

Article

**On the Viability of Small Endohedral Hydrocarbon Cage
 Complexes: X@CH, X@CH, X@CH, X@CH, X@CH, and X@CH**

Damian Moran, H. Lee Woodcock, Zhongfang Chen, Henry F. Schaefer, and Paul v. R. Schleyer

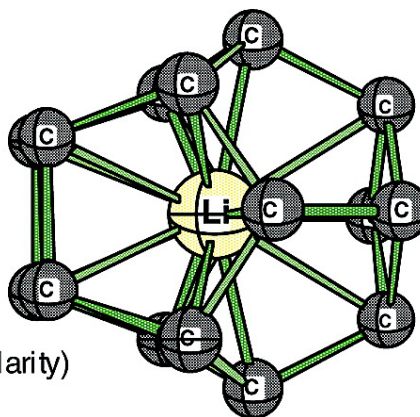
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Low host strain +
 Large host cavity +
 Small, charged guest

= Viable Endohedral
 Complex

E.g. $\text{Li}^+ @ \text{C}_{16}\text{H}_{16}$ (D_{4d})
 (Hydrogens omitted for clarity)



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On the Viability of Small Endohedral Hydrocarbon Cage Complexes: $X@C_4H_4$, $X@C_8H_8$, $X@C_8H_{14}$, $X@C_{10}H_{16}$, $X@C_{12}H_{12}$, and $X@C_{16}H_{16}$

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Abstract: Small hydrocarbon complexes ($X@cage$) incorporating cage-centered endohedral atoms and ions ($X = H^+$, H, He, Ne, Ar, $Li^{0,+}$, $Be^{0,+2+}$, $Na^{0,+}$, $Mg^{0,+2+}$) have been studied at the B3LYP/6-31G(d) hybrid HF/DFT level of theory. No tetrahedrane (C_4H_4 , T_d) endohedral complexes are minima, not even with the very small hydrogen atom or beryllium dication. Cubane (C_8H_8 , O_h) and bicyclo[2.2.2]octane (C_8H_{14} , D_{3h}) minima are limited to encapsulating species smaller than Ne and Na^+ . Despite its intermediate size, adamantane ($C_{10}H_{16}$, T_d) can enclose a wide variety of endohedral atoms and ions including H, He, Ne, $Li^{0,+}$, $Be^{0,+2+}$, $Na^{0,+}$, and Mg^{2+} . In contrast, the truncated tetrahedrane ($C_{12}H_{12}$, T_d) encapsulates fewer species, while the D_{4d} symmetric $C_{16}H_{16}$ hydrocarbon cage (see Table of Contents graphic) encapsulates all but the larger Be, Mg, and Mg^+ species. The host cages have more compact geometries when metal atoms, rather than cations, are inside. This is due to electron donation from the endohedral metals into C–C bonding and C–H antibonding cage molecular orbitals. The relative stabilities of endohedral minima are evaluated by comparing their energies (E_{endo}) to the sum of their isolated components ($E_{inc} = E_{endo} - E_{cage} - E_x$) and to their exohedral isomer energies ($E_{isom} = E_{endo} - E_{exo}$). Although exohedral binding is preferred to endohedral encapsulation without exception (i.e., E_{isom} is always exothermic), $Be^{2+}@C_{10}H_{16}$ (T_d ; -235.5 kcal/mol), $Li^+@C_{12}H_{12}$ (T_d ; 50.2 kcal/mol), $Be^{2+}@C_{12}H_{12}$ (T_d ; -181.2 kcal/mol), $Mg^{2+}@C_{12}H_{12}$ (T_d ; -45.0 kcal/mol), $Li^+@C_{16}H_{16}$ (D_{4d} ; 13.3 kcal/mol), $Be^+@C_{16}H_{16}$ (C_{4v} ; 31.8 kcal/mol), $Be^{2+}@C_{16}H_{16}$ (D_{4d} ; -239.2 kcal/mol), and $Mg^{2+}@C_{16}H_{16}$ (D_{4d} ; -37.7 kcal/mol) are relatively stable as compared to experimentally known $He@C_{20}H_{20}$ (I_h), which has an $E_{inc} = 37.9$ kcal/mol and $E_{isom} = -35.4$ kcal/mol. Overall, endohedral cage complexes with low parent cage strain energies, large cage internal cavity volumes, and a small, highly charged guest species are the most viable synthetic targets.

Introduction

Cage molecules^{1–7} with atoms and ions inside are not only significant theoretically^{8–17} but also may have intriguing practi-

cal uses.^{18–21} Endohedral cage complexes²² ($X@cage$) have potential applications as magnetic resonance imaging contrast agents,²³ semiconductors, and ferromagnets.²⁴ Saunders and co-workers²⁵ have used endohedral helium atoms and NMR to

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probe the internal electronic and magnetic cage environment of fullerenes and provide experimental conformation of computational results such as nucleus independent chemical shift^{26–28} predictions of cluster aromaticity.^{29–32}

Fullerene endohedral complexes, incorporating 60 or more cage atoms (e.g., ErSc₃N@C₈₀),³³ have been extensively prepared in covaporization experiments,^{33–35} using collisional insertion within a mass spectrometer,^{18–20} by forced incorporation under high pressure (3000 atm, 650 °C),²¹ and using molecular bombardment experiments.³⁶ The smallest endohedral hydrocarbon cage complex reported to date is He@C₂₀H₂₀, which was created by Cross, Saunders, and Prinzbach³⁷ when they blasted dodecahedrane^{38,39} with a helium molecular beam.³⁶ Prior computations on He@C₂₀H₂₀ predicted that the endohedral dodecahedrane derivative was 38 kcal/mol higher in energy than its isolated components.¹¹ Furthermore, Mascall⁴⁰ predicted that the barrier to He ingress via a C₂₀H₂₀ face (i.e., along C₅ axis) is >300 kcal/mol, making the achievement of Cross, Saunders, and Prinzbach³⁷ all the more remarkable.

Mascall⁴⁰ also predicted large (100–200 kcal/mol) endothermic C₂₀H₂₀ facial entrance barriers for Li⁺, Be⁺, and Mg²⁺. H⁺ and Be²⁺ dodecahedrane entrance along a C₅ axis, however, was exothermic by ~150 kcal/mol, and their concave potential energy profiles (energy vs distance from cage center) show points of inflection at cage face centers. Mascall's⁴⁰ Be²⁺ potential profile was in excellent agreement with our¹¹ previous computations showing that beryllium dication was a minimum with exothermically (>200 kcal/mol) bound internal and external cage faces (i.e., the potential energy profile is a double well potential with minima corresponding to exo- and endohedral facial binding). We¹¹ previously computed the relative energies of H, He, Ne, Ar, Li, Li⁺, Be, Be⁺, Na, Na⁺, Mg, Mg⁺, and Mg²⁺ dodecahedrane endohedral complexes and found that only Li⁺@C₂₀H₂₀ (*I_h*), Be⁺@C₂₀H₂₀ (*C_{5v}*), Be²⁺@C₂₀H₂₀ (*C_{5v}*), and Mg²⁺@C₂₀H₂₀ (*I_h*) had exothermic inclusion energies relative to their isolated components ($E_{\text{inc}} = E_{\text{endo}} - E_{\text{cage}} - E_{\text{x}}$). Although all of the endohedral dodecahedrane complexes were higher (>10 kcal/mol) in energy than their corresponding exohedral isomers, that is, external cage binding was favored, the Li⁺, Be²⁺, and Mg²⁺ relative energy differences were less than that of the known He complex, and they may also be synthesized in beam implantation experiments.

In light of the recent He@C₂₀H₂₀ preparative success,³⁷ we have now extended our previous DFT studies of endohedral dodecahedrane, borane, alane, and gallane complexes^{8–11,14,15,17} to the smaller hydrocarbon cage systems *T_d* tetrahedrane (C₄H₄, **1**),^{41–43} *O_h* cubane (C₈H₈, **2**),⁴⁴ *D_{3d}* bicyclo[2.2.2]octane (C₈H₁₄, **3**),^{45,46} *T_d* adamantane (C₁₀H₁₆, **4**),^{47–49} *T_d* truncated tetrahedrane (C₁₂H₁₂, **5**),^{50,51} *D_{3d}* diamantane (C₁₄H₂₀, **6**),^{52,53} and the *D_{4d}* symmetric 4,4-bitruncated tetragonal trapezohedron hydrocarbon isomer (C₁₆H₁₆, **7**) shown in Figure 1. We are seeking answers to a number of questions. Both H and Ar species are minima at the center of dodecahedrane,¹¹ but what are the analogous limits of encapsulation for the cages shown in Figure 1? Dodecahedrane is more compact when encapsulating a metal as compared to the corresponding cation/dication, due to donation of electron density from encapsulated metal atoms into the C–C bonding and C–H antibonding endohedral complex HOMO.¹¹ Do other endohedral hydrocarbon cage complexes respond to metal encapsulation similarly? M@C₂₀H₂₀ (M = Li, Na, Be, Mg) species possess lower first ionization potentials than the Cs atom (3.9 eV); that is, they are superalkalis.¹¹ Are the ionization potentials of metals encapsulated by the cages shown in Figure 1 also dramatically reduced? Relative to their isolated components, X@C₂₀H₂₀ (X = Li⁺, Be²⁺, Mg²⁺) complexes have endohedral inclusion energies comparable to that of He@C₂₀H₂₀ and are promising synthetic targets. Are endohedral X@cage complexes incorporating hosts smaller than dodecahedrane also likely to be experimentally observable; that is, are they viable? Our results, which extend earlier theoretical predictions, highlight the size dependence of endohedral complex stability and reveal the dramatic effects of encapsulation on the ionization potentials of the enclosed atoms.

