

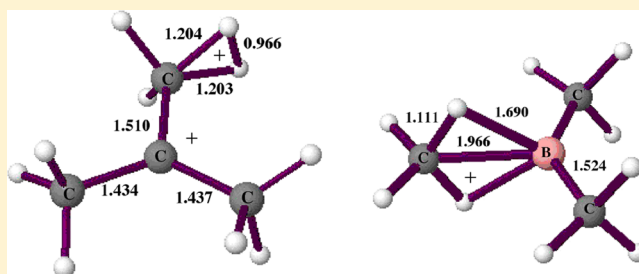
Comparative Study of Alkane Dications (Protonated Alkyl Cations, $C_nH_{2n+2}^{2+}$) and Their Isoelectronic Boron Cation Analogues[†]

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Supporting Information

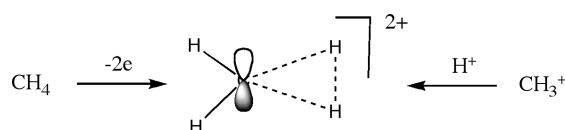
ABSTRACT: Comparative study of the superelectrophilic alkane dications ($C_nH_{2n+2}^{2+}$, $n = 1-5$) and their isoelectronic boron cation analogues was carried out using the ab initio method at the MP2/cc-pVTZ level. The structure, bonding, and relative stability of doubly charged alkane dications and monocharged boron cation analogues are discussed. These studies contribute to our general understanding of the superelectrophilic activation of alkyl cations as well as the electrophilic reactivity of C–H and C–C single bonds.



INTRODUCTION

Carbocations are of substantial significance both in solution and in gas-phase chemistry. Their structural properties have been addressed and reviewed.¹ The methane dication (CH_4^{2+}) is the parent of the alkane dications, RH^{2+} . It was studied theoretically by Radom² with ab initio methods and was generated experimentally in the gas phase by 2e oxidation of methane by Schwarz et al (Scheme 1).³ Protonation of the methyl cation as well as the reaction of CH_2^{2+} with H_2 can also be considered as alternative pathways for the generation of CH_4^{2+} .

Scheme 1



Boron and carbon are consecutive first-row elements. It follows that the trivalent carbocation is isoelectronic with the corresponding neutral trivalent boron compounds. The analogy between carbocations and boranes is quite apparent in the ability of CH fragments to replace BH_2 groups in polyboranes, leading to carboranes. On the basis of such an analogy, a 2,3,4,5-tetracarbahehexaborane ($C_4B_2H_6$) analogue,⁴ that is, pentagonal-pyramidal dication, $Me_6C_6^{2+}$, has been prepared and characterized based on 1H and ^{13}C NMR spectroscopic data by Hogeween and co-workers.⁵ The pentagonal-pyramidal structure of $C_4B_2H_6$ was established⁴ by Pasinski and Beaudet from the microwave spectra of 10 isotopic species. Similarly, BH_4^+ is isoelectronic with its corresponding carbon analogue CH_4^{2+} . Similar to the CH_4^{2+} dication, the BH_4^+ cation was also found to be the viable minimum on the potential energy surface.⁶ The structure of the BH_4^+ ion has been studied by Rasul and Olah.⁶

In continuation of our study of carbocations, we have carried out a comparative study on the structure and bonding of a series of superelectrophilic alkane dications and their corresponding isoelectronic boron cation analogues, as well as related mixed boron–carbon cations. For uniformity, all of the structures were calculated at the same MP2/cc-pVTZ level of theory.

CALCULATIONS

Geometry optimizations were performed at the MP2/cc-pVTZ level using the Gaussian 09 program.⁷ Vibrational frequencies at the MP2/cc-pVTZ level were used to characterize stationary points as minima (number of imaginary frequency (NIMAG) = 0) or transition state (NIMAG = 1) and to evaluate zero-point vibrational energies (ZPE), which were scaled by a factor of 0.95.⁸ Relative energies were computed at the MP2/cc-pVTZ//MP2/cc-pVTZ + ZPE level. Computed energies are given in Table 1.

