Theoretical Study of Stability, Structures, and Aromaticity of Multiply N-Confused Porphyrins

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The total electronic energy and nucleus-independent chemical shift (NICS) of 95 isomers of N-confused porphyrin (**NCP**: *normal* porphyrin (**N_0CP**), singly N-confused porphyrin (**N_1CP**), doubly N-confused porphyrin (**N_2CP**), triply N-confused porphyrin (**N_3CP**), and fully N-confused porphyrin (**N_4CP**)) have been calculated by the density functional theory (DFT) method. The stability of **NCP** decreased by increasing the number of *confused* pyrrole rings. Namely, the relative energies of the most stable isomers in each *confusion* level increased in a stepwise manner approximately by +18 kcal/mol: 0 (**N_0CP1**), +17.147 (**N_1CP2**), +37.461 (**N_2CPb3**), +54.031 (**N_3CPd6**), and +65.636 kcal/mol (**N_4CPc8**). In this order, the mean plane deviation of these isomers increased from 0.000 to 0.123, 0.170, 0.215, and 0.251 Å, respectively. The unusual tautomeric forms of pyrrole ring with an sp^3-carbon were found in the stable forms of **N_3CP** and **N_4CP**. The NICS values at the mean position of the 24 core atoms were nearly the same for the most aromatic isomers regardless of the *confusion* level: −15.1280 (**N_0CP1**), −13.8493 (**N_1CP2**), −13.7267 (**N_2CPd1**), −11.7723 (**N_3CPb5**), and −13.6224 ppm (**N_4CPa6**). The positive correlation between aromaticity and stability was inferred from the plots of NICS and the relative energy of **NCP** for **N_0CP**, **N_1CP**, and *trans*-**N_2CP**. On the other hand, the correlation was negative for *cis*-**N_2CP**, **N_3CP**, and **N_4CP** isomers.

1. Introduction

Syntheses and the metal coordination chemistry of porphyrin analogues have been attracting considerable attention due to the possibility of new porphyrin chemistry.[1] Among a variety of porphyrin analogues, an inverted porphyrin isomer, "N-confused porphyrin (**NCP**)", is unique in that it could form a family with a large number of *confused* isomers.[2] Even though only two types of isomers, singly N-confused porphyrin (**N_1CP**) and doubly N-confused porphyrin (*cis*-**N_2CP**), have been synthesized until now, the rich coordination chemistry and the unprecedented reactivity have been continuously disclosed.[2−6] For example, **N_1CP** forms square-planar complexes with both the divalent and trivalent d^8 metals such as Ni(II)[2b] and Ag(III),[4c] and **N_2CP** can coordinate higher oxidation state of metal like Cu(III)[6a] to afford the organometallic complex. The distinct outer-coordination at the peripheral nitrogen of the *confused* pyrrole ring was also demonstrated with Pd(II)[4g] and Rh(I)[4i] complexes. In a different level of the chemistry, a new porphyrinoid, N-fused porphyrin, was synthesized from **N_1CP** by using the ring-inversion property.[4d,e]

Previously, we have examined the stability and the structures of **N_2CP** isomers by using the density functional theory (DFT) method and shown that the less aromatic tautomers were not necessarily unstable and the balance between the steric repulsion in the core and

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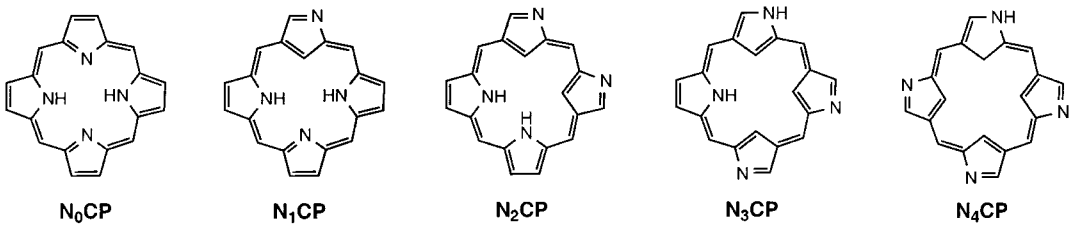
Chart 1. Structures of NCP Isomers



the aromaticity was main factor in determining the relative stability of each isomer.[6c] Since then, we have been wondering whether the result is general and applicable to other **NCP** isomers bearing more *confused* rings. To answer this question, we have extended the DFT calculations to all the isomers of the **NCP** family. In particular, the nucleus-independent chemical shift (NICS) was calculated to evaluate the aromaticity of each isomer.[7,8] In this paper, we describe the DFT calculation on all the **NCP** isomers and discuss their stability, structures, and aromaticity on the basis of the total energies and NICS values. Such calculations on a whole set of **NCP** isomers have never been reported, and thus, the results described here would become a general reference not only for the theoretical study but also for the synthetic attempts toward **NCP** family members in the future.

2. Method

Ab initio calculations were carried out with the Gaussian 98 program[9] for the skeleton of **NCP** isomers on the HPC-alpha UP264 (HIT) computer. The structures were optimized with B3LYP/6-31G**. The final estimation of the total electronic energies were performed at the B3LYP level with the 6-31G** basis set. The relative energies were calculated from the energy difference between each isomers and the *normal* porphyrin (**N_0CP1**). NICS values were determined at the mean position of the 24 heavy core atoms by the GIAO method[10] at the B3LYP/6-31G** level.

3. Results and Discussion

3-1. Relative Energy and NICS of NCP Isomers. The **NCP** isomers are grouped into five levels: *normal* porphyrin (**N_0CP**), N-confused porphyrin (**N_1CP**), doubly N-confused porphyrin (**N_2CP**), triply N-confused porphyrin (**N_3CP**), and fully N-confused porphyrin (**N_4CP**) (Chart 1). Multiply N-confused porphyrins (**N_2CP**, **N_3CP**, **N_4CP**) contain several regioisomers and tautomers that differ in the position of nitrogens and NH hydrogens, respectively. A total of 95 **NCP** structures (2-**N_0CP**, 6-**N_1CP**, 17-**N_2CP**, 24-**N_3CP**, 46-**N_4CP**) were subjected to the calculation (Table 1).[11] For discussion, the NCP isomers were further classified into *inner-2H*, *3H*, *4H*, *5H*, and *inner-6H* according to the number of hydrogens in the core.

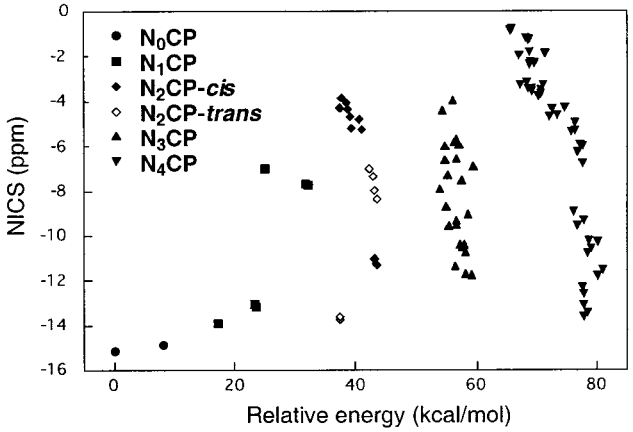


Figure 1. Plots of NICS (ppm) and the relative energies (kcal/mol) for **NCP** isomers.

The calculated relative energy and NICS values of **NCP** isomers are tabulated in Table 1 and plotted in Figure 1. When the number of *confused* pyrrole rings is increased, the macrocycles tend to be destabilized stepwise by approximately +18 kcal/mol. For example, the relative energies of the most stable isomers in each *confusion* level are 0 (**N_0CP1**), +17.147 (**N_1CP2**), +37.461 (**N_2CPb3**), +54.031 (**N_3CPd6**), and +65.636 kcal/mol (**N_4CPc8**), respectively. On the other hand, the magnitude of the aromaticity estimated by NICS for these isomers does not differ largely. Namely, the NICS values of the most aromatic isomers are −15.1280 (**N_0CP1**), −13.8493 (**N_1CP2**), −13.7267 (**N_2CPd1**), −11.7723 (**N_3CPb5**), and −13.6224 ppm (**N_4CPa6**), respectively. Interestingly, the most stable isomers of **N_2CP**, **N_3CP**, and **N_4CP** are not necessarily the most aromatic but rather nonaromatic, especially in the case of **N_4CP**. This is a marked contrast to **N_0CP** and **N_1CP**, where the most stable isomers show the highest negative NICS values. The details are discussed below.

