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Complexes of Guanidinium Ion $(NH_2)_3C^+$ with Super Lewis Acidic XH_4^+ (X = B and Al): Comparison with XH_3 Complexes and Protonated and Methylated Guanidinium Dications[1]

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Structures of the complexes (**1** and **8**) of the guanidinium ion $(H_2N)_3C^+$ with super Lewis acidic BH_4^+ and AlH_4^+ were calculated using the DFT method at the B3LYP/6-311+G** level. ^{13}C NMR chemical shifts were also calculated by the GIAO-MP2 method. Each of the dicationic complexes contains a hypercoordinate boron or aluminum atom with a two-electron three-center (2e-3c) bond. Guanidinium ion was found to form a strong complex with BH_4^+ but a relatively weak one with AlH_4^+. On the other hand, complexations of guanidinium ion with neutral BH_3 and AlH_3 lead only to very weak complexes (**5** and **9**). The structures of mono- and dicationic complexes were compared with the structures of protonated and methylated guanidinium dications.

Introduction

Guanidine and its derivatives are of significant biological importance. They are present as substructures in the amino acid arginine, the pyrimidine base of DNA, and many other biologically significant molecules. Protonated guanidine [guanidinium ion, $(NH_2)_3C^+$] is an abundant highly resonance-stabilized ion. The ion owes its thermodynamic stability to the efficient p−p interaction between the carbon atom and the nonbonded electron pairs on the three adjacent nitrogen atoms. The guanidinium ion is so stable that it is inert even in boiling water.[2]

We have previously reported[3] the protonation of guanidine in superacids. Guanidine was found to be diprotonated in superacids to give stable *N*,*N*-diprotonated guanidinium dication. No persistent triprotonated guanidine could be observed. However, Olah et al. suggested that the superelectrophilic[4] activation (protosolvolytic activation) of diprotonated guanidine in superacids (in the limiting case leading to the triprotonated guanidine) could be possible.[3] In superelectrophilic activation, nonbonded electron pairs of onium ions further interact with Brönsted or Lewis acids. In their studies, Thauer et al. have suggested that such activation might also play an important role in some enzyme-catalyzed reactions.[5] For example, a metal-free hydrogenase enzyme catalyzes the reversible dehyrogenation of methylenetetrahydromethaneopterin ($CH_2{=}H_4MPT$) to methenyltetrahydromethanopterin (CHH_4MPT^+) and H_2. It was suggested that the amidinium ion entity is further activated by N-protonation in the enzyme to bind a H_2 molecule via a two-electron three-center (2e-3c) bond.[5]

Lewis acid−base interactions are also involved in many important catalytic reactions. We have previously investigated[6] the structures of the complexes of CO_2, COS, and CS_2 with the super Lewis acidic BH_4^+ cation, as well as with neutral BH_3, by the density functional theory (DFT) method. Complexations with the BH_4^+ cation were calculated to be exothermic by 26−42 kcal/mol. However, complexations with neutral BH_3 led only to very weak complexes.[6] Such Lewis acid coordination of guanidinium ion $(NH_2)_3C^+$ has not yet been considered. The present theoretical study of guanidinium ion with the super Lewis acids XH_4^+ (X = B and Al), as well as with XH_3, is therefore also relevant to a better understanding of protolytic activation of guanidine-containing systems. We have previously reported the computed structures of four-coordinate boronium ion[7] BH_4^+ (**i**)

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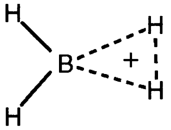
Table 1. Total Energies (−au) and ZPEs[a]

	B3LYP/6-311+G**	ZPE (kcal/mol)
1	232.61590	80.9
2	205.83555	54.2
3	205.94851	62.6
4	245.28879	80.0
5	232.45798	74.2
6	231.41066	68.8
7	231.31208	62.0
8	450.25664	73.1
9	450.06830	68.1
10	449.06447	63.8
11	448.91845	56.6
BH_3	26.62112	16.1
BH_4^+	26.85011	21.7
AlH_3	244.22910	11.4
AlH_4^+	244.51754	16.4
H_2	1.17957	6.2

