Research Article

Theoretical Studies on Structures and Electronic State of Alkyl-Substituted Ethyl Cations

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This paper describes the gas phase structural details for a series of alkyl-substituted ethyl cations **1–11** by mainly natural bond orbital (NBO) analysis. For the simplest ethyl cation, two kinds of optimized structures (nonclassical **1** and classical **2**) were found to have minima on the potential surface, and the nonclassical **1** was more stable than the corresponding classical **2** by 1.19 kcal/mol at Møller-Plesset (MP) level calculations in the gas phase. The calculated values of Wiberg's bond index revealed that the central ethylic C¹–C² bonds of the nonclassical cations **1**, **6**, **7**, and **10** have 1.10–1.46 bond multiplicities. The compliance constant (C_{ii}) values indicated that the cation center C¹ of nonclassical 2-butyl cation **6** (0.209 Å/mdyn) acquires stronger hyperconjugative stabilization from C²–R³ (C–H) bond than that of the nonclassical ethyl cation **1** (0.388 Å/mdyn). Moreover, the gas phase stabilities for the alkyl-substituted ethyl cations **1–11** were also estimated by the hydride affinities based on isodesmic equations.

1. Introduction

The carbocations are not only important chemical species as intermediates in various organic reactions but also have been gathering much attention on their structure and electronic state [1]. Since the 1960s, Von Schleyer and coworkers have examined alkyl cations (carbonium ions), in part alkyl dications, by magic acid techniques [2]. Yannoni et al. have also studied the alkyl cation and especially revealed the structural details of *tert*-butyl cation (1,1-dimethylethyl cation) by NMR methods in 1989 [3].

Fărcașiu et al. have theoretically investigated the conformations of carbocations and the reactions of their precursors with borane at high-level *ab initio* calculations [4, 5]. In 2007, Ricks and coworkers revealed that extraordinary stability of C₄H₉⁺ species is brought about the charge distribution and hyperconjugation by means of IR spectral analysis [6]. Feng et al. reported the structural properties and energetics at high-level MO calculations on *tert*-butyl cation [7].

Structural details of ethyl cation, which is the most basic and popular alkyl cation, were reported by Andrei and coworkers in 2008 [8]. They found that the ethyl cation takes the nonclassical structure from both the experimental results of Ar-tagging IRPD spectra and *ab initio* calculations. Furthermore, Reed and coworkers have recently isolated alkyl and any other cations as salts with carborane anions and characterized by X-ray crystallography [9].

However, the detailed information on the structure and electronic state of carbocation such as relative isodesmic energy, bond multiplicity, and the relative energy difference has not been fully elucidated in the past theoretical and experimental studies. Especially, systematical consideration on the detailed electronic state of alkyl cation is still needed to understand the mechanisms for several basic organic reactions and structural aspects of fundamental carbon species. The present study describes the results of theoretical investigations on the detailed structure and electronic state of

FIGURE 1: Optimized structures of alkyl-substituted ethyl cations at MP2/6-311+G(d,p) level of theory.

various carbocations (ethyl cation and its alkylsubstitutes) by using Møller-Plesset method.

2. Computational Methods

Ab initio theoretical calculations at second order Møller-Plesset perturbation theory (MP2) level were performed by using Gaussian 03 program for all the alkyl-substituted ethyl cations 1–11 (Table 1). First geometry optimization was performed at the B3LYP/6-31G(d) level and the optimized structure was used as an input structure for the calculation at the MP2/6-311+G(d,p) level of theory. The SCF energy, Wiberg's bond index, and compliance constant calculation for each optimized ethyl cation were verified using the same basis set, and their results were summarized in Tables 3 and 4. The isodesmic equation and the relative reaction energy (ΔE_{iso}) were summarized in Table 5.

3. Results and Discussions

3.1. Calculated Molecular Structures and Molecular Orbitals of Alkyl-Substituted Ethyl Cations 1–11. The optimized structures of cations 1–11 are shown in Figure 1, and their selected bond length and angle parameters are summarized in Table 2.

Our calculations for the simplest ethyl cation by MP2 level of theory demonstrated that the cation has two energies-minimized structures (1 and 2) in agreement with their previous studies [7, 8]. The cation center of optimized 2 is almost localized on one carbon atom, whereas the cation centers of 1 are splitting to two carbons (Figure 1). Therefore, the calculated structure of 1 is categorized into a nonclassical cation, while that of 2 is considered as a classical ethyl cation. The central $\text{C}^1\text{--C}^2$ bond length (1.39 Å) of nonclassical 1 is similar to that of a double bond (1.34 Å). On the other hand,

TABLE 1: Alkyl-substituted ethyl cations 1–11.

