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George A. Olah, G. K. Surya Prakash, and Golam Rasul

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## Ab Initio/GIAO-CCSD(T) Study of Structures, Energies, and $^{13}\text{C}$ NMR Chemical Shifts of $\text{C}_4\text{H}_7^+$ and $\text{C}_5\text{H}_9^+$ Ions: Relative Stability and Dynamic Aspects of the Cyclopropylcarbinyl vs Bicyclobutonium Ions

George A. Olah,\* G. K. Surya Prakash, and Golam Rasul

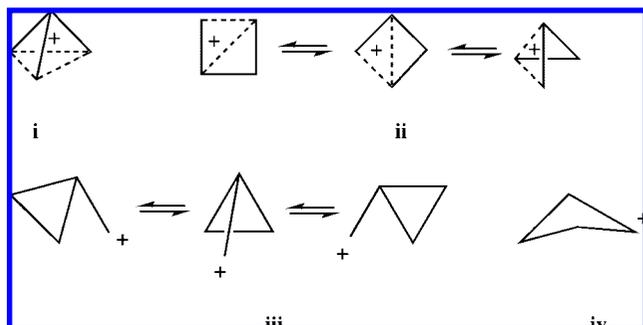
Loker Hydrocarbon Research Institute and Department of Chemistry, University of Southern California, University Park, Los Angeles, California 90089-1661

Received April 3, 2008; E-mail: olah@usc.edu.

**Abstract:** The structures and energies of the carbocations  $\text{C}_4\text{H}_7^+$  and  $\text{C}_5\text{H}_9^+$  were calculated using the ab initio method. The  $^{13}\text{C}$  NMR chemical shifts of the carbocations were calculated using the GIAO-CCSD(T) method. The  $\pi\sigma$ -delocalized bisected cyclopropylcarbinyl cation, **1** and nonclassical bicyclobutonium ion, **2** were found to be the minima for  $\text{C}_4\text{H}_7^+$  at the MP2/cc-pVTZ level. At the MP4(SDTQ)/cc-pVTZ//MP2/cc-pVTZ + ZPE level the structure **2** is 0.4 kcal/mol more stable than the structure **1**. The  $^{13}\text{C}$  NMR chemical shifts of **1** and **2** were calculated by the GIAO-CCSD(T) method. Based on relative energies and  $^{13}\text{C}$  NMR chemical shift calculations, an equilibrium involving the **1** and **2** in superacid solutions is most likely responsible for the experimentally observed  $^{13}\text{C}$  NMR chemical shifts, with the latter as the predominant equilibrating species. The  $\alpha$ -methylcyclopropylcarbinyl cation, **4**, and nonclassical bicyclobutonium ion, **5**, were found to be the minima for  $\text{C}_5\text{H}_9^+$  at the MP2/cc-pVTZ level. At the MP4(SDTQ)/cc-pVTZ//MP2/cc-pVTZ + ZPE level ion **5** is 5.9 kcal/mol more stable than the structure **4**. The calculated  $^{13}\text{C}$  NMR chemical shifts of **5** agree rather well with the experimental values of  $\text{C}_5\text{H}_9^+$ .

### Introduction

Among simple carbocationic systems, the cyclopropylcarbinyl cation, i.e.  $\text{C}_4\text{H}_7^+$  ion, has been one of the most extensively studied, yet its structure has not yet been fully established. The nature of the cyclopropylcarbinyl cation has been under intense scrutiny by many groups of researchers using various techniques, ever since J. D. Roberts first carried out his pioneering solvolytic studies on the cyclobutyl and cyclopropylcarbinyl derivatives. Roberts in 1951 initially proposed a pentacoordinated tricyclobutonium structure (**i**) for the cationic intermediate and named it as a “nonclassical” carbocation.<sup>1,2</sup> The tricyclobutonium ion structure was subsequently replaced by Roberts et al. with that of equilibrating bridged bicyclobutonium ions **ii** as further experimental results were not in agreement with the originally proposed structure.<sup>3</sup> H. C. Brown, on the other hand, on the basis of solvolysis of cyclopropylcarbinyl and cyclobutyl 2-naphthalene-sulfonates, proposed the intermediacy of a set of equilibrating cyclopropylcarbinyl cations **iii** involving the intermediacy of a relatively unpopulated puckered cyclobutyl cation, **iv**.<sup>4</sup>



