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Ab Initio/GIAO−CCSD(T) Study of Propenoyl ($H_2C{=}CH{-}CO^+$) and Isopentenoyl ($(CH_3)_2C{=}CH{-}CO^+$) Cations and Their Superelectrophilic Protonated Dications[1]

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Structures of superelectrophilic protonated propenoyl ($H_2C{=}CH{-}COH^{2+}$) and isopentenoyl ($(CH_3)_2C{=}CH{-}COH^{2+}$) dications and their parent cations were calculated using ab initio methods at the MP2/6-311+G** and MP2/cc-pVTZ levels. Energies were calculated using Gaussian-2 (G2) theory. The α-carbon (C_α) protonated **3** and **7** were found to be the global minima for protonated propenoyl and isopentenoyl dications, respectively. ^{13}C NMR chemical shifts of the cations were also calculated using the GIAO−CCSD(T), GIAO−MP2 and GIAO−SCF methods. ^{13}C NMR chemical shifts of the related *tert*-butyl cation ($(CH_3)_3C^+$) and protonated *tert*-butyl dication ($(CH_3)_2CCH_4{}^{2+}$) were also computed at the same level to compare and explore the effect of the additional charge in dications.

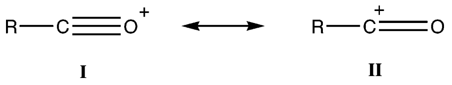
Introduction

Acyl cations are important intermediates in Friedel−Crafts type acylation of aromatics.[2] Many of the acyl cations were obtained as stable, long-lived ions and directly studied by ^1H and ^{13}C NMR spectroscopy.[3] These studies have indicated that acyl cations have a nearly linear structure, being resonance hybrids of the linear oxonium ion **I** and the oxocarbenium ion **II** forms, with **I** being the predominant contributor to the overall structure (Scheme 1).

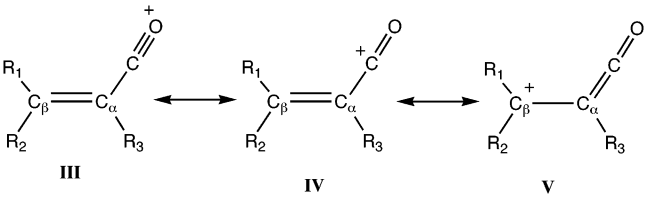
In 1967, Olah and Comisarow reported[4] the preparation and ^1H NMR spectroscopic studies of a series of alkenoyl cations (alkenyloxocarbenium ions). Later, Olah et al. used ^{13}C NMR spectroscopic methods to study the structures of alkenoyl cations.[5] From the ^{13}C NMR spectroscopic studies it has been shown that to the structure of alkenoyl cations **III** there is limited contribution from oxocarbenium ion structures **IV** but with substantial contribution from delocalized "ketene-like" resonance forms **V** (Scheme 2). This is due to the ability of the electrons of the carbon−carbon double bond to stabilize the adjacent positive charge. β-Carbon methyl substituents change the importance of **V** relative to **III**.

The important role of protosolvation of nonbonded electron pairs, π-, and even σ-electrons of carbocations and onium ions in superacid solutions is by now well recognized.[6] Such protosolvation in the limiting case can lead to dications.[6] Considerable interest has also centered on the elucidation of the structure and electronic properties of the dications by theoretical methods.[7] Previously, we have reported our theoretical studies on protonated oxonium,[7a] carboxonium,[7a] halonium,[7b] trihalomethylcarbenium,[7c] nitronium,[7d] sulfonium,[7a] and isopropyl[7e] and *tert*-butyl[7f] dications. However, no such investigations on protonated alkenoyl dications have been reported. In continuation of our work, we now report ab initio/GIAO−CCSD(T) studies to investigate the electronic structure and energies of protonated propenoyl and isopentenoyl dications. Besides activation by protonation of the oxygen nonbonded lone pair electrons, C=C or C−H bond protonation of the parent ion is also possible. For protonated isopentenoyl dications, the results were compared with the related *tert*-butyl cation and protonated *tert*-butyl dication.

