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Ab initio structural studies of cyclobutylmethyl cations: effect of fluoroalkyl groups on the relative stability of the carbocations

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Dedicated to Professor Kenneth K. Laali on the occasion of his 65th birthday

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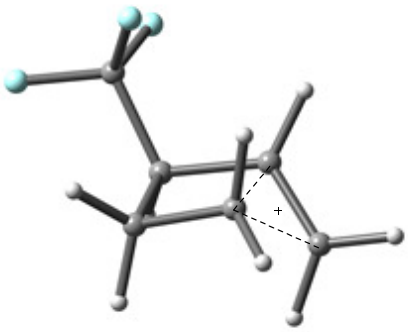
Abstract

Ab initio calculations at MP2/cc-pVTZ level show that the trifluoromethyl group has a strong destabilizing effect on the nonclassical, σ-bridged cyclobutylmethyl cations. The GIAO-MP2 derived ^{13}C NMR chemical shifts indicate substantial charge delocalization from the neighboring cyclobutyl ring for carbocations with an α-fluorolkyl group as compared to the 1-cyclobutylethyl cation, and this enhanced charge delocalization in case of the α-(trifluoromethyl)cyclobutylmethyl cation would lead to the ring-opening rearrangement to form the relatively more stable nonclassical primary cyclobutylmethyl cation, in which the carbocation center is farthest from the strongly electron-withdrawing trifluoromethyl group.

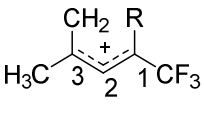


Keywords: Carbocations, ab initio, cyclobutylmethyl cation, trifluoromethyl, fluoroalkyl, GIAO-MP2

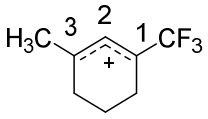
Introduction

The α-trifluoromethyl carbocations are exceptionally unstable as compared to their nonfluorinated analogs, and their formation is strongly disfavored under solvolysis as well as stable-ion conditions in superacidic media. Thus, there are only a few reports of the formation and characterization of the α-trifluoromethyl cations in stable-ion conditions, using superacidic media, as well as in solvolysis reactions. [1-5] Even the α-monofluoroalkyl carbocations are too strongly destabilized to be prepared and observed in the solution phase. However, an α-monofluoromethyl carbocation, 1-fluoro-2-propylium cation ($CH_3CH^+CH_2F$), was characterized as a transient intermediate in the gas phase,[6] and an extremely unstable α-trifluoromethylvinyl cation, 3,3,3-trifluoro-1-phenyl-2-propenium cation, was generated through a photochemical reaction.[7]

We have earlier demonstrated that the π-delocalized, α-trifluoromethylallyl cations **1**-**3**, formed in superacidic media at low temperatures, have relatively low C_1-C_2 rotational barriers of about 9 kcal/mol, implying that the positive charge is substantially localized on the tertiary carbon (C_3).[3] That is, the positive charge is disfavored at the C_1 due to the strong electron-withdrawing inductive effect of the trifluoromethyl group. Tidwell and coworkers have demonstrated the strong destabilizing effect of the trifluoromethyl group on the 9-(trifluoromethyl)fluorenyl cation (**4**) and 3-(trifluoromethyl)indenyl cation (**5**) through solvolysis studies.[1,2]



1; R = H,
2; R = CH_3



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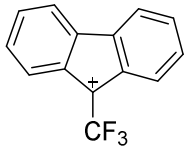

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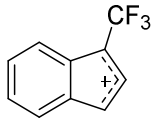

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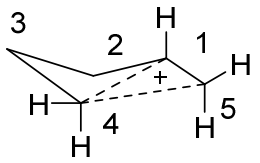
The cyclobutylmethyl cations involve extensive nonclassical σ-participation and the extent of this σ-participation correlates with the electronic characteristics the substituents on the carbocation center.[8] Our ab initio calculations, including ^{13}C NMR chemical shift calculations, at MP2/cc-pVTZ level showed that the primary cyclobutylmethyl cation (**6**), *exo*- and *endo*-secondary 1-methyl-1-cyclobutylmethyl cations (**7** and **8**), and the tertiary 1,1-dimethylcyclobutylmethyl cation (**9**) have σ-bridged, nonclassical structures, the relative extent of charge delocalization from the strained cyclobutyl ring being dependent on the stabilizing effects of the substituents on the carbocation center.[9] The tertiary 1,1-dimethylcyclobutylmethyl cation (**9**) is relatively more stabilized, by the methyl groups, as compared to the primary and secondary structures **6, 7,** and **8** so that the σ-delocalization from the adjacent cyclobutyl C_1-C_4 bond is relatively less significant, as reflected by the relatively less elongated C_1-C_4 bond ((C_1-C_4) = 1.903, 1.837, 1.819, and 1.766 Å, respectively for carbocations **6**, **7**, **8**, and **9**), and the relatively less deshielded ^{13}C NMR signal for the carbocationic center at C_1 ($\delta^{13}C(C_1)$ = 199.6, 155.7, 139.9, and 106.0, respectively for carbocations **6**, **7**, **8**, and **9**).



