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Comparative Study of the Hypercoordinate Ions $C_7H_9^+$ and $C_8H_9^+$ by the ab Initio/GIAO-CCSD(T) Method

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A comparative study of the hypercoordinate square-pyramidal carbocations $C_7H_9^+$ and $C_8H_9^+$ was performed by the ab initio/GIAO-CCSD(T) method. The structures and ^{13}C NMR chemical shifts of the cations were calculated at the GIAO-CCSD(T)/tzp/dz//MP2/cc-pVTZ level. The bishomo square pyramidal structure **1** was calculated for $C_7H_9^+$ at the MP2/cc-pVTZ level. The calculated ^{13}C NMR chemical shifts of structure **1** agree extremely well with the experimental values. However, unlike for $C_7H_9^+$ both the bishomo square pyramidal structure **3** and the trishomocyclopropenium type structure **4** were found to be minima on the potential energy surface of $C_8H_9^+$. They are very close energetically with cation **3**, only 0.7 kcal/mol less stable than cation **4** at the MP2/cc-pVTZ//MP2/cc-pVTZ + ZPE level. Neither structure **3** nor **4** yields NMR spectra that agree with experiment. However, a weighted average of the two reproduces the observed NMR spectrum of $C_8H_9^+$ (at −80 °C) quite well.

Introduction

Hypercoordinate square-pyramidal carbocations are of much interest and have been a subject of many experimental and theoretical studies.[1] In 1970, Williams[2] first suggested the hypercoordinate square-pyramidal structure for the $(CH)_5^+$ carbocation based on the structure of isoelectronic isostructural pentaborane (Scheme 1). In 1972, Stohrer and Hoffmann concluded[3] from a theoretical treatment using extended Hückel theory that the energy minimum for the $(CH)_5^+$ cation does not correspond to a planar classical structure. The proposed structure was a three-dimensional one in the form of a square-pyramid with multicenter bonding.

In the same year, Masamune and co-workers presented[4] experimental evidence for a dimethyl analogue $(CH_3)_2C_5H_3^+$ in the superacid solution (Scheme 2) and concluded that the structure is indeed square-pyramidal, and thus a close structural and isoelectronic relationship with 1,2-$(CH_3)_2B_5H_7$ was established. The square-pyramidal $(CH)_5^+$ cation has also been a subject of many theoretical studies, first by semiempirical and later by ab initio methods. Kollman et al.[5] and Dewar and co-workers[6] reported CNDO and MINDO/3 studies on $(CH)_5^+$, respectively. Ab initio calculation on capped annulene rings with six interstitial electrons was carried carried out by Schleyer et al.[7,8] Results of this calculation show that the favorable pyramidal structure follows the Hückel-like $4n + 2$ interstitial electron rule.

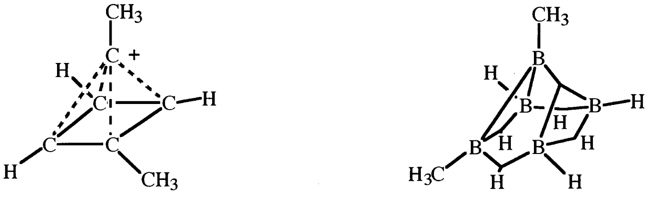
Although the parent cation, $(CH)_5^+$, has not yet been observed in superacids experimentally, a variety of related structures including the $C_7H_9^+$ cation[9] and the $C_8H_9^+$ cation[10] have been identified under stable ion conditions using ^{13}C and ^1H NMR spectroscopy. The pentagonal-pyramidal structure was also observed for the $(CCH_3)_6^{2+}$ dication.[11]

