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Structures and Properties of Closed Ladderanes $C_{24}H_{24}$, Laddersilanes $Si_{24}H_{24}$, and Their Nitrogen-Containing Isoelectronic Equivalents: A G3(MP2) Investigation

Xin Wang[†] **and Kai-Chung Lau***

Department of Biology and Chemistry, City University of Hong Kong, Kowloon, Hong Kong

Wai-Kee Li*

Department of Chemistry, The Chinese University of Hong Kong, Shatin, N.T., Hong Kong

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An investigation has been undertaken to study the large closed ladderanes $C_{24}H_{24}$ and their analogs. Thirteen isoelectronic species have been identified as local minima on the MP2(FU)/6-31G(d) potential energy surface, including three $C_{24}H_{24}$, four $Si_{24}H_{24}$, two N_{24}, and four $C_{24-x}H_{24-x}N_x$ ($x = 6, 8, 12$) isomers. Of these 13 species, 11 are reported for the first time. Their structures, stabilities, HOMO−LUMO gaps, and G3(MP2) heats of formations are computationally obtained and discussed. These results are also compared with those of the related species already available in the literature. Our results show that molecules with 12-membered rings are highly energetic and much less stable than their corresponding isomers that do not have such rings. Isomer **II** of $Si_{24}H_{24}$ with anticonformations has a very small HOMO−LUMO gap of 2.56 eV, approaching the semiconductor range. Therefore, it is a candidate of potential semiconductor materials. Meanwhile, the N_{24} and other nitrogen-containing species are candidates for high-energy density materials. Our results also indicate that $C_{18}H_{18}N_6$ and $C_{16}H_{16}N_8$ may be good hexa- and octadentate ligands for metal cations.

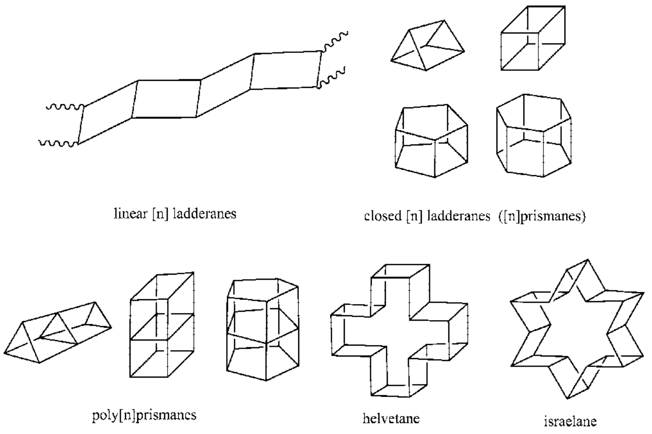
1. Introduction

Chemists have always been interested in novel compounds with structures containing tetracoordinated carbon atoms in nonstandard stereochemical environments.[1−4] As a family of interesting organic molecules, ladderanes have received extensive attention because of their novel structures.[5−11] For example, scientists have found that poly[*n*]prismanes or columnar closed ladderanes possess stable cage structures with half-planar or bisphenoidal (SF_4-like) carbon centers.[7]

Ladderanes contain two or more fused cyclobutane rings (Scheme 1), and their name is a portmanteau that comes from the fact that their serial cyclobutane rings look like a ladder and the bonds are all single bonds, just like those in alkanes. The geometry of ladderanes is highly strained because their carbon skeleton cannot extend to the ideal angles. Many ladderanes of various lengths have been synthesized, and ladderane lipids have been found in living organisms.[12,13] Specifically, there are two types of ladderanes: linear ladderanes and closed ladderanes, as shown in Scheme 1. Linear ladderanes have simpler structures and can fold back on themselves. If we fuse the last cyclobutane ring of a linear ladderane to the first one, then a closed ladderane is resulted. Because closed ladderanes contain prismatic structures, they are also called [*n*]-prismanes.[7,10,11]

Ladderanes are of fundamental interest to chemists, not only structurally but also electronically.[5] They have important applications in materials science[5,14−16] and biology.[5,12,13] In materials science areas, because of ladderanes' structural rigidity and unique electronic properties, they can be functionalized and used as molecular rods, stiff spacers, and molecular devices.[14−16] In some biological systems, the bacterial lipids containing ladderane substructures have been found and isolated from ammonium-oxidizing bacteria living approximately 90 m below the surface of the Black Sea.[12] Damsté and coworkers[12] discovered that the bacteria can utilize the lipids to encase cellular compartments known as anammoxosomes.

SCHEME 1: Structures of Ladderanes



Ladderanes have unique highly symmetrical structures and electronic properties.[5−11,17] In light of the important experiments involving ladderanes in materials sciences and biology,[5,12−16] it is highly desirable to characterize the electronic structure and properties of this family of molecules. A variety of theoretical approaches has been applied to study the electronic structures and properties of the ladderanes.[6−11,17] Santos[8] studied the electronic structure of linear [*n*]-ladderanes ($n = 1, 3, 5, 7$, and 9) by HF and B3LYP methods. Minyaev and Minkin[10,11] reported their quantum chemical studies on the structural

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* To whom correspondence should be addressed. E-mail: kaichung@cityu.edu.hk (K.-C.L.), wkli@cuhk.edu.hk (W.-K.L.).

