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Ab Initio/DFT/GIAO−CCSD(T) Calculational Study of the *t*-Butyl Cation: Comparison of Experimental Data with Structures, Energetics, IR Vibrational Frequencies, and ^{13}C NMR Chemical Shifts Indicating Preferred C_s Conformation

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The C_s conformation of the *tert*-butyl cation **3** was established to be the preferred global energy minimum using a combination of ab initio, DFT, and CCSD(T) methodology with correlation-consistent basis sets. The potential energy surface of methyl rotation involving the C_{3v}, C_s, and C_{3h} forms, however, in accord with previous studies, is quite flat. The computed IR absorptions of **3** indicate that it has the greatest degree of electron donation from C−H bonds into the C$^+$−C bonds. The experimental ^{13}C NMR chemical shifts also agree very well with the experimental data.

Introduction

NMR spectroscopic study of the persistent *tert*-butyl cation prepared by decarbonylation of the pivaloyl cation under superacid conditions was first reported[1] by Olah et al. in 1963 (Scheme 1).[2] Subsequently, in extensive studies, Olah et al. also showed that the *tert*-butyl cation could also be generated by the dissolution of *tert*-butyl halides and related precursors in SbF_5/SO_2ClF and varied other superacidic solutions (Scheme 2)[3] and may even be isolated as crystalline salts.

Yannoni and associates[4] used solid-state NMR to investigate the geometry of the *tert*-butyl cation and found that its C−C bond length is relatively short (1.46 Å). Recent X-ray studies on single crystals of *tert*-butyl cation salts confirmed that the cation carbon formally has a planar geometry, as expected for its sp^2-hybridized carbon center, in addition to having an overall C_{3h} symmetry. Furthermore, the C$^+$−C bond lengths were found to be short (1.440 to 1.445 Å in the crystal), indicating partial double-bond character resulting from substantial C−H hyperconjugation.[5,6]

The detailed global minimum structure of the *tert*-butyl cation has been a subject of debate over time. Olah and coworkers in 1971 concluded, on the basis of the early IR and Raman studies, that the cation exists in the C_{3v} conformation.[7] They observed C−H stretching at a very high frequency (2830 cm^{-1}) and asymmetric C−C−C stretching at a low frequency (1290 cm^{-1}), which they justified as a consequence of C−H hyperconjugation in the cation that results in a weaker C−H bond and a stronger C−C bond (Scheme 3).[8]

Subsequent ab initio calculations of the structure and NMR chemical shifts of the *tert*-butyl cation have been used to corroborate experimental findings and elucidate further details of the cation's nature. Radom and associates reported[9] the C_{3h} form to be 1.4 kcal/mol more stable than the C_{3v} form according to their computational results from the minimal STO-3G basis set. In 1993, Schleyer et al., who carried out extensive theoretical calculations on the various structural butyl cation isomers, identified the C_{3h} form as the minimum energy structure in accord with experimental IR spectral assignments.[10,11] At the MP4(SDTQ)/6-31G**//MP2/6-31G** + ZPE level, they found the C_{3h} structure to be the most stable structure, however, only 0.1 kcal/mol more stable than the C_s structure. At the MP2/6-31G* level, they reported peaks at 2803 (88 km/mol) and 2799 cm^{-1} (125 km/mol), corresponding to Olah's reported IR absorptions at 2830 and 1296 cm^{-1} (129 km/mol), in comparison with the experimental absorption at 1290 cm^{-1}. Recently, Douberly and his coworkers[12] carried out IR measurements on the *tert*-butyl cation in the gas phase with an improved spectral resolution over that reported by Olah. A multiplet involving peaks at 1278, 1302, and 1316 cm^{-1} was reported in support of the C_s and C_1 conformations, agreeing most with the IR spectra.

