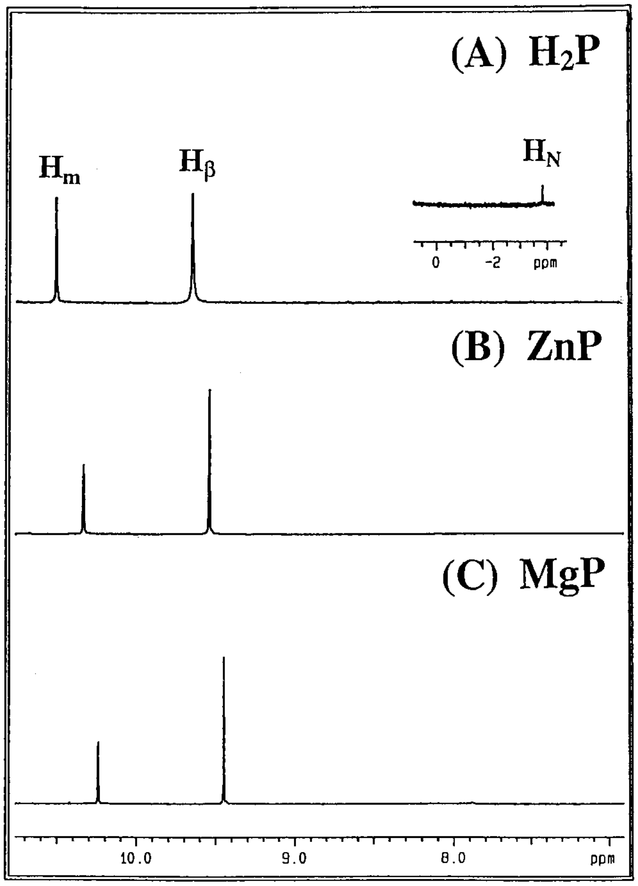

Figure 2. ^1H NMR spectra of free base porphyrin and zinc and magnesium metalloporphyrins. See text for the experimental conditions.

unit for many porphyrins, while MgP is related to chlorophyll. In this paper, we calculate the nuclear magnetic shielding tensor for all nonequivalent nuclei in H_2P, MgP, and ZnP at the SCF/GIAO level. In comparison with the usual experimental data in solution, only the isotropic average can be used. However, solid-state NMR can yield all principal components of a shielding tensor, and thus we present the full tensors. We hope that a detailed knowledge of these magnetic properties may lead to a better understanding of this important class of compounds and could guide future NMR experiments, besides demonstrating the possibilities of modern ab initio theory of NMR shifts. Porphyrins are large molecules on the ab initio scale and therefore the calculations are necessarily limited to isolated systems. A large body of previous evidence shows[21] that this approximation is adequate, especially for relative chemical shifts, unless there are strong specific interactions like H bonds with the solvent. As discusses below, this approach is justified by the agreement between the shifts measured in dilute solutions and the solid state.

