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^{13}C NMR Spectroscopic Study of Para-Substituent Effects in Highly Crowded 1,1′-Diadamantylbenzyl Cations[1]

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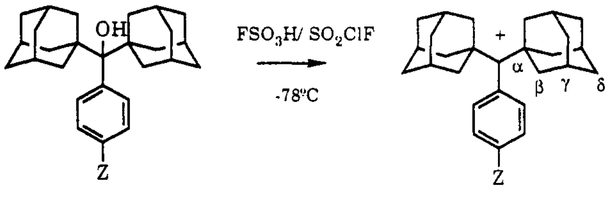
A series of para-substituted 1,1′-diadamantylbenzyl cations were studied under stable ion conditions at low temperatures in superacid solutions. These studies were informative in probing the effects of ring substituents and their ability to delocalize positive charge from the carbenium center in highly crowded systems. The observed ^{13}C NMR chemical shifts of the carbocation center in comparison with those of the corresponding cumyl cations indicate the effects of steric crowding of the diadamantyl substituents in minimizing p–π interactions. This renders the carbocationic ^{13}C NMR chemical shifts virtually unaffected by para-substituents.

Introduction

The Gassman–Fentiman tool of increasing electron demand[2] has been frequently employed in probing the substituent-induced electronic effects of electron-deficient systems using NMR spectroscopy. The technique involves systematic variation of the aryl ring substituents (varying from electron-releasing to electron-withdrawing) adjacent to a developing carbenium center in an effort to detect the onset of other electronic interactions such as π, $\pi\sigma$, and σ delocalization in the system. Although the "tool of increasing electron demand" applied to stable carbocations is more sensitive in detecting electronic interactions than the usual solvolysis studies wherein solvation significantly masks the electron demand of the cation center in the solvolytic transition state, the method has limitations. A phenyl group even with electron-withdrawing substituents can still delocalize positive charge in its π-system. This sometimes makes the method insensitive to detect subtle interactions which are operative, when the aryl group is replaced by a hydrogen substituent.

Our interest focused on a system where p–π delocalization is effectively screened from the carbocation center. Earlier work[3] established the tertiary α,α-di(1-adamantyl)phenylmethyl cation as showing interesting spectroscopic behavior since little charge is delocalized to the phenyl ring. The chemical shift comparison of cations 1 and 2 emphasizes the difference in charge distribution which result from very unfavorable steric interactions between the aryl ring and adamantyl β-hydrogens. The ring is forced to twist and largely eliminates conjugation with the empty p-lobe of the cationic center. This exceptional exclusion of resonance effects in association with carbocationic intermediates with adjacent aromatic systems prompted us to investigate this unique system for inductive effects only.

Scheme I



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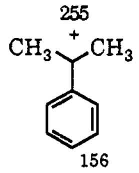

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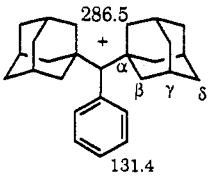

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Consequently, we prepared a series of related para-substituted 1,1′-diadamantylbenzyl cations and studied them by ^{13}C NMR spectroscopy. The needed precursors, para-substituted 1,1′diadamantylbenzyl alcohols suitable for studies of increasing electron demand were prepared from 1,1′-diadamantyl ketone[4] with aryllithiums.[5] Ionization of the alcohol in FSO_3H/SO_2ClF at −78 °C generated the benzyl cation as a dark red solution (Scheme I).

Results and Discussion

The ^{13}C NMR spectrum (Figure 1) of 1,1′-diadamantyl-*p*-tolyl cation shows a highly deshielded benzylic cationic center at ^{13}C δ 286 as compared to the cumyl cation resonance at 255 ppm.[2,6] Such extraordinary deshielding

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[1] Stable Carbocations 288. For part 287 see Olah, G. A.; Liao, Q.; Casanova, J.; Bau, R.; Prakash, G. K. S. *J. Am. Chem Soc.*, in press.