We have previously investigated the structures and ^{13}C NMR chemical shifts of a number of hypercoordinate square-pyramidal carbocations by the ab initio/IGLO/GIAO-MP2 method.[12] The structures were obtained at the MP2/6-31G* level. The IGLO calculated ^{13}C NMR chemical shifts show only a reasonable correlation with the experimental data. The correlated GIAO-MP2 calculated ^{13}C NMR shifts, however, showed significant improvements over the SCF IGLO calculated chemical shifts. Recent studies indicate that extensive electron correlation contributions are necessary to calculate the accurate chemical shifts. These types of correlated ^{13}C NMR chemical shift calculations can be carried out by the GIAO-CCSD(T) and other coupled cluster methods. The GIAO-CCSD(T) method of calculating the accurate ^{13}C NMR chemical shifts of carbocations and other organic molecules have been demonstrated in several recent studies.[13−17] The GIAO-CCSD(T) calculations for these hypercoordinate carbocations would be expected to closely correspond with the experimental data.

SCHEME 1

$(CH)_5^+$ pentaborane

SCHEME 2



$(CH_3)_2C_5H_3^+$ 1,2-$(CH_3)_2B_5H_7$

In our previous study[12] we found two isomeric, bishomo square pyramidal and the trishomocyclopropenium type minimum structures corresponding to $C_8H_9^+$. They are almost

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TABLE 1: Total Energies (−au), ZPE,[a] and Relative Energies (kcal/mol)[b]

	MP2/6-31G*	ZPE	MP2/6-311G*	MP2/cc-pvtz	rel. energy (kcal/mol)
1	270.86694	85.4	270.95415	271.19054	0.0
2	270.85748	84.2	270.94339	271.18057	5.1
3	308.85725	88.7	308.95665	309.21470	0.7
4	308.85835	88.9	308.95859	309.21626	0.0
5ts	308.85692	88.6	308.95655	309.21450	0.8
6	308.88584	88.7	308.98320	309.24095	−15.7

[a] Zero-point vibrational energies (ZPE) at MP2/6-31G*//MP2/6-31G* scaled by a factor of 0.96. [b] Relative energy at MP2/cc-pVTZ//MP2/cc-pVTZ + ZPE level.

isoenergetic. A calculated 1:2 equilibrium mixture of these ions seems to best represent the experimentally observed NMR spectrum of $C_8H_9^+$ at −80 °C.[12] We now report our ab initio/GIAO-CCSD(T) detailed investigation of the intriguing $C_8H_9^+$ cation and compare the results with the closely related $C_7H_9^+$ cation.

Calculations

Geometry optimizations and frequency calculations were carried out with the Gaussian 03 program.[18] The geometry optimizations were performed at the MP2/6-31G* level. Vibrational frequencies at the MP2/6-31G*//MP2/6-31G* level were used to characterize stationary points as minima (number of imaginary frequency (NIMAG) = 0) or transition state (NIMAG = 1). The MP2/6-31G* geometries were further optimized at the higher MP2/6-311G* and MP2/cc-pVTZ levels. Calculated energies are given in Table 1. NMR chemical shifts were calculated by the GIAO (Gauge invariant atomic orbitals) method[19] using MP2/cc-pVTZ geometries. GIAO-CCSD(T), GIAO-MP2, and GIAO-SCF calculations using tzp/dz and qzp/tzp basis sets[20,21] have been performed with the ACES II program.[22] The ^{13}C NMR chemical shifts were computed using TMS (calculated absolute shift, i.e. σ(C), tzp/dz = 193.9 (GIAO-SCF), 199.6 (GIAO-MP2), 197.9 (GIAO-CCSD(T); qzp/tzp = 196.3 (GIAO-CCSD(T)) as a reference.

Results and Discussion

$C_7H_9^+$. The C_{2v} symmetrical structure **1** was found to be a minimum on the potential energy surface of $C_7H_9^+$ at the MP2/cc-pVTZ level (Figure 1). The bishomo square pyramidal ion **1** was originally prepared by Masamune et al.[9] in the superacid solution (in SbF_5–SO_2ClF at −110 °C). The computed C1−C2 (apical carbon−basal carbon) bond length of **1** was found to be 1.626 Å, which indicates nonclassical nature of the structure. There is no significant bonding interaction between C5 and C7 carbons as the distance between them was found to be 2.104 Å.