[†] Permanent address: Faculty of Chemistry and State Key Laboratory of Biotherapy, Sichuan University, Chengdu 610064, People's Republic of China.

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TABLE 1: G3(MP2) Energy at 0 K (E_0), G3(MP2) Enthalpies at 298 K (H_{298}), and Heats of Formation at 0 and 298 K (ΔH_{f0} and ΔH_{f298}) of the 13 Stable Titled Compounds

molecule	E_0 (a.u.)	H_{298} (a.u.)	ΔH_{f0} (kcal mol^{-1})	ΔH_{f298} (kcal mol^{-1})
helvetane (D_{2d})	−926.83630	−926.82160	393.9	375.0
israelane (D_{3d})	−926.38660	−926.37101	676.1	657.8
$C_{24}H_{24}$ **IV** (C_2)	−926.86533	−926.84975	375.6	357.4
$Si_{24}H_{24}$ **I** (D_{2d})	−6952.14873	−6952.10974	309.5	297.3
$Si_{24}H_{24}$ **II** (D_{3d})	−6952.02100	−6951.98231	389.6	377.2
$Si_{24}H_{24}$ **III** (D_{12h})	−6951.90812	−6951.86718	460.4	449.5
$Si_{24}H_{24}$ **IV** (D_{3h})	−6952.12562	−6952.08607	324.0	312.1
N_{24} **I** (D_{4h})	−1310.87208	−1310.85632	1277.7	1262.9
N_{24} **IV** (D_{3h})	−1310.85226	−1310.83561	1290.1	1275.9
$C_{12}H_{12}N_{12}$ **I** (D_{2h})	−1119.10706	−1119.09243	677.1	659.9
$C_{12}H_{12}N_{12}$ **V** (D_{3h})	−1119.13998	−1119.12493	656.4	639.5
$C_{18}H_{18}N_6$ (D_{3h})	−1023.02121	−1023.00560	504.4	487.0
$C_{16}H_{16}N_8$ (D_{4h})	−1054.99335	−1054.97843	597.4	579.9

stability of [*n*]-prismanes, with $n = 3$ to 10 with D_{nh} symmetry. Hoffmann and coworkers[7] have designed a series of poly[*n*]-prismanes computationally, with the main goal of identifying novel nonclassical organic structures.

Helvetane and israelane (Scheme 1) are large closed ladderanes with two 12-membered rings. The structures of the two molecules were proposed by Israeli chemist Ginsberg.[18] Their names were given because of their characteristic shapes: helvetane resembles the cross on the Swiss flag, whereas israelane looks like the Star of David on the Israeli flag. These two molecules have been studied at the semiempirical level.[19,20] However, high-level ab initio approaches have not been applied to them. This is what we intend to do in this work. In addition, we will study a host of related molecules, including other $C_{24}H_{24}$ isomers as well as isoelectronic $Si_{24}H_{24}$, N_{24}, and $C_{24-x}H_{24-x}N_x$ isomers. Quite recently, a theoretical study on linear ladder polysilanes has shown that the chain elongation of $R_4Si_2-(Si_2R_2)_n-Si_2R_4$ ($n = 0$ to 7) will result in a reduction of the HOMO−LUMO gap.[21] When $n = 7$, the gap becomes 3.4 eV, which is significantly smaller than the predicted gap of 4.7 eV for regular polysilanes.[21] Compared with the linear ladder polysilanes, the electronic structures and properties of the closed ladder polysilanes are interesting but unknown.

In the present work, we perform the high level G3(MP2)[22] calculations on the double-layer closed ladderane isomers with 12-membered rings. In addition to revisiting helvetane and israelane with ab initio methods, other stable isomers with different shapes are also explored. The corresponding ladder polysilanes with the same number of atoms are computationally designed to study the structures and properties of the closed ladder polysilanes. Finally, the isoelectronic equivalents of closed ladderanes with full or partial nitrogen substitution are studied with the aim of identifying candidates of high-energy density materials (HEDMs) and multidentate ligands for metal cations.