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Table I. ^{13}C NMR Spectroscopic Data[a] on Para-Substituted Diadamantylbenzyl Cations in SO_2ClF at −78 °C

4-Z	C^+	α	β	γ	δ	ipso	*o*	*m*	*p*	*Z*	$C^+_{(arylcp)}$
OCH_3	283.0	67.2	39.6	29.2	33.7	135.8	130.3	112.9	157.7	57.6	237
CH_3	286.1	66.7	39.7	29.5	33.8	145.4	127.7	125.6	134.7	20.6	260
F	284.7	67.6	39.7	29.5	33.7	132.9	128.3[b]	115.1[c]	164.6[d]		265
H	286.5	65.9	38.3	26.4	32.5	136.2	125.9	122.8	131.4		271
CF_3	287.1	68.5	39.8	27.9	33.7	140.7	124.8	123.9[e]	133.1[f]	121.3[g]	285[h]

[a] Carbon-13 chemical shifts are in parts per million from the external acetone (capillary) signal. [b] ($^3J_{C-F}$) = 3.2 Hz. [c] ($^2J_{C-F}$) = 22.4 Hz. [d] ($^1J_{C-F}$) = 257.4 Hz. [e] ($^3J_{C-F}$) = 11.9 Hz. [f] ($^2J_{C-F}$) = 33.4 Hz. [g] ($^1J_{C-F}$) = 256.6 Hz. [h] ^{13}C NMR chemical shifts of 1-aryl-1-cyclopentyl cations are included for comparison.

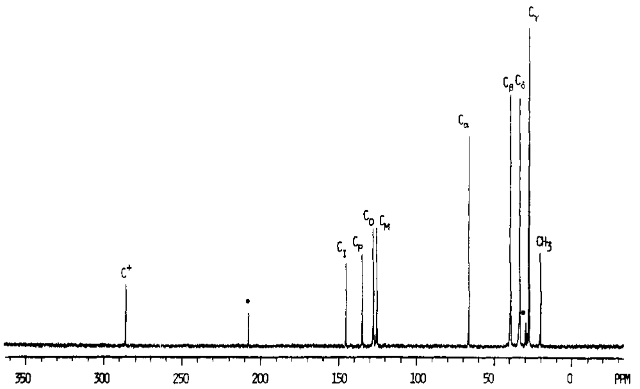

Figure 1. ^{13}C NMR spectrum (75.4 MHz, proton decoupled) of 1,1′-diadamantyl-*p*-tolyl carbocation. Absorptions due to acetone-d_6 are indicated by asterisks.

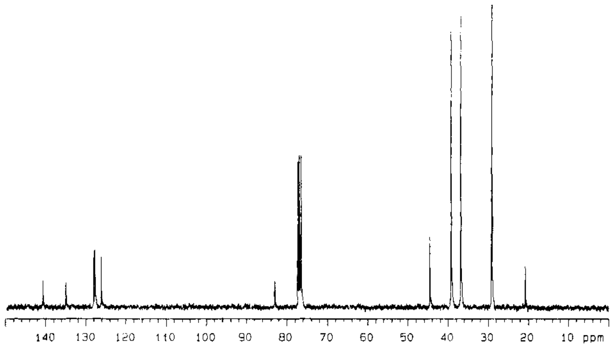

Figure 2. ^{13}C NMR spectrum (75.4 MHz, proton decoupled) of 1,1′-diadamantyl-*p*-tolylmethanol.

can be explained only by the decreased (if not nonexistent p–π overlap) with the carbocationic center. This observation also indicates that the two bulky adamantyl groups prohibit coplanar ring rotation of the phenyl group into conjugation with the empty p-orbital of the cationic center. MMX calculations of the cationic species complement this interpretion via high rotational energy barriers as the phenyl ring rotates through its molecular axis.[7] The ^{13}C resonances of the ortho and meta carbons shown in Figure 1 indicate one peak each, which we attribute to the adopted ground state C_{2v} symmetry of the cation. However, full 360° rotation of the aryl group cannot be excluded. The observation at room temperature of diastereotopic ^{13}C aromatic resonances (Figure 2) from the parent neutral alcohol (C_s symmetry) was interpreted as a "freezing" of the phenyl ring about the C_{ipso}–C^+ bond into a fixed position, suggesting strong steric interactions imposed by the adamantyl substituents.

