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Notes

^{1}H and ^{13}C NMR Spectroscopic Investigation of Long-Lived *Ortho*- and *Meta*-Substituted Di-1-adamantylbenzyl Cations: Highly Deshielded Crowded Benzylic Cationic Centers[1a]

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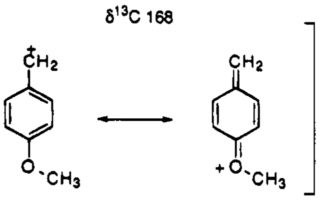
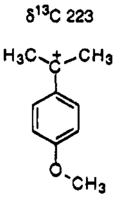
Introduction

In 1971 Olah and co-workers reported proton and ^{13}C NMR spectroscopic studies of the first stable monosubstituted primary benzyl cation, the *p*-methoxybenzyl cation (**1**). The ^{13}C NMR resonance signal was observed at δ 168.[1b] Extensive p–π aromatic quinonoid delocalization was attributed to the high C_{para}-OCH_3 and C_{ipso}-C^+ bond rotational barriers and the overall stability of the ion.[2] These p–π resonance interactions were shown to be dramatically reduced with the introduction of two methyl groups at the benzylic position as in the the cumyl cations **2** and **3** which displayed ^{13}C NMR chemical shifts at 223 and 255 ppm for the *p*-OCH_3 (**2**) and *p*-H (**3**) derivatives, respectively.



1a **1b**



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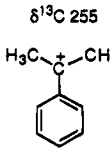

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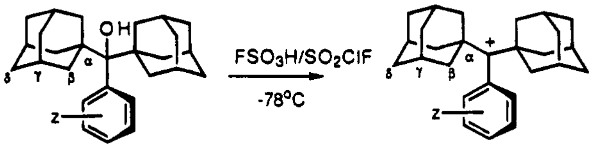
More recently we have shown that with increased steric congestion about the benzylic center of the carbocationic intermediate, much larger deshielding of the cationic center is observed.[3] In the case of di-1-adamantylbenzyl cations we reported a highly deshielded benzylic cationic center with a ^{13}C NMR resonance at δ 286.[4] Application of the Gassman–Fentiman tool of increasing electron demand with *para*-substituted derivatives indicated very little p–π aromatic delocalization. We now report a ^{1}H and ^{13}C NMR spectroscopic study of the *o*-methyl, *m*-methyl, and *m*-*tert*-butyl derivatives of 1,1-di-1-adamantylbenzyl cations, possibly the most hindered benzyl cations that have yet been observed as long-lived ions. In such systems the p–π conjugation is almost completely annulled.

Results and Discussion

The necessary precursors *o*-tolyldi-1-adamantylmethanol (**4a**), *m*-tolyldi-1-adamantylmethanol (**4b**), and (*m*-*tert*-butylphenyl)di-1-adamantylmethanol (**4c**) were prepared according to published procedures.[5] Lack of rotational symmetry with respect to the sp^3–sp^2 bond between the Ad_2COH group and the aryl ring results in two diastereomerically distinct (*syn, anti*) rotamers for each compound. It is of no importance which rotamer of the *meta*-substituted compounds is used; in practice mixtures were employed. For **4a**, ease of synthesis and rapidity of reaction advocated the use of the *anti* rotamer in preference to the *syn*.

Benzyl carbocations were successfully generated by ionization of the corresponding alcohols by FSO_3H in SO_2ClF at −78 °C. In the case of the *meta*-substituted benzylic cations a clear orange solution was obtained. Ionization of the *anti*-*o*-tolyl derivative was extremely rapid, generating a dark red solution.



4a-d **5a-d**

a= *o*-CH_3; b= *m*-CH_3: c= *m*-*tert*-butyl
d= H

The cationic carbon of **5a** displays the highest chemical shift recorded for benzylic systems with a ^{13}C δ 301, whereas **5b** and **5c** (Table 1) show slightly less deshielding, with the C^+ signals at 289 and 288 ppm, respectively. ^{13}C NMR data for these cations recorded at −80 °C are given in Table 1 along with ^{13}C NMR data of phenyl- (**5d**) and alkyl-substituted (**6a,b**) diadamantylmethyl cations.

