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Structure and Stability of 2-Aza-21-carbaporphyrin Tautomers Prearranged for Coordination

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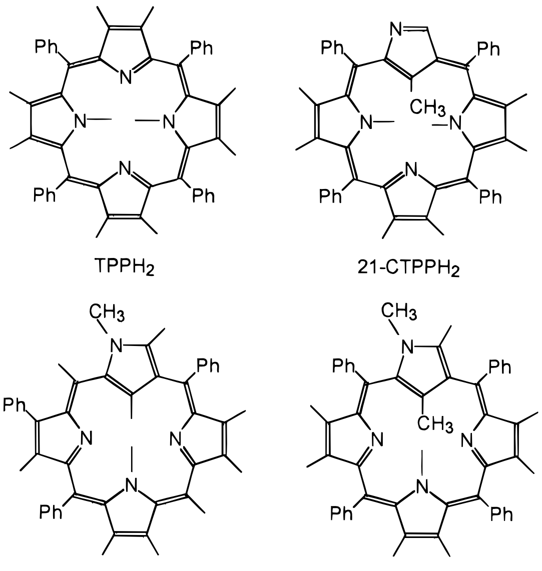
2-Aza-21-carba-5,10,15,20-tetraarylporphyrin (CTPPH$_2$, inverted porphyrin) and its methylated derivatives, acting as ligands, can be structurally related to the following hypothetical tautomers: 2-aza-5,10,15,20-tetraphenyl-21-carbaporphyrin (2-NH-CTPPH); 2-aza-5,10,15,20-tetraphenyl-21-methyl-21-carbaporphyrin (21-H-21-CH$_3$CTPPH); 2-aza-5,10,15,20-tetraphenyl-21-methyl-21-carbaporphyrin (2-NH-21-CH$_3$CTPPH); 2-aza-2,21-dimethyl-5,10,-15,20-tetraphenyl-21-carbaporphyrin (2-NCH$_3$-21-CH$_3$CTPPH). Their structures and electronic energies have been investigated applying the density functional theory (DFT) for idealized 21-carbaporphyrin, created by a replacement of phenyl and methyl groups with hydrogen, yielding CPH$_2$, 21-H-CPH, 2-NH-CPH, and 2-NH-21-H-CP. The B3LYP/6-31G optimized bond lengths and angles of 21-carbaporphyrin skeletons are in satisfactory agreement with X-ray crystallographic values when compared in structurally related pairs, i.e., CPH$_2$ and CTPPH$_2$, 21-H-CPH and (21-CH$_3$TPP)Ni^{II}, and 2-NH-CPH and (2-NCH$_3$-21-CH$_3$CTPP)Ni^{II}I. The calculated total electronic energies, using the B3LYP/6-31-G**//B3LYP/6-31G approach, demonstrate that relative stability of the postulated tautomers decreases in the order CPH$_2$ > 21-H-CPH > 2-NH-CPH ≫ 2-NH-CPH$_2$ > 2-NH-21-H-CP. The difference between the electronic energy of the regular porphyrin PH$_2$ and the fundamental tautomer 21-carbaporphyrin CPH$_2$ is calculated to be 20.41 kcal/mol. The DFT calculation reproduced properly the distribution of mobile protons for the tautomer of the lowest energy for each stable 21-carbaporphyrin and provided some insight into the analysis of energy required for the suggested prearrangement process imposed by insertion of a metal ion. The spectacular flexibility of the ligand structure including a reversible trigonal-pyramidal geometry change at the C(21) center has been also discussed.

Introduction

Formal permutation of a pyrrole nitrogen and a β-methine pyrrolic group of 5,10,15,20-tetraarylporphyrin (TPPH$_2$) results in creation of the porphyrin-like skeleton 2-aza-21-carba-5,10,-15,20-tetraarylporphyrin (CTPPH$_2$, inverted porphyrin) although with drastically changed electronic and coordination properties (Chart 1).[1,2] Synthetically, 21-carbaporphyrin is readily accessible through a one-step alteration of cyclopolymerization in the classical Rothemund condensation of pyrrole and arylaldehyde, typically used to generate 5,10,15,20-tetraarylporphyrin.[3] Recently the peralkylated, meso-unsubstituted inverted porphyrin[4] and core-modified meso-substituted inverted porphyrins[5] have been stepwise synthesized.