3-2. The Structures of the Most Stable NCP Isomers. The optimized structures of the most stable tautomers in each *confusion* level (**N_0CP1**, **N_1CP2**, **N_2CPb3**, **N_3CPd6**, **N_4CPc8**) are illustrated in Figure 2. The mean plane deviation and the dihedral angles of the pyrrole rings to the mean plane are shown in Table 2.[12]

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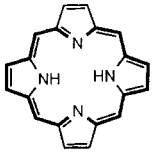
(11) To avoid the complexity, the nonconjugated isomers of the isoporphyrin type that bears an sp^3-carbon at the *meso* position were not included in the present study. See also ref 18.

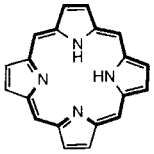
(12) Cartesian coordinates of **NCP** family are shown in Supporting Information.

Table 1. Structures, Calculated Total Energies (Hartree), Relative Energies (kcal/mol), and NICS (ppm) of NCP Isomers and Tautomers[a]

N_0CP

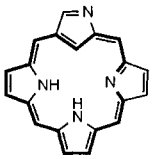


N_0CP1
-989.5777539 (standard)
0 kcal/mol
NICS = -15.1280 ppm

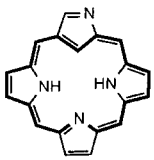


N_0CP2
-989.5647101
8.185 kcal/mol
NICS = -14.8949 ppm

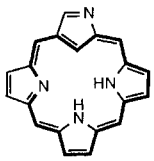
N_1CP



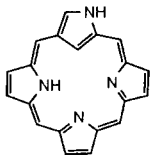
N_1CP1
-989.540095075
23.631 kcal/mol
NICS = -13.1522 ppm



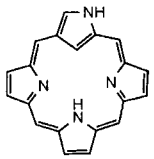
N_1CP2
-989.5504271
17.147 kcal/mol
NICS = -13.8493 ppm



N_1CP3
-989.540622688
23.300 kcal/mol
NICS = -13.0547 ppm



N_1CP4
-989.526588787
32.107 kcal/mol
NICS = -7.7155 ppm



N_1CP5
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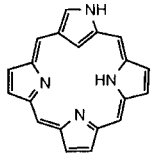
24.928 kcal/mol
NICS = -7.0308 ppm



N_1CP6
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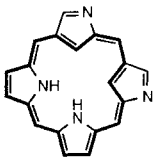
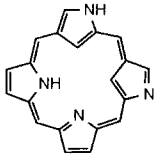
31.683 kcal/mol
NICS = -7.7019 ppm

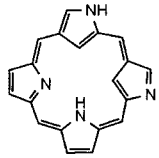
cis-N_2CP



N_2CPa1
-989.5090252
43.127 kcal/mol
NICS = -11.0261 ppm



N_2CPa2
-989.5122223
41.121 kcal/mol
NICS = -5.2836 ppm



N_2CPa3
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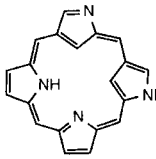
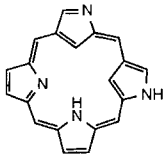
39.392 kcal/mol
NICS = -5.1993 ppm



N_2CPa4
-989.517809160
37.615 kcal/mol
NICS = -3.8481 ppm



N_2CPa5
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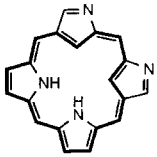
38.569 kcal/mol
NICS = -4.0591 ppm



N_2CPb1
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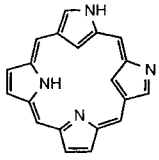
43.352 kcal/mol
NICS = -11.2278 ppm



N_2CPb2
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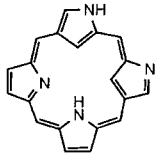
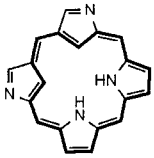
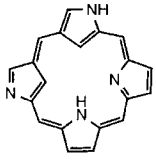
38.744 kcal/mol
NICS = -4.3425 ppm



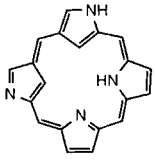
N_2CPb3
-989.5180558
37.461 kcal/mol
NICS = -4.2840 ppm



N_2CPc1
-989.508425
43.504 kcal/mol
NICS = -11.2985 ppm



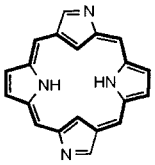
N_2CPc2
-989.5150862
39.324 kcal/mol
NICS = -4.6654 ppm



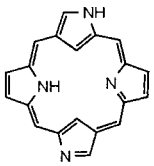
N_2CPc3
-989.5129892
40.640 kcal/mol
NICS = -4.8122 ppm

Table 1 (Continued)

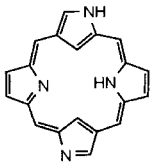
trans-N_2CP



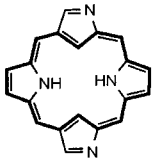
N_2CPd1
-989.5179548
37.524 kcal/mol
NICS = -13.7267 ppm



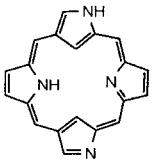
N_2CPd2
-989.5082536
43.612 kcal/mol
NICS = -8.3734 ppm



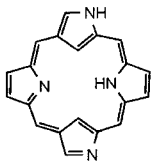
N_2CPd3
-989.5104415
42.239 kcal/mol
NICS = -7.0076 ppm



N_2CPe1
-989.517989
37.503 kcal/mol
NICS = -13.6328 ppm

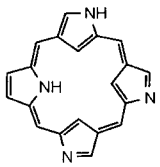


N_2CPe2
-989.5094258
42.876 kcal/mol
NICS = -7.3698 ppm

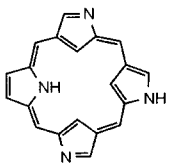


N_2CPe3
-989.509004
43.141 kcal/mol
NICS = -7.9410 ppm

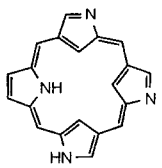
N_3CP



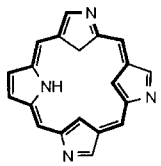
N_3CPa1
-989.483161851
59.357 kcal/mol
NICS = -6.9223 ppm



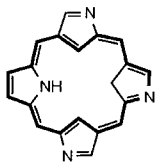
N_3CPa2
-989.489654560
55.283 kcal/mol
NICS = -7.2644 ppm



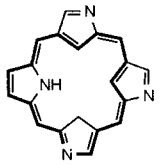
N_3CPa3
-989.490310344
54.871 kcal/mol
NICS = -5.9661 ppm



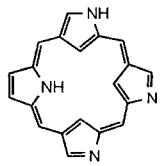
N_3CPa4
-989.486306569
57.384 kcal/mol
NICS = -10.3923 ppm



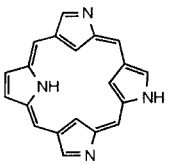
N_3CPa5
-989.485735497
57.742 kcal/mol
NICS = -10.5250 ppm



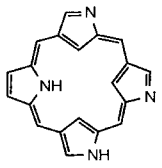
N_3CPa6
-989.489268707
55.525 kcal/mol
NICS = -9.5548 ppm



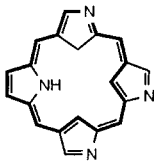
N_3CPb1
-989.488350442
56.101 kcal/mol
NICS = -3.9419 ppm