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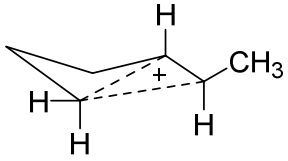

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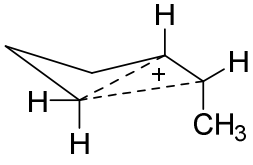

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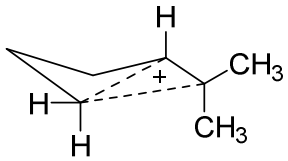

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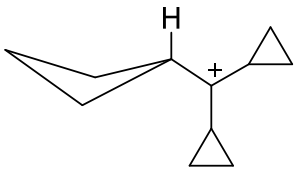
We have also located the transition structure for the interconversion of the nonclassical cyclobutylmethyl cation **6** to the classical C_2-symmetric cyclopentyl cation, which is the global minimum on the potential energy surface and is 10.3 kcal/mol more stable than the nonclassical structure **6**.[9] This transition state is very similar in structure to that of the nonclassical structure **6** and is only 0.7 kcal/mol higher in energy. The GAIO-MP2 calculated ^{13}C NMR chemical shifts unequivocally show that the positive charge is significantly delocalized among the C_2 and C_5 carbons in carbocations **6**-**9**.

The experimental observation of the destabilized cyclobutylmethyl cations remains challenging, and all attempts of preparing such carbocations, including relatively stabilized secondary cyclobutylmethyl cations have been unsuccessful to date.[8,10,11] However, we were able to prepare and characterize the cylobutyldicyclopropylmethyl cation (**10**) in superacidic media at low temperature. The latter carbocation, although predominantly a classical carbocation, involves significant delocalization into the neighboring cyclobutyl and the cyclopropyl rings.[10]



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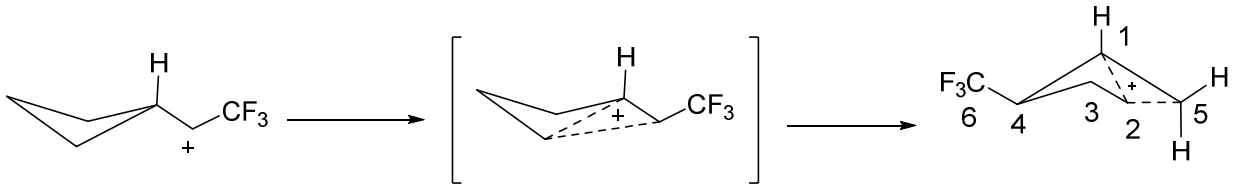


11-classical
(input geometry)

11-nonclassical

12

The destabilized cyclobutylmethyl cations are expected to involve extensive charge delocalization into the cyclobutyl ring, potentially leading to further rearrangements. Thus, it would be interesting to explore the structural characteristics of the destabilized carbocations, such as cyclobutyl(trifluoromethyl)methyl cation (**11**), at high level *ab initio* calculations. We have accordingly calculated structures of the cyclobutyl-(fluoroalkyl)methyl cations at high-level *ab initio* calculations, at MP2/cc-pVTZ level, which reveal that the α-trifluoromethyl group strongly destabilizes the nonclassical σ-delocalized carbocation, and the optimization resulted in the rearranged carbocation, a primary σ-bridged cyclobutylmethyl cation **12**, with the trifluoromethyl group being placed at a distant carbon from the carbocation center.

