^{13}C NMR spectroscopic comparison of sterically stabilized *meta*- and *para*-substituted *o*-tolyldi(adamant-1-yl)methyl cations with conjugatively stabilized benzyl cations

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A series of *meta*- and *para*-substituted *anti-o*-tolyldi(adamant-1-yl)methyl cations has been generated by reaction of *anti-o*-tolyldi(adamant-1-yl)methanols with trifluoroacetic acid in chloroform. ^{13}C NMR spectroscopy indicates small but significant variations in the chemical shifts of the charged carbon and its nearest neighbours on the adamantyl groups, and departures from additivity of substituent effects on the shifts of the aromatic carbons. Previous work on the closely related di(adamant-1-yl)benzyl cations is discussed. Comparison with data on aryl-substituted carbocations in superacid media reveals marked differences in the aromatic carbon shifts in the two types of carbocation. The dihedral angle between aryl and carbocation planes in aryldi(adamant-1-yl)methyl cations is estimated to be about 60°.

In the 1970s and the early 1980s there was much debate concerning the application of the Gassman–Fentiman tool of increasing electron demand (TIED)[1] to the question of non-classical carbonium ions. This technique involves systematic variation of the substituent on an aryl ring at the developing or fully developed carbocation centre, the idea being to detect the onset of electronic interactions other than stabilization by the aryl group. This was usually revealed by a deviation from a linear relationship with a reference system when highly electron-withdrawing substituents were introduced.[2] Controversy arose, however, as to the interpretation of these deviations, which were variously attributed to π, $\pi\sigma$, *n* or σ delocalization or participation, depending not only on the system but also on the viewpoint of the author.[3–7]

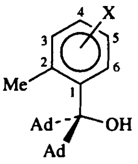
The approach was applied both to solvolysis studies (transition states)[8] and to the ^{13}C NMR study of stable carbocations (intermediates).[3–6] In the latter, attention was focused on the chemical shift of the charged carbon, which lies for most aryl-substituted carbocations between about 210 and 290 ppm. For many simple systems, where all 'extraordinary' electronic interactions can be ruled out, there are good linear correlations (with slopes close to unity) between the chemical shifts for variously substituted compounds, frequently ranging from 4-methoxy to 3,5-di(trifluoromethyl), and those of the 1-aryl-1-cyclopentyl cations with the same substituents. Following work by Kelly and Spear,[9] who proposed 'super sigma constants' to accommodate the much stronger resonance interactions between *para* substituents and the cationic carbon centre, Brown *et al.*[10] devised a set of σ^{C+} NMR substituent constants, based on *tert*-cumyl cations, which take into account the increased electron demand of carbocations in superacids. Good correlations of C$^+$ chemical shifts against these constants are found for many systems. He also proposed a further set of substituent constants, denoted $\sigma^{\alpha C+}$, again based on *tert*-cumyl cations, to express the effect of the charged carbon on the neighbouring aliphatic carbon shifts.[11]

NMR investigations of stable carbocations were previously performed exclusively in very strongly acid or superacid media, the latter generally at low temperature. Recently, we have found that *anti-o*-tolyldi(adamant-1-yl)methanol can be ionized in chloroform containing trifluoroacetic acid at room temperature to give relatively long-lived *o*-tolyldiadamantylmethyl cations.[12] In this paper results will be presented on *meta*- and *para*-substituted *o*-tolyldiadamantylmethyl cations and their ^{13}C NMR spectra compared with those of aryl-stabilized carbocations, in order to see how these non-coplanar cations differ from those in which the aryl group is in the plane of the charged centre and the charge is to a large extent delocalized over the aromatic system. Results on the analogous di(adamant-1-yl)benzyl cations will also be discussed.[13,14]

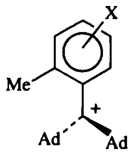
Results

Alcohol synthesis and identification

Substituted *anti-o*-tolyldi(adamant-1-yl)methanols, **1a–j**, were synthesized by reaction of the appropriate aryllithium compounds with di(adamant-1-yl)ketone and their structures established by ^{13}C and ^{1}H NMR spectroscopy (Table 1). In all cases one aromatic proton is very downfield of the others, its shift ranging from 7.8 to 8.1 ppm (except prehnityl, **1j**: 7.63 ppm). This is characteristic of H6 in the *anti* rotamers, that in the *syn* isomers being at 7.5 ppm or less.[15] The spectra of the parent compound, **1a**, having been completely assigned in previous work,[15] it is easy to check the aromatic part of the ^{13}C NMR spectrum by applying the substituent effect additivity rule.[16] The *ipso*, *ortho*, *meta* and *para* effects of the various substituents are taken directly from literature tabulations.[17,18] Summation of these effects with the CH and C$_q$ shifts for the parent compound gives values which correspond well with those found for the substituted *anti-o*-tolyldi(adamant-1-yl)methanols, the root mean square (rms) of the difference between calculated and experimental aromatic carbon shifts being in all cases less than 0.8 ppm.



1a–j



2a–j

a: X = H; **b**: 4-Me; **c**: 5-Me; **d**: 5-(Bu^t); **e** 4-Cl; **f**: 5-Cl; **g**: 4-F; **h**: 5-F **i**: 4-OMe; **j**: 3, 4, 5-Me$_3$

In some cases the aromatic CH attributions were confirmed by ^{13}C-^{1}H correlation experiments, the *ortho* proton (H6) being readily recognizable and, in the case of 5-substituted com-

Table 1 ^{13}C and ^{1}H chemical shifts (ppm) for 4- and 5-substituted *anti-o*-tolyldi(adamant-1-yl)methanols, **1a–j**, in CDCl$_3$ at 22 °C

Compound	**1a**	**1b**	**1c**	**1d**	**1e**	**1f**	**1g**	**1h**	**1i**	**1j**
Substituent	H	4-Me	5-Me	5-(Bu^t)	4-Cl	5-Cl	4-F[a]	5-F[b]	4-OMe	3,4,5-Me$_3$
^{13}C										
C1	144.2	141.1	143.7	143.5	142.7	146.4	139.7	147.1	136.7	141.6[c]
C2	135.5	135.1[d]	132.3	132.3	137.4	134.0	137.7	131.0	136.3	135.7[c]
C3	133.0	133.8	133.0	132.5	133.1	134.1	118.8	134.0	118.2	132.5[c]
C4	126.0	135.2[d]	126.6	122.4	131.4	125.8	160.7	112.4	157.0	132.2[c]
C5	124.9	125.7	133.8	147.0	124.8	131.3	111.3	161.0	109.4	131.8[c]
C6	131.1	131.1	131.7	128.7	132.2	131.2	133.3	117.1	132.5	129.6
rms (C$_{Ar}$)	—	0.1	0.2	0.2	0.5	0.5	0.7	0.9	0.5	—
C$_q$-OH	87.3	87.2	87.2	87.5	87.2	87.2	87.2	87.1	87.1	87.5
Ad C$_q$	45.6	45.5	45.5	45.4	45.5	45.6	45.6	45.6	45.5	46.0
Ad α-CH$_2$	39.4	39.4	39.4	39.3	39.3	39.3	39.4	39.4	39.4	39.8
Ad β-CH	29.4	29.4	29.4	29.4	29.3	29.3	29.4	29.4	29.4	29.6
Ad γ-CH$_2$	37.0	36.9	36.9	36.9	36.8	36.8	36.9	36.9	36.9	37.0
2-Me	29.5	29.3	29.2	29.2	29.2	28.9	29.4	28.6	29.5	25.1
Substituent	—	20.4	21.6	31.4, 34.4	—	—	—	—	54.9	16.2, 17.2, 21.6
^{1}H										
H3	7.13	6.95[e]	7.03[h]	7.04[k]	7.12[n]	7.06[q]	6.83[t]	7.07[w]	6.67[z]	—
H4	7.13	—	6.97[i]	7.13[l]	—	7.07[r]	—	6.81[x]	—	—
H5	7.13	6.97[f]	—	—	7.09[o]	—	6.83[u]	—	6.70[aa]	—
H6	8.03	7.89[g]	7.84[j]	8.10[m]	7.98[p]	8.06[s]	8.01[v]	7.81[y]	7.93[bb]	7.63
Ad γ-CH$_2$	1.61	1.62	1.63	1.61	1.61	1.61	1.62	1.62	1.62	1.62
Ad	1.75–2.1	1.8–2.1	1.8–2.1	1.75–2.1	1.75–2.1	1.7–2.1	1.7–2.1	1.7–2.1	1.8–2.1	1.8–2.1
2-Me	2.75	2.69	2.69	2.68	2.70	2.69	2.71	2.68	2.69	2.48
Substituent	—	2.29	2.33	1.31	—	—	—	—	3.80	2.22, 2.22, 2.30