2. Computational Details

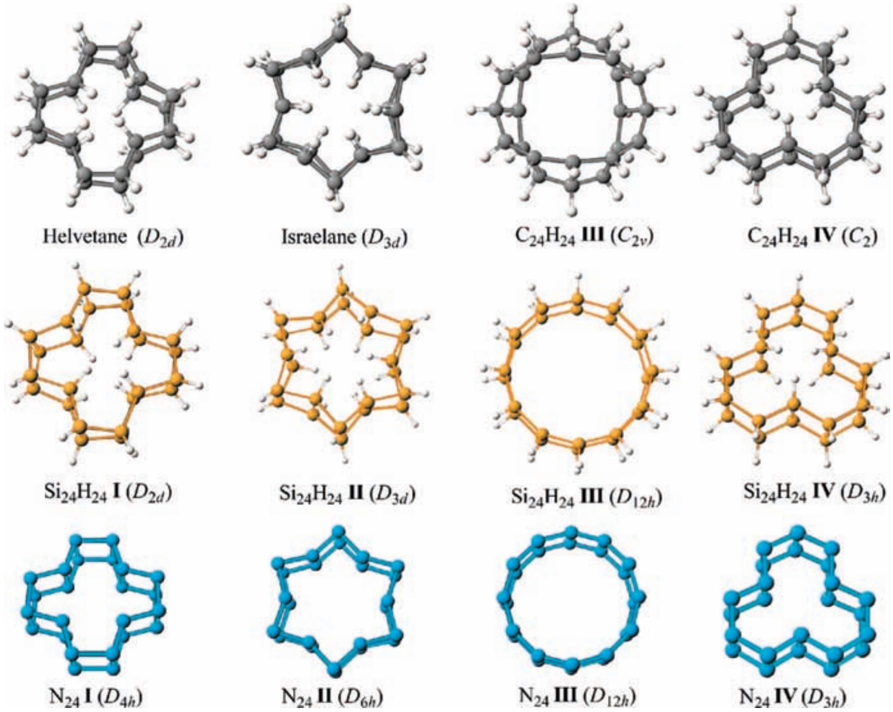
All calculations in this study were carried out using the Gaussian 03 program.[23] Geometrical structures were optimized at the HF/6-31G(d) and B3LYP/6-31G(d) levels, followed by vibrational frequency calculations at the same levels of theory. In addition, for the structures with all positive vibrational frequencies at the two aforementioned levels, their heats of formation (ΔH_f) were calculated by the G3(MP2) method[22] with the atomization scheme.[24] In view of the excellent track record of this method, the ΔH_f values obtained should be reliable estimates. In these calculations, for the $C_{24}H_{24}$ isomers and their nitrogen-containing isoelectronic equivalents, the MP2(FU)/6-31G(d) vibrational frequencies were scaled by 0.9661.[25] But for the $Si_{24}H_{24}$ isomers, the calculations of vibrational frequencies at the MP2(FU)/6-31G(d) level are prohibitively expensive. Therefore the corresponding zero-point vibrational energy (ZPE) corrections for $Si_{24}H_{24}$ isomers were obtained with the HF/6-31G(d) vibrational frequencies scaled by 0.8929.[22] For two FeL^{3+} (L = $C_{16}H_{16}N_8$ and $C_{18}H_{18}N_6$) complexes studied in this work, the structures were optimized with the B3LYP method, and the relativistic effective core potential (ECP)[26] for iron was employed. The basis functions for iron are a modified LANL2DZ double-ζ basis set plus an f type polarization function,[27] in which the two 4p functions of the standard LANL2DZ are replaced by the optimized 4p functions from Couty and Hall.[28] The standard 6-31G(d) basis set is employed for all of the nonmetal atoms.

3. Results and Discussion

The G3(MP2) total energies, enthalpies, and the heats of formation ΔH_{f0} and ΔH_{f298} of 13 stable isomers are listed in Table 1. The theoretical infrared spectra of these compounds and two FeL^{3+} (L = $C_{16}H_{16}N_8$ and $C_{18}H_{18}N_6$) complexes are displayed in Figure S2 of the Supporting Information.

3.1. Double-Layer Closed Ladderane Isomers with Twelve-Membered Rings. The structures of four $C_{24}H_{24}$ isomers with different shapes (having symmetry D_{2d}, D_{3d}, C_{2v}, and C_2) have been optimized at the HF, B3LYP, and MP2 levels with the 6-31G(d) basis set. The structures of these isomers are shown in Figure 1, and the structural parameters optimized at the MP2(FU)/6-31G(d) level are presented in Figure S1 of the Supporting Information.

Ab initio calculations on two known $C_{24}H_{24}$ isomers, helvetane (with D_{2d} symmetry) and israelane (D_{3d}), called $C_{24}H_{24}$ **I** and $C_{24}H_{24}$ **II**, respectively, in this work are reported here for the first time. At the three computational levels mentioned above, these two structures have all real vibrational frequencies and represent minima on the potential energy surface (PES). At the MP2(FU)/6-31G(d) level, the lowest vibrational frequencies of these two structures are 204 and 194 cm^{-1}, respectively. Their respective HOMO−LUMO gaps are 15.11 and 11.50 eV at the HF/6-31G(d) level. These results show that these two $C_{24}H_{24}$ isomers are stable and have fairly rigid structures. The C−C bond distances of the two isomers are in the range of 1.54 to 1.60 Å at the MP2(FU)/6-31G(d) and B3LYP/6-31G(d) levels, which are close to the calculated bond lengths in linear ladderanes at the same level.[8] These results indicate that all C−C bonds in helvetane and israelane are typical single C−C bonds. The bond angles between three carbon atoms of the cyclobutane rings are in the range of 86 and 94°, implying the presence of



Helvetane (D_{2d}) Israelane (D_{3d}) $C_{24}H_{24}$ **III** (C_{2v}) $C_{24}H_{24}$ **IV** (C_2)

$Si_{24}H_{24}$ **I** (D_{2d}) $Si_{24}H_{24}$ **II** (D_{3d}) $Si_{24}H_{24}$ **III** (D_{12h}) $Si_{24}H_{24}$ **IV** (D_{3h})

