

Molecular Structures and Energetics of Corrole Isomers: A Comprehensive Local Density Functional Theoretical Study

Abhik Ghosh* and Knut Jynge

Abstract: By using geometry optimizations with local density functional theory and double- ζ plus polarization basis sets, an extensive study has been carried out on the molecular structures and stabilities of free-base and metal-complexed corrole isomers. The optimized structures of normal metallocorroles have been found to agree well with crystallographic results. For both free-base and metal-complexed derivatives, the [1.1.1] ring system is found to be the most stable. The [2.0.1]- and [2.1.0]corrole isomers are unequivocally predicted to exist as stable materials. Of these, the [2.0.1] ring system, known as isocorrole, has been recently synthesized. Various derivatives of these two ring systems lie only about 10–20 kcal mol⁻¹ above analogous derivatives of normal corrole. In general, the *cis*- and *trans*-[3.0.0]corrole derivatives are predicted to be significantly less stable than the other

corrole isomers. However, the Sc^{III} complexes of these two stereoisomeric ring systems are surprisingly stable. Direct C _{α} –C _{α} linkages between pyrrole rings are identified as a principal source of strain in the molecular structures of corrole isomers. The N₄ cores of [1.1.1]- and [2.0.1]corrole isomers are significantly smaller than the porphyrin core. Thus, these corrole isomers are predicted to have a strong preference for smaller metal ions such as Ga^{III}. The [2.1.0] core is somewhat larger, as evidenced by longer metal–nitrogen distances in [2.1.0]-metallocorroles. These differences in core

geometry account for an interesting reversal of the relative stabilities of [2.0.1]- and [2.1.0]metallocorroles with increasing ionic radius of the complexed metal ion. Analogous to porphyrin isomer chemistry, the *trans* stereoisomer of [3.0.0]corrole is found to be more stable than the *cis* stereoisomer for the free-base and for the Sc^{III} and In^{III} derivatives. For the free bases of any particular isomer, the tautomers are quite similar in energy, differing by only 2–7 kcal mol⁻¹. This, together with the presence of short, strong N–H···N hydrogen bonds, suggests that N–H tautomerization in at least some free-base corrole isomers should be considerably faster than that in porphyrins. Overall, it has been possible in most cases to establish a good correlation between the energetics trends and structural differences among molecules.

Keywords

corroles · density functional calculations · metallocorroles · porphyrinoids

1. Introduction

Recent syntheses of porphyrin and corrole isomers have opened up a new direction in the chemistry of tetrapyrroles.^[1] Conceptually, the tetrapyrrole isomers are related to classical porphyrin and corrole^[2] by various redistributions of the methine bridges linking the pyrrole rings. The new molecules are of great interest for a variety of reasons. They are stable aromatic compounds based on the [18]annulene framework, and their optical properties promise applications in such areas as electronic devices and photodynamic cancer therapy.^[1] As tetradentate ligands, porphyrin and corrole isomers furnish rigid, planar coordination environments of various shapes that differ from ideal square-planar. In this work, we have obtained a fairly comprehensive picture of the molecular structures and energetics of free-base

and metal-complexed corrole isomers from geometry optimizations performed at the local density functional (LDF) level.

Corrole isomers can be described by a system of nomenclature similar to that used for porphyrin isomers.^[2] A molecule of a corrole isomer consists of a bipyrrrole unit and two pyrrole rings bridged by various distributions of three CH units. Accordingly, a corrole isomer can be described as $[a.b.c]$, where a , b , and c are the numbers of CH units in the “interpyrrole bridges”. Permissible values of a , b , and c are limited to 0, 1, 2, and 3, with the constraint that $a + b + c = 3$. Disregarding the possibility of *cis*–*trans* isomerism and inverted structures, four corrole isomers with N₄ cores are possible: [1.1.1], [2.1.0], [2.0.1], and [3.0.0]. In view of our recent finding that both *cis* and *trans* stereoisomers of certain porphyrin isomers should be thermodynamically stable,^[3] we also investigate here the *cis* and *trans* stereoisomers of [3.0.0]corrole. Figure 1 depicts the most stable tautomers of five isomeric corroles. The chemistry of normal or [1.1.1]corrole is fairly extensive.^[2] [2.0.1]Corrole has been recently synthesized and has been named isocorrole.^[1a] Here we provide evidence that at least one other corrole isomer,

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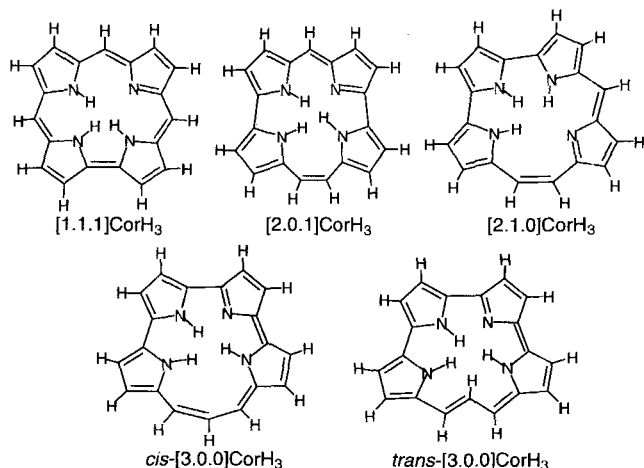


Figure 1. Stable tautomeric forms of free-base corrole isomers.

the [2.1.0] ring system, should also be isolable as a stable material.

The coordination chemistry of corroles is of considerable current interest.^[2] In contrast to porphyrins, which have two central protons in their free-base forms and four interpyrrole CH bridges, normal and isomeric corroles have three central NH groups in their free-base forms and only three interpyrrole CH units. This has several consequences. Corroles, as contracted porphyrins, have smaller core sizes than porphyrins and they are typically trianionic ligands. Recently, high-valent transition metal corroles have been isolated as stable materials,^[4] and a similarly rich coordination chemistry can also be expected for the isomeric corroles. Accordingly, we have begun to explore this area by examining the structures and stabilities of three series of isomeric metalcorroles. The three series involve three closed-shell tripositive cations of different sizes: Ga^{III}, Sc^{III}, and In^{III}.

Relatively little is known about N–H tautomerism in free-base corrole and its isomers. Accordingly, we have fully optimized the structures of all twelve N–H tautomers of the five corrole isomers. The results provide insights into hydrogen bonding and H–H repulsive interactions in the crowded cores of these macrocycles.

Overall, LDF geometry optimizations^[5] have furnished an extensive database of structures of twenty-seven free-base and metal-complexed corrole-isomers. While crystallographic data on [1.1.1]metalcorroles are used to verify the quality of our calculations, the majority of this paper is of an exploratory nature: it seeks to provide a comprehensive preview of the structural chemistry and thermochemistry of the corrole isomers ahead of the experiments. A satisfying aspect of this study is that the energetics trends can be fairly well interpreted in terms of structural differences among the different molecules.

2. Methods

Given the large number of moderately large molecules that needed to be fully optimized, we sought a good compromise between quality of the results and affordability. In recent studies, we have found that LDF theory gives excellent structures and energetics for a variety of tetrapyrroles in their ground states.^[5] Elsewhere, we have calibrated LDF results against those obtained

from gradient-corrected or nonlocal density functional theory (NLDF)^[5g] and ab-initio second-order Møller–Plesset perturbation theory (MP2).^[6] Accordingly, we chose LDF theory for the present calculations. Specifically, we have used the local exchange–correlation functional due to Hedin and von Barth,^[7] numerical double- ζ plus polarization (DNP) basis sets, and a very fine mesh for numerical integrations, as implemented in the DMol program system.^[8]

Ab-initio Hartree–Fock theory is not applicable for the present purpose: One of us, in cooperation with Almlöf et al., has previously reported that minimum-energy tetrapyrrole structures on Hartree–Fock potential energy surfaces correspond to frozen resonance forms with localized single and double bonds rather than to realistic, aromatic structures.^[6] This problem is solved by relatively simple schemes of electron correlation such as MP2 theory or DFT.^[6]

Metal-complexed corrolato ligands are in general approximately planar.^[2] In contrast, steric congestion caused by the three central hydrogen atoms in free-base corroles results in some macrocycle nonplanarity.^[9] In the crystal structure determination of free-base 8,12-diethyl-2,3,7,13,17,18-hexamethylcorrole, Harrison et al.^[9] found one of the directly linked pyrrole rings to be tilted by 8–10° relative to the rest of the molecular skeleton, which was approximately planar. This is a significant but still quite modest level of buckling. Moreover, because of the relative flatness of the potential energy surfaces associated with out-of-plane distortions, accurate conformational analyses of tetrapyrroles by means of automated geometry optimization routines are apt to be troublesome. Thus, in this initial study, we have constrained most of the molecules to a plane in the geometry optimizations. We believe that this simplification will introduce only very minor errors in optimized bond lengths and bond angles of the free bases. Nonplanar structures were considered only for the [3.0.0]corroles.