Apart from the very high C^+ shift in **5a** (301 ppm), the ^{13}C NMR data for **5a**, **5b**, and **5c** indicate no great differences between the effects of the *ortho* substituent adjacent to the cation and those of *meta* substituents. The chemical shifts of the C_α adamantyl carbons are displaced up to *ca.* 25 ppm downfield (as compared to the precursor alcohols), which indicates the extensive hyperconjugative contribution required of the bridgehead centers whereas, with the exception of the *ipso* carbon, the aromatic carbons remain relatively unaffected in comparison to neutral compounds. Similar bridgehead stabilization is observed in compounds in which phenyl participation is absent, such as the alkyl-substituted series **6a** and **6b**

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[1] (a) Stable Carbocations 295. For part 294 see Prakash, G. K. S.; Rasul, G.; Yudin, A. K.; Bausch, J.; Olah, G. A. *Gaz. Chim. Ital.*, in press. (b) Olah, G. A.; Porter, R. D.; Jeuell, C. L.; White, A. M. *J. Am. Chem. Soc.* **1972**, *94*, 2044.

[2] C–O rotation "freezes" in the NMR time scale below −25 °C giving rise to non-equivalent *ortho* protons.

[3] Olah, G. A.; Prakash, G. K. S.; Liang, G.; Schleyer, P. v. R.; Graham, W. D. *J. Org. Chem.* **1982**, *47*, 1040.

[4] Olah, G. A.; Heagy, M. D.; Prakash, G. K. S. *J. Org. Chem.* **1993**, *58*, 4851.

[5] (a) Lomas, J. S.; Bru-Capdeville, V. *J. Chem. Soc. Perkin Trans. 2* **1994**, 459. (b) Lomas, J. S.; Luong, P. K.; Dubois, J. E. *Tetrahedron* **1981**, *37*, 2273. (c) Lomas, J. S.; Dubois, J. E. *J. Org. Chem.* **1976**, *41*, 3033.

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Table 1. ^{13}C NMR Chemical Shifts of *Ortho*- and *Meta*-Substituted Di-1-adamantylbenzyl Cations 5a–c in FSO_3H-SO_2ClF at −80 °C[a]

ion	C^+	α	β	γ	δ	aromatic[b]	Z
5a	300.7	68.9	40.1	27.9	33.7	138.7 (s, C_i)*, 132.9 (d), 134.4 (s, C_o)*, 131.2 (d), 122.1 (d), 124.2 (d)	CH_3, 23.6
5b	289.1	67.6	40.1	28.2	34.3	138.0 (s, C_i)*, 127.6 (d), 124.5 (d), 138.4 (s, C_m)*, 121.6 (d), 133.8 (d)	CH_3 20.4
5c	288.0	66.9	39.5	27.7	33.7	137.4 (s, C_i), 121.1 (d), 129.7 (d), 150.3 (s, C_m), 121.5 (d), 126.9 (d)	C_q, 34.3; CH_3, 29.5
5d[c]	286.5	65.9	38.3	26.4	32.5	136.2 (s, C_i), 125.9 (d, C_o, $C_{o'}$), 122.8 (d, C_m, $C_{m'}$), 131.4 (d, C_p)	
6a[d]	327.1	68.1	39.9	27.9	34.6		CH_3, 39.9
6b[d]	323.3	67.2	39.9	29.3	34.7		CH_2, 41.9; CH_3, 11.0

[a] All chemical shifts are in ppm (±0.1) and are referenced to external acetone-d_6 capillary. [b] Multiplicity in parenthesis with assignment wherever possible. [c] Reference 4. [d] Reference 3. *Assignment interchangeable.

Table 2. ^{13}C NMR Chemical Shifts of *Ortho*- and *Meta*-Substituted Di-1-adamantylbenzyl Cations 5a–c in FSO_3H-SO_2ClF at 25 °C[a]