N_{24} **I** (D_{4h}) N_{24} **II** (D_{6h}) N_{24} **III** (D_{12h}) N_{24} **IV** (D_{3h})

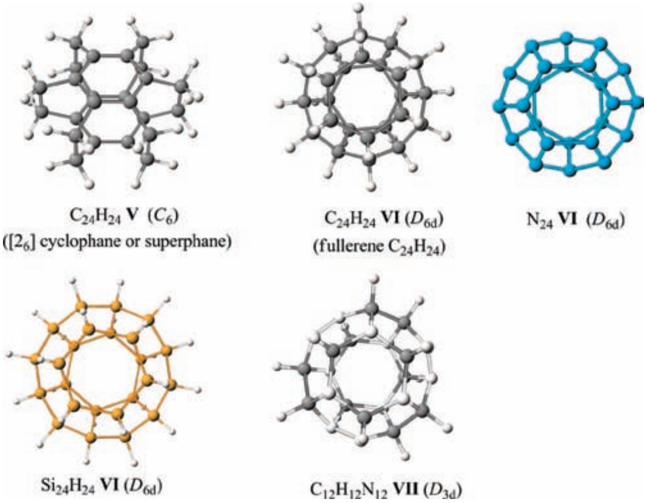
Figure 1. Structures of the $C_{24}H_{24}$, N_{24}, and $Si_{24}H_{24}$ isomers.

strong angular strain in the two structures. At the G3(MP2) level, helvetane is 282 kcal mol^{-1} more stable than israelane, whereas previous MNDO calculations showed that helvetane is more stable by 200 kcal mol^{-1}.[19]

Isomers $C_{24}H_{24}$ **III** and $C_{24}H_{24}$ **IV** have not been previously reported. The former has two dodecagonal closed rings. Originally, we tried to optimize a $C_{24}H_{24}$ isomer with D_{12h} symmetry. But this highly symmetrical structure is not a stable stationary point on the PES, having two imaginary vibrational frequencies at both the HF and B3LYP levels. The normal modes of the imaginary frequencies involve the bending of the planar dodecagonal ring. After removing these two imaginary frequencies, we obtained a minimum with a distorted bowl-shaped structure, $C_{24}H_{24}$ **III** (C_{2v}), at the B3LYP/6-31G(d) level. It should be noted that this bowl-shaped structure has one imaginary frequency at the HF/6-31G(d) level. The energy of $C_{24}H_{24}$ **III** is 203 kcal mol^{-1} less stable than that of helvetane ($C_{24}H_{24}$ **I**) at the B3LYP/6-31G(d) level. Considering that $C_{24}H_{24}$ **III** has a very high energy and also one imaginary frequency at the HF level, we will not give this isomer any further consideration.

The shape of the 12-membered rings in $C_{24}H_{24}$ **IV** (C_2 symmetry) is similar to those of perinaphthane[29] or *s*-triazine.[30] The calculated C−C bond lengths at the MP2 level of theory are in a range of 1.54 to 1.64 Å. At the HF, MP2, and B3LYP levels, $C_{24}H_{24}$ **IV** is found to be a minimum with all positive vibrational frequencies. Compared with the other three $C_{24}H_{24}$ isomers, $C_{24}H_{24}$ **IV** has a lower symmetry, and its energy is much lower than that of israelane and very close to that of helvetane. At the G3(MP2) level, $C_{24}H_{24}$ **IV** is 18 kcal mol^{-1} more stable than helvetane. As shown in Figure 1, three "endo" hydrogen atoms on each ring of $C_{24}H_{24}$ **IV** point toward the center of the ring (albeit slightly upward for the upper ring and downward for the lower ring), whereas helvetane and israelane have four and six "endo" hydrogen atoms on each ring, respectively. These "endo" hydrogen atoms would sterically interfere with each other and increase the overall energy of the structures. The number of "endo" hydrogen atoms on each isomer may well be correlated with the isomers' relative stabilities.

SCHEME 2: Related Isomers That Have Been Reported in the Literature



$C_{24}H_{24}$ **V** (C_6)
([2_6] cyclophane or superphane)

$C_{24}H_{24}$ **VI** (D_{6d})
(fullerene $C_{24}H_{24}$)

N_{24} **VI** (D_{6d})

$Si_{24}H_{24}$ **VI** (D_{6d})

$C_{12}H_{12}N_{12}$ **VII** (D_{3d})

Among the three stable $C_{24}H_{24}$ isomers, $C_{24}H_{24}$ **IV** is reported for the first time, and it has a lower energy than the two better-known isomers. The calculated ΔH_{f298} values of $C_{24}H_{24}$ **IV** and helvetane are about 360 kcal mol^{-1}. These three isomers' large positive ΔH_f values show that they are high-energy species. Here we also compare these three structures with two other $C_{24}H_{24}$ isomers (Scheme 2) that have been previously reported.[31,32] Isomer $C_{24}H_{24}$ **V** (C_6 symmetry), also known as [2_6]cyclophane or superphane, has a fairly symmetric and multibridged structure, and it has been synthesized. [31] Fullerene $C_{24}H_{24,}$ isomer **VI**, has a polyhedral caged structure with D_{6d} symmetry.[33] In Table 2, the relative energies of the five $C_{24}H_{24}$ isomers are presented. It is seen that helvetane is about 301 and 353 kcal mol^{-1} less stable than superphane and fullerene $C_{24}H_{24}$, respectively. Although these results show that the three double-layer closed

