The Aromatic Character of Magnesium Porphyrins

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The aromaticity of magnesium porphyrins have been studied by calculating the nuclear magnetic shieldings in selected points outside the molecules. The strength of the induced ring currents for a given magnetic field have been obtained by using the aromatic-ring-current-shielding (ARCS) method. Nucleus-independent chemical shift (NICS) calculations provide additional information about the current routes in the multiple-ring systems. The total aromatic pathway of magnesium porphyrins must be considered as a superposition of several $(4n + 2)$ π-electron Hückel pathways. We found that all β-unsaturated pyrrolic rings have local ring currents the strength of which is 70−90% of the current strength for the pyrrole molecule. The present study also shows that the 18π-[16]annulene aromatic pathway does not exist in magnesium porphyrins until all four pyrrolic units are saturated in the β-position.

Introduction

In aromatic molecules an external magnetic field induces a ring current in the conjugated π-electron system.[1−16] The ring current in turn creates a magnetic field that is observed as a long-range magnetic shielding. This implies that the strength of the ring current of aromatic molecules can be estimated by studying the long-range magnetic shielding function.[17] The short-range contribution to the magnetic shielding functions as a result of the local motion of the electrons around the atoms and in the chemical bonds vanishes outside the electron density.

Magnesium porphyrins consist of four pyrrole units connected by conjugated bonds to form a larger ring with a magnesium atom at the center. Traditionally, porphyrins have been considered as 18π-[18]annulenes.[18−21] However, there are several other possible routes for the induced ring current. The common denominator for feasible paths is that $(4n + 2)$ π-electrons are involved,[22,23] which implies that all pathways consisting of 18, 22, or 26 π-electrons might come in question. The total aromatic pathway may in fact consist of a linear combination of several routes.

In the present work, the aromatic pathways of magnesium porphin, magnesium chlorin, and magnesium bacteriochlorins have been studied by performing aromatic ring current shieldings (ARCS)[17] and nucleus-independent chemical shift (NICS)[24] calculations. The ARCS calculations yield the overall current strengths, while the NICS values provide information about the fine structure of the currents in the multiple-ring systems. Since the magnesium porphyrins have the magnesium atom at the center of the porphyrin nucleus, the NICS method cannot be used to study the degree of aromaticity of magnesium porphyrins. In the ARCS approach, the ring current is deduced from the long-range behavior of the shielding function and the magnesium atom at the molecular center does not prevent the determination of the strength of the induced ring current.

The molecules were chosen to enable us to probe different aspects of the aromaticity of the magnesium porphyrins. The saturation of the β-carbons effectively prevents the $\pi-\pi$ conjugation of the $C_\beta-C_{\beta'}$ bond. By saturating one or more pyrrolic rings in the β-position, the current can be forced to take certain paths in the porphyrin nucleus.

Theory

A simple relation between the long-range behavior of the isotropic nuclear magnetic shielding function $\sigma(z)$ and the current susceptibility with respect to the applied