	Cation	R ¹	R ²	R ³	R ⁴	R ⁵
	1 ^a	H	H	H	H	H
	2	H	H	H	H	H
	3	Me	H	H	H	H
	4	Me	Me	H	H	H
	5	H	H	Me	H	Me
	6 ^a	H	Me	H	Me	H
	7 ^a	Me	H	H	Me	H
	8	Me	H	H	Me	H
	9	Me	Me	Me	Me	H
	10 ^a	Me	Me	H	Me	Me
	11	Me	Me	Me	Me	Me

^aNonclassical cation.

TABLE 2: Calculated structural parameters for multisubstituted ethyl cations 1–11. Selected bond lengths are in angstrom (Å) and selected torsion angles in degrees (°).

Cation	Bond lengths (Å)				Torsion angles (°)			
	C ¹ –C ²	R ¹ –C ¹	C ² –R ³	C ² –R ⁵	C ¹ –C ² –R ³	R ¹ –C ¹ –C ²	R ¹ –C ¹ –R ²	C ¹ –C ² –R ⁵
1	1.39	1.09	1.31	1.09	58.1	120.5	119.1	120.5
2	1.42	1.09	1.11	1.11	106.3	120.1	116.8	106.3
3	1.44	1.44	1.12	1.09	97.9	125.3	117.4	114.1
4	1.46	1.46	1.11	1.09	102.7	119.5	120.7	113.8
5	1.41	1.09	1.58	1.58	109.4	118.1	120.0	109.4
6	1.40	1.09	1.31	1.49	58.0	116.5	118.5	124.8
7	1.40	1.49	1.32	1.09	57.4	126.9	117.4	115.5
8	1.41	1.48	1.66	1.08	76.2	124.1	118.2	118.8
9	1.45	1.47	1.60	1.09	96.8	121.2	118.7	110.5
10	1.42	1.50	1.32	1.50	57.2	122.4	115.1	122.5
11	1.45	1.48	1.62	1.53	92.6	121.2	116.5	116.8

the C¹–C² bond length of classical **2** is to be 1.42 Å. The C²–R³ bond lengths of **1** and **2** are envisaged to be 1.31 and 1.11 Å, and the bond angles of each C¹–C²–R³ are 58.1 and 106.3°, respectively. The single point energies of each structure involving ZPE showed that nonclassical **1** is more stable than classical **2** by 1.19 kcal/mol.

The gas phase structural feature of isopropyl cation **3** was also investigated by the same level of theory as **1** and **2**. The C¹–C² bond length of the calculated **3** is 1.44 Å, which became shorter than that of the corresponding alkane **3-H** (1.53 Å). In case of **3**, the cation center is almost localized on the C¹ carbon. Actually, the C¹–C²–R³ bond angle of the calculated **3** is 97.9°, which is much smaller than an ideal sp³ bond angle (109.3°) due to the hyperconjugative effect from C–H bond to the cation center. Whereas LUMO of the 2-isopropyl cation **3** is mainly formed in C¹ cation center, HOMO is bound on the C–H bonds of two methyl groups (Figure 2).

With respect to optimized structures of *tert*-butyl cation **4** and isobutyl cation **5**, the C¹–C² bond lengths are 1.46 and 1.41 Å at MP2 level in the gas phase, respectively. The calculation predicted that **4** has a C_s symmetric structure where

the four carbons are coplanar (R¹–C¹–C² angle is 119.5°), and its cation center (C¹) takes almost sp² hybridization. In fact, one C¹–C²–H (R³) bond angle of the optimized **4** becomes smaller (102.7°) than that of **4-H** (110.2°). The isobutyl cation **5** possesses a classical form, in which the cationic charge is localized on the C¹ (Figure 3). Two methyl groups connected to the C² are located on up and down sides of the cation plane (R¹R²–C¹–C²), because efficient hyperconjugation from the two C–C bonds to the cation center contributes for this conformation. The *tert*-butyl cation **4** is much more stable (by >35 kcal/mol) than **5** in gas phase, due to a strong hyperconjugative stabilization effect from three methyl groups as discussed later (Section 3.3).