[a] Aromatic carbon J_{C-F} in order: 3.4, 6.6, 20.3, 245.3, 18.8, 7.4 Hz. [b] Aromatic carbon J_{C-F} in order: 5.6, 3.1, 7.2, 20.7, 240.0, 24.6 Hz. [c] Interchangeable. [d] Interchangeable. [e] 1.6 Hz (benzene). [f] 1.6 and 8.5 Hz (benzene). [g] 8.5 Hz (benzene). [h] 7.6 Hz. [i] 1.3 and 7.6 Hz. [j] 1.3 Hz. [k] 7.8 Hz. [l] 2.0 and 7.8 Hz. [m] 2.0 Hz. [n] 2.5 Hz (benzene). [o] 2.5 and 9.1 Hz (benzene). [p] 9.1 Hz (benzene). [q] 7.0 Hz. [r] 2.0 and 7.0 Hz. [s] 2.0 Hz. [t] 2.9 and 9.9 Hz (benzene). [u] 2.9, 7.4 and 9.3 Hz (benzene). [v] 6.7 and 9.3 Hz (benzene). [w] 6.9 and 8.3 Hz. [x] 2.9, 6.9 and 8.3 Hz. [y] 2.9 and 14.6 Hz. [z] 0.7 and 3.1 Hz. [aa] 3.1 and 8.6 Hz. [bb] 0.7 and 8.6 Hz.

Table 2 ^{13}C and ^{1}H chemical shifts (ppm) for 4- and 5-substituted *o*-tolyldi(adamant-1-yl)methyl cations, **2a–j**, in CDCl$_3$/TFA at 22 °C

Compound	**2a**	**2b**	**2c**	**2d**	**2e**	**2f**	**2g**	**2h**	**2i**	**2j**
Substituent	H	4-Me	5-Me	5-(Bu^t)	4-Cl	5-Cl	4-F[a]	5-F[b]	4-OMe	3,4,5-Me$_3$
^{13}C										
C1	139.6	137.2	139.7	139.4	137.3	139.9	135.1	139.5	133.0	138.3[c]
C2	134.1	135.1	131.2	131.6	136.6	132.5	138.8	129.5	140.5	132.6[c]
C3	132.1	132.6	132.1	132.0	132.2	133.3	119.3	134.5	117.2	138.4[c]
C4	133.9	146.3	134.9	131.3	140.7	133.8	165.5	120.5	165.7	144.2[c]
C5	125.2	125.6	135.6	148.6	125.8	132.3	113.4	159.7	110.8	134.3[c]
C6	122.1	122.9	121.8	118.6	124.2	121.7	125.9	110.0	127.4	120.5
rms (C$_{Ar}$)	—	1.1	0.5	0.6	0.7	0.9	2.1	0.9	2.9	—
C$^+$	303.2	300.2	303.2	302.3	299.8	300.9	298.8	301.0	290.7	301.9
Ad C$_q$	70.4	69.6	70.1	69.8	70.8	71.4	70.0	71.4	68.1	69.2
Ad α-CH$_2$	41.6	41.4	41.5	41.5	41.6	41.8	41.6	41.8	41.4	41.8
Ad β-CH	28.5	28.5	28.4	28.4	28.5	28.5	28.5	28.5	28.5	28.5
Ad γ-CH$_2$	34.7	34.7	34.7	34.7	34.6	34.6	34.6	34.6	34.8	34.8
2-Me	24.6	24.5	24.0	24.0	24.2	23.7	24.5	23.4	25.2	24.4
Substituent	—	21.3	20.8	30.8, 35.0	—	—	—	—	56.0	15.3, 16.7, 20.9
^{1}H										
H3	7.48	7.29	7.35[e]	7.41[h]	7.49	7.42[l]	7.20[o]	7.45[r]	6.98[u]	—
H4	7.62	—	7.42[f]	7.65[i]	—	7.57[m]	—	7.30[s]	—	—
H5	7.48	7.27	—	—	7.47	—	7.20[p]	—	6.98[u]	—
H6	6.88	6.78[d]	6.61[g]	6.74[j]	6.89[k]	6.86[n]	6.96[q]	6.64[t]	6.95[u]	6.45
Ad γ-CH$_2$	1.6–2.0	1.6–2.0	1.6–2.0	1.6–2.0	1.6–2.1	1.6–2.0	1.6–2.0	1.6–2.0	1.6–2.0	1.65–1.95
Ad	2.31	2.28	2.30	2.29	2.31	2.29	2.29	2.26	2.25	2.27
2-Me	2.31	2.28	2.26	2.29	2.31	2.29	2.32	2.32	2.31	2.36
Substituent	—	2.45	2.43	1.34	—	—	—	—	3.95	2.15, 2.27, 2.33

[a] Aromatic carbon J_{C-F} in order: 3.3, 9.6, 21.9, 255.3, 22.9, 9.8. [b] Aromatic carbon J_{C-F} in order: 6.5, 3.8, 8.2, 25.9, 253, 25.8 Hz. [c] Tentative assignments. [d] 8.5 Hz. [e] 8.1 Hz. [f] <1 and 8.1 Hz. [g] <1 Hz. [h] 8.3 Hz. [i] 1.9 and 8.3 Hz. [j] 1.9 Hz. [k] 8.4 Hz. [l] 8.4 Hz. [m] 2.0 and 8.4 Hz. [n] 2.0 Hz. [o] 3.1 and 9.5 Hz. [p] 3.1, 7.1 and 9.4 Hz. [q] 5.1 and 9.4 Hz. [r] 5.2 and 8.6 Hz. [s] 2.5, 7.7 and 8.6 Hz. [t] 2.5 and 8.3 Hz. [u] Interchangeable.

pounds, it being easy to distinguish the *para* proton (H4) by its larger coupling constant with this proton. For 4-substituted compounds the proton between the two substitutents to the benzene ring appears as a singlet or a doublet with a small coupling constant to H5, while H5 and H6 are strongly coupled. Not unexpectedly, for the highly congested prehnityl (2,3,4,5-tetramethylphenyl) derivative, **1j**, substituent effects are clearly not additive, and we were unable to attribute the aromatic C$_q$ carbon signals. Nevertheless, the aromatic CH signal is very close to its predicted value. The carbons of the methyl groups could not be assigned either, but we assume that the one whose shift is closest to the normal value for the *ortho*-methyl in the other derivatives corresponds also to *ortho*-methyl in the prehnityl derivative.

o-Tolyldi(adamant-1-yl)benzyl cations, 2a–j

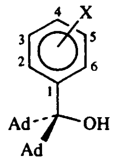
Reaction of the alcohols in deuteriated chloroform (containing trifluoroacetic anhydride) and approx. 10% v/v trifluoroacetic acid at room temperature gave an immediate deep red colouration in all cases, except for the 5-chloro and 5-fluoro derivatives which required about 15 min for complete conversion.