Olah et al. characterized in 1972 the  $\text{C}_4\text{H}_7^+$  ion by  $^{13}\text{C}$  NMR spectroscopy under stable ion conditions.<sup>5</sup> Cyclopropylcarbinol or cyclobutanol upon ionization in superacids gave identical ions. The  $^{13}\text{C}$  NMR spectrum showed only two signals:  $\delta^{13}\text{C}$  108.4 (CH), and 55.2 ( $\text{CH}_2$ ).<sup>5</sup> Temperature-dependent chemical shifts for the  $\text{C}_4\text{H}_7^+$  ion, prepared from cyclopropylcarbinol- $1-^{13}\text{C}$ , between  $-61$  to  $-132$  °C were also reported in the late 1970s by the Roberts and Olah groups.<sup>6</sup> The ion shows two absorptions at  $\delta^{13}\text{C}$  107.6 and 57.4 for the methine and methylene carbons, respectively, at  $-70$  °C. The  $^{13}\text{C}$  label was randomly distributed, indicating facile hydride shifts in the cation. At  $-132$  °C, the methine and methylene carbons moved to  $\delta^{13}\text{C}$  111.3 and 50.9, respectively. This indicates that more than one species is involved in the rapid equilibration process. On the basis of these observations, an equilibration involving the  $\pi\sigma$ -delocalized bisected cyclopropylcarbinyl cation, **1**, and nonclassical bicyclobutonium ion, **2**, was suggested with the former as a minor equilibrating species.<sup>6</sup> Such a proposal has

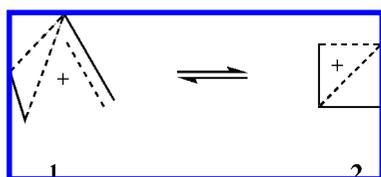
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**Table 1.** Previous and Present Calculated of Relative Energies<sup>a</sup> of **1** and **2**

level of calculation	<b>1</b>	<b>2</b>	refs
MINDO/3	0.0	5.6	10
STO-3G	0.0	collapses to <b>1</b>	11
HF/3-21G	0.0	10.2	12
HF/4-31G	0.0	10.9	13
HF/6-31G*	0.0	2.5	12,14,15
MP2/6-31G**//MP2/6-31G*	0.0	-1.8	12,14,15 <sup>b</sup>
MP4(SDTQ)/6-31G**//MP2(full)/6-31G*	0.0	-0.4	14
MP4(SDTQ)/6-311G**//MP2/6-31G**	0.0	-0.5	15
MP4(SDTQ)/6-311G**//MP2/6-31G** + ZPE	0.0	0.0	15
MP2/6-311G*	0.0	-1.9	<i>b</i>
MP2/cc-pVTZ	0.0	-2.4	<i>b</i>
MP2/cc-pVQZ	0.0	-2.6	<i>b</i>
MP2/cc-pVQZ//MP2/cc-pVQZ + ZPE	0.0	-2.0	<i>b</i>
MP4(SDTQ)/cc-pVTZ//MP2/cc-pVTZ + ZPE	0.0	-0.4	<i>b</i>

<sup>a</sup> Relative energies in kcal/mol. <sup>b</sup> Present calculations.

been affirmed by deuterium isotopic NMR studies of Saunders et al.,<sup>7,8</sup> and low-temperature solid-state NMR studies of Myhre and Yannoni.<sup>9</sup>