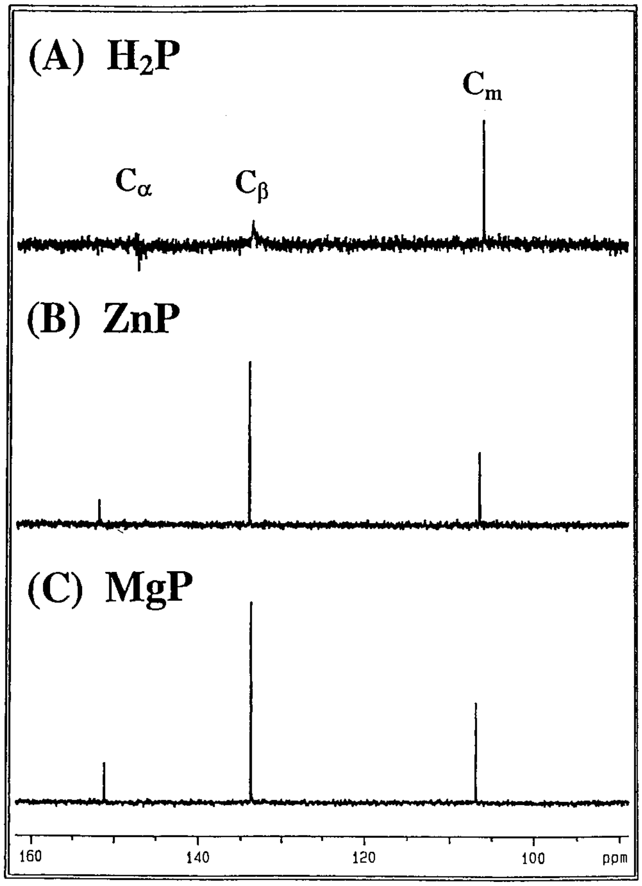

Figure 3. ^{13}C NMR spectra of free base porphyrin and zinc and magnesium metalloporphyrins. See text for the experimental conditions.

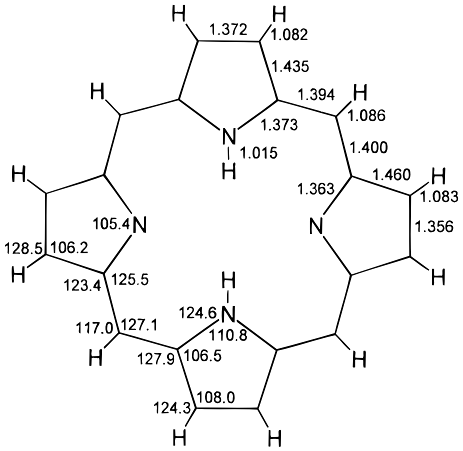

Figure 4. Optimized geometry of H_2P (with D_{2h} symmetry constraint) at the DFT/Becke-3LYP level of theory and with the 6-31G* basis set.

2. Experimental Section

Chromatographically pure free base porphyrin (H_2P) and its Mg(II) and Zn(II) complexes were purchased from Mid-Century (Posen, IL) and used as received. The purity of samples was checked by UV-vis and FT-IR before being used for NMR measurements. H_2P and its metallocomplexes have a fairly low solubility in almost all common organic solvents. To guarantee good comparisons, we used the same solvent, perdeuterated tetrahydrofuran (THF-d_8), for all our measurements. NMR spectra were recorded on a Bruker ARX-300 NMR spectrometer at room temperature (298 ± 1 K). The THF-d_8 signal was used to lock the field. All chemical shifts are given relative to TMS.

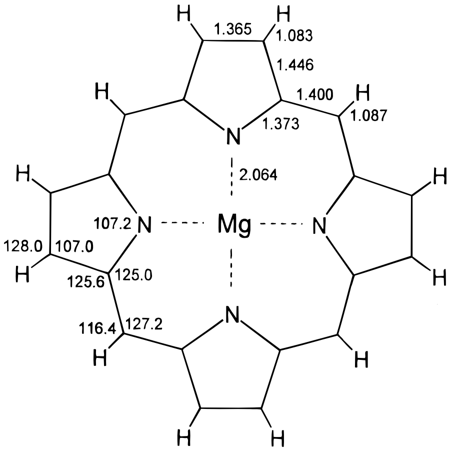

Figure 5. Optimized geometry of MgP (with D_{4h} symmetry constraint) at the DFT/Becke-3LYP level of theory and with the 6-31G* basis set.

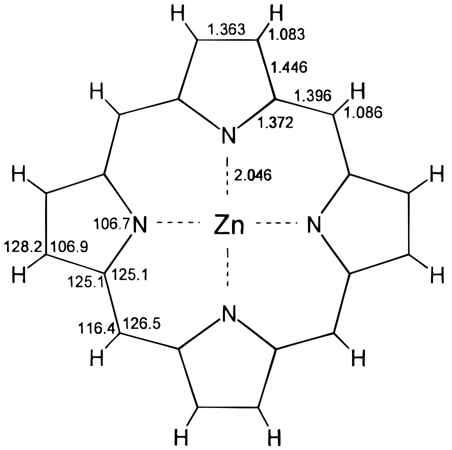

Figure 6. Optimized geometry-of ZnP (with D_{4h} symmetry constraint) at the DFT/Becke-3LYP level of theory and with the 6-31G*/Ahlrichs VTZ basis set.

