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Hexa- and Octacoordinate Carbon in Hydrocarbon Cages: Theoretical Design and Characterization

Yang Wang, Yuanhe Huang,* and Ruozhuang Liu[a]

Abstract: A new series of hydrocarbon cages containing hexa- and octacoordinate carbon centers were designed theoretically by performing DFT calculations at the B3LYP/6–311+G** level. Among these non-classical structures that were found to still obey the 8e rule, the two tetracations with octacoordinate carbons may be the first examples found in pure hydrocarbons. Structural characteristics, as well as thermodynamic and kinetic stabilities, were also investigated theoretically for these two octacoordinate tetracations. These hydrocarbon compounds containing hypercoordinate carbon centers provide a challenge for synthetic organic chemists.

Keywords: cage compounds · carboranes · density functional calculations · hydrocarbons · octacoordinate carbon

Introduction

The search for novel structures containing hypercoordinate carbons has received increasing attention from both theoreticians and experimentalists, due to the potentially unique properties of these structures, as well as the importance of fundamental research.[1] Many compounds with planar or nonplanar hypercoordinate carbon centers have been predicted theoretically[2] and exemplified experimentally.[3] Among these compounds, hypercoordinate carbon in a pure hydrocarbon is particularly attractive, for the following reasons: First, hydrocarbons are ordinary organic compounds with many applications. Second, because there are no "hetero" atoms in these compounds, the neighboring atoms contacting with the hypercoordinate carbon center are all carbons, except for some compounds with hydrogen ligands, such as protonated methane[4] and the pyramidal hydrocarbon cations.[5] The hexamethyl derivative of the pyramidal dication $(CH)_5^+$ containing a hexacoordinate carbon atom was prepared[6] in superacid media by using various precursors. Recently, a neutral saturated hydrocarbon cage containing an exact-planar tetracoordinate carbon atom was proposed[7] by computational design, which was expected to have an ionization energy comparable to that of alkali metals. More recently, a hydrocarbon cage dication (**2**, see below) with a nonplanar hexacoordinate carbon atom was also predicted theoretically.[8] However, compounds with all-carbon ligands are still relatively rare among those compounds identified or predicted to contain hypercoordinate carbons. Are there more possible hydrocarbon structures containing hypercoordinate carbons with all-carbon ligands? Moreover, apart from the penta- and hexacoordination of carbon, the examples for octacoordination of carbon are relatively few. Recently, an effectively octacoordinate carbon center in a planar cyclic compound CB_8[9] was predicted computationally. Because CB_8 is highly fluxional and undergoes rapid low-barrier rearrangement among several distorted structures, the central carbon atom in CB_8 is, in fact, linked to only five boron ligands, though it is *effectively* octacoordinate. More recently, an *exact*-octacoordinate carbon center was designed in a carborane sandwich tetraanion $C[(BH)_4]_2^{4-}$.[10] However, this compound is not a pure hydrocarbon. Does an *exact*-octacoordinate carbon with all-carbon ligands indeed exist in the strict sense?

To address these questions, we designed and constructed a series of novel hydrocarbon cages containing hexa- and octacoordinate carbon centers by using a strategy similar to that proposed by Minkin and Minyaev.[11] The structures designed were expected to give the first examples of exact-octacoordinate carbon centers in pure hydrocarbons, and were investigated theoretically. In contrast to previous studies, in which different atoms and cations were squeezed into small hydrocarbon cages,[12] these novel compounds are interesting because they can be considered as hydrocarbon cage complexes incorporating endohedral carbon cations.

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Computational Methods

The geometric optimizations and energy calculations were performed by using the Gaussian 98 program[13] based on the density functional theory (DFT) method. The Becke's three-parameter hybrid functional with the Lee–Yang–Parr correlation functional (B3LYP)[14–16] was used at the 6–311+G** level. Once an optimized geometry was obtained, imaginary frequencies were checked at the same level of theory by vibration analysis to verify the genuine minimum on the potential energy surfaces (PES) and to evaluate zero-point energy correction (ZPE).

The orbital-correlation diagram was obtained by using the CACAO[17] program based on the extended Hückel method (EHMO),[18] which is incorporated in the CACAO package.

Results and Discussion

Structure design and the 8e rule: Two series of hydrocarbon cages with hypercoordinate carbons were designed from two fragments, triangular prism C_6 and cuboid C_8 (Figure 1).

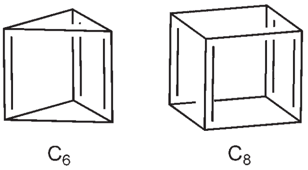
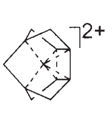
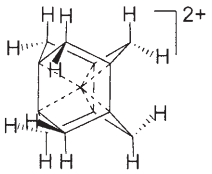


Figure 1. The two basic structural fragments, triangular prism C_6 and cuboid C_8.