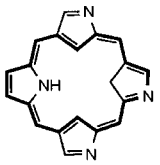
N_3CPb2
-989.490977916
54.452 kcal/mol
NICS = -4.4231 ppm



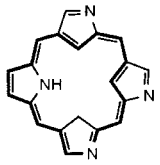
N_3CPb3
-989.487948664
56.353 kcal/mol
NICS = -5.8334 ppm



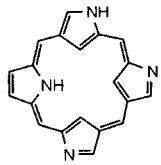
N_3CPb4
-989.487478837
58.649 kcal/mol
NICS = -9.0236 ppm



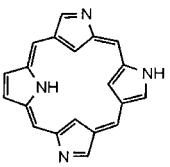
N_3CPb5
-989.483259186
59.296 kcal/mol
NICS = -11.7723 ppm



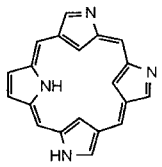
N_3CPb6
-989.485474118
57.906 kcal/mol
NICS = -10.3754 ppm



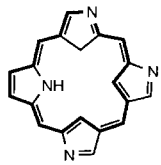
N_3CPc1
-989.486874995
57.027 kcal/mol
NICS = -5.9189 ppm



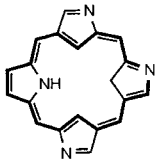
N_3CPc2
-989.490552102
54.720 kcal/mol
NICS = -6.5945 ppm



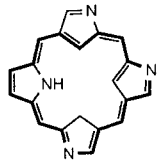
N_3CPc3
-989.487446450
56.668 kcal/mol
NICS = -6.5462 ppm



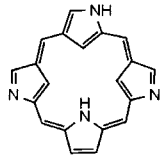
N_3CPc4
-989.484907469
58.262 kcal/mol
NICS = -11.6985 ppm



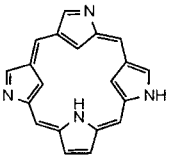
N_3CPc5
-989.484905844
58.263 kcal/mol
NICS = -10.7238 ppm



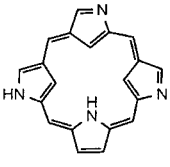
N_3CPc6
-989.490134498
54.982 kcal/mol
NICS = -8.7214 ppm



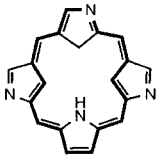
N_3CPd1
-989.487378575
56.711 kcal/mol
NICS = -9.3328 ppm



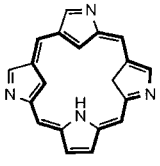
N_3CPd2
-989.487375568
56.713 kcal/mol
NICS = -5.7304 ppm



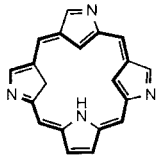
N_3CPd3
-989.485891389
57.644 kcal/mol
NICS = -7.5281 ppm



N_3CPd4
-989.487536035
56.613 kcal/mol
NICS = -9.5006 ppm



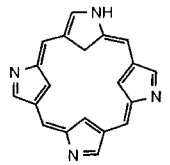
N_3CPd5
-989.487768255
56.467 kcal/mol
NICS = -11.3402 ppm



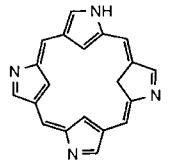
N_3CPd6
-989.491650435
54.031 kcal/mol
NICS = -7.9181 ppm

Table 1. (Continued)

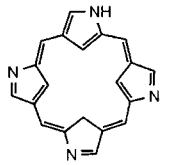
N_4CP



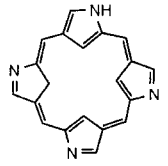
N_4CPa1
-989.458747010
74.682 kcal/mol
NICS = -4.3134 ppm



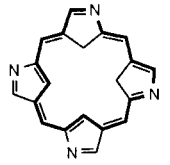
N_4CPa2
-989.468718571
68.420 kcal/mol
NICS = -3.1643 ppm



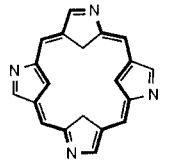
N_4CPa3
-989.468672974
68.449 kcal/mol
NICS = -1.2930 ppm



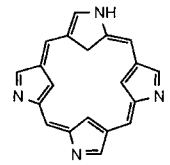
N_4CPa4
-989.462831343
72.115 kcal/mol
NICS = -4.6724 ppm



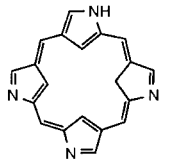
N_4CPa5
-989.453623397
77.893 kcal/mol
NICS = -9.3503 ppm



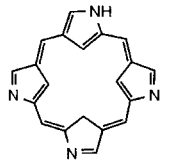
N_4CPa6
-989.453676560
77.859 kcal/mol
NICS = -13.6224 ppm



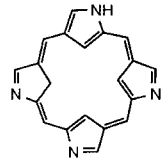
N_4CPb1
-989.455933595
76.443 kcal/mol
NICS = -4.9878 ppm



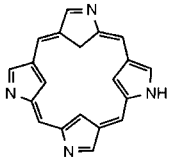
N_4CPb2
-989.465159800
70.653 kcal/mol
NICS = -3.4828 ppm



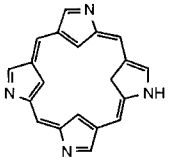
N_4CPb3
-989.463875110
71.460 kcal/mol
NICS = -1.8652 ppm



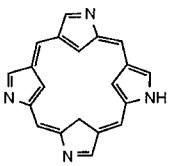
N_4CPb4
-989.460688858
73.459 kcal/mol
NICS = -4.6061 ppm



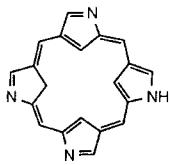
N_4CPb5
-989.465272097
70.583 kcal/mol
NICS = -3.6573 ppm



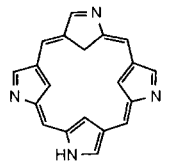
N_4CPb6
-989.456102010
76.337 kcal/mol
NICS = -5.3072 ppm



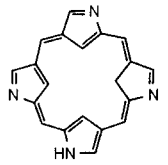
N_4CPb7
-989.468257733
68.709 kcal/mol
NICS = -1.8244 ppm



N_4CPb8
-989.464528802
71.049 kcal/mol
NICS = -3.2641 ppm



N_4CPb9
-989.472935151
65.774 kcal/mol
NICS = -0.8065 ppm



N_4CPb10
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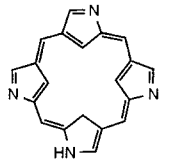
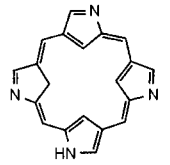
70.147 kcal/mol
NICS = -3.7774 ppm



N_4CPb11
-989.457046592
75.745 kcal/mol
NICS = -5.3507 ppm



N_4CPb12
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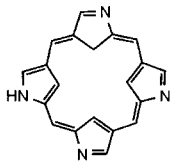
67.281 kcal/mol
NICS = -3.2654 ppm



N_4CPb13
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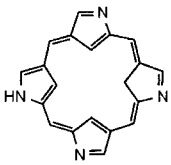
69.155 kcal/mol
NICS = -3.4610 ppm



N_4CPb14
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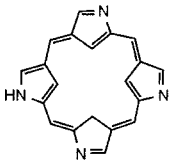
68.004 kcal/mol
NICS = -1.1870 ppm



N_4CPb15
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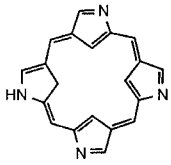
69.638 kcal/mol
NICS = -2.2302 ppm



N_4CPb16
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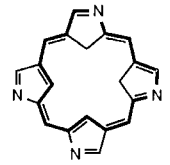
77.707 kcal/mol
NICS = -6.7700 ppm



N_4CPb17
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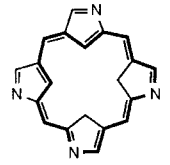
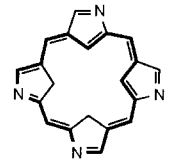
78.510 kcal/mol
NICS = -10.7942 ppm