TABLE 2: Relative Energy (E_{rel}, kcal mol^{-1}) of Stable $C_{24}H_{24}$ Isomers at the B3LYP/6-31G(d) and MP2(FU)/6-31G(d) Levels

molecule	E_{rel} (MP2)	E_{rel} (B3LYP)
helvetane (D_{2d})	0.0	0.0
israelane (D_{3d})	305.6	299.0
$C_{24}H_{24}$ **IV** (C_2)	−16.9	−27.1
$C_{24}H_{24}$ **V** (C_6)	−300.7	−290.9
$C_{24}H_{24}$ **VI** (D_{6d})	−352.5	−338.3

ladderane isomers with 12-membered rings are of high energy with respect to other $C_{24}H_{24}$ isomers, they are located in relatively deep potential energy wells, and thus there may be high activation barriers hindering their decomposition or isomerization. These conclusions are consistent with their relatively high values of the lowest harmonic vibrational frequencies and large HOMO−LUMO gaps. Finally, it is noted that among the five isomers considered in Table 2, only $C_{24}H_{24}$ **V** cannot be expressed as $(CH)_{24}$.

3.2. Double-Layer Closed Laddersilane Isomers with Twelve-Membered Rings. Ladder polysilanes or laddersilanes are analogs of carbon ladderanes, but their electronic properties are significantly different. Recent theoretical investigations[21] on a series of linear laddersilanes indicate that a chain elongation results in a reduction of HOMO−LUMO gaps. For example, at the B3LYP/6-31G(d) level, the HOMO−LUMO gap of $R_4Si_2-(Si_2R_2)_7-Si_2R_4$ is calculated to be 3.4 eV, which is very close to the semiconductor range.[21] To our knowledge, the closed laddersilanes have not been studied either theoretically or experimentally. That is, the structures and electronic properties of the closed laddersilanes are still unknown. In this light, we replace the carbon atoms of the four $C_{24}H_{24}$ isomers (**I** to **IV**) with silicon atoms to arrive at four new laddersilane isomers. Their structures and properties are then studied computationally.

In Figure 1, four $Si_{24}H_{24}$ isomers with high symmetry are shown. At the HF and B3LYP levels of theory, they are stable structures with all positive vibrational frequencies. The Si−Si bond lengths range from 2.35 to 2.41 Å at the MP2(FU)/6-31G(d) level. The experimentally estimated Si−Si bond lengths in the tetrahedral core of the $Si_4(^tBu_3Si)_4$ molecule are between 2.315 and 2.341 Å.[34] The calculated values of polyhedral caged Si_6H_6 and Si_8H_8 are about 2.37 and 2.4 Å, respectively.[35] The present calculated Si−Si bond distances are consistent with these values.

The structures of $Si_{24}H_{24}$ **I** and $Si_{24}H_{24}$ **II** are similar to those of helvetane and israelane, respectively. Because the Si−Si length is longer than the C−C distances, the "endo" hydrogens of each ring in $Si_{24}H_{24}$ **I** and $Si_{24}H_{24}$ **II** are not as crowded as those in the carbon analogs, thus improving their relative stability among the $Si_{24}H_{24}$ isomers. The $C_{24}H_{24}$ isomer with two dodecagonal rings (D_{12h} symmetry) is not a stable stationary point on the PES. But its silicon analog, $Si_{24}H_{24}$ **III** with this symmetry, does represent a stable structure at the HF and B3LYP levels. Compared with $C_{24}H_{24}$ **IV** (with C_2 symmetry), $Si_{24}H_{24}$ **IV** has a higher symmetry of D_{3h}.

Among the four $Si_{24}H_{24}$ isomers, $Si_{24}H_{24}$ **I** with the cross shape is the most stable one, and $Si_{24}H_{24}$ **III** with dodecagonal rings has the highest energy. At the G3(MP2) level, the energy difference between them is 151 kcal mol^{-1}. The G3(MP2) calculations show that all four $Si_{24}H_{24}$ isomers have high positive ΔH_f values, which are between 300 and 460 kcal mol^{-1}.