Computational Details

Endohedral complexes were optimized at the B3LYP/6-31G(d) hybrid HF/DFT level of theory; vibrational frequency analyses (at the same level) characterized the optimized structures as minima or higher and provided zero-point energies which are included throughout (ZPE; unscaled).^{54–56} The B3LYP functional was chosen because the inclusion of electron correlation was important for accurate geometry prediction. For example, Mg@C₁₀H₁₆ (*T_d*) and Mg⁺@C₁₀H₁₆ (*T_d*) were minima at

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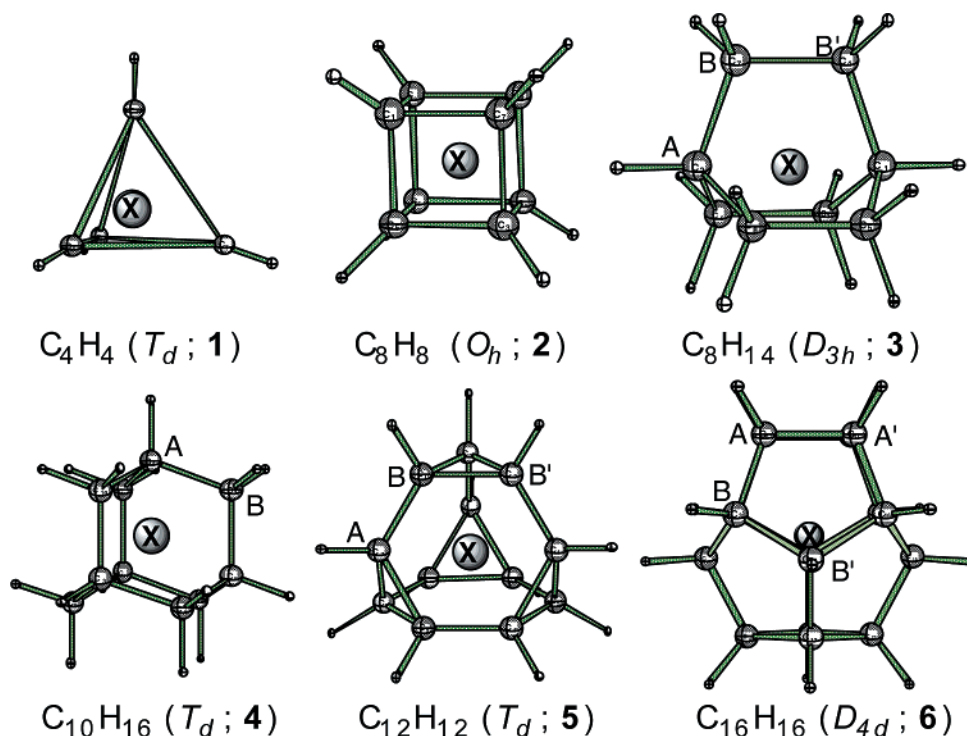


Figure 1. Hydrocarbon cages with endohedrally encapsulated “X” species.

HF/6-31G(d); however, they had five (doubly degenerate $789i\text{ cm}^{-1}$ and triply degenerate $461i\text{ cm}^{-1}$) and three (triply degenerate $2222i\text{ cm}^{-1}$) imaginary frequencies, respectively, at B3LYP/6-31G(d). DFT methods were used in preference to correlated ab initio methods such as MP2 because of the large basis set superposition errors^{11,57,58} and lengthy execution times associated with the latter. Furthermore, consistent with our¹¹ previous He@C₂₀H₂₀ and Ne@C₂₀H₂₀ results, agreement between, for example, Be²⁺@C₈H₈ B3LYP/6-31G(d) ($E_{\text{inc}} = -69.8\text{ kcal/mol}$; $E_{\text{bind}} = -222.0\text{ kcal/mol}$; and $E_{\text{isom}} = -152.2\text{ kcal/mol}$) and MP2/6-31G(d) ($E_{\text{inc}} = -68.7\text{ kcal/mol}$; $E_{\text{bind}} = -216.7\text{ kcal/mol}$; and $E_{\text{isom}} = -148.5\text{ kcal/mol}$) relative energies (see below for energy term definitions) was $<5\text{ kcal/mol}$. The 6-31G(d) basis set was used throughout because B3LYP/6-31G(d) + ZPE and B3LYP/6-311+G(d,p) + ZPE relative energies are generally in good agreement ($<1\text{ kcal/mol}$). For example, H@C₂₀H₂₀ and He@C₂₀H₂₀ inclusion energies (*vide infra*) are (B3LYP/6-31G(d) + ZPE) 36.3 and 38.0 kcal/mol,¹⁷ respectively, and (B3LYP/6-311+G(d,p) + ZPE) 35.8 and 37.9 kcal/mol,¹¹ respectively. Endohedral complexes where the cage was possibly overly “stretched” were checked for wave function instabilities, for example, Be@C₁₀H₁₆ (T_d); however, none were found.

The inclusion energies, E_{inc} (kcal/mol), of endohedral complex minima were evaluated by comparing the energy of X@cage (E_{endo}) to the sum of the energies of the isolated components, E_{cage} and E_{x} . For comparison, their corresponding exohedral binding energies (E_{bind} , kcal/mol), which is the energy difference between the most stable exohedral structures (E_{exo}) and the sum of the isolated component energies, were also computed. We designated the energy difference between the most stable exohedral structures and their endohedral isomers as the “isomerization energy”, E_{isom} (kcal/mol). The values of E_{inc} , E_{bind} , and E_{isom} are represented graphically in Figure 2. All energies were corrected using unscaled zero-point energies (ZPE).

The optimized endohedral complexes were used to calculate adiabatic ionization potentials and to obtain NBO⁵⁹ natural charges. Cage and

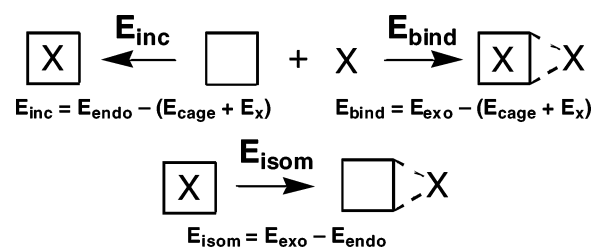


Figure 2. Graphical summary of inclusion, binding, and isomerization energies (kcal/mol).

ring cyclic electron delocalization was assessed using NICS at the GIAO/B3LYP/6-31G(d)//B3LYP/6-31G(d) level.^{26–28} All calculations were performed using Gaussian 98.⁶⁰ Absolute energies, ZPE, optimized endohedral bond lengths, and unscaled lowest (real or imaginary) vibrational frequencies are summarized in the Supporting Information.

Results and Discussion

X@C₄H₄ (T_d). As could be expected, all endohedral complexes of tetrahedrane (X@C₄H₄) are B3LYP/6-31G(d) higher order stationary points (NImag ≥ 2), with both the small internal volume (0.143 \AA^3 ; Table 1) of the cage and the tetrahedrane’s large, unfavorable strain (141 kcal/mol)⁶¹ leading to cage rupture. For example, the primary imaginary mode of H⁺@C₄H₄ (T_d) leads to the cage-ruptured C₄H₅⁺ C_s minimum shown in

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Table 1. Distances between Cage Centers and the Closest Carbon Atom and C–C Bond Center (Å)^a

	C ₄ H ₄ (T _d)	C ₈ H ₈ (O _h)	C ₈ H ₁₄ (D _{3h})	C ₁₀ H ₁₆ (T _d)	C ₁₂ H ₁₂ (T _d)	C ₁₆ H ₁₆ (D _{4d})	C ₂₀ H ₂₀ (I _h)
cage	0.906	1.360	1.299 ^b	1.546	1.772	1.816 ^c	2.180
face	0.302	0.785	0.726	0.771	0.927	1.410	1.732
bond	0.523	1.110	1.268 ^b	1.478	1.601	1.639 ^c	2.037
volume	0.143	1.368	2.039	3.229	4.104	4.403	8.452

^a Cage faces are not useful because they are not often flat, and this makes the assignment of position and its implications arbitrary. ^b C₁₀H₁₆ bridgehead carbon and C–C bond. ^c Carbon and C–C bond in cage “equator”.