N_4CPb18
-989.451687969
79.107 kcal/mol
NICS = -10.5675 ppm



N_4CPb19
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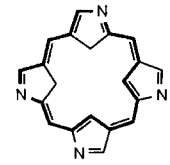
76.086 kcal/mol
NICS = -8.9142 ppm



N_4CPb20
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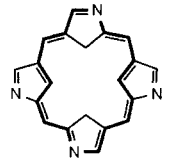
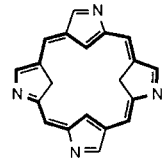
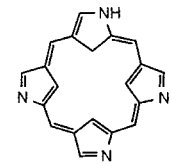
80.085 kcal/mol
NICS = -10.2937 ppm



N_4CPb21
-989.453561447
77.932 kcal/mol
NICS = -12.5862 ppm



N_4CPb22
-989.453764146
77.804 kcal/mol
NICS = -13.1394 ppm



N_4CPc1
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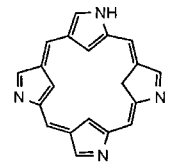
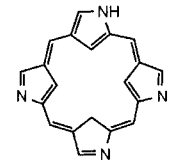
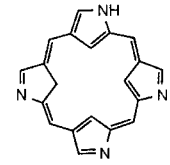
77.559 kcal/mol
NICS = -5.9645 ppm



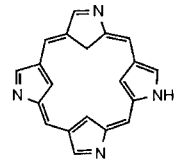
N_4CPc2
-989.462008597
72.631 kcal/mol
NICS = -4.3773 ppm



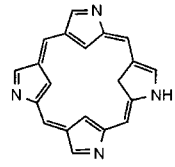
N_4CPc3
-989.464080740
71.331 kcal/mol
NICS = -1.8774 ppm



N_4CPc4
-989.467798628
68.998 kcal/mol
NICS = -2.2494 ppm

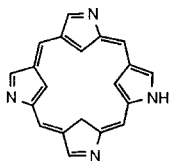
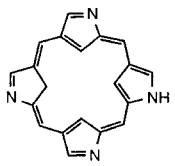
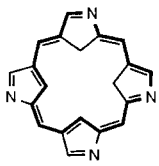
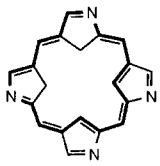
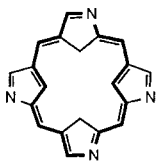
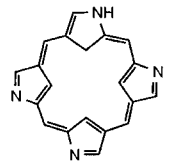
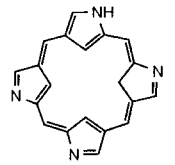
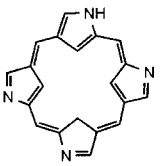
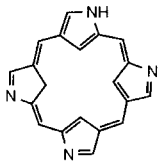
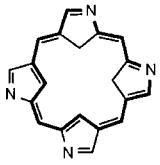
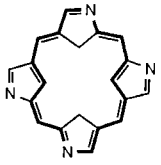
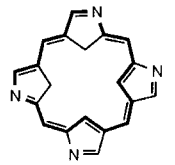


N_4CPc5
-989.468558621
68.521 kcal/mol
NICS = -3.4558 ppm



N_4CPc6
-989.455398172
76.779 kcal/mol
NICS = -6.2971 ppm

Table 1. (Continued)

				
N_4CPc7 -989.470739455 67.152 kcal/mol NICS = -2.0035 ppm	**N_4CPc8** -989.473155718 65.636 kcal/mol NICS = -0.8204 ppm	**N_4CPc9** -989.452328269 78.705 kcal/mol NICS = -10.2497 ppm	**N_4CPc10** -989.449898743 80.230 kcal/mol NICS = -11.8075 ppm	**N_4CPc11** -989.454165717 77.552 kcal/mol NICS = -12.3401 ppm
					
N_4CPd1 -989.454611335 77.273 kcal/mol NICS = -5.9453 ppm	**N_4CPd2** -989.467421681 69.234 kcal/mol NICS = -3.5825 ppm	**N_4CPd3** -989.468214595 68.737 kcal/mol NICS = -1.2459 ppm	**N_4CPd4** -989.468186216 68.752 kcal/mol NICS = -2.3515 ppm	**N_4CPd5** -989.456045145 76.737 kcal/mol NICS = -9.5629 ppm	**N_4CPd6** -989.452570386 78.553 kcal/mol NICS = -13.4757 ppm
					
N_4CPd7 -989.44851709 81.097 kcal/mol NICS = -11.5193 ppm					

[a] [18]-Annulenic pathways are indicated in bold.

An almost completely flat structure is calculated for **N_0CP1**, but the structures for other **NCP** are largely distorted. To illustrate the distortion clearly, the linear displays of deviations of the macrocyclic atoms of **N_1CP2**, **N_2CPb3**, **N_3CPd6**, and **N_4CPc8** are presented in Figure 3. The mean plane deviation of **N_1CP2** is 0.123 Å, and the dihedral angles of the four pyrrole rings to the macrocycle are +16.152 (*confused*), −2.017 (*normal*), +1.666 (*normal*), and −2.090° (*normal*), respectively. The tilting angles of **N_2CPb3** (mean plane deviation: 0.170 Å) are +16.601 (*confused*), −16.748 (*confused*), +2.162 (*normal*), and −0.066° (*normal*), respectively. In the case of **N_3CPd6** (0.215 Å), the two *confused* pyrroles consisted of sp^2 atoms are tilted +20.982° and −15.402° at the opposite direction of the mean plane. The remaining *confused* sp^3-carbon-containing-pyrrole and the *normal* pyrrole are tilted +4.154° and +8.066°, respectively. With **N_4CPc8** (0.251 Å), the tilting angles of the three *confused* pyrrole rings with sp^2-carbons are up (+17.628°), down (−19.267°), up (+19.975°), respectively, and the sp^3-carbon-containing-pyrrole is tilted downward slightly (−5.771°). The dihedral angles of the *confused* pyrrole rings are larger than those of the *normal* one in the **NCP** family in general.

3-3. *Normal* Porphyrin (N_0CP). At first, the relative energy between the two tautomers of the *normal* porphyrin (**N_0CP1**, **N_0CP2**) was estimated.[13] **N_0CP1**, bearing 2 NH at the opposite site, is more stable than **N_0CP2** (+8.185 kcal/mol), where the repulsion between the two neighboring NH hydrogens is significant.[14] Structurally, **N_0CP1** is more planar than **N_0CP2**: the mean plane deviation and the maximum dihedral angle are (0.000 Å, 0.000°) for **N_0CP1** and (0.000 Å, 0.048°) for **N_0CP2**, respectively. The NICS values of these structures are −15.1280 and −14.8949 ppm, respectively, which suggest that the stable planar tautomer, **N_0CP1**, is more aromatic than distorted **N_0CP2**. Thus, in the *normal* porphyrin (**N_0CP**), the stability and the aromaticity are correlated positively.

3-4. Singly N-Confused Porphyrin (N_1CP). **N_1CP** is classified into two kinds of NH-tautomers, *inner-3H* type (**N_1CP1-3**) and *inner-2H* type (**N_1CP4-6**).[15] The optimized structures of the *inner-2H* (**N_1CP4-6**) showed the planarity more than the *inner-3H* (**N_1CP1-3**): the mean plane deviations for **N_1CP4-6** are 0.046, 0.054, and 0.053 Å, and those of **N_1CP1-3** are 0.125, 0.123, and 0.129 Å, respectively. The dihedral angles of the *confused* pyrrole ring of **N_1CP1-3** are +14.589, +16.152, and +14.448°, and those of **N_1CP4-6** are +6.102, +5.184, and +6.971°, respectively. As expected from the Kekulé structures, the *inner-3H* type shows more negative NICS

(13) A considerable numbers of theoretical study on the NH tautomers of *normal* porphyrin have been reported. (a) Ghosh, A.; Lü, T. X.; Almlöf, J. *J. Phys. Chem.* **1995**, *99*, 1073−1075. (b) Reimers, J. R.; Lü, T. X.; Crossley, M. J.; Hush, N. S. *J. Am. Chem. Soc.* **1995**, *117*, 2855−2861. (c) Ghosh, A. *Acc. Chem. Res.* **1998**, *31*, 189−198, and references therein.

