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Empirical Quantitative Correlation of Substituent Size with Proton Nuclear Magnetic Resonance Chemical Shift Difference between Nonequivalent Geminal Methylene Protons of Hindered N-Substituted Acetanilides and Difluorooxyboranes

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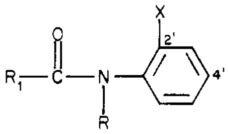
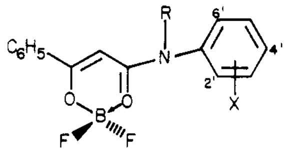
In *N*-ethyl- and *N*-benzyl-substituted difluorooxyboranes nonequivalence of the geminal methylene protons is exhibited in the ^{1}H NMR ($CDCl_3$) when the neighboring ortho X substituent on the arylamido moiety is sufficiently large. The observed chemical shift difference ($\Delta\delta_{AB}$) correlates quantitatively with the van der Waals radius (or a specially assigned "effective radius", r_X) of the X substituent, and the linear relationship ($\Delta\delta_{AB} = ar_X + b$) is rationalized in terms of a preferred conformation for the difluorooxyborane. The correlation also extends to the hindered N-substituted acetanilides.

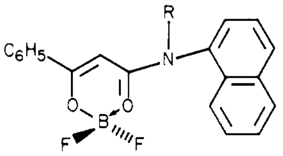
The chemical shift difference ($\Delta\delta_{AB}$) between nonequivalent methylene protons in hindered amides such as **1–3** has been investigated extensively,[1-4] and the subject has been reviewed.[5-7] Siddall[2] has observed that the degree of nonequivalence of the methylene protons for the *N*-ethyl derivatives is evidently very much a function of size of the groups R_1 and X: increasing the sizes of these moieties increases the value of $\Delta\delta_{AB}$ almost without exception. We have now found, from study with a series of hindered *N*-benzyl (**5**) and *N*-ethyl (**6**) difluorooxyboranes (Table I), a simple, empirical expression which correlates $\Delta\delta_{AB}$ quantitatively with the size of the substituent X in **5** and **6** and in the aforementioned amides.



1, R = $(CH_3)_2CHCH_2$; R_1 = CH_3
2, R = C_2H_5; R_1 = $(CH_3)_2CH$
3, R = C_2H_5; R_1 = CH_3
4, R = C_2H_5; R_1 = $C_6H_5COCCl_2$



5, R = $C_6H_5CH_2$
6, R = C_2H_5
7, R = CH_3
8, R = H



9, R = $C_6H_5CH_2$
10, R = C_2H_5

a, X = 3',5'-diCH_3; **b**, X = 3'-Cl; **c**, X = 2'-CH_3; **d**, X = 2'-C_2H_5; **e**, X = 2'-CH_3O; **f**, X = 2'-F; **g**, X = 2'-Cl; **h**, X = 2'-Br; **i**, X = 2'-C_6H_5; **j**, X = 4'-Br, 2'-Cl, 3',5'-diCH_3

In the ^{1}H NMR spectra of the hindered **5**, the benzylic protons were exhibited as a typical AB quartet, while in the analogous **6**, the methylene protons formed a symmetrical multiplet, consisting of two sets of six lines constituting the AB part of an apparent ABX_3 system with overlap of some signals. For purposes of comparison, the meta-substituted **5a** (X = 3',5'-diCH_3) and **5b** (X = 3'-Cl) showed no detectable barrier to rotation ($\Delta\delta_{AB}$ = 0) and neither did the *N*-methyl group in **7** (Table II). The respective $\Delta\delta_{AB}$ magnitudes in **5** and **6** were clearly a function of both the size and the nature of the corresponding X substituent. Thus, in **5**, the $\Delta\delta_{AB}$ values, in the main, followed the intuitive ordering in size of X, increasing in the sequence F < OCH_3 < Cl < Br < C_6H_5, with the notable exceptions in this trend of the CH_3 and C_2H_5 groups (Table II). In the *N*-ethyl derivatives **6**, however, $\Delta\delta_{AB}$ varied as expected[2] in all instances (Table II).

