Ab Initio/IGLO/GIAO-MP2 Study of Hypercoordinate Square-Pyramidal Carbocations[1]

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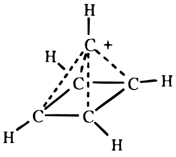
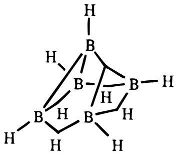
The structures of hypercoordinate square-pyramidal carbocations were calculated at the correlated MP2/6-31G* level. The ^{13}C NMR chemical shifts of the cations were also calculated using IGLO and GIAO-MP2 methods. The IGLO calculated data show only a reasonable correlation with the experimental ^{13}C NMR chemical shifts. The correlated GIAO-MP2 calculated ^{13}C NMR shifts, however, showed significant improvements over the SCF IGLO calculated chemical shifts. It was also found that among the $C_8H_9^+$ isomers, the bishomo square-pyramidal cation **7** is only 0.2 kcal/mol more stable than the trishomocyclopropenium-type ion **8** at the MP4(SDQ)/6-31G*//MP2/6-31G* + ZPE level. Almost a calculated 1:2 equilibrium mixture of ions **7** and **8** seems to best represent the experimental NMR spectrum of $C_8H_9^+$ at −80 °C. The structures and ^{13}C NMR chemical shifts for the elusive $(CH)_5^+$ **1** and its monomethyl-substituted analogues **2** and **3** were also computed.

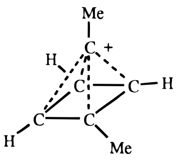
Introduction

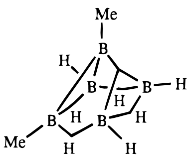
Hypercoordinate square-pyramidal carbocations have been the focus of much interest and speculation over the past two decades.[2,3] In 1971, Williams[4] first suggested the hypercoordinate square-pyramidal structure for the $(CH)_5^+$ carbocation based on the structure of isoelectronic isostructural pentaborane. In 1972, Stohrer and Hoffmann[5] concluded from a theoretical treatment using extended Hückel formalism that the energy minimum for the $(CH)_5^+$ cation does not correspond to a planar classical structure. The proposed structure was three-dimensional in the form of a square pyramid with multicenter bonding.


$(CH)_5^+$

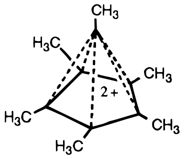

pentaborane

In the same year Masamune and co-workers[6] presented experimental evidence for a dimethyl analogue $(CH_3)_2C_5H_3^+$ in superacid solution and concluded that the structure is indeed a square pyramid, and thus, a structural and isoelectronic relationship with 1,2-$(CH_3)_2B_5H_7$ was established.


$(CH_3)_2C_5H_3^+$


1,2-$(CH_3)_2B_5H_7$

Although the parent cation $(CH)_5^+$ has not yet been observed experimentally, a variety of similar structures[6−10] have been identified under stable ion conditions using ^{13}C and ^{1}H NMR spectroscopy. The pentagonal-pyramidal structure was observed for the $(CCH_3)_6^{2+}$ dication:[11]


$(CCH_3)_6^{2+}$

The $(CH)_5^+$ cation has also been a subject of many theoretical studies first by semiempirical and later by ab initio methods. Kollman et al.[12] and Dewar and co-workers reported[13] CNDO and MINDO/3 studies on $(CH)_5^+$, respectively. Ab initio calculation on capped annulene rings with six interstitial electrons was carried out by Schleyer et al.[14,15] Results of this calculation show that the favorable pyramidal structure follows the Hückel-like $4n + 2$ interstitial electron rule.

We now wish to report our ab initio/IGLO/GIAO-MP2 studies of a series of square-pyramidal carbocations, which were characterized earlier by ^{1}H and ^{13}C NMR spectroscopy under long-lived stable ion conditions. This permits comparison of calculated data with the experimentally observed results. We have also calculated the structures and ^{13}C NMR chemical shifts for the still elusive $(CH)_5^+$ carbocation and its monomethyl analogues.

