Table III. Experimental and Calculated ^{1}H NMR[a] Chemical Shift Difference ($\Delta\delta_{AB}$) between Methylene Protons in Amides 1-3

		amide					
		1		2		3	
X	r_X[b]	exptl	calcd[c]	exptl	calcd[d]	exptl	calcd[e]
CH_3	2.0	1.24[f]	1.24	0.85[f]	0.87	0.84[g]	0.83
C_2H_5	2.15	1.37[f]	1.36			0.98[f]	1.00
F	1.35					-	0.08
Cl	1.80			0.67[h]	0.66	-	0.60
Br	1.95					0.77[h,i]	0.77
I	2.15					1.02[h]	1.00
C_6H_5	2.45	1.60[f]	1.60	1.30[f]	1.30	1.37[f]	1.35
C_4H_4	1.95					0.80[f]	0.77

[a] Data are reported as δ in parts per million from Me_4Si. [b] As for Table II. [c] $0.795r_X - 0.346$; $r^2 = 0.999$. [d] $0.974r_X - 1.09$; $r^2 = 0.994$. [e] $1.16r_X - 1.49$; $r^2 = 0.993$. [f] Determined in $CDCl_3$ at about 43 °C.[1] [g] Determined in $CDCl_3$ at 40 °C.[4] [h] Determined in $CDCl_3$ at about 43 °C.[2] [i] X = 2′-bromo-4′-methyl.

cumstances, whereas their conformational energies are similar.[14] This research provides a consistent framework for accommodating a host of previously apparently unrelated measurements and is being continued.

Experimental Section

Melting points were determined with a Kofler hot-stage apparatus and are uncorrected. ^{1}H NMR spectra were obtained (in $CDCl_3$) at 60 MHz, using a Hitachi Perkin-Elmer R-20 instrument, and chemical shifts (δ) are measured from internal tetramethylsilane as reference. The proton resonances of all compounds were integrated for confirmation of structure (s, singlet; d, doublet; t, triplet; m, multiplet).

***N*-Substituted Difluorooxyboranes.** The requisite parent difluorooxyboranes, 8, were prepared from the appropriate benzoylacetanilide and boron trifluoride.[15] The N-alkylation of 8 was carried out in dimethylformamide, using sodium hydride and either benzyl bromide, ethyl bromide, or methyl iodide (methyl tosylate) as appropriate,[16] and afforded the corresponding 5, 6, 7, 9, and 10, respectively, in good yields. The crude reaction products, isolated after trituration with ethanol,[16] were sufficiently pure (melting point) for most purposes (including ^{1}H NMR determination). Samples were obtained for elemental analysis by crystallization from chloroform–ethanol. New N-substituted difluorooxyboranes 5, 6, 7, 9, and 10 together with relevant details are listed in Table I. The mass spectra (measured (70 eV) on a Varian CH-5 spectrometer) which substantiated the respective structures featured the rearrangement ion, $Ar\dot{N}^+(R)BF_2$, thought to originate from a six-membered transition state in which the N and B atoms are suitably aligned or even coordinated.[17] It now seems more likely that the $Ar\dot{N}^+(R)BF_2$ (and other species[17]) arise after intervention of acyclic difluorooxyborane intermediates.[18]

Registry No. **1c**, 7128-76-9; **1d**, 7128-77-0; **1i**, 6930-93-4; **2c**, 6932-98-5; **2g**, 13936-57-7; **2i**, 7215-53-4; **3c**, 6932-92-9; **3d**, 7111-32-2; **3f**, 76359-25-6; **3g**, 76359-26-7; **3i**, 7097-82-7; **3** (X = I), 13936-59-9; **3** (X = C_4H_4), 6930-96-7; **3** (X = 2-Br, 4-Me), 13936-58-8; **5b**, 76377-14-5; **5c**, 76391-54-3; **5d**, 76377-15-6; **5e**, 76377-16-7; **5f**, 76377-17-8; **5g**, 76377-18-9; **5h**, 76377-19-0; **5i**, 76377-20-3; **6c**, 76377-21-4; **6d**, 76377-22-5; **6e**, 76377-23-6; **6f**, 76377-24-7; **6g**, 76377-25-8; **6h**, 76377-26-9; **6i**, 76377-27-0; **6j**, 76377-28-1; **7g**, 76377-29-2; **7i**, 76377-30-5; **8b**, 76377-31-6; **8c**, 76377-32-7; **8d**, 76377-33-8; **8e**, 76377-32-7; **8f**, 76377-34-9; **8g**, 76377-35-0; **8h**, 76377-36-1; **8i**, 76377-37-2; **8j**, 76377-38-3; **9**, 76377-39-4; **10**, 76391-55-4; boron trifluoride, 7637-07-2; 3′-chlorobenzoylacetanilide, 962-06-1; 2′-methylbenzoylacetanilide, 71599-78-5; 2′-ethylbenzoylacetanilide, 76359-27-8; 2′-methoxybenzoylacetanilide, 92-16-0; 2′-fluorobenzoylacetanilide, 349-25-7; 2′-chloroacetanilide, 7342-28-1; 2′-bromoacetanilide, 41084-99-5; 2′-phenylacetanilide, 76359-28-9; 4′-bromo-2-chloro-3′,5′-dimethylacetanilide, 76359-29-0.