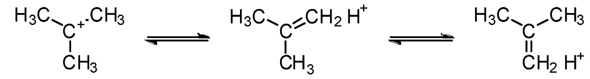
SCHEME 1

$$(CH_3)_3CCOF + SbF_5 \xrightarrow[-5^\circ C\ \text{to}\ -10^\circ C]{\text{Freon 113}} (CH_3)_3CCO^+SbF_6^- \underset{}{\overset{-CO}{\rightleftharpoons}} (CH_3)_3C^+SbF_5Cl^-$$

SCHEME 2

$$(CH_3)_3CCl + SbF_5 \xrightarrow[-78^\circ C]{SO_2ClF} (CH_3)_3C^+SbF_5Cl^-$$

SCHEME 3



Additionally, Schleyer et al. calculated[10] the NMR spectra of the C_s and C_{3h} forms of the *tert*-butyl cation at the IGLO/DZ level using the MP2/6-31G** geometries. They reported the ^{13}C NMR chemical shift to be δ^{13}C 346.5 for the cationic carbon center and δ^{13}C 45.6 for the methyl carbons of the C_s conformation. For the C_{3h} structure, they reported δ^{13}C 353.0 for the cationic carbon center and δ^{13}C 45.7 for the methyl carbons. In comparison, the observed experimental δ^{13}C values are 335.2 for the cationic carbon center and 47.5 for the methyl carbons, whereas the ^{1}H NMR spectrum consists of a sharp singlet peak at δ^1H 4.35, as previously reported by Olah.[2,3,13]

Recent studies indicate that electron correlation contributions are necessary to calculate the NMR chemical shifts more accurately. GIAO-MP2 is a widely used correlated method included in several widely used quantum chemistry programs including Gaussian 03.[14] Correlated ^{13}C NMR chemical shift calculations can also be carried out by GIAO−CCSD(T) and other coupled cluster methods. The GIAO−CCSD(T) method

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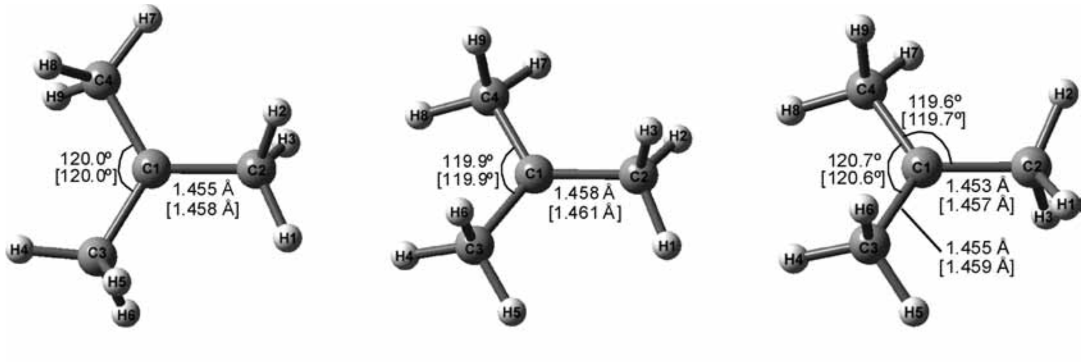


1 C_{3h} **2** C_{3v} **3** C_s

Figure 1. MP2/cc-pVTZ and B3LYP/cc-pVTZ structures of the *tert*-butyl cation. Parameters corresponding to B3LYP/cc-pVTZ are given in brackets.

TABLE 1: Total Energies (au), ZPE,[a] and Relative Energies (kcal·mol^{-1}) of the *tert*-Butyl Cation

structure	MP2/6-31G**	ZPE	relative energy	B3LYP/cc-pVTZ	ZPE	relative energy	MP2/cc-pVTZ	ZPE	relative energy
1 C_{3h}	157.00951	71.3	0.0	157.61245	69.8	0.0	157.16361	69.9	0.0
2 C_{3v}	157.00746	71.4	1.4	157.61004	69.6	1.3	157.16137	69.9	1.4
3 C_s	157.00972	71.6	0.1	157.61240	70.0	0.2	157.16410	70.2	0.0

[a] Zero point vibrational energies (ZPE) were scaled by a factor of 0.96 at B3LYP/cc-pVTZ//B3LYP/cc-pVTZ and 0.95 at MP2/6-31G**//MP2/6-31G** and MP2/cc-pVTZ//MP2/cc-pVTZ.

TABLE 2: Number of Imaginary Frequencies (NiMAG) in the *tert*-Butyl Cation

structure	MP2/6-31G**// MP2/6-31G**	B3LYP/cc-pVTZ// B3LYP/cc-pVTZ	MP2/cc-pVTZ// MP2/cc-pVTZ
1 C_{3h}	2	2	2
2 C_{3v}	1	1	1
3 C_s	1	1	0

is currently available through the ACES II program;[15] its accuracy for ^{13}C NMR chemical shifts of carbocations and other organic molecules has been demonstrated in several recent studies.[16−20] Herein we have reinvestigated various structures of the *tert*-butyl cation using available high-level ab initio/GIAO−CCSD(T) methods.