All free-base corrole structures were optimized with C_s symmetry constraints. In addition, a completely symmetry-unconstrained geometry optimization was carried out for the more stable tautomer (i.e., tautomer a) of *trans*-[3.0.0]corrole. All metal complexes of [1.1.1]-, [2.0.1]-, and *cis*-[3.0.0]corroles were optimized with C_{2v} constraints. All [2.1.0]metalcorroles were optimized with C_s symmetry constraints, with the entire molecules confined to the mirror plane. In addition, metal complexes of both *cis* and *trans* [3.0.0]corroles were optimized with C_s symmetry constraints, with the symmetry planes perpendicular to the mean planes of the molecules. These last optimizations allowed nonplanar structures to be examined.

3. Results and Discussion

Table 1 presents the calculated molecular total energies of the free-base and metal-complexed forms of different corrole isomers relative to the [1.1.1] system as zero level. The data for the

Table 1. Molecular total energies [kcal mol⁻¹] of corrole isomers relative to normal corroles. Unless otherwise indicated, all molecular point groups are C_{2v} .

Isomer	H ₃	Ga ^{III}	Sc ^{III}	In ^{III}
[1.1.1]	0.0 [a]	0.0	0.0	0.0
[2.0.1]	7.9 [a]	13.5	11.1	23.1
[2.1.0]	18.1 [a]	27.0 [a]	13.1 [a]	15.8 [a]
<i>cis</i> -[3.0.0]	50.7 [a]	63.2	33.6	56.4
<i>trans</i> -[3.0.0]	43.9 [b]	70.0 [c]	15.7 [c]	47.3 [c]

[a] Each of these molecules was assigned a C_s point group, with the entire molecule confined to the mirror plane. [b] This energy corresponds to a symmetry-unconstrained C_1 optimized geometry. [c] Each of these molecules was assigned a C_s point group, with the mirror plane perpendicular to the molecule's least-squares plane and bisecting the molecule; these molecules are thus nonplanar.

free bases refer to the most stable tautomers. The optimized molecular geometries of free-base (PH₂) and zinc(II) porphine (PZn), shown in Figure 2, are intended to facilitate a compari-

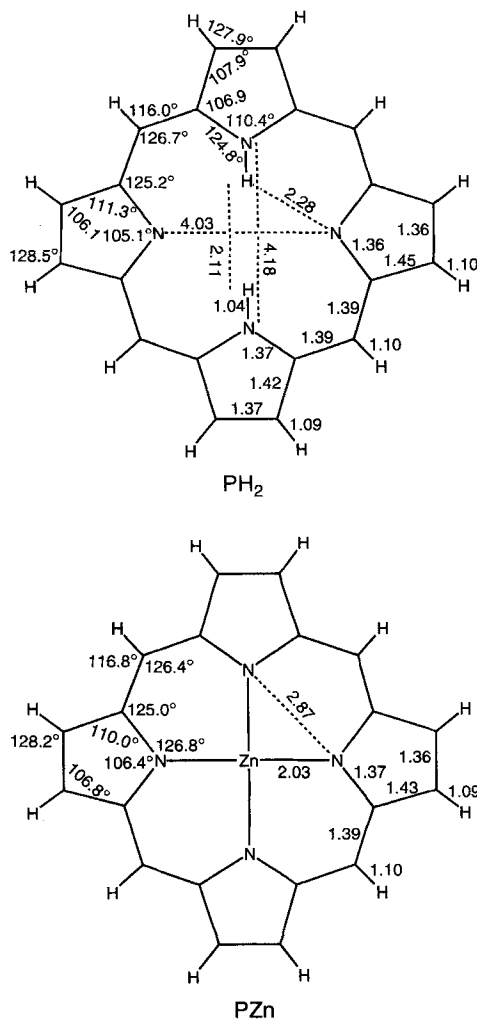


Figure 2. Optimized bond lengths [Å] and angles [°] of PH₂ (D_{2h}) and PZn (D_{4h}).

son of the structural features of porphyrin and corrole. Figures 3 and 4 present optimized molecular geometries of free-base and metal-complexed corrole isomers, respectively. Figures 2, 3, and 4 also show the abbreviations for the various molecules studied in this work. We encourage frequent cross-checking of Figures 3 and 4 and the written description, but to avoid repetition, we will refrain from continually citing Figures 3 and 4 in the remainder of the paper.

The discussion of our results is organized as follows: Section 3.1 discusses the optimized structures of normal corrole and compares it to experiment. Section 3.2 deals with the [2.0.1] and [2.1.0] isomers of corrole. Section 3.3 deals with [3.0.0]corrole and the possibility of a stereoisomer with a skeletal *trans*-CH=CH double bond. Section 3.4 focuses on the various tautomers of the free-base corrole isomers. As far as possible, the stabilities of the compounds are interpreted in terms of their molecular structures.

3.1. [1.1.1]Corroles: As Table 1 shows, normal or [1.1.1]corrole is the most stable corrole isomer. This is readily rationalized in terms of our optimized [1.1.1] structures (Figure 3 and 4). The bond lengths and bond angles of normal corrole derivatives are very similar to those in analogous porphyrins (Figure 2). Thus,

since porphyrin is one of the least strained tetrapyrroles, it becomes clear why normal corrole is also relatively strain free.

The order of bond lengths in [1.1.1]CorH₃ or [1.1.1]CorGa is largely identical to that in PH₂ or PZn, respectively: C_α-C_β (1.41–1.44 Å) > C_α-C_{meso} (1.39–1.40 Å) > C_β-C_β (1.37–1.38 Å) ≈ C_α-N (1.37–1.39 Å)^[6] (to use nomenclature similar to that in porphyrin chemistry, we will describe one-carbon interpyrrole bridges in corrole and its isomers as *meso*). In other words, as in typical porphyrins, the C_α-C_β bonds are significantly longer than the other bonds.^[6] We will see that this order of bond lengths holds somewhat less strictly for the Sc^{III} and In^{III} complexes, in which the C_α-C_{meso} bonds closely approach the C_α-C_β bonds in length. In the free-base corrole structures, note the subtle variation in the C_α-C_β bond lengths, depending on whether the nitrogen in the pyrrole ring in question is protonated or not, whereby the C_α-C_β bonds are slightly shorter in the *N*-protonated pyrrole rings. Compared to porphyrins, the main structural characteristic of corrole is the direct C_α-C_α linkage. In [1.1.1]CorH₃ or [1.1.1]CorGa, this bond (1.41–1.42 Å) is marginally longer than the C_α-C_{meso} bonds (1.39–1.40 Å).

There is also considerable similarity between the bond angles in [1.1.1]CorH₃ or [1.1.1]CorGa and those in PH₂ or PZn. The C_α-N-C_α angles in the *N*-protonated pyrrole rings in both [1.1.1]CorH₃-a and [1.1.1]CorH₃-b are significantly larger (111.5–114.3°) than those in the unprotonated pyrrole rings (106.5–107.8°). To compensate for this, the N-C_α-C_β angles in the *N*-protonated pyrrole rings in [1.1.1]CorH₃-a and [1.1.1]CorH₃-b are smaller (103.9–106.6°) than those in the *N*-unprotonated pyrrole rings (106.5–107.8°). These are features that the [1.1.1]CorH₃ tautomers share with PH₂. Even the C_α-C_{meso}-C_α angles (123.7–128.9°) in the central C₁₁N₄ rings of [1.1.1]CorH₃ or [1.1.1]CorGa are similar to those in the central C₁₂N₄ rings of PH₂ (126.5°) or PZn (126.4°) (Figure 2). The N-C_α-C_{meso} angles in [1.1.1]CorGa (119.6–125.5°) are also roughly equal to those in PZn (125.0°). The N-C_α-C_{meso} angles in the free bases, [1.1.1]CorH₃-a and [1.1.1]CorH₃-b, however, span a larger range of 116.5–129.0° owing to steric repulsion among the central nitrogen atoms and N-H···N hydrogen bonding. At the direct interpyrrole linkage, the N-C_α-C_α angles in [1.1.1]CorH₃ and [1.1.1]CorGa are in the range 110.8–116.2° and thus are unremarkable. However, the exocyclic C_α-C_α-C_β angles are large at approximately 140°. Thus, except for H···H repulsions, the direct C_α-C_α linkage is the only strained area in the [1.1.1]CorH₃ and [1.1.1]CorGa molecules.