The apparent discontinuities in the trend of $\Delta\delta_{AB}$ observations in **5** disappear on taking cognisance of two types of X substituent and R–X interactions. Thus, "α"-type X substituents, specifically alkyl groups, interact with all R (C_2H_5, $C_6H_5CH_2$) in a conventional "steric" manner, while "β"-type groups, i.e., those possessing lone pair(s) and/or π electrons (such as halogen, phenyl, methoxy), experience, in addition, a superimposed "electronic" repulsion from a similarly endowed R ($C_6H_5CH_2$ in **5**).[8] In consequence, the $\Delta\delta_{AB}$, which is a function of substituent "size" (vide infra), is greater, in, for example, **5g** (X = Cl) than in **5c** (X = CH_3), despite the Cl atom being the "smaller" substituent.

A simple linear regression analysis of the observed $\Delta\delta_{AB}$ with the size (r_X) of the X substituent in the two series **5** and **6** revealed that the variables were correlated satisfactorily by the relationship shown in eq 1.

$$\Delta\delta_{AB} = ar_X + b \qquad (1)$$

In eq 1, the r_X of simple X (F, Cl, Br, I, CH_3) is measured by the van der Waals radius (Å) and that of more complex X (such as C_2H_5 and C_6H_5) by an assigned "effective radius" which was selected to give the best overall agreement with the experimental data (Table II); *a* and *b* are constants for a particular amide series. The experimental $\Delta\delta_{AB}$ values and those calculated from eq 1 are compared in Table II and the correspondence is surprisingly good, considering that no provision is made for other factors[9] which affect the magnitude of geminal nonequivalence.

Equation 1 and other findings with **5** and **6** may be rationalized in terms of a preferred conformation for these compounds shown (Figure 1) with greater stereochemical

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[1] T. H. Siddall, III, and C. A. Prohaska, *J. Am. Chem. Soc.*, **88**, 1172 (1966).

[2] T. H. Siddall, III, *J. Org. Chem.*, **31**, 3719 (1966).

[3] T. H. Siddall, III, and W. E. Stewart, *J. Org. Chem.*, **34**, 2927 (1969).

[4] Y. Shvo, E. C. Taylor, K. Mislow, and M. Rabin, *J. Am. Chem. Soc.*, **89**, 4910 (1967).

[5] W. E. Stewart and T. H. Siddall, III, *Chem. Rev.*, **70**, 517 (1970).

[6] I. O. Sutherland, *Annu. Rep. NMR Spectrosc.*, **4**, 200 (1971).

[7] T. H. Siddall, III and W. E. Stewart, *Prog. NMR Spectrosc.*, **5**, 33 (1969).

[8] Siddall and Prohaska[1] have noted a similar distinction between steric and electronic effects for the pronounced interaction of the N-substituent with the CO group in certain amides.

[9] W. B. Jennings, *Chem. Rev.*, **75**, 307 (1975).

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Table I. Analytical Data of Difluorooxyboranes 5, 6, 7, 9, and 10