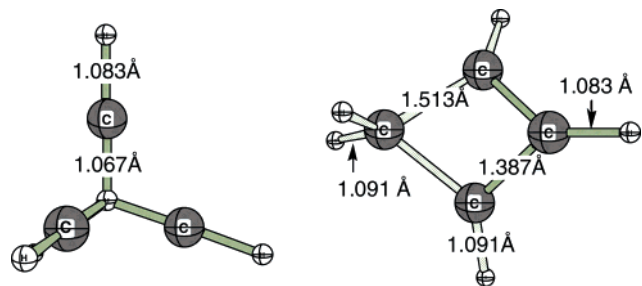
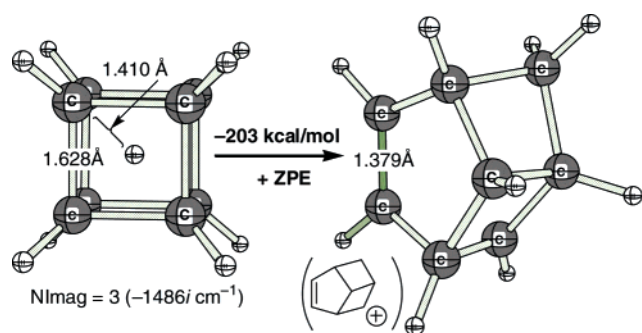
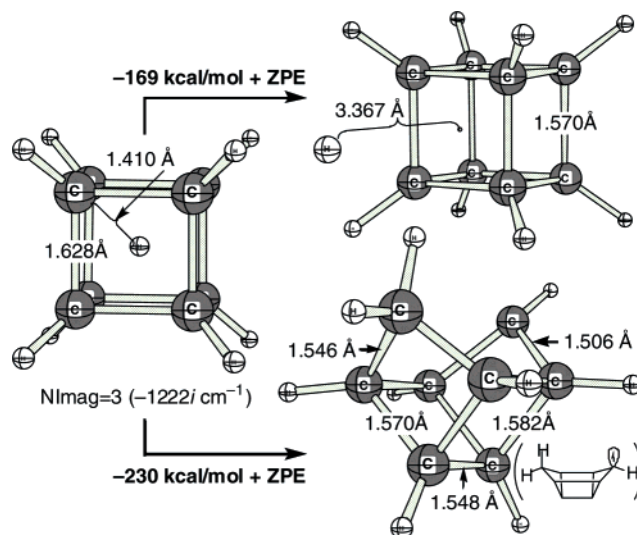
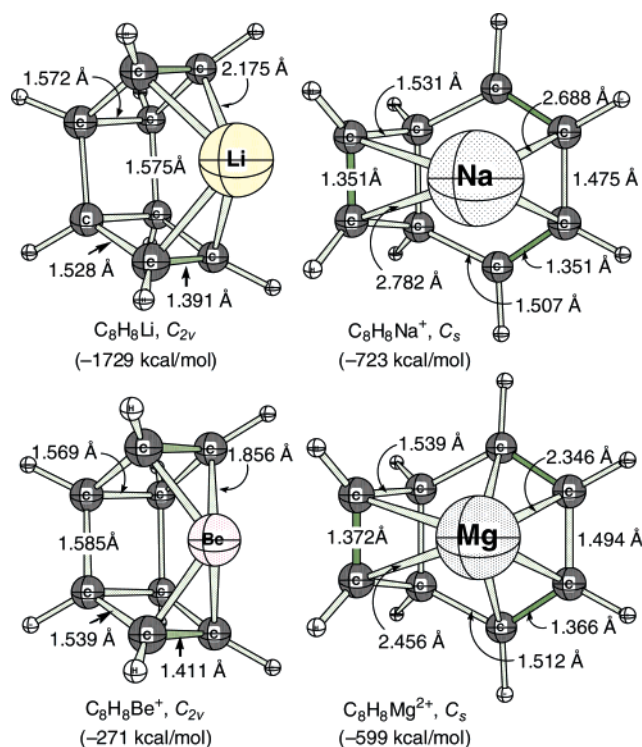
**Figure 3.** H⁺@C₄H₄ (T_d) higher order stationary point structure (NImag = 5) and its C_s symmetric C₄H₅⁺ cage-ruptured, isomeric minimum that is 331 kcal/mol more stable.**Figure 4.** The H⁺@C₈H₈ higher order stationary point structure and its C₈H₉⁺ cage-ruptured, isomeric minima.

Figure 3, which is 331 kcal/mol lower in energy than its endohedral T_d isomer.

X@C₈H₈ (O_h). With the exception of He@C₈H₈, Li⁺@C₈H₈, and Be²⁺@C₈H₈, all other O_h cubane endohedral species are higher order stationary points leading to cage rupture. Like tetrahedrane, the dearth of endohedral complex minima is mainly due to cubane's small internal cavity (1.368 Å³; Table 1) and highly unfavorable strain (~159 kcal/mol).⁶¹ Endohedral protonated cubane has three imaginary frequencies (triple degenerate 1486i cm⁻¹), and its cage-ruptured C₈H₉⁺ isomer is 203 kcal/mol more stable (Figure 4). H@C₈H₈ also has three imaginary frequencies (triple degenerate 1222i cm⁻¹) which lead, as shown in Figure 5, to C_{4v} expulsion of the endohedral hydrogen via a cubane face. The dissociated H and C₈H₈ complex is 169 kcal/mol more stable than O_h H@C₈H₈, but 60 kcal/mol less stable than an alternative cage-ruptured C_s minima, with a hydrogen inserted into a C–C bond. The ruptured cubane metal, cation, and dication complexes fall into the C_{2v} (Li, Be⁺, Na, Mg) and C_s (Be, Na, Mg, Na⁺, Mg⁺, Mg²⁺) symmetric structural categories shown in Figure 6. They are much lower (> 100 kcal/mol) in energy than their O_h endohedral higher order stationary point isomers. The NICS values at the C_{2v} and C_s complex ring centers (see Figure 7) are negative (diatropic) for

**Figure 5.** The H@C₈H₈ (O_h) higher order stationary point structure, which leads to a C_{4v} exohedral H+C₈H₈ minimum. A C_s cage-ruptured C₈H₉ structure also was located.**Figure 6.** Examples of cage-ruptured cubane complexes and their energies relative to their endohedral complexes which are higher order stationary points.

three-membered rings (3MR) and positive (paratropic) for four-membered rings (4MR), as expected from calculations on the cyclopropane, cyclobutane, etc. parent molecules.⁶²

He@C₈H₈, Li⁺@C₈H₈, and Be²⁺@C₈H₈ are O_h endohedral minima. In contrast to Be²⁺@C₈H₈, which is ~70 kcal/mol more stable than its isolated components, the He@C₈H₈ and Li⁺@C₈H₈ inclusion energies shown in Table 2 are >200 kcal/mol endothermic. Furthermore, Li⁺ and Be²⁺ have relatively large exothermic exohedral cubane binding energies, and all three endohedral complexes are > 150 kcal/mol unfavorable relative

(62) Moran, D.; Manoharan, M.; Heine, T.; Schleyer, P. v. R. *Org. Lett.* **2003**, *5*, 23.

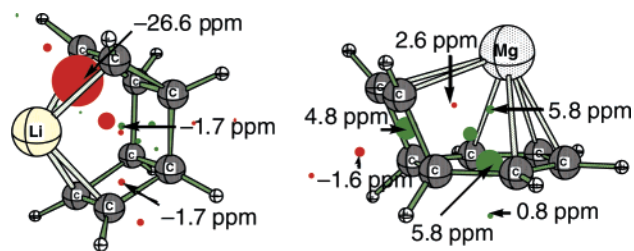


Figure 7. C_8H_8Li (C_{2v} ; left) and $C_8H_8Mg^{2+}$ (C_s ; right) nucleus independent chemical shifts (NICS).