Results and Discussion

We have optimized the structures of the secondary cyclobutylmethyl carbocations – cyclobutyl(fluoromethyl)-methyl cation (**16**), cyclobutyl(difluoromethyl)methyl cation (**15**), cyclobutyl(trifluoromethyl)methyl cation (**11**)—initially at MP2/6-311G(d,p) level and then re-optimized at the MP2/cc-pVTZ level. The zero-point energies (ZPE) were then calculated using the optimized geometries, which also revealed them as true minima by not having any imaginary (negative) frequencies. The ^{13}C NMR chemical shifts were calculated at the GIAOMP2/cc-pVTZ level using the final geometries of the MP2/cc-pVTZ calculations (Table 1). We have calculated the structure and $\delta^{13}C$ of **7** earlier at the same level of calculations using Gaussian 03 for structure

optimization and ACES II program for NMR.[9] In order to be consistent with the present NMR calculations using Gaussian 09, we have recalculated the structure and the ^{13}C NMR chemical shifts, and also obtained the zero-point energy at the MP2/cc-pVTZ level (the earlier reported ZPE value corresponds to MP2/6-31G* level). The extent of σ-delocalization from the strained cyclobutyl group in these carbocations is analyzed in terms of the C_1-C_2 and C_2-C_5 bond lengths and ^{13}C NMR chemical shifts of the carbocationic centers. Selected bond lengths of the carbocations **7** and **12**-**17**, along with their MP2/cc-pVTZ optimized structures are shown in Figures 1 and 2. The MP2-derived ^{13}C NMR chemical shifts are better correlated with the experimental values than those of the SCF-derived ones in the case of the parent cyclopentyl cation in our earlier calculations,[10] so we have focused on the GIAO-MP2/cc-pVTZ//MP2/cc-pVTZ values (Table 1) in analyzing the structural details of the carbocations studied here.

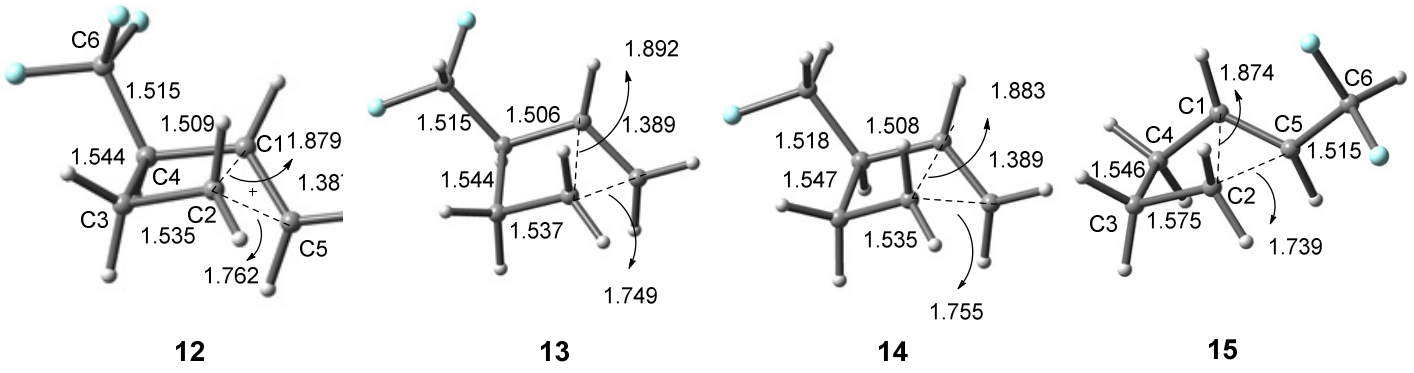


Figure 1. MP2/cc-pVTZ optimized structures and selected bond lengths (in Å) of carbocations **12**-**15**.