^1H NMR spectra were measured at 300.132 MHz with an average of 16 scans. ^{13}C NMR spectra were obtained at 74.475 MHz, using THF-d_8 as an external standard with wide band proton decouping. The spectra are averages of 34770, 1330, and 850 scans, respectively, for H_2P, ZnP, and MgP. Free base porphyrin and metalloporphyrins are often contaminated by small traces of impurity from a synthetic byproduct that is quite soluble in THF and can be removed by a thin layer chromatography. The atom labeling is shown in Figure 1 and the experimental ^1H and ^{13}C NMR spectra of free base porphyrin and its Mg(II) and Zn(II) complexes are presented in Figures 2 and 3.

As a result of fast tautomerization of the inner hydrogens, there is a significant broadening/weakening of the ^{13}C NMR peaks in H_2P. The broadening effect follows the order $C_\alpha \gg C_\beta \gg C_{meso}$. As a consequence, the C_α peak almost vanishes in the spectra, resulting in a relatively large uncertainty in the exact position of this peak. The broadening of ^{13}C chemical shifts is. consistent with the picture that tautomerization has the largest effect on the C_α carbons and the least effect on C_{meso} carbons. The latter have, of course, the same magnetic shielding in both tautomers.

3. Computational Details

The choice of molecular geometry has a marked effect on the calculated NMR parameters.[20,21] Kutzelnigg et al.[21] recommend the use of experimental equilibrium geometries for the calculation of magnetic properties. However, the study of Bühl and Schleyer on boranes showed superiority of optimized geometries.[22] For H_2P considered in this paper, there are no structural data for the free molecule, and until very recently even the symmetry of the ground-state geometry (D_{2h} or the symmetry-broken C_{2v}) had been uncertain.[24] The ground-state symmetry has been decided in favor of the symmetrical D_{2h} structure only recently by our simulation of the vibrational spectrum of H_2P.[25,26] The crystal structure, besides being affected by intermolecular forces, is not free of problems, as discussed in the Introduction. Therefore, we have decided to perform all chemical shift calculations at the geometries obtained with density functional theory, using the B3-LYP exchange−correlation functional as implemented in the Gaussian suite of programs[23] (G92-DFT). Modern density functional theory gives excellent ground-state potential energy surfaces for organic molecules; as shown by numerous recent studies, including some on porphyrins.[25,26] For geometry optimization, we used the 6-31G* basis, which we have found to be adequate in DFT theory. For Zn, the VTZ basis set of the Ahlrichs group[27] was used. The equilibrium geometries are shown in Figures 4−6. Both MgP and ZnP are planar in our calculations. It has been suggested that Zn is too large for the central cavity and that ZnP may pucker,[28] but we see no such effect. This can be understood by noting that Zn^{2+} is only slightly larger than Mg^{2+} because of the transition metal contraction. The calculated

TABLE 1: Basis Set Convergence of Calculated NMR Shielding Constants for Free Base Porphyrin

	6-311G[a]		6-311G (d,p)[b]		6-311G (2d,p)[c]	
atom[d]	σ_{iso}[e]	σ_{aniso}[f]	σ_{iso}[e]	σ_{aniso}[f]	σ_{iso}[e]	σ_{aniso}[f]
H(−N)	38.82	30.74	40.73	40.46	41.16	42.29
H_{meso}	22.91	12.17	21.04	14.33	20.84	14.86
H_β	23.40	6.19	21.91	8.84	21.70	9.38
H_β'	23.27	6.77	21.62	9.05	21.41	9.58
C_α	35.59	167.00	31.87	170.18	30.67	172.45
C_α'	53.07	165.83	50.13	169.07	49.59	170.96
C_β	55.69	149.08	50.68	144.38	50.44	143.91
C_β'	63.26	152.15	59.13	148.95	58.93	148.94
C_{meso}	88.76	137.12	87.85	130.83	88.00	131.09
N(−H)	116.44	204.14	119.85	199.80	119.96	201.11
−N=	−14.98	470.63	2.23	456.28	1.83	456.82