The ^{1}H NMR spectra (Table 2) show that the downfield (higher δ) *ortho* proton signal of the alcohol is replaced by an upfield (lower δ) signal, generally more upfield than the other aromatic protons. The *ortho*-methyl group also shifts about 0.4 ppm upfield. The ^{13}C spectra (Table 2) show with one exception, **2i** (X = 4-OMe), a signal for the positively charged carbon at 300–303 ppm. As previously noted,[12] the quaternary adamantyl carbons are shifted downfield from about 46 ppm in the alcohols to some 70 ppm in the cations, while the *ortho*-methyl group moves about 5 ppm upfield. Overall changes in the chemical shifts of the aromatic carbons are not very great, with the sum of the shifts for the alcohols slightly greater (except **2i** and **2j**) than for the cations; individual variations of carbon shifts will be discussed below.

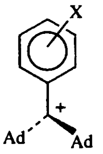
Discussion

In previous work it has been shown that the major product of the addition of *o*-tolyllithium to a highly congested ketone, such as 2,2,4,4-tetramethylpentan-3-one or di(adamant-1-yl)ketone, is the less stable *o*-tolyldi(*tert*-alkyl)methanol, the *anti* rotamer.[20] This is readily distinguished from the substantially more stable *syn* isomer by spectroscopic and chromatographic methods, these latter also providing an efficient means for the separation of the two isomers. More recently, it has been possible to separate and characterize *anti*- and *syn*-*m*-tolyl and *m*-(*tert*-butyl)phenyl derivatives obtained by the reaction of the appropriate organolithium reagents with di(adamant-1-yl)ketone.[15]

Aryldi(adamant-1-yl)methanols, **3a–g**, ionize in superacids to the corresponding benzylic cations, which have been investigated by Olah's group.[13,14] Substituted (*para* or *meta*) phenyldiadamantylbenzyl cations, **4a–g**, have very high ^{13}C NMR shifts for the charged carbon, ranging from 283 to 289 ppm, showing little dependence on substituent effects. Olah concludes that the bulk of the adamantyl substituents is such that p–π conjugation is minimized in these systems. The large downfield shift of the quaternary adamantyl carbons is an indication of extensive compensatory hyperconjugative interactions.



3a–g



4a–g

a: X = 4-OMe; **b**: 4-Me; **c**: 4-F; **d**: H
e: 4-CF$_3$; **f**: 3-Me; **g**: 3-(Bu^t)

We subsequently found that *anti*-*o*-tolyldi(adamant-1-yl)methanol, **1a**, could be ionized in chloroform containing 10% of TFA at room temperature, to give a relatively stable carbocation, **2a** with a C$^+$ shift of 303 ppm[12] (301 ppm in FSO$_3$H–SO$_2$ClF at −80 °C).[13] Its ready formation is due to the particularly high steric energy of the precursor alcohol, and its stability to steric hindrance to attack by nucleophiles and the reluctance of the adamantyl group to undergo rearrangement. The present work has extended this initial finding to several *meta*- or *para*-substituted derivatives of the parent compound.

We should consider the very remote possibility that in CDCl$_3$–TFA a carbocation is in rapid equilibrium with the corresponding trifluoroacetate and that, consequently, the observed NMR shift of the carbocationic carbon, for example, is the weighted mean of the true cation value and that of the tertiary carbon in the trifluoroacetate. However, in the case of **2a** the C$^+$ shift is **higher** in TFA than in superacid, while for the strongly electron-donating substituent, 4-OMe, it is **smaller** than for all other substituents. If there were an equilibrium, the cation would be favoured in **2i** and the weighted mean would tend to be high, not low. Furthermore, there is no evidence for trifluoroacetates except in very inert, bridgehead systems. In the present case, the trifluoroacetate would be a particularly strained species and, therefore, its equilibrium with a stabilized (by adamantyl hyperconjugation and aryl conjugation) carbocation is highly improbable. In previous work[12] evidence was found for a slow equilibrium between protonated *syn* alcohol and the carbocation, but this did not affect the carbocation NMR spectra.

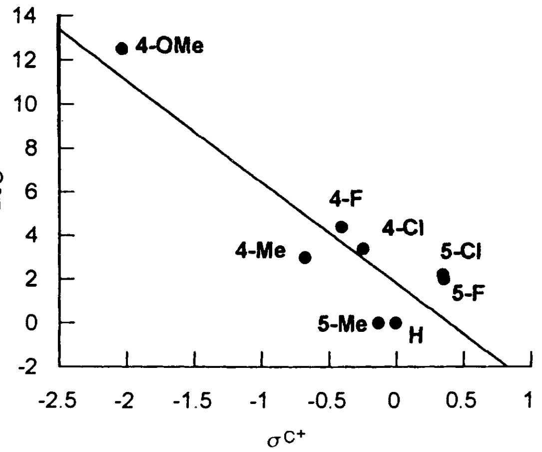


Fig. 1 Correlation of C$^+$ chemical shift difference, $\Delta\delta C^+ = \delta C^+_H - \delta C^+_X$, for cations **2** with σ^{C+} substituent constants

4- and 5-Substituted o-tolyldiadamantylmethyl cations, 2a–j

(i) Aliphatic carbons. It is convenient to consider first the ^{13}C NMR spectra (Table 2) of the non-aromatic part of the cation, including the charged carbon, and then the aryl system. The most surprising result is that, whereas the C$^+$ shift for all the other derivatives lies in the 300–303 ppm range, for the methoxy derivative it is 291 ppm. This leads to a virtually two-point correlation (Fig. 1) with Brown's σ^{C+} substituent constants,[10] with a ρ-value of -4.6 ± 1.0 (in the form of $\Delta\delta C^+ + \delta C^+_H - \delta C^+_X$; 8 points, not **2d** and **2j**; $r = 0.884$), as compared to values for classical cations ranging from about −14 to −18. This is in marked contrast to results[13] on 4-substituted phenyl(adamant-1-yl)methyl cations, **4a–e**, where the correlation is better ($r = 0.961$) but the ρ-value is very small, -1.5 ± 0.3, with the C$^+$ shift for the 4-OMe derivative, **4a**, not more than 4 ppm lower than those for the other cations.

In the *o*-tolyldiadamantylmethyl cations the average value for the adamantyl quaternary carbons is 70.1 ± 0.6 ppm (not 4-OMe, **2i**, nor 5-halo, **2f** and **2h**) while those for **2i**, **2f** and **2h** are 68.1, 71.4 and 71.4 ppm, respectively. If the downfield shift of the adamantyl carbons is due to hyperconjugative interactions which compensate for the lack of resonance stabilization from the aryl group, then this lack is apparently slightly less marked for **2i** and more marked for **2f** and **2h**. In fact, when the adamantyl C$_q$ shifts (in the form of $\Delta\delta C'' = \delta C''_H - \delta C''_X$; 8 points, not **2d** and **2j**) are plotted against Brown's σ''^{C+} constants[11] a fair linear correlation ($r = 0.983$) with a slope of −2.1 is obtained (Fig. 2).