The inverted porphyrin belongs to a larger group of recently emerged porphyrinic isomers,[6] although this particular molecule presents a sole case where the pattern of the porphyrinic framework is completely preserved. A complementary area of porphyrin modification involves the replacement of one pyrrole ring by cyclopentadiene, benzene, and its derivatives, azulene and cycloheptatriene.[7] Such a strategy implants a CH unit in the position of pyrrole nitrogen, establishing a (N,NH,NH,CH) central core as a common structural denominator of 21-carbaporphyrin-like macrocycles.

Chart 1



In the context of organometallic chemistry, facilitated by an appropriate construction of the polydentate macrocycle, the

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(1) Chmielewski, P. J.; Latos-Grażyński, L.; Rachlewicz, K. Głowiak, T. *Angew. Chem.* **1994**, *106*, 805; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 779.

(2) Furuta, H.; Asano, H.; Ogawa, T. *J. Am. Chem. Soc.* **1994**, *116*, 767.

(3) (a) Rothemund, P. *J. Am. Chem. Soc.* **1936**, *58*, 625; (b) Rothemund, P. *J. Am. Chem. Soc.* **1939**, *61*, 2912.

(4) Liu, B. Y.; Brückner, C.; Dolphin, D. *Chem. Commun.* **1996**, 2141.

(5) Heo, P.-Y.; Shin, K.; Lee, C.-H. *Tetrahedron Lett.* **1995**, 197.

(6) (a) Vogel, E.; Köcher, M.; Schmickler, H.; and J. Lex, J. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 257. (b) Vogel, E.; Koch, P.; Hou, X.-L.; Lex, J.; Lausman, M.; Kister, M.; Aukauloo, M. A.; Richard, P. Guilard, R. *Angew. Chem., Int. Ed. Engl.* **1993**, *32,* 1600. (c) Aukauloo, M. A.; Guilard, R. *New J. Chem.* **1994**, *18*, 1205. (d) Sessler, J. L.; Brucker, E. A.; Weghorn, S. J.; Kisters, M.; Schäfer, M.; Lex, J.; Vogel, E. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2308. (e) Callot, H. J.; Rohrer, A.; Tschamber, T.; Metz, B. *New J. Chem.* **1995**, *19*, 155.

(7) (a) Berlin, K.; Breitmaier, E. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1246. (b) Berlin, K.; Steinbeck, C.; Breitmaier, E. *Synthesis* **1996**, 336. (c) Berlin, K. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1820. (d) Lash, T. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2533.

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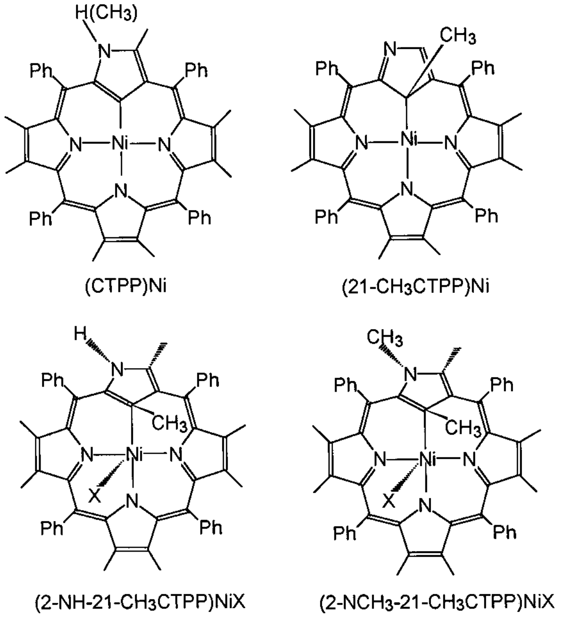
Chart 2