The significant number of available metalcorrole crystal structures provides an opportunity for judging the quality of the calculated molecular geometries.^[4, 10] For this purpose, Table 2 compares the calculated geometry of [1.1.1]CorGa with the crystallographic structure of [Rh(OMC)(AsPh₃)] (OMC = octamethylcorrolato).^[10a] This choice was based on the fact that Ga^{III} and Rh^{III} have similar ionic radii. Ionic radii for four-coordinate Rh^{III} are not available, but for sixfold coordination, Ga^{III} and Rh^{III} have ionic radii of 0.76 and 0.805 Å, respectively.^[11] Table 2 compares selected geometry parameters of the computed Ga^{III} and experimental Rh^{III} [1.1.1]corrole structures.^[10a] In the crystal, the [Rh(OMC)(AsPh₃)] molecule is completely asymmetric, with metrical parameters for the two halves of the corrole macrocycle somewhat unequal.^[10a] Accordingly, Table 2 provides two columns of data for

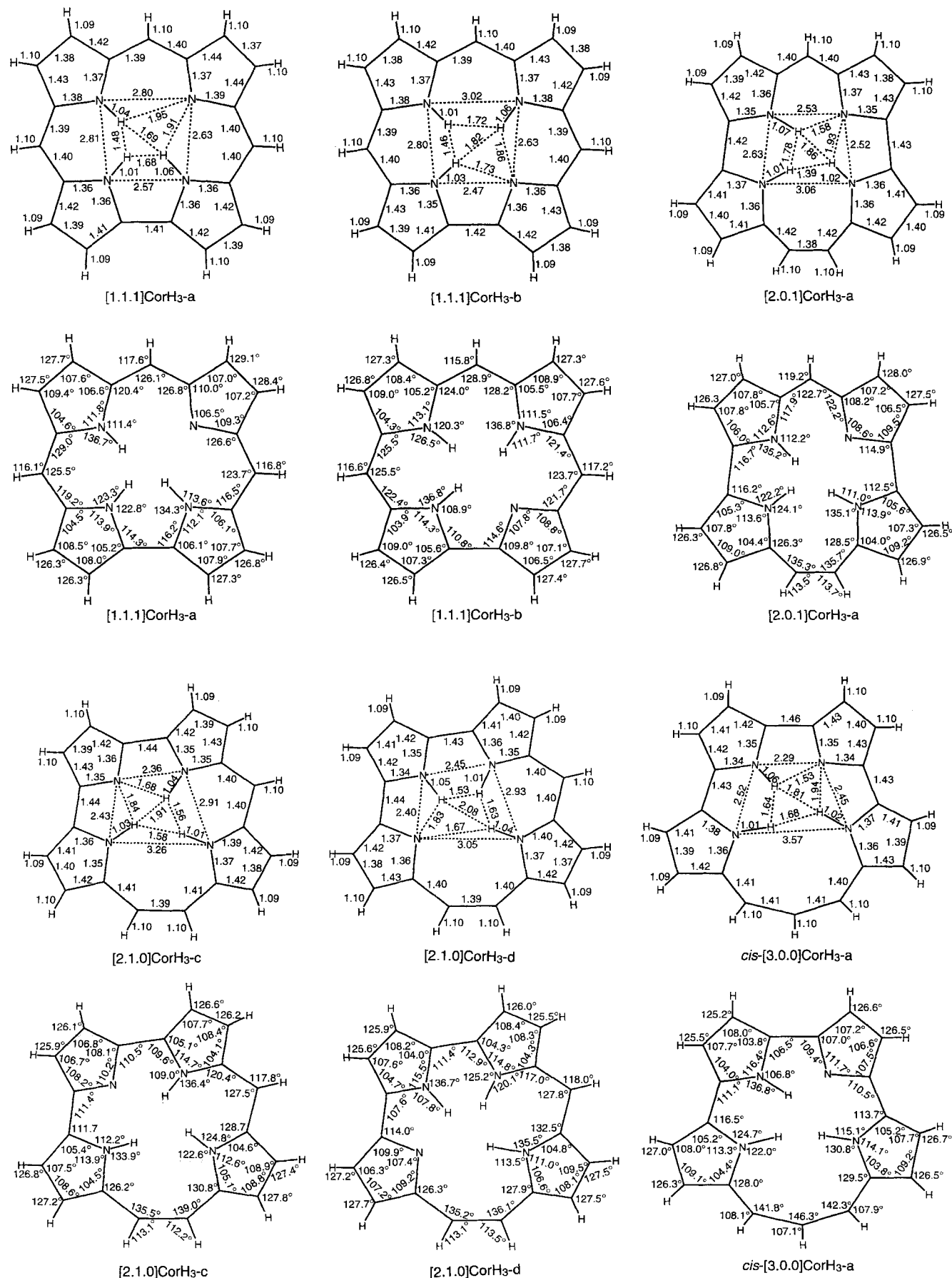
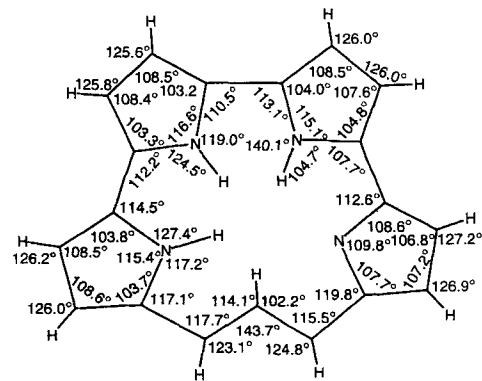
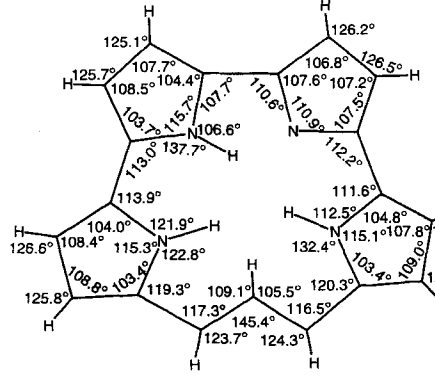
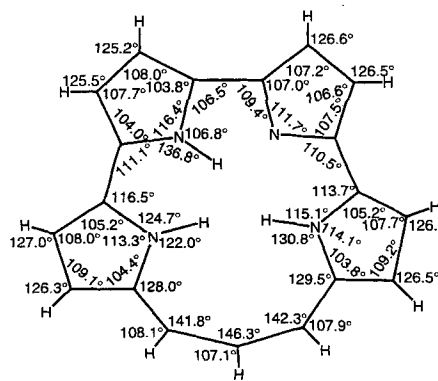
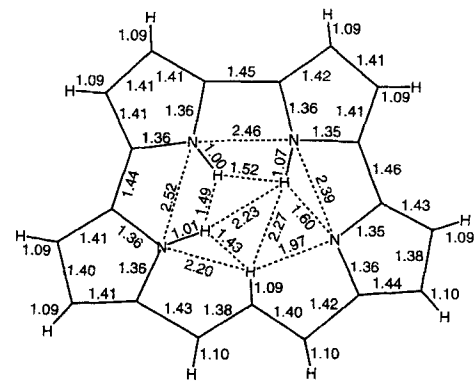
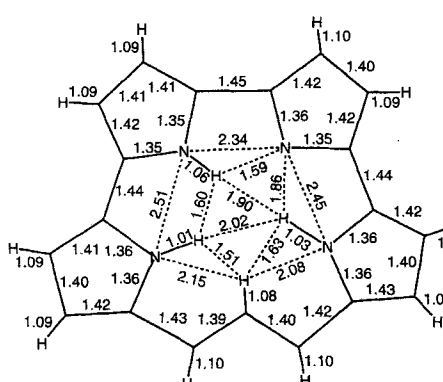
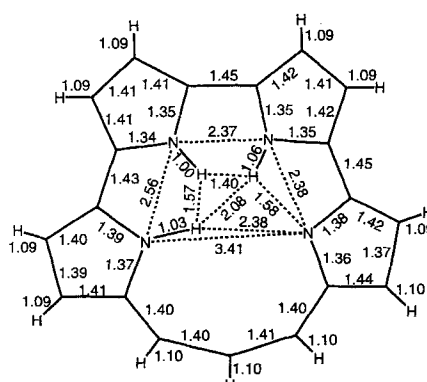
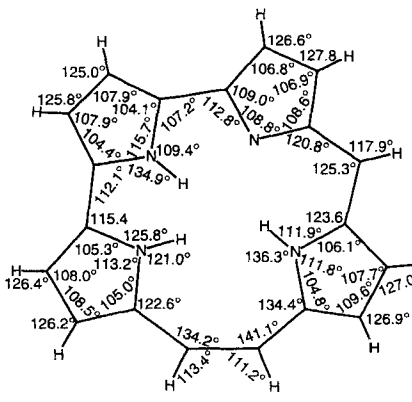
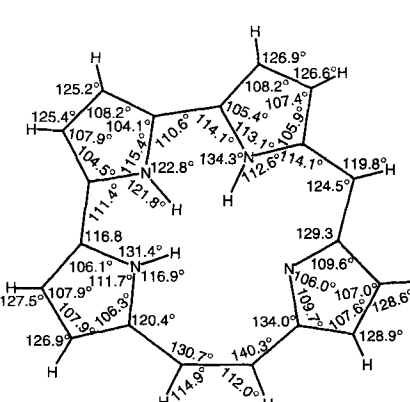
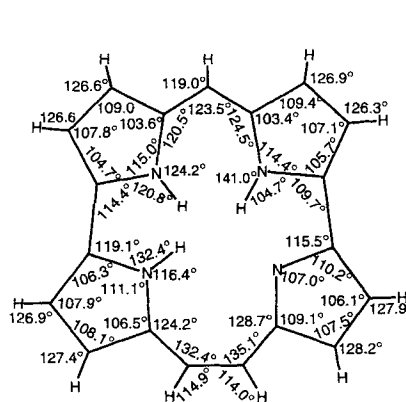
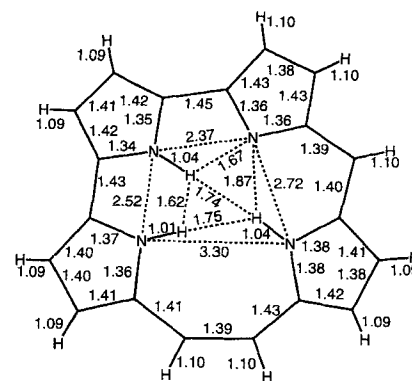
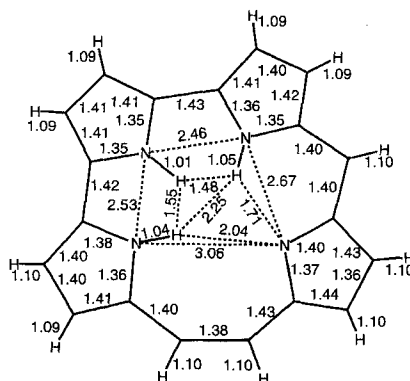
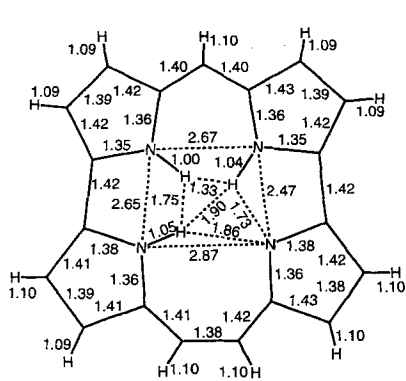
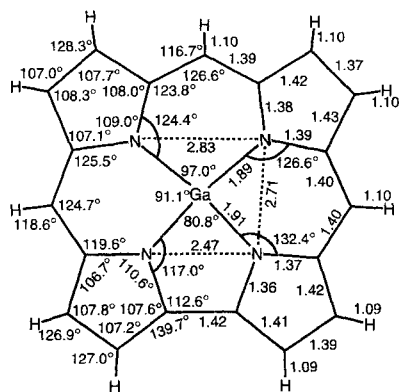
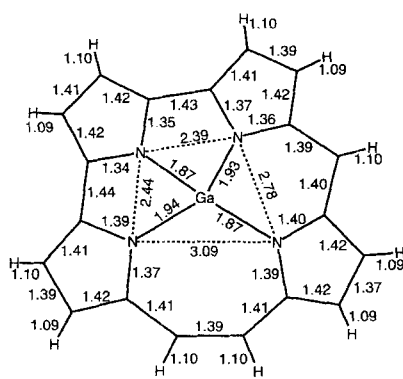