SCHEME 1



SCHEME 2



Calculations

Calculations were carried out with the Gaussian 03 program.[8] The geometry optimizations were performed at the MP2/6-311+G** level. Vibrational frequencies at the MP2/6-311+G**//MP2/6-311+G** level were used to characterize stationary points as minima (number of imaginary frequency (NIMAG) = 0)) or transition state (NIMAG = 1) and to evaluate zero-point vibrational energies (ZPE), which were scaled by a factor of 0.95.[9] Final energies were calculated using the Gaussian-2 (G2) theory.[10] Calculated energies are given in Table 1. For the larger isopentenoyl systems, final energies were computed at the MP4(SDTQ)/6-311+G**//MP2/6-311+G** + ZPE level. Atomic charges were obtained using the natural bond orbital analysis (NBO)[11] method at the MP2/6-311+G**//MP2/6-311+G** level. MP2/6-311+G** optimized geometrical parameters and final energies are discussed throughout, unless stated otherwise. For NMR shift calculations, some of the cations were further optimized at the higher MP2/cc-pVTZ level. NMR chemical shifts were calculated by the GIAO method.[12] GIAO−CCSD(T), GIAO−MP2, and GIAO−SCF calculations[13] using tzp/dz basis set[13,14] have been performed using the ACES II

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

no.	MP2/6-311+G**//MP2/6-311+G**	ZPE	energies MP2/cc-pVTZ	energies G2	rel. energy
1	190.540 74	30.3	190.647 88	190.696 10	3.0
2	190.522 11	35.5	190.630 82	190.676 49	15.3
3	190.556 55	35.4	190.659 67	190.700 90	0.0
4	190.518 24	33.0		190.664 60	22.8
2ts	190.431 49	30.6		190.588 89	70.3
3ts	190.425 03	30.3		190.576 85	77.8

no.	MP2/6-311+G**//MP2/6-311+G**	ZPE	energies MP2/cc-pVTZ	energies MP4(SDTQ)/6-311+G**//MP2/6-311+G**	rel. energy
5	268.966 98	63.8	269.128 56	269.054 71	52.4
6	269.000 44	68.3		269.092 97	32.8
7	269.053 28	68.2	269.211 47	269.145 14	0.0
8	269.005 15	67.3		269.093 75	31.4
9	269.040 10	69.5		269.130 74	10.5

[a] Zero point vibrational energies (ZPE) at MP2/6-311+G**//MP2/6-311+G** scaled by a factor of 0.95. [b] Structures **1**−**3** using G2 theory and **5**−**9** at MP4/6-311+G**//MP4/6-311+G**+ZPE level.

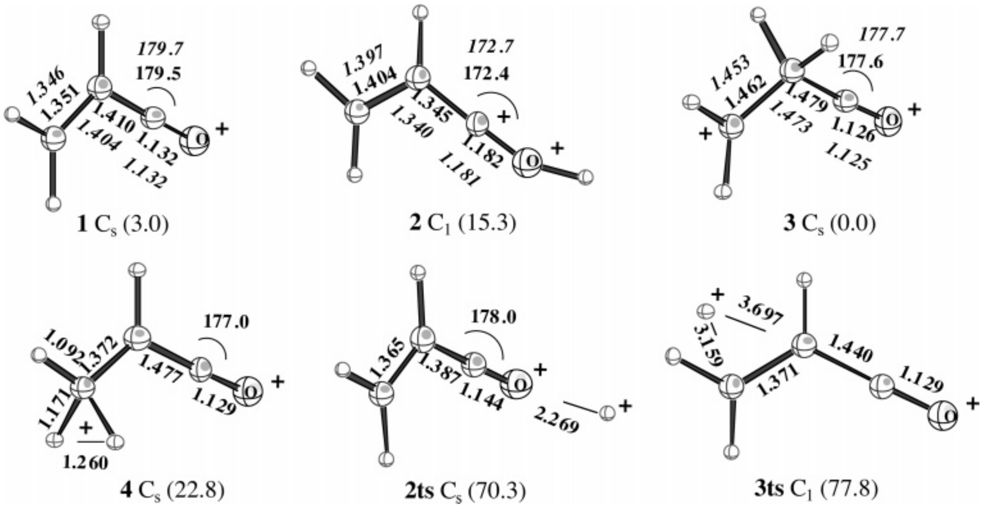


Figure 1. MP2/6-311+G** calculated structures **1**−**4**. MP2/cc-pVTZ parameters are given in italics; relative energies in kcal/mol are given in parentheses.