[a] Energy = −983.03277 3 a.u. (354 basis functions). [b] Energy = −983.451 181 a.u. (516 basis functions). [c] Energy = −983.480 948 a.u. (636 basis functions). [d] For atoms labeling, see Figure 1. [e] $\sigma_{iso} = 1/3(\sigma_{11} + \sigma_{22} + \sigma_{33})$. [f] $\sigma_{aniso} = \sigma_{33} - 1/2(\sigma_{22} + \sigma_{11})$ where $\sigma_{33} > \sigma_{11} > \sigma_{11}$.

TABLE 2: Components of the Magnetic Shielding Tensor for Free Base Porphyrin[a]

atom[b]	σ_{iso}	σ_{aniso}	σ_{11}	σ_{22}	σ_{33}	tensor orientation[c]
H(−N)	40.73	40.46	28.54	25.96	67.71	N−H
H_{meso}	21.04	14.33	30.60	26.93	5.60	$C_{meso}-H_{meso}$
H_β	21.91	8.84	27.80	24.54	13.37	$C_\alpha'-C_\beta'$
H_β'	21.62	9.05	27.65	25.63	11.57	$C_\alpha-C_\beta$
C_α	31.87	170.18	−47.33	−2.39	145.32	$C_\alpha-C_\beta$
C_α'	50.13	169.07	−35.57	23.10	162.84	$C_\beta'-C_\beta'$
C_β	50.68	144.38	64.31	−59.21	146.93	$C_\alpha'-C_\beta'$
C_β'	59.13	148.95	50.79	−40.83	158.43	$C_\alpha-C_\beta$
C_{meso}	87.85	130.83	1.45	87.03	175.07	$C_{meso}-H_{meso}$
N(−H)	119.85	199.80	26.06	80.45	253.05	N−H
−N=	2.23	456.28	−230.94	−68.79	306.42	N−H

[a] 6-311G (d,p) basis set; see Table 1 for energy. [b] See Figure 1. [c] Principal axis 1 is approximately aligned with the specified bond. Principal axis 3 is always the out-of-plane (*z*) direction.

TABLE 3: GIAO/6-311G(d,p) NMR Shielding Tensors for Magnesium and Zinc Porphyrins

	MgP[a]				ZnP[b]				
atom	σ_{iso}	σ_{11}	σ_{22}	σ_{33}	σ_{iso}	σ_{11}	σ_{22}	σ_{33}	tensor orientation[c]
H_β	21.65	24.84	27.76	12.35	21.67	25.09	27.59	12.32	$C_\alpha-C_\beta$
H_{meso}	20.96	30.72	26.74	5.43	20.99	30.41	27.14	5.41	$C_{meso}-H_{meso}$
C_α	36.69	−5.51	−37.69	153.28	36.71	−5.15	−36.89	152.16	$C_{meso}-H_\alpha$
C_β	53.46	−51.37	59.63	152.12	53.72	−51.26	60.05	152.38	$C_\alpha-C_\beta$
C_{meso}	85.37	85.81	−2.11	172.42	85.83	85.88	−1.49	173.11	$C_{meso}-H_{meso}$
N	55.29	−22.41	−106.10	294.36	55.66	−21.14	−104.13	292.26	N···Me
Me[d]	571.67	553.21	553.21	608.58	1887.15	1980.97	1980.97	1699.51	N···Me

[a] Energy = −1182.067 451 a.u. (536 basis functions). [b] Energy = −2760.142 381 a.u. (548 basis functions). [c] See Table 2. [d] Me = Mg or Zn, respectively.