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(18) The feasibility of the equilibrium below is supported from ^{1}H NMR observations with certain 6 in dimethyl-d_6 sulfoxide solution (N. J. Coville and B. Staskun, unpublished results).

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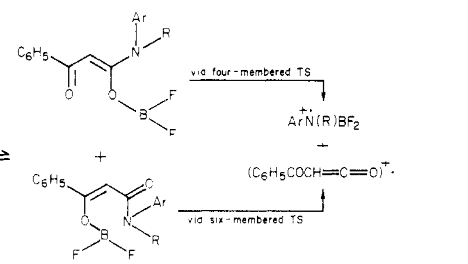

Structural Effects in Solvolytic Reactions. 35. Carbon-13 Nuclear Magnetic Resonance Studies of Carbocations. Effect of Increasing Electron Demand on the Carbon-13 Nuclear Magnetic Resonance Shifts in 2-Aryl-2-butyl and 4-Aryl-4-heptyl Carbocations. Correlation of the Data by a New Set of Substituent Constants, σ^{C^+}

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The ^{13}C NMR shifts of a series of meta- and para-substituted 2-phenyl-2-butyl and 4-phenyl-4-heptyl carbocations were measured in $SbF_5/FSO_3H/SO_2ClF$. The plots of the chemical shifts of the cationic carbon, $\Delta\delta^{C^+}$, in the various substituted derivatives against the values of substituent constants, σ and σ^+, reveal only relatively poor correlations. However, excellent linear correlations are realized in the plots of $\Delta\delta^{C^+}$ against the new σ^{C^+} values proposed for these systems. The 2-aryl-2-butyl system yields a ρ^{C^+} value of -17.78 with a correlation coefficient $r = 0.9998$. The 4-aryl-4-heptyl system gives a ρ^{C^+} value of -14.57 with $r = 0.999$. The nearly perfect linear correlations observed for these systems support the validity and utility of these new σ^{C^+} constants.

During a systematic investigation of electrophilic aromatic substitution reactions, it was recognized that the original Hammett σ constants, derived from the ionization of substituted benzoic acids, required modification to allow

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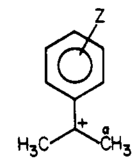
for the very different electron demand accompanying such electrophilic reactions.[3] This led to the development of electrophilic substituent constants σ^+.[4] These constants have been systematically applied in studies of structural effects in solvolytic and related reactions.[5] On the basis of the usual assumption of a late transition state[6] in such solvolytic reactions, it was not unreasonable to anticipate that these substituent constants could also be used to correlate the stabilities of the carbocationic intermediates produced in such solvolyses. Indeed, a large body of consistent information has been accumulated as to the effect of many substituents on the stabilities of such carbocations.[5]

In recent years it has become possible to prepare and observe such carbocations in superacid media.[7] The ^{13}C NMR chemical shifts in such carbocations have been taken as a measure of the electron delocalization and stabilization of the cations. Accordingly, numerous attempts seeking to correlate the ^{13}C NMR shifts with the σ^+ values have been reported.[8-10]

For example, Olah and co-workers[8] originally reported approximate linearity in the plot of ^{13}C NMR shifts of the cationic carbon of substituted *tert*-cumyl cations (δ^{C^+}) against the electrophilic substituent constants, σ^+. However, a critical examination of the proposed correlation reveals only a fair fit, with the correlation coefficient r being 0.976, considerably poorer than the excellent correlations usually realized in reactions involving solvolytic processes.[5]