We also searched for minimum-energy trishomocyclopropenium type structure **I** (Scheme 3). At the MP2/cc-pVTZ level, the structure **I** is not a minimum on the potential energy surface of $C_7H_9^+$ and converged into structure **1** upon optimization. The parent persistent trishomocyclopropenium ion **II** and other related ions were in fact prepared by Masamune et al.[23] in the superacid solutions and characterized by ^{13}C NMR spectroscopy. Ion **II** was also studied by the ab initio/IGLO method by Prakash et al.,[24] and its highly symmetrical C_{3v} structure was confirmed.

SCHEME 3

$C_7H_9^+$ $C_6H_9^+$

The isomeric classical C_s symmetrical structure **2** was also found to be a minimum on the PES of $C_7H_9^+$. Structure **2** can be considered as a dicyclopropylcarbinyl cation. However, structure **2** was found to be 5.1 kcal/mol less stable than the structure **1**. The calculated ^{13}C NMR chemical shifts of the structure **2** are shown in Table 2.

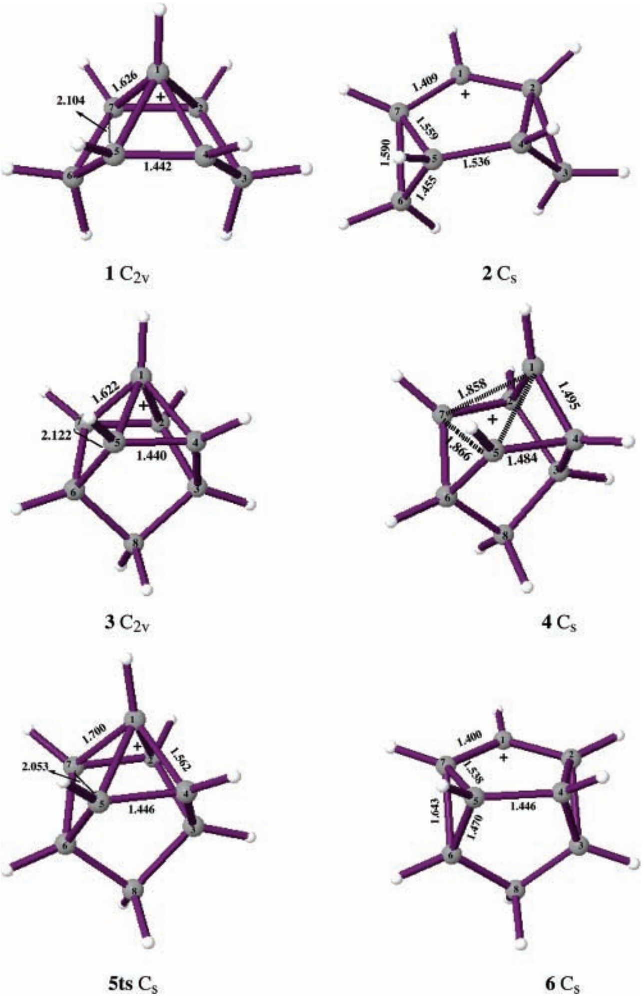
TABLE 2: Calculated[a] and Experimental ^{13}C NMR Chemical Shifts