TABLE 4: Theoretical and Experimental NMR Shieldings of Free Base Porphyrin Relative to Internal References[a]

atom	theor	exptl[b]	theor	exptl[c]
H(−N)	19.69	14.34	19.11	12.23
H_{meso}	0	0	−0.58	
H_β	0.87	0.86*	0.29	0.29
H_β'	0.58	0.86*	0	0

atom	theor	exptl[d]
C_α	0	0
C_α'	18.26	16*
C_β	18.81	16*
C_β'	27.26	25
C_{meso}	55.98	50

atom	theor	exptl[e]
N(−H)	117.62	109.1
−N=	0.0	0.0

[a] Results obtained with the 6-311G(d,p) basis set. Shieldings are given as differences from reference nucleus, i.e., the nucleus with the smallest absolute shielding. Note that this procedure yields chemical shifts which are of opposite sign to the usual ones. *designates average experimental values. [b] This work. These values are virtually identical with those quoted by T. R. Janson and J. J. Katz, in ref 1, Vol. IV (Physical Chemistry), p 14. [c] Reference 3. This value is in agreement with the 183 K spectra of ref 15. [d] Reference 13. [e] Reference 15 (from the plot). These values correspond closely to results obtained on *meso*-tetraphenyl porphyrin.[6,7]

TABLE 5: Theoretical and Experimental NMR Chemical Shifts of Free Base, Magnesium, and Zinc Porphyrins, Relative to TMS

	H_2P		MgP		ZnP	
atom[a,b]	theor	exptl	theor	exptl	theor	exptl
H(−N)	−8.25	−3.91				
H_β	10.72	9.57	10.83	9.45	10.81	9.54
H_{meso}	11.44	10.43	11.52	10.24	11.49	10.34
C_α	155.15	147.16[c]	159.46	151.16	159.44	151.84
C_β	141.24	133.56	142.69	133.75	142.43	133.95
C_{meso}	108.30	106.03	110.78	106.91	110.32	106.50

[a] Chemical shifts relative to tetramethylsilane (TMS). The calculated 6-311G(d,p) SCF isotropic shieldings of TMS are 32.48 ppm for ^1H and 196.15 ppm for ^{13}C. The geometry of TMS was optimized at the SCF level with the 3-21G* basis set. [b] The ^1H NMR spectrum for nickel porphyrin (NiP), in which Ni(II) exists as a low-spin ion, was also recorded in this work. Found: H_β, 9.43; H_{meso}, 10.21 in THF-d_8. NiP has the lowest solubility in THF compared with H_2P, ZnP, and MgP, making it extremely difficult to record high quality ^{13}C NMR spectrum. [c] As a result of the broadening associated with the H tautomerization, the uncertainty is larger for the position of the C_α peak, estimated to be ±0.25 ppm from the width.

TABLE 6: Coordination Effects in Magnesium Porphyrin, Changes in the Chemical Shifts Relative to Free Base Porphyrin

atom	Δ(0)[a]	A(l)[a,b]	A(2)[a,c]	exptl[d]	exptl[e]
H_β	0.12	0.01	−0.06	−0.12	−0.04
H_{meso}	0.08	−0.07	−0.16	−0.19	−0.07
C_α	4.31	4.25	3.46	4.00 ± 0.25[f]	2.5 ± 0.5[f]
C_β	1.45	0.72	0.85	0.19	0.51
C_{meso}	2.48	1.72	0.92	0.88	1.32
N	5.75	11.04	16.83		

[a] $\Delta(n) = \sigma[H_2P \text{ (tautomeric average)}] - \sigma[MgP(H_2O)_n]$. [b] C_{2v} geometry. The calculated Mg···O distance is 2.133 Å. The Mg atom is 0.283 Å out of the molecular plane. The shieldings are averaged over the two slightly different pyrrole rings. [c] D_{2d} configuration. The calculated Mg···O distances are 2.208 Å, and the H−O−H angles are 108.53°. [d] Dilute solution of "MgP" in THF. [e] Dilute solution of "MgP" in CD_2Cl_2. [f] As a result of the broadening of this band, the results are less accurate than for the other shifts.

geometry for H_2P is in good agreement with the experimental X-ray structure,[16] if the latter is averaged to D_{2h} symmetry.