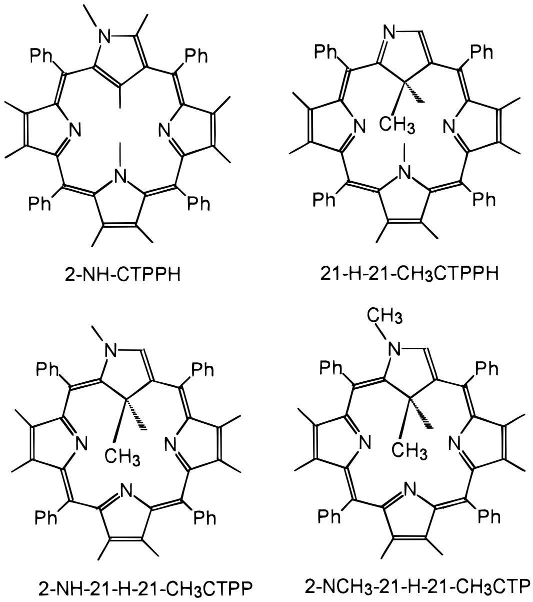
(CTPP)Ni

(21-CH$_3$CTPP)Ni

(2-NH-21-CH$_3$CTPP)NiX

(2-NCH$_3$-21-CH$_3$CTPP)NiX

Chart 3



2-NH-CTPPH

21-H-21-CH$_3$CTPPH

2-NH-21-H-21-CH$_3$CTPP

2-NCH$_3$-21-H-21-CH$_3$CTPP

inverted porphyrin offers an interesting coordinating environment, potentially accessible for a large variety of metal ions. Heretofore, organometallic chemistry involving 21-carbaporphyrin has been focused solely on nickel chemistry.[1,8−10] The localization of the 21-carbon atom imposes the extremely rare coordination of a carbon donor to nickel(III) or paramagnetic nickel(II).[9−12] Taking advantage of a peculiar reactivity of the nickel 21-carbaporphyrin and free 21-carbaporphyrin we have extended the group of inverted porphyrin to methylated derivatives: 2-aza-2-methyl-5,10,15,20-tetraphenyl-21-carbaporphyrin (2-NCH$_3$CTPPH), 2-aza-5,10,15,20-tetraphenyl-21-methyl-21-carbaporphyrin (21-CH$_3$-CTPPH$_2$), and 2-aza-2-methyl-5,10,-15,20-tetraphenyl-21-methyl-21-carbaporphyrin (2-NCH$_3$-21-CH$_3$CTPPH).[8,9] The series constitutes a group where a position of methylation has been essentially varied (Chart 1). 21-Carbaporphyrin and methylated 21-carbaporphyrin act as mono- or dianionic ligands toward the nickel(II) ion (Chart 2).

Nickel(II) coordination imposes the drastic rearrangement on the inverted porphyrin skeleton as illustrated at Charts 1 and 2. Consequently, 21-carbaporphyrin acting as a ligand, can be structurally related to the following hypothetical tautomers: 2-aza-5,10,15,20-tetraphenyl-21-carbaporphyrin (2-NH-CTPPH), 2-aza-5,10,15,20-tetraphenyl-21-methyl-21-carbaporphyrin (21-H-21-CH$_3$CTPPH), 2-aza-5,10,15,20-tetraphenyl-21-methyl-21-carbaporphyrin (2-NH-21-CH$_3$CTPPH), and 2-aza-2,21-dimethyl-5,10,15,20-tetraphenyl-21-carbaporphyrin (2-NCH$_3$-21-CH$_3$CTPPH), shown in Chart 3.

The spectacular flexibility of the ligand structure has been exemplified by a reversible trigonal-pyramidal geometry change at the C(21) center in the course of nickel(II) insertion or removal.[1,8−10] In this context, we have raised the question of the relative stability of the invoked tautomers of 21-carbaporphyrin and methylated 21-carbaporphyrins. To approach this problem, we have performed theoretical investigations applying the density functional theory (DFT).

Method

Ab initio methods were used for investigation of tautomeric equilibria of 21-carbaporphyrin. Calculations were carried out with the GAUSSIAN94 program.[13] All structures were optimized with unconstrained C_1 symmetry of the system using HF theory and density functional theory (DFT) with Becke's three-parameter exchange functionals and the gradient-corrected functionals of Lee, Yang, and Parr (DFT(B3-LYP)).[14] The final estimations of the total electronic energies were performed at the B3-LYP level with the 6-31G** basis set using the B3-LYP/6-31G reference structures.