Table 2. Symmetry-Optimized C_8H_8 (O_h), C_8H_{14} (D_{3d}), and $C_{10}H_{16}$ (T_d) Endohedral Complex Minima Inclusion, Binding, and Isomerization Energies and the Natural Charge on the Endohedral Species

	E_{inc} (kcal/mol)	E_{bind} (kcal/mol)	E_{isom} (kcal/mol)	charge X@
He@ C_8H_8	332.3	0.1	-332.1	0.13
Li+@ C_8H_8	245.1	-26.6	-271.8	0.60
Be ²⁺ @ C_8H_8	-69.8	-222.0	-152.2	1.46
He@ C_8H_{14}	214.2	0.1	-214.1	0.09
Li@ C_8H_{14}	178.9	-0.1	-178.9	0.33
Li+@ C_8H_{14}	103.7	-26.3	-130.0	0.75
Be ²⁺ @ C_8H_{14}	-208.3	-230.0	-21.8	1.63
H@ $C_{10}H_{16}$	101.2	-0.3	-101.5	0.23
He@ $C_{10}H_{16}$	159.9	-0.2	-160.2	0.09
Ne@ $C_{10}H_{16}$	364.5	-2.5	-367.0	0.12
Li@ $C_{10}H_{16}$	144.9	-0.5	-145.4	0.25
Li+@ $C_{10}H_{16}$	60.0	-23.8	-83.8	0.72
Na@ $C_{10}H_{16}$	359.1	-0.4	-359.5	0.15
Na+@ $C_{10}H_{16}$	284.7	-14.8	-299.5	0.76
Be@ $C_{10}H_{16}$	225.2	-0.4	-225.6	1.51
Be+@ $C_{10}H_{16}$	57.2	-50.5	-107.7	1.58
Be ²⁺ @ $C_{10}H_{16}$	-235.5	-245.1	-9.5	1.69
Mg ²⁺ @ $C_{10}H_{16}$	62.7	-117.7	-180.4	1.75

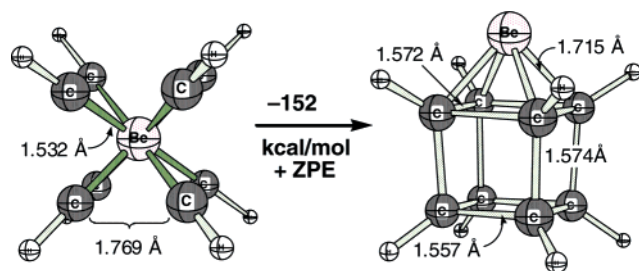


Figure 8. Endohedral and exohedral $C_8H_8Be^{2+}$ isomers and their relative energy, which is referred to in this paper as the “isomerization energy”.

to their exohedral complexes (see Figure 8). Overall, cubane is an unsuitable host, irrespective of the size or charge of the guest.

X@ C_8H_{14} (D_{3h}). With the exception of He, Li, Li⁺, and Be²⁺, no other species are minima when encapsulated by D_{3h} symmetric C_8H_{14} . A proton at the cage center is a third-order stationary point (doubly degenerate $1260i$ cm^{-1} and $759i$ cm^{-1}), with the primary mode leading to C_{2v} H⁺ expulsion (Figure 9) and the minor imaginary frequency corresponding to rapid ($759i$ cm^{-1}) proton oscillation between the cage bridgehead carbons. A hydrogen atom at the cage center also is a third-order stationary point, corresponding to the hydrogen atom oscillation between bridgehead carbons ($109i$ cm^{-1}) and C_{2v} hydrogen expulsion from the cage (doubly degenerate $104i$ cm^{-1} ; same motion as shown in Figure 9 for H⁺ expulsion). Following the mode of the first imaginary vibrational frequency of D_{3h} , H@ C_8H_{14} leads to a C_s cage-ruptured first-order stationary point

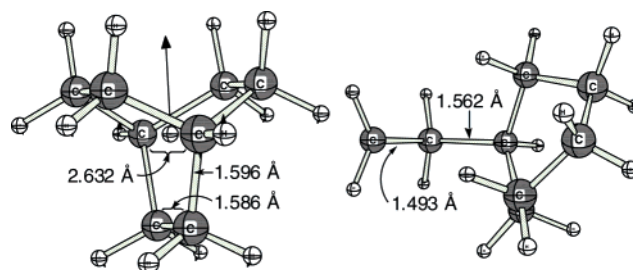


Figure 9. (Left) The H⁺@ C_8H_{14} (D_{3h}) third-order stationary point and its first imaginary mode ($1260i$ cm^{-1}) which corresponds to proton expulsion. (Right) Mode following the H@ C_8H_{14} (D_{3h}) first imaginary frequency ($109i$ cm^{-1}) leads in two steps to a cage-ruptured C_1 minima, which is 127 kcal/mol more stable than its D_{3h} parent.

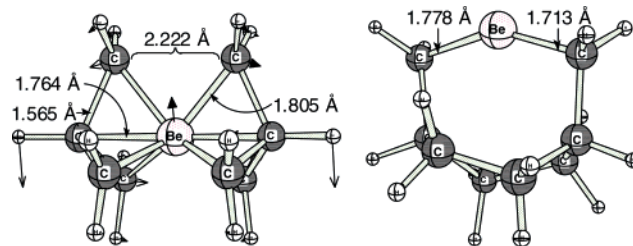


Figure 10. (Left) The first imaginary mode ($1362i$ cm^{-1}) of the second-order stationary point structure Be⁺@ C_8H_{14} (D_{3h}). (Right) Following the mode leads to the Be⁺ inserting into a cage C–C bond cage; the C_1 structure shown is 99 kcal/mol more stable than its D_{3h} parent.

($134i$ cm^{-1}), which is 121 kcal/mol lower in energy than its D_{3h} isomer. The C_s C_8H_{14} imaginary mode corresponds to ring twisting and leads to a C_1 twist boat minimum with a hyperconjugatively stabilized ethenyl radical substituent (see Figure 9), which is an additional 5 kcal/mol more stable than its D_{3h} endohedral parent isomer. Mode following the first D_{3h} H⁺@ C_8H_{14} imaginary frequency leads to an analogous cage-ruptured structure, 60 kcal/mol more stable than its D_{3h} parent isomer.

The remaining endohedral D_{3h} X@ C_8H_{14} complexes are at least second-order stationary points, with the cages split in half as shown for Be⁺@ C_8H_{14} (doubly degenerate $1362i$ cm^{-1}) in Figure 10. In the case of D_{3h} Ne@ C_8H_{14} , the 2.222 Å separation between cage halves shown in Figure 10 increases to 4.154 Å, and the limits of encapsulation are clearly demonstrated. Mode following and C_1 optimization for the beryllium and magnesium cation and dication systems lead to their insertion into non-bridgehead C–C bonds, as shown for $C_8H_{14}Be^+$ in Figure 10.

X@ $C_{10}H_{16}$ (T_d). The moderately sized adamantane^{47–49} molecule is possibly the most enigmatic host cage computed in this study, as the majority of adamantane endohedral complexes are minima (see Table 2). Species which are not T_d minima at the cage center include Ar (NImag = 9), Mg (NImag = 5), and Mg⁺ (NImag = 3), as they are too large to fit inside the $C_{10}H_{16}$ host. Internally protonated adamantane also is a third-order stationary point (triple degenerate $1396i$ cm^{-1}), leading to proton attack of a nonbridgehead cage carbon and the formation of secondary carbocation minima 67 kcal/mol lower in energy than its endohedral parent (Figure 11). Placing an endohedral proton C_{3v} along a three-fold axis of symmetry and optimizing did not lead to proton expulsion via a cage face as expected, but located a second-order stationary point (doubly degenerate $1342i$ cm^{-1}) that also leads to proton attack on a nonbridgehead cage carbon.

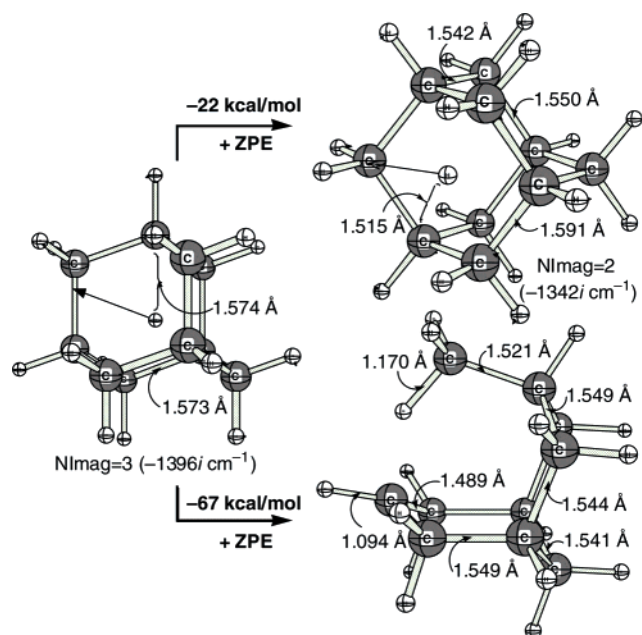


Figure 11. The $\text{H}^+@C_{10}\text{H}_{16}$ (T_d) third-order stationary point structure leading to a C_{3v} face localized second-order stationary point structure (top right) and C_s symmetric cage-ruptured $C_{10}\text{H}_{17}^+$ minima (bottom right).