In a reinvestigation of the behavior of the substituted *tert*-cumyl cations, Kelly and Spear[11] observed an even lower correlation coefficient, $r = 0.967$. Even more important, they pointed out that the least-squares line for their data failed to pass through the point for the parent *tert*-cumyl cation. They suggested that the difficulty might be due to enhanced charge delocalization in ions containing electron-donating substituents. They proposed to introduce new "super sigma" constants, σ^{++}, to allow for such enhanced charge delocalization. They proceeded to extrapolate the line for the three electron-withdrawing substituents *m*-F, *p*-CF_3, and 3,5-$(CF_3)_2$ through the origin and then calculated new σ^{++} constants for electron-donating substituents to place the points on the line. This treatment gave the following "super sigma" constants (σ^+ values[12] in parentheses): *p*-OCH_3, −1.50 (−0.778); *p*-CH_3, −0.60 (−0.311); *p*-F, −0.36 (−0.073); *p*-Cl, −0.21 (0.114); *p*-Br, −0.15 (0.150).

A critical examination of the studies of both Olah[8] and Kelly[11] revealed that they included very few meta derivatives in their studies. Accordingly, we reinvestigated the ^{13}C NMR data of the substituted *tert*-cumyl cations (1) utilizing derivatives containing eight different *meta* sub-



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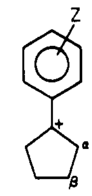


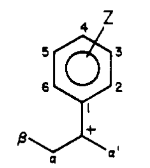
2

stituents [*m*-CH_3, *m*-$CH(CH_3)_2$, *m*-F, *m*-Cl, *m*-Br, *m*-CF_3, 3,5-Cl_2, and 3,5-$(CF_3)_2$] in addition to derivatives with six representative para substituents (*p*-OCH_3, *p*-CH_3, *p*-F, *p*-Cl, *p*-Br, and *p*-CF_3) as well as the parent *tert*-cumyl cation.[13]

The data revealed that the chemical shifts[14] for the cationic carbon, $\Delta\delta^{C^+}$, in the meta derivatives coorrelate reasonably well against σ^+_m values ($r = 0.990$ and slope = −18.18). However, a plot of all of the $\Delta\delta^{C^+}$ values, both meta and para, against σ^+ revealed that the data for the para derivatives deviate from the meta correlation line in a systematic manner, corresponding to the incursion of more resonance interactions for the para derivatives than estimated by the values of the σ^+_p constants. In this way, the need for enhanced substituent constants for the para derivatives is established. Consequently, we defined the following modified Hammett-type equation (eq 1), where

$$\Delta\delta^{C^+} = \rho^{C^+}\sigma^{C^+} \quad (1)$$

ρ^{C^+} is the slope (−18.18) obtained from the plot of $\Delta\delta^{C^+}$ against σ^+_m values. Using this equation, we calculated the following σ^{C^+} constants (σ^+ values[12] in parentheses): *p*-OCH_3, −2.02 (−0.778); *p*-CH_3, −0.67 (−0.311); *p*-F, −0.40 (−0.073); *p*-Cl, −0.24 (0.114); *p*-Br, −0.19 (0.150); *m*-CH_3, −0.13 (−0.066); *m*-F, 0.352 (0.35); *m*-Cl, 0.36 (0.399); *m*-Br, 0.33 (0.405); *m*-CF_3, 0.56 (0.52); 3,5-Cl_2, 0.66 (0.798); *p*-CF_3, 0.79 (0.612); 3,5-$(CF_3)_2$, 1.03 (1.04). We designated these constants as σ^{C^+} to indicate their relationship to the chemical shifts of the cationic carbon. A plot of these σ^{C^+} values against $\Delta\delta^{C^+}$ values of the 1-aryl-1-cyclopentyl cations (2) revealed an excellent correlation ($r = 0.999$ and $\rho^{C^+} = -16.84$). Encouraged by the good fit, we proceeded to apply these σ^{C^+} constants to various carbon structures. In this paper we report our studies of the aliphatic systems, the 2-aryl-2-butyl (3) and 4-aryl-4-heptyl (4) carbocations.



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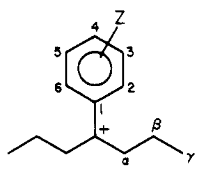

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Results and Discussion

2-Aryl-2-butanols (5) and 4-aryl-4-heptanols (6) were prepared by the addition of the corresponding ketone to Grignard reagents prepared from the corresponding bromo- or iodobenzenes.

