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Comparison and Search for CH_5^{3+} and CH_6^{4+} and Their Isoelectronic Boron Analogues BH_5^{2+} and BH_6^{3+} [1]

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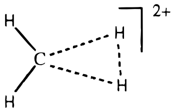
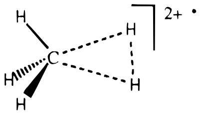
Abstract: The structures and stabilities of CH_5^{3+} and CH_6^{4+} and their isoelectronic boron analogues BH_5^{2+} and BH_6^{3+}, respectively, were calculated at the MP2/6-31G** and QCISD (T)/6-311G** levels. The planar D_{5h} symmetric structure **3** is a minimum for the CH_5^{3+} trication. The five hydrogens in structure 3 are bonded to the carbon atom by sharing the six valence electrons. Calculations showed that the CH_6^{4+} tetracation does not correspond to a minimum at the levels studied. The planar C_{2v} symmetric structure **6**, with two 3c−2e (three-center two-electron) bonds, on the other hand, was found to be a minimum for the BH_5^{2+} dication. The D_3 symmetric structure **8** also corresponds to a stable minimum for the BH_6^{3+} trication.

Introduction

The methane cation and dication are of great significance and have been the subject of many experimental and theoretical studies.[2] The methane cation $CH_4^{+\bullet}$ is the parent ion in mass spectrometry, and the methane dication CH_4^{2+} has been observed in the gas phase.[3] The planar C_{2v} symmetrical structure **1** is preferred for CH_4^{2+} as shown[4a] by Wong and Radom. Earlier calculations predicted[4b] a square pyramidal D_{4h} symmetrical structure for the CH_4^{2+} dication. The sp^2-hybridized carbon atom of **1** contains a three-center two-electron (3c−2e) bond and an empty p-orbital perpendicular to the plane of the molecule. The five-coordinated $CH_5^{2+\bullet}$ radical dication was studied[3d] by Stahl et al. by charge-stripping mass spectrometry and *ab initio* calculations. The theoretically determined structure of $CH_5^{2+\bullet}$ shows the C_s symmetric geometry **2**. Removal of an electron from the $CH_5^{2+\bullet}$ ion leads to the unprecedented CH_5^{3+} trication. We now wish to report our *ab initio* calculational studies and search for the CH_5^{3+} trication and the CH_6^{4+} tetracation. Because of the structural similarity[5] of carbocations and corresponding boron compounds, we also extended our studies to the isoelectronic BH_5^{2+} dication and BH_6^{3+} trication, respectively.



1 (C_{2v})



2 (C_s)

In multicharged small cations, charge−charge repulsion is difficult to overcome and the direct experimental study of these ions at the present time does not seem feasible. However, more stabilized analogues, including Schmidbaur[6] type gold complexes, could be considered. Schmidbaur et al. have prepared gold complexes of dipositively charged octahedral six-coordinate carbon[7] ($\{[(C_6H_5)_3PAu]_6C\}^{2+}$), five-coordinate triagonal bipyramidal nitrogen[8] ($\{[(C_6H_5)_3PAu]_5N\}^{2+}$), five-coordinate square pyramidal phosphorus[9] ($\{[(C_6H_5)_3PAu]_5P\}^{2+}$), four-coordinate tetrahedral sulfur[10] ($\{[(C_6H_5)_3PAu]_4S\}^{2+}$), and four-coordinate tetrahedral oxygen[11] ($\{[(o\text{-}CH_3C_6H_4)_3PAu]_4O\}^{2+}$) and determined their X-ray structures. These represent isolobal analogues of CH_6^{2+}, NH_5^{2+}, PH_5^{2+}, SH_4^{2+}, and OH_4^{2+}, respectively. Despite their significant metal−metal bonding that makes them stable and even isolable, these gold complexes greatly aid in understanding the bonding in hypercoordinate compounds.