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(1) Pauling, L. *J. Chem. Phys.* **1936**, *4*, 637.
(2) London, F. *J. Phys. Radium* **1937**, *8*, 397.
(3) Pople, J. A. *J. Chem. Phys.* **1956**, *24*, 1111.
(4) Pople, J. A. *Mol. Phys.* **1958**, *1*, 175.
(5) McWeeny, R. *Mol. Phys.* **1958**, *1*, 311.
(6) Elvidge, J. A.; Jackman, L. M. *J. Chem. Soc.* **1961**, 859.
(7) Abraham, R. J.; Sheppard, R. C.; Thomas, W. A.; Turner, S. *Chem. Commun.* **1965**, 43.
(8) Kutzelnigg, W.; van Wüllen, C.; Fleischer, U.; Franke, R.; v. Mourik, T. In *Nuclear Magnetic Shieldings and Molecular Structure*; Tossell, J. A., Ed., Kluwer Academic Publishers: Norwell, MA, 1993; pp 141−161.
(9) Minkin, V. I.; Glukhovtsev, M. N.; Simkin, B. Y. *Aromaticity and Antiaromaticity—Electronic and Structural Aspects*; Wiley: New York, 1994.
(10) Fleischer, U.; Kutzelnigg, W.; Lazzeretti, P.; Mühlenkamp, V. *J. Am. Chem. Soc.* **1994**, *116*, 5298.
(11) Bilde, M.; Hansen, A. *Mol. Phys.* **1997**, *92*, 237.
(12) Černušák, I.; Fowler, P. W.; Steiner, E. *Mol. Phys.* **1997**, *91*, 401.
(13) Zanasi, R.; Lazzeretti, P. *Mol. Phys.* **1997**, *92*, 609.
(14) Chesnut, D. B. *J. Chem. Phys.* **1998**, *231*, 1.
(15) Ligabue, A.; Pincelli, U.; Lazzeretti, P.; Zanasi, R. *J. Am. Chem. Soc.* **1999**, *121*, 5513.
(16) Morao, I.; Cossío, F. P. *J. Org. Chem.* **1999**, *64*, 1868.
(17) Jusélius, J.; Sundholm, D. *Phys. Chem. Chem. Phys.* **1999**, *1*, 3429.
(18) Vogel, E.; Haas, W.; Knipp, B.; Lex, J.; Schmickler, H. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 406.
(19) Vogel, E. *J. Heterocycl. Chem.* **1996**, *33*, 1461.
(20) Lash, T. D.; Chaney, S. T. *Chem. Eur. J.* **1996**, *2*, 944.
(21) Lash, T. D.; Romanic, J. L.; Hayes, J.; Spence, J. D. *Chem. Commun.* **1999**, 819.
(22) Lloyd, D. *J. Chem. Inf. Comput. Sci.* **1996**, *36*, 442.
(23) Schleyer, P. v. R.; Jiao, H. *Pure Appl. Chem.* **1996**, *28*, 209.
(24) Schleyer, P. v. R.; Maerker, C.; Dransfeld, A.; Jiao, H.; van Eikema Hommes, N. J. R. *J. Am. Chem. Soc.* **1996**, *118*, 6317.

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magnetic field can be derived from Biot-Savart's law[25] by assuming that the wire carrying the current is circular and infinitely thin.[17,26] The expression that relates the long-range shielding function to the ring-current susceptibility and to the size of the aromatic pathway then becomes

$$\sigma(z) = -\frac{\mu_0}{2}\frac{\partial I_{\mathrm{ring}}}{\partial B_{\mathrm{ext}}}\frac{R^2}{(z^2 + R^2)^{3/2}} \qquad (1)$$

In eq 1, μ_0 is the vacuum permeability, R is the radius of the current loop, B_{ext} is the external magnetic field, $\partial I_{\mathrm{ring}}/\partial B_{\mathrm{ext}}$ is the current susceptibility, and z is the perpendicular distance from the center of the current loop.

Computational Methods

The molecular structures of the magnesium porphyrins have been fully optimized without any symmetry constraints at the resolution-of-the-identity density-functional theory (RI-DFT) level[27] using the Becke-Perdew (B-P) parametrization[28−30] as implemented in TURBOMOLE.[31] The nuclear magnetic shieldings have been calculated at Hartree-Fock self-consistent-field (SCF) level.[32−34] To ensure origin-independence in the shielding calculations, the gauge-including-atomic-orbital (GIAO) approach has been employed.[2,35−37] In the structure optimization, the Karlsruhe split-valence basis sets[38] augmented with polarization functions on C, N,[39] and Mg were employed (SV(P)), while in the shielding calculations the basis set was further augmented with polarization functions on H (SVP).