			anal.					
			calcd			found		
compd	mp, °C	molecular formula	C	H	N	C	H	N
5b	155-157	$C_{22}H_{17}BClF_2NO_2$	64.19	4.16	3.40	64.39	4.19	3.37
5c	129-130	$C_{23}H_{20}BF_2NO_2$	70.61	5.15	3.58	70.66	5.30	3.63
5d	160-161	$C_{24}H_{22}BF_2NO_2$	71.13	5.47	3.46	71.17	5.60	3.59
5e	156-157	$C_{23}H_{20}BF_2NO_3$	67.84	4.95	3.44	67.38	4.78	3.25
5f	172-173	$C_{22}H_{17}BF_3NO_2$	66.86	4.34	3.55	66.53	4.29	3.49
5g	132-133	$C_{22}H_{17}BClF_2NO_2$	64.19	4.16	3.40	64.53	4.27	3.35
5h	156-157	$C_{22}H_{17}BBrF_2NO_2$	57.93	3.76	3.07	57.77	3.87	3.00
5i	151-153	$C_{28}H_{22}BF_2NO_2$	74.19	4.89	3.09	74.41	4.57	2.87
6c	165-166	$C_{18}H_{18}BF_2NO_2$	65.68	5.51	4.26	65.81	5.67	4.15
6e	120-121	$C_{18}H_{18}BF_2NO_3$	62.64	5.26	4.06	62.61	5.16	4.08
6f	155-156	$C_{17}H_{15}BF_3NO_2$	61.29	4.54	4.21	61.47	4.62	3.87
6g	129	$C_{17}H_{15}BClF_2NO_2$	58.41	4.33	4.01	58.36	4.36	4.13
6h	133-134	$C_{17}H_{15}BBrF_2NO_2$	51.82	3.84	3.56	52.12	3.83	3.57
6i	162-163	$C_{23}H_{20}BF_2NO_2$	70.61	5.15	3.58	70.37	4.95	3.71
7g	151	$C_{16}H_{13}BClF_2NO_2$	57.27	3.90	4.18	57.58	4.36	4.12
7i	185	$C_{22}H_{18}BF_2NO_2$	70.05	4.81	3.71	70.28	4.79	3.36
9	184-185	$C_{26}H_{20}BF_2NO_2$	73.09	4.72	3.28	73.55	4.62	3.36
10	177-178	$C_{21}H_{18}BF_2NO_2$	69.07	4.97	3.84	69.52	4.86	3.95

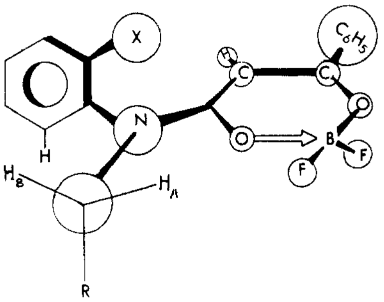

Figure 1. Lowest energy (preferred) conformation for hindered **5** and **6**.

explicitness than was feasible for the related conformer of **4j**.[10] Specifically, whereas the relative atomic dispositions in the flexible $C_6H_5COCCl_2$ appendage in **4j** were a matter of conjecture that of the difluorooxyborane cycle, which incorporates the corresponding (albeit modified) C chain in **5** and **6**, can be more easily discerned and specified.

Figure 1 shows an exo (coordinated) amide CO group[10] and features the plane of the benzene ring approximately perpendicular to that of the difluorooxyborane cycle and with the substituents R and X suitably staggered for minimal interactions.[11] In support of and explicable in terms of the preferred conformer, the ^1H NMR of hindered **5** showed a one-proton aromatic absorption near δ 6.7–6.8 (absent in **6** and **7**), attributed to shielding of the 6′-proton by the proximate benzyl group. In Figure 1, the methylene protons, H_A and H_B, reside in disparate magnetic environments, and this is reflected in the ^1H NMR by the $\Delta\delta_{AB}$ exhibited in the hindered **5** and **6**. Moreover, a consequence of coordination of the CO group in the latter structures is reduced deshielding of the H_A proton, leading to the expectation of a smaller $\Delta\delta_{AB}$ than that in the parent benzoylacetanilides.