Calculations

Geometry optimizations, frequency calculations, and natural bond orbital (NBO) analysis were carried out with the Gaussian 03 program.[14] The geometry optimizations were performed at the ab initio MP2/6-31G** and MP2/cc-pVTZ levels. For comparison, optimizations were also carried out with the DFT method at the B3LYP/cc-pVTZ level using the Gaussian 03 program.[14] Vibrational frequencies at the MP2/6-31G*, MP2/cc-pVTZ, and B3LYP/cc-pVTZ levels were used to characterize stationary points as minima (number of imaginary frequency (NIMAG) = 0) or transition sates (NIMAG = 1). NMR chemical shifts were calculated by the GIAO (gauge invariant atomic orbitals) method[21] using MP2/6-31G** and MP2/cc-pVTZ geometries. GIAO−CCSD(T), GIAO-MP2, and GIAO-SCF calculations using tzp (tzp is used for both carbon and hydrogen) and tz2p basis sets (same tz2p is used for both carbon and hydrogen)[22,23] have been performed with the ACES II program.[15] The ^{13}C NMR chemical shifts were computed using TMS (calculated absolute shift, i.e., σ(C), tzp = 195.5 (GIAO-SCF), 199.2 (GIAO-MP2), 197.3 (GIAO−CCSD(T); tz2p = 194.8 (GIAO-SCF), 198.5 (GIAO-MP2), 196.7 (GIAO−CCSD(T), 207.5 (GIAO-MP2/6-31G**) as reference.

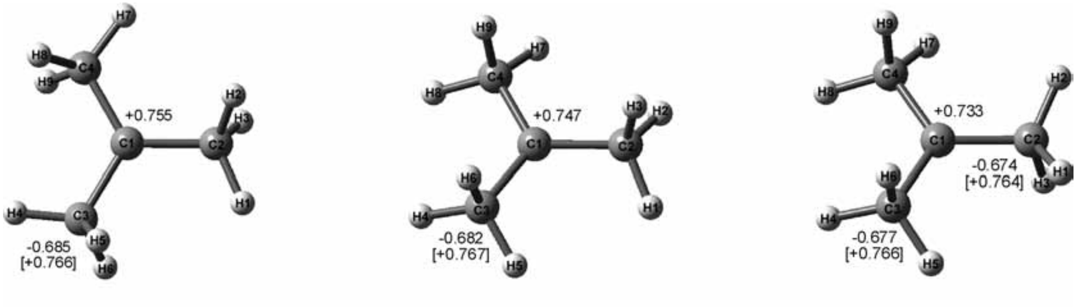
Results and Discussion

Geometries and Energies. The three symmetrical conformers (C_{3h} **1**, C_{3v} **2**, and C_s **3**) of *tert*-butyl cation were computed (Figure 1). Energy data on different conformations of the *tert*-butyl cation confirm Schleyer's argument that the potential energy surface of methyl group rotation is quite flat (Table 1).[10] Specifically, energy differences between any two of the computed conformations do not exceed 2.0 kcal/mol. Structure **1** is the most stable at the B3LYP/cc-pVTZ//B3LYP/cc-pVTZ + ZPE level, but the fact that it has two imaginary frequencies (−52.3 cm^{-1}, degenerate) means that it is likely not the true minimum (Table 2). At this level, the C_s structure **3** is 0.2 kcal/mol less stable than structure **1** and has one imaginary frequency.

Structure **2** has the highest energy along with one imaginary frequency at both B3LYP/cc-pVTZ and MP2/cc-pVTZ. Structures **1** and **3** are energetically the same at the MP2/cc-pVTZ//MP2/cc-pVTZ + ZPE level. However, structure **1** has two imaginary frequencies at this level, whereas structure **3** does not have any. This strongly indicates that structure **3** is the actual global minimum.