Since the ρ-values in the original work range from −3.6 to −5.9, the value of −2.1 would appear to indicate significant stabilization by the aryl group, despite the relative insensitivity

Table 3 Differences between chemical shifts of aromatic carbons in 4- and 5-substituent *o*-tolyldiadamantylmethanols, **1**, and the corresponding phenyldiadamantylmethyl ions, **2**

Substituent	H	4-Me	5-Me	5-(Bu^t)	4-Cl	5-Cl	4-F	5-F	4-OMe	3,4,5-Me$_3$
C1	4.6	3.9	4.0	4.1	5.4	6.5	4.6	7.6	3.3	
C2	1.4	0.1	1.1	0.7	0.8	1.5	−1.1	−1.5	−3.8	
C3	0.9	1.2	0.9	0.5	0.9	0.8	−0.5	−0.5	0.9	
C4	−7.9	−11.2	−8.3	−8.9	−9.3	−8.0	−4.8	−8.1	−8.7	
C5	−0.3	0.1	−1.8	−1.6	−1.0	−1.0	−2.1	1.3	−1.4	
C6	9.0	8.2	9.9	10.1	8.0	9.5	7.4	7.1	5.1	9.1
Total	7.7	2.3	5.8	4.9	4.8	9.3	3.5	8.9	−4.6	−4.9

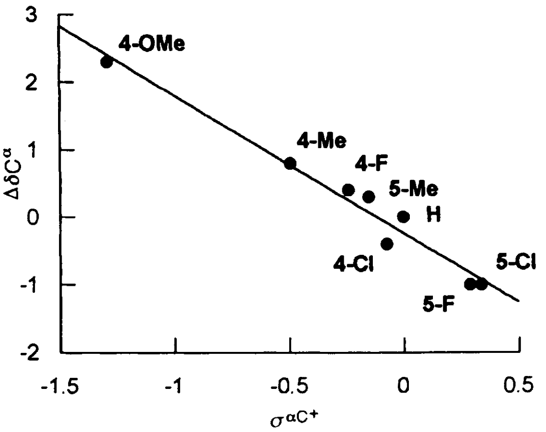


Fig. 2 Correlation of adamantyl C_q chemical shift difference, $\Delta\delta C^{\alpha} = \delta C^{\alpha}_{H} - \delta C^{\alpha}_{X}$, for cations **2** with $\sigma^{\alpha C^+}$ substituent constants

of the C$^+$ shift to all substituents except 4-OMe. In contrast, in the 3- and 4-substituted diadamantylbenzyl cations, **4a–g**, in superacid media[13,14] the chemical shifts of all the adamantyl carbons, not only the quaternary carbons, show random variations with the substituent, no trend of any sort being detectable and the parent compound giving the smallest shift values for all adamantyl carbons. We have no explanation for this difference in behaviour.

Electron-attracting *meta* substituents are included in both of the above correlations, though the fact that they operate inductively implies that their effects should be expressed by a normal 'reaction constant', while that for the electron-donating substituent(s) should be modulated, as in a Yukawa–Tsuno-type equation.[21] The available data, however, do not allow such a detailed analysis.

The two correlations with Brown's carbocation substituent constants suggest that in the *o*-tolyldiadamantylmethyl cations resonance stabilization by electron-donating substituents or relative destabilization by electron-attractors is not negligible, though attenuated compared to the situation in classical aryl-stabilized cations. That electron-attractors in the *meta* position, absent from the previous studies,[13,14] increase the demand upon the aliphatic carbons is not so surprising, since their effect is essentially inductive. Nevertheless, it is paradoxical that substituent effects are more easily detectable in the *ortho*-methyl-substituted cations, **2a–j**, than for the 3- and 4-substituted cations, **4a–g**. One would intuitively expect the presence of the 2-Me group to increase the dihedral angle between the aryl system and the plane of the di(adamant-1-yl)methyl cation and, thus, to quench conjugative effects further. A possibility is that the change of medium, from FSO_3H–SO_2ClF at −78 °C in Olah's work to $CDCl_3$–TFA at 22 °C in ours, has a critical effect on substituent effects. However, the *ortho*-tolyl cation has been studied both in $CDCl_3$–TFA[12] and FSO_3H–SO_2ClF,[14] and comparison of the two sets of shifts shows that the values in the two solvents run closely parallel. If there are no inversions in the sequence of values on going from one solvent to the other, then the difference for a given aromatic carbon is never greater than 1 ppm. Similar differences are seen for all the other atoms, with the shifts systematically 1–2 ppm lower in the superacid than in $CDCl_3$–TFA. This would appear to indicate that the change of solvent and temperature has no great effect upon the cation spectrum.

The 2-Me shift is 24.3 ± 0,3 ppm in all the cations except **2i**, **2f** and **2h** for which it is 25.2, 23.7 and 23.4 ppm, respectively. However, since very similar differences are seen in the precursor alcohols, this observation is irrelevant to the central problem of possible substituent effects on the cations.

(ii) Attribution of aromatic carbons. In previous work[12,14] the aromatic carbons of the parent cation, **2a**, were not attributed. There are two ways of tackling this problem. One is to assume that substituent effects are additive[16] and seek the appropriate pattern of shifts for the parent ion (the *o*-tolyldiadamantylmethyl cation), the 4- and 5-methyl and the 5-(*tert*-butyl) derivatives, **2a–d**. Since these substituents have very small effects on the *meta* position, the C_q which changes the least in the 5-substituted derivatives is clearly that which bears the Ad_2C^+ group (139.6 ppm in the parent). The CH in the 3 position is identified in the same way (132.1 ppm). The shift of the CH in the 6 position should be little changed by the 4-Me group, raised by the 5-Me and depressed by the 5-Bu^t, which suggests it is that at 122.1 ppm. This is readily confirmed by ^{13}C-^{1}H correlation, since the proton *ortho* to the charged substituent has a characteristic upfield shift. Reasoning along these lines gave complete assignments for the four above-mentioned ions.

A second method, which is limited to the CH carbons and can be used only for the *meta*-substituted compounds (except the fluoro derivative), is to identify the proton signals by simple inspection of the ^{1}H NMR spectrum, bearing in mind that the coupling constants for *ortho* and *meta* proton pairs are about 8 and 1–2 Hz, respectively. A correlation experiment then identifies the corresponding carbon signals.

These two methods gave self-consistent results, making it possible to assign the aromatic carbon signals in our entire series of carbocations, except the prehnityl derivative, **2j**. In this case the experimental C_q shift values could not be matched with the predictions, though the C6 value was close to that expected. For most of the cations in the present study substituent effects are accurately additive [rms = 0.5 (5-Me) − 1.1 (4-Me) ppm] except for **2i** (4-OMe, rms = 2.9 ppm) and **2g** (4-F, rms = 2.1 ppm) for which the major discrepancies lie in the prediction of the C2 and C6 shifts, both being higher than expected; for **2g** the C4 shift, on the other hand, is overestimated.

(iii) Effects of ionization on shifts of aromatic carbons. Comparison of the cations, **2a–j**, with the corresponding alcohols, **1a–j**, reveals a certain regularity in the effects of ionization on the chemical shifts of the aromatic carbons. Differences, C*n*(**1**) − C*n*(**2**), are listed in Table 3. Not unexpectedly, the values are small for the *meta* positions, whether substituted or not, and there is also little change for C2 which bears the methyl group. On the other hand, C1 and C6 show large, regular upfield shifts, both of which must be due to the change in hybridization of the carbon attached to C1 and the accompanying steric changes. The carbon in the *para* position, C4, which is the most reliable probe for electronic effects, shows a significant downfield shift, consistent with deshielding by removal of electron density from this atom. Overall, the shifts of the aromatic carbons are greater in the precursor alcohols than in the cations, being greatest for the electron-withdrawing 5-halo substituents, and only the 4-OMe and 3,4,5-Me$_3$ substituents are associated with negative totals. This is the opposite of what would be expected and what is found for aryl-stabilized cations (see below); the main reason is that the upfield shifts of C1 and C6 are greater than the modest downfield shift of C4, other contributions being of negligible importance.