Figure 3. Internuclear distances [Å] and angles [°] in C_s symmetry-constrained optimized geometries of free-base corrole isomers.

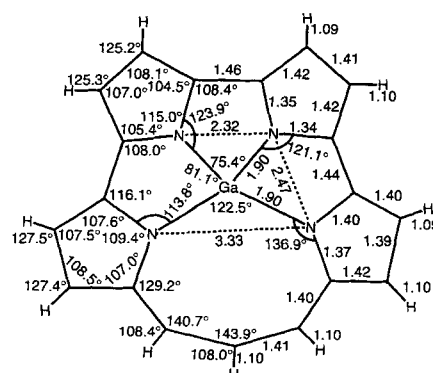




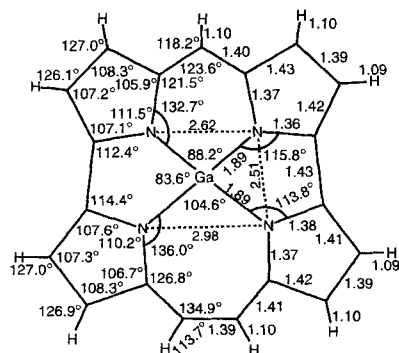
[1.1.1]CorGa



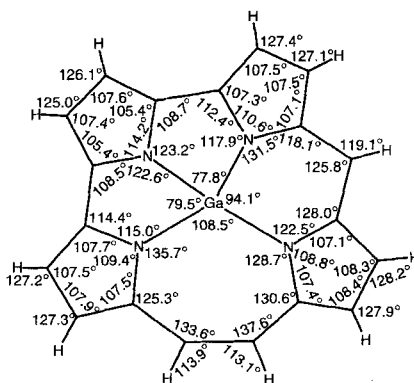
[2.1.0]CorGa



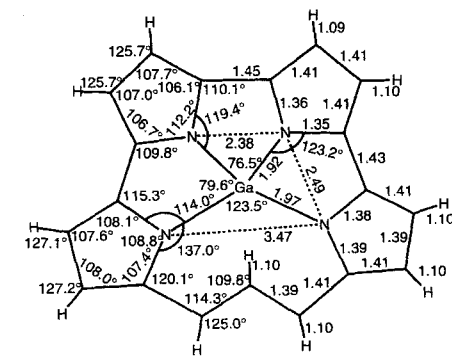
cis-[3.0.0]CorGa



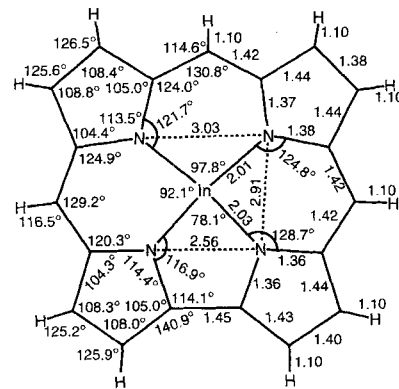
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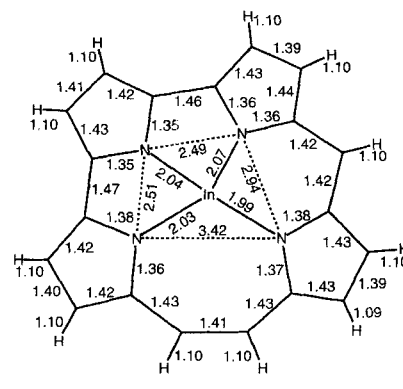
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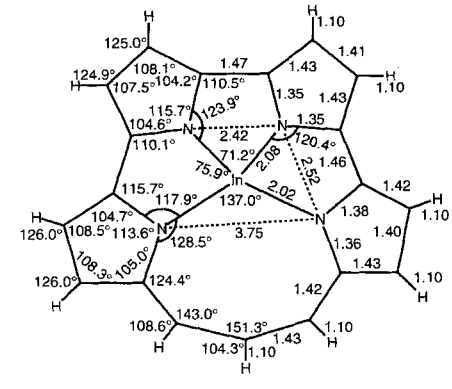
trans-[3.0.0]CorGa