Results and Discussion

The nuclear magnetic shieldings have been studied for magnesium porphin (MgP), magnesium chlorin (MgC), magnesium bacteriochlorin (MgBC), and magnesium isobacteriochlorin (MgIBC). The molecular structures together with the calculated ^{1}H NMR shieldings are shown in Figure 1. The optimized B-P DFT structure for MgP is slightly distorted from the expected D_{4h} symmetry. The difference in the Mg−N distances though is only 0.24 pm. However, at second-order Møller−Plesset (MP2) level,[40] MgP possesses D_{4h} symmetry. Two other magnesium porphyrins were also studied. Magnesium hexahydroporphyrin with three of the pyrrolic rings saturated in the β position is denoted Mg3BC and magnesium octahydroporphyrin with four β-saturated pyrrolic rings is denoted Mg4BC. The molecular structures of Mg3BC and Mg4BC and the calculated ^{1}H NMR shieldings are shown in Figure 2. The Cartesian coordinates of the optimized molecular structures can be downloaded from our world wide web (www) server.[41] The optimized MP2 structure for MgP is also available on our world wide web (www) server. To check whether nonplanar distortions are significant, the molecular structures of MgP and MgIBC were reoptimized starting from a strongly nonplanar structure. The reoptimized structures were practically planar. The obtained ruffling angle of MgIBC was about 1°.

The total energies and the hydrogenation energies of the magnesium porphyrins are compared in Table 1. As seen in Table 1, MgIBC lies energetically lower than MgBC. This is remarkable since the current susceptibility for MgBC is 2.5 times larger than for MgIBC and one would expect that the electron delocalization stabilizes the molecule. The hydrogenation energies are the energy gain when two hydrogens are added to the β-carbons of a pyrrolic ring. From the differences in the hydrogenation energies (ΔE_{hyd}), it can be seen that the hydrogenation energies decrease with the number of β-saturated rings. That means that magnesium porphin is more stable than magnesium chlorin and that Mg4BC is the least stable magnesium porphyrin among the studied ones. The hydrogenation energy for the hydrogenation of Mg3BC to Mg4BC is 46 kJ mol^{-1} smaller than for the hydrogenation of MgP to MgC.

The current susceptibilities and the ARCS indices have been deduced from the long-range shielding function as previously described.[17,26] In Figure 3, the ARCS plots for MgP are shown. The ARCS plots for the other molecules are very similar and can be downloaded from our world wide web (www) server.[41] MgP has the largest current susceptibility of 10.5 nA T^{-1}. MgBC, Mg4BC, and MgC can also be considered to be aromatic molecules since their current susceptibilities are 8.5, 6.9, and 6.2 nA T^{-1}, respectively. MgIBC and Mg3BC have significantly smaller current susceptibilities of 3.5 and 2.9 nA T^{-1}, respectively, and one may question whether they can be considered aromatic. The current radii are in general somewhat larger than the geometrical radii. The lower limit for the given geometrical radii is the distance between the meso carbons. For Mg4BC, the only possible aromatic pathway is the 18π-[16]annulene inner-cross path. As expected, Mg4BC has a smaller ring-current radius than the other magnesium porphyrins. The ARCS calculations are summarized in Table 2.

As seen in Table 3, the relative ring-current susceptibilities for the magnesium porphyrins can be obtained from the NICS values calculated for β-saturated rings. The larger the ring current the more negative is the NICS value of the β-saturated rings. The current susceptibilities also correlate with the ^{25}Mg NMR shieldings. However, since the ^{25}Mg nucleus is unfortunately not a very useful NMR nucleus, ^{25}Mg NMR can probably not be used as an experimental measure for the aromaticity of magnesium porphyrins. As seen from the ^{1}H NMR shieldings in Figures 1 and 2, the degree of aromaticity for magnesium porphyrins cannot be unambiguously obtained using ^{1}H NMR spectroscopy. The ARCS index in Table 3 is the obtained current susceptibility relative to the benzene value. Judged from the ARCS index, MgP and MgBC would be slightly more aromatic than benzene.

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(25) Arfken, G. *Mathematical Methods for Physicists*; Academic Press: Orlando, FL, 1985.

(26) Jusélius, J.; Sundholm, D. *Phys. Chem. Chem. Phys.* **2000**, *2*, 2275.

(27) Eichkorn, K.; Treutler, O.; Öhm, H.; Häser, M.; Ahlrichs, R. *Chem. Phys. Lett.* **1995**, *240*, 283.

(28) Vosko, S. H.; Wilk, L.; Nusair, M. *Can. J. Phys* **1980**, *58*, 1200.