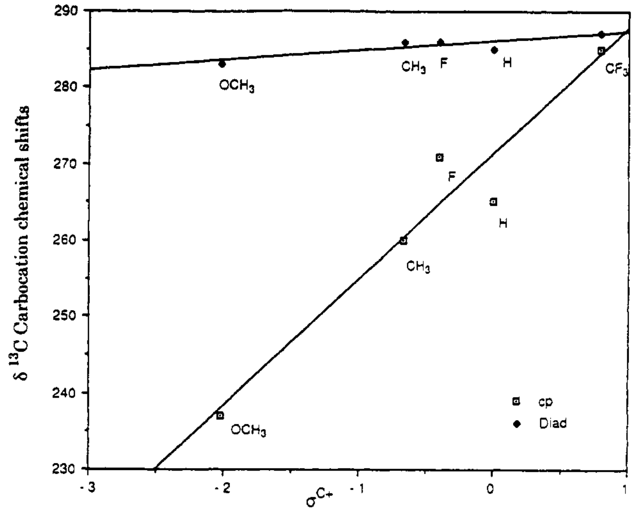

Figure 3. Chemical shift correlation plot of 1-aryl-1-cyclopentyl and 1,1′-diadamantylbenzyl cation chemical shifts versus σ^{c+} substituent constants.

The ^{13}C NMR data for the 1,1′-diadamantylbenzyl ions are summarized in Table I. We have also included the ^{13}C NMR chemical shifts of the cationic center of model 1-aryl-1-cyclopentyl cations (a system similar to cumyl)[8] for comparison. The range of ^{13}C chemical shifts for the 1,1′-diadamantylbenzyl cationic centers varies by only ±2 ppm throughout the series. The aromatic carbons remain relatively unaffected by the charge as evidenced by their ^{13}C NMR resonances in comparison to parent neutral compounds. Concomitantly, we observe up to ca. 23 ppm downfield chemical shift of the C_α adamantyl carbons which indicates extensive hyperconjugative interactions that compensate for the lack of resonance stabilization from the aryl group.

A plot of the carbocationic chemical shifts of 1,1′-diadamantylbenzyl cations and 1-aryl-1-cyclopentyl cations versus σ^{C+} indicates a near unity slope for 1-aryl-1-cyclopentyl cations with excellent correlation (Figure 3). However, these two systems appear to have considerably different carbocationic environments as indicated by their slopes. The 1,1′-diadamantylbenzyl cations appear to have almost zero slope in comparison to that of the 1-aryl-1-cyclopentyl system. Removal of π-resonance interaction with the adjacent carbocationic center in these highly crowded systems plays a significant role in dampening the effects of substituents 'Z' at the para position. Not surprisingly, the inductive effects of the various substituents are negligible since the interaction of bond dipoles is transmitted through the bonds by successive polariza-

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(7) MMX Molecular modeling calculations were carried out using PCModel version 4.0 *Serena Software*. Single point calculations without optimization were carried out at 10° increments of rotation about C_{ipso}–C^+ bond.

(8) σ^{c+} substituent constants were based on the cationic chemical shifts of substituted cumyl cations previously developed by Brown et al.[9] These constants taken into account the increased electron demand of carbocations in superacid medium. 1-Aryl-1-cyclopentyl cations provide a model set of "ordinary" cations for comparison.

Table II. Carbocation Charge-Densities Data Based on Semiempirical PM3 Calculations[a]

Z	benzyl	1-aryl-1-cyclopentyl	1,1′-diadamantylbenzyl
OCH_3	0.200	0.265	0.422
CH_3	0.250	0.303	0.471
F	0.271	0.317	0.485
H	0.285	0.325	0.489
CF_3	0.325	0.352	0.509

[a] Calculations were performed with the Spartan program on an IBM RS/6000 Model 560 computer.