A similar trend in **1** and **2** was also observed in cases of 2-butyl cations **6**, **7**, and **8**. Both **6** and **7** are considered as nonclassical cations because the optimized structure has almost planar framework whose cation center is splitting between C¹ and C². In contrast, another “kinked” form (classical cation) **8** was inferred by MP2 optimizations. LUMOs of the nonclassical cations **6** and **7** mainly exist on C¹ and C² carbons, while they spread to the hydrogen of the “kinked”

TABLE 3: Bond length, Wiberg’s bond index (WBI), and compliance constants (C_{ii}) for multisubstituted ethyl cations **1**, **3**, **6**, and **9** and corresponding alkanes.

Bond	Bond length (Å)	WBI	C_{ii} (Å/mdyn)
C^1-C^2			
(1)	1.39	1.46	0.388
(1-H)	1.53	1.04	0.510
(3)	1.44	1.17	0.377
(3-H)	1.53	1.02	0.617
(6)	1.40	1.38	0.209
(6-H)	1.53	1.02	0.578
(9)	1.45	1.10	0.436
(9-H)	1.54	0.99	0.644
C^2-R^3			
(1)	1.31	0.45	2.236
(1-H)	1.09	0.96	0.755
(3)	1.12	0.83	2.718
(3-H)	1.10	0.95	0.702
(6)	1.31	0.45	3.609
(6-H)	1.10	0.95	0.702
(9)	1.60	0.90	1.126
(9-H)	1.53	1.01	0.612

methyl group for the classical **8**. Both the central C^1-C^2 bond lengths of **6** (nonclassical: *trans*) and **7** (nonclassical: *cis*) are estimated to be 1.40, whose value is almost the same as that of the classical **8** (1.41 Å). The C^2-R^3 (C–C) bond length of the classical **8** is expected to be 1.66 Å, which is elongated from a typical $C(sp^3)-C(sp^3)$ bond length (1.54 Å) due to the hyperconjugative effect. The $C^1-C^2-R^3$ bond angles of the nonclassical **6** and **7** are 57.8 and 58.1°, respectively, whereas the classical **8** has a larger angle (76.2°). The nonclassical **6** and **7** are estimated to be more stable than the classical **8** by 3.77 and 2.51 kcal/mol, respectively, suggesting that the hyperconjugations of the methyl groups of **6** and **7** are more effective for the stabilization than that of “kinked” methyl group of **8**. Moreover, the *trans*-nonclassical **6** is a little more stable than the *cis*-nonclassical **7** by 1.26 kcal/mol.

The 2,3-dimethylbutyl cations **9** (classical: 1.44 Å for C^1-C^2 bond length, 1.60 Å for C^2-R^3 bond length, and 96.8° for $C^1-C^2-R^3$ torsion angle) and **10** (nonclassical: 1.42 Å for C^1-C^2 bond length, 1.32 Å for C^2-R^3 bond length, and 57.2° for $C^1-C^2-R^3$ torsion angle) possess the similar structural features with the ethyl and 2-butyl cations. However, our calculations revealed that classical **9** is more stable than nonclassical **10** by 8.79 kcal/mol in the gas phase. Although the reason is not clear, there is a possibility that four methyl groups of nonclassical **10** are more sterically hindered. LUMO orbital of classical **9** exists at the cation center (C^1) and methyl groups connecting to the C^1 and C^2 , whereas the LUMO of nonclassical **10** is almost localized on C^1 and C^2 carbons in a similar manner to ethyl and 2-butyl cations (Figure 3).

As a result of MP2 calculation, trimethylbutyl cation **11** is clearly categorized into a classical cation, because the cation center is localized on the C^1 (Figure 3). The central ethylic C^1-C^2 bond length (1.45 Å) of **11** is significantly shorter than that of corresponding alkane **11-H** (1.55 Å) and slightly longer than those of classical ethyl and 2-butyl cations **2** and **4**. The C^2-R^3 bond length of **11** (1.62 Å) is longer than typical sp^3-sp^3 single bond length (1.54 Å). The $C^1-C^2-R^3$ bond angle of **11** (92.6°) is smaller than that of corresponding alkane **1-H** (111.9°).

3.2. The Comparison of Structural and Bond Strength Parameters between Selected Cations and Their Alkanes. Structural and bond strength parameters at MP2 level calculations between cations **1–11** and corresponding alkanes **1-H–11-H** were compared in order to estimate the hyperconjugative effect (Figure 4 and Table 3).