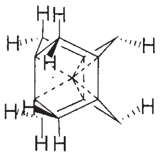
Structures **1**–**7** containing hexacoordinate carbon were constructed from the fragment C_6, and structures **8** and **9** containing octacoordinate carbon were constructed from the fragment C_8. Note that some adjacent carbon atoms in the fragments C_6 and C_8 are linked by CH_2 groups to obtain these hydrocarbon cages. These structures were all confirmed to be energy minima on the PES with no imaginary frequency. Apart from dication **2**, which has already been predicted by Minyaev et al.,[8] all the other structures are proposed for the first time. We wish to stress that structures **8** and **9** are the first pure hydrocarbon structures predicted theoretically to contain exact-octacoordinate carbon atoms.



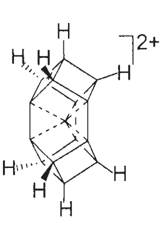
1 (C_{2v})



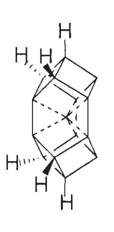
2 (D_{3h})



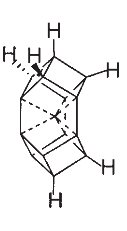
3 (C_{2v})



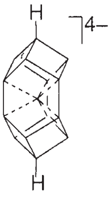
4 (D_{3h})



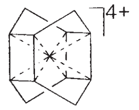
5 (C_{2v})



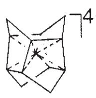
6 (C_s)



7 (D_{3h})



8 (D_{4h})



9 (D_{2d})

Unlike the $2(N+1)^2$ rule for spherical molecules,[19] the electron-counting rule for this series of cage structures is the 8e rule, which is similar to the case in the pyramidal cations and carbon sandwich compounds.[1,9,11] That is, the number of electrons for the multicenter bond formed between the central carbon atom and the peripheral carbon atoms is eight. This can be understood if we consider the multicenter bond as the donor–accepter interaction between the central carbon atom (electron acceptor) and the surrounding C=C bonds (electron donors), as shown in Figure 2. The stabilization of the system requires the eight-electron configuration of the central atom. As a result, among the designed structures derived from the C_6, **1**, **2**, and **4** are all dications, which satisfy the requirements of the 8e rule. In addition, neutral compounds **3** and **5**, **6** are obtained by stripping two H^+ from dications **2** and **4**, respectively. By removing four further H^+ from isomers **5** or **6**, we get tetraanion **7**. Likewise, for the structures derived from the C_8, C^{4+} is introduced into the neutral cage to satisfy the 8e rule, thus, we obtain the octacoordinate tetracations **8** and **9**. We failed to obtain neutral structures with energy minima on the PES by stripping four H^+ from tetracations **8** and **9**. However, we obtained several neutral carboranes (**11**–**14**) with energy minima on the PES after replacing four peripheral carbon atoms of tetracations **8** and **9** by four boron atoms.

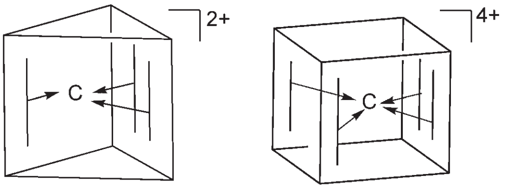


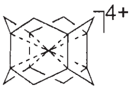
Figure 2. Donor–acceptor interaction interpretation of the multicenter bond.

We considered other possible structures based on the fragments C_6 and C_8. For example, we initially constructed the two simplest structures, C_7^{2+} and C_9^{4+}, by placing C^{2+} and C^{4+} directly into the centers of C_6 and C_8, respectively.

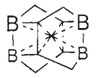
Table 1. Calculated ΔE [kcal mol^{-1}], smallest vibration frequencies $\omega_{\min}$ [cm^{-1}], natural charges on the central carbon atom q [|e|], and WBIs for the C–C bonds between the central and the peripheral carbon atoms.

	Structure	ΔE	$\omega_{\min}$	q	WBI
$C_{13}H_{12}^{2+}$	**2**	456.7	349	+0.172	0.63
$C_{15}H_{8}^{2+}$	**4**	449.9	346	+0.222	0.61
$C_{12}H_{8}^{4+}$	**8**	2041.7	291	−0.248	0.49
$C_{12}H_{8}^{4+}$	**9**	2012.8	354	−0.183	0.49

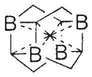
However, both optimized structures have several imaginary frequencies, thus, do not correspond to energy minima on the PES. This is due mainly to the high steric strain induced by the adjacent three- or four-membered rings in the cage framework. In addition, we also considered structure **10** with D_{4h} symmetry. However, **10** was ultimately optimized into a D_{2d} structure with an ordinary tetracoordinate carbon center, possibly because the size of the outer cage of **10** with eight-membered rings is too large to bind a carbon atom in the center stably. Therefore, besides the 8e rule, another crucial factor in the design of hydrocarbon cages with a hypercoordinate carbon center is the size of the hydrocarbon cage, which must be appropriate for the hypercoordinate central carbon to bind inside.