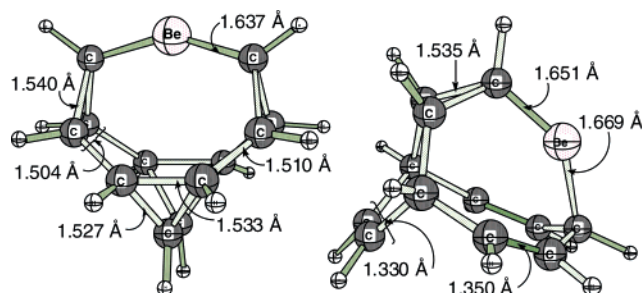


Figure 12. The $\text{Be}@C_{12}\text{H}_{12}$ (T_d) complex is a third-order stationary point. Mode following leads to the C_{2v} (left) and C_s (right) $C_{12}\text{H}_{12}\text{Be}$ complexes shown, which are 252 and 262 kcal/mol, respectively, more stable than their endohedral isomer.

$\text{X}@C_{12}\text{H}_{12}$ (T_d). Despite its increased internal cavity (Table 1), fewer endohedral species are minima at the $C_{12}\text{H}_{12}$ cage center as compared to adamantane (see Table 2). Species which are not T_d minima at the cage center include Ar (NImag = 5) and Be (NImag = 3), while Na, Mg, and Mg^+ T_d endohedral complex geometry optimizations failed to converge. An endohedral argon atom roughly exits the cage via an edge (i.e., no C–C bonds are broken) without barrier. In contrast, an endohedral Be inserts into a cage C–C bond, as shown in Figure 12, to form a C_{2v} symmetric complex favored by 252 kcal/mol. Relaxing symmetry constraints and reoptimizing the C_{2v} symmetric $C_{12}\text{H}_{12}\text{Be}$ structure lead to a C_s minimum, a further 10 kcal/mol (i.e., 262 kcal/mol total) more stable than the T_d third-order stationary point. NICS values at the C_{2v} and C_s $C_{12}\text{H}_{12}\text{Be}$ cage and ring centers (Figure 13) show the shielding effects due to the 3MRs,⁶² with the later possessing an aromatic (–11.1 ppm) cage center.

As expected from the smaller host cage rearrangements (*vide supra*), internally protonated $C_{12}\text{H}_{12}$ is a third-order T_d stationary structure (triply degenerate $1467i$ cm^{-1}) corresponding to proton attack on a strained cyclopropane C–C bond (see Figure 14). With two double bond centers forming and the cation center localizing in a cyclopropenium moiety, the $C_{12}\text{H}_{13}^+$ cage

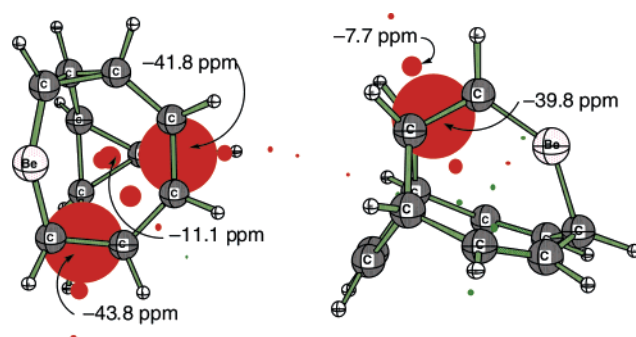


Figure 13. C_{2v} (left) and C_s (right) $C_{12}\text{H}_{12}\text{Be}$ NICS.

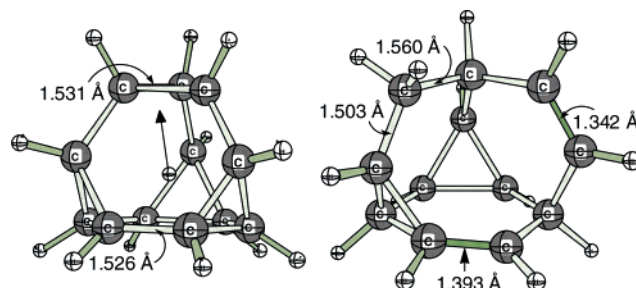


Figure 14. (Left) $\text{H}^+@C_{12}\text{H}_{12}$ (T_d) is a third stationary structure (triply degenerate $1467i$ cm^{-1}) corresponding to proton attack of the strained cyclopropane C–C bond. (Right) Mode following leads to a C_1 cage-ruptured structure 149 kcal/mol lower in energy.

ruptures, and the new structure is 149 kcal/mol more stable than its T_d endohedral isomer.

$C_{12}\text{H}_{12}$ offers three (3MRF)- and six (6MRF)-membered ring cage faces for coordination with exohedral species. He and Ne weakly prefer 3MRF coordination by 0.1 and 0.6 kcal/mol, respectively. Hydrogen and lithium atoms have a weak (3.3 and 3.8 kcal/mol, respectively) preference for the 6MRF, while charged species strongly favor (>20 kcal/mol) the larger cage face; Li^+ , Na^+ , Be^{2+} , and Mg^{2+} favor the 6MRF by 28, 19, 88, and 61 kcal/mol, respectively.

$\text{X}@C_{16}\text{H}_{16}$ (D_{4d}). The majority of endohedral $\text{X}@C_{16}\text{H}_{16}$ species have D_{4d} minima. The expected (*vide supra*) exceptions are mostly higher order saddle points leading to $C_{16}\text{H}_{16}$ cage rupture: H^+ (NImag = 2, cage rupture); Be (NImag = 3, cage rupture); Mg^+ (NImag = 2, cage rupture); and Mg (geometry optimization failed to converge). Unexpectedly, neither Be^+ ($2604i$ cm^{-1} and doubly degenerate $532i$ cm^{-1}) nor Be^{2+} ($257i$ cm^{-1}) are minima at the cage center; however, following their primary imaginary modes leads to the C_{4v} face localized minima shown in Figure 15. This is the same behavior as that for $\text{Be}^+@C_{20}\text{H}_{20}$ and $\text{Be}^{2+}@C_{20}\text{H}_{20}$, which in preference to I_h cage-centered structures are C_{5v} symmetrically localized against an interior dodecahedrane face.¹¹ The tendency for small species to face localize was tested by placing an endohedral helium atom against a four-membered ring cage face, in the same geometry as was observed for C_{4v} $\text{Be}^{2+}@C_{16}\text{H}_{16}$. However, optimization results in movement of the helium atom back to the cage center; that is, an approximately D_{4d} structure develops. $\text{Be}@C_{16}\text{H}_{16}$ is a D_{4d} minimum, although it spontaneously dissociates into a (cyclobutadiene)Be(*nido*- $C_{12}\text{H}_{12}$) upon C_{4v} geometry optimization (see Supporting Information).

Endohedrally protonated $C_{16}\text{H}_{16}$ undergoes a variety of interesting rearrangements, as shown in Figure 16. At the cage center (D_{4d}), the proton encapsulating complex is a second-order

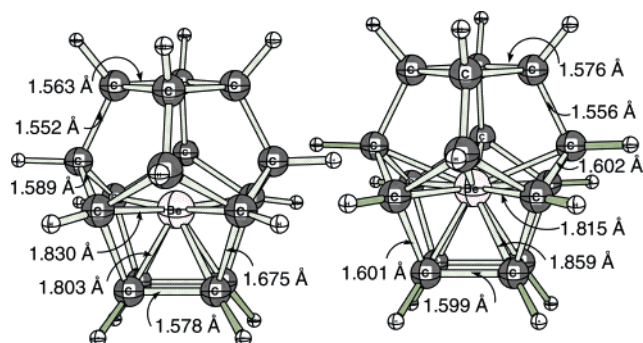


Figure 15. Face localized $\text{Be}^+@C_{16}H_{16}$ (left) and $\text{Be}^{2+}@C_{16}H_{16}$ (right) C_{4v} symmetric minima. They are 10 and 2 kcal/mol, respectively, more stable than their D_{4d} cage-centered isomers.