[a] ZPEs at B3LYP/6-311+G** scaled by a factor of 0.98.

and alonium ion[8] AlH_4^+ (**ii**). Structures of the cations are planar with a 2e-3c bond. Recently, the ion BH_4^+ was prepared in the gas phase by reacting BH_2^+ and H_2.[9]



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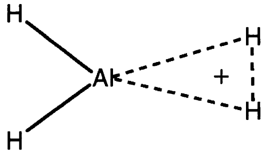

ii

Calculations

Calculations were performed using the Gaussian 98 program.[10] The geometry optimizations and vibrational frequency calculations were performed at the B3LYP/6-311+G** level.[11] Vibrational frequencies were used to characterize stationary points as minima [number of imaginary frequencies (NIMAG) = 0] and to evaluate zero-point vibrational energies (ZPEs), which were scaled by a factor of 0.98.[12] Final energies were calculated at the B3LYP/6-311+G** + ZPE level. Calculated energies are given in Table 1. Atomic charges and Wiberg bond indices[13] (bond order) were obtained using the natural bond orbital analysis (NBO)[14] method at the B3LYP/6-311+G** level. The ^{13}C NMR chemical shifts were calculated using the B3LYP/6-311+G** optimized geometries by the GIAO method.[15] The GIAO-MP2 calculations[16] were performed with the following basis sets:[16,17] triple-ζ polarization (tzp), consisting of a (9s5p1d/5s3p1d) contraction for B, C, and N with d exponents of 0.5 for B, 0.8 for C, and 1.2 for O, and double-ζ (dz), consisting of a (4s1p/2s1p) contraction for H with a p exponent of 0.8 for H. For comparison, GIAO-SCF calculations using the tzp/dz basis set were also performed. The GIAO calculations were performed with the ACES II program.[18] The ^{13}C NMR chemical shifts were referenced to $(CH_4)_4Si$ [calculated absolute shift, i.e., $\sigma(C) = 193.0$ for GIAO−SCF and $\sigma(C) = 198.7$ for GIAO-MP2].

Results and Discussions

Complexation of guanidinium ion $[(H_2N)_3C^+]$ with BH_4^+ leads to **1**, which was found to be a stable minimum at the B3LYP/6-311+G** level (Figure 1). The structure **1** contains a five-coordinate boron atom involving a 2e-3c bond. The B−N bond distance of **1** is 1.662 Å, 0.004 Å shorter than that in the neutral ammonia borane complex H_3BNH_3 calculated at the same B3LYP/6-311+G** level. For comparison, the structures of guanidinium ion **2** and protonated and methylated guanidinium dications **3** and **4**, respectively, were also calculated (Figure 1). The computed C−N(BH_4) and C−N(NH_2) bond distances of **1** are 1.467 and 1.309 Å, respectively, 0.132 Å longer and 0.026 Å shorter than the C−N bond distance of **2**. However, these bond lengths are very close to the C−N(NH_3) and C−N(NH_2) bond distances of **3** and the C−N(CH_3) and C−N(NH_2) bond distances of **4**, which indicates a strong $(H_2N)_3C^+$ and BH_4^+ interaction in dication **1** despite charge−charge repulsion. The relative bond strengths were estimated using the Wiberg bond index[13] analysis at the B3LYP/6-311+G** level (Figure 2). The strong interaction is in agreement with the calculated bond index of 0.63 for the B−N bond of **1**. This value is three-fourths of the C(CH_3)−N bond index of **4** (0.84).