These alcohols were ionized by solution in "magic acid", FSO_3H/SbF_5 (1:1 molar ratio), and the mixtures diluted with SO_2ClF at −78 °C, taking care to ensure the presence of a fourfold excess of acid.[15] The ^{13}C NMR shifts of the

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(14) In order to reproduce the Hammett-type plots, we defined $\Delta\delta^{C^+}$ as the cationic carbon substituent chemical shift, which is the difference between the cationic carbon chemical shift for the parent *tert*-cumyl cation and that for the substituted *tert*-cumyl cation; i.e., $\Delta\delta^{C^+} = \delta^{C^+}$ (Z = H) − δ^{C^+} (Z = Z).
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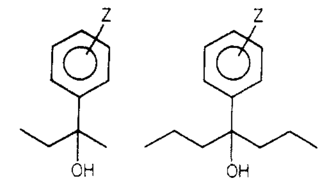

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resulting solutions of 3 and 4 are summarized in Tables I and II.

A plot of the $\Delta\delta^{C^+}$ values for the 2-aryl-2-butyl cations (**3**) against the Hammett σ constants gives a poor correlation ($r = 0.877$ and $\rho = -36.3$). A plot of the data against the Brown σ^+ constants gives only a fair correlation ($r = 0.960$ and $\rho^+ = -27.8$). However, a plot of the data against the new σ^{C^+} constants reveals an excellent correlation, with $r = 0.9998$ and $\rho^{C^+} = -17.78$ (Figure 1).

Similar treatment of the data for the 4-aryl-4-heptyl cations (**4**) yields poor correlations with σ and σ^+ constants (σ, $r = 0.858$, $\rho = -31.5$; σ^+, $r = 0.961$, $\rho^+ = -24.5$). However, a plot of the data against the σ^{C^+} constants gives an excellent correlation with $r = 0.999$ and $\rho^{C^+} = -14.57$ (Figure 2).

Although it is too early to come to a definite conclusion about the significance of the magnitude of the ρ^{C^+} values for the four systems so far studied, it may be of interest to note the variations observed in these values (see Chart I).

This observed variation suggests that it may be possible to use the ρ^{C^+} values as a measure of electronic or steric interactions in carbocations.

Another interesting item is the variation of the α-carbon shifts with electron demand (Tables I and II). These α-carbon chemical shifts vary approximately in the same order as the σ^{C^+} constants.

Another interesting feature is the marked variation of the β-carbon chemical shifts with electron demand in different systems. In the case of 2-aryl-2-butyl carbocations (**3**), the β-CH_3 carbon chemical shift changes by only 1.2 ppm from p-OCH_3 to p-CH_3, with essentially no further change from p-CH_3 to 3,5-$(CF_3)_2$ (Table I). On the other hand, in the case of 4-aryl-4-heptyl cations (**4**), the β-CH_2 carbon exhibits larger chemical shifts, varying by 4.2 ppm from p-OCH_3 to p-CF_3 (Table II), approximately in the same order as the σ^{C^+} constants. This variation in the magnitude of the β-carbon shifts suggests that the extent of the attenuation of charge through the carbon skeleton may be sensitive to the substituent at the β-carbon and other structural characteristics.

The possibility of correlating these α- and β-carbon chemical shifts with various substituent constants will be examined in detail later.

Experimental Section

NMR Spectra. The ^{13}C NMR spectra were recorded at −70 or −80 °C on a Varian CFT-20 spectrometer using 8-mm tubes containing a concentric 3-mm (o.d.) capillary tube of acetone-d_6 and Me_4Si and with 8192 data points, a spectral width of 6500 Hz, and a pulse angle of 45°. Chemical shifts are in parts per million downfield from external Me_4Si.

Precursors. 2-Aryl-2-butanols (**5**) and 4-aryl-4-heptanols (**6**) were prepared by the addition of the corresponding ketone to Grignard reagents prepared from the corresponding substituted bromo- and iodobenzenes. The boiling point data for these precursors are summarized in Table III. All of these compounds gave ^1H NMR and ^{13}C NMR data in accordance with the assigned

Table I. ^{13}C NMR Shifts of 2-Aryl-2-butyl Carbocations 3 in $SbF_5/FSO_3H/SO_2ClF$ at −70 °C