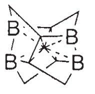
10 (D_{4h})



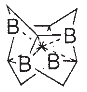
11 (D_{2h})



12 (D_{2d})



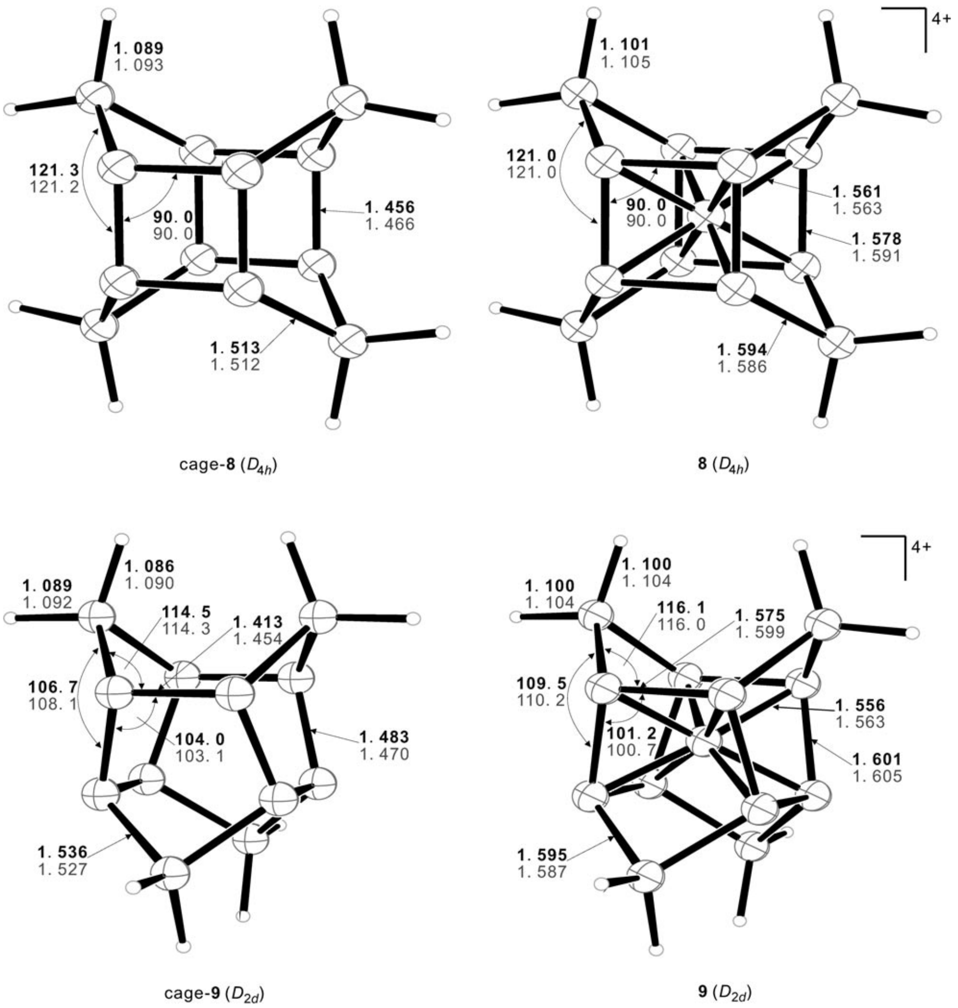
13 (D_2)



14 (S_4)

Theoretical characterizations: Among the hexacoordinate structures, dication **2** was investigated in detail theoretically by using the B3LYP/6–311G** method,[8] and the results are in excellent agreement with those obtained by our B3LYP/6–311+G** calculations. The structure characteristics, stability, and electronic properties for dication **4** are similar to those for dication **2**, as shown in Table 1. Here, we focus on theoretical characterizations for the novel structures **8** and **9** with octacoordinate carbon centers.