Complexation of guanidinium ion with neutral BH_3 leads to a relatively weak complex **5** with a long B−N bond of 1.951 Å. The weak interaction between $(H_2N)_3C^+$ and BH_3 is also in agreement with the calculated bond index of 0.34 for B−N bond, which is almost one-half that of the **1** (Figure 2). The C−N(BH_3) and C−N(NH_2) bond distances of **5** are 1.392 and 1.320 Å, respectively, only 0.057 Å longer and 0.015 Å shorter than C−N bond distance of **2**. Both BH_4^+ and BH_3 contain an empty p orbital, which can formally accept an electron pair. However, only BH_4^+ forms (because of greater electrostatic attraction) a stronger B−N bond with a relatively poor base such as guanidinium ion **2**. Consequently, BH_4^+ can be classified as a super Lewis acid, being a significantly stronger electron acceptor than BH_3.

NBO charges[14] of structures **1**−**5** were also calculated (Figure 2). The charge of the carbon of the dication **1** (+0.72)

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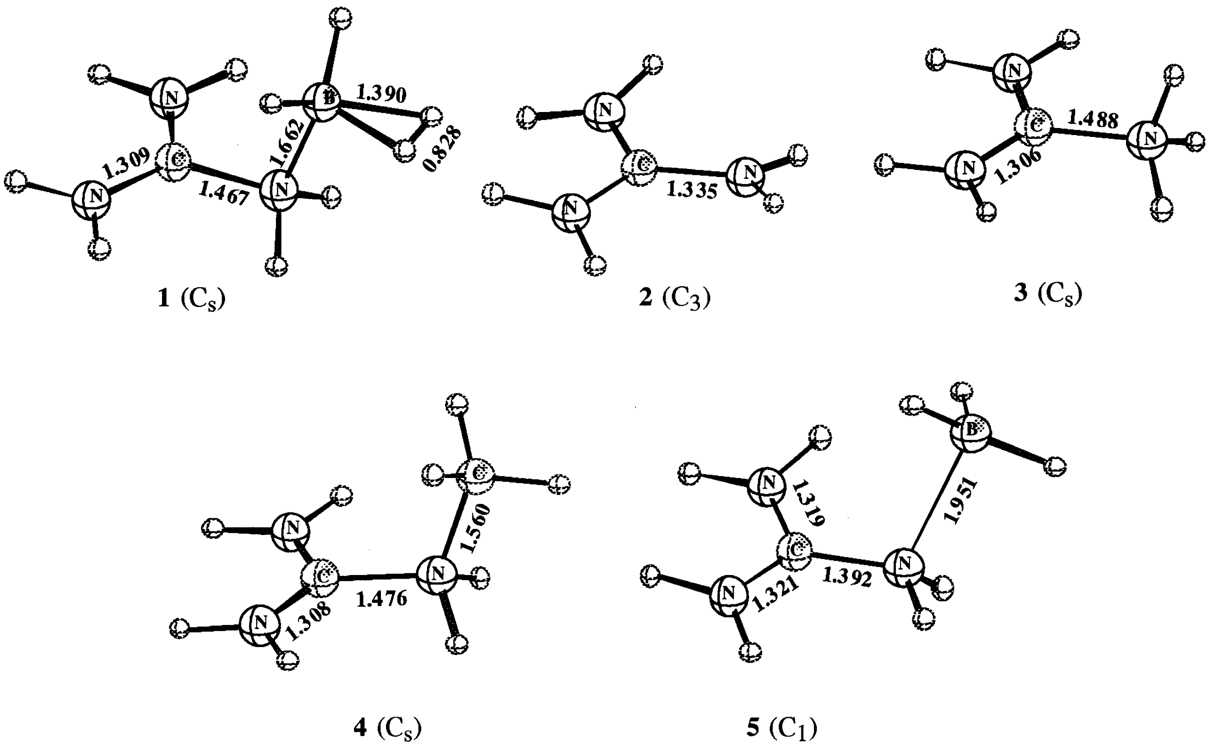
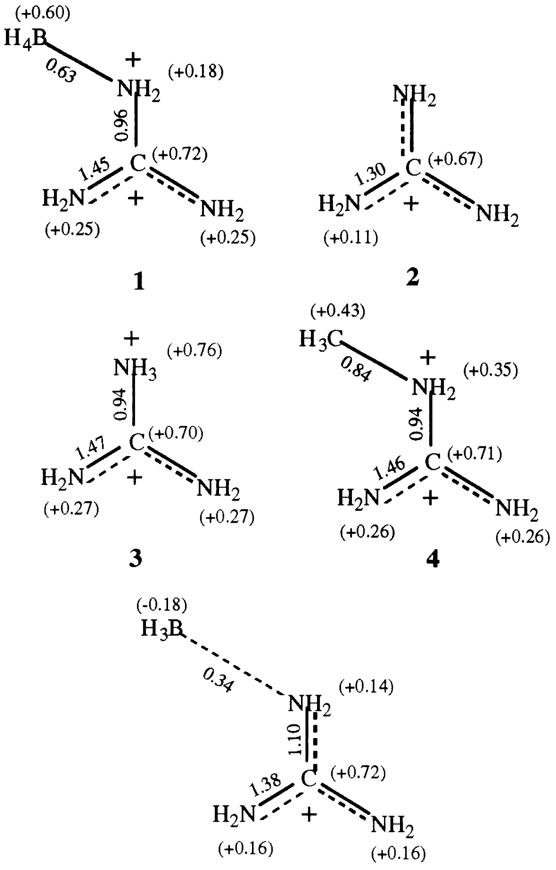