3- and 4-Substituted diadamantylbenzyl cations, 4a–g

(i) Attribution of aromatic carbons in alcohols. In order to make a site-by-site comparison of the precursor alcohols, **3a–g**, and the corresponding carbocations, **4a–g**, it was necessary first to assign the aromatic carbon chemical shifts in the alcohols. Some complete assignments are given in previous work,[15] but not for the 4-OMe, 4-F and 4-CF$_3$ derivatives, **3a**, **3c** and **3e**, respectively. Moreover, for the 4-CF$_3$ derivative the reported ^{13}C NMR spectrum[13] was incompatible with the structure. This material was therefore reexamined. The assignments of the aromatic carbon signals (Table 4) are based on the assumption that substituent effects are additive; rms values are never greater than 1.0 ppm.

(ii) Attribution of aromatic carbons in cations. It is not clear how some of the aromatic carbons in 4-substituted di(adamant-1-yl)benzyl cations, **4a–e**,[13] were assigned, and certain of the shift values appear incompatible with those for the *ortho*-tolyl cations. Moreover, in the most recent study[14] on the 3-substituted cations, **4f–g**, we neglected to assign the CH carbons. This problem can be resolved, as for the substituted *ortho*-tolyl cations, by assuming approximate substituent effect additivity; we chose the parent cation, **4d**, the two methyl-substituted derivatives, **4b** and **4f**, and the 3-(*tert*-butyl)-substituted cation, **4g**, as a basis. In the parent cation only the quaternary carbon at 136.2 ppm and the *para* CH carbon at 131.4 ppm can be assigned with confidence. If now we examine the *tert*-butyl derivative, **4g**, we note that the quaternary carbon signals are at 137.4 and 150.3 ppm. Given that *meta* substituent effects are small and that *tert*-butyl has a large *ipso* effect, we attribute these signals to C1 and C3, respectively. Now, subtracting the *ipso* effect (22.4 ppm) from 150.3 ppm we obtain a value of 129.4 ppm, which should be close to the value for C3/C5 in the parent compound, **4d**, and a little greater than that for C5 in the *tert*-butyl derivative. Applying the *ortho* effect of a *tert*-butyl to the value for C4 in the parent ion, we get a value of 128.1 ppm for C4 in **4g**. This reasoning leads us to associate the signals at 126.9 and 129.7 ppm with C5 and C4, respectively, leaving those at 121.1 and 121.5 ppm for C2 and C6, probably in this order. We therefore conclude that the lower values (122.8 ppm) in the parent ion correspond to the *ortho* CH groups and the higher (125.9 ppm) to the *meta* CH, in contradiction with the published assignments.[13] This conclusion is in better agreement with the fact that C6 in **2a** shows a similar upfield shift.

Table 4 Substituent effects on aryl carbon shifts (ppm) in 4-substituted phenyldi(adamant-1-yl)methanols, **3a–e**. (Data from ref. 13, except **3e**)

Compound	**3a**	**3b**	**3c**	**3d**	**3e**
Substituent	4-OMe	4-Me	4-F	H	4-CF$_3$^{a}
C1	137.4	140.8	139.3	144.1	148.1
C2	130.3	128.2	130.7	128.4	128.5
C3	111.8	126.3	111.6	125.3	122.2^b
C4	158.7	135.0	161.2	125.7	127.9^c
C5	112.5	127.9	114.4	127.3	124.2^b
C6	129.9	127.7	128.5	127.9	128.4
rms	1.0	0.2	0.6	—	0.3

^{a} CF$_3$ 124.5 ppm, J_{C-F} 272 Hz. ^{b} J_{C-F} 3.8 Hz. ^{c} J_{C-F} 32.0 Hz.

Now that the parent ion is assigned, it is easy to calculate values for the various sites in the methyl-substituted cations and to match them with the experimental data (Table 5). For the 3-methyl ion, **4f**, this works fairly well (rms = 2.0 ppm) but for the 4-methyl derivative, **4b**, it is necessary to reverse the C$_q$ assignment given by Olah, and even then the fit is noticeably poorer (rms = 2.7 ppm), with the shifts of the C4 and C2/C6 carbons somewhat underestimated. The assignments for the fluorine-containing cations, **4c** and **4e**, are supported by the C–F coupling constants, and that for **4a** appears reasonable in view of the OMe substituent effects. Nevertheless, the shifts for the aromatic carbons in these cations are not generally in good agreement with additivity calculations. While shifts are fairly well predicted for **4e** (4-CF$_3$, rms = 1.7 ppm), for **4c** and **4a** the fit is poor, with rms values of 2.7 and 5.3 ppm, respectively. In **4c** the greatest error lies in the C2/C6 shifts which are underestimated, while for **4a** both C1 and C2/C6 are underestimated and C4 severely overestimated.

(iii) Effects of ionization on aromatic carbon shifts. Differences between the chemical shifts of the aromatic carbons in the alcohols and the derived cations are listed in Table 6. It should be noted that the *ortho* and *meta* carbons are distinguished in the alcohols **3a–e** but not in the corresponding cations; the changes for C2 and C6 and for C3 and C5 should therefore be averaged. In the same way, for alcohols **3f–g** the shifts in the *syn* and *anti* isomers are different; we have taken average values of equivalent carbons. The results are somewhat less regular than for the *o*-tolyldiadamantylmethyl cations. Ionization generally results in modest upfield shifts for the *ipso* and *ortho* carbons, little change for the *meta* carbons and downfield shifts for the *para* carbon. The 4-methoxy derivative behaves anomalously, there being very little change at any aromatic carbon.

Aryl-stabilized benzyl cations

(i) The average phenyl group. Inspection of the large body of data on aryl-stabilized benzyl cations produced by the laboratories of Brown, Olah and their co-workers[3] reveals that, despite variations in the experiment temperature and the nature of the superacid mixture, for many cations the chemical shifts of the aromatic carbons are almost independent of the alicyclic or acylic alkyl system which includes the charged carbon, and depend only on the ring substituent. Standard values can be

Table 5 Aromatic carbon shifts (in ppm) for di(adamant-1-yl)benzyl cations, **4a–g** and **2a**, in FSO$_3$H–SO$_2$ClF at −80 °C (data for 2-Me derivative, **2a**, in TFA–CDCl$_3$ at 22 °C in parentheses)

Compound	**4a**	**4b**	**4c**	**4d**	**4e**	**4f**	**4g**	**2a**
Substituent	4-OMe	4-Me	4-F	H	4-CF$_3$	3-Me	3-(Bu^t)	2-Me
C1	135.8	134.7	132.9	136.2	140.7	138.4	137.4	138.7 (139.6)
C2	130.3	125.6	128.3	122.8	124.8	124.5	121.1	134.4 (134.1)
C3	112.9	127.7	115.1	125.9	123.9	138.0	150.3	131.2 (132.1)
C4	157.7	145.4	164.6	131.4	133.1	133.8	129.7	132.9 (133.9)
C5	112.9	127.7	115.1	125.9	123.9	127.6	126.9	124.2 (125.2)
C6	130.3	125.6	128.3	122.8	124.8	121.6	121.5	122.1 (122.1)
rms	5.3	2.7	2.7	—	1.7	2.0	1.7	2.4

Table 6 Differences between chemical shifts of aromatic carbons in 3- and 4-substituted phenyldiadamantylmethanols, **3a**–**g**, and the corresponding phenyldiadamantylmethyl ions, **4a**–**g**