The optimized geometries for tetracations **8** and **9** and their corresponding empty cages (denoted as cage-**8** and cage-**9**, respectively) are shown in Figure 3. These geometric structures were also optimized by using the second-order Møller–Plesset perturbation theory (MP2)[20] at the 6–311+G** level. The geometry parameters obtained by the DFT and MP2 methods are indicated by bold and plain text, respectively, in Figure 3. With the exception of the relatively large discrepancies in bond lengths between these two methods for cage-**9** (~0.041 Å) and **9** (~0.024 Å), the differences in bond lengths and angles for the structures shown are less



cage-**8** (D_{4h}) **8** (D_{4h})

cage-**9** (D_{2d}) **9** (D_{2d})

Figure 3. Optimized geometries (bond lengths [Å], bond angles [°]) for structures **8** and **9** and their corresponding empty cages.

than 0.013 Å and 1.4°, respectively. Because the geometry parameters calculated by the DFT method are comparable to those obtained by the MP2 method, the following discussions are based on the DFT results only.

The four C=C bond lengths in cage-**8** and cage-**9** are about 1.46–1.48 Å, and are stretched to about 1.58–1.60 Å in **8** and **9**. The other C−C bonds in the outer cage of **8** and **9** are also elongated upon the encapsulation of C^{4+}, similarly to those in **2**[8] and **4**. Each of the eight C−C bonds between the central atom and the peripheral atoms in **8** and **9** has a bond length of about 1.56 Å, which is close to the length of an ordinary C−C single bond (~1.54 Å). However, natural bond-orbital (NBO)[21] analyses reveal that the Wiberg bond indexes (WBIs)[22] of these C−C bonds are only 0.49 (see Table 1), indicating that these bonds are much weaker than an ordinary C−C single bond. The total WBI for the central carbon atom in **8** and **9** is 3.98 and 4.07, respectively. Hence, the octet rule is not violated for these octacoordinate carbon atoms.

Besides the octacoordinate central carbon, the eight peripheral carbon atoms with an inverted umbrella-like configuration[23] make the structures of **8** and **9** more intriguing. All four carbons attached to the umbrella-like carbon lie on one side of a plane. Thus, the plane drawn through the three carbon atoms attached to the umbrella-like carbon would intersect the central bond that links the fourth carbon atom and the umbrella-like carbon atom. Let us simply call the distance from the intersection point to the umbrella-like carbon center the "inverted distance". The inverted distance of the peripheral carbons in **8** and **9** is 0.51 and 0.58 Å, respectively. Hence, these peripheral carbons have an inverted umbrella-like geometry. Compared with the inverted distance of about 0.1 Å for the bridgehead carbon in the dichloropropellane, the eight peripheral carbons in **8** and **9** seem to be greatly "inverted". As a result, structures **8** and **9** would have considerably high strain energy, which will be discussed in detail below.

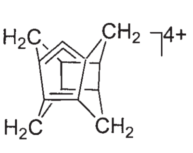
To investigate the thermodynamic stabilities of tetracations **8** and **9**, we considered some possible isomers (**15**–**25**). All of these isomers were calculated to be energy minima on the PES. Table 2 lists the calculated relative energies and the smallest vibration frequencies for tetracations **8** and **9** and their isomers. Among these isomers, the phenalene-like tetracation **24** is probably the global minimum for the $C_{13}H_8^{4+}$ and lies 352 and 404 kcal mol^{-1} below **8** and **9**, respectively. Other planar (**20**, **24**, **25**) or bowl-like (**21**–**23**) structures are at least 300 kcal mol^{-1} lower in energy than **8**. Compared with the above isomers, isomers **15**–**19**, which have cage frameworks, have relatively high energy, due to the strain of the cage. Nevertheless, they are still at least 80 kcal mol^{-1} lower in energy than **8**. Therefore, tetracations **8** and **9** are higher in energy than their isomers. This may be due to the large strain induced by the eight umbrella-like carbons in **8** and **9**.

Table 2. Calculated relative energies E_{rel} [kcal mol^{-1}] and smallest vibration frequencies ω_{min} [cm^{-1}] for the tetracations **8** and **9** and their isomers.

Compound	E_{rel}	ω_{min}	Compound	E_{rel}	ω_{min}
8	−51	291	**20**	−351	73
9	0	354	**21**	−362	131
15	−167	318	**22**	−371	135
16	−147	205	**23**	−357	70
17	−136	192	**24**	−404	113
18	−177	318	**25**	−381	130
19	−156	254			

A better way to estimate the strain energy of the molecule with small rings is to calculate the energy change for an appropriately-designed isodesmic[24] or homodesmotic[25] reaction. Therefore, we calculated the strain energies for the neutral empty cages of **8** and **9**, based on the following homodesmotic reaction:

$$\begin{aligned} & C_{12}H_8\ (\text{cage-}\mathbf{8}\text{ or cage-}\mathbf{9}) + 4\ CH_2{=}CH_2 + 8\ CH_3{-}CH_3 \\ & \rightarrow 4\ H_2C{=}C(CH_3){-}C(CH_3){=}CH_2 + 4\ CH_3{-}CH_2{-}CH_3 \end{aligned} \tag{1}$$