Figure 1. B3LYP/6-311+G** structures of **1**−**5**.



1 **2** **3** **4** **5**

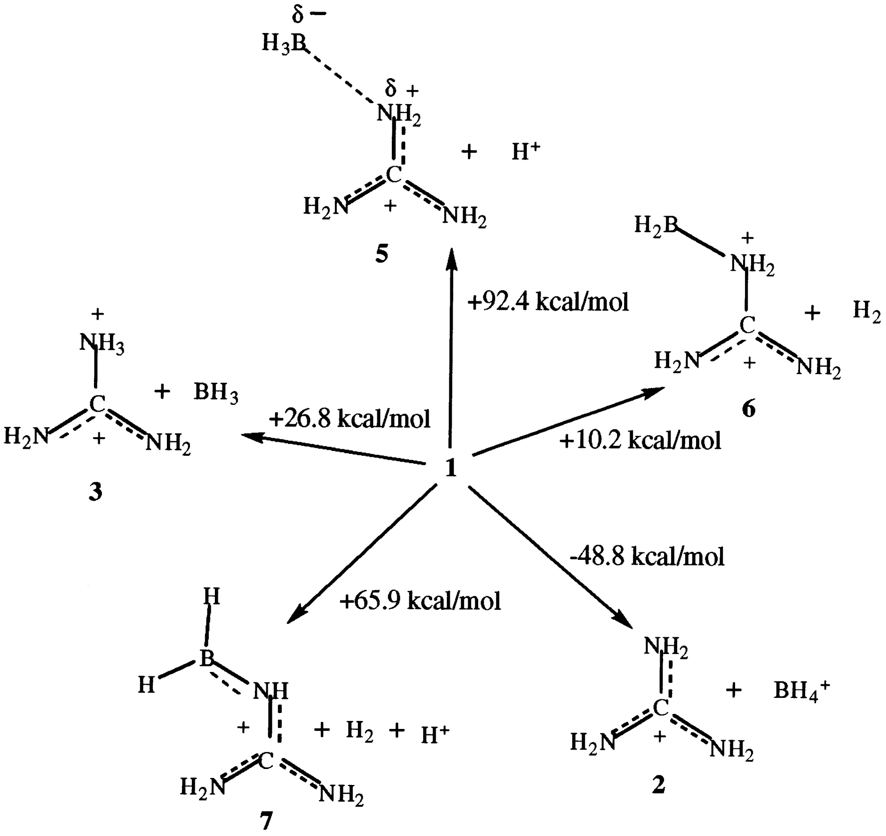
Figure 2. B3LYP/6-311+G** calculated Wiberg bond index and NBO charges (given in parentheses) of **1**−**5**.