(14) Schlabach, M.; Scherer, G.; Limbach, H.-H. *J. Am. Chem. Soc.* **1991**, *113*, 3550−3558.

(15) (a) Szterenberg, L.; Latos-Grażyński, L. *Inorg. Chem.* **1997**, *36*, 6287−6291. (b) Ghosh, A.; Wondimagegn, T.; Nilsen, H. J. *J. Phys. Chem. B* **1998**, *102*, 10459−10467.

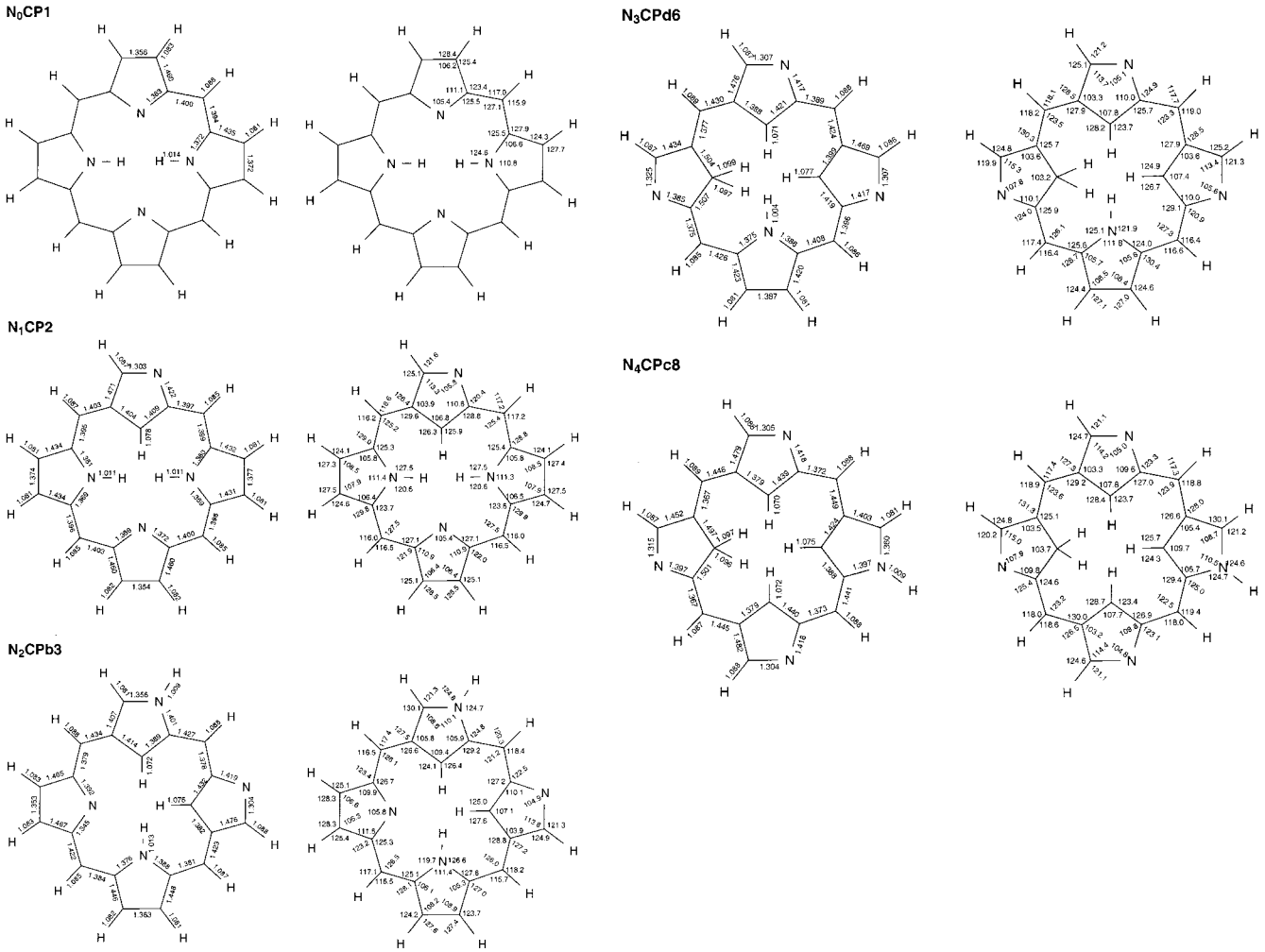


Figure 2. Optimized geometries (Å, deg) of **NCP** isomers.

values (∼−13 ppm) than the *inner-2H* type (∼−7 ppm) (Figure 4).[16] The weak aromaticity of the *inner-2H* may be due to the contribution of the zwitterionic resonance form.[17]

N_1CP2, the most stable (+17.147 kcal/mol) and aromatic (−13.8493 ppm) isomer in the **N_1CP** family, shows the effective hydrogen bonding between both the NHs and N in the core. Such inner-core hydrogen bondings play an important role to lower the energy in the *inner-2H* type as well, as judged by the structure of more stable **N_1CP5**. On the other hand, the magnitude of the aromaticity seems to be related to the planarity of **N_1CP**, because the less distorted **N_1CP2** and **N_1CP4** are the most aromatic in the *inner-3H* and *inner-2H* type, respectively.

3-5. Doubly N-Confused Porphyrin (N_2CP). The five regioisomers of **N_2CP** are grouped into two types, cis and trans, according to the relative position of the *confused* rings, that is, the two *confused* pyrroles are neighboring in cis (**N_2CPa-c**) and countered in trans (**N_2CPd**, **e**). Each isomer has *inner-3H* and *inner-4H* tautomers, and thus, 17 structures in total are possible in the **N_2CP** family. The results of the DFT calculation on the structures and the relative stability of **N_2CP** have been previously reported in which the *inner-3H* are more stable than the *inner-4H* in cis isomers but the *inner-4H* are more stable in the trans isomers.[6c]

The most stable isomer, **N_2CPb3**, has +37.461 kcal/mol higher energy than **N_0CP1**. The *inner-4H* tautomers (**N_2CPa1**, **b1**, **c1**, **d1**, **e1**) can form a complete 18π conjugation system; thus, the aromaticity inferred from NICS is larger than that of the *inner-3H* type. Among the *inner-4H*, the trans isomers (**N_2CPd1**, **e1**) are more stable (ca. −6 kcal/mol) and more aromatic (ca. −2.5 ppm) than the cis isomers (**N_2CPa1**, **b1**, **c1**). Due to the repulsive interaction in the core, the aromatic *cis*-**N_2CP** is more distorted than the *trans*-**N_2CP**. In the *inner-3H* tautomers, on the other hand, the cis isomers are less aromatic (ca. +3 ppm) and distorted but are more stable (ca. −3 kcal/mol) than the trans isomers (Figure 5). The inner-core hydrogen bonding is crucial for the stabilization of cis isomers as shown in **N_1CP**.

3-6. Triply N-Confused Porphyrin (N_3CP). **N_3CP** has four regioisomers (**N_3CPa**−**d**) according to the position of the peripheral nitrogens. Each isomer has six NH tautomers, and thus, the 24 isomers in total are grouped into two types: *inner-4H* (**N_3CP1**−**3**) and *inner-5H*

(16) In the solid state, the *confused* pyrrole ring is canted +26.9° in the *inner-3H* tautomer of tetraphenyl N-confused porphyrin (NC-TPP), on the other hand, the pyrrole rings are tilted only 0.2−4.7° in the *inner-2H* isomer. In $CDCl_3$, the ^{1}H NMR signals derived from inner CH and NH of the aromatic *inner-3H* type were observed at −4.99 and −2.41 ppm, respectively. On the other hand, in DMF-d_7, those signals of *inner-2H* type were downfield shifted at +0.76 and +2.27 ppm, respectively, reflecting the weak aromaticity. See ref 4h.