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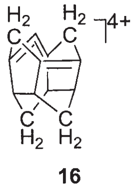

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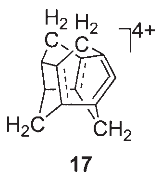

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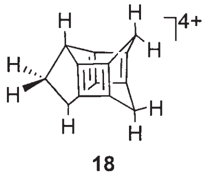

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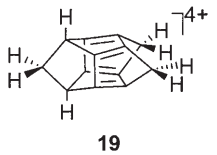

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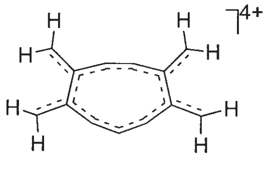

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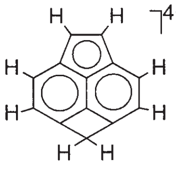

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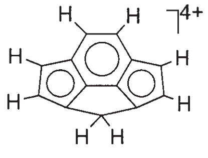

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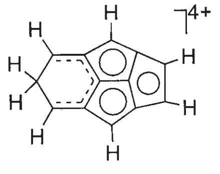

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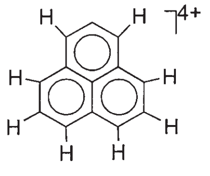

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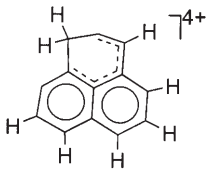

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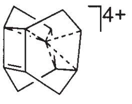
The strain energy is calculated as the energy difference between reagents and products in Equation (1), and was determined for cage-**8** and cage-**9** to be 187 and 209 kcal mol^{-1}, respectively. Another isomer of $C_{12}H_8$, dicubane,[26] has a strain energy of 347 kcal mol^{-1}, which is much higher than that of cage-**8** or cage-**9**, and is in accordance with that (373 kcal mol^{-1}) reported by Minyaev et al.[27] Thus, both cage-**8** and cage-**9** are more stable than dicubane.

It is impossible, however, to describe appropriate homodesmotic reactions for tetracations **8** and **9**, as we could not find any aliphatic hydrocarbon containing an octacoordinate carbon center that could be regarded as one of the products of the homodesmotic reactions. As mentioned above, tetracations **8** and **9** contain eight greatly inverted umbrella-like carbons, each of which would contribute to a considerable strain energy, compared to the strain energies of about 100 kcal mol^{-1} for propellanes.[23] Therefore, tetracations **8** and **9** are of even higher energy than other cage isomers (**15**–**19**).

Although tetracations **8** and **9** are thermodynamically unstable with respect to their isomers, the relatively high values of the smallest vibration frequencies (291 and 354 cm^{-1} for **8** and **9**, respectively) suggest that structures **8** and **9** correspond to relatively deep local minima, which is similar to the case of prismanes.[27] Therefore, we considered whether tetracations **8** and **9** would have relatively high dynamic stabilities. We studied the rearrangement reactions of **8** to **15** and of **9** to **16** and **17**, as shown in Scheme 1, and found that the rearrangement of **8** to **15** has a transition state **26** and an energy barrier of about 15 kcal mol^{-1}. In comparison, there are two possible low-energy-barrier rearrangements for **9**. One is from **9** to **16** through the transition state **27** with an energy barrier of about 6 kcal mol^{-1}, and the other is from **9** to **17** through **28** with a barrier of about 7 kcal mol^{-1}. Both rearrangements have a rather low energy barrier. Furthermore, as both **16** and **17** are about 140 kcal mol^{-1} lower in energy than **9**, the rearrangements of **9** to **16** and **17** are almost irreversible. As a result, tetracation **9** would have a lower kinetic stability. However, for the rearrangement of **8**, the energy barrier of about 15 kcal mol^{-1} is much higher than that for the rearrangements of **9**. Hence, tetracation **8** should be kinetically more stable than **9**. It is expected that tetracation **8** would be kinetically relatively stable, if it can indeed be produced.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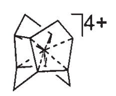
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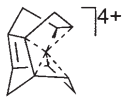
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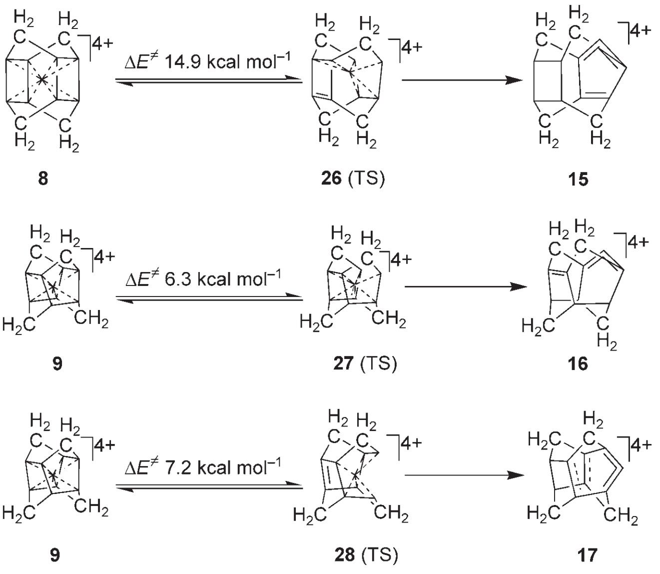

Scheme 1. Rearrangement reactions of **8** to **15** and of **9** to **16** and **17**.