RESULTS AND DISCUSSION

Methane Dication CH_4^{2+} . The planar C_{2v} , symmetrical **1** (Figure 1) is the preferred structure at the MP3/6-311G** level for the methane dication (CH_4^{2+}), as shown² by Wong and Radom. Earlier calculations at the HF/6-31G* level have predicted^{9,10} a square D_{4h} symmetrical structure for the CH_4^{2+} dication. The MP2/cc-pVTZ calculated structure of **1** is depicted in Figure 1. The sp^2 -hybridized carbon atom of **1** contains a two-electron three-center ($2e-3c$) bond and two two-electron two-center ($2e-2c$) bonds with an empty p orbital perpendicular to the plane of the molecule. The four hydrogen atoms of **1** are bonded to the central carbon atom by sharing only six valence electrons. The electron-deficient $2e-3c$ C–H bonds (1.264 Å)

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Table 1. Total Energies (au), ZPE^a, and Relative Energies^b

	MP2/cc-pvtz	ZPE (kcal/mol)	rel energy (kcal/mol)
CH ₄ ²⁺			
1	39.21724	20.9	
BH ₄ ⁺			
2	26.74205	21.7	
C ₂ H ₆ ²⁺			
3	78.61462	39.9	0.0
4	78.59775	40.7	11.4
B ₂ H ₆			
5	53.09722	38.4	
CBH ₆ ⁺			
6	66.01624	40.8	0.0
7	66.00551	32.2	4.1
C ₃ H ₈ ²⁺			
8	117.92142	57.1	
C ₂ BH ₈ ⁺			
9	105.27207	57.6	0.0
10	105.19997	55.3	42.9
11	105.24928	58.5	15.2
12	105.22778	55.7	25.8
C ₄ H ₁₀ ²⁺			
13	157.17770	72.9	0.0
14	157.15272	72.2	14.5
C ₃ BH ₁₀ ⁺			
15	144.52551	74.1	0.0
16	144.48311	75.7	28.2
17	144.50263	75.3	15.6
C ₅ H ₁₂ ²⁺			
18	196.45199	90.9	0.0
19	196.40146	91.4	32.2
C ₄ BH ₁₂ ²⁺			
20	183.70531	90.7	29.0
21	183.70060	89.4	30.7
22	183.74623	91.4	4.1
23	183.67784	88.5	44.1
24	183.68981	88.4	36.5
25	183.75349	91.9	0.0
26	183.73386	92.5	12.9

^aZero-point vibrational energies (ZPE) at MP2/cc-pvtz//MP2/cc-pvtz scaled by a factor of 0.95. ^bRelative energy at the MP2/cc-pVTZ//MP2/cc-pVTZ + ZPE level.

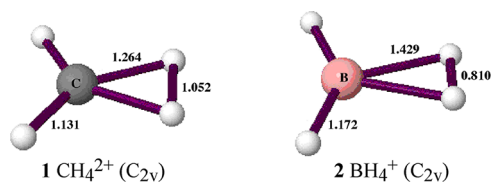


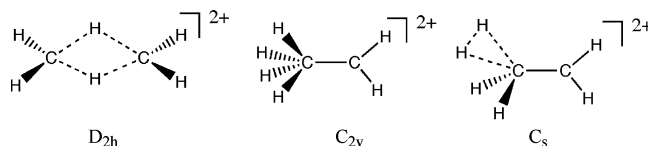
Figure 1. MP2/cc-pVTZ calculated structures of 1 and 2.

of 1 are expectedly longer than those of the 2e–2c C–H bonds (1.131 Å).

BH₄⁺ is isoelectronic with its corresponding carbon analogue CH₄²⁺. Similar to CH₄²⁺ 1, the C_{2v} symmetric form 2 (Figure 1) is also found to be the only minimum for BH₄⁺.⁶ Structure 2 resembles a complex between BH₂⁺ and H₂, resulting in the formation of a 2e–3c bond with an empty p orbital orthogonal to the plane of the molecule. The electron-deficient 2e–3c B–H bonds (1.429 Å) of 2 are substantially longer than those of the 2e–2c B–H bonds (1.172 Å).