The C–C bond of ethane **1-H** is 1.53 Å in length, which should be an almost ideal sp^3 C–C bond, whereas that of **1** generated by hydride elimination from **1-H** becomes shorter by 0.15 Å (Figure 4). As shown in Table 3, the compliance constant C_{ii} of C^1-C^2 bond is changed from 0.510 (**1-H**) to 0.388 Å/mdyn (**1**), indicating that the central C^1-C^2 bond of simple ethyl cation **1** is stronger than that of **1-H**. Such a change is attributed to the hyperconjugative effect caused by the electron transfer from C–H covalent bond to the cation center. In contrast, the C^2-R^3 (C–H) bond strength of cation **1** becomes much weaker than that of **1-H** (from 0.755 to 2.236 Å/mdyn), indicating that the bonding electrons of C^2-R^3 are moved to the unfilled p orbital (cation center). In fact, the value of Wiberg’s bond index (WBI) is changed from 1.04 (**1**) to 1.46 (**1-H**) (Figure 3), meaning that the C^1-C^2 bond becomes stronger by the hydride elimination. Details of the WBIs with bond orders of the **1–11** are discussed in the following section.

The C^1-C^2 bond length of 2-propylcation **3** (1.44 Å) became shorter than that of **3-H** (1.53 Å) by the hydride elimination (Figure 4). A similar tendency is observed for the bond strengths and WBI values of **3** and **3-H**. Thus, the compliance constant C_{ii} of C^1-C^2 bond changed from 0.617 (1.04) to 0.377 Å/mdyn (1.17). On the other hand, the C^2-R^3 bond strength of **3** became weaker (from 0.702 to 2.718 Å/mdyn) from that of **3-H**. Moreover, the bond angle of $C^1-C^2-R^3$ changed from 110.7° (**3-H**) to 97.94° (**3**) according to our calculations. These structural changes can also be explained by the concept of hyperconjugative effect.

Similarly, gas phase calculations predict that the ethylic C^1-C^2 bond of *trans*-2-butyl cation **5** is shorter and stronger (1.40 Å and 0.578 Å/mdyn) than that of corresponding alkane **5-H** (1.53 Å and 0.209 Å/mdyn), while the C^2-R^3 bond strength of **5** (0.702 Å/mdyn) becomes much weaker than that of **5-H** (3.609 Å/mdyn) by hydride elimination.

On the other hand, MP2 level calculation in gas phase demonstrated that both 2,3-dimethylbutyl cations **8** and its hydride adduct **8-H** have the same central C^1-C^2 bond length (1.54 Å). Also, accompanied by the structural change from **8** to **8-H**, a decrease of C_{ii} (from 0.644 to 0.436 Å/mdyn) and a

TABLE 4: Bond orders, bond indexes, hybridizations, and occupancies parameters for multisubstituted ethyl cations **1–11**.

Cation	Wiberg's bond indexes (NAO bond orders)				Hybridizations		Occupancies	
	C ¹ –C ²	R ¹ –C ¹	C ² –R ³	C ² –R ⁵	C ¹	C ²	C ¹ –C ²	C ² –R ⁵
1	1.46 (1.20)	0.92 (0.78)	0.45 (0.46)	0.92 (0.78)	sp ^{2.69}	sp ^{2.69}	1.99493	0.69157
2	1.23 (1.06)	0.95 (0.77)	0.84 (0.75)	0.84 (0.75)	sp ^{1.00}	sp ^{3.16}	1.99705	1.91297
3	1.17 (1.02)	1.17 (1.02)	0.83 (0.75)	0.91 (0.77)	sp ^{2.32}	sp ^{3.17}	1.99051	1.88072
4	1.12 (0.99)	1.12 (0.99)	0.86 (0.76)	0.92 (0.78)	sp ^{2.37}	sp ^{3.21}	1.98454	1.91306
5	1.16 (1.01)	0.95 (0.78)	0.93 (0.79)	0.93 (0.79)	sp ^{2.12}	sp ^{3.27}	1.99111	1.91993
6	1.38 (1.16)	0.91 (0.77)	0.45 (0.47)	1.05 (0.91)	sp ^{2.47}	sp ^{2.47}	1.98604	0.69074
7	1.38 (1.16)	1.05 (0.91)	0.44 (0.46)	0.91 (0.77)	sp ^{2.90}	sp ^{2.90}	1.98649	0.70556
8	1.22 (1.07)	1.07 (0.93)	0.77 (0.63)	1.05 (0.92)	sp ^{2.67}	sp ^{2.13}	1.98615	1.73687
9	1.10 (0.97)	1.10 (0.97)	0.90 (0.75)	0.90 (0.76)	sp ^{2.40}	sp ^{3.39}	1.97682	1.88461
10	1.32 (1.13)	1.03 (0.90)	0.43 (0.46)	1.04 (0.90)	sp ^{3.05}	sp ^{3.05}	1.97706	0.71843
11	1.10 (0.96)	1.09 (0.96)	0.87 (0.72)	0.99 (0.83)	sp ^{3.05}	sp ^{3.06}	1.97307	1.85722