Calculations

The geometry optimizations and frequency calculations were performed at the MP2/6-31G** level.[12] From calculated frequencies, the optimized structures were characterized as minima, saddle point, or transition structure. For the MP2/6-31G**-optimized structures, further geometry optimizations were carried out at the QCISD(T)/6-311G** level. For improved energy, the Gaussian-2 (G2) energies[13] and single-

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Table 1. Total Energies (−au) and ZPE (kcal/mol)

	3	**6**	**7**	**8**	**9**
MP2/6-31G**//MP2/6-31G**	38.73214	26.62656	26.60220	26.26619	26.19448
a	(16.4)	(25.5)	(23.7)	(24.2)	(20.1)
QCISD(T)/6-311G**//QCISD(T)/6-311G**	38.77491	26.66592	26.64167	26.31471	26.24666
G2	38.78353	26.65272	26.63327	26.29974	26.24363
CCSD(T)/cc-pVTZ//QCISD(T)/6-311G**	38.79913	26.68290	26.65961	26.33066	26.26406

[a] Zero-point vibrational energies (ZPE) at MP2/6-31G**//MP2/6-31G** scaled by a factor of 0.93.

Table 2. MP2/6-31G**(QCISD(T)/6-311G**)-Calculated Lowdin Bond Orders and Charges[a]

no.	bond	Lowdin bond order	atom	charge
3	C−H	0.56 (0.59)	C	−0.54 (−0.46)
	H−H	0.06 (0.02)	H	+0.71 (+0.69)
6	$B-H_a$	0.91 (0.93)	B	+0.64 (+0.74)
	$B-H_b$	0.45 (0.43)	H_a	+0.16 (+0.13)
	$B-H_c$	0.49 (0.47)	H_b	+0.37 (+0.36)
	H_b-H_c	0.40 (0.44)	H_c	+0.24 (+0.21)
8	B−H	0.48 (0.46)	B	+0.69 (+0.80)
	H_a-H_b	0.34 (0.38)	H	+0.39 (+0.37)

[a] For numbering scheme see Figures 1, 2, and 3.

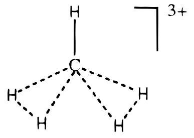
Table 3. MP2/6-31G**-Calculated Frequencies and IR Intensities

no.	frequencies in cm^{-1} (IR intensities in KM/mol)
3	416 (0), 831 (56), 911 (0), 1102 (658), 1130 (0), 1445 (2675), 1808 (0)
6	562 (29), 649 (0), 765 (63), 853 (0), 1016 (10), 1397 (22), 1466 (168), 1546 (148), 1717 (32), 2762 (146), 3203 (23), 3231 (485)
8	82 (0), 230 (0), 614 (1), 685 (154), 754 (326), 840 (28), 1448 (0), 1574 (241), 2856 (707), 2904 (0)

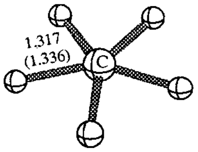
point energies at CCSD(T)/cc-pVTZ[14a] level on QCISD(T)/6-311G**-optimized geometries were computed. Calculated energies are given in Table 1. Atomic charges and Lowdin[14b] bond orders were obtained using the natural bond orbital analysis (NBO)[14c] method (Table 2). Calculated vibrational frequencies are given in Table 3.