(17) Lash, T. D. *Synlett* **2000**, 279−295.

Table 2. Mean Plane Deviation Δ (Å) and Dihedral Angles (deg) of NCP Isomers and Tautomers[a]

	Δ (Å)	dihedral angles (deg)					Δ (Å)	dihedral angles (deg)			
N_0CP1	0.000	0.000	0.000	0.000	0.000	**N_0CP2**	0.000	0.048	−0.048	0.048	−0.048
N_1CP1	0.125	*14.589*	1.082	−3.014	−5.639	**N_1CP4**	0.046	*6.102*	1.071	0.560	−0.813
N_1CP2	0.123	*16.152*	−2.017	1.666	−2.090	**N_1CP5**	0.054	*5.184*	0.523	−0.391	1.353
N_1CP3	0.129	*14.448*	−6.723	3.237	0.813	**N_1CP6**	0.053	*6.971*	−0.996	0.518	1.928
N_2CPa1	0.164	*12.714*	*−16.776*	−6.443	8.528	**N_2CPc2**	0.157	*16.112*	0.206	1.778	*−14.174*
N_2CPa2	0.162	*17.451*	*−13.599*	−0.502	−2.245	**N_2CPc3**	0.161	*19.183*	−1.840	0.911	*−10.797*
N_2CPa3	0.159	*14.593*	*−16.251*	1.319	0.404	**N_2CPd1**	0.145	*14.513*	−2.810	*−14.558*	−2.789
N_2CPa4	0.166	*14.203*	*−17.387*	−0.523	−2.412	**N_2CPd2**	0.127	*8.544*	−2.953	*13.059*	4.047
N_2CPa5	0.172	*11.114*	*−20.826*	1.571	−1.065	**N_2CPd3**	0.135	*14.997*	−4.094	*7.435*	2.707
N_2CPb1	0.172	*15.959*	*−16.012*	−7.050	7.304	**N_2CPe1**	0.146	*14.736*	1.770	*−14.725*	−2.607
N_2CPb2	0.175	*19.484*	*−14.126*	0.271	−1.663	**N_2CPe2**	0.123	*14.172*	−1.855	*15.086*	−4.394
N_2CPb3	0.170	*16.601*	*−16.748*	2.162	−0.066	**N_2CPe3**	0.141	*12.434*	−4.123	*12.147*	3.516
N_2CPc1	0.157	*15.434*	6.992	−8.852	*−11.709*						
N_3CPa1	0.200	*9.879*	*−20.616*	*−17.093*	2.502	**N_3CPc1**	0.207	*13.226*	*−20.668*	*−17.624*	2.523
N_3CPa2	0.211	*3.104*	*−28.765*	*−13.982*	3.511	**N_3CPc2**	0.205	*6.302*	*−26.662*	*−13.234*	3.728
N_3CPa3	0.214	*12.269*	*−18.261*	*−20.652*	3.664	**N_3CPc3**	0.218	*12.461*	*−19.890*	*−21.521*	3.297
N_3CPa4	0.207	*(9.224)*	*25.385*	*12.966*	−4.306	**N_3CPc4**	0.210	*(8.788)*	*25.039*	*15.591*	−2.970
N_3CPa5	0.165	*15.074*	*(7.194)*	*−15.411*	1.293	**N_3CPc5**	0.166	*15.941*	*(−7.066)*	*−14.758*	1.697
N_3CPa6	0.198	*10.031*	*−20.638*	*(−2.961)*	−6.510	**N_3CPc6**	0.213	*15.644*	*−20.640*	*(−4.237)*	−6.502
N_3CPb1	0.252	*17.715*	*−18.415*	*17.480*	−1.925	**N_3CPd1**	0.236	*28.737*	*13.575*	−1.443	*15.335*
N_3CPb2	0.218	*10.502*	*−29.078*	*−4.930*	−2.552	**N_3CPd2**	0.201	*9.526*	*−11.163*	3.004	*19.519*
N_3CPb3	0.198	*8.625*	*−23.139*	*−14.646*	4.942	**N_3CPd3**	0.210	*17.115*	*−12.740*	2.609	*22.427*
N_3CPb4	0.214	*(4.135)*	*21.098*	*−15.324*	6.458	**N_3CPd4**	0.175	*(7.382)*	*−16.622*	−1.285	*15.836*
N_3CPb5	0.157	*15.393*	*(−6.344)*	*−14.573*	0.338	**N_3CPd5**	0.209	*24.038*	*(9.686)*	−3.469	*15.455*
N_3CPb6	0.198	*12.993*	*−21.296*	*(−3.731)*	−6.442	**N_3CPd6**	0.215	*20.982*	*−15.402*	8.066	*(4.154)*
N_4CPa1	0.250	*(6.731)*	*19.757*	*−15.764*	*19.133*	**N_4CPb18**	0.158	*15.562*	*(3.380)*	*(−2.727)*	*−13.845*
N_4CPa2	0.238	*24.855*	*(8.540)*	*−17.129*	*12.477*	**N_4CPb19**	0.173	*15.338*	*−16.575*	*(−3.269)*	*(3.790)*
N_4CPa3	0.246	*16.622*	*−19.218*	*(−6.961)*	*−19.009*	**N_4CPb20**	0.171	*3.811*	*15.326*	*−26.544*	*−2.806*
N_4CPa4	0.223	*24.922*	*10.924*	*−16.109*	*(7.832)*	**N_4CPb21**	0.246	*(11.563)*	*22.702*	*(12.299)*	*22.579*
N_4CPa5	0.172	*(2.812)*	*(−3.848)*	*−16.186*	*15.798*	**N_4CPb22**	0.249	*21.356*	*(11.961)*	*23.172*	*(11.672)*
N_4CPa6	0.251	*(23.230)*	*23.475*	*(12.058)*	*23.737*	**N_4CPc1**	0.244	*(8.856)*	*20.139*	*−16.072*	*17.700*
N_4CPb1	0.252	*(0.510)*	*7.305*	*−19.967*	*16.298*	**N_4CPc2**	0.226	*24.764*	*(7.960)*	*−15.951*	*10.395*
N_4CPb2	0.234	*22.651*	*(7.830)*	*−14.426*	*17.836*	**N_4CPc3**	0.239	*14.867*	*−20.301*	*(−6.850)*	*−18.155*
N_4CPb3	0.240	*14.549*	*−19.841*	*(−6.960)*	*−19.264*	**N_4CPc4**	0.265	*21.003*	*−15.105*	*21.010*	*(6.618)*
N_4CPb4	0.226	*21.900*	*−2.665*	*−21.611*	*(−8.095)*	**N_4CPc5**	0.240	*(8.453)*	*26.747*	*12.668*	*−16.660*
N_4CPb5	0.219	*(6.686)*	*16.131*	*22.268*	*−13.025*	**N_4CPc6**	0.232	*17.439*	*(8.616)*	*20.068*	*−13.165*
N_4CPb6	0.241	*16.936*	*(6.636)*	*20.921*	*−15.767*	**N_4CPc7**	0.266	*10.851*	*−24.600*	*(−8.083)*	*−22.070*
N_4CPb7	0.264	*11.281*	*−23.278*	*(−7.340)*	*−22.853*	**N_4CPc8**	0.251	*17.628*	*−19.267*	*19.975*	*(−5.771)*
N_4CPb8	0.234	*10.720*	*−22.769*	*−20.422*	*(−7.883)*	**N_4CPc9**	0.170	*(3.665)*	*(−2.991)*	*−16.416*	*15.055*
N_4CPb9	0.254	*(5.427)*	*18.064*	*−19.219*	*19.185*	**N_4CPc10**	0.178	*(3.440)*	*16.541*	*−16.914*	*(−3.537)*
N_4CPb10	0.233	*21.766*	*(9.167)*	*−21.729*	*8.451*	**N_4CPc11**	0.250	*(9.172)*	*23.189*	*(11.775)*	*22.427*
N_4CPb11	0.239	*13.934*	*−18.982*	*(−7.879)*	*−19.531*	**N_4CPd1**	0.243	*(8.848)*	*19.400*	*−14.267*	*19.874*
N_4CPb12	0.243	*15.468*	*−14.318*	*−26.522*	*(−8.410)*	**N_4CPd2**	0.240	*25.072*	*(8.032)*	*−14.666*	*17.323*
N_4CPb13	0.239	*(9.072)*	*21.953*	*24.762*	*−0.963*	**N_4CPd3**	0.247	*17.123*	*−19.451*	*(−6.810)*	*−18.504*
N_4CPb14	0.247	*17.812*	*(6.352)*	*19.571*	*−17.306*	**N_4CPd4**	0.264	*23.315*	*−13.409*	*21.619*	*(5.471)*
N_4CPb15	0.245	*12.707*	*−21.057*	*(−6.412)*	*−21.019*	**N_4CPd5**	0.182	*(3.277)*	*(−3.777)*	*−16.308*	*16.996*
N_4CPb16	0.236	*18.030*	*−14.113*	*20.232*	*(8.225)*	**N_4CPd6**	0.250	*(12.426)*	*23.016*	*(11.851)*	*22.603*
N_4CPb17	0.180	*(3.642)*	*(−3.340)*	*−26.533*	*16.167*	**N_4CPd7**	0.156	*(2.720)*	*14.717*	*−14.428*	*(−3.022)*