Substituent	4-OMe	4-Me	4-F	H	4-CF_3	3-Me[a]	3-(Bu^t)[a]
C1	1.6	6.1	6.4	7.9	7.4	5.5	6.0
C2	0.0	2.6	2.4	5.6	3.7	4.4	4.4
C3	−1.1	−1.4	−3.5	−0.6	−1.7	−2.5	−1.5
C4	1.0	−10.4	−3.4	−5.7	−5.3	−7.4	−7.6
C5	−0.4	0.2	−0.7	1.4	0.3	−1.4	−0.9
C6	−0.4	2.1	0.2	5.1	3.6	3.7	3.8
Total	−0.4	−0.6	1.4	13.5	8.0	2.3	4.2

[a] For the alcohols, average values are taken for equivalent carbons in the *syn* and *anti* isomers.

established by considering the aryl-2-propyl (*tert*-cumyl),[10] 2-butyl,[22] 3-pentyl,[22] 4-heptyl,[22] cyclopentyl,[10] cyclohexyl,[19] cycloheptyl[19] and 2-adamantyl[22] cations, data for 8–9 substituents being available for these species. For 2-aryl-2-adamantyl cations, however, substituent effects on the *ipso* and *ortho* carbons were somewhat unusual, shifts being significantly smaller than for the other series; these data were not included in the means. A small number of apparently anomalous or uncertain (because of difficulties in assignment) data were also discarded. Average shifts for the phenyl group are 139.4 ± 0.9, 141.8 ± 0.9, 133.2 ± 0.3 and 155.5 ± 1.0 ppm for C1, C2/C6, C3/C5 and C4, respectively (Table S7). The result is displayed below in structure **5**. Considering the dialkyl cation as a substituent on benzene (base value 128.5 ppm), the substituent effect on the aromatic carbon shifts is seen to be uniformly positive, *i.e.* downfield, and that it is greatest at the *para* carbon, large at the *ipso* and *ortho* carbons, but relatively minor at the *meta* carbons, though much greater than for non-ionic substituents.†

(ii) Substituent effects. It is interesting now to consider how other substituents modify the response of the aromatic carbons to the charged centre. Any attempt to predict the chemical shifts, by taking individual or averaged parent ions as the starting point and applying the increments found in standard tables, is relatively unsuccessful: these ions do not obey the additivity principle (Table S8). The data in Tables S7 and S8 can be summarized as follows: (i) Mean values for the *para* carbon in 4-substituted compounds differ considerably from the calculated values. (ii) For *meta* substituents the behaviour of C3 is somewhat more normal, the mean shifts being close to expected values except for 3-F. (iii) Effects of both *meta* and *para* substituents on C1 are reasonably normal. (iv) In the same way, the effects of *para* substituents on the *meta* carbons, C3 and C5, are very homogeneous and in close agreement with the additivity principle. These data are valid for a much greater range of cations, including several which are believed to be affected by 'extraordinary' electronic effects, only the 7-aryl-7-norbornenyl cations[23] showing significant deviations from the norm. (v) Conversely, the effects of *para* substituents on the shifts of the *ortho* carbons, C2 and C6, are much less predictable, the greatest deviations being for the 4-OMe and 4-F substituents.

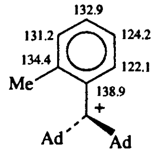
The conclusion of this brief survey is that the additivity rule breaks down, probably because of conjugative interactions between the cation and the substituent, particularly when this latter is in the *para* position, the effects of 4-OMe and 4-F being especially unpredictable, and that the aromatic carbon atoms most affected by these interactions are C4 and C2/C6.

We have not considered in detail the various systems which are believed to display deviations in the C^+ shift indicative of 'extraordinary' stabilization. Not infrequently the aromatic carbon shifts are somewhat smaller than normal, but the differences are generally barely significant and doubtless even more difficult to interpret than the C^+ shifts, which vary over much greater ranges. The 7-aryl-7-norbornyl system[23] is distinguished by having positive deviations for C4 and C2/C6 whereas the shifts for C1 are 6–7 ppm smaller than normal. The 2-norbornyl system,[5] on the other hand, shows small C1 shifts for all substituents, except 3- and 4-CF_3 and 3-Cl, slightly small values for C4, and normal values everywhere else. Whether this constitutes evidence for the involvement of an 'extraordinary' electronic interaction is a very moot point.

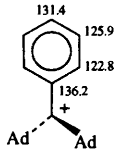
Without a theoretical model to explain in detail the various deviations from substituent effect additivity observed in aryl-stabilized cations, it is perhaps rather dangerous to assume that analogous deviations in diadamantylbenzyl cations are indicative of aryl stabilization. Nevertheless, certain similarities can be discerned, in particular the persistence of large errors at the C4 and C2/C6 atoms for the 4-OMe and 4-F derivatives, whether *ortho*-methyl-substituted or not. In general, the deviations from additivity are greater for the 'phenyl' than for the '*ortho*-tolyl' cations, which is what one would expect intuitively, but these data do not allow a quantitative estimate of the importance of resonance stabilization in the di(adamant-1-yl)-benzyl cations.

Comparison of stabilized cations with diadamantylbenzyl cations

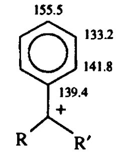
We can now compare the chemical shifts of three aryl-substituted carbocations: the average aryl-stabilized cation, **5**, the phenyldiadamantylmethyl cation, **4d**, and the *o*-tolyldiadamantylmethyl cation, **2a**. These are displayed below with the ^{13}C NMR shifts for the aromatic carbons.



2d



3a



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The obvious difference between the aryl-stabilized and the phenyl cations is that the chemical shifts are all greater in the former, and that the differences are the most pronounced at the positions most likely to be concerned with conjugative delocalization of the charge. The introduction of the *ortho*-methyl substituent modifies the C1 and C2 shifts somewhat more than would be expected, but this is no doubt attributable to steric effects. However, the most outstanding difference lies in the chemical shift of C2/C6 in the aryl-stabilized cation as compared with that for the 'phenyl' cations and C6 in the '*ortho*-tolyl' ions, which goes from 141.8 ppm in the first to 122.8 and 122.1 ppm in the latter.

Various attempts have been made to correlate substituent effects on ^{13}C NMR chemical shifts by means of Hammett-type substituent parameters, either singly or in duel parameter correlations (DSP).[24] For obvious reasons *ortho* substituents are excluded, and there is little interest in *meta* substituents, since the shift variations are so small. Two of the best correlations[25]

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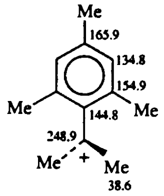
† Tables S7 and S8 summarizing literature data on substituent effects on aryl carbon shifts in aryl-stabilized benzyl cations are available as a Supplementary Publication [Supp. Pub. no. 57179 (3 pp.)]. For details of the deposition scheme, see 'Instructions for Authors (1996),' *J. Chem. Soc., Perkin Trans. 2*, 1996, issue 1.

can be used to extract successively Taft's constants, σ_{R° and σ_I, from the *meta* and *para* effects on the average aryl-stabilized cation, **5**, giving values of 0.89 and 1.73, respectively, both much higher than for conventional substituents. In the same way, for **4d** we obtained values of 0.20 and −0.37 for σ_{R° and σ_I, respectively. These results are in good agreement with another DSP relationship based on a modified substituent set.[26] That the inductive effect should become electron-donating is rather surprising, and is perhaps an artefact, while the fall in σ_{R° is consistent with a decrease in the importance of resonance stabilization, but not its total elimination.