Results and Discussion

CH_5^{3+}. The D_{5h} symmetrical structure **3** is found to be the only minimum on the potential energy surface of CH_5^{3+} at the MP2/6-31G** level. The possible C_2 structure **4**, with two 3c−2e bonds is not a minimum and converted to **3** upon optimization at the MP2/6-31G** level. In structure **3**, five hydrogen atoms are bonded to the carbon atom by sharing only six valence electrons resulting in a planar five-coordinated carbon atom with a vacant p-orbital perpendicular to the plane of the molecule (Figure 1). Thus, the electron deficient, weaker C−H bonds (1.317 Å) of **3** are expectedly longer than those found in the 3c−2e C−H bonds (1.181 Å) of the C_s structure of CH_5^+ at the same theoretical level. This is in agreement with the calculated Lowdin[14b] bond order of C−H bond (Table 2), which was found to be only 0.56. There is no significant bonding interaction between two adjacent hydrogens, separated by 1.549 Å. Thus, the calculated Lowdin bond order between two adjacent hydrogen atoms was found to be only 0.06. We also calculated the NBO charges[14c] of the ion **1** (Table 2). The calculated charges of carbon and hydrogen are −0.54 and +0.71 au, respectively, at the MP2/6-31G** level. Using G2 theory, the dissociation of **3** into CH_4^{2+} (**1**) and H^+ is calculated to be exothermic by 274.6 kcal/mol. The transition structure for the dissociation lies only 0.1 kcal/mol higher in energy than structure **3** at the MP2/6-31G** level and 0.01 kcal/mol at the QCISD(T)/6-311G** level. At our highest level of theory (CCSD(T)/cc-pVTZ//QCISD(T)/6-311G** + ZPE(MP2/6-31G**//MP2/6-31G** level), the transition structure lies 0.2 kcal/mol lower in energy than structure **3**. This shows that the trication **3** if formed will dissociate spontaneously into CH_4^{2+} (**1**) and H^+. In comparison, in CH_5^+ there is a small but definite barrier for the equilibration of the five hydrogens, as recently shown (using Car−Perrrinello high-level *ab initio* simulation) by Marx and Parrinello.[15] The completely delocalized 6c−8e structure as suggested by Schreiner et al.[16] is not the lowest energy minimum for CH_5^+. Increasing charge−charge repulsion in CH_5^{3+}, however, makes **3** the only minimum structure.

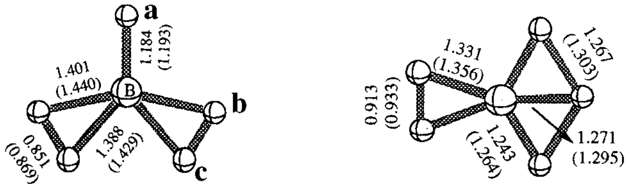


4 (C_2)



CH_5^{3+} **3** (D_{5h})

Figure 1. MP2/6-31G**(QCISD(T)/6-311G**)-optimized structure of **3**.



BH_5^{2+} **6** (C_{2v})

BH_5^{2+} **7** TS (C_{2v})

Figure 2. MP2/6-31G**(QCISD(T)/6-311G**)-optimized structures of **6** and **7**.

BH_5^{2+}. BH_5^{2+} dication is isoelectronic with the CH_5^{3+} trication. But unlike the D_{5h} minimum energy structure of CH_5^{3+}, the planar C_{2v} symmetric structure **6** is found to be the only minimum on the potential energy surface of BH_5^{2+} at both the MP2/6-31G** and QCISD (T)/6-311G** levels. The planar D_{5h} symmetrical structure of BH_5^{2+} was characterized as the saddle point, since there are two imaginary frequencies (i.e., NIMAG = 2) in its calculated IR spectrum. Structure **6**, resembling a complex between BH^{2+} and two hydrogen molecules, results in the formation of two 3c−2e bonds with an empty p-orbital orthogonal to the plane of the molecule. The calculated structural parameters are given in Figure 2, and the calculated Lowdin bond orders and NBO charges are given in Table 2. We have located a transition structure (**7**) for the

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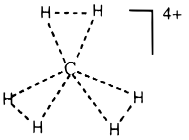
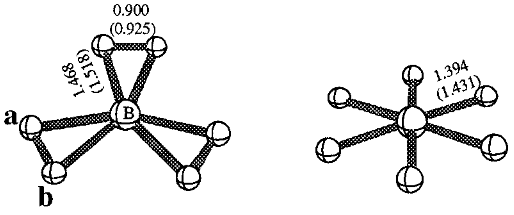
hydrogen scrambling in **6**. With G2 theory the calculated barrier for hydrogen scrambling through transition state **7** is 12.2 kcal/mol (12.8 kcal/mol at the CCSD(T)/cc-pVTZ//QCISD(T)/6-311G** + ZPE (MP2/6-31G**//MP2/6-31G** level). Such barriers for intramolecular hydrogen migration for CH_4^{2+},[4a] CH_5^+,[16] CH_6^{2+},[17] and CH_7^{3+} [1] carbocations are calculated to be even lower. We have also located the transition state for dissociation (deprotonation) of **6** into BH_4^+ and H^+. The G2-calculated barrier for the proton loss is 4.4 kcal/mol, and the deprotonation process is exothermic by 57.7 kcal/mol. This expectedly high exothermicity is, however, smaller than the exothermicity of 103.0 kcal/mol calculated for the deprotonation of CH_4^{2+} into CH_3^+ and H^+ with the G2 theory. The activation barrier of 4.4 kcal/mol for the deprotonation of **6** is smaller than the activation barrier of 18.8 kcal/mol for the deprotonation of CH_4^{2+}, also obtained with the G2 theory. In fact, the doubly electron deficient boron compounds, such as *nido*-μ-(2,3-Me_2B)-B_5H_8, are known experimentally,[18] the structure of which has recently been reconfirmed by Onak and Williams with *ab initio* calculations.[19]