no.	atom	GIAO-SCF	GIAO-MP2	GIAO CCSD(T)	expt
1[b]	C1	−34.5	−17.0	−17.6	−17.2
	C2, C4, C5, C7	37.4	42.2	41.5	39.4
	C3, C6	6.5	10.6	10.2	8.1
2	C1	285.7	265.3	265.0	
	C2, C7	38.2	54.6	52.2	
	C3, C6	41.9	55.0	52.7	
	C4, C5	52.0	68.5	64.7	
3[c]	C1	−44.9	−28.4	−28.5	2.4
	C2, C4, C5, C7	37.8	42.6	41.8	30.4
	C3, C6	21.8	30.8	29.3	29.0
	C8	39.2	47.3	44.7	41.7
4	C1	1.5	12.9	12.8	
	C2, C4	26.9	36.9	34.5	
	C5, C7	9.8	18.5	18.7	
	C3	32.4	40.8	38.6	
	C6	13.0	21.7	20.7	
	C8	35.1	43.6	41.1	
6	C1	261.6	235.4	237.4	
	C2, C7	45.5	63.7	59.9	
	C3, C6	73.8	95.7	90.3	
	C4, C5	55.0	71.2	66.9	
	C8	27.3	37.0	35.8	

[a] ^{13}C NMR chemical shifts were referenced to TMS; for numbering scheme, please see Figure 1. [b] Experimental values were taken from ref 9. [c] Experimental values taken from ref 10.

The ^{13}C NMR chemical shifts of **1** were calculated by the GIAO-coupled cluster method at the GIAO-CCSD(T)/tzp/dz level using MP2/cc-pVTZ geometry (Table 2). The calculated $\delta^{13}C$ values agree extremely well with the available experimental values. For comparison, the ^{13}C NMR chemical shifts of **1** were also computed at the GIAO-MP2/tzp/dz and GIAO-SCF/tzp/dz levels (Table 2). The GIAO-CCSD(T)/tzp/dz calculated $\delta^{13}C$ of the C1 (apical) and C2 (basal) carbons of **1** are −17.6 and 41.5, respectively, and are close to the experimentally reported values[9] of −17.2 and 39.4 ppm. The corresponding GIAO-MP2/tzp/dz calculated $\delta^{13}C$ values are −17.0 and 42.2. They are remarkably close to the GIAO-CCSD(T)/tzp/dz values. This indicates that the GIAO-MP2 method is probably adequate for NMR chemical shift calculations for nonclassical carbocations. However, the corresponding GIAO-SCF/tzp/dz calculated $\delta^{13}C$ values (C1, −34.5 and C2, 37.4) are significantly more shielded than those of the GIAO-CCSD(T)/tzp/dz values.

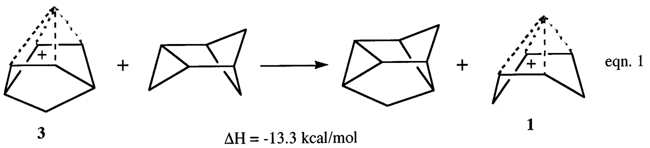
$C_8H_9^+$. Unlike $C_7H_9^+$, both the bishomo square pyramidal **3** and the trishomocyclopropenium type structure **4** were found to be minima on the PES of $C_8H_9^+$ at the MP2/cc-pVTZ level (Figure 1). Structure **3** is very similar to the structure **1** with the C1−C2 (apical carbon − basal carbon) bond length of 1.622 Å. On the other hand, the C1−C5 and C5−C7 bond distances of **4** are 1.858 Å and 1.866 Å, respectively, indicating the three-center two-electron (3c-2e) bonding in the ion. Structure **4** is 0.7 kcal/mol more stable than **3**. We have located a transition structure, **5ts** (Figure 1), at the MP2/cc-pVTZ level for the interconversion of the ions **3** and **4**. However, structure **5ts** lies only 0.1 kcal/mol higher in energy than structure **3**. The interconversion between **3** and **4** through transition state **5ts**, therefore, is very facile.



1 C_{2v} **2** C_s **3** C_{2v} **4** C_s **5ts** C_s **6** C_s

Figure 1. MP2/cc-pVTZ structures of **1**−**6**.