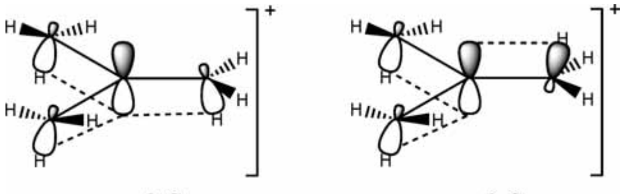
MP2/cc-pVTZ calculated C$^+$−C bond lengths of 1.453 to 1.455 Å for C_s structure **3** were found to be in good agreement with Yannoni's nutation NMR experimental value (1.46 Å).[4] In comparison, X-ray studies showed C$^+$−C lengths to be shorter, notably between 1.440 and 1.445 Å, as reported earlier.[5,6] The calculated C$^+$−C bond length at the MP2/cc-pVTZ level is 1.455 Å for C_{3h} structure **1** and 1.458 Å for the C_{3v} structure **2** (Figure 1). In comparison, calculated bond lengths (1.458 to 1.462 Å) at the B3LYP/cc-pVTZ level were slightly closer to Yannoni's experiment. However, the MP2/cc-pVTZ results are within the ~1% error range reported for measurements made with nutation NMR spectroscopy.[4] The methyl carbons were very close to 120.0° from each other, as expected for a trigonal planar carbon skeleton. Compared with the *tert*-butyl cation, the MP2/cc-pVTZ calculated C−C length of isobutane is higher at 1.524 Å. This indicates substantial hyperconjugation in the *tert*-butyl cation.

Comparing all three structures, the NBO charge of C$^+$ in structure **1** is the most positive, and its methyl groups are the most negative over all. On the other hand, the NBO charge of C$^+$ in structure **3** is the least positive, whereas its methyl groups, correspondingly, are the least negative. This means that structure



1 C_{3h} **2** C_{3v} **3** C_s

Figure 2. Carbon and hydrogen NBO charges of the *tert*-butyl cation. Sums of hydrogen charges for unique, individual methyl groups are shown in brackets.



2 C_{3v} **3** C_s

Figure 3. C−H hyperconjugation in the *tert*-butyl cation.

3 may involve the greatest amount of hyperconjugation and structure **1** may involve the least amount of hyperconjugation (Figure 2).

Also notable is the fact that the C_1 structure that was optimized at the MP2/cc-pVTZ level was readily transformed into a C_s-like conformation, further corroborating earlier evidence of the C_s structure being the energy minimum. The results may be explained on the basis of hyperconjugation along both sides of the plane of the carbon skeleton stabilizing the cation much more in the C_s form than that from only one side in the C_{3v} structure (Figure 3). The *tert*-butyl cation is efficiently stabilized by intramolecular C−H hyperconjugative interactions with the cationic carbon.[24] The C_s and C_{3v} structures each have three hydrogen atoms that are parallel to the empty p orbital of the center carbon, but two lie on one side of the plane of the carbon skeleton and one on the other in the former, whereas all three are on the same side in the latter.

Infrared Frequencies

Frequency calculations carried out at the MP2/cc-pVTZ//MP2/cc-pVTZ level show three absorptions at 1271 (37 km/mol), 1291 (129 km/mol), and 1338 cm^{-1} (134 km/mol) for structure **3** (Table 3) as a triplet, which agrees with Duncan's experimental values.[12] All three bands correspond to an asymmetric C−C stretch and the methyl bend. In contrast, asymmetric C−C stretching/methyl bending within the same range of frequencies is observed as a doublet in the calculated spectrum

TABLE 3: MP2/cc-pVTZ//MP2/cc-pVTZ Calculated and Experimental Frequencies and IR Intensities of the *tert*-Butyl Cation[a,b]