TABLE 3: HOMO−LUMO Gaps (eV) at the B3LYP/6-31G(d) Level and Relative Energy (E_{rel}, kcal mol^{-1}) of $Si_{24}H_{24}$ Isomers at the B3LYP/6-31G(d) and MP2(FU)/6-31G(d) Levels

molecule	E_{rel} (MP2)	E_{rel} (B3LYP)	HOMO−LUMO gap
$Si_{24}H_{24}$ **I** (D_{2d})	0.0	0.0	3.83
$Si_{24}H_{24}$ **II** (D_{3d})	87.8	93.2	2.56
$Si_{24}H_{24}$ **III** (D_{12h})	159.1	105.2	3.31
$Si_{24}H_{24}$ **IV** (D_{3h})	16.0	−2.3	3.95
$Si_{24}H_{24}$ **VI** (D_{6d})	−144.0	−147.2	4.78

We have also optimized the structure of silicon fullerene, $Si_{24}H_{24}$ **VI**, in Scheme 2, which has been previously reported.[35,36] The relative energies and HOMO−LUMO gaps of five $Si_{24}H_{24}$ isomers are listed in Table 3. Compared with the other four $Si_{24}H_{24}$ isomers, $Si_{24}H_{24}$ **VI** is the most stable and has the largest HOMO−LUMO gap. Meanwhile, $Si_{24}H_{24}$ **I** is 144 kcal mol^{-1} less stable than $Si_{24}H_{24}$ **VI** at the MP2(FU)/6-31G(d) level. Among the five $Si_{24}H_{24}$ isomers, star-shaped $Si_{24}H_{24}$ **II** is the most unstable, and it has the smallest HOMO−LUMO gap. The calculated gaps at the B3LYP level of the first four $Si_{24}H_{24}$ isomers are 3.83, 2.56, 3.31, and 3.95 eV, respectively. These gaps are significantly smaller than the corresponding values of linear laddersilanes computed at the same level of theory.[21] The HOMO−LUMO gap of $Si_{24}H_{24}$ **II** with a value of 2.56 eV is close to the semiconductor range. If synthesized, it may be a good candidate for semiconductor materials.

The HOMO and LUMO molecular orbital plots of the four $Si_{24}H_{24}$ isomers (**I** to **IV**) are displayed in Figure 2. The HOMOs of $Si_{24}H_{24}$ **I** and $Si_{24}H_{24}$ **II** have considerable $3p_z$ character, and the LUMOs have mainly 3s character. The HOMO−LUMO gaps are determined by the conformations of the two isomers. The fused cyclobutane rings of $Si_{24}H_{24}$ **I** have gauche conformation, whereas $Si_{24}H_{24}$ **II** is an anticonformer. The orbital analysis by Karni and Apeloig[21] shows that anti and gauche conformations have different effects on the HOMO and LUMO orbitals. In the antiperiplanar conformation, the 1−4 σ-conjugated interaction destabilizes the HOMO and stabilizes the LUMO. In the gauche conformations, the effects of the interaction are just the opposite. The former effects will lead to a smaller HOMO−LUMO gap. As a result, the structure $Si_{24}H_{24}$ **II** with the anticonformation will have a smaller energy gap.

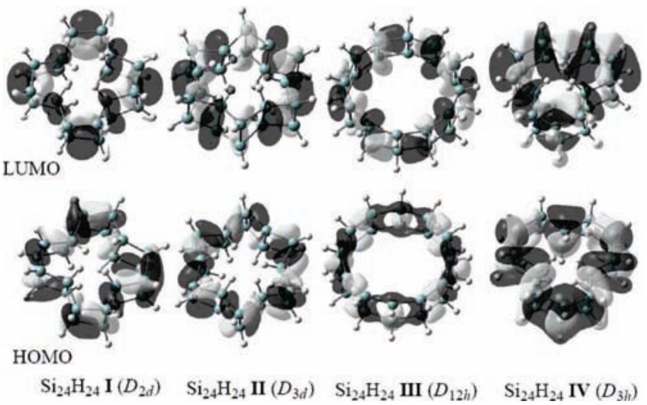


Figure 2. HOMO and LUMO molecular orbital plots of the four $Si_{24}H_{24}$ isomers.

TABLE 4: Relative Energy (E_{rel}, kcal mol^{-1}) of Stable N_{24} Isomers at the B3LYP/6-31G(d) and MP2(FU)/6-31G(d) Levels

molecule	E_{rel} (MP2)	E_{rel} (B3LYP)
N_{24} **I** (D_{4h})	0.0	0.0
N_{24} **IV** (D_{3h})	15.7	9.5
N_{24} **VI** (D_{6d})	−119.7	−125.6

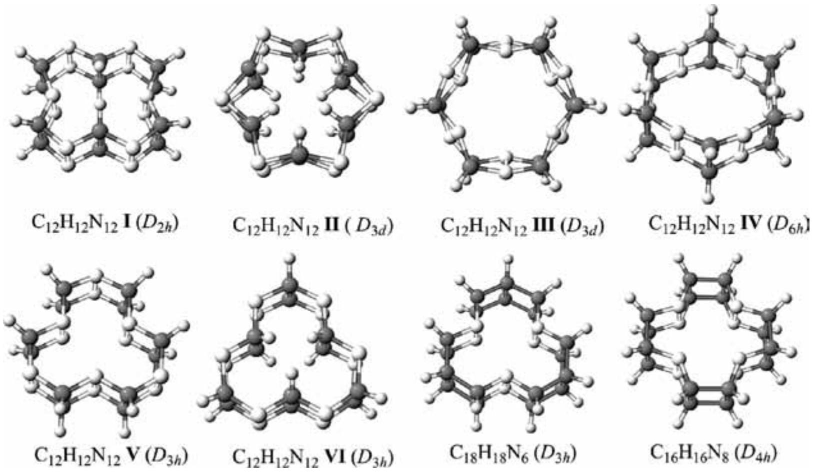


Figure 3. Structures of the six $C_{12}H_{12}N_{12}$ isomers, $C_{16}H_{16}N_8$, and $C_{16}H_{16}N_8$ molecules at the HF/6-31G(d) level of theory.