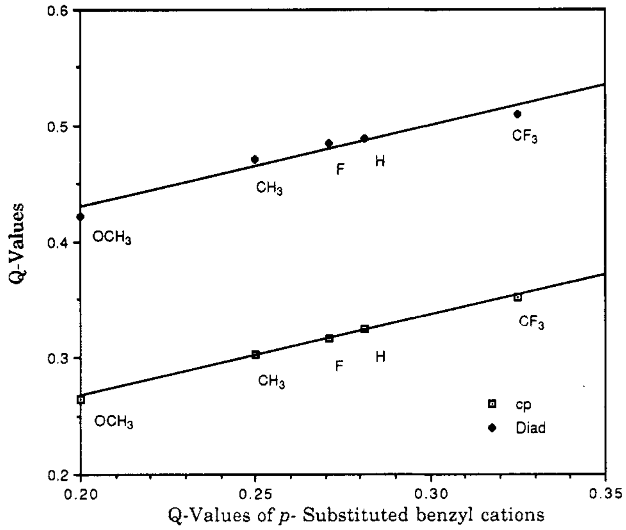

Figure 4. PM3 charge density correlation plot of carbocationic centers for 1,1′-diadamantylbenzyl cations and arylcyclopentyl versus benzyl cations.

tion. Thus, inductive effects drop off rapidly as the cationic site is four bonds removed from the substituent. The subtle differences in chemical shift shown in Table I may arise from solvation effects of the carbocationic center depending on slight differences in acid concentration of the sample. However, although lesser in magnitude, the positive slope follows the same trend as the 1-aryl-1-cyclopentyl system as well as other substituted aromatic systems adjacent to a cationic center.

To coordinate the NMR study with molecular modeling, theoretical calculations on the studied carbocationic systems were carried out at the PM3 level.[10] Charge densities (Q-values shown in Table II) at the carbocationic centers were calculated for para-substituted 1,1′-diadamantylbenzyl, 1-aryl-1-cyclopentyl, as well as para-substituted benzyl cations. The calculated Q-values of both 1,1′-diadamantylbenzyl and 1-aryl-1-cyclopentyl cations were plotted against those of the sterically unencumbered benzyl cations (see Figure 4). The plots from Figure 4 clearly indicate that more positive charge is localized in the sterically congested 1,1′-diadamantylbenzyl system (as reflected by higher Q-values) compared to 1-aryl-1-cyclopentyl cations. These observations support our experimental findings that little positive charge is dispersed into the aryl ring due to steric inhibition of resonance posed by the two bulky adamantyl groups. However, the nearly identical slopes shown in Figure 4 is misleading for both systems and does not corroborate with the ^{13}C chemical shift/σ^{C+} correlations reported in Figure 3. A possible explanation for this discrepancy may be due to the inability of semiempirical calculations (such as PM3) to handle carbocationic structures with shallow energy minima.

In summary, the para-substituted 1,1′-diadamantylbenzyl cation system shows a remarkably deshielded carbocationic center for benzylic cations in solution. This extraordinary deshielding is the result of high steric strain associated with the 1,1′-diadamantyl framework. The prohibitively high rotational barriers prevent complete p–π resonance overlap with the adjacent empty p-orbital. To compensate for the lack of resonance stabilization, significant hyperconjugative interactions via the adamantyl substituents are observed from the ^{13}C NMR chemical shifts. The subtle chemical shift differences of the cationic center are virtually independent of substituent effects in the para position.

Experimental Section

THF and diethyl ether were distilled from sodium–benzophenone immediately before use. Lithium metal dispersion in mineral oil was obtained from Aldrich and used as received. 70-eV Mass spectra were recorded on a Finnigan-Mat/Incos-50 mass spectrometer, using DEP probe. Melting points were determined using a Mettler FP1 melting point apparatus. ^1H and ^{13}C NMR spectra were recorded on a Varian VXR-200 or Varian UNITY-300 equipped with a variable temperature probe. The ^1H and ^{13}C NMR chemical shifts for the carbocations were referenced with respect to the external capillary d_6-acetone.