One of the reasons for the relative stability of tetracation **8** is the delocalization of the positive charge of the central C^{4+}. We calculated the energy effect ΔE for the insertion of C^{4+} into the neutral hydrocarbon cage-**8**, with consideration of the zero-point energy correction. As listed in Table 1, the insertion reaction is significantly exothermal, with $\Delta E =$ 2041.7 kcal mol^{-} for tetracation **8**, similar to the case for **2**,[8] **4**, and **9**. The large exothermal effect may be due mainly to the delocalization of the positive charge in the combined system. Results of NBO analyses show that the central carbon atom in tetracation **8** carries a negative charge of -0.248. The positive charges of C^{4+} are transferred and dispersed to the peripheral carbon and the hydrogen atoms. This delocalization of the positive charge accounts for the relative stability of tetracation **8**.

On the other hand, the relative stability of tetracation **8** is also attributed to the formation of a multicenter bond between the central carbon atom and the peripheral carbon atoms. The multicenter bond in **8** was investigated by conducting molecular orbital (MO) analyses to elucidate the octacoordination of the central carbon atom. As shown in the orbital-correlation diagram illustrated in Figure 4, the stability of **8** is due mainly to the two bonding MOs with a_{2u} and e_u symmetries. The a_{2u} bonding MO is formed by the interaction of the a_{2u} MO of the empty cage with the p_z atomic orbital (AO) of C^{4+}. The e_u bonding MO results from the interaction of the e_u MO with the p_x,p_y AOs. Because the e_u MO of **8** is the highest-occupied MO (HOMO) and has the bonding character of the central carbon, the stripping of more electrons from this tetracation would destabilize the system. In fact, the hexacation obtained by removing two electrons from **8** is found to be a second-order saddle point (two negative force constants) on the PES. Similarly, we failed to obtain energy minima on the PES for the dication and neutral structure of **8**, because the lowest-unoccupied MO (LUMO) (b_{1g}) and LUMO+1 (e_g) have antibonding character.