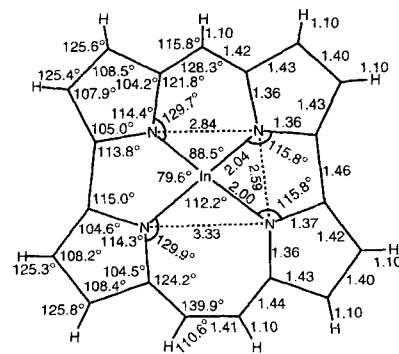
[1.1.1]CorIn



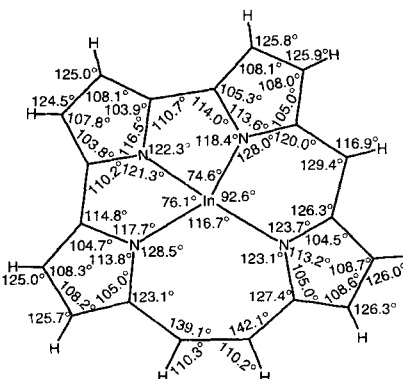
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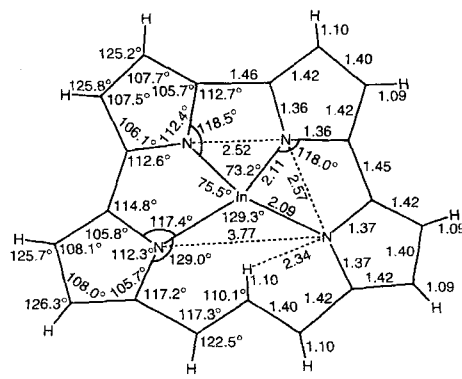
cis-[3.0.0]CorIn



[2.0.1]CorIn



[2.1.0]CorIn



trans-[3.0.0]CorIn

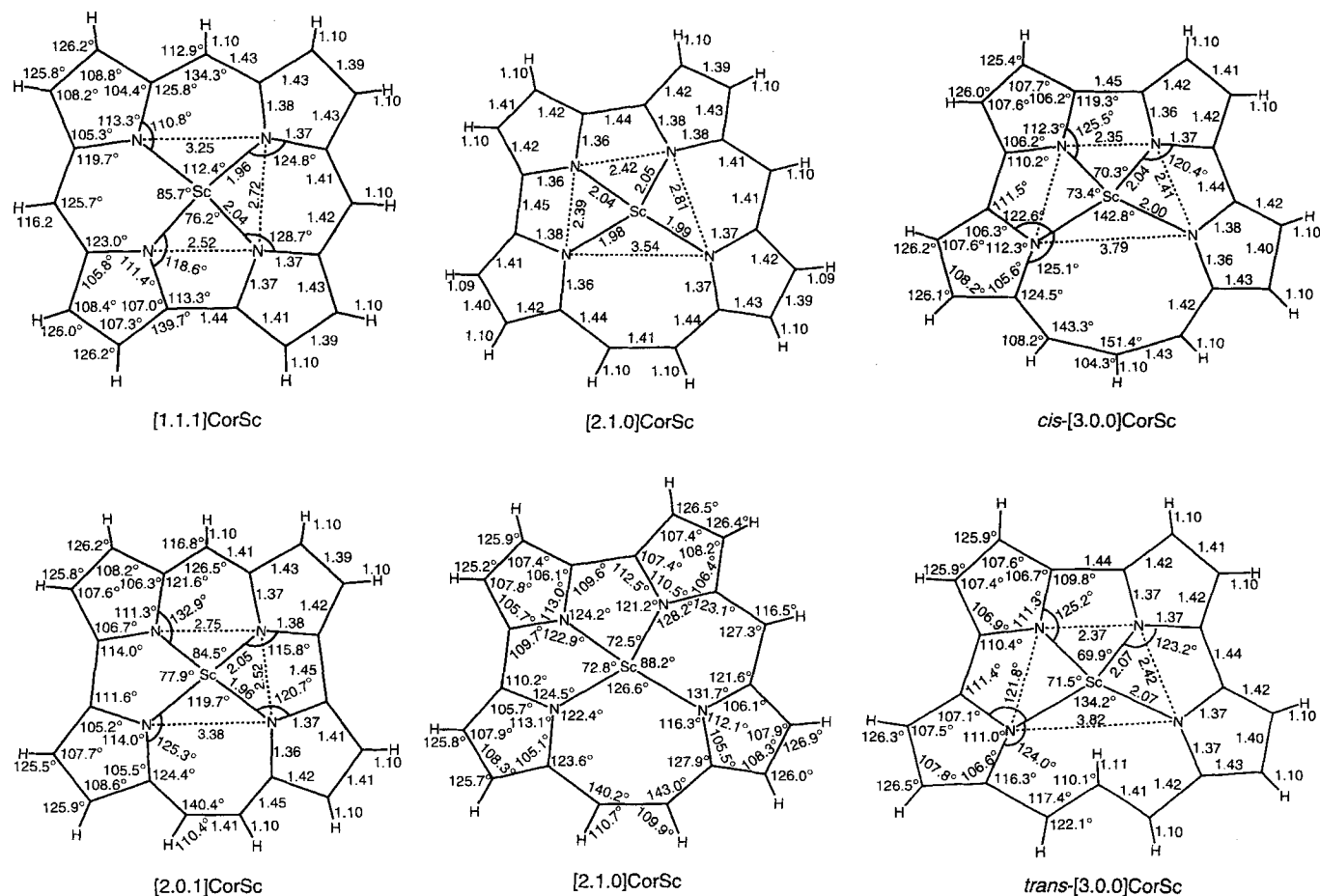


Figure 4. Optimized internuclear distances [Å] and angles [°] in metalcorrole isomers.

[Rh(OMC)(AsPh₃)], but only one for the optimized C_{2v} symmetric structure of [1.1.1]CorGa. Overall, the optimized and crystallographic data are in excellent agreement. Thus, the comparison presented in Table 2 validates LDF theory as a good structure determination tool for tetrapyrrolic molecules. This has also been found in some of our other work.^[5, 6]

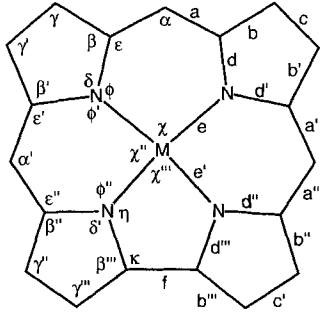
We now proceed to examine the geometry of the central metal-binding region of [1.1.1]corrole in some detail. As expected, [1.1.1]corrole has a smaller core than porphyrin. For instance, in PZn, adjacent pyrrole nitrogen atoms are separated by 2.87 Å, and opposite pyrrole nitrogen atoms by 4.06 Å (Figure 2). In [1.1.1]CorGa, adjacent pyrrole nitrogen atoms are separated by 2.47, 2.71, or 2.83 Å, while opposite pyrrole nitrogen atoms are separated by only 3.78 Å. Similarly, as expected, the [1.1.1]CorH₃ tautomers have smaller cores and shorter separations between adjacent nitrogen atoms than PH₂. The shortest separation (ca. 2.5 Å) is between the nitrogen atoms of the two directly linked pyrrole rings, as is observed experimentally.^[4, 9, 10] Thus, although metal–nitrogen bond lengths shorter than or equal to 1.90 Å are uncommon for metalloporphyrins, the optimized Ga–N bond lengths of 1.89 and 1.91 Å in [1.1.1]CorGa are typical for metalcorroles (see the data on [Rh(OMC)(AsPh₃)]^[10a] in Table 2). In this connection, it may be worth recalling Vogel's recent finding that the corrolato ligand stabilizes high-valent transition metals.^[5] This special property of corroles is not analyzed in this paper. Clearly, this property of corrole is intimately linked to its being a trianionic lig-

and. What is relevant here is that the small core size of corrole is ideally suited for coordination of small, high-valent first-row transition metal ions. Thus, the average Fe^{IV}–N bond lengths in [Fe(OEC)]₂O (1.904 Å), [Fe(OEC)Cl] (1.906 Å), [Fe(OEC)Ph] (1.871 Å), and [Fe(OEC)py] (1.893 Å) [OEC = octaethylcorrole, py = pyridine] are all very similar to the optimized Ga–N bond lengths (1.89 and 1.91 Å) in [1.1.1]CorGa.^[5]