	chemical shift[a]										
substituent (Z)	C^+	$C_{\alpha}(CH_2)$	$C_{\alpha'}(CH_3)$	$C_{\beta}(CH_3)$	C_Z	C_1	C_2	C_3	C_4	C_5	C_6
4-OCH_3	225.1	35.8	27.1	16.3	60.1	133.5	146.0[b]	119.8[c]	182.3	120.1[c]	145.2[b]
4-CH_3	248.3	38.6	30.2	17.5	25.1	137.8	142.6[b]	134.4	175.0	134.4	141.5[b]
4-F	253.0 (5.2)	39.7	31.3	17.4		136.8	147.8[b] (16.6)	121.8 (22.3)	180.8 (294.8)	121.8 (22.3)	146.7[b] (16.6)
4-Cl	256.0	40.2	31.7	17.6		138.0	143.1[b]	134.0	166.1	134.0	142.0[b]
3-CH_3	258.0	40.1, 40.0	31.7	17.8, 17.7	20.7	140.4	142.1,[b] 141.0[c]	144.5	157.5	133.1	140.1[b] 139.3[c]
H	260.4	40.4	32.0	17.7		139.8	142.6[b]	133.3	156.0	133.3	141.4[b]
3-F	266.9	42.1	33.7	18.0, 17.5		141.4 (7.8)	126.0 (22.1), 124.9 (22.8)	164.4 (255.4)	142.3 (21.5)	134.9 (7.2)	139.5 138.3
3-Cl	266.8	42.0	33.6	17.9, 17.6		140.1	139.8,[b] 139.6[c]	140.9	154.1	134.3	139.6[b] 138.9[c]
3-CF_3	270.5	42.8	34.2	17.6, 17.4	d	139.5	145.0[b]	136.7 (35.7)	149.9 (2.6)	134.0	143.7[b]
3,5-Cl_2	272.7	43.7	35.0	17.7		141.3	138.6[b]	140.0	151.8	140.0	137.4[b]
4-CF_3	274.6	43.8	35.1	17.7	122.5 (259.5)	141.0	142.3[b]	129.6[c]	150.5 (34.1)	129.5[c]	141.5[b]
3,5-$(CF_3)_2$	279.0	45.3	36.3	17.2	122.6 (272.9)	135.1	139.8	136.0 (36.5)	144.8	136.0 (36.5)	139.8

[a] In parts per million downfield from Me_4Si (capillary). Assignments for aliphatic carbons are based on SFOR experiments. Assignments for aromatic carbons are based on SFOR experiments and comparison with previously reported values for other systems.[13] ^{13}C–F coupling constants (in hertz) are in parentheses. [b] Assignments may be interchanged. [c] Assignments may be interchanged. [d] CF_3 carbon signals are too weak to measure.

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Table II. ^{13}C NMR Shifts of 4-Aryl-4-heptyl Carbocations 4 in $SbF_5/FSO_3H/SO_2ClF$ at −80 °C

substituent (Z)	chemical shift[a]										
	C^+	$C_{\alpha}(CH_2)$	$C_{\beta}(CH_2)$	$C_{\gamma}(CH_3)$	C_Z	C_1	C_2	C_3	C_4	C_5	C_6
4-OCH_3[b]	228.5	43.8	28.7	15.2	60.9	133.8	145.5	120.0	180.8	120.0	145.5
4-CH_3	246.8	46.0	30.4	15.6	25.1	137.3	141.9	134.5	174.5	134.5	141.9
4-F	250.8 (4.8)	47.2	30.9	15.7		136.3	147.2	122.0	180.6	122.0	147.2
4-Cl	253.6	47.7	31.3	15.9		137.4	142.5	134.1	165.5	134.1	142.5
3-CH_3	255.4	47.5	31.3	15.8	20.7	139.4	139.8[c]	144.7	157.0	133.2	141.4[c]
H	257.4	47.8	31.5	15.8		139.1	141.9	133.4	155.7	133.4	141.9
3-F	262.6	49.4	32.3	16.1		140.4 (7.8)	125.5 (23.8)	164.7 (255.5)	142.0 (23.0)	138.9	135.1 (6.3)
3-Cl	262.4	49.3	32.4, 32.3	16.1		139.9	140.4[c]	139.7	153.7	134.4	139.4[c]
3-CF_3[d]	265.8	49.9	32.7, 32.2	16.1							
3,5-Cl_2	267.2	50.8	33.1	16.3		137.9	140.3	137.9	151.5	137.9	140.3
p-CF_3[d]	268.9	50.8	32.9	16.2							

[a] In parts per million downfield from Me_4Si (capillary). Assignments for aliphatic carbon shifts are based on SFOR experiments and comparison with previously reported assignments for the 4-methyl-4-heptyl carboaction.[16] The aromatic carbon signals are assigned by comparison with the previously reported values for other systems.[13] ^{13}C–F coupling constants (hertz) are in parentheses. Attempts to prepare the 3,5-$(CF_3)_2$ ion were unsuccessful. [b] Ion prepared from the corresponding olefin. [c] Assignments may be interchanged. [d] The ions decompose when the spectrum is run for a longer time (i.e., new small peaks start appearing). The CF_3 and aromatic carbon signals are comparatively weak and difficult to assign.