Numerous computational studies were reported on the structure and energetics of **1** and **2**. Relative energies of these ions are given in Table 1. Semiempirical MINDO/3 studies by Dewar and Reynolds found that the structure **1** is 5.6 kcal/mol less stable than the structure **2**.<sup>10</sup> However, using the ab initio method at the STO-3G level the structure **1** is found to be the only minimum on the potential energy surface (PES) of  $C_4H_7^+$ .<sup>11</sup> On the other hand, using the ab initio method at the HF/3-21G,<sup>12</sup> HF/4-31G<sup>13</sup> and HF/6-31G\*<sup>12,14,15</sup> levels **1**, is more stable than **2** by 10.2, 10.9, and 2.5 kcal/mol, respectively. At the correlated MP2/6-31G\*\*//MP2/6-31G\*<sup>12,14,15</sup> MP4(SDTQ)/6-31G\*\*//MP2(full)/6-31G\*<sup>14</sup> and MP4(SDTQ)/6-311G\*\*//MP2/6-31G\*\*<sup>15</sup> levels **1** is less stable than **2** by 1.8, 0.4 and 0.5 kcal/mol, respectively. Including zero-point vibrational energy (ZPE) i.e. at the MP4(SDTQ)/6-311G\*\*//MP2/6-31G\*\* + ZPE<sup>15</sup> level the energy difference between **1** and **2** vanished. More recently, quantum-mechanical calculations of the stabilities of isomers of  $C_4H_7^+$  in solutions were reported.<sup>16</sup> However, solvent effects on the relative stabilities of **1** and **2** are found to be rather small

and insignificant. In water, structure **1** was found to be only 0.3 kcal/mol more stable than the structure **2**.<sup>16</sup>

Siehl et al. generated 1-(trimethylsilyl)bicyclobutonium ion in  $SbF_5/SO_2ClF/SO_2F_2$  solution at  $-128\text{ }^\circ\text{C}$ .<sup>17</sup> The NMR spectroscopic data are in accord with a bridged puckered bicyclobutonium structure undergoing a 3-fold rapid degenerate rearrangement. <sup>13</sup>C NMR chemical shifts of 1-silylbicyclobutonium cation and the (1-silylcyclopropyl)methyl cation were calculated using the GIAO-MP2 method. The experimental shifts of 1-silylbicyclobutonium ion agree well with the GIAO-MP2 computed chemical shifts.<sup>17</sup>

Saunders et al. have previously investigated the structures and <sup>13</sup>C NMR chemical shifts of **1** and **2** by ab initio/IGLO method.<sup>14</sup> The structures were obtained at the MP2/6-31G\* level. The <sup>13</sup>C NMR chemical shifts of both **1** and **2** deviate from the experimental chemical shifts. The experimentally observed <sup>13</sup>C NMR spectrum of the  $C_4H_7^+$  ion at  $-61\text{ }^\circ\text{C}$  shows only two signals at  $\delta^{13}\text{C}$  106.8 (CH) and 59.0 (CH<sub>2</sub>).<sup>14</sup> On the other hand, IGLO calculated  $\delta^{13}\text{C}$  of the C1 (CH), C2 (CH<sub>2</sub>), and C4 (CH<sub>2</sub><sup>+</sup>) carbons of **1** were found to be 70.0, 75.0, and 244.3, respectively. The IGLO calculated  $\delta^{13}\text{C}$  of the C1 (CH<sup>+</sup>), C2 (CH<sub>2</sub>), and C3 (CH<sub>2</sub>) carbons of **2** were found to be 167.0, 71.3, and  $-14.3$ , respectively.<sup>14</sup> The deviation of the observed chemical shifts from the IGLO values also suggests the presence of two isomers in equilibrium. The mole fractions of these isomers were determined by assuming the observed chemical shifts as weighted average of the chemical shifts of the static ion. The IGLO calculated <sup>13</sup>C NMR chemical shifts show reasonable correlation with the experimental data.

DFT calculations at the GIAO-B3LYP/6-311G(d,p)//B3LYP/6-31G(d) level of theory indicate that the accurate prediction of <sup>13</sup>C chemical shifts for a number of carbocations could be achieved through scaling.<sup>18</sup> The study shows that after proper scaling, a very good correlation of predicted and experimental chemical shifts of these carbocations could be obtained using the relatively inexpensive DFT method. Recent studies<sup>19–23</sup> indicate that extensive electron correlation contributions are necessary to compute the accurate chemical shifts. These types of correlated <sup>13</sup>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 <sup>13</sup>C NMR chemical shifts of carbocations and other organic molecules have been demonstrated in several recent studies.<sup>19–23</sup> The GIAO-CCSD(T) calculations for these carbocations would be expected to closely correspond with the experimental data. We now report high level ab initio/GIAO-CCSD(T) investigations on the  $C_4H_7^+$  and related  $C_5H_9^+$  cations.