The proportion of preferred conformer (Figure 1) in the conformer population (i.e., ρ) is expected to increase with the size of either or both R and X. A simplistic rationalization of eq 1 supposes that ρ varies directly with the "extent of steric hindrance" between R and X in **5** and **6** and that a measure of the latter is the difference between the combined "size" of X and R (i.e., $r_X + r_R$) and a magnitude, r_H, pertaining to incipient hindrance in the molecule.[12] Accordingly, $\rho \propto [(r_X + r_R) - r_H]$. Another assumption is that the less favored conformers in the population make hardly any contribution to the magnitude of $\Delta\delta_{AB}$ in **5** and **6**, perhaps because of intrinsic factors and/or owing to fortuitous cancellation of opposing effects. This permits ρ to be equated with the observed $\Delta\delta_{AB}$[9] and leads to $\Delta\delta_{AB} \propto [r_X - (r_H - r_R)]$. The value of r_H is determined by the spacial interrelationships of the various groups around the N atom and is expected to remain more or less the same in a particular series having specific N substituents, as in **5**. Thus, with the proviso that the term $(r_H - r_R)$ is invariant in a series, and introduction of an appropriate proportionality factor (fortuitously $\simeq 1$),[13] $\Delta\delta_{AB}$ is seen to vary with r_X as in eq 1.

This simplistic derivation, in the absence of a more rigorous treatment, was useful in helping to coordinate a number of diverse concepts and observations. In particular, since the relative spatial orientations of the benzene ring bearing X, the amide group, and the methylene protons in Figure 1 are similar to those in the model proposed[2] for amides such as **3**, it was expected that eq 1 would be valid also for the latter compounds. Gratifyingly, good linear correlations were confirmed by simple regression analysis in the series of amides **1**–**3**, and the results are collected in Table III.

Application of eq 1 offers a means of estimating the size of a substituent appropriate to steric hindrance in amides as opposed to an "A" value which pertains to the cyclohexane system. For example, the I atom (2.15 Å) is significantly "bigger" than Cl (1.80 Å) in the present cir-

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[10] B. Staskun, *J. Org. Chem.*, **45**, 2482 (1980).

[11] The postulated relative spatial orientations depicted in Figure 1, as well as the individual B (sp^3) and N (sp^2) hybridizations, are supported from a subsequent X-ray structure determination of the related difluorooxyborane from *N*-ethyl-2′-chloroferrocenoylacetanilide and BF_3 (J. S. Field, private communication).

[12] This "extent of steric hindrance" is clearly analogous to the "interference value" in hindered biphenyls [R. Adams and H. C. Yuan, *Chem. Rev.*, **12**, 285 (1933)].

[13] Values of $\Delta\delta_{AB}$ approximating closely those derived from eq 1 are generated from the simplified expression $\Delta\delta_{AB} = r_X - c$ (c = 0.65 for **5**; 1.31 for **6**; 0.79 for **1**; 1.14 for **2**; 1.15 for **3**). In this latter equation, the relation $c = (r_H - r_R)$ is convenient for rationalizing other observations in Tables II and III. Thus, it may be inferred that in two series of amides with a common R_1 (such as **5** and **6** or **1** and **3**), the one bearing the "bigger" R substituent will show the more substantial $\Delta\delta_{AB}$ values; this result follows [from $c = (r_H - r_R)$] when the geometry around the N atom (and hence r_H) is much the same in both instances. Further, it has been reported that $\Delta\delta_{AB}$ is roughly proportional to the "A" value of the R_1 group,[4] and this leads to the proposal that a "large" R_1 should correlate with a "small" r_H.

Table II. Experimental and Calculated ^{1}H NMR[a] Chemical Shift Differences ($\Delta\delta_{AB}$) between Methylene Protons in Difluorooxyboranes 5, 6, 7, 9, and 10