The optimized structures of [1.1.1]CorSc and [1.1.1]CorIn illustrate the effects of core expansion in corroles. Although core-expansion effects are well-characterized for porphyrins,^[12] this aspect of metalcorrole chemistry remains essentially unexplored experimentally. The ionic radii of six-coordinate Sc^{III} and In^{III} are 0.885 and 0.94 Å, respectively, and are comparable to those of six-coordinate zinc (0.88 Å). The ionic radius of four-coordinate Sc^{III} is unavailable, but the radii of four-coordinate In^{III} and Zn^{II} (0.76 and 0.74 Å) are very similar.

Compared to a mean Ga–N bond length of 1.90 Å for [1.1.1]CorGa, the metal–nitrogen bond lengths in [1.1.1]CorSc (1.96 and 2.04 Å) and [1.1.1]CorIn (2.01 and 2.03 Å) are considerably longer and lie in the range typical for metalloporphyrins. The longer metal–nitrogen distances in [1.1.1]CorSc and [1.1.1]CorIn imply that the mean distance between nearest-neighbor nitrogen atoms in either of these molecules is also significantly larger than that in [1.1.1]CorGa. The Sc–N bond lengths in [1.1.1]CorSc have two rather different values (1.96 and 2.04 Å), which differ considerably more than the metal–nitrogen bond lengths in [1.1.1]CorGa and [1.1.1]CorIn. Also, the

Table 2. Comparison of optimized internuclear distances [\AA] and angles [$^\circ$] in the corrole rings in the X-ray crystal structure of $[\text{Rh}(\text{OMC})(\text{AsPh}_3)]$ and the C_{2v} optimized geometry of $[1.1.1]\text{CorGa}$.



	$[\text{Rh}(\text{OMC})(\text{AsPh}_3)]$	$[1.1.1]\text{CorGa}$		$[\text{Rh}(\text{OMC})(\text{AsPh}_3)]$	$[1.1.1]\text{CorGa}$
<i>a</i>	1.382	1.394	α	130.8	126.6
<i>a'</i>	1.398	1.389	α'	126.0	128.1
<i>a''</i>	1.398	1.364	β	106.9	108.2
<i>b</i>	1.433	1.424	β'	106.5	105.4
<i>b'</i>	1.434	1.464	β''	106.2	105.5
<i>b''</i>	1.462	1.445	β'''	105.9	106.0
<i>b'''</i>	1.431	1.459	γ	108.0	109.6
<i>c</i>	1.365	1.331	γ'	108.8	108.5
<i>c'</i>	1.349	1.352	γ''	107.1	109.2
<i>d</i>	1.388	1.379	γ'''	109.5	107.6
<i>d'</i>	1.383	1.430	δ	109.9	108.2
<i>d''</i>	1.361	1.376	δ'	111.3	111.7
<i>d'''</i>	1.373	1.368	ϵ	122.8	119.7
<i>e</i>	1.960	1.956	ϵ'	124.5	124.1
<i>e'</i>	1.930	1.931	ϵ''	121.6	120.8
<i>f</i>	1.438	1.419	κ	110.9	113.0
			ϕ	124.4	127.7
			ϕ'	125.3	124.1
			ϕ''	129.8	130.3
			η	118.9	117.8
			χ	93.3	97.0
			χ'	91.4	92.1
			χ''	79.2	80.8

shapes of the expanded N_4 cores of $[1.1.1]\text{CorSc}$ and $[1.1.1]\text{CorIn}$ differ considerably. For instance, the nitrogen–metal–nitrogen angles are rather different in the two compounds. This suggests that, like the central $C_{12}N_4$ ring of porphyrins,^[5d] the central $C_{11}N_4$ ring of corroles is quite soft toward bond angle deformation. Other structural effects of core expansion in $[1.1.1]\text{CorSc}$ and $[1.1.1]\text{CorIn}$ include the following: The C_2-N-C_2 angles are wider in $[1.1.1]\text{CorSc}$ ($111.4, 113.3^\circ$) and $[1.1.1]\text{CorIn}$ ($113.5, 114.4^\circ$) than in $[1.1.1]\text{CorGa}$ ($109.0, 110.6^\circ$). The $C_\alpha-C_{meso}$ bonds are also slightly longer in $[1.1.1]\text{CorSc}$ and $[1.1.1]\text{CorIn}$ than in $[1.1.1]\text{CorGa}$. The direct $C_\alpha-C_\alpha$ linkage is stretched in $[1.1.1]\text{CorSc}$ (1.44\AA) and $[1.1.1]\text{CorIn}$ (1.45\AA) compared to that in $[1.1.1]\text{CorGa}$ (1.42\AA). Overall, these structural data suggest that the $[1.1.1]$ corrole ligand has a strong thermodynamic preference for binding smaller metal ions of approximately the size of Ga^{III} rather than Sc^{III} or In^{III} .

Finally, a comment is in order on the shape and local symmetry^[13] of the N_4 core of normal corrole. As the C_{2v} symmetry of $[1.1.1]$ metallocorroles implies, the central N_4 core has a trapezoidal shape with C_{2v} local symmetry. Also, the N_4 core of $[1.1.1]$ corrole is rather close to square-planar. This minimizes nitrogen–metal–nitrogen bond-angle strain in $[1.1.1]$ metallocorroles relative to, for instance, $[2.1.0]$ and $[3.0.0]$ metallocorroles.

3.2. [2.0.1]- and [2.1.0]Corroles: Table 1 shows that the $[2.0.1]$ and $[2.1.0]$ ring systems are of comparable stability. This is not surprising since both isomers have one one-carbon bridge and one two-carbon bridge, which are simply distributed differently among the pyrrole rings. Both isomers are thermodynamically less stable than analogous normal corrole derivatives by $10\text{--}20 \text{ kcal mol}^{-1}$. These are rather small differences and it seems safe to predict on the basis of these calculations that both isomers should be isolable as stable materials. As mentioned before, $[2.0.1]$ corrole derivatives have already been synthesized.^[1a] Both the $[2.0.1]$ and $[2.1.0]$ systems are generally more stable than the $[3.0.0]$ isomers.

Not surprisingly, many of the structural features of $[1.1.1]$ corrole derivatives, such as most of the geometry parameters of the pyrrole rings, are essentially unchanged in the corrole isomers. What, then, are the features that make these two isomers less stable than normal corrole? While a variety of factors are at play, the main one seems to be that the two isomers each have two bipyrrrole units or two direct $C_\alpha-C_\alpha$ linkages, compared to only one in the $[1.1.1]$ system. As mentioned before, these linkages, as part of the central $C_{11}N_4$ rings of corrole isomers, are a source of strain. In terms of their bond lengths, these $C_\alpha-C_\alpha$ bonds are all rather elongated, being $1.42\text{--}1.45 \text{\AA}$ in the free-base and Ga^{III} derivatives and even longer ($1.44\text{--}1.47 \text{\AA}$) in the Sc^{III} and In^{III} complexes. The very wide exocyclic $C_\alpha-C_\alpha-C_\beta$ angles ($\geq 140^\circ$) are also a source of strain.