Results and Discussions

Ab initio calculations were carried out by using the Gaussian 94[16] package of programs. Geometries were optimized at the HF/6-31G* and MP2/6-31G* levels. Vibrational frequencies at the HF/6-31G*//HF/6-31G* level were used to characterize stationary points as minima and to evaluate zero-point vibrational energies (ZPE). For some of the cations single-point energies at the MP4(SDQ)/6-31G* level on MP2/6-31G*

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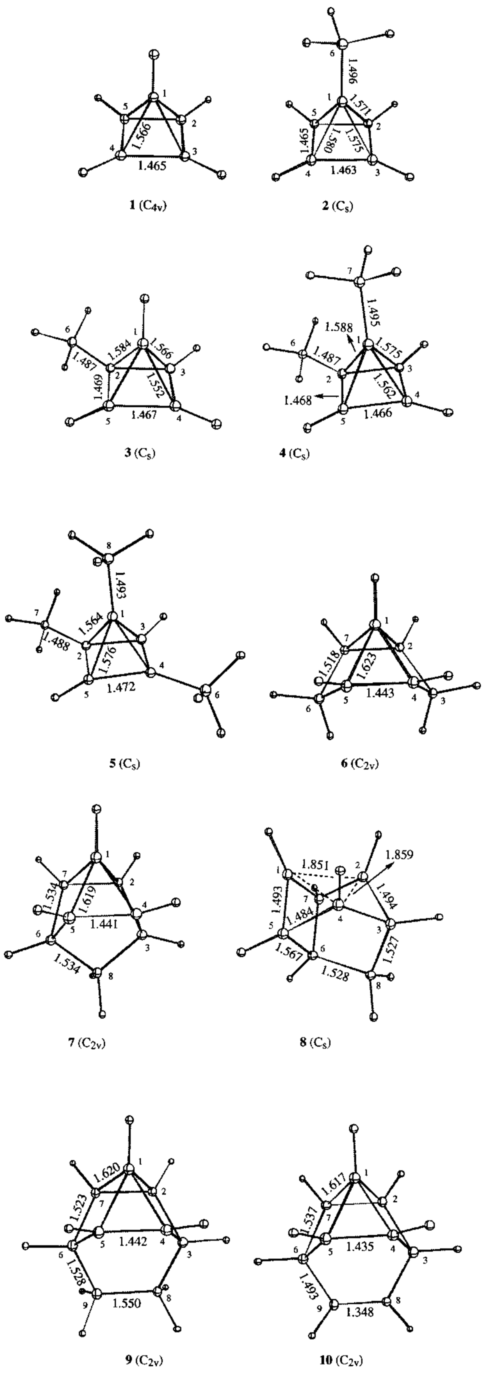


Figure 1. MP2/6-31G* optimized structures of **1**−**10**.

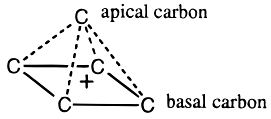
geometries were calculated. Selected parameters of the ions at the MP2/6-31G* level are given in Figure 1. IGLO calculations were performed according to a reported method[17−19] at IGLO DZ and II levels using MP2/6-31G* geometries. Huzinaga[20a] Gaussian lobes were used as follows. Basis DZ: C, 7s3p contracted to [4111, 21]; H, 3s contracted to [21]. Basis II: C, 9s5p1d contracted to [51111, 2111, 1]; d exponent, 1.0; H, 5s1p contracted to [311, 1]; p exponent, 0.70. GIAO-MP2 calculations using 3-21G,[20b] dzp/dz,[21,22] and tzp/dz basis sets[21,22] on MP2/6-31G* geometries have been performed with the ACES II program.[23] Relevent computed and reported chemical shifts are listed in Table 1.