**Calculations.** Geometry optimizations were carried out with the Gaussian 03 program.<sup>24</sup> The geometries were first optimized at the MP2/6-311G\* level. Vibrational frequencies at the MP2/6-311G\*\*//MP2/6-311G\* level were used to characterize stationary points as minima (NIMAG (number of imaginary frequency) = 0 or transition state NIMAG = 1). The MP2/6-311G\*

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**Table 2.** Total Energies (-au), ZPE and Relative Energies (kcal/mol) of Cations 1–5.

	MP2/6-311G*	ZPE (kcal/mol)	MP2/cc-pVTZ	rel. energy <sup>a</sup> (kcal/mol)	MP4(SDTQ)/cc-pVTZ//MP2/cc-pVTZ	rel. energy <sup>b</sup> (kcal/mol)	MP2/cc-pVQZ	rel. energy <sup>c</sup> (kcal/mol)
<b>1</b>	155.77599	58.8	155.92530	1.8	155.99310	0.4	155.97416	2.0
<b>2</b>	155.77898	59.4	155.92917	0.0	155.99473	0.0	155.97830	0.0
<b>3ts</b>	155.77557	59.0	155.92529	2.0	155.99310	0.6	155.97415 <sup>d</sup>	2.2
<b>4</b>	194.96624	75.6	195.15770	6.8	195.24266	5.9	195.21964	6.8
<b>5</b>	194.97729	76.2	195.16947	0.0	195.25298	0.0	195.23168	0.0

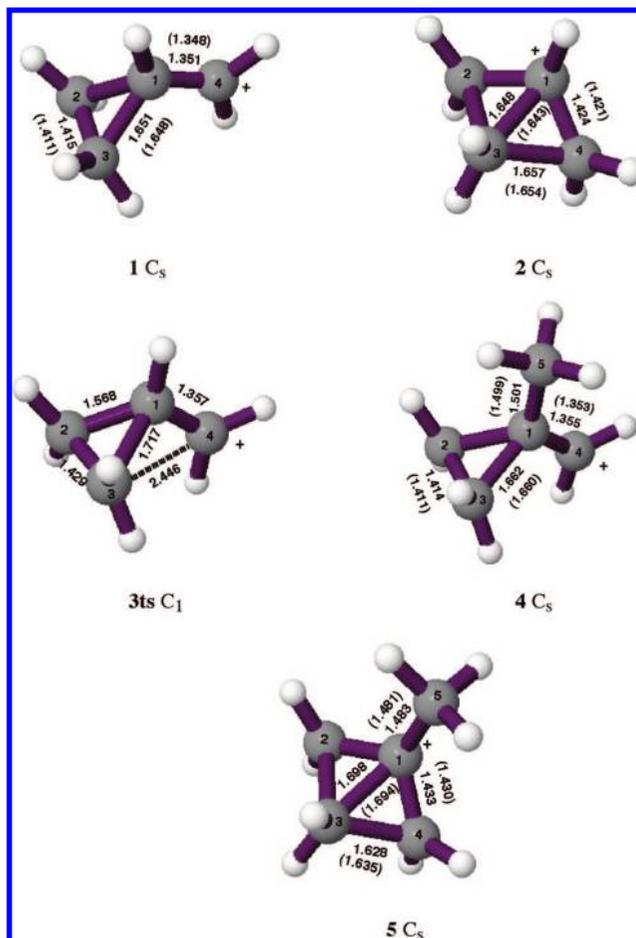
<sup>a</sup> At MP2/cc-pVTZ//MP2/cc-pVTZ + ZPE level. <sup>b</sup> At MP4(SDTQ)/cc-pVTZ//MP2/cc-pVTZ + ZPE level. <sup>c</sup> At MP2/cc-pVQZ//MP2/cc-pVQZ + ZPE level. <sup>d</sup> Single-point energy at MP2/cc-pVQZ//MP2/cc-pVTZ level.