The energetics results for $[2.0.1]$ - and $[2.1.0]$ metallocorroles exhibit an interesting trend: the relative stability of the two ring systems undergoes a reversal as the ionic radius of the complexed metal ion increases from Ga^{III} to In^{III} , with the two corrole isomers being essentially equienergetic for their Sc^{III} complexes. An explanation for this can be found from an examination of the optimized geometries. The $[2.0.1]$ ring system has a significantly smaller core than the $[2.1.0]$ system. More precisely, the mean separation among nearest-neighbor nitrogen atoms is significantly smaller in various $[2.0.1]$ free-base tautomers than in $[2.1.0]$ tautomers. The smaller core of either tautomer of $[2.0.1]\text{CorH}_3$ is optimally suited for coordination to the relatively small Ga^{III} ion. All Ga-N bond lengths in $[2.0.1]\text{CorGa}$ are 1.89\AA , that is, about the same as those in $[1.1.1]\text{CorGa}$. In contrast, two Ga-N bonds in $[2.1.0]\text{CorGa}$ are as long as $1.93\text{--}1.94 \text{\AA}$, and these elongated bonds appear to be a major factor contributing to the thermodynamic instability of $[2.1.0]\text{CorGa}$ relative to $[2.0.1]\text{CorGa}$. The opposite scenario holds for the largest ion, In^{III} , which is better coordinated by the larger $[2.1.0]$ core than by the $[2.0.1]$ core. Thus, all but one In-N bonds in $[2.1.0]\text{CorIn}$ are 2.03\AA or longer, whereas two In-N bonds, at 2.00\AA , are relatively compressed in $[2.0.1]\text{CorIn}$. The Sc^{III} ion appears to represent the crossover point between the two scenarios, with both the $[2.0.1]$ and $[2.1.0]$ complexes being of similar stability. Overall, for each of the three metal ions we have considered, the average metal–nitrogen bond length is significantly shorter in the $[2.0.1]$ complexes than in the $[2.1.0]$ complexes.

In view of the above discussion, caution must be exercised in comparing the thermodynamic stabilities of metallotetrapyrrole isomers solely on the basis of the coordination geometry of the metal center. This is successful for $[2.0.1]$ - and $[2.1.0]$ corrole complexes because most of their skeletal structural features are

identical, but simply distributed differently. Thus, there is no great mystery in the apparent paradox that [1.1.1]corrole, which has a relatively small core size, forms the most stable complexes for all three metal ions, Ga^{III}, Sc^{III}, and In^{III}. The [1.1.1]corrole ring system does not have the same degree of skeletal strain as the other isomers that have multiple direct C_α–C_β linkages.

Finally, the molecular total energies of the two most stable free-base tautomers, [2.0.1]CorH₃-a and [2.1.0]CorH₃-a, differ by almost 10 kcal mol⁻¹. It is not yet clear how this energy difference can be divided into contributions from differences in skeletal geometry, H···H repulsions, and NH···N hydrogen-bonding interactions.

3.3. [3.0.0]Corroles: Recently, LDF calculations similar to the present ones predicted that [3.0.1.0] and [3.1.0.0] porphyrin isomers should be thermodynamically stable. The three-carbon interpyrrole bridges in these compounds were predicted to accommodate a *trans*-CH=CH bond at little or no energy cost.^[3] These findings prompted us to study both *cis* and *trans* [3.0.0]corroles.

The energies listed in Table 1 refer to perfectly planar *cis*-[3.0.0] structures and nonplanar C₁ or C_s *trans*-[3.0.0] structures. These symmetry constraints were based on the finding that the *cis*-[3.0.0] compounds have relatively little tendency to buckle.

With the exception of *trans*-[3.0.0]CorSc (discussed below), all the [3.0.0]corrole derivatives have substantially higher energies than analogous [1.1.1], [2.0.1], or [2.1.0] derivatives. The reasons for this are rather diverse and are discussed in the following.

Bond-angle strain is rather severe in all the *cis*-[3.0.0] structures, with nine very wide C–C–C angles of about 140° or greater. Six of these angles are exocyclic C_α–C_α–C_β angles. The other three are endocyclic, one subtended at each methine unit in the (CH)₃ interpyrrole bridge.

The especially high energies of both *cis*- and *trans*-[3.0.0]CorGa are partially attributable to the mismatch between the small ionic radius of Ga^{III} and the large core sizes of both stereoisomers of [3.0.0]corrole.

Bond-angle strain is significantly less severe in *trans*-[3.0.0] structures than in the *cis* ones. The former have only about seven very wide C–C–C angles per molecule, six of these being exocyclic C_α–C_α–C_β angles and the seventh being the exocyclic angle at the central methine unit of the (CH)₃ bridge. A significant factor contributing to the high energy of *trans*-[3.0.0]CorIn appears to be steric interactions between the large In^{III} ion and the inward-pointing methine hydrogen atom.

In addition to bond-angle strain, a destabilizing factor unique to the tautomers of *trans*-[3.0.0]CorH₃ is that they have four hydrogen atoms, including the inner methine hydrogen, in the central cavity of the macrocycle. This results in as many as five H···H repulsive interactions.

A curious result that warrants discussion is the low energy of *trans*-[3.0.0]CorSc. The size of the Sc^{III} ion appears to be such that both the Sc–N bond lengths are relatively unstrained (2.07 Å) and the repulsion between the Sc^{III} ion and inward-pointing methine hydrogen is not prohibitive. Note that only one of these criteria applies to *trans*-[3.0.0]CorGa or *trans*-[3.0.0]CorIn. The orientation of the inward-pointing C–H bond in *trans*-[3.0.0]CorSc can be seen from the ball-and-stick dia-

grams shown in Figure 5. This C–H bond makes an angle of 34.9° with the least-squares plane of the carbon and nitrogen atoms of the four pyrrole rings, that is, the planar portion of the molecule. The methine groups on either side of the inward-pointing C–H bond are also significantly tilted.

The plane of the three carbon atoms of the (CH)₃ bridge in *trans*-[3.0.0]CorSc makes an angle of 30.4° with the planar part of the molecule. The Sc^{III} ion and the central methine hydrogen are 0.47 Å above and 0.28 Å below the planar section of the molecule, respectively. These deviations from planarity are substantial but probably not severe enough to completely disrupt the aromaticity of the molecule.

It is interesting to speculate what these results imply for the isolability of *cis*- or *trans*-[3.0.0]corrole derivatives. Based on an examination of the stabilities of the majority of [3.0.0]corrole molecules we have studied, one would make a bleak prognosis. Most of the [3.0.0]corrole derivatives examined here appear to be very unstable thermodynamically. If isolated, they would probably be considerably more vulnerable to decomposition than derivatives of the other corrole isomers. However, since *trans*-[3.0.0]CorSc appears to be surprisingly stable, a synthetic route involving a metal-ion template may ultimately provide access to the *trans*-[3.0.0]corrole ring system. Such a synthetic route would avoid some of the steric repulsion among the four central hydrogen atoms in the free-base *trans*-[3.0.0]CorH₃ tautomers. Finally, in analogy to porphyrin isomer chemistry,^[5] the *trans* stereoisomers of certain [3.0.0]-corrole derivatives are more stable than the corresponding *cis* stereoisomers.

3.4. Free-Base Tautomers: X-ray crystallography provides only a rather inaccurate picture of the positions of hydrogen atoms. Quantum chemical approaches have an advantage in this regard and can provide a detailed description of the positions and dynamics of hydrogen atoms in molecules, information which may be difficult to obtain experimentally. Theoretical approaches are therefore ideally suited for studies of tautomeric phenomena. This work is the first major study of the free-base tautomers of normal and isomeric corroles.

Table 3 shows that all tautomers of any particular corrole isomer are of comparable energy. The maximum energy difference between the tautomers of any particular corrole isomer is about 7 kcal mol⁻¹. This is intuitively reasonable since, for a given corrole isomer, the central cavities of all the tautomers have approximately the same repulsive and attractive interactions. For instance, for tautomers of [1.1.1]- and [2.0.1]CorH₃, there are three H···H repulsions and two N–H···N hydrogen-bonding interactions per molecule. Both tautomers of *trans*-[3.0.0]CorH₃ have five H···H repulsions and two N–H···N hydrogen-bonding interactions.