We have carried out a series of preliminary calculations on H_2P to establish the convergence behavior of the calculated shielding tensors with respect to the basis set. For first-row elements, a triple-ζ type basis set is sufficient to describe the sp region in NMR calculations.[29] The effect of polarization functions was determined by calculations with the 6-311G, 6-311G (d,p), and 6-311G (2d,p) basis sets[30] presented in Table 1. As this table shows, the second set of polarization functions on the heavy atoms has only a minor influence on the calculated shieldings (less than 1−2 ppm for ^{13}C and ^{15}N, less than 0.4 ppm for ^1H). The relative shifts of chemically similar nuclei (e.g., H bond to C) converge, in general, faster than the absolute shieldings. Thus, we decided to use the 6-311G(d,p) basis set for first-row elements and the analogous McLean−Chandler basis for Mg.[31] On the basis of our former experience,[29] we have decontracted this basis set in the 2p region. For Zn, we used the VTZ basis referenced above. Results of calculations for H_2P, showing all tensor components, are summarized in Table 2. The results for MgP and ZnP are presented in Table 3. Table III shows that NMR shielding tensors are very similar for magnesium and zinc porphyrins, a fact that is not surprising in view of the closed-shell configurations of both ions. The values averaged over the tautomeric configurations of H_2P are also quite similar.

The strong electron correlation effect on the geometry of porphyrin raises the question of the reliability of SCF NMR results. Traditional correlation methods like MP2 are still too expensive for a system of this size. We have run a DFT calculation for free base porphyrin using the BLYP exchange−correlaton functional. While the results, especially for the absolute ^{15}N shieldings, change somewhat, the shifts relative to internal standards are similar. For. ^{13}C, the largest change is the $C_{meso} - C_\alpha$ differencem which is reduced to 51.84 ppm from 55.98 (Table 4). The chemical shift of the two nitrogens shows the largest effect going from 117.6 ppm at the SCF level

TABLE 7: Shieldings for Zinc and Magnesium Porphyrins and Nonplanarity Effects

	ZnP^a		MgP^a		MgP^b		$MgP(H_2O)$	
atom	σ_{iso}	σ_{aniso}	σ_{iso}	σ_{aniso}	σ_{iso}	σ_{aniso}	σ_{iso}	σ_{aniso}
H_β	21.68	8.89	21.66	9.13	21.72	9.08	21.76	8.92
H_{meso}	21.01	14.16	21.00	14.60	21.01	14.59	21.11	14.31
C_α	36.40	173.31	36.39	174.98	35.87	175.11	36.75, 36.65	174.45, 173.89[c]
C_β	53.72	148.42	53.45	148.23	53.91	148.13	54.19, 53.73	146.50, 146.16[c]
C_{meso}	85.56	130.99	85.42	130.83	85.01	131.00	86.13	129.08
N	48.62	364.24	49.59	365.81	50.73	363.33	51.83, 48.18	365.90, 372.64[c]
Zn/Mg	1977.80	85.75	590.41	52.13	588.09	52.77	586.62	54.01

[a] Metal moved out of molecular plane by 0.5 Å. [b] Domed structure with the Mg atom 0.5 Å out of the plane of the four nitrogens. [c] As a result of the presence of the water molecule, the symmetry is lowered to C_{2v} and formerly equivalent atoms have slightly different shieldings. These differences may be detectable at low temperature in the solid state, and thus, we quote both values. For H_β, H_{meso}, and C_{meso}, the differences in the shielding tensors are very small and the tabulated values refer to average shieldings.

to 83.7 at the DFT level. These values bracket the experimental result of 109.1 ppm. None of our conclusions are significantly affected.