geometries were further optimized at the MP2/cc-pVTZ (cc-pVTZ defined as correlation-consistent polarized valence-triple- $\zeta$  (Dunning) basis set) and MP2/cc-pVQZ (correlation-consistent polarized valence-quadruple- $\zeta$  (Dunning) basis set) levels. For improved energy, MP4(SDTQ)/cc-pVTZ calculations on MP2/cc-pVTZ level geometry were carried out. NMR chemical shifts were calculated by the gauge invariant atomic orbitals (GIAO) method<sup>25</sup> using MP2/cc-pVTZ and MP2/cc-pVQZ geometries. GIAO-CCSD(T), GIAO-MP2, and GIAO-SCF calculations using triple- $\zeta$  polarization (tzp) and quadruple- $\zeta$  polarization (qzp) basis sets, which were optimized by Schäfer, Horn, and Ahlrichs,<sup>26,27</sup> have been performed with the ACES II program.<sup>28</sup> The <sup>13</sup>C NMR chemical shifts were computed using TMS (calculated absolute shift i.e.  $\sigma$  (C), tzp (MP2/cc-pVTZ geometry) = 195.5 (GIAO-SCF), 199.2 (GIAO-MP2), 197.4 (GIAO-CCSD(T)); tzp/tzp (MP2/cc-pVTZ geometry) = 197.7 (GIAO-CCSD(T)); qzp/tzp (MP2/cc-pVQZ geometry) = 196.3 (GIAO-CCSD(T)) as reference.

## Results and Discussion

**C<sub>4</sub>H<sub>7</sub><sup>+</sup>.** We have optimized the geometries at the MP2/6-311G\* level. Both the C<sub>s</sub> symmetric structures **1** and **2** are minima on the potential energy surface (PES) of C<sub>4</sub>H<sub>7</sub><sup>+</sup>. Similar to previous calculations at the MP2/6-311G\* level,<sup>12,14,15</sup> our present calculations at the MP2/6-311G\*\* level also show that the structure **2** is 1.9 kcal/mol more stable than the structure **1** (Table 2). No other minima corresponding to partially bridged bicyclobutonium ions **ii** type structure were found. The structures were further optimized at the MP2/cc-pVTZ level. For improved energy, single-point energies at MP4(SDTQ)/cc-pVTZ level on MP2/cc-pVTZ optimized geometries were computed. At this level (MP4(SDTQ)/cc-pVTZ//MP2/cc-pVTZ) the energy difference reduces to 1.0 kcal/mol. Including ZPE i.e. at the MP4(SDTQ)/cc-pVTZ//MP2/cc-pVTZ + ZPE level the energy difference further reduces to 0.4 kcal/mol.

The MP2/cc-pVTZ structures were further optimized at the MP2/cc-pVQZ level. At the MP2/cc-pVQZ level the structure **2** is also 2.6 kcal/mol more stable than the structure **1** (Table 2). Including ZPE i.e. at the MP2/cc-pVQZ//MP2/cc-pVQZ +



**Figure 1.** MP2/cc-pVTZ structures (MP2/cc-pVQZ values are given in parentheses) of 1–5.

ZPE level the energy difference reduces to 2.0 kcal/mol. We tried but could not calculate energies at the MP4(SDTQ)/cc-pVQZ//MP2/cc-pVQZ level because of the size of the systems. The MP2/cc-pVTZ and MP2/cc-pVQZ calculated structures are shown in Figure 1.

At the MP2/cc-pVQZ level the C1–C3 bond distance of **2** is 1.643 Å. This indicates that the methylene C3 carbon of **2** is pentacoordinated and the formal charge-bearing methine C1 carbon is tetracoordinated. A transition structure, **3ts** (Figure 1), was located for interconversion of **1** and **2** at the MP2/cc-pVTZ level. Structure **3ts** lies only 0.6 kcal/mol higher in energy than structure **2** at the MP4(SDTQ)/cc-pVTZ//MP2/cc-pVTZ + ZPE level. Interconversion of the ions **1** and **2** therefore is very facile.