TABLE 1: Calculated and Experimental ^{13}C NMR Chemical Shifts[a]

			IGLO		GIAO-MP2			
no.	position	atom	DZ[b]	II[b]	3-21G	dzp/dz	tzp/dz[b]	exptl
1	apical	C1	−36.2	−52.0	−34.1	−35.3	−37.4	
	basal	C2	78.4	62.7	65.9	68.3	71.5	
2	apical	C1	−36.7	−44.9	−28.9	−26.3		
	basal	C2	76.7	63.4	66.7	70.0		
		C3	80.3	66.9	69.2	72.9		
		C4	83.9	70.5	71.7	75.8		
	other	C6	3.6	−0.8	5.4	3.4		
3	apical	C1	−33.6	−47.7	−29.8	−30.4		
	basal	C2	93.4	83.4	83.2	89.8		
		C3	77.8	62.8	66.5	68.6		
		C4	70.2	53.8	58.1	59.7		
	other	C6	10.0	5.6	12.3	10.2		
4	apical	C1	−34.6	−41.2	−25.4			−23.0
	basal	C2	90.4	81.6	82.2			93.7
		C3	79.4	66.5	69.4			73.0
		C4	75.0	61.5	64.0			61.0
	other	C6	9.5	5.3	12.0			7.5
		C7	2.8	−2.2	4.4			−1.0
5	apical	C1	−33.3	−38.6	−21.9			−20.9
	basal	C2	84.0	75.2	76.1			78.5
		C3[b]	79.3	67.0	70.3			72.6
	other	C6	8.5	4.2	11.5			5.4
		C8	1.6	−3.4	3.2			−3.2
6	apical	C1	−36.2	−36.9	−15.1	−17.3	−17.0	−17.2
	basal	C2	43.0	35.9	37.9	40.3	41.9	39.4
	other	C3	6.5	4.8	12.7	9.8	5.0	8.1
7	apical	C1	−41.1	−48.1	−23.7	−28.9		2.4
	basal	C2	48.1	36.2	38.9	40.3		30.4
	other	C3	24.9	20.3	30.5	29.4		29.0
		C8	40.8	38.1	44.4	47.1		41.7
8		C1	18.2	0.2	14.1			
		C2	20.4	7.9	16.4			
		C3	16.6	10.5	18.7			
		C5	32.5	24.7	32.9			
		C6	36.2	31.4	39.6			
		C8	36.3	33.8	40.7			
9	apical	C1	−43.2	−47.8	−24.0	−28.6		−27.9
	basal	C2	42.4	34.6	36.6	38.8		37.7
	other	C3	8.0	10.0	17.5	16.9		14.9
		C8	9.5	11.6	16.4	17.0		14.2
10	apical	C1	−49.1	−54.2	−29.3	−35.6		−33.6
	basal	C2	42.3	34.6	36.0	38.3		35.3
	other	C3	13.4	11.8	21.2	20.6		17.5
		C8	141.3	139.7	112.6	124.7		129.9

[a] Calculated ^{13}C NMR chemical shifts were performed on MP2/6-31G* optimized geometries and referenced to TMS (absolute shift, i.e., σ(C) = 222.6 (IGLO DZ), 197.4 (IGLO II), 218.7 (GIAO-MP2/3-21G), 205.7 (GIAO-MP2/dzp/dz), 198.8 (GIAO-MP2/tzp/dz)). For numbering scheme, see Figure 1. [b]Average calculated values of C3 and C5.

Square-Pyramidal Carbocations. *$(CH)_5^+$ **1**, $CH_3C_5H_4^+$ **2**, $CH_3C_5H_4^+$ **3**, $(CH_3)_2C_5H_3^+$ **4**, and $(CH_3)_3C_5H_2^+$ **5**.* The parent square-pyramidal ion **1** has not yet been observed. The MP2/6-31G* optimized structure of **1** is shown in Figure 1. The calculated apical carbon−basal carbon bond length of 1.566 Å is 0.1 Å longer than basal carbon−basal carbon bond length (1.465 Å).