[a] The dihedral angles of the four pyrrole rings are represented clockwise from the upper ring of the corresponding structure in Table 1. The values of the *confused* pyrrole ring are shown in *italic*, and those of the *confused* sp^3-carbon-containing pyrroles are shown in parentheses.

(**N_3CP4**−**6**). The most stable **N_3CPd6** has +54.031 kcal/mol higher energy than **N_0CP1**, but the energy difference between **N_3CPd6** and the most unstable **N_3CPa1** is only +5.326 kcal/mol; thus, the stability does not differ largely in the **N_3CP** isomers (Figure 6). The mean plane deviations (0.157−0.252 Å) are larger than **N_2CP** (0.123−0.175 Å), and the dihedral angles of the *confused* rings become larger up to 29.078°. Interestingly, the sp^3-carbon-containing-pyrroles are tilted only 9.686° in maximum. Such small dihedral angles of the sp^3-rings are probably due to the steric interaction of CH_2-hydrogens pointing upside and downside in the core.[18] The *inner-5H* tautomers (**N_3CP4**−**6**) can form a complete aromatic circuit, and their NICS values (−7.9181 to −11.6985 ppm) are more negative than those of *inner-4H* type (**N_3CP1**−**3**, −3.9419 to −9.3328 ppm). Thus, the correlation between the stability and aromaticity of **N_3CP** is weak and shows the intermediate tendency between *trans*-**N_2CP** and *cis*-**N_2CP**; in other words, the aromatic property is not directly related to the stability in **N_3CP**.

3-7. Fully N-Confused Porphyrin (N_4CP). **N_4CP** are classified by four regioisomers (**N_4CPa-d**), and the 46 **N_4CP** tautomers are grouped into two types: *inner-5H* and *inner-6H*. The structures of the all **N_4CP** tautomers are distorted, but the deviation (0.156−0.264 Å) and the maximum dihedral angles (+26.8°) are almost in the same range as observed in **N_3CP**. The *inner-6H* tautomers are less stable (ca. +10 kcal/mol) compared

(18) Internal CH_2 structures were reported in the protonated carbaporphyrin and *trans*-dicarbaporphyrin. (a) Lash, T. D.; Hayes, M. J. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 840−842. (b) Lash, T. D.; Romanic, J. L.; Hayes, M. J.; Spence, J. D. *Chem. Commun.* **1999**, 819−820.

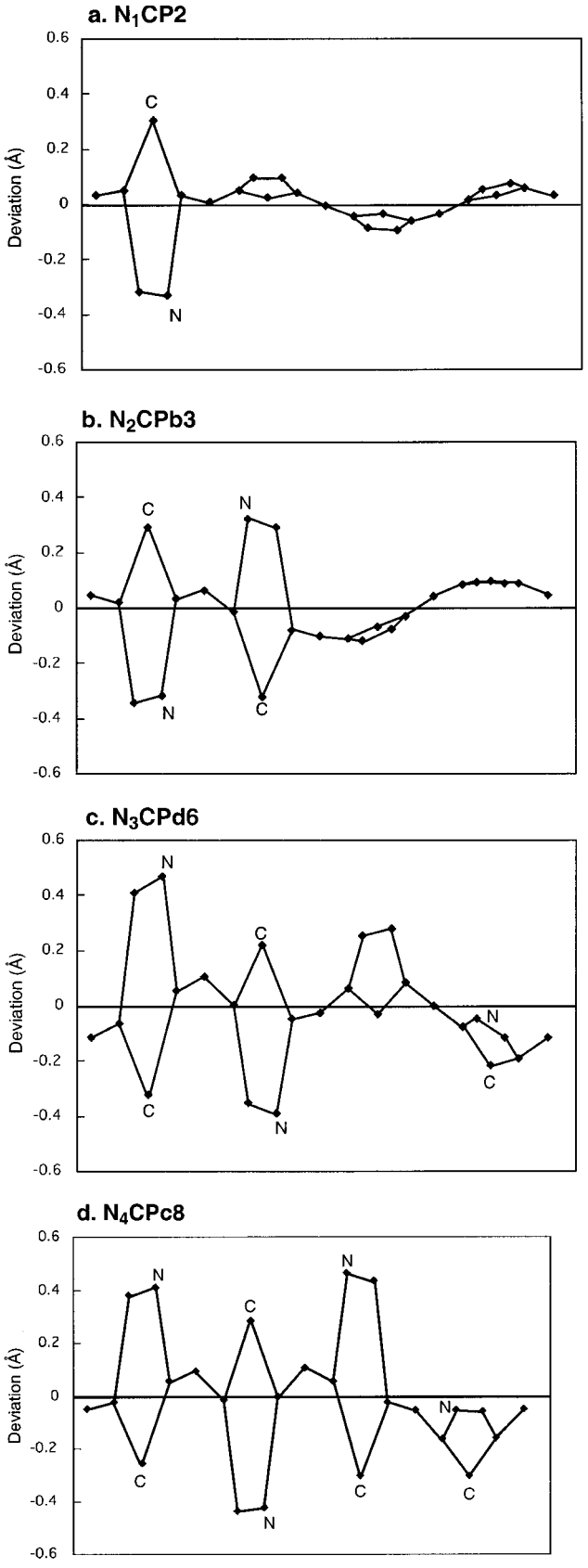


Figure 3. Linear display of deviations (Å) of the macrocycle atoms from the least-squares plane of the 24 heavy atoms.

to the *inner-5H* type due to the repulsion of the inner hydrogens. In the *inner-6H* type, the tautomers with neighboring two *confused* sp^3-carbon-containing-pyrroles make the macrocycle more planar (0.156−0.182 Å); on the other hand, the tautomers with a countered arrangement cause a dome-shaped deviation (0.246−0.251 Å).

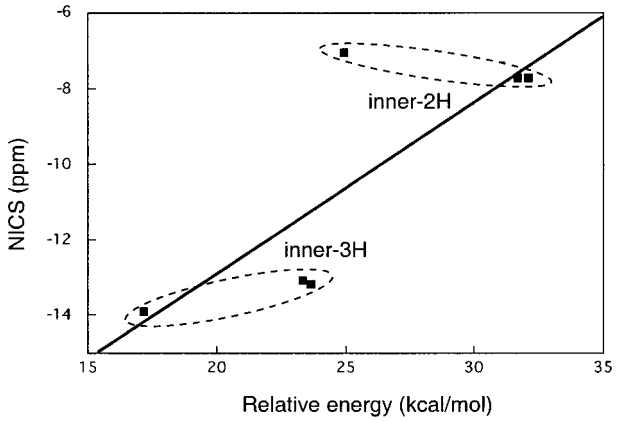


Figure 4. Plots of NICS (ppm) and the relative energies (kcal/mol) for **N_1CP**. The solid line denotes the least-squares line for the all isomers.