(29) Perdew, J. P. *Phys. Rev. B* **1986**, *33*, 8822.

(30) Becke, A. D. *Phys. Rev. B* **1988**, *38*, 3098.

(31) Ahlrichs, R.; Bär, M.; Häser, M.; Horn, H.; Kölmel, C. *Chem. Phys. Lett.* **1989**, *162*, 165.

(32) Häser, M.; Ahlrichs, R.; Baron, H. P.; Weis, P.; Horn, H. *Theor. Chim. Acta* **1992**, *83*, 551.

(33) Kollwitz, M.; Gauss, J. *Chem. Phys. Lett.* **1996**, *260*, 639.

(34) Kollwitz, M.; Häser, M.; Gauss, J. *J. Chem. Phys.* **1998**, *108*, 8295.

(35) Hameka, H. *Mol. Phys.* **1958**, *1*, 203.

(36) Ditchfield, R. *Mol. Phys.* **1974**, *27*, 789.

(37) Wolinski, K.; Hinton, J. F.; Pulay, P. *J. Am. Chem. Soc.* **1990**, *112*, 8251.

(38) Schäfer, A.; Horn, H.; Ahlrichs, R. *J. Chem. Phys.* **1992**, *97*, 2571.

(39) Dunning, T. H., Jr. *J. Chem. Phys.* **1989**, *90*, 1007.

(40) Weigend, F.; Häser, M. *Theor. Chem. Acc.* **1997**, *97*, 331.

(41) http://www.chem.helsinki.fi/~sundholm/qc/mg_porphin_arcs/.