The C4 shift as a probe for twisting

In recent work on twisted benzyl cations Timberlake and coworkers[27] studied the 2-mesityl-2-propyl cation, **6**, which according to *ab initio* calculations at the 3-21G level has a dihedral angle of 35°. The most revealing comparison is with the corresponding 2,4-dimethyl-[28] **7** and 4-methyl-*tert*-cumyl[10] **8** cations. It is quite clear that C4 serves as a probe of twisting and concomitant changes in charge distribution, falling from 175.2 to 172.0 and 165.9 ppm as methyl groups are introduced at the *ortho* positions. This should have little direct electronic effect on the C4 shift, but charge delocalization by the carbon *para* to the charge centre clearly falls. Since the ρ-value for correlation of the C^+ shifts of 4- and 5-substituted 2-methyl-*tert*-cumyl cations with σ^{C+} is virtually identical with that for *tert*-cumyl cations, Brown states that the 'cationic centre must be able to accommodate the difficulties in achieving coplanarity with only minor costs in energy.'[28] Nonetheless, it is noteworthy that in all the *ortho*-methyl-substituted cations the C4 shift is smaller than in the corresponding *tert*-cumyl cations.



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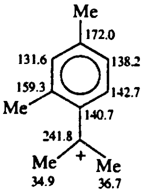

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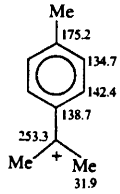

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The shifts of the methyl carbons at the carbonium centre also show a progressive change, going from 31.9 to 34.9/36.7 to 38.6 ppm as the ion is further twisted from coplanarity, thus compensating for the loss of resonance stabilization. The shifts of the charged carbon, on the other hand, show no correlation with twisting. The behaviour of the *meta* carbons, C3/C5, seems somewhat anomalous, and one is tempted to suggest that their attribution in the 2,4-dimethyl ion, **7**, should be reversed. The behaviour of C2/C6 is no doubt affected both by the introduction of the methyl groups and by direct steric effects.

Applying this C4 probe to cations **3** and **4** is a somewhat delicate operation in that the data on **3** were obtained in $CDCl_3$–TFA[12] and those on **4** in FSO_3H–SO_2ClF,[13,14] only **3a** having been studied in both media.[12,14] In this particular case, shifts in superacid are 0–1 ppm lower than in TFA. The differences in the C4 shift for 4-Me and 4-F are then insignificantly small, less than 1 ppm, that for the unsubstituted compound (X = H) significantly less (1.5 ppm) for **3d** than for **4a** (both in FSO_3H–SO_2ClF) while for the *para*-methoxy cations, **2i** and **4a**, the former is substantially greater than the latter, 165.7 ($CDCl_3$–TFA) and 157.7 (FSO_3H–SO_2ClF) ppm, respectively. This would suggest that, contrary to other indications (lower adamantyl C_q and C^+ shifts) and expectation, there is less resonance stabilization of cations **4** than **2**.

Empirical relationships involving $\cos^2\theta$, where θ is the dihedral angle,[29] have been proposed to interpret the variation of ^{13}C NMR shifts in aromatic carbonyl and other compounds.[30] Here, if we assume a value of 175.2 ppm for $\theta = 0°$ and 165.9 ppm for the *ab initio* value of 35°, then 172.0 ppm (2,4-dimethyl-*tert*-cumyl cation) corresponds to an angle of 20° and orthogonality ($\theta = 90°$) requires a value of 146.9 ppm. The value of 20° suggests that, if the $\cos^2\theta$ relationship is applicable to the 'reaction constants', *i.e.* the ρ-values, of the correlations with Brown's σ^{C+} parameters, the 2-methyl-*tert*-cumyl ion should be about 10% smaller than usual, whereas it is amongst the highest found. However, unexplained variations in the reaction constant of this order of magnitude, albeit to lower values, are not uncommon in Brown's work.[10] The value for an 'orthogonal' cation is perhaps coincidentally close to that of 146.3 ppm in **2b**, as it conflicts with other indications that ions **2** are not entirely free from resonance stabilization. Applying the $\cos^2\theta$ relationship to the reaction constants for **2** and **4** (assuming an average value of −17 for fully aryl-stabilized cations), we calculate θ-values of 59 and 73°, respectively (though values in the opposite order would be expected). Angles are small as this could be accommodated if the *ab initio* value in Timberlake's work were about 5° on the high side. It should be noted that if the same $\cos^2\theta$ relationship is applied to the σ_{R° values calculated above for **5** and **4d**, a dihedral angle of 62° is indicated.

To compare alcohol and cation shifts for aryl-stabilized systems, it was necessary to resynthesize a few typical precursor alcohols, as very few ^{13}C NMR spectra were published. For the phenyl-2-propyl (*tert*-cumyl), 2-butyl, 3-pentyl, 3-hexyl, 4-heptyl, cyclopentyl, cyclohexyl, cycloheptyl and 2-adamantyl alcohols the shift of the *para*-carbon, C4, is at 126.6, 126.4, 126.2, 126.2, 126.1, 126.7, 126.6, 126.4 and 127.2 ppm, respectively, averaging 126.5 ± 0.3 ppm. Comparison with the average C4 shift in aryl-stabilized cations indicates that ionization results in a downfield shift of some 29.0 ppm, whereas for $\mathbf{3} \longrightarrow \mathbf{4}$ the change is only 5.9 ± 1.7 (mean of the five coherent values, not 4-OMe or 4-Me; Table 6), it being necessary to assume in both cases that the change of solvent has no effect upon the shifts. Application of the $\cos^2\theta$ relationship to these data again gives an angle of *ca.* 63°. It may seem, however, rather naive to consider in this way that the alcohol is the appropriate reference for the shift variation, simply because it is the chemical precursor of the cation. Both in practice and in theory, other references could be chosen. The C4 shifts in the corresponding alkanes, for example, are about 0.6 ppm lower than for the alcohols,[15] which would slightly increase the relative change for $\mathbf{3} \longrightarrow \mathbf{4}$ and reduce the estimated dihedral angle to 62°.

Conclusions

The results of ^{13}C NMR spectroscopic studies of 4- and 5-substituted *o*-tolyldi(adamant-1-yl)methyl cations, **2**, under mildly acidic conditions at room temperature differ in several respects from those for the analogous 3- and 4-substituted di(adamant-1-yl)benzyl cations, **4**, previously investigated in FSO_3H–SO_2ClF at −80 °C. Contrary to previous statements concerning the lack of resonance stabilization in cations **4**,[13,14] and despite the fact that the C^+ shift is substantially higher for **2** than for **4**, the available evidence clearly indicates stabilization of the former by the conjugatively electron-donating substituent, 4-OMe, and relative destabilization by the inductively electron-withdrawing 5-halo substituents. Correlations with Brown's carbocation substituent constants, σ^{C+} and σ^{nC+}, give ρ-values significantly different from zero for **2** (but smaller than for classical aryl-stabilized ions). Analogous correlations for **4** give either a smaller ρ-value (σ^{C+}) or a scatter diagram (σ^{nC+}). Results obtained by applying a $\cos^2\theta$ relationship to various ^{13}C NMR data suggest that the dihedral angle in both **2** and **4** is of the order of 60°, the data being, however, somewhat less coherent for **4**. The reasons for this are not clear, but may be related to the use of superacid medium in the study of **4**. A recent study by Prakash[31] of **2f** (5-Cl) and **2i** (4-OMe) in superacid at −80 °C suggests that this solvent tends to reduce the difference between differently substituted cations and, furthermore, has a specific effect on the shift of the C4 carbon in *para*-methoxy derivatives, this being much lower than in TFA, 158.2 as against 165.7 ppm.

A review of the abundant literature on aryl-stabilized benzyl cations indicates that qualitative information can be extracted from the previously neglected data on aromatic carbon shifts, by applying the principle of additivity of substituent effects. Analysis of the early data serves to highlight the differences between aryl-stabilized cations and those which survive in solution for reasons of chemical inertia, largely resulting from steric hindrance to attack and the reluctance of adamantyl groups to rearrange. Differences in the geometries of the two types of ion, resulting in changes in the mode of stabilization of the ions and their charge distribution, obviously have an important bearing upon the chemical shifts of the aromatic carbons. The calculation of ^{13}C NMR shifts by quantum mechanical methods (*ab initio*-IGLO–NMR)[32] has progressed enormously in recent years, and it should be possible to find a theoretical explanation for the unusual *ortho*-carbon shifts in ions **2** and **4**. For the moment, however, these remain rather large systems for *ab initio* methods.