CH_6^{4+}. We also searched for a minimum energy structure of CH_6^{4+}. At the MP2/6-31G** or QCISD(T)/6-311G** level, no structure of CH_6^{4+} on its potential energy surface could be found as a minimum (including **5**, with three 3c−2e bonds or a 7c−6e delocalized form). Thus, in CH_6^{4+} charge−charge repulsion may have reached its prohibitive limit.



5 (D3)

BH_6^{3+}. The BH_6^{3+} trication is isoelectronic with the CH_6^{4+} tetracation. The MP2/6-31G** optimization shows that the propeller-shaped D_3 symmetrical structure **8** is the only minimum on the potential energy surface of BH_6^{3+}. Further optimization and frequency calculations were carried out using the higher QCISD (T)/6-311G** level. The calculated geometries are given in Figure 3, and calculated Lowdin bond orders and NBO charges are given in Table 2. The structure **8**, resembling a complex between a tripositive boron atom B^{3+} and three hydrogen molecules, results in the formation of three 3c−2e bonds. The plane of each of the 3c−2e unit is slightly rotated (1.6° at the MP2/6-31G** and 17° at the QCISD(T)/6-311G** level) around its axis from the plane of the molecule. The B−H bond distance of **8** is 1.468 Å, slightly longer than those found in similar 3c−2e B−H bonds (1.388 and 1.401 Å) of BH_5^{2+} (**6**) at the MP2/6-31G** level. The D_{6h} symmetrical structure **9** is identified as a transition structure (NIMAG = 1) which may be the transition state for hydrogen scrambling in the trication **8**. The structure **9** lies 35.2 kcal/mol higher in energy than structure **8**. We have also calculated (with G2) the barrier and exothermicity of the dissociation of **8** into **6** and H^+ and found them to be 1.0 and 221.5 kcal/mol, respectively.



BH_6^{3+} **8** (D_3) BH_6^{3+} **9** TS (D_{5h})

Figure 3. MP2/6-31G**(QCISD(T)/6-311G**)-optimized structures of **8** and **9**.

In conclusion, the present *ab initio* study indicates that the D_{5h} symmetrical structure **3** and the C_{2v} symmetrical structure **6** are the stationary points on the potential energy surfaces of CH_5^{3+} and its isoelectronic boron analogue BH_5^{2+}, respectively. The optimized structure shows that the five hydrogen atoms in structure **3** are bonded to the carbon atom by sharing the six valence electrons. On the other hand, five hydrogen atoms in structure **6** are bonded to the boron atom by two 3c−2e bonds and a 2c−2e bond. No stationary point on the CH_6^{4+} potential energy surface could be located. However, the propeller-shaped D_3 symmetrical structure **8**, with three 3c−2e bonds, corresponds to a stable minimum for isoelectronical boron analogue BH_6^{3+}. The instabilities of many small multicharged cations are mainly due to the charge−charge repulsion. A significant implication of the study of multicharged carbocations and their boron analogues is the relationship of their bonding nature to carbon and boron superelectrophiles[20] involved in superacid media. Better stabilization of these polycations by Schmidbaur type auration[6] with $(C_6H_5)_3PAu$, an isolobal analogue of H^+, should be possible.

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