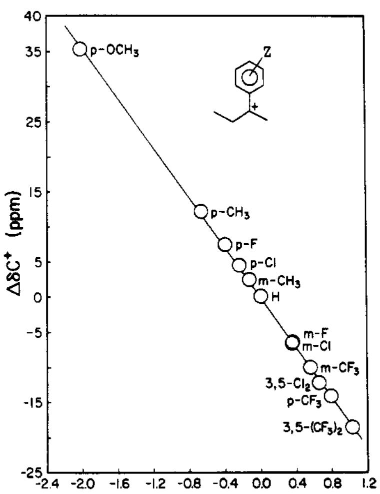


Figure 1. Plot of $\Delta\delta^{C^+}$ against σ^{C^+} values for the 2-aryl-2-butyl cations: correlation coefficient, r = 0.9998; slope ρ^{C^+} = −17.78; standard deviation, SD (ρ^{C^+}) = 0.11; standard deviation, SD ($\Delta\delta^{C^+}$) = 0.27.

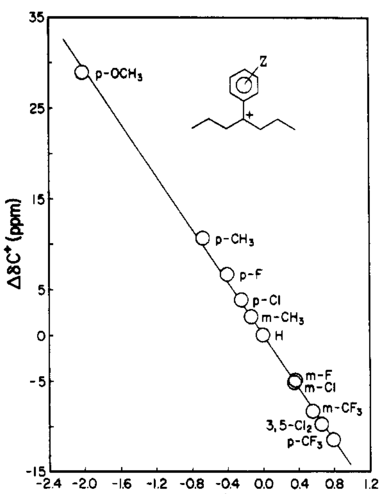
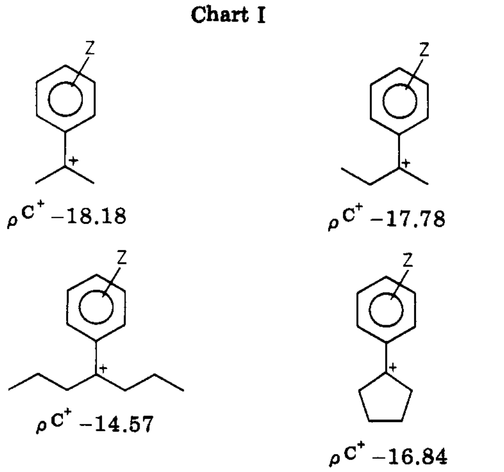


Figure 2. Plot of $\Delta\delta^{C^+}$ against σ^{C^+} values for the 4-aryl-4-heptyl cations: correlation coefficient, r = 0.999; slope, ρ^{C^+} = −14.57; standard deviation, SD(ρ^{C^+}) = 0.17; standard deviation, SD($\Delta\delta^{C^+}$) = 0.39.

Chart I



structures. Satisfactory elemental analyses were obtained for all of the new compounds.

Carbocations. The ions were prepared by slow addition of the appropriate precursor as a solution in SO_2ClF at −78 °C to a solution of FSO_3H/SbF_5 (1:1 molar ratio)/SO_2ClF cooled to −78°

Table III. Boiling Point Data for the 2-Aryl-2-butanols 5 and 4-Aryl-4-heptanols 6[a]

substituent (Z)	alcohol 5		alcohol 6, bp, °C (mm)
	bp, °C (mm)	lit. bp, °C (mm)	
4-OCH_3	76 (0.05)	99 (2.0)[b]	c
4-CH_3	56 (0.1)	78–81 (3.0)[b]	76–77 (0.1)
4-F	50 (0.1)		68–70 (0.1)
4-Cl	60 (0.1)		86–87 (0.1)
3-CH_3	54 (0.1)		76–77 (0.1)
H	54 (0.1)	82 (3.9)[b]	68 (0.1)[d]
3-F	49 (0.1)		72 (0.1)
3-Cl	58 (0.1)		86 (0.1)
3-CF_3	42 (0.05)		62 (0.1)
3,5-Cl_2	78 (0.1)		96 (0.1)
p-CF_3	48 (0.1)	80 (4.0)[b]	72 (0.1)
3,5-$(CF_3)_2$	48 (0.1)		62 (0.1)