1,1′-Diadamantylphenylmethanol (3a). Under an argon atmosphere in flame-dried glassware, a solution of chlorobenzene (0.85 mL, 8 mmol) and (0.5 g, 1.7 mmol) 1,1′-diadamantyl ketone in THF (10 mL) was added dropwise at 0 °C with vigorous stirring to a mixture of lithium dispersion (21 mmol, 3.3% Na) in THF over a 5-min period. Following overnight stirring at room temperature, the excess lithium was destroyed by careful addition of saturated aqueous ammonium chloride solution, and the mixture was extracted with pentane. The pentane extract was then washed with concd brine, dried (Na_2SO_4), and concentrated *in vacuo*. Purification by elution over a silica gel column (hexane–ether, 60:10) followed by recrystallization from pentane–ether (90:10) gave pure alcohol 0.233 g (46%): mp 212.4 °C; IR (CCl_4) ν 3348, 2908, 2840, 1549, 1250, 1006, 825 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.5–6.8, 1.98, 1.6; ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.1, 128.4, 127.9, 127.3, 125.7, 125.3, 83.1, 44.7, 39.4, 36.9, 29.2. Anal. Calcd for $C_{27}H_{36}O$: C, 86.12; H, 9.70. Found: C, 85.89; H, 9.90.

1,1′-Diadamantyl-*p*-tolylmethanol (3b). Preparation similar to 1,1′-diadamantylphenylmethanol (**3a**). A solution of *p*-chlorotoluene (1.01 mL, 8.4 mmol) and 1,1′-diadamantyl ketone (0.5 g, 1.7 mmol) in THF (10 mL) was added dropwise at 0 °C with vigorous stirring to a mixture of lithium dispersion (21 mmol, 3.3% Na) in THF over a 5-min period. Following overnight stirring at room temperature, the excess lithium was destroyed by careful addition of saturated aqueous ammonium chloride solution, and the mixture was extracted with pentane. The pentane extract was then washed with concd brine, dried (Na_2SO_4), and concentrated *in vacuo*. Purification by elution over silica gel column (hexane–ether, 60:10) followed by recrystallization from pentane–ether (90:10) gave pure alcohol 0.185 g (38%): mp 274.7 °C; IR (CCl_4) ν 3348, 2908, 2840, 1549, 1256, 1006, 780 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.6–7.0, 2.1, 1.9, 1.6; ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.8, 135, 128.2, 127.9, 127.7, 126.3, 83.1, 44.7, 39.4, 37.0, 29.4, 20.8. Anal. Calcd for $C_{28}H_{38}O$: C, 86.09; H, 9.81. Found: C, 86.13; H, 9.76.

1,1′-Diadamantyl-*p*-anisylmethanol (3c). Under an argon atmosphere in flame-dried glassware, a solution of *p*-chloroanisole (2.38 mL, 17 mmol) and 1,1′-diadamantyl ketone (0.5 g, 1.7 mmol) in THF (10 mL) was added dropwise at 0 °C with vigorous stirring to a mixture of lithium dispersion (21 mmol, 3.3% Na) in THF over a 5-min period. The temperature was maintained at constant ice-bath temperature for 5 h and the excess lithium was destroyed

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(10) Calculations were performed with the Spartan program on an IBM RS/6000 Model 560 computer.

by careful addition of saturated aqueous ammonium chloride solution. The mixture was extracted with ether. The ether extract was then washed with concd brine, dried (Na_2SO_4), and concentrated *in vacuo*. Purification by elution over silica gel column (hexane–ethyl acetate, 90:10) followed by recrystallization from boiling ethanol yielded 0.300 g (60%) of the alcohol: mp 294 °C; IR (CCl_4) ν 3348, 2908, 2840, 1549, 1250, 1006, 780 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.6–6.8, 3.5, 1.9, 1.6; ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.7, 137.4, 130.3, 129.9, 112.5, 111.8, 83.4, 55.2, 45.6, 40.2, 38.1, 30.5. Anal. Calcd for $C_{28}H_{38}O_2$: C, 82.71; H, 9.42. Found: C, 82.29; H, 9.64.