The <sup>13</sup>C NMR chemical shifts of **1** and **2** were calculated by the GIAO-coupled cluster method<sup>19–23</sup> at the GIAO-CCSD(T)/tzp level using the MP2/cc-pVTZ geometry (Table 3). Chemical

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**Table 3.** GIAO Calculated<sup>a</sup> and Experimental <sup>13</sup>C NMR Chemical Shifts of **1–5**.

	atom	SCF/tzp/tzp//MP2/cc-pVTZ	MP2/tzp/tzp//MP2/cc-pVTZ	CCSD(T)/tzp/tzp//MP2/cc-pVTZ	CCSD(T)/tzp/tzp//MP2/cc-pVQZ	CCSD(T)/qzp/tzp//MP2/cc-pVQZ	exptl
<b>1<sup>b</sup></b>	C1	71.8	82.7	81.9	81.7	83.5	106.8
	C2,C3	71.1	81.8	81.1	81.0	83.1	59.0
	C4	246.1	224.8	222.0	221.7	224.8	59.0
	total	460.0	471.1	466.2	465.4	474.4	283.8
<b>2</b>	C1	120.4	115.0	115.5	114.8	116.9	
	C2,C4	70.8	76.6	74.0	73.7	75.3	
	C3	−20.0	−15.2	−14.0	−14.3	−13.9	
	total	242.1	253.0	249.5	247.9	253.6	
<b>4</b>	C1	83.6	96.5	95.0	94.8	97.1	
	C2,C3	78.7	89.6	88.2	88.1	90.5	
	C4	241.2	218.3	215.8	215.3	218.7	
	C5	18.4	22.3	21.6	21.6	22.5	
	total	500.6	516.3	508.8	507.9	519.5	
<b>5<sup>c</sup></b>	C1	159.8	153.0	153.6	152.9	157.2	162.1
	C2,C4	67.6	75.0	72.0	71.8	74.9	72.7
	C3	−10.3	−4.7	−3.9	−3.9	−1.8	−2.8
	C5	25.8	28.4	27.4	27.4	29.1	25.8
	total	310.6	326.7	321.1	319.9	334.3	330.5

<sup>a</sup> <sup>13</sup>C NMR chemical shifts were referenced to TMS; for numbering scheme please see Figure 1; tzp/tzp means tzp on C and tzp on H; qzp/tzp means qzp on C and tzp on H. <sup>b</sup> Experimental values were taken from ref 6. <sup>c</sup> Experimental values were taken from ref 29.

shifts were also calculated at the GIAO-CCSD(T)/qzp/tzp level using the MP2/cc-pVQZ geometry. However, calculations at the CCSD(T)/qzp/tzp//MP2/cc-pVQZ level changed the magnitude of chemical shifts very little. Calculated (CCSD(T)/qzp/tzp//MP2/cc-pVQZ)  $\delta^{13}\text{C}$  of the C1 (CH), C2 (CH<sub>2</sub>), and C4 (CH<sub>2</sub><sup>+</sup>) carbons of **1** are 83.5, 83.1, and 224.8, respectively. These data are different from the experimentally observed <sup>13</sup>C NMR spectrum of the  $C_4H_7^+$  ion at −61 °C, which shows only two signals at  $\delta^{13}\text{C}$  106.8 (CH) and 59.0 (CH<sub>2</sub>).<sup>5</sup> On the other hand, calculated  $\delta^{13}\text{C}$  of the C1 (CH<sup>+</sup>), C2 (CH<sub>2</sub>), and C3 (CH<sub>2</sub>) carbons of **2** are 116.9, 75.3, and −13.9, respectively.<sup>5</sup> These results are also different from the experimentally observed results. Previously reported<sup>14</sup> noncorrelated IGLO calculated  $\delta^{13}\text{C}$  of the C1 (CH), C2 (CH<sub>2</sub>), and C4 (CH<sub>2</sub><sup>+</sup>) carbons of **1** were found to be 70.0, 75.0, and 244.3, respectively, and the IGLO calculated  $\delta^{13}\text{C}$  of the C1 (CH<sup>+</sup>), C2 (CH<sub>2</sub>), and C3 (CH<sub>2</sub>) carbons of **2** were found to be 167.0, 71.3, and −14.3, respectively.