Ethane Dications. The ethane dication (C₂H₆²⁺) was first investigated theoretically by Olah and Simonetta,¹¹ who found that a doubly bridged, diborane-like D_{2h} symmetric structure (Scheme 2) is a minimum. Later, Schleyer and Pople¹² calculated

Scheme 2



the structures at the HF/6-31G* level and showed that the C_{2v} symmetrical structure is energetically favored over the diborane-like D_{2h} structure by 9.0 kcal/mol at the MP4SDQ/6-31G**//HF/6-31G* level. Subsequently, Olah et al.¹³ showed that the global minimum of C₂H₆²⁺ is a C_s symmetrical structure with a 2e–3c bond. The C_s structure is, in fact, a carbonium–carbenium dication and can be considered either as a complex between the ethylene dication (C₂H₄²⁺) and H₂ or as the protonated ethylene cation (protonated at the C–H bond of the methyl group). The C_s structure is 3.5 kcal/mol more stable than the C_{2v} structure. The C₂H₆²⁺ dication has also been observed experimentally under high vacuum by charge stripping of the ethylene radical cation (C₂H₆^{•+}) in mass spectrometry.¹⁴ The structures and stabilities of the ethane dications C₂H₆²⁺ (C_s structure 3 and D_{2h} structure 4) were also carried out by Olah, Prakash, and Rasul¹⁵ at the ab initio MP2/6-31G** and QCISD(T)/6-311G** levels as well as using G2 theory. Similar to Olah et al.'s previously reported HF/6-31G* results,¹³ the study¹⁵ using G2 theory also indicates that the 2e–3c bonded carbonium–carbenium C_s structure 3 is more stable than the doubly hydrogen-bridged diborane-type D_{2h} structure 4 by 12.4 kcal/mol. The difference slightly decreases to 11.4 kcal/mol based on our present calculations at the MP2/cc-pVTZ//MP2/cc-pVTZ + ZPE level (Table 1). MP2/cc-pVTZ calculated structures of 3 and 4 are depicted in Figure 2.

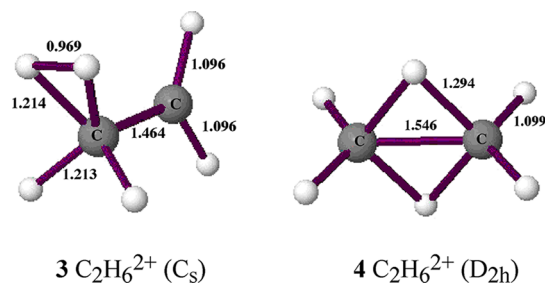
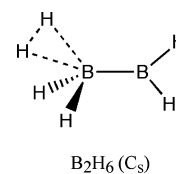


Figure 2. MP2/cc-pVTZ calculated structures of 3 and 4.

MP2/cc-pVTZ calculations on isoelectronic boron analogue B₂H₆, however, indicated that the 2e–3c bonded boronium–boronium structure (C_s structure, Scheme 3) is not a minimum at

Scheme 3



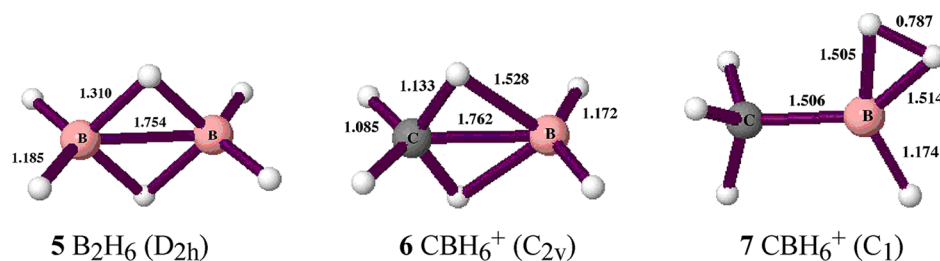


Figure 3. MP2/cc-pVTZ calculated structures of 5–7.

the MP2/cc-pVTZ level and converted into doubly hydrogen-bridged diborane D_{2h} structure **5** (Figure 3) upon optimization. Thus, at the MP2/cc-pVTZ level, structure **5** was found to be the only viable minimum for B_2H_6 .

For comparison, the mixed carbon- and boron-containing CBH_6^+ cation was also calculated at the MP2/cc-pVTZ level. In this case, there are two structures, doubly hydrogen-bridged **6** and $2e-3c$ bonded **7**, that were found to be the viable minima for CBH_6^+ (Figure 3). The structure **7** contains a planar four coordinate boron atom and a tetrahedral carbon atom and can be considered as methylated BH_4^+ **2**. The structure **6** can be considered as a complex between CH_4 and BH_2^+ . However, **6** was computed to be more stable than **7** by 4.1 kcal/mol.