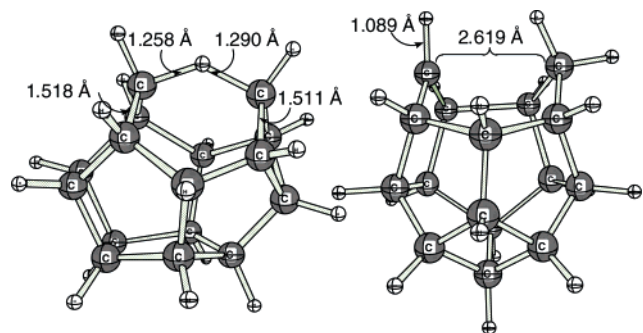


Figure 16. C_s (left) and C_1 (right) $C_{16}H_{17}^+$ minima. They are 90 and 109 kcal/mol, respectively, more stable than their D_{4d} cage-centered $\text{H}^+@C_{16}H_{16}$ isomer.

stationary point (doubly degenerate $1612i\text{ cm}^{-1}$) with the imaginary modes corresponding to proton attack of an “equatorial” C–H carbon. Mode following leads to a C_s minimum with a structure very similar to that of protonated dodecahedrane, $C_{20}H_{21}^+$ (C_{2v}), in which the proton symmetrically bridges two carbon atoms.¹⁷ With an endohedral proton against a four-membered ring cage face, in the same geometry as observed for C_{4v} $\text{Be}^{2+}@C_{16}H_{16}$, optimization results in barrierless proton migration through the face to the cage exterior, that is, exohedral coordination. An endohedral hydrogen atom placed against a four-membered ring cage face, however, simply moves back to the cage center, reproducing the D_{4d} symmetric minimum structure. The exohedral $C_{16}H_{16}$ bound proton structure also is a second-order stationary point (doubly degenerate $916i\text{ cm}^{-1}$); mode following leads to a C_1 , cage-ruptured minimum 109 kcal/mol more stable than its endohedral D_{4d} cage-centered $\text{H}^+@C_{16}H_{16}$ isomer.

$C_{16}H_{16}$ also has two different kinds of exterior faces, incorporating four (4MRF)- and five (5MRF)-membered rings, to which exohedral species can coordinate. The small species H and He weakly prefer 4MRF coordination, while neon, lithium, and sodium atoms have a weak preference for the 5MRF. Charged species favor the larger cage face with Li^+ , Na^+ , Be^+ , Be^{2+} , and Mg^{2+} 5MRF binding energies of -3.8 , -2.6 , -6.6 , -24.5 , and -12.0 kcal/mol, respectively.

Complex Stabilities. The theoretical inclusion, binding, and isomerization energies are summarized in Tables 2 and 3. The inclusion energies are related to the size and charge of the endohedral species and the volume of host cavity. The latter point is demonstrated in Figure 17, which shows He and Li^+ inclusion energies plotted as a function of cage volume (the volume is calculated using the distance from the cage center to

Table 3. Symmetry-Optimized $C_{12}H_{12}$ (T_d) and $C_{16}H_{16}$ (D_{4d}) Endohedral Complex Minima Inclusion, Binding, and Isomerization Energies and the Natural Charge on the Endohedral Species

	E_{inc} (kcal/mol)	E_{bind} (kcal/mol)	E_{isom} (kcal/mol)	charge X@
$\text{H}@C_{12}H_{12}$	86.4	-3.5	-89.9	0.15
$\text{He}@C_{12}H_{12}$	119.3	-0.1	-119.4	0.07
$\text{Ne}@C_{12}H_{12}$	287.0	-2.3	-289.3	0.12
$\text{Li}@C_{12}H_{12}$	143.4	-3.6	-147.0	0.21
$\text{Li}^+@C_{12}H_{12}$	50.2	-47.7	-97.8	0.73
$\text{Na}^+@C_{12}H_{12}$	237.2	-31.0	-268.2	0.80
$\text{Be}^{2+}@C_{12}H_{12}$	-181.2	-290.0	-108.8	1.75
$\text{Mg}^{2+}@C_{12}H_{12}$	45.0	-154.6	-199.7	1.77
$\text{H}@C_{16}H_{16}$	65.2	0.0	-65.2	0.13
$\text{He}@C_{16}H_{16}$	90.3	-0.1	-88.2	0.06
$\text{Ne}@C_{16}H_{16}$	207.3	-4.7	-212.0	0.12
$\text{Ar}@C_{16}H_{16}$	548.0	-0.9	-546.1	0.46
$\text{Li}@C_{16}H_{16}$	105.8	-0.8	-106.5	0.28
$\text{Li}^+@C_{16}H_{16}$	13.3	-35.0	-48.3	0.70
$\text{Na}@C_{16}H_{16}$	237.9	0.0	-237.9	0.16
$\text{Na}^+@C_{16}H_{16}$	157.5	-21.5	-179.1	0.75
$\text{Be}^+@C_{16}H_{16}^a$	31.8	-59.6	-91.4	1.59
$\text{Be}^{2+}@C_{16}H_{16}^a$	-239.2	-257.1	-17.8	1.73
$\text{Mg}^{2+}@C_{16}H_{16}$	-37.7	-130.6	-92.9	1.65

^a C_{4v} minimum.

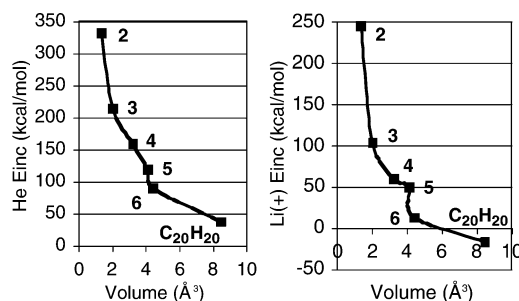


Figure 17. Relationship between cage volume and helium and lithium inclusion energies. The different cages are distinguished by the labels 2–6 (see Figure 1). Cage volumes were calculated using the distance from cage centers to the midpoints of the closest adjacent C–C bonds.

the midpoint of the nearest C–C bond). For both neutral (closed shell) helium and lithium cation, the inclusion energies smoothly decrease as the cage volume increases from 1.4 (C_3H_8) to 8.5 Å^3 ($C_{20}H_{20}$). There is no evidence of cage strain effects, that is, cages with different intrinsic strain energies having particularly poor inclusion energies, although qualitatively cage strain energies are indicative of the maximum species size a cage can encapsulate (*vide infra*). For example, $C_{12}H_{12}$ has a large strain energy (101 kcal/mol),⁵⁰ and yet there is a linear relationship ($R = 0.997$) between its E_{inc} and those for $C_{10}H_{16}$, which is only strained by 7 kcal/mol⁵⁰ (see Figure 18).

Dodecahedrane encapsulation of hydrogen ($E_{\text{inc}} = 36$ kcal/mol)¹⁷ and helium ($E_{\text{inc}} = 38$ kcal/mol)¹⁷ is much preferred to encapsulation by $C_{16}H_{16}$ or smaller cages. The $C_{10}H_{16}$ endohedral complex inclusion energies increase in the series (Figure 19): Be^{2+} ($E_{\text{inc}} = -236$ kcal/mol) > Li^+ ($E_{\text{inc}} = 60$ kcal/mol) > H ($E_{\text{inc}} = 101$ kcal/mol) > Li ($E_{\text{inc}} = 145$ kcal/mol) > He ($E_{\text{inc}} = 160$ kcal/mol). The surprising preference for lithium metal encapsulation as compared to helium is explained by its significant (+0.25 electrons) positive partial charge. Isomerization energies are always exothermic, and exohedral coordination is preferred to endohedral encapsulation without exception. Of note are $\text{Be}^{2+}@C_8H_{14}$ ($E_{\text{isom}} = -22$ kcal/mol), $\text{Be}^{2+}@C_{10}H_{16}$ ($E_{\text{isom}} = -10$ kcal/mol), $\text{Li}^+@C_{16}H_{16}$ ($E_{\text{isom}} = -45$ kcal/mol),

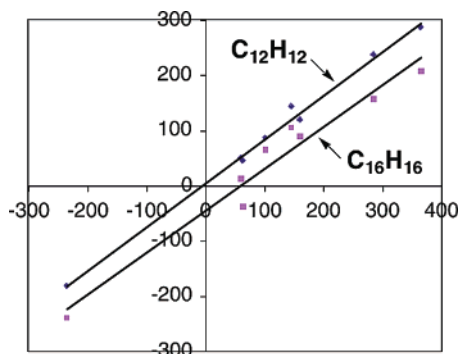


Figure 18. $C_{12}H_{12}$ and $C_{16}H_{16}$ inclusion energies (kcal/mol) plotted versus the $C_{10}H_{16}$ inclusion energies (kcal/mol) summarized in Tables 2 and 3. The highly correlated ($r \geq 0.98$) lines of best fit highlight the lack of relationship between intrinsic cage strain and endohedral complex inclusion energy.