We have yet to undertake kinetic studies, but the 5-halo substituents have a clear impact on the rate of formation of the carbocation, which is noticeably slower than for other substituents. This aspect of stable carbocation chemistry seems to have received no attention to date.‡

Experimental

General methods

NMR measurements were performed on a Bruker AS 200 FT instrument operating at 200 MHz (proton) or 50 MHz (carbon). Unless stated otherwise, all measurements were made in $CDCl_3$ and are referenced to internal TMS ($\delta_H = 0.00$ ppm for ^{1}H) or to the solvent ($\delta_C = 77.0$ ppm for ^{13}C). Details concerning measurements on carbocations are given below. Melting points were determined in capillary glass tubes on a Mettler FP5 instrument with a heating rate of 3 °C min^{-1}.

Synthesis of substituted *anti-o*-tolydi(adamant-1-yl)methanols, 1a–j

Alcohols were synthesized by reaction of the appropriate organolithium compound (prepared directly or by halogen exchange with BuLi or Bu^tLi) with di(adamant-1-yl)ketone in diethyl ether under argon at room temperature. The crude products were purified by chromatography on alumina in light petroleum–diethyl ether mixtures and recrystallization from hexane or hexane–benzene mixtures. The *anti* isomer, the major component of the product mixture, was obtained in this way; no attempt was made to isolate the *syn* isomers.

***anti*-2-Methylphenyldi(adamant-1-yl)methanol, 1a.** Details have already been described.[15]

***anti*-2,4-Dimethylphenyldi(adamant-1-yl)methanol, 1b.** 66%, mp 243 °C (Found: C, 85.7; H, 10.1. $C_{29}H_{40}O$ requires C, 86.08; H, 9.96%).

***anti*-2,5-Dimethylphenyldi(adamant-1-yl)methanol, 1c.** 76%, mp 187–188 °C (Found: C, 86.2; H, 10.1. $C_{29}H_{40}O$ requires C, 86.08; H, 9.96%).

***anti*-2-Methyl-5-(*tert*-butyl)phenyldi(adamant-1-yl)methanol, 1d.** 36%, mp 249 °C (Found: C, 86.2; H, 10.4. $C_{32}H_{46}O$ requires C, 86.04; H, 10.38%).

***anti*-2-Methyl-4-chlorophenyldi(adamant-1-yl)methanol, 1e.** 23%, mp 254 °C (Found: C, 79.1; H, 8.8; Cl, 8.3. $C_{28}H_{37}OCl$ requires C, 79.12; H, 8.77; Cl, 8.34%).

***anti*-2-Methyl-5-chlorophenyldi(adamant-1-yl)methanol, 1f.** 57%, mp 214–215 °C (Found: C, 79.4; H, 8.8; Cl, 8.3. $C_{28}H_{37}OCl$ requires C, 79.12; H, 8.77; Cl, 8.34%).

***anti*-2-Methyl-4-fluorophenyldi(adamant-1-yl)methanol, 1g.** 30%, mp 186 °C (Found: C, 82.2; H, 9.1; F, 4.6. $C_{28}H_{37}OF$ requires C, 82.31; H, 9.13; F, 4.65%).

***anti*-2-Methyl-5-fluorophenyldi(adamant-1-yl)methanol, 1h.** 24%, mp 203 °C (Found: C, 82.3; H, 9.1; F, 4.5. $C_{28}H_{37}OF$ requires C, 82.31; H, 9.13; F, 4.65%).

***anti*-2-Methyl-4-methoxyphenyldi(adamant-1-yl)methanol, 1i.** 47%, mp 250 °C (Found: C, 82.5; H, 9.5. $C_{29}H_{40}O_2$ requires C, 82.81; H, 9.58%).

***anti*-2,3,4,5-Tetramethylphenyldi(adamant-1-yl)methanol, 1j.** 72%, mp 220 °C (Found: C, 86.3; H, 10.5. $C_{31}H_{44}O$ requires C, 86.05; H, 10.25%).

Preparation of carbonium ions, 2a–j

For NMR studies the substituted *anti-o*-tolyldi(adamant-1-yl)methanol (25 mg, 0.056–0.064 mmol) was dissolved in $CDCl_3$ (0.5 cm^3) at room temperature with trifluoroacetic anhydride (5–10 mm^3) and TFA (50 mm^3) added from a Petersen pipette. Except for the 5-halo derivatives, shaking for a few seconds resulted in complete conversion of the alcohol to the carbocation; the 5-chloro and 5-fluoro derivatives required several minutes. Under these conditions decomposition of the carbocations was sufficiently slow for heteronuclear correlation experiments taking up to 12 h to be performed.

^{13}C NMR spectra of phenyl-substituted tertiary alcohols

Samples of tertiary alcohols were prepared by addition of the appropriate ketones to an excess of phenylmagnesium bromide in diethyl ether under argon at room temperature. Standard work-up was followed by chromatographic purification on alumina.

2-Phenylpropan-2-ol. δ_C 31.6 (2 CH_3), 72.5 (C-OH), 124.3 (2 CH), 126.6 (CH), 128.1 (2 CH) and 149.0 (C_q).

2-Phenylbutan-2-ol. δ_C 8.3 (CH_3), 29.5 (CH_3), 36.6 (CH_2), 74.9 (C-OH), 124.8 (2 CH), 126.4 (CH), 128.0 (2 CH) and 147.7 (C_q).

3-Phenylpentan-3-ol. δ_C 7.8 (2 CH_3), 34.9 (2 CH_2), 77.4 (C-OH), 125.4 (2 CH), 126.2 (CH), 127.9 (2 CH) and 145.7 (C_q).

3-Phenylhexan-3-ol. δ_C 7.7 (CH_3), 14.4 (CH_3), 16.7 (CH_2), 35.3 (CH_2), 44.9 (CH_2), 77.3 (C-OH), 125.3 (2 CH), 126.2 (CH), 127.9 (2 CH) and 146.0 (C_q).

4-Phenylheptan-4-ol. δ_C 14.4 (2 CH_3), 16.7 (2 CH_2), 45.2 (2 CH_2), 77.1 (C-OH), 125.2 (2 CH), 126.1 (CH), 127.9 (2 CH) and 146.4 (C_q).

1-Phenylcyclopentanol. δ_C 23.8 (2 CH_2), 41.7 (2 CH_2), 83.5 (C-OH), 125.0 (2 CH), 126.7 (CH), 128.2 (2 CH) and 147.0 (C_q).

1-Phenylcyclohexanol. δ_C 22.1 (2 CH_2), 25.5 (CH_2), 38.8 (2 CH_2), 73.1 (C-OH), 124.5 (2 CH), 126.6 (CH), 128.2 (2 CH) and 149.3 (C_q).

1-Phenylcycloheptanol. δ_C 22.5 (2 CH_2), 29.1 (2 CH_2), 43.1 (2 CH_2), 76.8 (C-OH), 124.4 (2 CH), 126.4 (CH), 128.1 (2 CH) and 150.7 (C_q).

2-Phenyl-2-adamantanol. δ_C 26.9 (CH), 27.4 (CH), 32.9 (2 CH_2), 34.8 (2 CH_2), 35.5 (2 CH), 37.6 (CH_2), 75.6 (C-OH), 125.4 (2 CH), 127.2 (CH), 128.6 (2 CH) and 145.3 (C_q).

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