Results and Discussion

For simplification, all calculations have been carried out for 2-aza-21-carbaporphyrin and its tautomers. Therefore, the corresponding phenyl and methyl groups of 2-aza-5,10,15,20-tetraphenyl-21-carbaporphyrins and its methylated derivatives presented in Charts 1 and 3 have been replaced by hydrogen, yielding CPH$_2$, 21-H-CPH, 2-NH-CPH, and 2-NH-21-H-CP, respectively, as shown in Chart 4. To evaluate the relative stability of 21-cabaporphyrin with respect to the regular porphyrin skeleton, we have also included porphine (PH$_2$). Our calculation resulted in the similar geometry of PH$_2$ as determined previously.[15] In addition, we have taken into account the tautomeric derivative 2-NH-CPH$_2$, which was suggested by Ghosh[16] to promote the hypothetical and intriguing carbene-

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(8) Chmielewski, P. J.; Latos-Grażyński, L. *J. Chem. Soc., Perkin Trans. 2* **1995**, 503.

(9) Chmielewski, P. J., Latos-Grażyński, L.; Głowiak, T. *J. Am. Chem. Soc.* **1996**, *118*, 5690.

(10) Chmielewski, P. J.; Latos-Grażyński, L. *Inorg. Chem.* **1997**, *36*, 840.

(11) (a) D'Anielo, M. J., Jr.; Barefield, E. K. *J. Am. Chem. Soc.* **1976**, *98,* 1610. (b) Ram, M. S.; Riordan, C. G.; Yap, G. P. A.; Liable-Sands, L. A.; Rheingold, L.; Marchaj, A.; Norton, J. R. *J. Am. Chem. Soc.* **1997**, *119*, 1648. (c) Kläui, W.; Huhn, M.; Herbst-Irmer, R. *J. Organomet. Chem.* **1991**, *415*, 133.

(12) Grove, D. M.; van Koten, G.; Mul, P; Zoet, R.; van der Linden, J. G. M.; Legters, J.; Schmitz, J. E. J.; Murral, N. W.; Welch, A. J. *Inorg. Chem.* **1988**, *27,* 2466.

(13) (a) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A. Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzales, C. and Pople, J. A. Gaussian, Inc., Pittsburgh PA, 1995.

(14) (a) Becke, A. D. *Phys. Rev.* A **1988**, *38*, 3098. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev.* B **1988**, *37*, 785. (c) Johnson, B. G.; Gill, P. M. W.; Pople, J. A. *J. Chem. Phys*. **1993**, *98*, 5612. (d) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(15) Almöf, J.; Fischer, T. H.; Gassman, P. G.; Ghosh, Häser, M. *J. Phys. Chem.* **1993**, *97*, 10964.

Chart 4

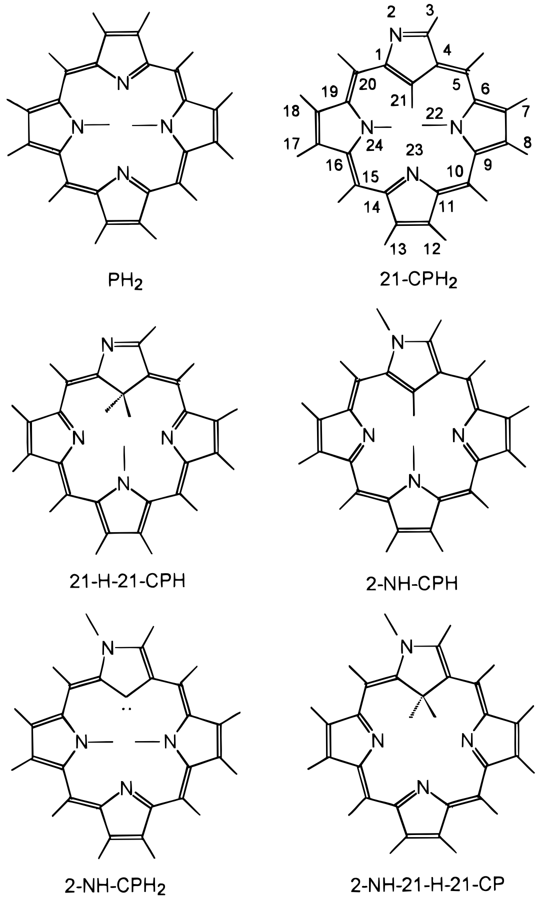

Table 1. Calculated Relative Electronic Energies[a]

macrocycle	B3LYP/3-21G//B3LYP/3-21G	B3LYP/6-31G//B3LYP/6-31G	B3LYP/6-31G**//B3LYP/6-31G
PH_2	−22.95	−21.08	−20.41
CPH_2	0	0	0
21-H-CPH	6.20	8.22	3.00
2-NH-CPH	3.39	4.56	4.56
2-NH-CPH_2	31.44	33.82	34.56
2-NH-21-H-CP	41.31	43.93	36.00