TABLE 5: Total energies E_{total} (Hartree) of alkyl-substituted ethyl cations **1–11** and reaction energies (kcal/mol) of corresponding isodesmic reactions^a.

Cation	R ¹	R ²	R ³	R ⁴	R ⁵	E_{total}	Alkane	E_{total}	ΔE_{iso}
1	H	H	H	H	H	−78.2804	1-H	−79.1823	31.75
2	H	H	H	H	H	−78.2785	1-H	−79.1823	30.56
3	Me	H	H	H	H	−117.339	3-H	−118.200	57.11
4	Me	Me	H	H	H	−156.380	4-H	−157.220	70.59
5	H	H	Me	H	Me	−156.323	5-H	−157.220	34.83
6	H	Me	H	Me	H	−156.353	6-H	−157.219	54.28
7	Me	H	H	Me	H	−156.351	6-H	−157.219	53.02
8	Me	H	H	Me	H	−156.347	6-H	−157.219	50.51
9	Me	Me	Me	Me	H	−234.418	9-H	−235.251	74.99
10	Me	Me	H	Me	Me	−234.407	9-H	−235.251	68.08
11	Me	Me	Me	Me	Me	−273.433	11-H	−274.265	75.61

^aThe structural optimizations and total energies E_{total} (Hartree) of methane and methyl cation were separately carried out at the same basis sets, respectively.

slight increase of bond order (from 0.99 to 1.10) of the C¹–C² bond were estimated by the calculation. Moreover, the C²–R³ bond length and strength of **8** (1.53 Å and 0.612 Å/mdyn) were shorter and stronger than those of **8-H** (1.60 Å and 1.126 Å/mdyn), respectively. Although the hyperconjugative effect from C²–R³ bond to cation center of **8** is expected from the MP2 calculation, steric repulsion between the methyl groups would be inhibiting the shrinking of C¹–C² bond. The pronounced deformation of C¹–C²–R³ bond angle of the cation **8** (96.77°) relative to alkane **8-H** (111.3°) supports the occurrence of the steric repulsion.

3.3. NBO Analysis of the Alkyl-Substituted Ethyl Cations.

Table 3 summarizes Wiberg's bond indexes (WBIs) and bond

orders of ethyl cations **1–11** evaluated by the NBO analysis at MP2/6-311++G(3df,3pd) level of theory. The character of chemical bond can be intuitively understood by the use of WBI bond indexes. For example, a bond index of 1 means that the bond takes single bond.

The WBIs of nonclassical **1** and classical **2** are evaluated to be 1.46 and 1.23, respectively, meaning that the more stable nonclassical ethyl cation **1** is essentially the same as a protonated ethylene. Actually, the NBO calculation by MP2/6-311++G(3df,3pd) level suggests that both the C¹ and C² of **1** possess sp^{1.99} hybridization which is nearly equal to sp². On the other hand, the C¹ and C² of **2** are sp^{1.55} and sp^{2.45} carbons, respectively, indicating that **2** is a classical cation.

A similar trend was also observed in 2-butyl cations **6** (*trans*-nonclassical), **7** (*cis*-nonclassical), and **8** (classical) in

FIGURE 2: HOMO orbitals of ethyl cations 1–11.

the gas phase. The WBIs for **6**, **7**, and **8** are 1.38, 1.38, and 1.22, respectively. The hybridizations of C^1 and C^2 of both **6** and **7** are $sp^{2.09}$ and $sp^{2.08}$, while those of **8** are $sp^{2.00}$ and $sp^{2.26}$, respectively.