compd	X	r_X[b]	methylene (benzylic) protons: H_A[c]	methylene (benzylic) protons: H_B[c]	$\Delta\delta_{AB}$ ($H_A - H_B$): exptl	$\Delta\delta_{AB}$ ($H_A - H_B$): calcd[d]	H_C	other (multiplicity, no. of protons, assignment)
5b			5.0	5.0	0		5.36	6.7–7.8 (m, 14 H, Ar H)
5c	CH_3	2.0	5.33, 5.12 (5.23)	4.76, 4.53 (4.65)	0.58		5.21	1.96 (s, 3 H, $ArCH_3$), 6.77 (dd, 1 H, 6′-H), 7.0–7.7 (m, 13 H, Ar H)
5d	C_2H_5	2.15[e]	5.45, 5.22 (5.34)	4.67, 4.46 (4.57)	0.77		5.22	1.07 (t, 3 H, $J = 7.5$ Hz, $ArCH_2CH_3$), 2.37 (q, 2 H, $J = 7.5$ Hz, $ArCH_2CH_3$), 6.72 (dd, 1 H, 6′-H), 7.0–7.7 (m, 13 H, Ar H)
5e	CH_3O	1.52[f]	5.49, 5.26 (5.38)	4.59, 4.36 (4.48)	0.90	0.90	5.33	3.68 (s, 3 H, OCH_3), 6.7–7.7 (m, 14 H, Ar H)
5f	F	1.35	5.46, 5.22 (5.34)	4.72, 4.50 (4.61)	0.73	0.75	5.36	6.7–7.7 (m, 14 H, Ar H)
5g	Cl	1.80	5.71, 5.48 (5.60)	4.50, 4.26 (4.38)	1.22	1.15	5.22	6.75 (dd, 1 H, 6′-H), 6.9–7.7 (m, 13 H, Ar H)
5h	Br	1.95	5.80, 5.55 (5.68)	4.45, 4.21 (4.33)	1.35	1.28	5.22	6.75 (m, 1 H, 6′-H), 7.0–7.9 (m, 13 H, Ar H)
5i	C_6H_5	2.45[e]	5.42, 5.18 (5.30)	3.70, 3.46 (3.58)	1.72	1.73	5.60	6.71 (dd, 1 H, 6′-H), 6.9–7.8 (m, 18 H, Ar H)
9	C_4H_4	1.95[e]	5.80, 5.56 (5.68)	4.61, 4.37 (4.49)	1.19	1.28	5.15	6.90 (m, 1 H, 6′-H), 7.2–8 (m, 16 H, Ar H)