is slightly more positive than that of the dication **3** (+0.70). In **1**, the BH_4 group as a whole bears a +0.60 charge, and the guanidinium $[(NH_2)_3C^+]$ group as a whole bears a +1.40 charge, which indicates that a +0.40 charge was transferred from BH_4^+ to the $(NH_2)_3C^+$ group upon complexation. In comparison, in dication **4**, a +0.57 charge was transferred from CH_3^+ group to the $(NH_2)_3C^+$ group upon methylation of guanidinium ion. In monocation **5**, a +0.18 charge was transferred from the BH_3 group to the $(NH_2)_3C^+$ group upon complexation. From these comparisons, the dications **1**, **3**, and **4** can be considered as similarly charged delocalized ions where one of the positive charges is located on the $NH_2{-}BH_4$, NH_3, or $NH_2{-}CH_3$ group and the second positive charge is delocalized among $H_2N{-}C{-}NH_2$, as shown in Figure 2. On the other hand, in monocations **2** and **5**, the positive charge is delocalized among $(H_2N)_2C{-}NH_2$, as shown in Figure 2.

Several different dissociation paths for dication **1** were computed (Scheme 1). Deprotonation of **1** to form **5** is unfavorable by 92.4 kcal/mol. Possible proton transfer from BH_4^+ to guanidinium ion **2** to form protonated guanidinium dication **3** was also computed and was found to be unfavorable by 75.6 kcal/mol. Expectedly, the dissociation of **1** into BH_4^+ and guanidinium ion **2** was calculated to be exothermic by 48.8 kcal/mol. In comparison, the dissociation of monocation **5** into BH_3 and **2** is endothermic by 3.1 kcal/mol. The dissociation of **1** into **6** and H_2 is unfavorable by 10.2 kcal/mol (Scheme 1). Structure **6** can be considered as a complex of the guanidinium ion and BH_2^+.

Dissociation into protonated guanidinium dication **3** and BH_3 was also considered and found to be substantially endothermic by 26.8 kcal/mol. Dissociation into monocation **7**, H_2, and H^+ was calculated to be even more endothermic by 65.9 kcal/mol. However, dissociation of **1** into **7** and H_3^+

Scheme 1



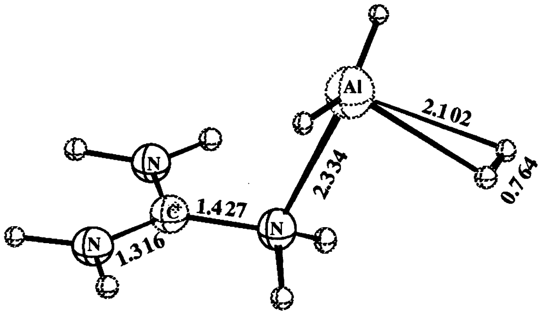
was calculated to be exothermic by 33.1 kcal/mol. Structure **7** can be considered as a complex of the neutral guanidine $(NH_2)_2CNH$ and BH_2^+.

We have also calculated the structure of the complex of guanidinium ion with AlH_4^+, **8** (Figure 3). Structure **8** also contains a 2e-3c bond involving aluminum and two hydrogens. The Al−N bond distance of **8** is 2.334 Å. However, from the calculated bond index of Al−N (0.21) in **8**, it appears that the interaction between $(H_2N)_3C^+$ and AlH_4^+ is rather weak. Complexation of guanidinium ion with neutral AlH_3 leads to the even weaker complex **9**, with an Al−N bond length of 2.538 Å. The calculated Al−N bond index of **9** (0.12) is one-half the Al−N bond index of **8**.