TABLE 5: Relative Energy (E_{rel}, kcal mol^{-1}) of Stable $C_{12}H_{12}N_{12}$ Isomers at the B3LYP/6-31G(d) and MP2(FU)/6-31G(d) Levels

molecule	E_{rel} (MP2)	E_{rel} (B3LYP)
$C_{12}H_{12}N_{12}$ **I** (D_{2h})	0.0	0.0
$C_{12}H_{12}N_{12}$ **V** (D_{3h})	−23.5	−27.5
$C_{12}H_{12}N_{12}$ **VII** (D_{3d})	−385.0	−369.9

3.3. Double-Layer N_{24} Isomers with Twelve-Membered Rings.

Nitrogen clusters, N_x, have been the subject of intense interest in the past 20 years for their potential as HEDMs.[37−39] The nitrogen atom is isoelectronic to the CH group. The substitution of all CH groups in the closed ladderane $C_{24}H_{24}$ isomers by N atoms results in N_{24} isomers with 12-membered rings. In previous theoretical investigations,[40] various cage isomers of N_{24} with five- and six-membered rings have been reported. But no N_{24} isomers with 12-membered rings have been studied. Here we report the results on the double-layer N_{24} isomers with 12-membered rings.

Four N_{24} isomers were designed and optimized at the HF and B3LYP levels. The results are shown in Figure 1. Isomers N_{24} **I** (D_{4h}) and N_{24} **IV** (D_{3h}) are confirmed to be minima at the HF, B3LYP, and MP2 levels. Vibrational frequency analysis shows that isomers N_{24} **II** and N_{24} **III** are not stable structures. At the HF/6-31G(d) level, the two isomers have eight and two imaginary frequencies, respectively.

For N_{24} **I** and N_{24} **IV**, the atoms in each layer are nearly coplanar. The N−N bond distances are between 1.45 and 1.59 Å at the MP2(FU)/6-31G(d) level. These lengths are slightly longer than the experimental N−N single bond length of hydrazine N_2H_4, which is 1.446 Å.[41] The calculated N−N bond distance of N_8 cubane at the same level of theory is 1.531 Å,[42] which is close to those calculated for N_{24} **I** and N_{24} **IV**.

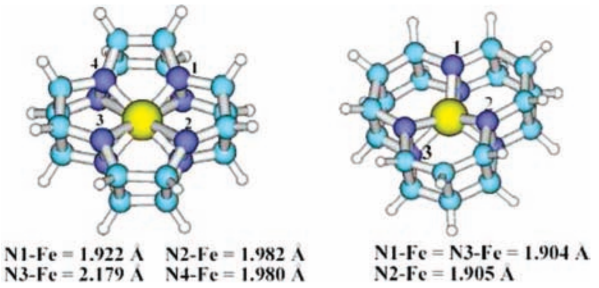


Figure 4. Optimized structures of FeL^{3+} (L = $C_{16}H_{16}N_8$ and $C_{18}H_{18}N_6$) complexes.

Isomer N_{24} **I** has a lowest vibrational frequency of 184 cm^{-1}, but that of N_{24} **IV** is very small, at about 5 cm^{-1} (the second-lowest vibrational frequency is 172 cm^{-1}). At the G3(MP2) level, N_{24} **I** is thermochemically more stable than N_{24} **IV** by about 12 kcal mol^{-1}. It is noted that N_{24} **IV** is not a very rigid molecule. In Table 4, we compare the energies of these two stable N_{24} isomers with that of the fullerene N_{24} (N_{24} **VI** in Scheme 2), which has been computationally studied by Strout.[40] Isomer N_{24} **VI** with D_{6d} symmetry is about 120 kcal mol^{-1} more stable than the N_{24} **I**. This result shows that the large N_x molecules with 12-membered rings are less stable than the corresponding isomers with pentagonal rings. The calculated ΔH_{f298} values of the two new N_{24} isomers are very high (1270 kcal mol^{-1}), indicating that these two isomers are indeed highly energetic species.

3.4. $C_{24-x}H_{24-x}N_x$ (x = 6, 8, and 12) Isomers, Isoelectronic Equivalents of $C_{24}H_{24}$ with Partial Nitrogen Substitution.

Although numerous N_x molecules have been studied theoretically, oftentimes, the highly energetic species are not sufficiently stable to be practical HEDMs. Recent theoretical investigations have identified carbon−nitrogen cages to be potential stable HEDMs.[43−46] Strout carried out extensive calculations on the carbon−nitrogen cages, including $C_6H_6N_6$,[43,44] $C_{10}H_{10}N_{10}$, $C_{12}H_{12}N_{12}$,[45] etc. Different degrees of CH substitution into N_{12}, N_{20}, and N_{24} cages result in these stable isomers. Following this approach, we have designed six $C_{12}H_{12}N_{12}$ isomers, one $C_{18}H_{18}N_6$, and one $C_{16}H_{16}N_8$ for theoretical investigation. We obtained the initial structures by replacing CH groups with nitrogen atoms on our four $C_{24}H_{24}$ isomers (**I** to **IV**).