ion	β	γ	δ	aromatic	Z
5a	$\delta_A = 0.99$, $\delta_B = 0.89$ (q, $J_{AB} = 12.8$ Hz, 12H)	1.41 (s, 6H)	1.49 (s, 12H)	6.68 (t, $J = 7.5$ Hz, 1H), 6.58 (t, J = 7.5 Hz, 1H), 6.56 (d, J = 7.5 Hz, 1H), 6.06 (d, J = 7.5 Hz, 1H)	CH_3, 1.44 (s, 3H)
5b	$\delta_A = 0.98$, $\delta_B = 0.89$ (q, $J_{AB} = 12.6$ Hz, 12H)	1.41 (s, 6H)	1.46 (s, 12H)	6.62 (t, $J = 7.6$ Hz, 1H), 6.59 (t, J = 7.3 Hz, 1H), 6.12 (s, 1H), 6.08 (d, J = 7.4 Hz, 1H)	CH_3, 1.44 (s, 3H)
5c	$\delta_A = 0.99$, $\delta_B = 0.88$ (q, $J_{AB} = 12.5$ Hz, 12H)	1.41 (s, 6H)	1.46 (s, 12H)	6.85 (t, $J = 8.2$ Hz, 1H), 6.67 (t, J = 7.9 Hz, 1H), 6.31 (s, 1H), 6.12 (d, J = 7.9 Hz, 1H)	CH_3, 0.5 (s, 9H)

[a] All chemical shifts are in ppm (±0.1) and are referenced to the external acetone-d_6 capillary.

(methyl and ethyl derivatives).[6] This similarity suggests that in the presently studied highly deshielded benzylic systems there is complete loss of resonance interaction with the neighboring aryl group.

Cations **5a**, **5b**, and **5c** could also be generated in trifluoromethanesulfonic acid, and their 500 MHz ^{1}H NMR spectra were readily obtained at room temperature. The ^{1}H NMR shifts of the aromatic hydrogens of all three ions (Table 2) indicate very little positive charge dispersal into the ring (≤6.85 ppm).

Interestingly, ion **5a** was previously generated[6] in 10% trifluoroacetic acid (TFA) in $CDCl_3$ solution at room temperature giving a ^{13}C NMR spectrum nearly identical with that in FSO_3H-SO_2ClF. Apparently, despite the decrease of the intermediate $C_{ispo}-{}^+C$ bond length,[7] rehybridization results in a substantial reduction of the energy in all such systems, but particularly in the most strained *ortho*-substituted derivative, the corresponding *meta*- or *para*-substituted cations being formed incompletely under these relatively mildly acidic conditions (TFA/$CDCl_3$).[8] That the alcohol **4a** should be converted completely to carbocation **5a** under such mild conditions underlines the importance of ground state steric strain in this system; MM3-calculated steric energies of *anti*-**4a**, *syn*-**4a**, and **4b** are 84.6, 78.4 and 71.9 kcal mol^{-1}, respectively.[5a] Moreover, the ion, once formed, is stable because it is sterically inaccessible to quenching by the trifluoroacetate anion. Nevertheless, it reacts slowly with water to give the protonated *syn* alcohol rotamer in equilibrium with the cation, and with silanes to give the corresponding hydrocarbon.[6]

Conclusion

To our knowledge, the *o*-tolyldi-1-adamantylmethyl cation shows the most deshielded carbocationic center for a tertiary benzylic cation in solution. The severe steric constraints about the cationic center virtually exclude p−π resonance overlap with the adjacent empty p-orbital. Significant hyperconjugative contribution from the two adamantyl groups compensates for the lack of resonance stabilization.

Experimental Section

The precursor alcohols *m*-tolyl -, and *o*-tolyl-, and *m*-*tert*-butylphenyldi-1-adamantylmethanols were synthesized according to procedures established by Lomas *et al.* [5a] ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 500 MHz NMR or Varian VXR-300 equipped with a variable-temperature probe. The ^{1}H and ^{13}C NMR chemical shifts for the carbocations were referenced with respect to external acetone-d_6 capillary. Multiplicities in the ^{13}C NMR were determined by obtaining proton-coupled spectra.

Preparation of Carbocations. FSO_3H was freshly distilled before use. A 1:1 mixture of FSO_3H and SO_2ClF was added to a suspension of the precursor alcohols in SO_2ClF contained in 5-mm NMR tubes at −78 °C in a dry ice/acetone bath. Efficient mixing of the solution was effected using a vortex stirrer. Ionizations in trifluoromethanesulfonic acid were similarly carried out at −18 °C (ice/salt mixture).

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[6] Lomas J. S.; Anderson, J. E.; *J. Org. Chem.* **1995**, *60*, 3246.

[7] Olah, G. A.; Prakash, G. K. S.; Krishnamurti, R. *J. Am. Chem. Soc.* **1990**, *112*, 6422.

[8] Lomas, J. S. Unpublished results.