[a] In kilocalories per mole with respect to the inverted porphyrin CPH_2.

like coordination of 21-carbon. The calculated total electronic energies and optimized structural parameters are presented at Tables 1−3, respectively. For the sake of comparison, the relevant X-ray structural data of porphyrin,[17] inverted porphyrin,[2] and nickel(II) methylated 21-carbaporphyrins[9] are included in Tables 2 and 3.

Comparison of bond distances within the pyrrole and inverted pyrrole (inverted methylated pyrrole) portions demonstrates that extensive delocalization exists through out the macrocycle and extends to the inverted pyrrole fragment. Generally bond distances of the regular pyrroles $C_\alpha-C_\beta > C_\alpha-C_{meso} > C_\alpha-C_N > C_\beta-C_\beta$, are similar to the pattern, within the normal porphyrin macrocycle PH_2. The largest differences in the bond lengths are in the range of a few hundred of angstroms. Thus, the inversion of the pyrrole ring and its methylation plays a rather moderate role in determination of the electronic and molecular structure of the complementary part of the macrocycle. By contrast, there is an appreciable effect within the inverted pyrrole fragment as well as on the overall properties of 21-carbaporphyrin. Here we have distinguished two cases of essentially trigonal (CPH_2, 2-NH-CPH, 2-NH-CPH_2) and tetrahedral (21-H-CPH, 2-NH-21-H-CP) geometry around the C(21) carbon atom. Accordingly the N(2)−C(3), N(2)−C(1), and C(3)−C(4) bond distances of 21-H-CPH, 2-NH-21-H-CP are markedly shorter than the bond distances C(1)−C(21) and C(4)−C(21). The environment of the C(21) atom approaches tetrahedral geometry, as illustrated by the respective bond angles and distances in Tables 2 and 3. Remarkably, the optimized C(21)−C(1) and C(21)−C(4) bond distances are 1.51 Å characteristic for of tetrahedral geometry. Thus, the pattern of bond lengths within this fragment of the macrocycle is modified to allow π-delocalization exclusively via the outer path. The planar trigonal geometry is acquired for the remaining tautomers (CPH_2, 2-NH-CPH, 2-NH-CPH_2). The bond length pattern, determined for CPH_2, 2-NH-CPH tautomers, suggests two alternative π-delocalization pathways as the bond distances are in the range expected for porphyrins, although the C(1)−N(2) and N(2)−C(3) bond lengths of CPH_2 approach limits of isolated single and double carbon−nitrogen bonds but acquire a more aromatic character for the 2-NH-CPH tautomer. The optimized bond lengths and angles show satisfactory agreement with X-ray crystallographic values when compared in structurally related pairs, i.e., CPH_2 and $CTPPH_2$,[2] 21-H-CPH and (21-CH_3TPP)-Ni^{II},[9] and 2-NH-CPH and (2-NCH_3-21-CH_3CTPP)Ni^{II}I,[9] respectively (Tables 2 and 3).

The calculated total electronic energies, using the B3LYP/6-31-G**//B3LYP/6-31G approach, demonstrate that relative stability of the postulated tautomers decreases in the order CPH_2 > 21-H-CPH > 2-NH-CPH ≫ 2-NH-CPH_2 > 2-NH-21-H-CP. The total electronic energy difference between the regular porphyrin PH_2 and the fundamental tautomer of 21-carbaporphyrin CPH_2 is calculated to be 20.41 kcal/mol.