4. Comparison of Experiment and Theory

Table 4 compares the experimental and theoretical NMR shifts of H_2P relative to internal references. With the exception of our ^1H results, the experimental data were recorded in the solid state at low temperature and thus resolve tautomerically equivalent nuclei. As usual at the SCF level, the calculated shifts are somewhat (~10%) larger than the experimental ones. The most important conclusion from Table 5 is that small shifts, e.g., the difference between the H_{meso} and the average H_β shieldings, or that between H_β and $H_{\beta'}$, are reproduced accurately. This has been found in previous studies as well, e.g., for stilbene.[29]

Table 5 compares the calculated and room-temperature experimental ^1H and ^{13}C chemical shifts of H_2P, MgP, and ZnP. Chemical shifts are listed relative to TMS (calculated absolute shieldings for TMS are 32.48 and 196.15 ppm for H and C, respectively, using the 6-311G(d,p) basis). The calculated values for H_2P have been averaged over the tautomers.

The calculated chemical shifts have significant errors (up to 8 ppm for the β carbon), as expected for comparing systems as dissimilar as TMS and porphyrins. However, these errors largely cancel in comparing atoms in similar chemical environment (free base and metalloporphyrin), or different geometries of the same system. Our experience shows that it is often possible to predict chemical shift differences between similar atoms to within a few tenths of a ppm. Indeed, the calculations correctly reproduce the deshielding that occurs when metal ion replaces the protons. As expected, this effect is largest for the C_α nuclei; its calculated magnitude (4−5 ppm) agrees well with the experimental value. The C_β and the C_{meso} nuclei are also deshielded, although the calculated changes are too large compared to experimental ones. Agreement is much better if the coordination effect is taken into account. For MgP this is shown in Table 6, which compares the calculated results for MgP, $MgP(H_2O)$, and $MgP(H_2O)_2$ with the experimental results obtained in THF and CD_2Cl_2 solvents. The geometries of the coordinated molecules were also optimized; see the footnotes to Table 6. In THF solvent, the best overall agreement is obtained for $MgP(H_2O)_2$. In CD_2Cl_2 solvent, the results are about halfway between $MgP(H_2O)$ and $MgP(H_2O)_2$. MgP is coordinatively unsaturated, and it is likely that the species observed in the THF solution contains at least one but probably two coordinated solvent molecules. This is corroborated by infrared spectral data.[32] The situation is less clear for the CD_2Cl_2 solution. It is difficult to free MgP of all water, especially in very dilute solution. Alternatively, the solvent may also coordinate weakly the exposed Mg atom.

It is well known that NMR shielding tensors may be quite sensitive to geometry changes.[21] An interesting question arises here as to whether NMR may be a useful probe of planarity in metalloporphyrins. These molecules are planar according to our DFT calculations; this is also supported by a comparison of the calculated and experimental vibrational spectra.[32] However, it is generally accepted that some metalloporphyrins, especially these containing high-spin transition metals, are nonplanar. The most important nonplanar distortion is doming, which corresponds to an A_{2u} vibration under D_{4h} symmetry. To answer this question, we have investigated three plausible models.

(a) The metal atom was moved from the planar ring by 0.5 Å (without geometry reoptimization).

(b) The metal atom was moved from the planar ring by 0.5 Å, and the pyrrole rings were tilted around the $C_\alpha-C_\alpha$. The structure was then reoptimized with a fixed Mg distance to the plane of the four nitrogenes.

(c) $MgP(H_2O)$ complex with fully optimized DFT/6-31G* geometry was used. The system remains essentially planar, with the Mg atom only 0.283 Å out of the average plane of the four nitrogens. The results of these calculations are shown in Table 7.

In all cases, only the nitrogen shielding tensors are affected significantly by nonplanarity. Changes in the shielding tensors of ^{13}C and ^1H are much smaller. Table 7 shows that the important factor determining the N shifts is the distance of the metal from the average ring plane rather than geometrical changes in the ring structure. The isotropic ^{15}N shielding decreases by 7 ppm in ZnP, about 5−6 ppm for MgP, and on the average by about 5 ppm in $MgP(H_2O)$. These changes are similar to those occuring upon water coordination (cf. the nonplanar MgP and the $MgP(H_2O)$ values in Table 7. Therefore, ^{15}N NMR may be a useful probe of the out-of-plane displacement of the metal or the ligation state. It is possible that the effect of the out-of-plane displacement of the metal is due simply to the increase of the metal−N distance.

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