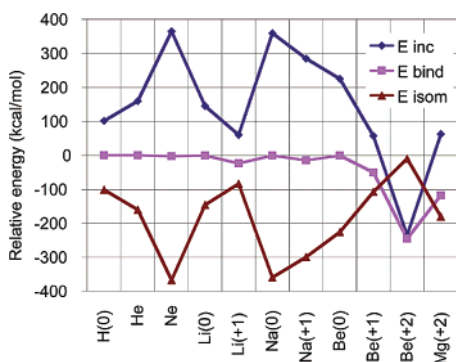


Figure 19. Adamantane inclusion, binding, and isomerization energy trends.

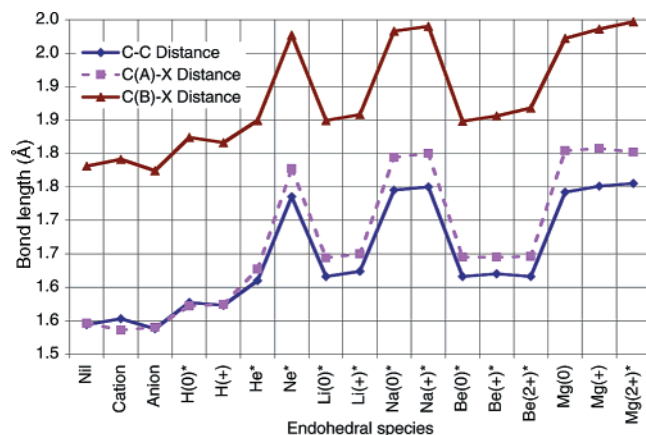


Figure 20. Endohedral T_d $C_{10}H_{16}$ derivative bond length trends.

and $Be^{2+}@C_{16}H_{16}$ ($E_{isom} = -18$ kcal/mol), which are stabilized by the combination of strong charge polarization stabilization and the relatively small endohedral species radii (Be^{2+} , after all, is the smallest possible metal cation, followed by Li^+). $Be^{2+}@C_{20}H_{20}$ (C_{5v}) also has an exothermic isomerization energy ($E_{isom} = -17$ kcal/mol),¹¹ although the dodecahedrane complex has a large inclusion energy (-236 kcal/mol), Be^{2+} binds the $C_{20}H_{20}$ cage exterior more tightly, and hence its isomerization energy is unfavorable.

Optimized Geometries. $X@C_{10}H_{16}$, $X@C_{12}H_{12}$, and $X@C_{16}H_{16}$ -optimized C–C bond lengths are summarized graphically in Figures 20–22, respectively. Reviewing these plots, it is obvious that cage C–C bond lengths are shorter when hosting a neutral metal as compared to its corresponding cation/dication. For example, the C–C bond length of $Li@C_{10}H_{16}$ is

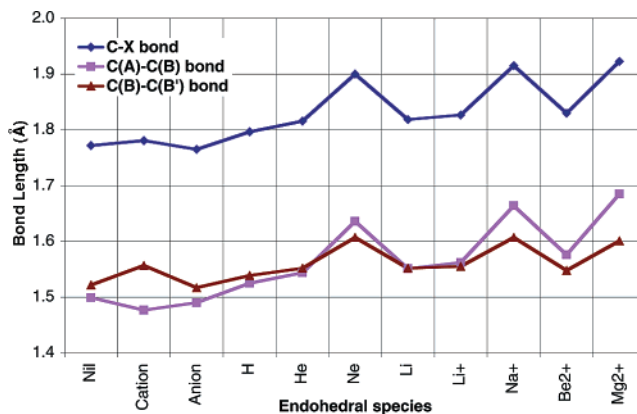


Figure 21. Endohedral T_d $C_{12}H_{12}$ complex C–C and CX bond lengths.

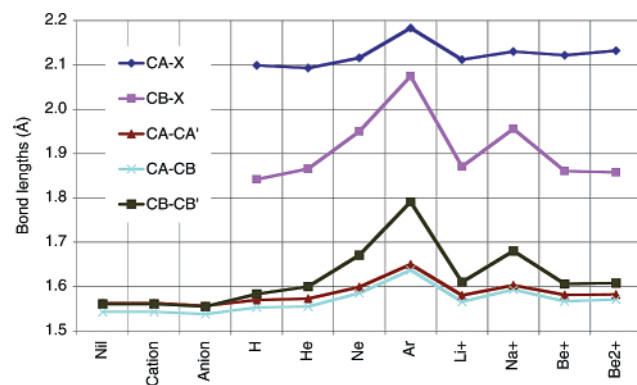


Figure 22. Endohedral $C_{16}H_{16}$ complex C–C and CX bond lengths.

1.616 Å, while that of $Li^+@C_{10}H_{16}$ is 1.624 Å. Previously,¹¹ we observed analogous behavior for the optimized geometries of $X@C_{20}H_{20}$ endohedral complexes, which was caused by donation of electron density from the encapsulated metal atom into their C–C bonding and C–H antibonding endohedral complex highest occupied molecular orbitals (HOMOs). Note that these HOMOs had structures closely resembling the lowest unoccupied molecular orbital (LUMO) of dodecahedrane. Surveying Tables 2 and 3, it is clear that, independent of the cage, encapsulated metals (Li, Na, Be) are significantly ionized through charge donation to the host. Hence the same molecular orbital argument explains the trend of $C_{10}H_{16}$, $C_{12}H_{12}$, and $C_{16}H_{16}$ cages becoming more compact upon metal encapsulation, as all three cages have C–C bonding and C–H antibonding LUMOs (see Figure 23). The optimized geometries of cage-encapsulated noble gas atoms are more straightforward and increase on going from He to Ne, as expected due to their increasing atomic radii down the periodic table.

When comparing $C_{10}H_{16}$, $C_{12}H_{12}$, and $C_{16}H_{16}$, there is a qualitative relationship between cage strain, internal volume, and potential to form an endohedral complex potential energy minima. This is best illustrated using examples and by focusing on adamantane, which is strained by a mere 6.6 kcal/mol⁶³ and has a moderate endohedral volume of ~ 3.2 Å³. T_d symmetric $C_{10}H_{16}$ is able to form endohedral complexes with large metal species such as Na and Be, while strained (101 kcal/mol)⁵⁰ $C_{12}H_{12}$, in contrast, which has a larger internal cavity (~ 4.1 Å³), ruptures when species larger than Ne and Li are placed inside, with large associated enthalpic gains. $C_{16}H_{16}$, the largest

(63) Schleyer, P. v. R.; Williams, J. E.; Blanchard, K. R. *J. Am. Chem. Soc.* **1970**, *92*, 2377.

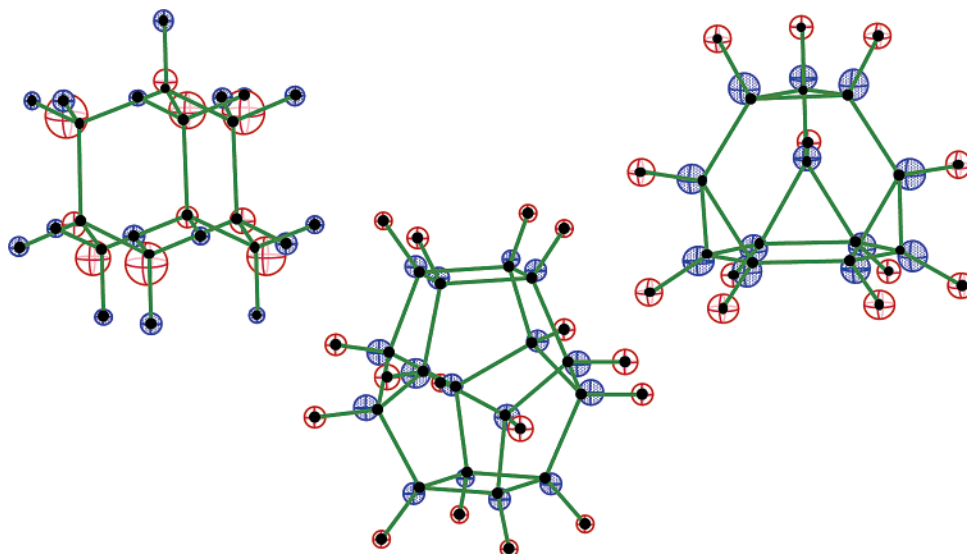


Figure 23. T_d $C_{10}H_{16}$ (left; A_1), T_d $C_{12}H_{12}$ (right; A_1), and D_{4d} $C_{16}H_{16}$ (center; B_2) lowest unoccupied molecular orbitals (LUMOs). Note that they are C–C bonding and C–H antibonding.