program.[15] The ^{13}C NMR chemical shifts were referenced to $(CH_4)_4Si$ (calculated absolute shifts, i.e., $\sigma(C) = 197.9$ (GIAO−CCSD(T)), 199.6 (GIAO−MP2), and 193.9 (GIAO−SCF)).

Results and Discussion

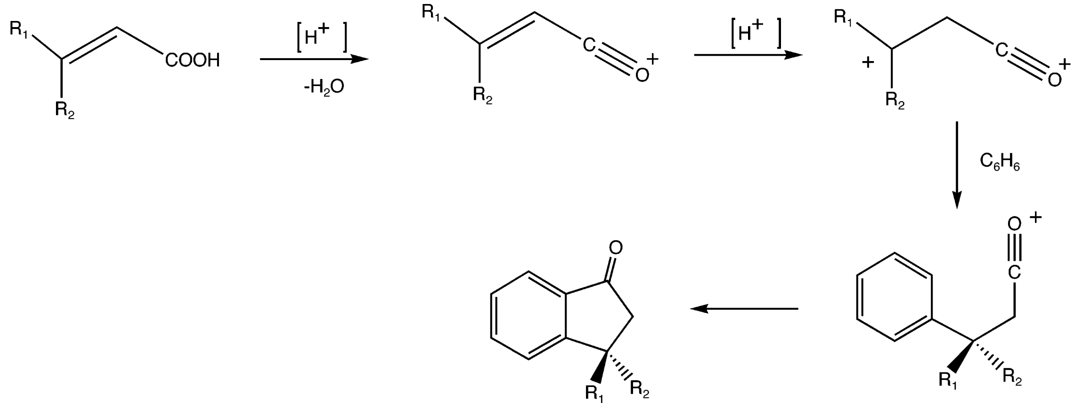
Protonation of Propenoyl Cation, $H_2C{=}CH{-}CO^+$, 1. Three structures of protonated propenoyl dications, oxygen protonated **2**, α-carbon (C_α) protonated **3**, and β-carbon (C_β) protonated **4**, were found to be minima on the potential energy surface at the MP2/6-311+G** level (Figure 1). The structure of the propenoyl cation **1** was also calculated at the same level and displayed in Figure 1. The C−O bond length of 1.182 Å in oxygen protonated **2** is only 0.050 Å longer than that of **1**. Due to $C_\alpha{=}C_\beta$ double bond conjugation, a significant shortening of the C_α−C(O) bond (1.345 Å) and lengthening of the $C_\alpha{=}C_\beta$ bond (1.404 Å) in **2** were found as compared to those of the propenoyl cation **1** (1.410 and 1.351 Å). Deprotonation of **2** was computed to be exothermic by 12.3 kcal/mol. The transition structure **2ts** for the dissociation of **2** lies 55.0 kcal/mol higher in energy than the structure **2**.

The C_α protonated structure **3** was found to be the global minimum for protonated propenoyl dications. The structure **3** contains a carbenium ion and an acylium ion center separated by a CH_2 group. Thus, the structure can be considered as a carbenium−acylium dication with greatly increased electrophilic reactivity. The structure **3** is 15.3 kcal/mol more stable than **2** (Table 1). The transition structure **3ts** for deprotonation of **3** lies 77.8 kcal/mol higher in energy than structure **3**. Deprotonation of **3** to the propenoyl cation **1** is computed to be endothermic by 3.0 kcal/mol. Thus, the propenoyl cation **1** and its protonated structure **3** are almost isoenergetic in the gas phase. The results are in accord with the recent experimental studies of cyclialkylacylation reactions in strong acid media.[16] The method is an extension of the Friedel−Crafts chemistry and can be applied to a variety of aromatics and unsaturated carboxylic derivatives. The two-step intermolecular alkylation−intramolecular acylation mechanism may involve a superelectrophilic dication such as **3** (Scheme 3).