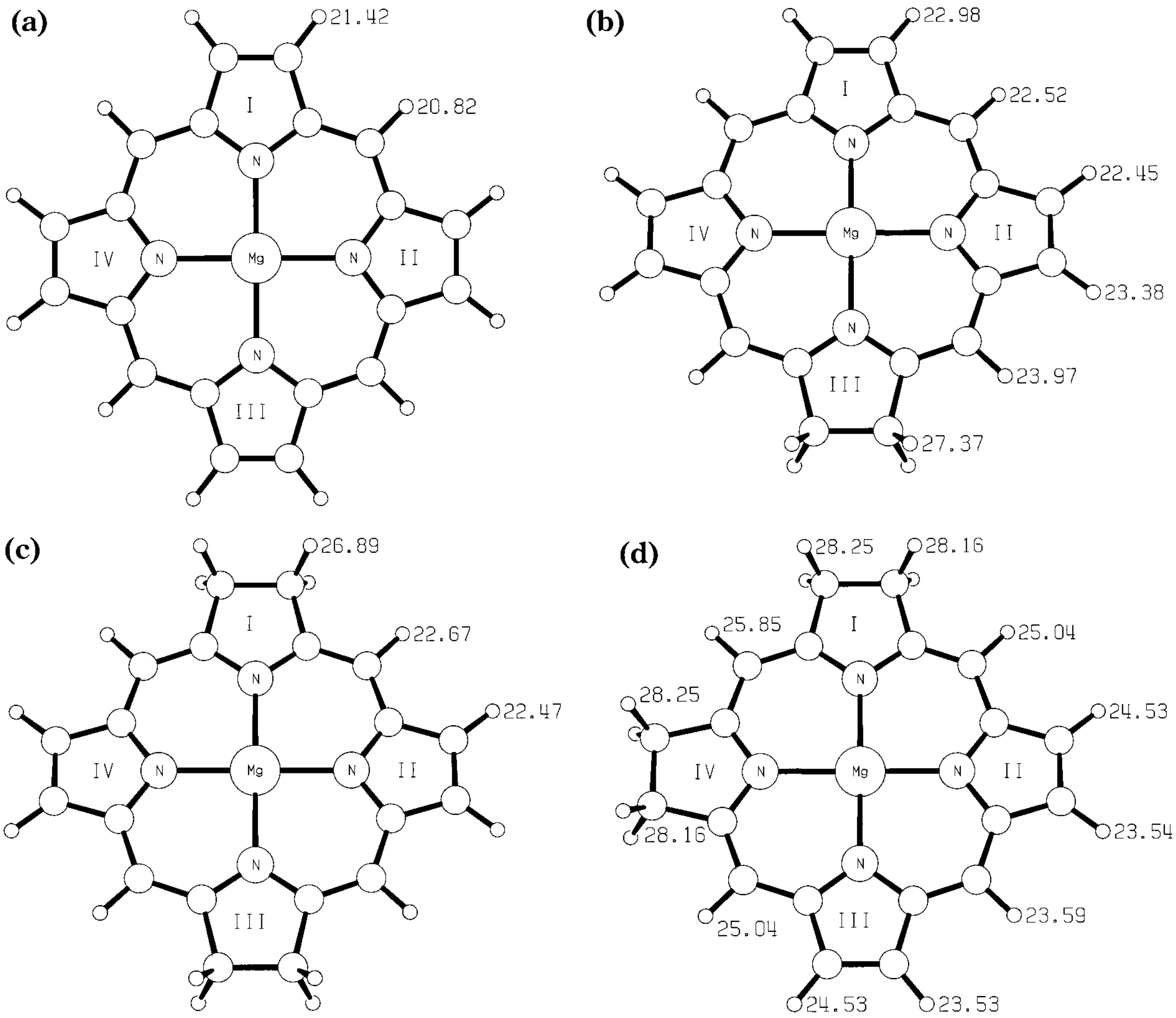

Figure 1. The molecular structures of the studied magnesium porphin, magnesium chlorin, and magnesium bacteriochlorins, their ^{1}H NMR shieldings (in ppm), and current susceptibilities ($\partial I/\partial B$ in nA T^{-1}). Key: (a) MgP ($\partial I/\partial B = 10.49$); (b) MgC ($\partial I/\partial B = 6.21$); (c) MgBC ($\partial I/\partial B = 8.52$); (d) MgIBC ($\partial I/\partial B = 3.49$).

The calculated NICS values for the pyrrolic rings are given in Table 4. The NICS values show that the β-unsaturated pyrrolic rings have their own local ring current. Note that the sign convention for the NICS values differs from that introduced by Schleyer et al.[24] This observation has previously been supported by planar aromatic schieldings calculations (PARCS)[26] on free-base porphyrins. The PARCS calculations on the free-base porphyrins showed that the noncircular symmetric part of the long-range shielding function has local maxima above the β-unsaturated pyrrolic rings, which indicates that the ring sustain a local ring current. For MgP, the NICS value of the pyrrolic rings is 10.0 ppm. MgC has two pyrrolic rings with NICS values of 8.6 ppm, and for one unsaturated ring the NICS value is 12.1 ppm, indicating a larger local ring current than for the other two unsaturated rings. For MgBC and MgIBC, the NICS values are 12.6 and 10.7 ppm, respectively. The only unsaturated pyrrolic ring for Mg3BC has a NICS value of 14.1 ppm. These values can be compared to the NICS value for the pyrrole molecule of 15.9 ppm.

The NICS values for the unsaturated pyrrolic rings help us to determine the aromatic pathway of the magnesium porphyrins. In the magnesium porphyrins, each β-unsaturated pyrrolic ring contribute 5 π-electrons. The meso carbons contribute 4 π-electrons, and the porphyrin nucleus in magnesium porphyrins can be considered to has a formal charge of -2, yielding two additional π-electrons that are mainly located on the nitrogens.

Since the four pyrrolic rings in MgP are aromatic, the aromatic pathway must be considered to consist of all the 26 π-electrons. MgC has 24 π-electrons, which as a result of the ($4n + 2$) rule cannot directly form the aromatic pathway. Since all the unsaturated pyrrolic rings are aromatic, all 24 π-electrons are, however, part of the total aromatic pathway. That means that the total aromatic pathway must be considered to consist of a superposition of two 22 π-electron paths. This notion is also supported by the NICS values that show that one of the pyrrolic rings have a stronger local ring current than the two other unsaturated rings. The obvious explanation is that ring I (See Figure 1) belong to both paths. For MgBC and MgIBC with 18 π-electrons, the aromatic pathway consists of all 18 electrons. However, the current susceptibility of MgIBC is only 3.5 nA T^{-1}, and one may question whether it should be considered aromatic. MgBC on the other hand has a current susceptibility of 8.5 nA T^{-1}, which is a typical value for aromatic molecules.