Previously Vogel et al. calculated, using the B3LYP/3-21-G**//B3LYP/3-21-G method, that other porphyrin isomers, namely, porphycene (−1.5 kcal/mol), hemiporphycene (5.1 kcal/mol), corrphycene (12.0 kcal/mol), and isoporphycene (19.0 kcal/mol), show comparable stability of relative total electronic energy with respect to regular porphyrin.[18] Thus, the energy of 21-carbaporphyrin, calculated by a similar method, approaches the electronic energy calculated for isoporphycene and fits properly in a series of isomeric porphyrins. The calculated energies of the other hypothetical porphyrinic isomers increased considerably (E > 30 kcal/mol) leading to doubts that these species will be stable molecules.[18]

To mimic the behavior of C-methylated or 2-N-methylated derivatives, we have excluded intramolecular mobility of 21-CH or 2-NH protons, into Chart 4. Consequently, for 21-CH_3-$CTPPH_2$ we have eliminated the 2-NH-CPH_2 species, which requires the carbene-like electronic structure at the 21-carbon, to obtain the relative stability. Accordingly, the methylation at the peripheral nitrogen will generate the following sequence of stability: 2-N*H*-CPH ≫ 2-N*H*-CPH_2 > 2-N*H*-21-H-CP (immobilized proton marked in italic).

At present, the experimental thermodynamic values necessary for comparison with the calculated relative stabilities of tautomers are not accessible. However, we have determined by ^{1}H NMR the structures of the fundamental tautomers of inverted porphyrins, i.e., $CTPPH_2$, 2-NCH_3-CTPPH, 21-CH_3CTPPH, and 2-NCH_3-21-CH_3CTPPH.[1,8,9] Our studies do reproduce properly the distribution of mobile protons for the tautomer of the lowest energy for each stable 21-carbaporphyrin. Thus, the following

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(16) Gosh, A. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1028.

(17) Chen, B. M. L.; Tulinsky, A. *J. Am. Chem. Soc.* **1972**, *94*, 4144.

(18) Vogel, E.; Bröring, M.; Fink, J.; Rosen, D.; Schmickler, H.; Lex, J.; Chan, K. W. K.; Wu, Y.-D. Plattner, D. A.; Nendel, M.; Houk, K. N. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2511.

Table 2. Selcted Optimized and X-ray Determined[a−c] Bond Lengths (Å)

	PH_2	CPH_2	21-H-CPH	2-NH-CPH	2-NH-CPH_2	2-NH-21-H-CP	PH_2[a]	$CTPPH_2$[b]	(21-CH_3CTPP)Ni^{II}[c]	(2-NCH_3-21-CH_3CTPP)Ni^{II}I[c]
C(1)−N(2)		1.446	1.390	1.420	1.456	1.393		1.443	1.372(9)	1.406(14)
N(2)−C(3)		1.317	1.345	1.361	1.342	1.375		1.336	1.344(9)	1.332(14)
C(3)−C(4)		1.480	1.430	1.416	1.429	1.388		1.454	1.392(9)	1.407(14)
C(1)−C(21)		1.404	1.500	1.389	1.415	1.507		1.355	1.480(8)	1.390(14)
C(4)−C(21)		1.404	1.500	1.420	1.448	1.520		1.378	1.468(9)	1.41(2)
C(4)−C(5)	1.394	1.404	1.380	1.429	1.424	1.407	1.382	1.410	1.393(9)	1.436(14)
C(5)−C(6)	1.398	1.400	1.417	1.380	1.381	1.393	1.382	1.366	1.401(9)	1.379(14)
C(6)−C(7)	1.465	1.441	1.468	1.469	1.444	1.468	1.431	1.441	1.445(9)	1.435(14)
C(7)−C(8)	1.362	1.381	1.365	1.362	1.373	1.366	1.366	1.352	1.349(10)	1.36(2)
C(8)−C(9)	1.465	1.438	1.466	1.472	1.451	1.476	1.476	1.475	1.419(9)	1.439(2)
C(6)−N(22)	1.379	1.391	1.368	1.403	1.396	1.381	1.380	1.430	1.385(8)	1.421(13)
C(9)−N(22)	1.379	1.378	1.383	1.355	1.370	1.357	1.380	1.366	1.378(8)	1.354(12)
C(9)−C(10)	1.398	1.397	1.391	1.416	1.400	1.413	1.382	1.411	1.396(9)	1.401(14)
C(20)−C(1)	1.394	1.404	1.404	1.385	1.397	1.391		1.436	1.394(9)	1.44(2)

[a] Reference 15. [b] Reference 2. [c] Reference 9.