The optimized structures of eight $C_{24-x}H_{24-x}N_x$ isomers are shown in Figure 3. Among the six $C_{12}H_{12}N_{12}$ isomers shown, only $C_{12}H_{12}N_{12}$ **I** and $C_{12}H_{12}N_{12}$ **V** have all positive vibrational frequencies at the HF, B3LYP, and MP2 levels of theory. At the HF/6-31G(d) level, isomers $C_{12}H_{12}N_{12}$ **III** and $C_{12}H_{12}N_{12}$ **IV** have three and six imaginary vibrational frequencies, respectively. Although $C_{12}H_{12}N_{12}$ **II** and $C_{12}H_{12}N_{12}$ **VI** have all real frequencies at the HF level; there are, respectively, four and one imaginary vibrational frequencies at the B3LYP/6-31G(d) level. Therefore, these four isomers ($C_{12}H_{12}N_{12}$ **II**, **III**, **IV**, and **VI**) do not represent stable stationary points on the PES. Interestingly, isomer $C_{12}H_{12}N_{12}$ **V** has no “endo” hydrogens in each 12-membered ring. For $C_{12}H_{12}N_{12}$ **I**, there are still two “endo” hydrogens in each ring, indicating the presence of some steric interaction. As a result, $C_{12}H_{12}N_{12}$ **V** is more stable than $C_{12}H_{12}N_{12}$ **I** by 21 kcal mol^{-1} at the G3(MP2) level. We also studied isomer $C_{12}H_{12}N_{12}$ **VII** with D_{3d} symmetry (Scheme 2), which was previously studied by Strout and found to be the most stable among the six $C_{12}H_{12}N_{12}$ cage isomers.[45] In Table 5, the calculated relative energies show that the $C_{12}H_{12}N_{12}$ **VII** is more stable than $C_{12}H_{12}N_{12}$ **V** by 361 kcal mol^{-1}. These results indicate that the cage structure is energetically more favorable for the isomers of $C_{12}H_{12}N_{12}$.

Species $C_{18}H_{18}N_6$ and $C_{16}H_{16}N_8$ (shown in Figure 3) are stable structures at the HF, B3LYP, and MP2 levels of theory. The nitrogen substitution leads to the removal of the "endo" hydrogens. The six nitrogen atoms in $C_{18}H_{18}N_6$ occupy the apical positions of a trigonal prism. In other words, it is a potential hexadentate ligand. Similarly, $C_{16}H_{16}N_8$ may be a octadentate ligand. As a test, we place a Fe^{3+} cation at the center of the cavity of these two (potential) ligands. The optimized structures of the resultant complexes are shown in Figure 4. These two structures are stable minima at the B3LYP level of theory. Calculations show that both complexes have a doublet ground state, as most inorganic chemists would have predicted. The Fe−N bond lengths are in the range of 1.9 to 2.2 Å. These results show that $C_{18}H_{18}N_6$ and $C_{16}H_{16}N_8$ may be effective ligands for various metal cations.

For the four aforementioned stable carbon−nitrogen isomers, $C_{12}H_{12}N_{12}$ **I**, $C_{12}H_{12}N_{12}$ **V**, $C_{18}H_{18}N_6$, and $C_{16}H_{16}N_8$, their G3(MP2) ΔH_{f298} values are in the range of 480−660 kcal mol^{-1}, implying that they are potential stable HEDMs.

4. Conclusions

High level ab initio calculations have been carried out to study the structure and properties of large closed ladderane and laddersilane isomers and their nitrogen-containing isoelectronic equivalents. Thirteen stable structures have been identified, which include three $C_{24}H_{24}$, four $Si_{24}H_{24}$, two N_{24}, and four $C_{24-x}H_{24-x}N_x$ isomers. Of these 13 species, 11 are reported for the first time. In addition, G3(MP2) calculations show that they have very positive ΔH_f values. The optimized structures are compared with the corresponding isomers that have been previously reported. The calculated results show that the present isomers with 12-membered rings are highly energetic species and much more unstable than their fullerene isomers. The HOMO−LUMO gaps of the four closed laddersilanes are smaller than those of linear laddersilanes at the same level of theory. The structure $Si_{24}H_{24}$ **II** with anticonformations has a very small gap of 2.56 eV, approaching the semiconductor range. If synthesized, it may be a viable candidate for semiconductor materials. When CH groups in $C_{24}H_{24}$ isomers are fully or partially substituted by nitrogens, the resultants species may form a series of potential HEDMs. Finally, the structures of $C_{18}H_{18}N_6$ and $C_{16}H_{16}N_8$ are shown to be good multidentate ligands for various metal cations.

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Supporting Information Available: Optimized structures, electronic energy, zero-point energy, and the lowest harmonic frequency and theoretical infrared spectra of 13 stable isomers. This material is available free of charge via the Internet at http://pubs.acs.org.

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