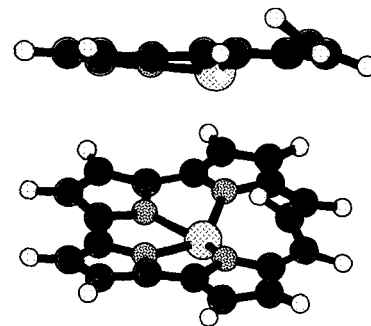


Figure 5. Two views of a ball-and-stick model of *trans*-[3.0.0]CorSc. The inward-pointing C–H bond makes an angle of about 45° with the mean plane of the rest of the molecule (top).

Table 3. Molecular total energies [kcal mol⁻¹] of C_s symmetry-constrained optimized geometries of free-base tautomers (a–d) of corrole isomers relative to [1.1.1]CorH₃-a as zero level. The nomenclature of the tautomers follows that of Figure 3.

Isomer	a	b	c	d
[1.1.1]	0.00	2.45		
[2.0.1]	7.88	12.37		
[2.1.0]	18.08	20.80	23.27	24.66
<i>cis</i> -[3.0.0]	50.65	55.45		
<i>trans</i> -[3.0.0]	47.67	53.78		

Can one predict the relative energetics of the tautomers by merely examining the optimized geometries? Given the small energy differences between the tautomers of any particular corrole isomer, this is not easy in all cases. Moreover, we have made the simplifying assumption of perfectly planar structures for free-base corroles. Nevertheless, it is worthwhile to at least attempt to answer the question posed above.

For normal corrole, the small energy difference of 2.45 kcal mol⁻¹ between the two tautomers does not seem to be attributable to any particular structural difference. Indeed, it is unsafe to make a definitive prediction regarding which free-base [1.1.1]corrole tautomer is more stable on the basis of these calculations. In the crystallographic study by Harrison et al.,^[9] the electron density was fitted with a "three-quarter" hydrogen attached to each nitrogen. In other words, our calculated result that both tautomers of corrole are approximately equienergetic is supported by experimental data.

In contrast, for [2.0.1]CorH₃, the stability of tautomer a relative to tautomer b seems to be more or less safely attributable to the presence of a short strong hydrogen bond (1.58 Å) in the former. Each of the four tautomers of [2.1.0]CorH₃ has a relatively short hydrogen bond of about 1.7 Å, and a simple structure-based prediction of the most stable tautomer does not seem to be feasible.

Both tautomers of *cis*-[3.0.0]CorH₃ have one short N–H···N hydrogen-bonding contact of about 1.55 Å. However, only *cis*-[3.0.0]CorH₃-a has a second N–H···N contact of moderate length (1.94 Å), the second N–H···N contact being as long as 2.38 Å in tautomer b. This may account for the stability of tautomer a relative to tautomer b. On a different note, one should observe that both tautomers of *cis*-[3.0.0]CorH₃ have high energies relative to [1.1.1]CorH₃-a and, accordingly, it is uncertain whether they can be synthesized.

Both tautomers of *trans*-[3.0.0]CorH₃ have a short N–H···N hydrogen-bonding contact of about 1.60 Å. Once again, the energy difference of about 6 kcal mol⁻¹ between the two tautomers does not seem to be attributable to any one specific structural difference. For the more stable tautomer (tautomer a), a completely symmetry-unconstrained geometry optimization lowered the molecular total energy to 43.9 kcal mol⁻¹ above [1.1.1]CorH₃-a (Table 1), which is about 4 kcal mol⁻¹ lower than the energy of the C_s symmetry-constrained optimized geometry of *trans*-[3.0.0]CorH₃-a (Table 3). Thus, the existence of *trans*-[3.0.0]CorH₃ as a stable substance is doubtful.

The optimized free-base structures offer a very detailed picture of N–H···N hydrogen bonding geometries in the central cavities of the macrocycles. Structural features worth noting in this regard include many short and moderate hydrogen bonding

contacts ranging from as short as 1.58 Å in [2.0.1]CorH₃-a to 2.04 Å in [2.1.0]CorH₃-a. These contacts are appreciably shorter than the N–H···N contact of 2.27 Å that is found in the optimized geometry of PH₂ (Figure 2). Of course, the bifurcated hydrogen bonding that is found in PH₂, in which each N–H proton is symmetrically hydrogen bonded to the two nearest unprotonated nitrogen atoms, has no analogue in corrole chemistry. Another noteworthy feature of the central regions of the free-base macrocycles is the considerable inequality of the H–N–C_α angles at the hydrogen-bonded N–H centers. For example, the H–N–C_α angles at one of the N–H groups of [1.1.1]CorH₃-a are 136.7 and 111.4°, and thus differ by about 25°. This is a consequence of both N–H···N hydrogen bonding and H···H repulsion in the interior of the macrocycle.

Finally, although we have not addressed the dynamics of N–H tautomerism in corroles here, some pertinent comments can be made on the basis of the calculated results. All the tautomeric structures can be reasonably expected to be minima on ground-state potential energy surfaces. Short hydrogen-bonding contacts and the very similar energies of the different tautomers suggests that N–H tautomerism should be extremely facile in all free-base corrole isomers. To put the energetics of the tautomers of corrole isomers in perspective, we recall that the two tautomers of PH₂, which have the central hydrogen atoms on opposite and adjacent pyrrole nitrogen atoms, differ in energy by about 7–8 kcal mol⁻¹.^[5d] For common porphyrins under normal conditions (i.e., not matrix isolated or the like), the *cis* tautomer is only a fleeting intermediate, which does not exist in detectable amounts. Thus, for any corrole isomer, the tautomers differ less in energy than do the PH₂ tautomers. This, together with the short N–H···N hydrogen bonds, suggests that NH tautomerism in free-base corrole isomers should be even faster than in PH₂. However, it is more difficult to predict whether multiple tautomers should exist in observable quantities for any corrole isomer. Based on the energetics data in Table 3, the chances for this seem to be best for the free-base [1.1.1] and [2.1.0]corrole isomers.

4. Summary and Conclusions

By using geometry optimizations with local density functional theory and double- ζ plus polarization basis sets, an extensive study has been carried out on the molecular structures and stabilities of free-base and metal-complexed corrole isomers. For each isomer, all possible N–H tautomers and Ga^{III}, Sc^{III}, and In^{III} complexes have been studied.

The optimized structures of normal metalcorroles have been found to agree well with crystallographic results. These points of agreement between theory and experiment lend credence to the remaining calculated results, which seek to investigate areas of corrole isomer chemistry that remain unexplored experimentally.

The [2.0.1]- and [2.1.0]corrole isomers are unequivocally predicted to exist as stable materials. Various derivatives of these ring systems lie about 10–20 kcal mol⁻¹ above analogous derivatives of normal corrole.

The N₄ cores of [1.1.1]- and [2.0.1]corrole isomers are significantly smaller than the porphyrin core. Thus, these corrole iso-

mers are predicted to have a strong preference for smaller metal ions such as Ga^{III}. The [2.1.0] core is somewhat larger, as evidenced by longer metal–nitrogen distances in [2.1.0]-metallocorroles. These differences in core geometries account for an interesting reversal of the relative stabilities of [2.0.1]- and [2.1.0]metallocorroles with increasing ionic radius of the complexed metal ion.

Direct C_α–C_α linkages between pyrrole rings are identified as a principal source of strain in the molecular structures of corrole isomers, and the structural features of these strained zones have been examined in detail.

Both *cis*- and *trans*-[3.0.0]corrole derivatives are predicted to be significantly more unstable than other corrole isomers. Both stereoisomers of [3.0.0]corrole are most stable for their Sc^{III} complexes and the surprising stability of *trans*-[3.0.0]CorSc is examined in detail. The possible synthesis and isolation of *cis*- and *trans*-[3.0.0]corrole derivatives remains an intriguing goal for the synthetic chemist.

In analogy to porphyrin isomer chemistry, the *trans* stereoisomer has been found to be more stable than the *cis* one for the free-base, Sc^{III}, and In^{III} derivatives of [3.0.0]corrole. This possibility has not been considered previously by experimental chemists.

Extensive structural data have been obtained for the N–H tautomers of corrole isomers. For any particular isomer, the tautomers are quite similar in energy, differing by only 2–7 kcal mol⁻¹. This, coupled with the presence of short strong N–H···N hydrogen bonds, suggests that N–H tautomerism in at least some free-base corrole isomers should be considerably faster than that in porphyrins.

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