($\sim 4.4 \text{ \AA}^3$) cage computed herein, encapsulates large species up to and including Ar, reflecting its relatively generous host cavity.

Excluding highly reactive proton and hydrogen moieties, which tend to destroy their hosts from the inside out, the situation for the smaller cages C_4H_4 , C_8H_8 , and C_8H_{14} is more straightforward. Tetrahedrane is highly strained (141 kcal/mol)⁶¹ and has a relatively small internal volume ($\sim 0.2 \text{ \AA}^3$); hence all encapsulation ruptures the cage due to either mechanical effects or polarization of the bent⁶¹ bonds. Cubane also is highly strained (159 kcal/mol);⁶¹ however, it has sufficient volume ($\sim 1.2 \text{ \AA}^3$) to encapsulate very small species He, Li^+ , and Be^{2+} . In contrast with C_4H_4 and C_8H_8 , bicyclo[2.2.2]octane is strained by a mere 11 kcal/mol⁶¹ and has a volume of $\sim 2.0 \text{ \AA}^3$. It is able to encapsulate Li in addition to He, Li^+ , and Be^{2+} and further exemplifies the encapsulation size effect highlighted by adamantane. Bicyclo[2.2.2]octane also illustrates that cage structure affects endohedral complex formation, as its non-bridgehead C–C bonds are exposed to endohedral electrophilic attack (see Figure 10 for examples of what happens) and the relatively large “windows” into the C_8H_{14} interior allow species to migrate out of the endohedral space (*vide supra*).

The proton affinities of the ruptured cages are as follows: 331 kcal/mol (C_4H_4); 230 kcal/mol (C_8H_8); 60 kcal/mol (C_8H_{14}); 67 kcal/mol ($C_{10}H_{16}$); 149 kcal/mol ($C_{12}H_{12}$); and 90 kcal/mol ($C_{16}H_{16}$). For comparison, the proton affinity (PA) of protonated dodecahedrane, $C_{20}H_{21}^+$ (C_{2v}), in which the proton bridges two carbon atoms symmetrically, is 185 kcal/mol;¹⁷ protonated ethane also has a proton-bridged C–C bond, but with a lower PA (143 kcal/mol).⁶⁴ The difference in PA between $C_{20}H_{20}$ and C_2H_6 is due to dodecahedrane’s superior ability to disperse the resulting positive charge. In addition to size effects, there also is an important contribution from strain to C_4H_4 – $C_{16}H_{16}$ PA trends.

Ionization Potentials. Adiabatic ionization potentials (IP) for Li, Na, Be, and Be^+ endohedral complexes are summarized in Table 4. The IPs of encapsulated species are reduced consider-

Table 4. Adiabatic Ionization Potentials for Free and Cage Encapsulated Metals (eV)

X	exp. ^a	free	C_8H_4	$C_{10}H_{16}$	$C_{12}H_{12}$	$C_{16}H_{16}$
$Li \rightarrow Li^+ + e^-$	5.39	5.61	2.23	1.83	1.32	1.44
$Na \rightarrow Na^+ + e^-$	5.14	5.42		2.11		1.85
$Be \rightarrow Be^+ + e^-$	9.32	9.11		1.45		
$Be^+ \rightarrow Be^{2+} + e^-$		18.59		5.48		6.83

^a NIST Physics Laboratory – Physical Reference Data (www.nist.gov/chemistry).

ably relative to the free metal. This is consistent with our previous¹¹ results where Li, Na, Be, and Mg $X@C_{20}H_{20}$ first ionization potentials ranging from 2.7 (62 kcal/mol) to 3.4 eV (86 kcal/mol) were computed. Boldyrev and co-workers^{65–67} defined species with first ionization potentials less than the Cs atom (3.9 eV; 90 kcal/mol) as “superalkalis”, and that label is equally applicable to the metals in Table 4.

Comparison of the IP in Table 4 reveals obvious size effects. For example, the lithium first ionization potentials go down in the series: C_8H_{14} (2.2 eV) > $C_{10}H_{16}$ (1.8 eV) > $C_{12}H_{12}$ (1.3 eV) \approx $C_{16}H_{16}$ (1.4 eV). This trend is explicable in terms of molecular orbital arguments, as C_8H_{14} has less orbitals than $C_{16}H_{16}$, charge-transfer stabilization of its C–C LUMO will be greater, and hence an endohedral metal atom is more stable inside the larger cage. Sodium also has a higher IP when $C_{10}H_{16}$ (2.1 eV) is encapsulated as compared to $C_{16}H_{16}$ (1.9 eV).

Conclusions

As an encapsulating hydrocarbon framework, tetrahedrane has neither practical nor theoretical utility as the highly strained cage always ruptures. The next largest systems computed, C_8H_8 (O_h) and C_8H_{14} (D_{3h}), encapsulated He, Li^+ , and Be^{2+} ; however, their relatively small internal cavities produce highly unfavorable endohedral inclusion energies or endo \rightarrow exo isomerization energies. For example, $Li^+@C_8H_{14}$ (D_{3h}) $E_{inc} = 103.7$ kcal/mol and $E_{isom} = -130.0$ kcal/mol. Cubane and bicyclo[2.2.2]-octane, therefore, do not offer much promise as encapsulating

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hosts either. Endohedrally protonated and hydrogenated cages undergo a myriad of structural rearrangements leading to caged-ruptured minima that are significantly lower (>100 kcal/mol) in energy than their cage-centered endohedral complex isomers, and they are not particularly viable synthetic targets.

The larger endohedral minima include: $T_d X@C_{12}H_{12}$ ($X = H, He, Ne, Li, Li^+, Na^+, Be^{2+},$ and Mg^{2+}); $T_d X@C_{10}H_{16}$ and $D_{4d} X@C_{16}H_{16}$ ($X = H, He, Ne, Li, Li^+, Na, Na^+,$ and Mg^{2+}); cage-centered $Be^{0,+2+}@C_{10}H_{16}$ (T_d) and $Ar@C_{16}H_{16}$ (D_{4d}); and face localized $Be^{+,2+}@C_{16}H_{16}$ (C_{4v}). Endohedral hydrogen and noble gas atoms (He, Ne, and Ar) stretch the cages roughly in proportion to their atomic radii, expanding, for example, the $X@C_{10}H_{16}$ (T_d) C–C bond lengths from 1.577 Å ($H@C_{10}H_{16}$) to 1.735 Å ($Ne@C_{10}H_{16}$). However, the trend is somewhat different, and the cages are slightly more compact when encapsulating metal atoms as compared to their corresponding cations or dications. For example, adamantane C–C bond lengths increase from 1.616 Å ($Li@C_{10}H_{16}$) to 1.624 Å ($Li^+@C_{10}H_{16}$). This is due to donation of electron density from encapsulated metal atoms into the C–C bonding and C–H antibonding endohedral complex HOMOs, which have structures closely resembling the LUMOs of their hosts.

$X@C_{10}H_{16}$, $X@C_{12}H_{12}$, and $X@C_{16}H_{16}$ inclusion energies are most favorable (i.e., <50 kcal/mol) for small, charged Li^+ and Be^{2+} species. The ZPE corrected inclusion energies of $Be^{2+}@C_{10}H_{16}$ (T_d ; -235.5 kcal/mol), $Li^+@C_{12}H_{12}$ (T_d ; 50.2 kcal/mol), $Be^{2+}@C_{12}H_{12}$ (T_d ; -181.2 kcal/mol),

$(T_d$; -45.0 kcal/mol), $Li^+@C_{16}H_{16}$ (D_{4d} ; 13.3 kcal/mol), $Be^+@C_{16}H_{16}$ (C_{4v} ; 31.8 kcal/mol), $Be^{2+}@C_{16}H_{16}$ (D_{4d} ; -239.2 kcal/mol), and $Mg^{2+}@C_{16}H_{16}$ (D_{4d} ; -37.7 kcal/mol) are exothermic or approaching thermoneutral as compared to their isolated components, due to polarization stabilization of these charged complexes. However, all of the endohedral complexes are higher in energy than their corresponding exohedral isomers; that is, exohedral binding is favored over endohedral encapsulation.

Although the prospects for preparing small ($<C_{20}H_{20}$) endohedral hydrocarbon cage complexes are poor, the complexes are not prohibitively unstable as compared to the experimentally known $He@C_{20}H_{20}$ endohedral complex ($E_{inc} = 38.0$ kcal/mol and $E_{isom} = -35.4$ kcal/mol). We conclude that the recipe for a viable endohedral cage complex is low parent cage strain energy, large cage internal cavity volume, and a small, highly charged guest species.

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Supporting Information Available: Absolute energies, zero-point vibrational energies, and optimized endohedral bond lengths and HOMO/LUMO gaps (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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