[a] Satisfactory analytical data (±0.3% for C, H, Cl, and F) were obtained for all new compounds. [b] Reference 9. [c] Alcohol dehydrated to olefin on distillation. The olefin was characterized as 4-p-anisyl-3-heptene (IR, ^1H NMR, ^{13}C NMR, and elemental analysis). [d] Lit. bp 134–138 °C (18 mm).[17]

C with rapid vortex mixing. The "magic acid", SbF_5/FSO_3H (1:1 molar ratio) concentration in the solution was 3 M. The concentration of the ion based on the alcohol added was ~0.5 M. Transfer of the solutions under nitrogen to an 8-mm NMR tube was achieved via a cooled double-ended syringe, as described previously.[15]

Registry No. **3** (Z = 4-OCH_3), 35144-43-5; **3** (Z = 4-CH_3), 14290-14-3; **3** (Z = 4-F), 51804-44-5; **3** (Z = 4-Cl), 76499-76-8; **3** (Z = 3-CH_3), 76499-77-9; **3** (Z = H), 14290-13-2; **3** (Z = 3-F), 76499-78-0; **3** (Z = 3-Cl), 76499-79-1; **3** (Z = 3-CF_3), 76499-80-4; **3** (Z = 3,5-Cl_2), 76499-81-5; **3** (Z = 4-CF_3), 36043-26-2; **3** (Z = 3,5-$(CF_3)_2$), 76499-82-6; **4** (Z = 4-OCH_3), 76499-83-7; **4** (Z = 4-CH_3), 76499-84-8; **4** (Z = 4-F), 76499-85-9; **4** (Z = 4-Cl), 76499-86-0; **4** (Z = 3-CH_3), 76499-87-1; **4** (Z = H), 76499-88-2; **4** (Z = 3-F), 76499-89-3; **4** (Z = 3-Cl), 76499-90-6; **4** (Z = 3-CF_3), 76499-91-7; **4** (Z = 3,5-Cl_2), 76499-92-8; **4** (Z = *P*-CF_3), 76499-93-9; **5** (Z = 4-OCH_3), 30068-21-4; **5** (Z = 4-CH_3), 5398-04-9; **5** (Z = 4-F), 7119-12-2; **5** (Z = 4-Cl), 3947-53-3; **5** (Z = 3-CH_3), 76499-94-0; **5** (Z = 3-F), 76529-20-9; **5** (Z = 3-Cl), 58977-34-7; **5** (Z = 3-CF_3), 10015-15-3; **5** (Z = 3,5-Cl_2), 76499-95-1; **5** (Z = *P*-CF_3), 10015-16-4; **5** (Z = 3,5-$(CF_3)_2$), 76499-96-2; **6** (Z = 4-CH_3), 76499-97-3; **6** (Z = 4-F), 76499-98-4; **6** (Z = 4-Cl), 76499-99-5; **6** (Z = 3-CH_3), 76500-00-0; **6** (Z = H), 4436-96-8; **6** (Z = 3-F), 76500-01-1; **6** (Z = 3-Cl), 76500-02-2; **6** (Z = 3-CF_3), 76500-03-3; **6** (Z = 3,5-Cl_2), 76500-04-4; **6** (Z = *p*-CF_3), 76500-05-5; **6** (Z = 3,5-$(CF_3)_2$), 76500-06-6; 4-*p*-anisyl-3-heptene, 6465-99-2.

Carbon-13 Nuclear Magnetic Resonance Studies of Carbocations. 5.[1] Effect of Increasing Electron Demand on the Carbon-13 Chemical Shifts of 3-Aryl-3-pentyl and 2-Aryl-2-adamantyl Carbocations. Correlation of $\Delta\delta^{C^+}$ with Enhanced Substituent Constants σ^{C^+}

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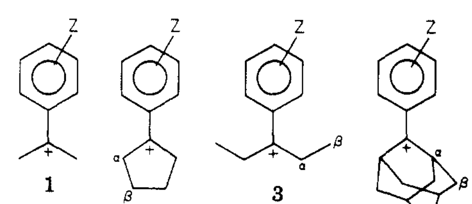
The ^{13}C chemical shifts for a range of meta- and para-substituted 3-phenyl-3-pentyl and 2-phenyl-2-adamantyl carbocations have been measured in $FSO_3H/SbF_5/SO_2ClF$ solutions. The cationic carbon substituent chemical shifts ($\Delta\delta^{C^+}$) show only a fair correlation with σ^+ constants, but when plotted against the new σ^{C^+} constants, excellent linear correlations are obtained. The 3-aryl-3-pentyl system gives a correlation coefficient of $r = 0.999$ with a slope of $\rho^{C^+} = -17.17$, and the 2-aryl-2-adamantyl system gives $r = 0.998$ with $\rho^{C^+} = -16.08$. These nearly perfect linear correlations, together with that realized previously for 1-aryl-1-cyclopentyl cations, confirm the validity and usefulness of the enhanced substituent constants.