The C_β−H protonated structure **4** is characterized by a short C_α−C_β bond length of 1.372 Å. The structure is characterized by a 2e−3c bond involving a tetracoordinate sp^2 type carbon and two hydrogens. The structure **4**, however, is significantly less stable than **3** by 22.8 kcal/mol.

NBO charges[11] of the structures **1**−**3** were also calculated and depicted in Figure 2. In monocation **1**, the acyl CO group as a whole bears +0.74 of charge and the CH and CH_2 groups as a whole bear −0.24 and +0.50 of charge, respectively,

SCHEME 3



indicating that the positive charge is shared by only the terminal CO and CH_2 groups. In the O-protonated dication **2**, the COH group as a whole bears +1.31 of charge and the CH and CH_2 groups as a whole bear −0.17 and +0.86 of charge, respectively. Thus, the electron deficiency of the terminal CH_2 group of the dication **2** becomes substantially more enhanced than that of the monocation **1**. On the other hand, the charge of the middle CH group of the dication **2** (−0.17) is closer to that of the monocation **1** (−0.24). In the dication **3**, the CO group bears +0.90 of charge and the middle and terminal CH_2 groups bear +0.08 and +1.02 of charge, respectively. In dications **2** and **3**, the positive charges are shared by the both CO and the terminal CH_2 groups.

For NMR shift calculation, the structure of cations **1**−**3** were further optimized at the higher MP2/cc-pVTZ level. The ^{13}C NMR chemical shifts of the cations were calculated (Figure 2) at the GIAO−CCSD(T)/tzp/dz level using MP2/cc-pVTZ geometries. Accurate ^{13}C NMR chemical shift calculations by the GIAO−CCSD(T) method has been demonstrated in several studies.[17−20] For comparison, GIAO−MP2 calculated ^{13}C NMR chemical shifts together with GIAO−SCF/tzp/dz values are given in Table 2. Calculated δ ^{13}C of C(O), C_α, and C_β carbons of the propenoyl cation **1** are 153.2, 90.6, and 172.2, respectively. These agree very well with the reported experimental values of δ ^{13}C 147.0, 92.7, and 177.1.[5] The total δ ^{13}C of C(O), C_α, and C_β is 421.0, deviated by only 4.2 ppm from the experimental value of 416.8. GIAO−MP2 calculated values of **1** are also very close to the experimental values (Table 2). The total δ ^{13}C of C(O), C_α, and C_β calculated by GIAO-MP2 method is 425.8, also slightly (9 ppm) different from the experimental value. However, the corresponding value calculated by GIAO−SCF method is 450.3, deviated by 33.5 ppm from the experimental value. The δ ^{13}C of C(O), C_α, and C_β of protonated form **2** are 208.9, 80.8, and 277.6. The δ ^{13}C shift of C(O) and C_β carbons of dication **2** are deshielded by about 56 and 100 ppm, respectively, compared to those of the monocation **1**. In contrast, the δ ^{13}C shift of C_α carbon of dication **2** is shielded by about 10 ppm with respect to the monocation **1**. The calculated δ ^{13}C of C(O), C_α, and C_β carbons of dication **3** are 142.1, 55.6, and 351.5, respectively.