MP2/cc-pVTZ//MP2/cc-pVTZ IR absorptions						
1 C_{3h}		**2** C_{3v}		**3** C_s		
frequency (cm^{-1})	intensity (km/mol)	frequency (cm^{-1})	intensity (km/mol)	frequency (cm^{-1})	intensity (km/mol)	exptl frequency
949.4	37.5	800.7	1.3	826.5	7.0	
949.4	37.5	949.3	0.0	950.5	40.9	970
961.8	0.0	1010.4	1.8	962.1	1.8	
1080.7	21.7	1010.4	1.8	1000.8	0.3	
1246.8	118.7	1100.7	17.4	1070.7	35.0	1098
1246.8	118.7	1278.0	10.2	1270.9	37.3	1278
1280.9	0.0	1278.0	10.2	1277.5	6.1	
1317.9	64.8	1296.7	159.1	1290.8	128.7	1302
1317.9	64.8	1296.7	159.1	1298.3	11.1	
1391.8	0.0	1319.5	35.9	1338.4	133.6	1316
1391.8	0.0	1335.5	0.0	1357.5	2.0	
1426.4	44.7	1393.6	0.3	1382.2	0.6	
1444.7	0.0	1393.6	0.3	1401.5	17.3	1410
1468.2	24.4	1463.7	23.0	1464.7	6.3	1465
1468.2	24.4	1463.7	23.0	1466.9	28.4	
2925.4	95.0	1492.2	24.0	1479.4	29.6	1476
2925.4	95.0	2881.6	86.8	2868.0	119.5	
2935.8	0.0	2881.6	86.8	2876.4	90.1	2834
2981.0	64.1	2901.2	42.8	2891.5	27.6	
2981.9	0.0	3039.0	1.6	3031.7	1.5	2965
2981.9	0.0	3039.0	1.6	3033.3	3.0	
3114.5	0.0	3045.1	17.2	3036.0	16.7	
3114.8	8.7	3112.0	0.0	3111.5	7.5	3036
3114.8	8.7	3119.6	6.1	3113.2	0.1	
		3119.6	6.1	3117.9	4.7	

[a] Frequencies were scaled by a factor of 0.97. [b] Experimental values for *tert*-butyl cation were taken from ref 12.

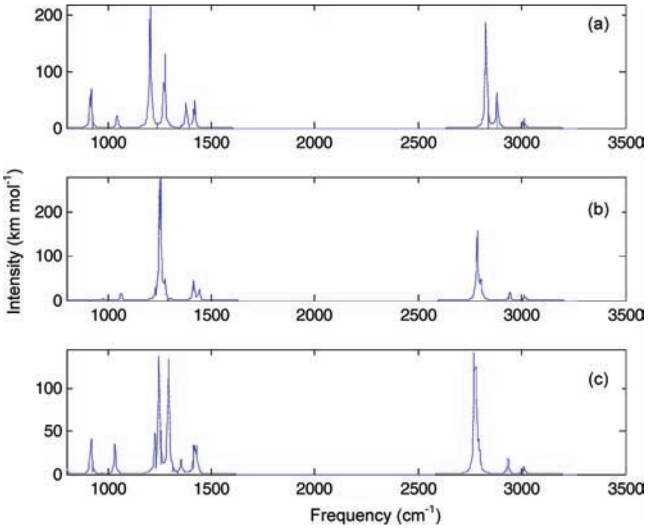


Figure 4. MP2/cc-pVTZ//MP2/cc-pVTZ calculated IR spectra of the *tert*-butyl cation. Spectra shown are of structures (a) **1**, (b) **2**, and (c) **3**.

for structure **1** and a singlet for structure **2**. Strong absorptions between 2860 (120 km/mol) and 2930 cm^{-1} (90 km/mol) for each structure corresponding to C−H stretching agree with Duncan's assignment of the same motion to a peak at 2834 cm^{-1} from his experiment. The C−C stretching triplet for structure **3** lies at higher frequencies than the doublet and singlet corresponding to the same motion for structures **1** and **2**, respectively, which shows that this structure has the greatest partial double-bond character. Its C−H stretching frequency is also the lowest, which indicates a weaker than normal C−H bond resulting from electron donation to the C−C bond. At the same time, the doublet for structure **1** lies at the lowest frequencies, whereas its C−H stretching frequency is the highest. This means that structure **1** has the weakest hyperconjugative stabilization. IR spectra of the three structures are displayed in Figure 4.

^{13}C NMR Chemical Shifts

The NMR chemical shift data calculated at the relatively low GIAO-MP2/6-31G**//MP2/6-31G** level appear to come close to the experimental values, with C^+ predicted to have $\delta^{13}C$ 335.1 for structure **2** and $\delta^{13}C$ 336.0 for structure **1**. (See Table 4.) At the same level, C^+ in the C_s structure **3** was predicted to have $\delta^{13}C$ 329.0. Because calculations at the same level as well as those using the cc-pVTZ basis set instead of 6-31G** predicted two (degenerate) imaginary frequencies for structure **1** and the highest energy for structure **2**, neither of them can be the true minimum.