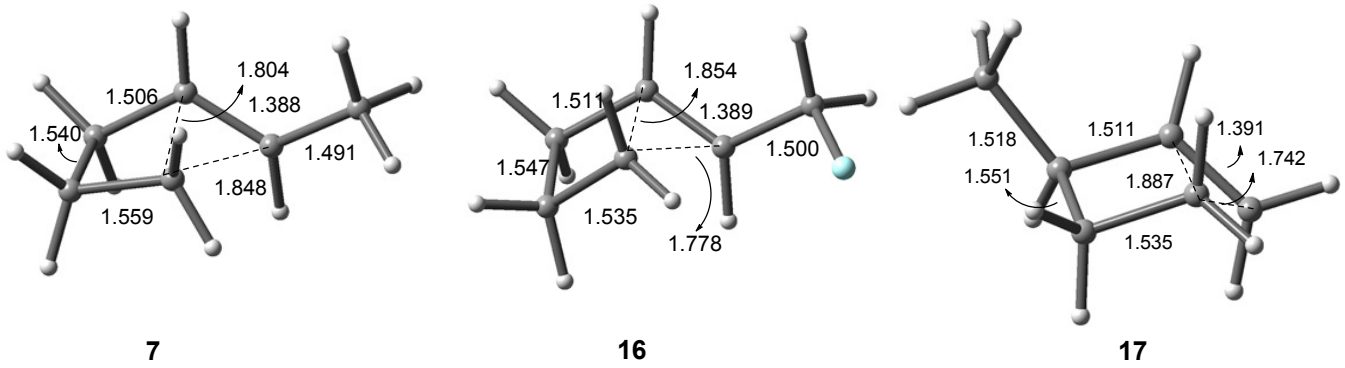


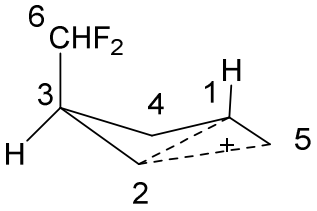
Figure 2. MP2/cc-pVTZ optimized structures and selected bond lengths (in Å) of carbocations **7**, **16**, and **17**.

The optimization of the secondary cyclobutyl(trifluoromethyl)methyl cation, starting from the classical geometry, **11**-classical, resulted in its spontaneous rearrangement to the nonclassical primary cyclobutyl-methyl cation **12**, which involves the migration of the trifluoromethyl group farther from the carbocationic centers, C_1 and C_5. The C_1-C_2 bond (1.879 Å) and the C_2-C_5 bond (1.762 Å) in the carbocation **12** are significantly smaller than in the parent cyclobutylmethyl cation[10] (1.903 Å and 1.738 Å, respectively for C_1-C_2 and C_2-C_5), calculated at the same level (MP2/cc-pVTZ), while the other bond lengths are comparable in both cases,

showing relatively lower C_1-C_2 σ-bond participation in case of the carbocation **12**. In agreement with this hypothesis, $\delta^{13}C$ of the carbocationic center C_1 in **12** (174.9 ppm; Table 1) is also relatively shielded as compared to that of the unsubstituted primary cyclobutylmethyl cation ($\delta^{13}C$ (C1) = 196.6).[9]

The carbocation **12** can also be considered as unsymmetrically delocalized 2-(trifluoromethyl)cyclopentyl carbocation, where the C_2-C_5 bond is stabilizing the carbocation center C_1 through the σ-delocalization. The MP2-derived ^{13}C NMR chemical shifts for the carbocation **12** show extensive charge delocalization among the C_1 and C_5 carbons, with a significant amount of charge residing on the methine carbon C_1, as shown by its relatively highly deshielded absorption, $\delta^{13}C$ = 174.9. The methylene carbon C_5, although relatively less deshielded ($\delta^{13}C$ 94.9) than that of the C_1, indicates substantial positive charge at C_5. The relatively strong electron-withdrawing field effect of the trifluoromethyl group thus disfavors extensive C_1-C_2 charge delocalization, even when it relatively farther from the carbocationic center.

The unexpected spontaneous rearrangement of cation **11** during its optimization indicates the much lower relative stability of **11**-nonclassical structure over the structure **12**, in which the trifluoromethyl group is relatively much farther than in **11**-nonclassical. We have then calculated the structures of the relatively lightly fluorinated versions of carbocations, the α-difluoromethyl substituted carbocation **15** and α-fluoromethyl-substituted carbocation **16**, starting from the corresponding classical structures, and also calculated the structures, energies, and $\delta^{13}C$ of the **13** and **14**, the rearrangement products of the latter carbocations, in order to probe their relative stabilities. Unlike the trifluoromethyl-substituted cation, the nonclassical structures **15** and **16** did not spontaneously rearrange to the carbocations **13** and **14** during structural optimization, reflecting their enhanced stabilities as compared to **12**.



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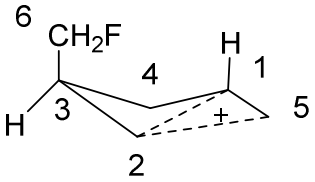

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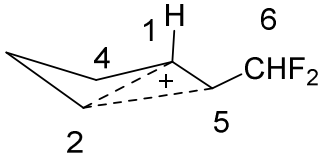

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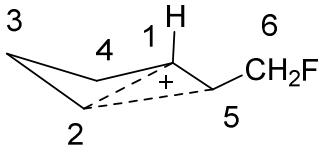

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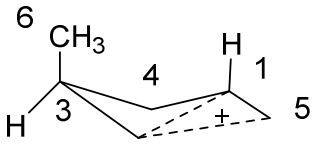