Table 3. Selected Optimized and X-ray Determined Bond Angles (deg)[a]

	CPH_2	21-H-CPH	2-NH-CPH	2-NH-CPH_2	2-NH-21-H-CP	21-$CTPPH_2$[b]	(21-CH_3CTPP)Ni^{II}[c]	(2-NCH_3-21-CH_3CTPP)Ni^{II}I[c]
C(1)−C(21)− C(4)	108.54	102.69	109.26	106.28	103.99	109.9	100.2(5)	106.7(9)
C(1)−C(21)−H(37)	125.48	112.63	125.05		112.94		113.1(5)	125.0(11)
C(4)−C(21)−H(37)	125.98	112.87	125.68		113.90		113.8(5)	125.0(9)
N(2)−C(1)−C(21)	109.30	110.56	106.14	110.10	106.09	110.7	111.5(6)	107.8(10)
C(1)−N(2)−C(3)	105.78	107.76	109.89	108.04	112.47	103.5	108.3(6)	109.3(9)
N(2)−C(3)−C(4)	112.62	113.70	108.39	108.43	110.12	112.3	110.5(6)	108.7(10)
C(3)−C(4)−C(21)	103.76	105.32	106.32	110.17	107.32	104.2	109.6(5)	107.4(9)
C(5)−C(4)−C(21)	128.29	125.63	126.77	126.77	127.17	131.6	124.4(6)	128.8(10)

[a] The relevant optimized angle values (deg) for porphyrin are equal (the X-ray data are given in parentheses): $C_\alpha NC_\alpha$, 110.75 (108.6); $NC_\alpha C_\beta$, 106.5 (107.9); $C_\alpha C_\beta C_\beta$, 108.14 (107.9); $NC_\alpha C_{meso}$, 125.9 (125.2), as in ref 15. [b] Reference 2. [c] Reference 9.

Table 4. Rearangement Energy[a]

fundamental tautomer	preorganization product	stability difference	adequate nickel(II) complex
CPH_2	2-N*H*-CPH	4.56	(CTPP)Ni^{II}
CPH_2	21-H-21-CPH	3.00	(21-CH_3-CTPP)Ni^{II}
2-N*H*-CPH	2-N*H*-CPH	0	(2-NCH_3CTPP)Ni^{II}
2-N*H*-CPH	2-N*H*-CPH	0	(2-NCH_3-21-CH3CTPP)Ni^{II}I
21-H-CPH	2-N*H*-CPH	1.56	(21-CH_3-21-CTPP)Ni^{II} + HI $\rightleftharpoons$ (2-NH-21-CH_3-21-CTPP)Ni^{II}I
2-N*H*-CPH	2-N*H*-21-H-CP	31.44	not found

[a] In kilocalories per mole.

structural correspondences have been unambiguously established: CPH_2 ↔ $CTPPH_2$, CPH_2 ↔ 21-CH_3-$CTPPH_2$, and 2-N*H*-CPH ↔ 2-NCH_3-CTPPH or 2-NCH_3-21-CH_3CTPPH, respectively. This observation provides an appropriate experimental criterion for the correctness of the DFT calculations carried out for 21-carbaporphyrins.

The small calculated energy difference between CPH_2 and 21-H-CPH or 2-NH-CPH species suggests the possibility of equilibrium with the less stable tautomer and raises the question of their simultaneous detection. At present, the ^{1}H NMR evidence the supports the exclusive presence of a single species for each considered inverted tetrarylporphyrin.[2,8,9] Here, one has to keep in mind that our calculations offer only an evaluation of the energy of isolated meso-unsubstituted structures. Therefore, the actual differences in solution may be more pronounced. In a relevant comparison, the exchange of NH protons of regular porphyrin involves two fundamental tautomeric structures: trans and cis. The recently calculated energy of the cis tautomer with respect to the trans equals ca. 6−11 kcal/mol.[19] In spite of the small difference in stability the cis porphyrin structure has yet to be directly observed spectroscopically.