Propane Dications. The long-lived stable isopropyl cation was found to undergo C–H protonation (determined by facile hydrogen–deuterium exchange) to form a highly electron-deficient propane dication in superacids.¹⁶ As the long-lived isopropyl cation in superacids is not involved in any deprotonation equilibrium with propene that would immediately lead to cyclization and oligomerization, the observed isotopic exchange indicates protonation of methyl C–H bonds.

The possible structures of the propane dication¹⁶ were also investigated by ab initio methods. The structure **8** (Figure 4) was

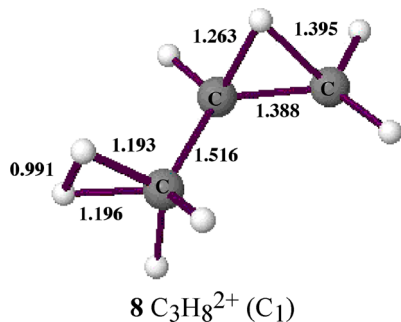


Figure 4. MP2/cc-pVTZ calculated structure of **8**.

found to be the lowest-energy structure for the propane dication ($C_3H_8^{2+}$). The structure **8** contains a hydrogen-bridged unit and a five pentacoordinate carbon atom with a $2e-3c$ bond.

Calculations at the MP2/cc-pVTZ level indicate that the doubly hydrogen-bridged structure and the $2e-3c$ bonded carbonium–cabenium structure (Scheme 4) are not minima on the potential energy surface (PES) and converted into **8** (Figure 4) upon optimization without any energy barrier.

Structures of the mixed carbon–boron analogue $C_2BH_8^+$ were also calculated at the MP2/cc-pVTZ level. Four structures, two doubly hydrogen-bridged **9** and **10** and two $2e-3c$ bonded **11** and **12**, were found to be viable minima on the PES of $C_2BH_8^+$ (Figure 5). The structure **9** can be considered as a complex between CH_4 and $B(CH_3)H^+$. On the other hand, **10** can be

Scheme 4

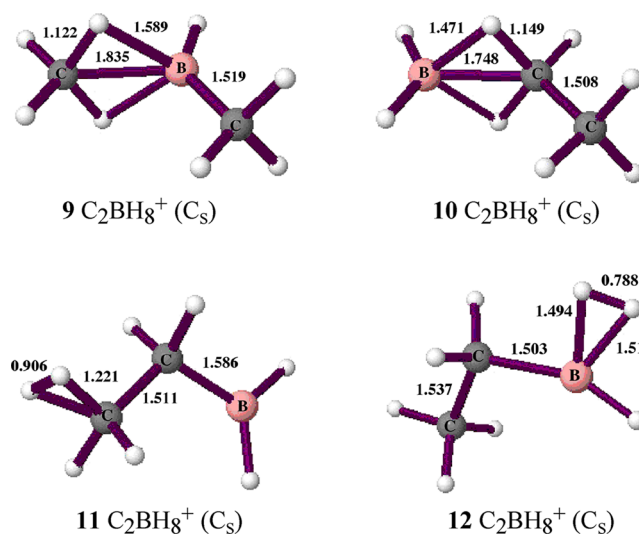
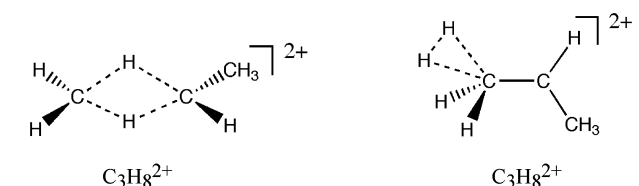


Figure 5. MP2/cc-pVTZ calculated structures of 9–12.

considered as a complex between CH_3CH_3 and BH_2^+ . The structure **11** contains a planar three coordinate boron atom and a pentacoordinate carbon atom separated by a CH_2 group. The structure **12** contains a planar four coordinate boron atom and can be considered as ethyl-substituted BH_4^+ **2**. The structure **9** is the global minimum, being more stable than the structures **10**, **11**, and **12** by 42.9, 15.2, and 25.8 kcal/mol, respectively. Unlike dication $C_3H_8^{2+}$ **8**, isoelectronic monocation $C_2BH_8^+$ **9** is a doubly hydrogen-bridged structure. This shows the importance of such bridging in stabilization of boron compounds.