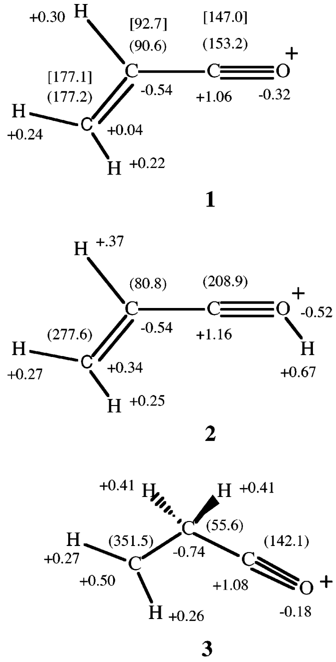


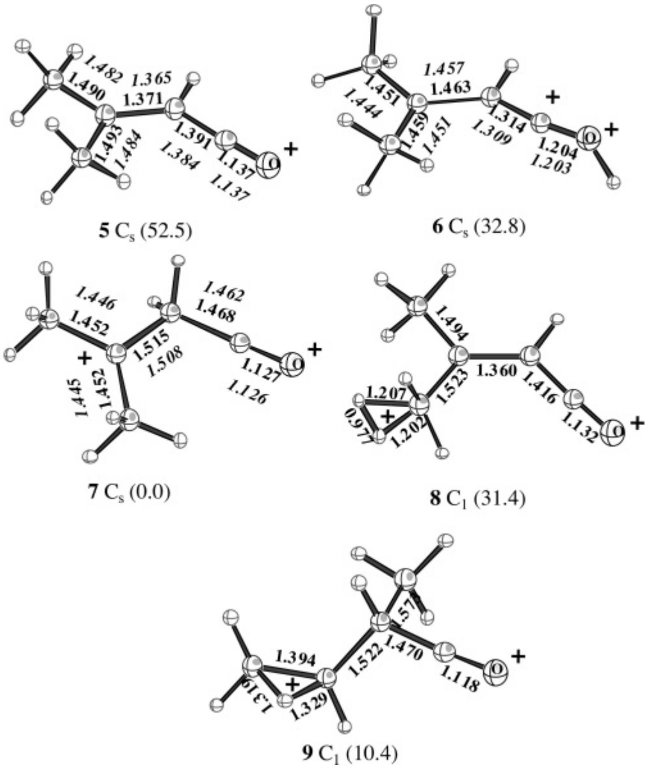
Figure 2. Calculated NBO charges and GIAO−CCSD(T) ^{13}C NMR chemical shifts (given in parentheses) of **1**−**3**. Experimental ^{13}C NMR chemical shifts are given in brackets.

TABLE 2: GIAO Calculated $^{13}C^{a}$ NMR Chemical Shifts

no.	atom	GIAO−SCF	GIAO−MP2	GIAO−CCSD(T)	expt[b]
1	C(O)	167.3	153.4	153.2	147.0
	C_α	86.2	92.0	90.6	92.7
	C_β	200.8	180.4	177.2	177.1
	total[c]	450.3	425.8	421.0	416.8
2	C(O)	229.2	205.6	208.9	
	C_α	70.7	78.7	80.8	
	C_β	288.1	276.4	277.6	
	total[c]	588.0	560.7	567.3	
3	C(O)	160.9	139.9	142.1	
	C_α	44.7	54.4	55.6	
	C_β	339.5	353.9	351.5	
	total[c]	545.1	548.2	549.2	
5	C(O)	171.0	158.3	158.1	154.2
	C_α	71.8	79.2	77.7	79.0
	C_β	245.9	227.2	225.4	223.0
	total[c]	488.7	464.7	461.2	456.2
7	C(O)	165.2	144.7	147.1	
	C_α	42.0	47.7	46.9	
	C_β	336.5	334.2	330.1	
	total[c]	543.7	526.6	524.1	
VI	C+	342.8	345.6	341.9	335.7[d]
VII	C+	319.5	314.9	310.7	

[a] ^{13}C shifts are referenced to TMS. [b] From ref 5. [c] (C(O) + C_α + C_β). [d] From ref 21.