compd	X	r_X[b]	methylene protons: multiplicity [first signal, twelfth signal (center)]	$\Delta\delta_{AB}$[g]: exptl	$\Delta\delta_{AB}$[g]: calcd[h]	H_C	other (multiplicity, no. of protons, assignment)
6c	CH_3	2.0	12-line multiplet [4.50, 3.27 (3.88)]; lines 6 and 7 separated by ~3 Hz	0.62	0.71	5.22	1.27 (t, 3 H, $J = 7.2$ Hz, NCH_2CH_3), 2.22 (s, 3 H, $ArCH_3$), 7.0–7.7 (m, 9 H, Ar H)
6d	C_2H_5	2.15[e]	12-line multiplet [4.60, 3.20 (3.90)]; lines 6 and 7 separated by ~14 Hz)	0.80	0.85	5.25	1.30 (t, 3 H, $J = 7.5$ Hz, CH_2CH_3), 1.22 (t, 3 H, $J = 7.5$ Hz, CH_2CH_3), 2.55 (q, 2 H, $J = 7.5$ Hz, $ArCH_2CH_3$), 7.0–7.7 (m, 9 H, Ar H)
6e	CH_3O	1.52[f]	apparent 10-line multiplet centered near δ 3.85	~0.4[i]	0.26	5.33	1.21 (t, 3 H, $J = 7$ Hz, NCH_2CH_3), 3.79 (s, 3 H, OCH_3), 7–7.7 (m, 9 H, Ar H)
6f	F	1.35	quartet (3.93)	0	0.10	5.34	1.25 (t, 3 H, $J = 7.0$ Hz, NCH_2CH_3), 3.93 (q, 2 H, $J = 7.0$ Hz, NCH_2CH_3), 7.1–7.7 (m, 9 H, Ar H)
6g	Cl	1.80	12-line multiplet [4.47, 3.47 (4.0)]; lines 6 and 7 separated by ~7 Hz	0.52	0.52	5.25	1.28 (t, 3 H, $J = 7.0$ Hz, NCH_2CH_3), 7.2–7.7 (m, 9 H, Ar H)
6h	Br	1.95	12-line multiplet [4.50, 3.26 (3.88)]; lines 6 and 7 separated by ~5 Hz	0.64	0.66	5.15	1.25 (t, 3 H, $J = 7$ Hz, NCH_2CH_3), 7–7.8 (m, 9 H, Ar H)
6i	C_6H_5	2.45[e]	12-line multiplet [4.25, 2.48 (3.38)]; lines 6 and 7 separated by ~37 Hz	1.18	1.13	5.6	1.05 (t, 3 H, $J = 7$ Hz, NCH_2CH_3), 7.1–7.8 (m, 14 H, Ar H)
6j	Cl	1.80	12-line multiplet [4.5, 3.4 (3.9)]; lines 6 and 7 separated by ~12 Hz	0.61	0.52	5.28	1.25 (t, 3 H, $J = 7.0$ Hz, NCH_2CH_3), 2.47 (s, 3 H, Ar CH_3), 2.66 (s, 3 H, $ArCH_3$), 7.07 (s, 1 H, 6′-H), 7.3–7.7 (m, 5 H, Ar H)
10	C_4H_4	1.95[e]	12-line multiplet [4.63, 3.38 (4.0)]; lines 6 and 7 separated by ~8 Hz	0.67	0.66	5.14	1.29 (t, 3 H, $J = 7$ Hz, NCH_2CH_3), 7–8.1 (m, 12 H, Ar H)
7g	Cl	1.80		0		5.29	3.45 (s, 3 H, NCH_3), 7.1–7.8 (m, 9 H, Ar H)
7i	C_6H_5	2.45		0		5.57	3.07 (s, 3 H, NCH_3), 7.1–7.8 (m, 14 H, Ar H)

[a] Approximately 10% solutions in $CDCl_3$. Data are reported as δ in parts per million from Me_4Si; spectra determined at about 36 °C. [b] van der Waals radius (Å) of X ("Handbook of Chemistry and Physics", 57th ed., R. C. Weast, Ed., CRC Press, Cleveland, OH, 1976–1977). [c] Downfield signal; upfield signal (center). [d] $0.887r_X - 0.446$; $r^2 = 0.966$. [e] Assigned "radius" (Å). [f] van der Waals radius (Å) of O atom; a value of 1.52 Å [cf. J. P. Idoux, J. M. Scandrett, and J. A. Sikorski, *J. Am. Chem. Soc.*, **99**, 4577 (1977)] seems more appropriate than 1.4 Å.[b] [g] Measured distance between corresponding signals of the halves of the AB spectrum (i.e., first and seventh lines) in parts per million. [h] $0.935r_X - 1.16$; $r^2 = 0.936$. [i] Measured distance between first and fifth lines (in parts per million).

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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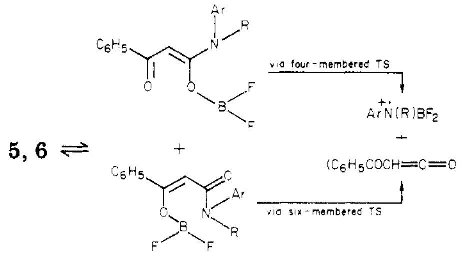

Structural Effects in Solvolytic Reactions. 35. Carbon-13 Nuclear Magnetic Resonance Studies of Carbocations. Effect of Increasing Electron Demand on the Carbon-13 Nuclear Magnetic Resonance Shifts in 2-Aryl-2-butyl and 4-Aryl-4-heptyl Carbocations. Correlation of the Data by a New Set of Substituent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