The correlation of ^{13}C chemical shifts with Hammett–Brown σ^+ constants has received considerable attention over the past few years.[2-4] On the assumption (i) of a late transition state for the solvolysis of cumyl chlorides in acetone[5] and (ii) that ^{13}C chemical shifts were linearly proportional to charge density, it was not unreasonable to expect the σ^+ constants to correlate ^{13}C shifts of the fully formed carbocations in superacids. Thus Olah and coworkers noted an approximate linearity in the plot of cationic carbon shifts (δ^{C^+}) against σ^+ for a series of substituted *tert*-cumyl cations.[3] However, reinvestigation of these cations showed that the correlation was only fair ($r = 0.967$) and that the line of best fit failed to pass through the point for the parent *tert*-cumyl cation (**1**, Z = *p*-H).[4] We suggested that the problem was due to our failure to allow for the extra electron demand in these fully formed cations compared to that for the solvolytic transition states. That is, there is enhanced charge delocalization in the cations containing electron-donating substituents. Consequently, we proposed a new set of "super sigma" values, σ^{++}, for correlation of cationic carbon shifts which were derived by extrapolating the line of best fit for electron-withdrawing substituents through the origin (i.e., for δ^{C^+} of **1** (Z = *p*-H), $\sigma^+ = 0$).

As the data in the earlier studies were relatively few, we have recently obtained the ^{13}C spectra of an extended range of both meta- and para-substituted *tert*-cumyl cations.[1] When plotted against σ^+_m, the cationic carbon substituent chemical shifts ($\Delta\delta^{C^+}$)[6] for the meta cations give a good correlation ($r = 0.990$, $\sigma^+ = -18.18$). Using the original approach of Brown and Okamoto,[7] we therefore used the slope of the line (−18.18) for the meta substituents to calculate new constants, values of which would place the $\Delta\delta^{C^+}$ values for the para derivatives on the line. Thus a modified Hammett–Brown constant was derived (eq 1),

$$\Delta\delta^{C^+} = \rho^{C^+}\sigma^{C^+} \quad (1)$$

where σ^{C^+} is the enhanced substituent constant having the following values: −2.02, *p*-OCH_3; −0.67, *p*-CH_3; −0.40, *p*-F; −0.24, *p*-Cl; −0.19, *p*-Br; 0.79, *p*-CF_3; 0.13, *m*-CH_3; −0.14, *m*-$CH(CH_3)_2$; 0.35, *m*-F; 0.36, *m*-Cl; 0.33, *m*-Br; 0.56, *m*-CF_3; 0.66, 3,5-Cl_2; 1.03, 3,5-$(CF_3)_2$. When applied to the data for the 1-aryl-1-cyclopentyl cations **2**, the σ^{C^+} constants give an excellent correlation: $r = 0.999$, $\sigma^{C^+} = -16.84$.



1 **2** **3** **4**

We now report similar excellent correlations for the plots against $\Delta\delta^{C^+}$ for two different systems, the 3-aryl-3-pentyl (**3**) and the multicyclic 2-aryl-2-adamantyl (**4**) cations.

(1) For Part 4, see: Brown, H. C.; Kelly, D. P.; Periasamy, M. *Proc. Natl. Acad. Sci. U.S.A.* **1980**, *77*, 6956.
(2) Kelly, D. P.; Spear, R. J. *Aust. J. Chem.* **1977**, *30*, 1993 and references therein.
(3) Olah, G. A.; Porter, R. D.; Jeuell, C. L.; White, A. M. *J. Am. Chem. Soc.* **1972**, *94*, 2044.
(4) Kelly, D. P.; Spear, R. J. *Aust. J. Chem.* **1978**, *31*, 1209.
(5) Stock, L. M.; Brown, H. C. *Adv. Phys. Org. Chem.* **1963**, *1*, 35.
(6) In order to reproduce the form of the Hammett–Brown plot, we define $\Delta\delta^{C^+} = [\delta^{C^+}(R = H) - \delta^{C^+}(R \neq H)]$ ppm (see ref 1).
(7) Brown, H. C.; Okamoto, Y. *J. Am. Chem. Soc.* **1958**, *80*, 4979.