Protonation of the Isopentenoyl Cation, $(CH_3)_2C{=}CH{-}CO^+$, 5: Comparison with the Related *tert*-Butyl Cation ($(CH_3)_3C^+$) and the Protonated *tert*-Butyl Dication ($(CH_3)_2CCH_4^{2+}$). Three isomeric protonated isopentenoyl cations, oxygen protonated **6**, C_α protonated **7**, and methyl C−H protonated **8** were located as minima (Figure 3). The C_β



5 C_s (52.5)

6 C_s (32.8)

7 C_s (0.0)

8 C_1 (31.4)

9 C_1 (10.4)

Figure 3. MP2/6-311+G** calculated structures **5**−**9**. MP2/cc-pVTZ parameters are given in italics; relative energies in kcal/mol are given in parentheses.

protonated structure does not correspond to a minimum and converted into **9** upon optimization. The structure **7** is the global minimum being 32.8 kcal/mol more stable than **6** (Table 1). The structure **7** contains a trivalent carbenium ion center and acylium ion center separated by a CH_2 group. Thus, the structure is a tertiary carbenium−acylium dication. The calculated C_α−C_β and C_α−C(CO) distances of **7** are 1.515 and 1.468 Å, respectively. Protonation of **5** to form dication **7** is calculated to be substantially exothermic by 52.5 kcal/mol. In comparison, protonation of **1** to form the dication **3** is calculated to be exothermic by only 3.0 kcal/mol. This is due to the hyperconjugative stabilizations by the methyl groups attached to the C_β of **7**.

The C−H (CH_3) protonated **8** is characterized by a pentacoordinate carbon involving a 2e−3c bond. The structure **8** contains a carbonium ion center and acylium ion centers separated by two carbons. Therefore, the structure can be considered as a carbonium−acylium dication. The structure **8** is significantly less stable than **7** by 31.4 kcal/mol. In **7**, the formal positive charge bearing carbenium and acylium centers are separated by one carbon whereas in **8** they are separated by two carbon atoms. Despite this the structure **8** is significantly less stable than **7**.

Attempts to find a stable minimum for a C_β protonated isopentenoyl cation failed because of spontaneous rearrangement to form the thermodynamically more stable dication structure **9**. The structure **9** is less stable than **7** by only 10.4 kcal/mol.

The structure of the dication **7** is particularly interesting because it can be considered a CO^+ substituted *tert*-butyl cation. The *tert*-butyl cation **VI** is stabilized not only by weak external solvation but also intramolecularly by C−H hyperconjugation. These hyperconjugative interactions with the carbocationic center contribute to the overall stability of the ion. The more stable an alkyl cation is, the lower its reactivity. On the other hand, with an adjacent positively charged CH_2CO^+ group of **7**, the electron deficiency and the reactivity of the carbocationic center would be further increased. This would lead to enhanced reactivity of the carbocationic center. Thus the structure **7** should be compared not with the *tert*-butyl cation **VI** but with C−H protonated *tert*-butyl dication **VII** (Figure 4).[7f] Olah et al. have been able to show[7f] by hydrogen/deuterium exchange experiments and theoretical studies that the long-lived stable *tert*-butyl cation **VI** undergoes C−H protonation in superacids to form the highly electron deficient protio *tert*-butyl dications **VII**. With further protonation of **VI** in superacidic solutions, C−H hyperconjugative stabilization of the trivalent carbenium center is enhanced (vide supra). This leads also to an enhanced overall electron deficiency and reactivity.

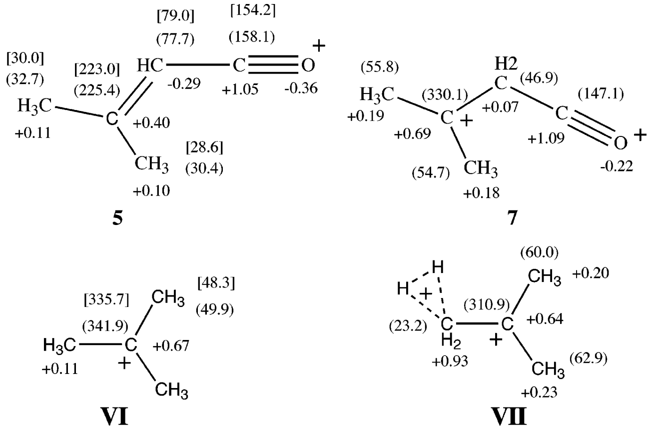


Figure 4. Calculated NBO charges and GIAO−CCSD(T) ^{13}C NMR chemical shifts (given in parentheses) of **5**, **7**, **VI**, and **VII**. Experimental ^{13}C NMR chemical shifts are given in brackets.