Butane Dications. The butane dication ($C_4H_{10}^{2+}$)¹⁷ was theoretically and experimentally investigated by Olah et al. Two minimum structures were located at the MP2(FU)/6-31G* level. The carbonium–carbonium structure **13** corresponds to a C–H protonated *tert*-butyl cation (Figure 6).¹⁷ The structure **13** with a $2e-3c$ bond was characterized as the most stable structure for $C_4H_{10}^{2+}$. Two C–H bonds on the two methyl groups are aligned with the empty p orbital on the tertiary carbon atom. The corresponding HCC bond angles are significantly smaller (104°) compared with those of the other C–H bonds (111°). The corresponding bonds are slightly elongated to 1.12 Å on these positions. The doubly hydrogen-bridged structure **14** was also

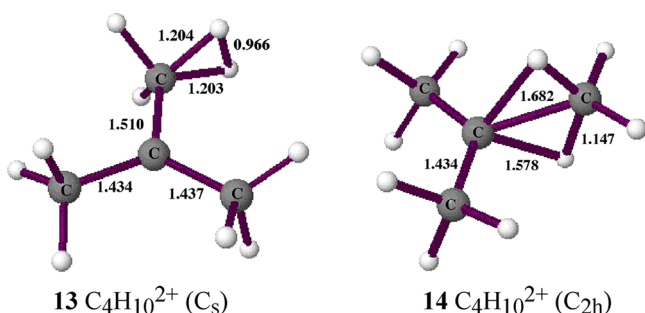


Figure 6. MP2/cc-pVTZ calculated structures of 13 and 14.

characterized as a minimum for $C_4H_{10}^{2+}$. The structure 14 corresponds to a complex between $H_3CCCH_3^{2+}$ and CH_4 and lies about 14.9 kcal/mol above 13 at the MP2/cc-pVTZ + ZPE level.

Structures of the mixed carbon–boron analogue $C_3BH_{10}^+$ were computed at the MP2/cc-pVTZ + ZPE level. Three doubly hydrogen-bridged structures 15, 16, and 17 were found to be viable minima on the PES of $C_3BH_{10}^+$ (Figure 7). The structure

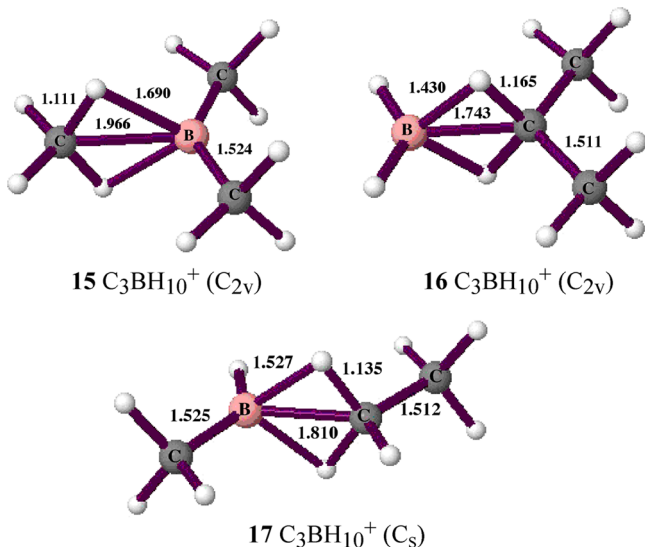


Figure 7. MP2/cc-pVTZ calculated structures of 15–17.

15 can be considered as a complex between CH_4 and $B(CH_3)_2^+$. The structure 16 can be considered as a complex between $H_2C(CH_3)_2$ and BH_2^+ . On the other hand, the structure 17 can be considered as a complex between CH_3CH_3 and $BH(CH_3)^+$. Structure 15 is the most stable, being 28.2 and 15.6 kcal/mol

more stable than 16 and 17, respectively, at the MP2/cc-pVTZ//MP2/cc-pVTZ + ZPE level.