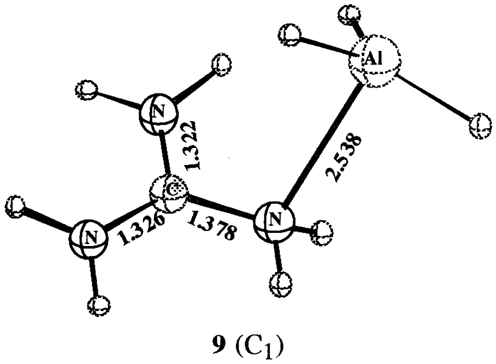
NBO charges of structures **8** and **9** were calculated and are given in Figure 4. In **8**, the AlH_4 group as a whole bears a +0.88 charge, and the $(NH_2)_3C^+$ group as a whole bears a +1.12 charge, which indicates that very little (+0.12) charge was transferred from AlH_4^+ to the $(NH_2)_3C^+$ group upon complexation.

As for **1**, several dissociation paths for complex **8** were also computed, and they are presented in Scheme 2. Dissociation of **8** into AlH_4^+ and $(NH_2)_3C^+$ was computed to be exothermic by 62.5 kcal/mol. On the other hand, dissociation of **9** into AlH_3 and $(NH_2)_3C^+$ is endothermic by only 0.2 kcal/mol. Deprotonation (into **9**) and dehydrogenation (into **10**) of **8** were computed to be unfavorable by 113.2 and 6.8 kcal/mol, respectively. Dissociation of **8** into **3** and AlH_3 and dissociation of **8** into **11**, H_2, and H^+ were also calculated and found to be endothermic by 50.5 and 65.9 kcal/mol, respectively. Dissociation of 8 into **11** and H_3^+ was calculated to be exothermic by 9.1 kcal/mol.

We have also calculated the ^{13}C NMR chemical shifts of **1**−**5**, **8**, and **9** by the correlated GIAO-MP2 method[15] using



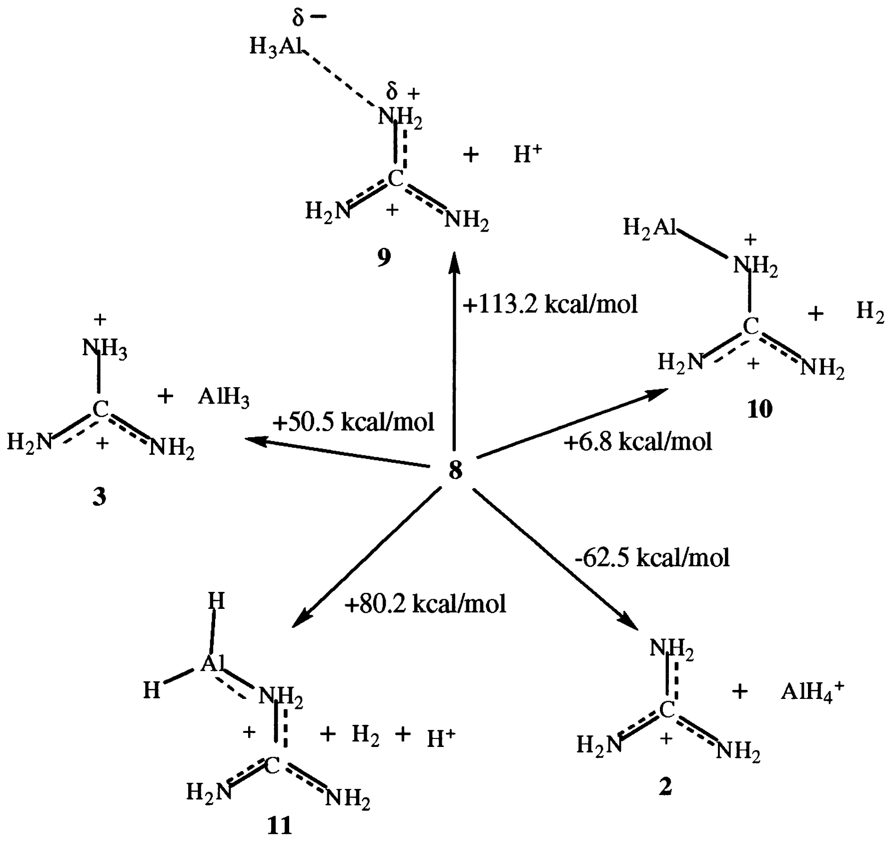
8 (C_s)



9 (C_1)

Figure 3. B3LYP/6-311+G** structures of **8** and **9**.