We have also computed the ^{13}C chemical shifts of **5** and **7** at the GIAO−CCSD(T)/tzp/dz level using MP2/cc-pVTZ geometries, and they are shown in Figure 4. The ^{13}C chemical shifts of **5** and **7** were also calculated using the GIAO−MP2 and GIAO−SCF theories and are given in Table 2. The GIAO−CCSD(T) calculated δ ^{13}C of C(O), C_α, and C_β of **5** are 158.1, 77.7, and 225.4, respectively. These agree extremely well with the reported experimental values of δ ^{13}C 154.2, 79.0, and 223.0.[5] The total δ ^{13}C of C(O), C_α, and C_β of 461.2 is only 5.0 ppm different from the experimental value of 456.2. GIAO−MP2 calculated values of **5** are also very close to experimental values (Table 2). The total δ ^{13}C of C(O), C_α, and C_β calculated by the GIAO−MP2 method is 464.7, also slightly (8.5 ppm) deviated from the experimental value. However, the corresponding value calculated by the GIAO−SCF method of 488.7 is 32.5 ppm different from the experimental value. These differences show the importance of correlation in ^{13}C NMR chemical shift calculation in cations. The ^{13}C NMR chemical shifts of the structurally related *tert*-butyl cation **VI** were also calculated at the same level to explore the effect of an additional charge in dication **7**. The GIAO−CCSD(T) calculated δ ^{13}C of the central carbenium carbon of **VI** is 341.9, which is only 6.2 ppm deshielded compared to that of the experimental value of 335.7.[21] The calculated δ ^{13}C of the carbenium carbon of **7** (δ ^{13}C 330.1) was found to be 11.8 ppm shielded relative to the calculated value of **VI**. For comparison, ^{13}C NMR chemical shifts of the protonated *tert*-butyl dication **VII** were also calculated (Figure 5). The calculated δ ^{13}C of central carbenium carbon of **VII** is 310.9 and is also 31.0 ppm shielded compared to that of the calculated value of **VI**. Such ^{13}C NMR shieldings in the dications compared to the monocation can be rationalized by enhanced dissipation of the positive charge by hyperconjugative effects. This can be noticed in the computed NBO charges[10] (Figure 4). In fact, the charge of the carbenium carbon of **VII** (+0.64) is slightly less positive than that of **VI** (+0.67). In the *tert*-butyl cation **VI**, each of the CH_3 groups as a whole bears +0.11 of charge, whereas in the protonated *tert*-butyl dication **VII**, as well as in **7**, each of the CH_3 groups as a whole bears about +0.20 of charge. This indicates enhanced dissipation of the positive charge in these types of dications.

Conclusion

The structures of superelectrophilic protonated propenoyl ($H_2C{=}CH{-}COH^{2+}$) and isopentenoyl ($(CH_3)_2C{=}CH{-}COH^{2+}$) dications and their parent cations were calculated at the MP2/6-311+G** level. The α-carbon (C_α) protonated forms **3** and **7** were found to be the most stable structures for protonated propenoyl and isopentenoyl dications, respectively, in accord with recent experimental studies.[16] Deprotonation energies of the global minimum structures were also calculated. The ^{13}C NMR chemical shifts of the intriguing dications **3** and **7** and their corresponding parents cations were calculated using the GIAO−CCSD(T) method. These calculated ^{13}C NMR chemical shifts of the parent monocations agree extremely well with the reported experimental values in superacid solutions. The charges and the ^{13}C NMR chemical shifts of the related *tert*-butyl cation ($(CH_3)_3C^+$) and the protonated *tert*-butyl dication ($(CH_3)_2CCH_4^{2+}$) were also calculated at the same level for comparison to explore the effect of an additional charge in the dication **7**. For comparison, ^{13}C NMR chemical shifts of the cations were also computed using the GIAO−MP2 and GIAO−SCF methods.

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