17

As can be seen from Table 1, it is evident that the secondary nonclassical structures **7**, **16**, and **15** are relatively more stable than the corresponding isomeric primary nonclassical structures **17**, **14**, and **13**, by 3.6, 2.6, and 0.1 kcal/mol, respectively, and thus there is no driving force for their spontaneous rearrangements during their structural optimization, unlike that for **11**. Thus, the nonclassical structures are increasingly destabilized as the α-substituent in the carbocations is varied from methyl to trifluoromethyl. These relative stability differences are also in accordance with the $\delta^{13}C(C_1)$ values; the $\delta^{13}C(C_1)$ of **7**, **16**, and **15** are 133.3, 162.0 and 168.5, respectively (Table 1) indicating the gradual increase of the positive charge density at the C_1

carbon for carbocations when the α-substituents are varied with progressively electron-withdrawing groups, methyl, fluoromethyl, and difluoromethyl.

Table 1. Electronic energies (E_{el}), zero-point energies (ZPE), relative total energies (at MP2/cc-pVTZ//MP2/cc-pVTZ level; the relative energies shown are for color-coded compounds), and ^{13}C NMR chemical shifts (at GIAO-MP2/cc-pVTZ//MP2/cc-pVTZ level) of carbocations **7**, and **12–17**; the numbering schemes for the carbons are shown on the structures

Carbocation	E_{el} (–a.u.)	ZPE (kcal/mol)	Relative energy (kcal/mol)	$\delta^{13}C$	
				C1 133.3	C4 21.0
7	234.39047	98.7	0	C2 31.0	C5 114.3
				C3 8.2	C6 19.1
				C1 174.9	C4 40.9
12	531.78849	84.2		C2 26.5	C5 94.9
				C3 23.9	C6 133.5
				C1 184.5	C4 41.7
13	432.63918	89.3	0.1	C2 24.9	C5 92.4
				C3 23.1	C6 120.7
				C1 180.9	C4 35.0
14	333.50090	94.1	2.6	C2 26.5	C5 93.3
				C3 25.0	C6 83.5
				C1 168.5	C4 21.8
15	432.63977	89.6	0	C2 15.0	C5 87.5
				C3 -1.2	C6 114.1
				C1 162.0	C4 21.4
16	333.50526	94.2	0	C2 30.9	C5 116.9
				C3 20.3	C6 83.2
				C1 194.9	C4 30.7
17	234.38441	98.5	3.6	C2 22.8	C5 90.5
				C3 28.9	C6 20.1

Calculations

Geometry optimizations were initially performed at MP2/6-311G(d,p) level, and the resulting structures were then optimized at MP2/cc-pVTZ level, using Gaussian 09 program.[12] Vibrational frequency calculations for all the carbocations were carried out at MP2/cc-pVTZ level to characterize the stationary points as minima (NIMAG = 0). The total energies (*i.e.*, sum of electronic and vibrational zero point energies (ZPE)), denoted as MP2/cc-pVTZ// MP2/cc-pVTZ + ZPE, were then used to calculate the relative energies of the carbocations, and are shown in Table 1. GIAO-MP2 ^{13}C NMR calculations carried out for MP2/cc-pVTZ optimized structures (σC for TMS at GIAO-MP2/cc-pVTZ//MP2/cc-pVTZ = 199.1) and the chemical shifts are summarized in Table 1.

Conclusions

In summary, we have carried out high-level *ab initio* calculations (MP2/cc-pVTZ and GIAO-MP2/cc-pVTZ at the same basis set) on the cyclobutylmethyl cations, and investigated the effect of the fluoroalkyl groups on the σ-delocalization from the strained cyclobutyl ring. Whereas the α-methyl, α-fluoromethyl-, α,α-difluoromethyl-cyclobutylmethyl cations converged into the corresponding nonclassical, σ-delocalized structures, without any attendant rearrangements during the structure optimization, the strongly destabilized α–trifluoromethylcyclobutylmethyl cation spontaneously rearranges during optimization to give the nonclassical 2-(trifluoromethyl)cyclobutylmethyl cation. The σ-bond participation from the strained cyclobutyl ring, as shown by the calculated ^{13}C NMR chemical shifts and the bond distances, is correlated with the electron-withdrawing effects of the substituents on the carbocationic center: the higher the electron demand, the greater the σ-bond participation.

Supplementary Material

Cartesian coordinates for structures **7**, and **12**-**17**.

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