The relative stability of the structurally similar ions **1** and **3** were compared by the isodesmic eq 1. The reaction was computed to be exothermic by 13.3 kcal/mol, indicating more stabilization of **1** compared to **3**. This is probably due to the fact that the overlap between the p-orbitals of the cap and the p-orbitals of the 1,4-cyclohexadiene ring decreases with the bending of the p-orbitals away from the cap. The calculated highest occupied molecular orbitals (HOMO) of **1**, **3**, and **4** are shown in Figure 2. The HOMO of **1** shows that the good overlap between the cap p-orbital and 1,4-cyclohexadiene p-orbitals is possible because of the right geometry. However, in ion **3**, since the 3,6 positions of the cyclohexadiene moiety are tied (constrained) with a methylene group, the corresponding p-orbitals cannot easily bend toward the cap to allow a good overlap. On the other hand, the HOMO of the trishomocyclopropenium structure **4** is showing the 3c-2e bonding nature of the ion resulting from good orbital overlap among C1, C5, and C7 carbons.



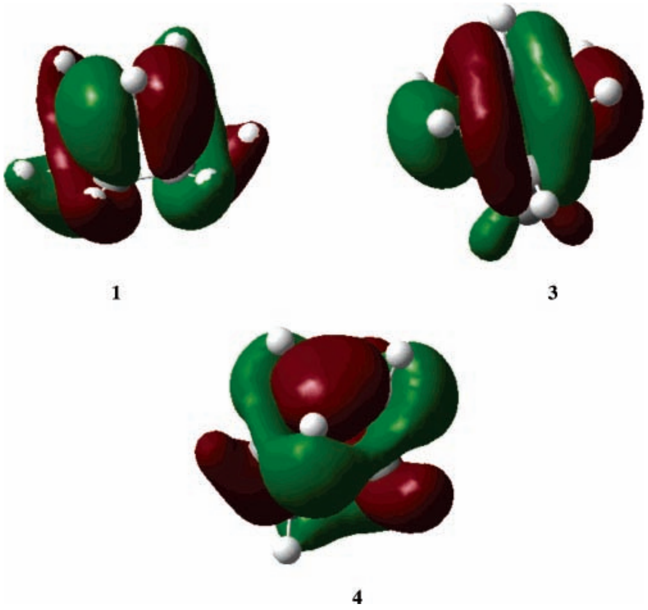
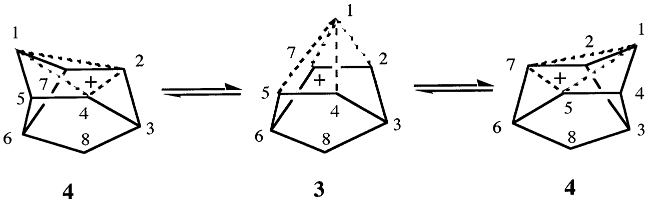


Figure 2. Calculated HOMO of **1**, **3**, and **4**.

SCHEME 4



The ^{13}C NMR chemical shifts of **3** were calculated at the GIAO-CCSD(T)/tzp/dz level using MP2/cc-pVTZ geometry (Table 2). The calculated $\delta^{13}C$ value of the C1 (apical) carbon of −28.5 strongly deviates from the experimental value of 2.4 ppm.[10] The calculated $\delta^{13}C$ of the C2 (basal) carbon of 41.8 also deviates from the experimental value of 30.4 ppm. The ^{13}C NMR chemical shifts of **4** were also calculated at the GIAO-CCSD(T)/tzp/dz level using MP2/cc-pVTZ geometry (Table 2). The calculated $\delta^{13}C$ of the C1, C2, and C5 carbons of **4** are 12.8, 34.5, and 18.7, respectively, also show strong deviation from the experimental value. As the ions (**3** and **4**) are very close energetically, an equilibrium mixture (undergoing rapid exchange on the NMR time scale as shown in Scheme 4) involving ions **3** and **4** (in 1:2 ratio) can best represent the structure of $C_8H_9^+$. Thus, the calculated average $\delta^{13}C$ of C1, C2, C3, and C8 are −1.0 (example for averaging procedure for C1 carbon: $(-28.5 + 12.8 \times 2)/3)$), 31.7 $(41.8 \times 4 + (34.5 \times 2 + 18.7 \times 2) \times 2)/12$, 29.5 $(29.3 \times 2 + (38.6 + 20.7) \times 2)/6$ and 42.3 $(44.7 + 41.1 \times 2)/3)$ match extremely well with the corresponding experimental values of 2.4, 30.4, 29.0, and 41.7, respectively (Table 2).