Computations performed using the GIAO−CCSD(T) method with the tz2p basis set yielded predicted cationic carbon $\delta^{13}C$ 349.2 for structure **1**, 347.9 for structure **2**, and 340.3 for structure **3**; the latter value agrees extremely well with the experimental data. Additionally, it is consistent with previously discussed findings that structure **3** is the lowest energy and contains no imaginary frequencies. That the carbocationic carbon in structure **3** is the most shielded among the different conformations indicates that it has the greatest stabilization from the most effective hyperconjugation. NMR properties predicted with GIAO-MP2 and the same basis set resulted in slightly higher ^{13}C NMR shifts for the same carbon.

Chemical shifts of the methyl carbons calculated with tzp and tz2p basis sets using the GIAO-SCF method are further from experimental results than those found with GIAO-MP2 and GIAO−CCSD(T) levels. This indicates the importance of factoring in the electron correlation effects when carrying out computations. However, better agreement of GIAO-SCF with experiment than GIAO-MP2 for the center carbon may be fortuitous. In general, the greater accuracy of GIAO−CCSD(T) compared with GIAO-MP2 results from its better treatment of electron correlation contributions.[16] Computations carried out using the tzp basis set, however, did not differ much from those that used the larger tz2p basis set.

Conclusions

The C_s structure **3** was found to be the preferred conformation of the *tert*-butyl cation on the basis of its assignment as the global

TABLE 4: Calculated and Experimental ^{13}C and ^1H NMR Chemical Shifts of the *tert*-Butyl Cation[a,b]

			GIAO-SCF		GIAO-MP2		GIAO−CCSD(T)		
no.	atom	GIAO-MP2/6-31G**	tzp	tz2p	tzp	tz2p	tzp	tz2p	exptl
1 C_{3h}	C_1	336.0	352.9	351.4	352.4	352.9	349.1	349.2	
	C_2	47.3	43.9	43.3	50.5	50.4	49.2	49.1	
	C_3	47.3	43.9	43.3	50.5	50.4	49.2	49.1	
	C_4	47.3	43.9	43.3	50.5	50.4	49.2	49.1	
	H_{1-3}	4.0	3.9	3.9	4.0	4.0	3.9	4.0	
	H_{4-6}	4.0	3.9	3.9	4.0	4.0	3.9	4.0	
	H_{7-9}	4.0	3.9	3.9	4.0	4.0	3.9	4.0	
2 C_{3v}	C_1	335.1	350.5	349.2	351.1	351.6	347.9	347.9	
	C_2	46.4	42.9	42.5	49.3	49.4	48.0	48.1	
	C_3	46.4	42.9	42.5	49.3	49.4	48.0	48.1	
	C_4	46.4	42.9	42.5	49.3	49.4	48.0	48.1	
	H_{1-3}	4.0	3.9	3.9	3.9	4.0	3.9	3.9	
	H_{4-6}	4.0	3.9	3.9	3.9	4.0	3.9	3.9	
	H_{7-9}	4.0	3.9	3.9	3.9	4.0	3.9	3.9	
3 C_s	C_1	329.0	343.4	342.0	343.4	343.8	340.4	340.3	335.2
	C_2	48.1	45.2	44.6	51.8	51.7	50.4	50.3	47.5
	C_3	46.6	43.2	42.7	49.5	49.5	48.2	48.1	
	C_4	46.6	43.2	42.7	49.5	49.5	48.2	48.1	
	H_{1-3}	3.9	3.8	3.8	3.9	3.9	3.9	3.9	4.35
	H_{4-6}	3.9	3.8	3.8	3.9	3.9	3.9	3.9	
	H_{7-9}	3.9	3.8	3.8	3.9	3.9	3.9	3.9	

[a] ^{13}C and ^1H NMR chemical shifts were referenced to TMS. See Figure 1 for numbering scheme. [b] Experimental values of *tert*-butyl cation were taken from refs 2 and 3.

minimum energy structure. The computed IR absorptions indicate that structure **3** has the greatest amount of electron donation from C−H bonds to C^+−C bonds and predicted ^{13}C NMR chemical shifts that agree the most with the experimental data. The isolation and characterization of the individual conformations of *tert*-butyl cation are beyond the scope of existing experimental techniques because of their closely related energetics and the low energy barriers of rotation between the different conformations. This necessitates the use of available high-level ab initio computational methods to differentiate and elucidate their structure.

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