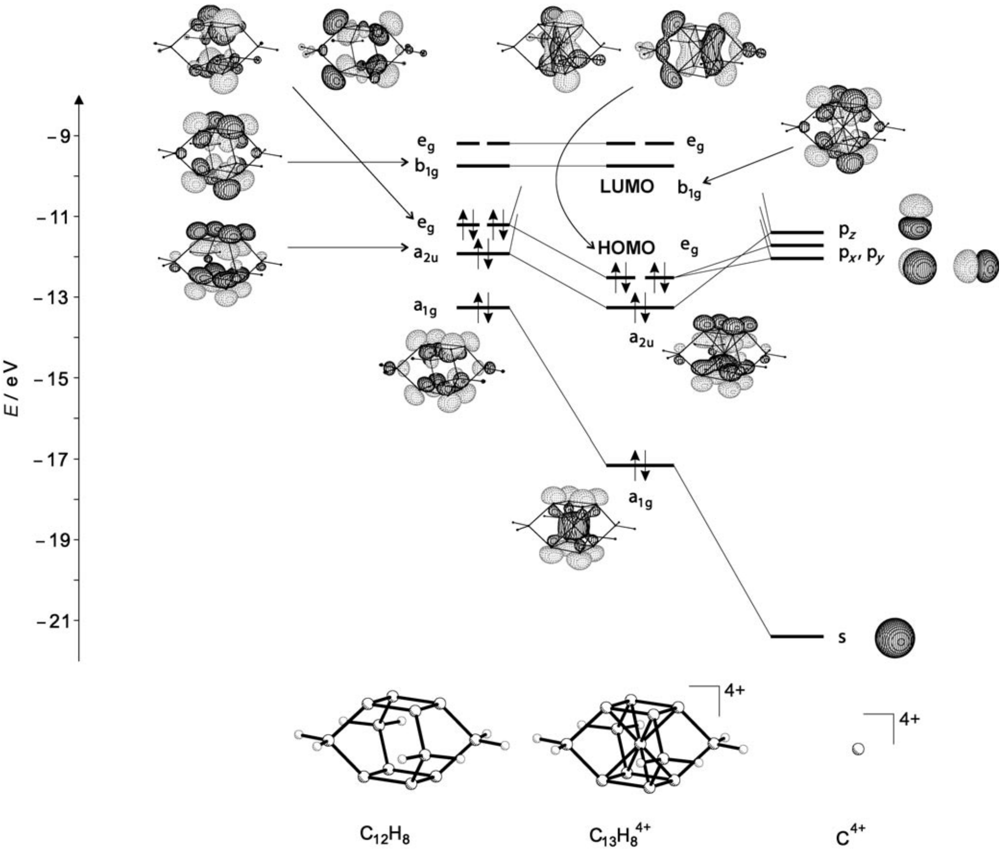

Figure 4. Orbital-correlation diagram of the formation of the multicenter bond in structure **8**.

Conclusion

We have designed computationally several possible hydrocarbon cages with hexa- and octacoordinate carbon centers. These non-classical compounds were verified by the results of DFT calculations to be energy minima on the PES. The two tetracations, **8** and **9**, may be the first examples of pure hydrocarbon compounds containing exact-octacoordinate carbons.

There are several crucial factors in the strategy for constructing these hydrocarbon cages with hypercoordinate carbons. First, these compounds originate from a fragment composed of a carbon center acting as an electron-acceptor and several surrounding C=C double bonds acting as electron-donors. Second, to stabilize the system, the number of electrons should obey the 8e rule. Finally, the cage framework should have sufficient structural rigidity and a suitable size to accommodate stably the hypercoordinate carbon center inside.

The tetracations **8** and **9** are particularly interesting because these structures contain not only octacoordinate central carbons, but also eight greatly inverted umbrella-like carbons. Tetracations **9** can be more easily converted into other energetically more stable cage isomers than tetracation **8**. The stabilization of tetracation **8** is attributed to the redistribution of charge from the central C^{4+} over the whole cage and the multicenter bond formed between the a_{2u} and e_u bonding MOs of the central carbon atom and the peripheral carbon atoms.

The synthesis of the hydrocarbon compounds **8** and **9** is a challenge to organic chemists. Tetracation **9** should be more difficult to produce, due to its relatively low thermodynamic and kinetic stabilities. However, the relatively high kinetic stability of tetracation **8** should make its synthesis in practice a possibility. We hope to motivate synthetic organic chemists to synthesize these intriguing hydrocarbon cages containing hypercoordinate carbons.

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[1] V. I. Minkin, R. M. Minyaev, R. Hoffmann, *Russ. Chem. Rev.* **2002**, *71*, 869–892, and references therein.

[2] See, for example, a) Z.-X. Wang, P. v. R. Schleyer, *Science* **2001**, *292*, 2465–2469; b) S.-D. Li, G.-M. Ren, C.-Q. Miao, Z.-H. Jin, *Angew. Chem.* **2004**, *116*, 1395–1397; *Angew. Chem. Int. Ed.* **2004**, *43*, 1371–1373; c) P. v. R. Schleyer, J. Kapp, *Chem. Phys. Lett.* **1996**, *255*, 363–366; d) G. A. Olah, G. Rasul, *Acc. Chem. Res.* **1997**, *30*, 245–250; e) Z.-X. Wang, P. v. R. Schleyer, *Angew. Chem.* **2002**, *114*, 4256–

4259; *Angew. Chem. Int. Ed.* **2002**, *41*, 4082–4085; f) S.-D. Li, J.-C. Guo, C.-Q. Miao, G.-M. Ren, *Angew. Chem.* **2005**, *117*, 2196–2199; *Angew. Chem. Int. Ed.* **2005**, *44*, 2158–2161.

[3] See, for example, a) R. Choukroun, P. Cassoux, *Acc. Chem. Res.* **1999**, *32*, 494–502; b) X. Li, H.-F. Zhang, L.-S. Wang, G. D. Geske, A. I. Boldyrev, *Angew. Chem.* **2000**, *112*, 3776–3778; *Angew. Chem. Int. Ed.* **2000**, *39*, 3630–3632; c) E. D. Jemmis, J. Chandrasekhar, E.-U. Würthwein, P. v. R. Schleyer, J. W. Chinn, F. J. Landro, R. J. Lagow, B. Luke, J. A. Pople, *J. Am. Chem. Soc.* **1982**, *104*, 4275–4276; d) H. Schmidbaur, F. P. Gabbaï, A. Schier, J. Riede, *Organometallics* **1995**, *14*, 4969–4971; e) J. Vicente, M. T. Chicote, M. D. Abrisqueta, P. González-Herrero, R. Guerrero, *Gold Bull.* **1998**, *31*, 126–130; f) M. Yamashita, Y. Yamamoto, K.-y. Akiba, D. Hashizume, F. Iwasaki, N. Takagi, S. Nagase, *J. Am. Chem. Soc.* **2005**, *127*, 4354–4371.