1,1′-Diadamantyl-*p*-fluorophenylmethanol (3d). Under an argon atmosphere in flame-dried glassware, a solution of 1-bromo-4-fluorobenzene (2.08 mL, 17 mmol) and 1,1′-diadamantyl ketone (0.5 g, 1.7 mmol) in diethyl ether (10 mL) was added dropwise at 0 °C with vigorous stirring to a mixture of lithium dispersion (21 mmol, 3.3% Na) in ether over a 5-min period. The reaction was allowed to warm to room temperature, stirred vigorously for 5 days, and tracked by TLC analysis. The excess lithium was destroyed by careful addition of saturated aqueous ammonium chloride solution and the mixture was extracted with ether. Purification by elution through silica gel column (hexane–ethyl acetate, 90:10) followed by recrystallization from boiling cyclohexane yielded 0.15g (32%) of the alcohol: mp 213 °C; IR (CCl_4) ν 3348, 2908, 2840, 1540, 1280, 1069, 785 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.8–6.9, 1.9, 1.6; ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.2 ($^1J_{C-F}$ = 243.6 Hz), 139.3, 130.7 ($^3J_{C-F}$ = 7.2 Hz), 128.5 ($^3J_{C-F}$ = 7.2 Hz), 114.4 ($^2J_{C-F}$ = 20.7 Hz), 111.6 ($^2J_{C-F}$ = 20.7 Hz), 83, 44.2, 1, 39.4, 37.1, 29.5; ^{19}F NMR (188 MHz, $CDCl_3$) δ −118. Anal. Calcd for $C_{27}H_{35}FO$: C, 82.19; H, 8.94; F, 4.81. Found: C, 81.73; H, 8.50; F, 4.57.

1,1′-Diadamantyl-*p*-(trifluoromethyl)phenylmethanol (3e). Under an argon atmosphere in flame-dried glassware, a solution of 1-bromo-4-(fluoromethyl)benzene (2.7 mL, 17 mmol) and 1,1′-diadamantylketone (0.5 g, 1.7 mmol) in diethyl ether (10 mL) was added dropwise at 0 °C with vigorous stirring to a mixture of lithium dispersion (21 mmol, 3.3% Na) in ether over a 5-min period. The reaction was allowed to warm to room temperature followed by sonication for 8 h and stirred vigorously for 5 days. The excess lithium was destroyed by careful addition of saturated aqueous ammonium chloride solution and the mixture was extracted with ether. Purification by elution through silica gel column (hexane–ethyl acetate, 90:10) followed by recrystallization from boiling cyclohexane yielded 0.20g (42%) of the alcohol: mp 237.5 °C; IR (CCl_4) ν 3348, 2908, 2840, 1540, 1260, 1003, 784 cm^{-1}; ^{1}H NMR (300 MHz, THF-d_8) δ 7.7–7.4, 2.0, 1.59; ^{13}C NMR (75 MHz, THF-d_8) δ 150.4, 130.0, 129.5 ($^2J_{C-F}$ = 30.2 Hz), 128.4 ($^2J_{C-F}$ = 30.2 Hz), 125.9 ($^1J_{C-F}$ = 301.8 Hz), 124.6 ($^3J_{C-F}$ = 3.8 Hz), 122.6 ($^3J_{C-F}$ = 3.8 Hz), 83.9, 45.5, 40.1, 37.8, 30.2; ^{19}F NMR (188 MHz, $CDCl_3$) δ −62.66. Anal. Calcd for $C_{28}H_{35}F_3O$: C, 75.65; H, 7.94; F, 12.81. Found: C, 75.05; H, 8.30; F, 12.42.

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 dry ice/acetone bath. Efficient mixing of the solution was effected using a vortex stirrer.

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