According to our calculations, the hybridizations of C^1 and C^2 for classical 2,3-dimethylbutyl cation **9** are provided as $sp^{1.86}$ and $sp^{2.51}$, respectively. On the other hand, both of them were $sp^{1.86}$ for nonclassical 2,3-dimethylbutyl cation **10** by NBO calculation in the gas phase. The bond order and bond index of central ethylic C^1-C^2 bond for **10** are 0.96 and 1.10, respectively.

Our calculations revealed that the hybridization values of central C^1 and C^2 ($sp^{1.77}$ and $sp^{2.66}$) of the trimethylbutyl cation **11** are also close to those of **9** (Table 4).

3.4. Total Energies and Hydrogen Affinities of Each Cation. The zero point corrected total energies [E_{total} 's] of alkyl-substituted ethyl cations and their isodesmic reaction energy

[ΔE_{iso}] by MP2/6-311++G(3df,3dp) level are summarized in Table 5.

Each ΔE_{iso} is derived from the difference of total energies between alkane plus methyl cation and alkyl cation plus methane according to the equation shown in Table 5. The difference of ΔE_{iso} ($\Delta\Delta E_{\text{iso}}$) between nonclassical ethyl cation **1** and classical cation **2** is 1.19 kcal/mol. The gas phase MP2 calculation revealed that the hydride affinity of the *t*-butyl cation **3** is considerably lower than that of simple ethyl cation by 38–40 kcal/mol. This fact means that the *tert*-butyl cation **3** is much more stable than ethyl, propyl, and other butyl cations.

2-Methylpropan-1-yl cation **5** with a similar stability to ethyl cation is less stable than *tert*-butyl cation **4** (35.8 kcal/mol). In case of 2-butyl cations, both the non-classical cations **5** and **6** possess almost the same isodesmic reaction energy ($\Delta E_{\text{iso}} = 54.28$ kcal/mol for **5** and 53.02 kcal/mol for **6**) in the gas phase. On the other hand,

FIGURE 3: LUMO orbitals of ethyl cations 1–11.

MP2 calculations revealed that classical **7** is less stable than nonclassical **5** and **6** by 3 kcal/mol.

Although nonclassical ethyl and butyl cations are more stable than the corresponding classical cations, classical and nonclassical 2,3-dimethylbutyl cations **9** and **10** showed an opposite trend ($\Delta\Delta E_{\text{iso}} = 6.91$ kcal/mol). That classical **9** is more stable than nonclassical **10** is attributed to a higher steric repulsion between four methyl groups in **10** with a shorter $\text{C}^1\text{--C}^2$ bond length than the corresponding alkane.

Tetramethylbutyl cation **11** had the highest gas phase isodesmic reaction energy ($\Delta E_{\text{iso}} = 75.61$ kcal/mol), indicating the most stable cation among a series of alkyl-substituted ethyl cations in this report.

4. Conclusions

Gas phase structural and electronic properties of alkyl-substituted ethyl cations **1–11** were investigated at MP2 level.

It was revealed that there are nonclassical and classical forms for ethyl, 2-butyl, and 2,3-dimethylbutyl cations, whose nonclassical cationic state is more stable than the classical one (1.19 and 3.48 kcal/mol). On the contrary, the calculation for 2,3-dimethylbutyl cation demonstrated that the classical cation is more stable by 8.79 kcal/mol than the nonclassical one. The WBI parameters of the central $\text{C}^1\text{--C}^2$ bonds for the nonclassical and classical cations were 1.32–1.46 and 1.10–1.23 multiplicities in the gas phase, respectively. It was estimated from compliance constant C_{ii} that the $\text{C}^1\text{--C}^2$ bonds for the nonclassical cations are stronger than those of the classical cations, while the former $\text{C}^2\text{--R}^3$ bonds are weaker than the latter ones due to the hyperconjugative effects. The gas phase hydride affinities based on isodesmic equations demonstrated that the nonclassical cations are strongly stabilized by electron donations from $\text{C}^2\text{--R}^3$ bond. In case of 2,3-dimethylbutyl cations, however, the classical cation

FIGURE 4: Structural comparisons between alkyl-substituted ethyl cations **1**, **3**, **5**, and **9** and their alkanes calculated by MP2/6-311+G(d,p) level of theory.

was predicted to be more stable than nonclassical one by 8.79 kcal/mol due to the steric repulsions between four methyl groups substituted on the C¹ and C² carbons.

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