Scheme 2



B3LYP/6-311+G** geometries (Table 2). The calculated δ^{13}C of guanidinium ion **2** is 158.6, which agrees very well the experimental value of 156.7.[3] The calculated δ^{13}C of protonated guanidinium dication **3**, 148.5, is almost identical to the experimental value of 148.9.[3] The δ^{13}C shift of dication **3** is, in fact, shielded by about 8 ppm from that of the monocation **2**. The calculated δ^{13}C shifts of guanidinium−BH_4^+ complex **1** (155.4) and methylated guanidinium dication **4** (155.9) are also shielded by about 3 ppm from that of guanidinium ion **2**. However, the δ^{13}C shift of monocation guanidinium−BH_3 complex **5** (165.4) is deshielded by about 7 ppm from that of **2**. The calculated δ^{13}C shifts of guanidinium−AlH_4^+ complex **8** and guanidinium−AlH_3 complex **9** are 158.4 and 163.6, respectively.

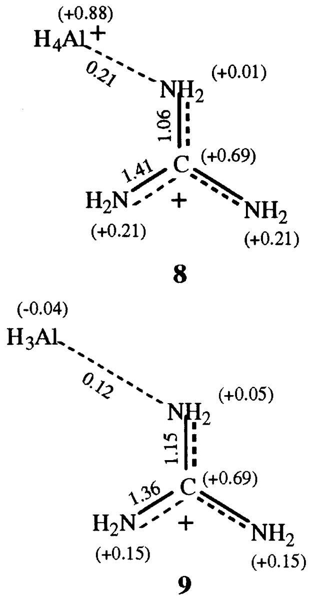


Figure 4. B3LYP/6-311+G** calculated Wiberg bond index and NBO charges (given in parentheses) of **8** and **9**.

Table 2. Calculated[a] and Experimental[b] ^{13}C NMR Chemical Shifts

	GIAO−SCF/tzp/dz//B3LYP/6-311+G**	GIAO-MP2/tzp/dz//B3LYP/6-311+G**	expt
1	164.5	155.4	
2	165.4	158.6	156.7
3	158.8	148.5	148.9
4	164.7	155.9	
5	172.8	165.4	
8	167.1	158.4	
9	171.3	163.6	

[a] ^{13}C NMR chemical shifts were referenced to $(CH_3)_4Si$. [b] Experimental values were taken from ref 3.

Olah previously reported[4] that superelectrophilic interactions offer an adequate explanation of the observed experimental data for a variety of superacid-catalyzed reactions. Our present studies will help in elucidating the nature of such interactions of electrophilic guanidinium ion with Lewis and super Lewis acids. If the nitrogen atom of guanidinium ion is further coordinated with Lewis and super Lewis acids, the electron deficiency of the systems would become more pronounced, resulting in enhanced reactivity.[4]

Conclusion

Complexes (**1** and **8**) of guanidinium ion with super Lewis acidic BH_4^+ and AlH_4^+ were found to be stable minima at the B3LYP/6-311+G** level of calculation. Each of the dications **1** and **8** contains a 2e-3c bond. The structures of **1** and **8** were compared with the structures of protonated and methylated guanidinium dications (**3** and **4**), indicating that guanidinium ion forms a strong complex with BH_4^+ but a relatively weak complex with AlH_4^+. Complexation of guanidinium ion with neutral BH_3 and AlH_3 leads to weak complexes (**5** and **9**). Energies of possible different dissociation paths of **1** and **8** were computed. The ^{13}C NMR chemical shifts of the ions were also calculated by the GIAO-MP2 method.

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