For Mg3BC, which has 20 π-electrons, there are two

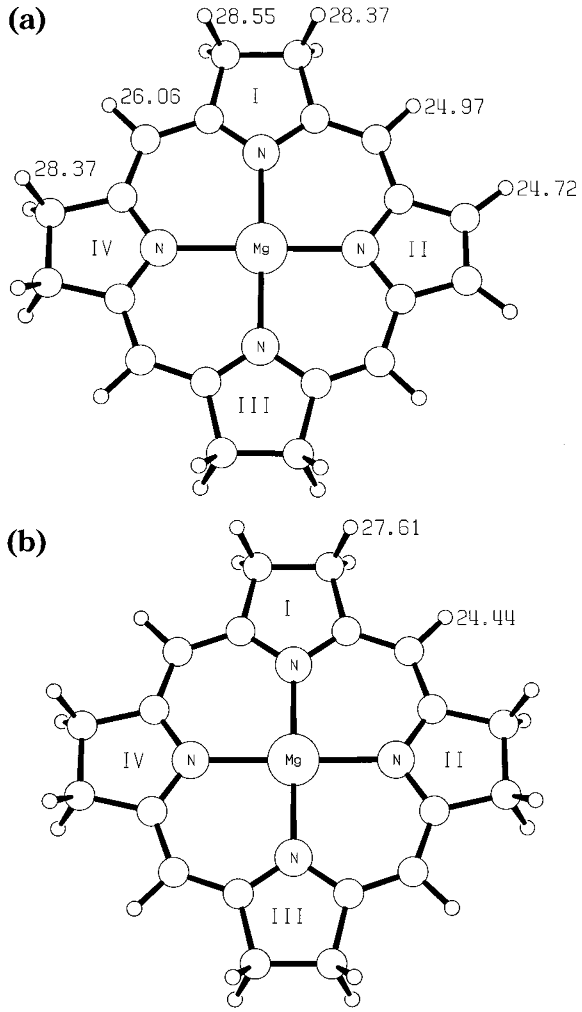

Figure 2. The molecular structures of Mg3BC and Mg4BC, their ^{1}H NMR shieldings (in ppm) ,and current susceptibilities ($\partial I/\partial B$ in nA T^{-1}). Key: (a) Mg3BC ($\partial I/\partial B = 2.93$); (b) Mg4BC ($\partial I/\partial B = 6.90$).

Table 1. Total Energy of the Magnesium Porphyrins, Hydrogenation Energies. and Differences in Hydrogenation Energies Relative to the Hydrogenation of MgP to MgC

molecule	total energy (au)	E_{hyd} (au)	ΔE_{hyd} (kJ mol^{-1})
MgP	−1187.878690		
MgC	−1189.078801	1.200111	
MgBC	−1190.274220	1.195419	12.3
MgIBC	−1190.276926	1.198125	5.2
Mg3BC	−1191.468317	1.194097[a]	15.8[a]
Mg4BC	−1192.650901	1.182584	46.0

[a] Relative to MgBC.