[4] a) V. L. Talroze, A. K. Lyubimova, *Dokl. Akad. Nauk SSSR* **1952**, *86*, 909–912; b) V. L. Talrose, A. K. Ljubimova, *J. Mass Spectrom.* **1998**, *33*, 502–504; c) G. A. Olah, R. H. Schlosberg, *J. Am. Chem. Soc.* **1968**, *90*, 2726–2727; d) K. Lammertsma, M. Barzaghi, G. A. Olah, J. A. Pople, P. v. R. Schleyer, M. Simonetta, *J. Am. Chem. Soc.* **1983**, *105*, 5258–5263; e) G. A. Olah, G. A. Rasul, *J. Am. Chem. Soc.* **1996**, *118*, 8503–8504.

[5] V. I. Minkin, R. M. Minyaev, *Dokl. Chem.* **2002**, *385*, 203–206.

[6] H. Hogeveen, P. W. Kwant, *Acc. Chem. Res.* **1975**, *8*, 413–420.

[7] D. R. Rasmussen, L. Radom, *Angew. Chem.* **1999**, *111*, 3051–3054; *Angew. Chem. Int. Ed.* **1999**, *38*, 2875–2878.

[8] R. M. Minyaev, V. I. Minkin, T. N. Gribanova, A. G. Starikov, *Mendeleev Commun.* **2004**, 47–48.

[9] R. M. Minyaev, T. N. Gribanova, A. G. Starikov, V. I. Minkin, *Mendeleev Commun.* **2001**, 213–214.

[10] R. M. Minyaev, V. I. Minkin, T. N. Gribanova, *Mendeleev Commun.* **2004**, 96–98.

[11] V. I. Minkin, R. M. Minyaev, *Mendeleev Commun.* **2004**, 43–46.

[12] D. Moran, H. L. Woodcock, Z. F. Chen, H. F. Schaefer, P. v. R. Schleyer, *J. Am. Chem. Soc.* **2003**, *125*, 11 442–11 451.

[13] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, J. A. Pople, *Gaussian 98*, *Revision A.8*, Gaussian, Inc., Pittsburgh PA, **1998**.

[14] A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648–5652.

[15] C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785–789.

[16] S. H. Vosko, L. Wilk, M. Nusair, *Can. J. Phys.* **1980**, *58*, 1200–1211.

[17] C. Mealli, D. M. Proserpio, *J. Chem. Educ.* **1990**, *67*, 399–402.

[18] R. Hoffmann, *J. Chem. Phys.* **1963**, *39*, 1397–1412.

[19] a) A. Hirsch, Z. Chen, H. Jiao, *Angew. Chem.* **2000**, *112*, 4079–4081; *Angew. Chem. Int. Ed.* **2000**, *39*, 3915–3917; b) A. Hirsch, Z. Chen, H. Jiao, *Angew. Chem.* **2001**, *113*, 2916–2920; *Angew. Chem. Int. Ed.* **2001**, *40*, 2834–2838; c) Z. Chen, H. Jiao, A. Hirsch, P. v. R. Schleyer, *Angew. Chem.* **2002**, *114*, 4485–4488; *Angew. Chem. Int. Ed.* **2002**, *41*, 4309–4312; d) Z. Chen, A. Hirsch, S. Nagase, W. Thiel, P. v. R. Schleyer, *J. Am. Chem. Soc.* **2003**, *125*, 15 507–15 511.

[20] C. Møller, M. S. Plesset, *Phys. Rev.* **1934**, *46*, 618–622.

[21] a) A. E. Reed, F. Weinhold, *J. Chem. Phys.* **1985**, *83*, 1736–1740; b) A. E. Reed, L. A. Curtiss, F. Weinhold, *Chem. Rev.* **1988**, *88*, 899–926.

[22] K. B. Wiberg, *Tetrahedron* **1968**, *24*, 1083–1096.

[23] K. B. Wiberg, *Acc. Chem. Res.* **1984**, *17*, 379–386.

[24] W. J. Hehre, L. Radom, P. v. R. Schleyer, J. A. Pople, *Ab Initio Molecular Orbital Theory*, Wiley-Interscience, New York, **1985**, p. 271.

[25] P. George, M. Trachtman, C. W. Bock, A. M. Brett, *Tetrahedron* **1976**, *32*, 317–323.

[26] E. T. Seidl, H. F. Schaefer, *J. Am. Chem. Soc.* **1991**, *113*, 1915–1917.

[27] R. M. Minyaev, V. I. Minkin, T. N. Gribanova, A. G. Starikov, *J. Org. Chem.* **2003**, *68*, 8588–8594.

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