The ^1H NMR chemical shifts of **3** were also calculated at the GIAO-CCSD(T)/tzp/dz level using MP2/cc-pVTZ geometry (Table 3). The calculated δ^1H of the H(C1), H(C2), H(C3), and H(C8) of 0.74, 4.03, 3.11, and 2.01 ppm differ somewhat from the experimental values of 1.8, 3.84, 3.37, and 1.8 ppm. The calculated average δ^1H of the H(C1), H(C2), H(C3), and H(C8) of the equilibrium mixture involving ions **3** and **4** (in 1:2 ratio) are 1.3, 3.43, 3.11, and 1.92 ppm, respectively, match very well with the corresponding experimental values of 1.8, 3.84, 3.37, and 1.8 ppm.

The possibility of structures **3** and **4** being in rapid equilibrium is not only indicated from their average chemical shifts but also from their nearly identical energies. In fact, such an equilibrium was already suggested by Masamune et al.[10] but has never been further investigated.

TABLE 3: Calculated[a] and Experimental ^{1}H NMR Chemical Shifts

no.	atom	GIAO-SCF	GIAO-MP2	GIAO-CCSD (T)	expt
3[b]	H(C1)	−0.06	0.91	0.74	1.80
	H(C2, C4, C5, C7)	4.44	4.43	4.03	3.84
	H(C3, C6)	3.06	3.21	3.11	3.37
	H(C8)	1.99	2.08	2.01	1.80
4	H(C1)	1.36	1.62	1.58	
	H(C2, C4)	4.09	4.37	4.18	
	H(C5, C7)	1.94	2.13	2.08	
	H(C3)	2.73	2.88	2.76	
	H(C6)	3.33	3.61	3.46	
	H(C8)	1.84	1.94	1.87	

[a] ^{13}C NMR chemical shifts were referenced to TMS (calculated absolute shift, i.e. σ(H), SCF = 31.92, MP2 = 31.71, and CCSD(T) = 31.92); for numbering scheme, please see Figure 1. [b] Experimental values were taken from ref 10.

Similar to **2**, the classical C_s symmetrical structure **6** was also found to be a minimum on the PES of $C_8H_9^+$ (Figure 1). The structure **6** can also be considered as a dicyclopropylcarbinyl cation. The structure **6** was found to be 16.4 kcal/mol more stable than the structure **3**. However, the structure **6** was not observed in superacid solutions at low temperature.[10] The ^{13}C NMR chemical shifts of the structure **6** were also calculated and are shown in Table 2.

Conclusion

The structures and ^{13}C NMR chemical shifts of the hypercoordinate square-pyramidal carbocations $C_7H_9^+$ and $C_8H_9^+$ were calculated using the ab initio/GIAO-CCSD(T) method. The bishomo square pyramidal structure **1** was found to be a minimum on the PES $C_7H_9^+$ at the MP2/cc-pVTZ level. The calculated ^{13}C NMR chemical shifts of structure **1** agree extremely well with the experimental values. On the other hand, both the bishomo square pyramidal structure **3** and the trishomocyclopropenium type structure **4** were found to be minima on the PES of $C_8H_9^+$ at the MP2/cc-pVTZ level. Structure **4** is 0.7 kcal/mol more stable than structure **3** at the MP2/cc-pVTZ//MP2/cc-pVTZ + ZPE level. The calculated ^{13}C NMR chemical shifts of neither structures **3** nor **4**, however, agree with the experimental values. An equilibrium mixture of ions **3** and **4** (in 1:2 ratio) seems to best represent the experimental NMR spectrum of $C_8H_9^+$ (at −80 °C).

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