Earlier calculations of the ion **1** at the HF/3-21G level showed the corresponding bond lengths to be 1.589 and 1.477 Å, respectively.[15] In structure **1** the apical carbon is bonded to the four carbon atoms and a hydrogen atom by sharing only eight valence electrons. Thus, the electron-deficient apical carbon−basal carbon bonds are as anticipated longer than basal carbon−basal carbon bonds. The IGLO DZ calculated ^{13}C NMR chemical shifts of the apical and basal carbons of **1** are

SCHEME 1

trishomocyclopropenium structure of $C_7H_9^+$

trishomocyclopropenium ion

δ^{13}C −36.2 and 78.4, respectively. The IGLO calculations using a larger basis set (i.e., basis II) gave chemical shifts of **δ**^{13}C −52.0 and 62.7 significantly different from the corresponding IGLO DZ values. It is known[24] that IGLO provides relatively poor data in calculations of ^{13}C NMR chemical shift of tertiary carbons. Thus, correlated calculations using the GIAO-MP2 method showed significant effect on the ^{13}C NMR chemical shifts of **1**. GIAO-MP2 calculations using the 3-21G basis set (i.e., GIAO-MP2/3-21G) gave corresponding values of **δ**^{13}C of −34.1 and 65.9. However, GIAO-MP2 calculations using a larger dzp/dz basis set (i.e., GIAO-MP2/dzp/dz; dzp basis set for carbons and dz basis set for hydrogens) gave **δ**^{13}C of −35.3 and 68.3 only slightly different from those of GIAO-MP2/3-21G values. By use of an even larger tzp/dz basis set (i.e., GIAO-MP2/tzp/dz; tzp basis set for carbons and dz basis set for hydrogens), the calculated **δ**^{13}C of −37.4 and 71.5 are also very close to those of the corresponding GIAO-MP2/3-21G and GIAO-MP2/dzp/dz results.

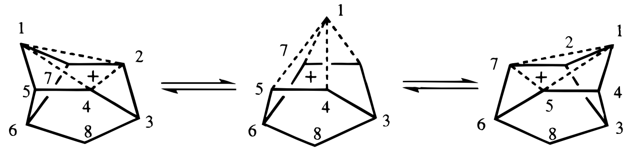
The monomethyl-substituted analogues of **1**, that is, C1 (apical) substituted **2** and C2 (basal) substituted **3**, have also not been observed. The structures of the cations were fully optimized at the MP2/6-31G* level (Figure 1). The cation **2** was found to be only 1.7 kcal/mol less stable than **3** at the MP4(SDQ)/6-31G*//MP2/6-31G* level. The ^{13}C NMR chemical shifts of **2** and **3** were calculated and are compiled in Table 1.

The 1,2-dimethyl-substituted analogue of **1**, that is, **4**, was observed[6] as a long-lived ion and characterized by ^{13}C NMR spectroscopy. The 2,4-dimethyl-substituted analogue of **1** was not observed experimentally. The MP2/6-31G* optimized geometry of **4** is similar to that of **1**. The GIAO-MP2/3-21G calculated δ^{13}C of the apical carbon of **4** is −25.4, which is very close to the experimental value of δ^{13}C −23.0. However, GIAO-MP2/3-21G calculated δ^{13}C of the basal carbons (82.2, 69.4, and 64.0) slightly deviate from the experimental data (93.7, 73.0, and 61.0). GIAO-MP2 calculations using larger basis sets, however, were not possible. This is because calculations using the ACES II program[23] are presently limited to only to smaller-sized molecules (limits strongly dependent on molecular symmetry).

Trimethyl analogue **5** was also characterized[7] in superacid solutions by ^{13}C NMR spectroscopy. The MP2/6-31G* optimized geometry of **5** is expectedly similar to that of **4**. As in **4**, the GIAO-MP2/3-21G calculated δ^{13}C of the apical carbon of **5** is −21.9, which is very close to the experimental value of δ^{13}C −20.9. GIAO-MP2/3-21G calculated δ^{13}C of the basal carbons of **5** (76.1 and 70.3) also corresponds very closely to the observed experimental values (78.5 and 72.6).

Bishomo Square-Pyramidal Cations. *$C_7H_9^+$ 6*. The bishomo square-pyramidal ion **6** was originally prepared by Masamune et al.[8] in superacid SbF_5-SO_2ClF solution at −110 °C. The MP2/6-31G* optimized structure of **6** is given in Figure 1. We also searched for minimum-energy trishomocyclopropenium-type structure (Scheme 1). At the MP2/6-31G* level the structure is not a minimum on the potential-energy surface of $C_7H_9^+$ and converged into structure **6** upon optimization. The parent persistent trishomocyclopropenium ion was also prepared by Masamune et al.[26] in superacid solutions and characterized by ^{13}C NMR spectroscopy. The trishomocyclopropenium ion was also studied by an ab initio/IGLO method by Prakash et al.,[26] and its highly symmetrical C_{3v} structure was confirmed.