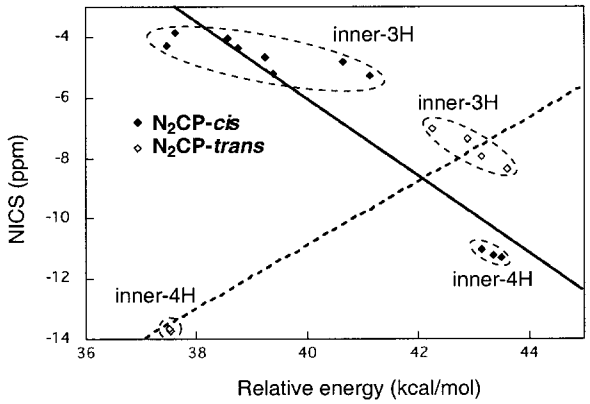


Figure 5. Plots of NICS (ppm) and the relative energies (kcal/mol) for **N_2CP**. The solid and the dotted lines denote the least-squares lines for the cis and trans isomers, respectively.

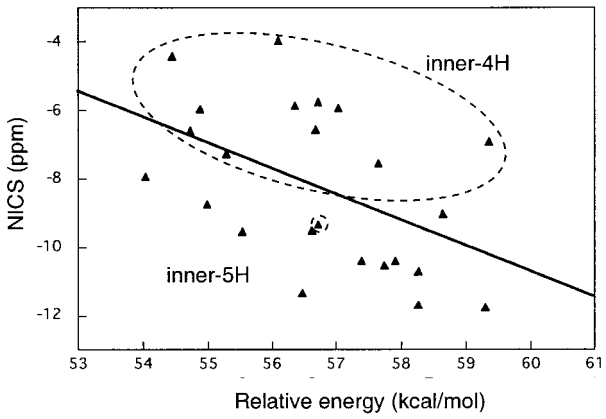
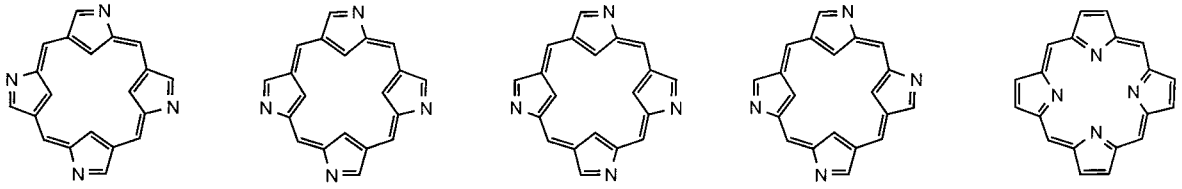


Figure 6. Plots of NICS (ppm) and the relative energies (kcal/mol) for **N_3CP**. The solid line denotes the least-squares line for the all isomers.

The larger aromaticity of the *inner-6H* type, which possesses the complete aromatic circuit, was illustrated by the lower NICS values (−8.9142 to −13.6224 ppm) compared to that of *inner-5H* tautomers (−0.8065 to −6.7700 ppm) (Figure 7). Surprisingly, the most stable isomers (**N_4CPb9**, **c8**) with the energies of 65.774 and 65.636 kcal/mol, respectively, are almost nonaromatic

Chart 2. Oxidized Forms of N_4CP and N_0CP



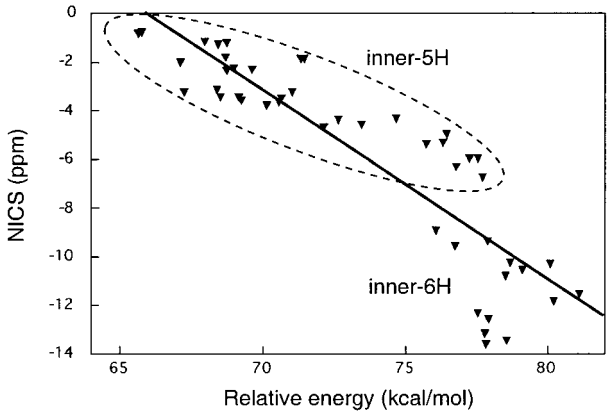


Figure 7. Plots of NICS (ppm) and the relative energies (kcal/mol) for **N_4CP**. The solid line denotes the least-squares line for the all isomers.

(−0.8065, −0.8204 ppm). Thus, in the fully *confused* level, the steric energy is predominant over the aromatic stabilization of the macrocycles.[19]

Finally, the oxidized form of **N_4CP** in Chart 2 is worth mentioning. The relative energies of these structures (**a**−**e**) are in the range of 0 to −9.661 kcal/mol. This proves that the *confused* forms (**a**−**d**) are more stable than the *normal* form (**e**) in the oxidized state.[20] The stability of the fully *confused* core could be explained by the lack of mutual repulsion of the lone pair electrons on the pyrrolic nitrogens in the core. Assuming the facile protonation at the peripheral nitrogens, such a fully *confused* configuration would be important for the design and the synthesis of **N_4CP**, especially in the metal coordination state.

4. Summary

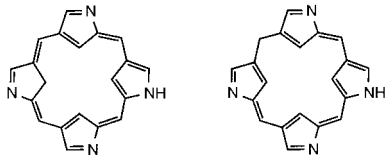
The structures, stability, and aromaticity of 95 isomers of **NCP** including the *normal* porphyrin have been estimated by DFT calculations. By increasing the number of the *confused* pyrrole rings, the total energies of the stable **NCP** isomers increase by approximately +18 kcal/mol for every *confusion* step. In the case of *normal* and singly *confused* porphyrin, the most stable isomers are the most aromatic. In the multiply *confused* porphyrins like *cis*-**N_2CP**, **N_3CP**, and **N_4CP**, on the other hand, the aromaticity was enhanced in the relatively unstable tautomers. The aromaticity and the stability of **NCP** are not simply correlated but the steric factor becomes more important than the aromatic stabilization of **NCP** in the upper *confusion* level.

Because of the involvement of the *confused* sp^3-carbon-containing pyrrole rings, the properties of the multiply *confused* porphyrin like **N_3CP** and **N_4CP** should be quite different from that of already synthesized **N_1CP** or **N_2CP**. The calculated results described here would be informative for the design of the synthetic pathway to the whole **NCP** family. Such efforts are continuously under way.

Supporting Information Available: Cartesian coordinates of the optimized structures of the isomers of **NCP** family. This material is available free of charge via the Internet at http://pubs.acs.org.

JO016051B

(19) We have examined the isoporphyrin type of **N_4CP** (**N_4CPc8'**) for the comparison with the most stable, nonaromatic isomer **N_4CPc8**.



N_4CPc8 **N_4CPc8'**

Interestingly, the relative energy and NICS value of **N_4CPc8'** are +69.257 kcal/mol and +1.3230 ppm, which indicates the disruption of π-conjugation by sp^3 *meso*-carbon destabilizes only at +3.621 kcal/mol.

(20) The relative energy (kcal/mol) and NICS (ppm) values for the oxidized structures **a**−**e** are (**a**: −9.661, +4.9361), (**b**: −7.415, +6.2178), (**c**: −5.960, +8.5820), (**d**: −5.669, +8.6553), and (**e**: 0, +19.7167), respectively. The positive NICS values of these structures represent the antiaromatic nature of the oxidized forms. Minkin, V. L.; Glukhovtsev, M. N.; Simkin, B. Y. *Aromaticity and Antiaromaticity*; Wiley: New York, 1986.