Pentane Dications. The structures of the isopentane dication ($C_5H_{12}^{2+}$) were calculated at the MP2/cc-pVTZ level.¹⁸ Methonium (CH_4^+)-substituted *tert*-butyl cation form 18 was found to be the most stable isomer (Figure 8). The hypercoordinate structure 18 contains a formal positive-charge-bearing trivalent carbenium ion center and a pentacoordinated carbonium ion center involving a $2e-3c$ bond separated by a CH_2 group and can be considered as a carbenium–carbonium dication.

The diborane-type structure 19 was also found to be a minimum on the PES of $C_5H_{12}^{2+}$. Structure 19 can be considered as a complex between $H_3CCCH_3^{2+}$ and CH_3CH_3 , and lies 32.2 kcal/mol above 18. The central C2–C3 bond length of 18 was computed to be 1.682 Å.

Structures of the mixed carbon–boron analogue ($C_4BH_{12}^+$) of the isopentane dication were calculated at the MP2/cc-pVTZ levels (Figure 9). Seven minima (20–26) were located on the potential energy surface of $C_4BH_{12}^+$ at the MP2/cc-pVTZ level. Relative energies of the structures are given in Table 1. The structure 20 corresponds to a BH_4 -substituted *tert*-butyl cation, $(H_3C)_2C^+CH_2BH_4$. The structure contains a formal positive-charge-bearing trivalent carbenium and a pentacoordinate boron atom (involving a $2e-3c$ bond) center separated by a carbon atom and can be considered as a carbenium–boronium ion.

C–C protonated 21 can be considered as a borenium–carbonium ion. However, formal electron-deficient centers in 21 are now adjacent to each other. Despite this, the structure 21 is slightly (1.7 kcal/mol) less stable than ion 20. The structure 22, which is 26.6 kcal/mol more stable than 21, contains a doubly hydrogen-bridged unit and can be considered as a complex between $(CH_3)B(C_2H_5)^+$ and CH_4 . The structure 23 corresponds to a BH_4 -substituted *sec*-butyl cation, $(CH_3)_2C^+(C_2H_5)BH_4$. The structure 23 contains a formal positive-charge-bearing trivalent carbenium and a pentacoordinate boron atom adjacent to each other and can be considered as a carbenium–boronium ion. However, the structure 23 lies 15.0 kcal/mol above 20 (Table 1). The structure 24 can also be considered as a carbenium–boronium ion. The diborane-type structure 25 corresponds to a complex between $(CH_3)_2B^+$ and CH_3CH_3 and lies 29.0 kcal/mol below 20. The doubly hydrogen-bridged structure 25 was found to be the lowest-energy structure. The calculated central C–B bond length of 25 was found to be 1.908 Å. On the other hand, the doubly hydrogen-bridged structure 26 corresponds to a complex between CH_3BH^+ and $CH_3CH_2CH_3$ and lies 12.9 kcal/mol above 25. The calculated central C–B bond length of 26 is 1.804 Å.

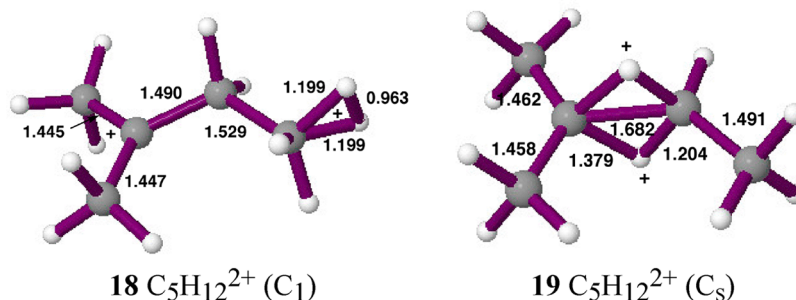


Figure 8. MP2/cc-pVTZ calculated structures of 18 and 20.