SCHEME 2



8 **7**

The ^{13}C NMR chemical shifts of **6** were calculated by the both IGLO and GIAO-MP2 methods. The IGLO II calculated δ^{13}C of the apical carbon of −36.9 deviates substantially from the experimental value by −17.2 ppm. However, GIAO-MP2/dzp/dz calculated δ^{13}C of the apical carbon of −17.3 is almost the same as the experimental value of −17.2. These comparisons clearly demonstrate the importance of electron correlations in the calculations of the ^{13}C chemical shift of the square-pyramidal carbocations. The GIAO-MP2/dzp/dz calculated δ^{13}C of the basal carbon of 40.3 ppm is also found to be very close to the experimental value of 39.4 ppm. With the larger tzp/dz basis set the GIAO-MP2 calculated δ^{13}C of the apical and basal carbons of **6** are −17.0 and 41.9, respectively, which are only slightly different from those of GIAO-MP2/dzp/dz values.

*$C_8H_9^+$, **7** and **8***. The $C_8H_9^+$ ion was prepared by Masamune et al.[9] in superacid solution. Jefford and co-workers[27] calculated the ion at the MINDO/3 level. Unlike $C_7H_9^+$, both the bishomo square-pyramidal **7** and the trishomocyclopropenium-type structure **8** were found to be minimum-energy structures on the potential-energy surface of $C_8H_9^+$ at the HF//6-31G* level as confirmed by the frequency calculations at the same level. The structures were further optimized at the MP2/6-31G* level. At the MP2/6-31G*//MP2/6-31G* level **7** is only 0.7 kcal/mol less stable than **8**. This difference is reduced to 0.1 kcal/mol at the higher MP4(SDQ)/6-31G*//MP2/6-31G* level. By inclusion of zero-point vibrational energies (ZPE), that is, at the MP4(SDQ)/6-31G*//MP2/6-31G* + ZPE (at the HF/6-31G*//HF/6-31G* level scaled by a factor of 0.89), **7** is only 0.2 kcal/mol more stable than **8**. Thus, structures **7** and **8** are almost isoenergetic.

The ^{13}C NMR chemical shifts of **7** were calculated by the both IGLO and GIAO-MP2 methods. The IGLO II calculated δ^{13}C of the apical carbon of −48.1 largely deviates from the experimental value by 2.4 ppm. The GIAO-MP2/dzp/dz calculated δ^{13}C of the apical carbon of −28.9 also deviates from the experimental value by 31.3 ppm.

The ^{13}C NMR chemical shifts of **8** were calculated at the GIAO-MP2/3-21G level. The calculated δ^{13}C values of **8** are given in Table 1. From calculated chemical shifts of **7** and **8** it seems that the ion **7** might not be the only species involved in superacid solutions. An equilibrium mixture (undergoing rapid exchange on the NMR time scale) (Scheme 2) involving ions **7** and **8** (in 1:2 ratio) can best represent the structure of $C_8H_9^+$. The calculated average chemical shifts (at the GIAO-MP2/3-21G level) of the equilibrating structures of Scheme 2 are depicted in Scheme 3 along with the experimental data obtained at −80 °C (in parentheses). Thus, the calculated δ^{13}C of C1−C4 are 1.5, 29.4, 29.6, and 41.9, respectively, and match very well with the corresponding experimental values of 2.4, 30.4, 29.0, and 41.7. The possibility of structures **7** and **8** in rapid equilibrium is not only indicated from their average chemical shifts but also from their nearly identical energies. In