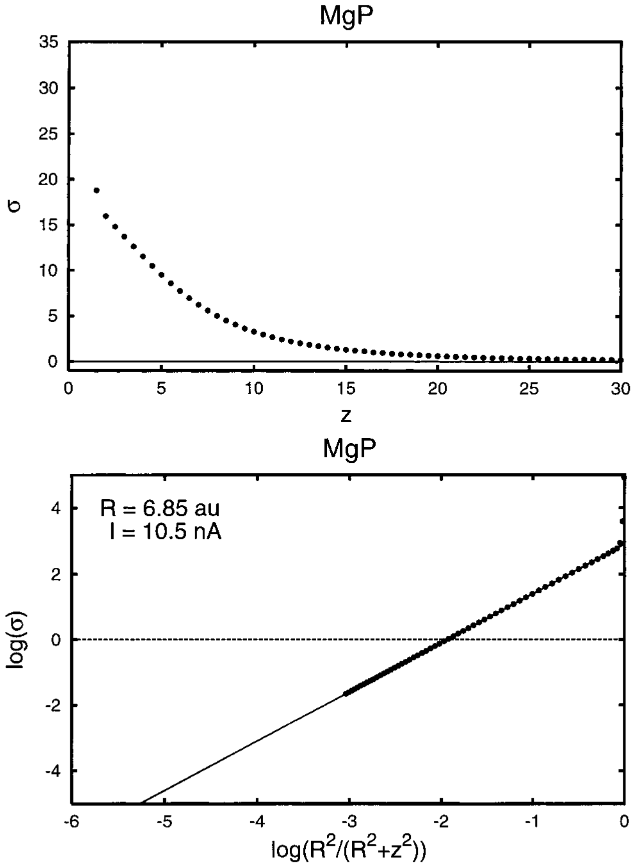

Figure 3. The calculated ARCS function (in ppm) for MgP and the logarithmic fit of the ARCS function to eq 1.

Table 2. Geometrical Ring Radius, Effective Radius of the Ring Current, and Induced Ring-Current Susceptibility

molecule	geometric radius (b)	current radius (b)	$\partial I_{ring}/\partial B_{ext}$ (nA T^{-1})
MgP	5.88−6.54	6.85	10.49
MgC	5.89−6.54	7.01	6.21
MgBC	5.88−6.54	6.42	8.52
MgIBC	5.89−6.54	7.26	3.49
Mg3BC	5.89−6.54	6.94	2.93
Mg4BC	5.88−6.54	5.65	6.90

Table 3. NICS Value of the β-Saturated Pyrrolic Ring, ARCS Aromaticity Indices Relative to Benzene, and ^{25}Mg NMR Shieldings

molecule	NICS	ARCS index[a]	$\sigma(^{25}$Mg) (ppm)
MgP		1.31	567.1
MgC	−5.2	0.78	562.1
MgBC	−7.5	1.07	567.5
MgIBC	−2.5	0.44	559.4
Mg3BC	−1.8[b]	0.37	560.4
Mg4BC	−6.0	0.86	570.4

[a] The aromaticity index for benzene is 1.0. [b] The other β-saturated rings have NICS values of −2.0 ppm.

possible aromatic pathways consisting formally of 18 π-electrons. The current can take the outer route at the unsaturated pyrrolic ring or it can take the inner route yielding the 18π-[16]annulene inner-cross path. Since the NICS value for the β-unsaturated pyrrolic ring is 14.1 nA T^{-1} the pyrrolic ring has a strong local ring current and the 18π-[16]annulene inner-cross path must be ruled out. However, the current susceptibility for Mg3BC is only 2.9 nA T^{-1}, which indicates that the Mg3BC nucleus is not very aromatic.

For Mg4BC, the 18π-[16]annulene inner-cross is the only possible aromatic pathway. The ARCS calculation shows that it has a large current susceptibility of 6.9 nA T^{-1}, and it must be considered to be aromatic. However, the hydrogenation energies show that Mg4BC lies energetically high as compared to the other magnesium porphyrins studied, indicating that the 18π-[16]annulene pathway is not energetically favorable. The 18π-[16]annulene internal cross pathway, the traditional 18π-[18]-annulene pathway, the symmetric 22π-electron pathway,

Table 4. NICS Values (ppm) Calculated at the Center of the Pyrrolic Rings[a]

molecule	I	II	III	IV
MgP	9.98	9.95	9.98	9.95
MgC	12.13	8.60	−5.19	8.60
MgBC	−7.52	12.57	−7.52	12.57
MgIBC	−2.45	10.68	10.68	−2.45
Mg3BC	−2.01	14.07	−2.01	−1.84
Mg4BC	−5.95	−5.96	−5.96	−5.96

[a] The ring numbers are given in Figures 1 and 2.