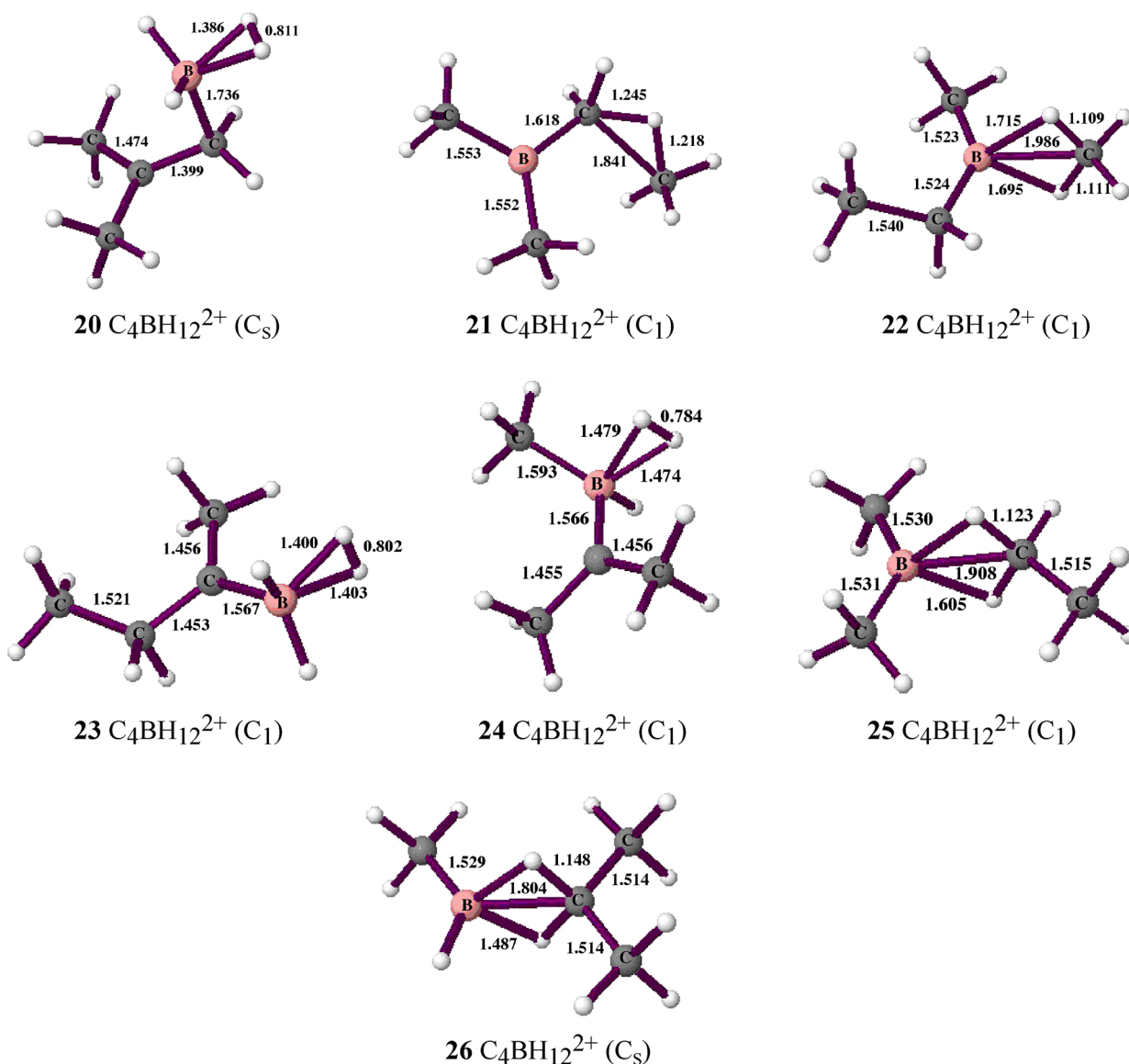


Figure 9. MP2/cc-pVTZ calculated structures of 20–26.

CONCLUSIONS

Comparative study of the structures and stabilities of the alkane dications (protonated alkyl cations, $C_nH_{2n+2}^{2+}$, $n = 1-5$) and their corresponding isoelectronic boron cation analogues was carried out at the ab initio MP2/cc-pVTZ levels. The structure, bonding, and relative stability of the structures are discussed. These studies contribute to our general understanding of the superelectrophilic activation of protonated alkyl dications. Such superelectrophilic activations are now well-recognized.¹⁹

ASSOCIATED CONTENT

Supporting Information

Cartesian coordinates and energies of the species involved in the calculations and complete citation for ref 7. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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DEDICATION

[†]In memory of the late Professor Howard Zimmerman.

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