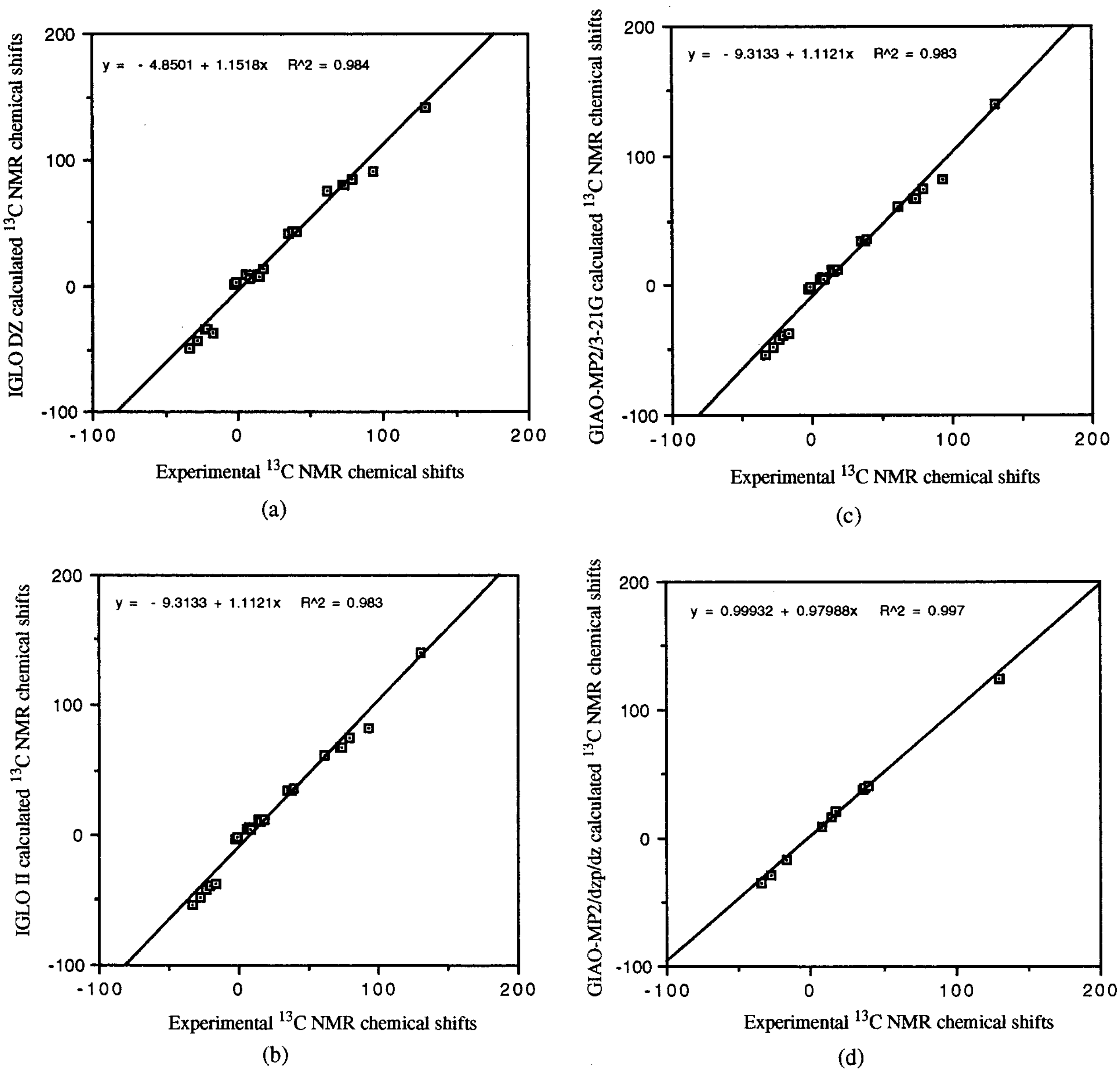
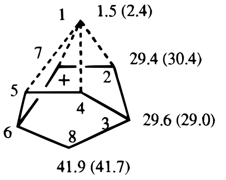
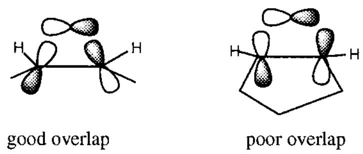


Figure 2. Plot of calculated vs experimental ^{13}C NMR chemical shifts of hypercoordinate carbocations **4**–**6**, **9**, and **10**: (a) IGLO DZ vs experimental results; (b) IGLO II vs experimental results; (c) GIAO-MP2/3-21G vs experimental results; (d) GIAO-MP2/dzp/dz vs experimental results.