Like in previous suggestions, the deviation of the observed chemical shifts from the GIAO-CCSD(T)/qzp/tzp values indicate the presence of two isomers **1** and **2** in rapid equilibrium as they are energetically extremely close (shallow potential energy surface). The mole fractions of these isomers were determined by assuming the observed chemical shifts as weighted average of the chemical shifts of the static ion. By using this assumption, we have estimated the  $\delta^{13}\text{C}$  values of  $C_4H_7^+$  ion based on computed  $\delta^{13}\text{C}$  of **1** and **2**. Thus, at −61 °C, the percentages of **1** and **2** were estimated to be 16 and 84, respectively (Table 4).<sup>6</sup> At these percentages, the calculated values of  $\delta^{13}\text{C}$  of CH and CH<sub>2</sub> are 111.5 and 59.1 (CCSD(T)/qzp/tzp//MP2/cc-pVQZ) agree very well with the corresponding experimental values 106.8 and 59.0. Similarly, at −132 °C the percentages of **1** and **2** were found to be 6 and 94, respectively. At these percentages, the calculated values of  $\delta^{13}\text{C}$  of CH and CH<sub>2</sub> are 114.8 and 50.6, also agree very well with the corresponding experimental values 111.3 and 50.9.<sup>6</sup> The results are listed in Table 4. Rapid equilibrium between structures **1** and **2** is not only indicated from their average chemical shifts but also from their very close energies. Based on calculated energies and <sup>13</sup>C NMR chemical shifts, a rapid equilibration involving the  $\pi\sigma$ -delocalized bisected cyclopropylcarbinyl cation, **1** and nonclassical bicyclobutonium ion, **2** is indicated, with the former as the lesser populated species. Present study shows the power of high level calculations

**Table 4.** Calculated<sup>a</sup> and Experimental<sup>b</sup> <sup>13</sup>C NMR Chemical Shifts of **1** and **2** at Various Temperatures

temp, °C	% of		calculated		experimental	
	<b>1</b>	<b>2</b>	$\delta^{13}\text{CH}$	$\delta^{13}\text{CH}_2$	$\delta^{13}\text{CH}$	$\delta^{13}\text{CH}_2$
−61	16	84	111.5	59.1	106.8	59.0
−70	14	86	112.2	57.4	107.6	57.5
−76	14	86	112.2	57.4	107.6	57.2
−80	13	87	112.5	56.6	108.0	56.6
−88	12	88	112.8	55.7	108.5	55.6
−99	10	90	113.5	54.0	109.2	54.3
−101	10	90	113.5	54.0	109.4	54.0
−107	9	91	113.8	53.2	109.7	53.5
−112	9	91	113.8	53.2	110.0	53.0
−115	8	92	114.2	52.3	110.3	52.6
−127	7	93	114.5	51.5	111.0	51.4
−132	6	94	114.8	50.6	111.3	50.9

<sup>a</sup> <sup>13</sup>C NMR chemical shifts were calculated at GIAO-CCSD(T)/qzp/tzp//MP2/cc-pVQZ level and referenced to TMS. <sup>b</sup> Experimental values were taken from ref 6. When the calculated values of  $\delta^{13}\text{C}$  of CH and CH<sub>2</sub> were plotted against the corresponding experimental values, good linear correlations with correlation coefficients of 0.98 and 0.99, respectively, were found.

(such as GIAO-CCSD(T)/qzp/tzp//MP2/cc-pVTZ method) to determine the accurate structures of still complex carbocationic systems.

The <sup>13</sup>C NMR chemical shifts of **1** and **2** were also computed at the GIAO-MP2/tzp/dz and GIAO-SCF/tzp/dz levels (Table 3). The calculated GIAO-MP2/tzp/dz  $\delta^{13}\text{C}$  values are reasonably close to the GIAO-CCSD(T)/tzp/dz values. However, the GIAO-SCF/tzp/dz calculated  $\delta^{13}\text{C}$  values are significantly more deviated than those of the GIAO-CCSD(T)/tzp/dz values.