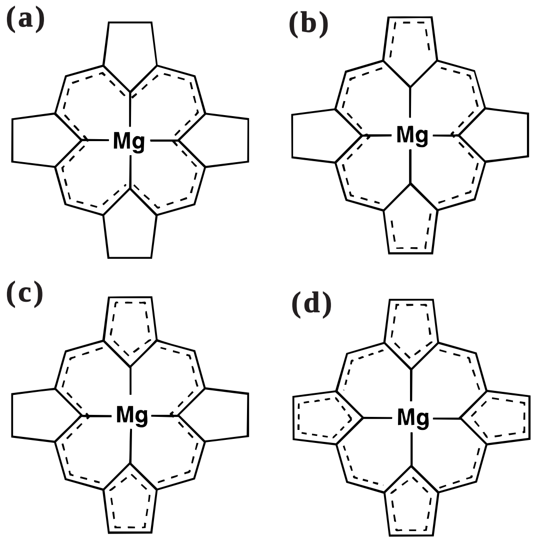

Figure 4. (a) The 18π-[16]annulene internal cross pathway; (b) the traditional 18π-[18]annulene pathway; (c) the symmetric 22π-electron pathway; and (d) the 26π-electron aromatic pathway for magnesium porphyrins.

and the 26π-electron aromatic pathway for magnesium porphyrins are sketched in Figure 4.

Recently, we performed similar calculations on free-base porphyrins.[26] A comparison of the NICS values given in Table 4 with the NICS values for the free-base porphyrins shows that the present NICS values of the β-unsaturated pyrrolic rings are close to the average of the NICS values for the isomers of the corresponding free-base porphyrins. For free-base porphin, the average NICS value is 10.04 ppm as compared to 10.0 ppm for MgP. The NICS values for MgC, MgBC, MgIBC, and Mg3BC are 10.2 (10.4), 12.6 (12.2), 10.7 (10.6), and 14.1 (14.0) ppm, respectively. The average NICS values for the isomers of the corresponding free-base porphyrins are given within the parentheses. Mg4BC and the corresponding free-base porphyrin have no β-unsaturated pyrrolic rings.

The ring current susceptibilities for the magnesium porphyrins are also about the average of the current susceptibilities for the isomers of the corresponding free-base porphyrins. The current susceptibilities for MgP, MgC, MgBC, MgIBC, Mg3BC, and Mg4BC are 10.5 (10.4), 6.2 (6.1), 8.5 (8.5), 3.5 (3.1), 2.9 (2.9), and 6.9 (7.2) nA T^{-1}, respectively. The average current susceptibilities for the corresponding isomers of the free-base porphyrins are given within parentheses.[26] The current radii of the magnesium porphyrins and the average of the current radii of the corresponding free-base porphyrins are also almost equal. These agreements show that the aromaticity of the magnesium porphyrins and the corresponding free-base porphyrins are very similar.

Summary

This study shows that the β-unsaturated pyrrolic rings in magnesium porphyrins have local ring currents that are integrated parts of the total aromatic pathway. The local aromaticity of the pyrrolic rings stabilizes energetically magnesium porphyrins and prevents the apparency of an 18π-[16]annulene inner-cross aromatic pathway before all pyrrolic rings are β-saturated. The aromatic pathway of magnesium porphyrins can be considered as a superposition of several pathways. For MgP, all 26 π-electrons contribute to the aromatic pathway. For MgC, the pathway is mainly a superposition of two 22 π-electron paths. For MgBC, all 22 π-electrons are involved in the aromatic pathway, while it is doubtful whether MgIBC can be considered aromatic. Mg3BC has also a very small current susceptibility as compared to 10.5, 8.5, and 6.2 nA T^{-1} for MgP, MgBC, and MgC, respectively. Mg4BC in turn is aromatic since its current susceptibility is 6.9 nA T^{-1}. However, Mg4BC lies energetically high as compared to the other aromatic magnesium porphyrins. The aromaticity of the magnesium porphyrins are very reminiscent of the aromaticity of the corresponding free-base porphyrins.

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Supporting Information Available: Optimized structures of the studied magnesium porphyrins. This material is available free of charge via the Internet at http://pubs.acs.org.

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