The analysis of the calculated relative stabilities of 21-carbaporphyrin tautomers sheds some light on 21-carbaporphyrins as macrocyclic organometallic ligands. In considering a mechanism of nickel(II) insertion into 21-carbaporphyrin and its methylated derivatives, one may conceive a crucial preorganization step in order to match the 21-carbaporphyrin geometry and the specific requirements of the nickel(II) coordination. A preorganization may contribute to the overall activation energy of the metal insertion. In fact, a hypothetical demetalation mechanism via a straightforward replacement of nickel(II) by protons will give the geometry of the preorganized ligands, illustrated in selection by the 21-carbaporphyrin tautomers (Chart 4). Consequently, we have evaluated the difference in stabilization energy between the idealized porphyrin and its preorganized ligand-like tautomer. The relevant comparison in Table 4 shows the preorganization energy within the lower limits of activation energy determined for metal ion insertion into regular porphyrin or N-methylated porphyrin. However, one has to be aware that the mechanistic reasons for activation enthalpy in the case of regular porphyrins and 21-carbaporphyrins may be essentially different.[20,21] The relatively small 21-HCPH ↔ 2-NH-CPH ligand preorganization energy accounts well for marked changes of geometry around the C(21) carbon (pyramidal vs planar one) in the reaction

$$(21\text{-}CH_3\text{-}CTPP)Ni^{II} + HI \rightleftharpoons (2\text{-}NH\text{-}21\text{-}CH_3\text{-}CTPP)Ni^{II}I$$

and in the reversible nickel removal/insertion.[10]

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(19) (a) Reimers, J. R.; Lü, T. X.; Crossley, M. J.; Hush, N. S. *J. Am. Chem. Soc.* **1995**, *117*, 2855. (b) Gosh, A.; Almlöf, J. *J. Phys. Chem.* **1995**, *99*, 1073 and reference cited therein.

(20) (a) Hambright, P.; Chock, P. B. *J. Am. Chem. Soc.* **1974**, *96*, 3123. (b) Longo, R. F.; Brown, E. M.; Quimby, D. J.; Adler, A. D.; Meot-Ner, M. *Ann. N.Y. Acad. Sci.* **1973**, *206*, 420. (c) Longo, R. F.; Brown, E. M.; Rau, G. W..; Adler, A. D. In *The Porphyrins*; Dolphin, D., Ed.; Academic Press: New York, 1978; Vol. 5, p 459.

(21) Bain-Ackerman, M. J.; Lavallee, D. K. *Inorg. Chem.* **1979**, *18*, 3358.

Chart 5

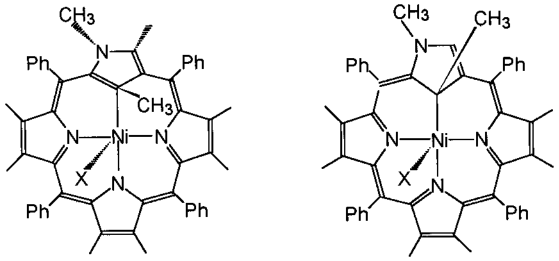
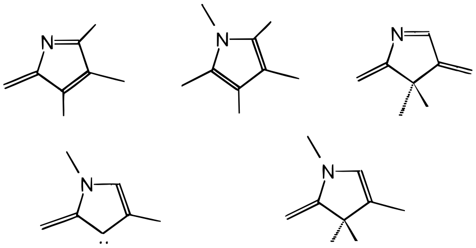


Chart 6



On the other hand, the hypothetical rearrangement of the ligand (Chart 5) in (2-NCH$_3$-21-CH$_3$-CTPP)Ni^{II}I to convert C(21) geometry from planar to pyramidal (2-N*H*-CPH to 2-N*H*-21-HCP) is strongly energetically disfavored, accounting for the preference for the unusual side-on η^1-pyrrole coordination.

Conclusion. The different tautomeric forms may be invoked to account for coordination of 21-carbaporphyrin and C- and N-methylated 21-carbaporphyrins. Some of these tautomers have not been experimentally reported but represent a useful presentation of the feasible coordination modes, adjusting the specific ligand structure to the requirements of the metal ion (Chart 6). The DFT calculations have revealed the relative stabilities of real and hypothetical structures and provided some insight into the analysis of energy required for the prearrangement process. Previously Ghosh considered the hypothetical carbene-like coordination of 2-NH-CPH$_2$.[16] In light of our calculations, it does not seem to be the preferred choice as far as the prearrangement step is considered.

Finally, we have shown that with the defined restrictions on the mobility of N(2) and C(21) protons in the model structures, the DFT calculation gives the proper distribution of protons in the dominating tautomeric form.

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Supporting Information Available: The complete table of calculated bond lengths (3 pages). Ordering information is given on any current masthead page.

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