SCHEME 3



SCHEME 4



fact, such an equilibrium was also suggested by Masamune et al.[9] $C_8H_9^+$ also showed[28] chemical behavior different from that of other related ions.

The relative instability of the ions **7** can also be justified from the molecular-orbital picture. 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. Therefore, the good overlap between cap p orbital and 1,4 cyclohexadiene p orbitals in ion **6** is possible because of the right geometry. However, in ion **7**, since the 3,6-positions of the cyclohexadiene moiety is tied (constrained) to a methylene group, the corresponding p orbitals cannot easily bend toward the cap to make a good overlap (Scheme 4; only part of the structures are shown for simplicity).

$C_9H_{11}^+$ 9 and $C_9H_9^+$ 10. Both ions **9** and **10** were prepared by Coates et al.[10] in superacid SbF_5–SO_2ClF solutions between −100 and −130 °C. The MP2/6-31G* optimized C_{2v} symmetrical structures of **9** and **10** are anticipated to be similar in nature (see Figure 1). Unlike in **7**, in ions **9** and **10** the 3,6-positions of the cyclohexadiene moiety are tied to two methylene and two methyne groups, respectively. Thus, p orbitals of the cyclohexadiene moieties of **9** and **10** can bend toward the cap, thus stabilizing the cationic center. However, no minimum-energy trishomocyclopropenium-type structures (Scheme 5) for $C_9H_{11}^+$ or $C_9H_9^+$ could be located. At the MP2/6-31G* level

SCHEME 5

trishomocyclopropenium structure of $C_9H_{11}^+$

trishomocyclopropenium structure of $C_9H_9^+$

the structures are not minima on the potential-energy surfaces and converged into corresponding pyramidal (i.e., **9** and **10**) structures upon optimization.

The GIAO-MP2/dzp/dz calculated δ^{13}C values of the apical carbons of **9** and **10** are −28.6 and −35.6, respectively. These values compare very well with the corresponding experimental results of δ^{13}C −27.9 and −33.6, respectively. Similarly, the GIAO-MP2/dzp/dz calculated δ^{13}C of both basal carbons of **9** and **10** are 38.8 and 38.3, respectively, which also compare very well with the experimental data of 37.7 and 35.3 ppm, respectively.

Chemical-Shift Correlation. Both IGLO and GIAO-MP2 calculated ^{13}C NMR chemical shifts of the hypercoordinate carbocations correlate very well with the experimental data (Figure 2). However, only the GIAO-MP2 calculated individual ^{13}C NMR chemical shifts are in excellent agreement with experimental results (Table 1) and are clearly superior to the IGLO calculated ^{13}C NMR chemical shifts.

Conclusions

We have calculated the structures and ^{13}C NMR chemical shifts of a series of hypercoordinate square-pyramidal carbocations that were earlier characterized by ^{13}C NMR spectroscopy under long-lived stable ion conditions by ab initio calculations. IGLO calculations with either the DZ or II basis set were found to be only reasonable in reproducing the ^{13}C NMR chemical shifts of these ions. However, calculations of ^{13}C NMR chemical shifts of these ions with the correlated GIAO-MP2 method showed significant improvements over the chemical-shift results computed at the SCF level (IGLO methods). The calculations suggest that **7** is nearly identical in energy with isomeric ion **8**. An almost 1:2 equilibrium mixture of ions **7** and **8** seems to best represent the observed NMR data of $C_8H_9^+$ at −80 °C. The structures and ^{13}C NMR chemical shifts for the elusive $(CH)_5^+$ ion **1** and its monomethyl-substituted analogues **2** and **3** were also computed.

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Supporting Information Available: Listing of Cartesian coordinates of the MP2/6-31G* optimized geometries and energies at the MP2/6-31G*//MP2/6-31G* level for **1**−**10** (4 pages). Ordering information is given on any current masthead page.

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