$C_5H_9^+$ . Not unlike  $C_4H_7^+$ , both the  $C_s$  symmetric structures **4** and **5** were found to be minima on the PES of  $C_5H_9^+$  at the MP2/6-311G\* level (Figure 1). The structures were also optimized at the MP2/cc-pVTZ level. At the MP2/cc-pVTZ//MP2/cc-pVTZ level the structure **5** is 7.4 kcal/mol more stable than the structure **4** (Table 2). For improved energy, single-point energies at the MP4(SDTQ)/cc-pVTZ level using MP2/cc-pVTZ optimized geometries were computed. At this level (MP4(SDTQ)/cc-pVTZ//MP2/cc-pVTZ) the energy difference reduces to 6.5 kcal/mol. Including ZPE, i.e. at the MP4(SDTQ)/cc-pVTZ//MP2/cc-pVTZ + ZPE level, the energy

difference further reduces to 5.9 kcal/mol. The structures were further optimized at the MP2/cc-pVQZ level and are shown in Figure 1.

The structure **5** is very similar to the structure **2** with the C1–C3 bond length of 1.694 Å (MP2/cc-pVQZ level). This also shows that the methylene C3 carbon of **5** is pentacoordinated and the formal charge bearing C1 carbon is tetracoordinated. We tried but could not locate a transition state for interconversion of **4** and **5** at the MP2/cc-pVTZ level.

The  $^{13}\text{C}$  NMR chemical shifts of **4** and **5** were calculated at the GIAO-CCSD(T)/qzp/tzp level using the MP2/cc-pVQZ geometry (Table 3). Calculated  $\delta^{13}\text{C}$  of the C1 (CH), C2 (CH<sub>2</sub>), and C4 (CH<sub>2</sub><sup>+</sup>) carbons of **4** are 97.1, 90.5, and 218.7, respectively. These calculated chemical shift values are different than the experimentally observed  $^{13}\text{C}$  NMR data on the C<sub>5</sub>H<sub>9</sub><sup>+</sup> ion at –156 °C.<sup>29</sup> On the other hand, calculated  $\delta^{13}\text{C}$  of the C1 ((CH<sub>3</sub>)C<sup>+</sup>), C2 (CH<sub>2</sub>), and C3 (CH<sub>2</sub>) carbons of **5** are 157.2, 74.9, and –1.8, respectively, and these are in good agreement with the observed experimental  $^{13}\text{C}$  NMR shifts of 162.1, 72.7, and –2.8 at –156 °C. The agreement between the observed chemical shifts and the GIAO-CCSD(T)/qzp/tzp values suggests that, unlike C<sub>4</sub>H<sub>7</sub><sup>+</sup>, the two isomers **4** and **5** are not in rapid equilibrium. This is in agreement with the fact that the energy difference (5.9 kcal/mol) between the isomeric ions **4** and **5** is sufficiently high precluding any involvement of **4** at –156 °C.

## Conclusion

The structures and  $^{13}\text{C}$  NMR chemical shifts of the C<sub>4</sub>H<sub>7</sub><sup>+</sup> and C<sub>5</sub>H<sub>9</sub><sup>+</sup> ions were calculated using the high level ab initio/GIAO-CCSD(T) method. The cyclopropylcarbinyl cation, **1** and

bicyclobutonium ion, **2** were found to be the minima on the C<sub>4</sub>H<sub>7</sub><sup>+</sup> energy surface at the MP2/cc-pVTZ level. At the MP4(SDTQ)/cc-pVTZ//MP2/cc-pVTZ + ZPE level structure **2** is 0.4 kcal/mol more stable than structure **1**. A rapid equilibrium involving ions **1** and **2** is in accord with the observed  $^{13}\text{C}$  NMR chemical shifts in superacid solutions, with the former only as the lesser populating species. The  $\alpha$ -methylcyclopropylcarbinyl cation, **4** and nonclassical bicyclobutonium ion, **5** were found to be the minima for the C<sub>5</sub>H<sub>9</sub><sup>+</sup> at the MP2/cc-pVTZ level. At the MP4(SDTQ)/cc-pVTZ//MP2/cc-pVTZ + ZPE level the ion **5** is 5.9 kcal/mol more stable than the ion **4**. The calculated  $^{13}\text{C}$  NMR chemical shifts of **5** agree well with the experimental values. It is rewarding to see that after half a century of intense studies, Roberts pioneering view of the nonclassical nature of these challenging carbocations prevails.

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