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A New Substituent Constant, σ^{c+} ; a Fit for π -Participation in Modified Hammett-Brown Equation

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A set of substituent constants, σ^+ , has been widely used comparing the stability of carbocation in super acid condition. Plotting of ^{13}C chemical shifts of cationic carbon ($\Delta\delta^{c+}$) against σ^+ constants yields an excellent correlation with a good correlation coefficient ($r=0.999$) for a cyclopentyl cation system. But these σ^+ constants show poor linearity in norbornenyl cations that well known to show homoallylic stabilization in a cationic condition. We calculated the new substituent constant, $\sigma^{c+\pi}$, and found that the new substituent constants give an excellent correlation in π - and $\pi\sigma$ -participating cation systems.

Introduction

The correlation of ^{13}C chemical shifts with Hammett-Brown σ^+ constants has received considerable attention over past few years. On the assumption that ^{13}C chemical shifts were linearly proportional to charge density, it was not unreasonable to expect the σ^+ constants to correlate ^{13}C chemical shifts of the fully formed carbocations in superacids. Accordingly, numerous attempts seeking to correlate the ^{13}C chemical shifts of the cationic carbons with Hammett-Brown σ^+ constants have been reported.

For example, Olah and co-worker¹ originally reported approximated linearity in the plot of C^+ chemical shifts of the substituted *tert*-cumyl cations ($\Delta\delta^{c+}$) against Hammett-Brown σ^+ constants. In a reinvestigation of the behavior of the substituted *tert*-cumyl cations, Kelly and Spear² observed an even lower correlation coefficient, $r=0.967$.

The use of Hammett-Brown σ^+ constants have shown to be inappropriate for this purpose. Thus Brown and coworkers³ developed the following modified Hammett-Brown equation,

$$\Delta\delta^{c+} = \rho^{c+} \cdot \sigma^{c+}$$

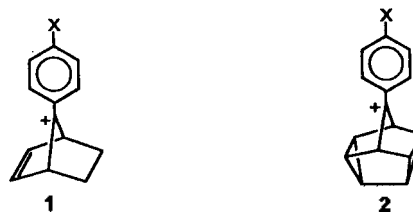
where ρ^{c+} is the slope obtained from the plot of $\Delta\delta^{c+}$ against σ_m^+ values of the *tert*-cumyl cations. Using this equation, their calculated the new substituent constants σ^{c+} .

A plot of σ^{c+} values against $\Delta\delta^{c+}$ values of the 1-aryl-1-cyclopentyl cations revealed an excellent correlation, with a correlation coefficient $r=0.999$.⁴ Therefore, a set of substituent constants, σ^{c+} , has been widely used for investigation of structure-reactivity relationship in acyclic, cyclic, and polycyclic cation systems.⁵

However, these new σ^{c+} constants reveals only a fair fit

in cation systems with neighboring π -participating groups. For example, when plotted against σ^{c+} , the cationic carbon substituent chemical shifts ($\Delta\delta^{c+}$) of 7-arylnorbornenyl cations **1** give a poor correlation ($r=0.961$), in which the cation **1** was well-known the presence of π -participation.⁶

We wish now to report the calculated the new σ^{c+} s constants and examined on their ability to correlate $\Delta\delta^{c+}$ values for π - and $\pi\sigma$ -participating cations such as 7-aryl-norbornenyl and 9-aryl-pentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}] cation **2**.



Results and Discussion

7-Arylnorbornen-7-ol derivatives were prepared by the addition of the ketone to the *Grignard* reagents that were prepared from the *m*-CH₃, *m*-F, *m*-Cl, *m*-CF₃, *m*-OCH₃, *p*-CH₃, *p*-OCH₃, *p*-Cl, *p*-F and *p*-H substituted bromobenzenes. The cations **1** were prepared by adding a measured quantity of the corresponding alcohol to the FSO₃H/SO₂ClF solution at $-120\text{ }^\circ\text{C}$, and ^{13}C NMR spectra of the cations were recorded at $-90\text{ }^\circ\text{C}$ and $-100\text{ }^\circ\text{C}$. The ^{13}C NMR chemical shifts of cationic carbon in these cations and $\Delta\delta^{c+}$ values summarized in Table 1 and 2.

When the $\Delta\delta^{c+}$ values for the *para*-substituted 7-arylnorbornenyl cations are plotted against the substituent constants σ^{c+} , the results are unsatisfactory with $r=0.961$, $\rho^{c+} =$

Table 1. ^{13}C NMR Chemical shifts of *m*-substituted 7-Arylnorbornenyl Cations

Substituent	<i>m</i> -CF ₃	<i>m</i> -F	<i>m</i> -Cl	<i>m</i> -OCH ₃	H
C ₇ ⁺	85.7	90.7	90.1	88.3	111.4
$\Delta\delta^+$	25.7	20.7	21.3	23.1	0

Table 2. ^{13}C NMR Chemical shifts of *p*-substituted 7-Arylnorbornenyl Cations

Substituent	<i>p</i> -Cl	<i>p</i> -F	<i>p</i> -CH ₃	<i>p</i> -OCH ₃	H
C ₇ ⁺	110.2	127.1	167.4	217.0	111.4
$\Delta\delta^+$	1.2	-15.7	-56	-105.6	0

Table 3. New Substituent Constants

Substituent	OCH ₃	CH ₃	H	F	Cl	CF ₃
σ^+_{sm}	0.387	0	0.347	0.363	0.434	
σ^+_{sp}	-0.778	-0.311	0	-0.073	0.114	0.612

55.174. Similar treatment of the data for the *meta*-substituted 7-arylnorbornenyl cations results in a somewhat satisfactory correlation against σ^+_{sm} , with $r=0.972$, $\rho^+=59.03$.

We used the previously reported methods in the development of σ^+ constants in order to obtain new substituent constants. We utilized the slope 59.03 of the line established by the *meta*-substituent derivatives. And, σ^+ values calculated by using the following equation.

$$\sigma^+_{s} = \rho^+ / \Delta\delta^+$$

The substituent constants obtained from this method are symbolized to the σ^+_{sp} for *para*-derivatives, the σ^+_{sm} for *meta*-derivatives, and these substituent constants are summarized in Table 3.

In order to investigate the validity and usefulness for these new substituent constants, σ^+_{s} , we have chosen the *Coates* cation system. Solvolysis of the *Coates* cation **2** proceeds with an exceptionally large rate (10^{12}) compared with that of the related 7-norbornyl derivatives. This major rate enhancement was attributed to the π -participation by the remote cyclopropyl group leading to the formation of a tris (homocyclopropenium) cation intermediate. However, it is well known that the degree of charge delocalization into neighboring cyclopropyl group in cation intermediates depends substantially on the geometric arrangement.

We reported previously the results of a ^{19}F NMR study on *Coates* cation, indicating the extreme stability compared to the 7-norbornyl cation.⁷

When we plotted the $\Delta\delta^+$ value of *Coates* cation against σ^+ constants (old), the results showed poor correlation, $r=0.902$, $\rho^+=30.43$. However the plot of these values against the σ^+ constants (new) revealed an excellent correlation with $r=0.999$ and $\rho^+=21.43$.

In the present ^{13}C NMR study, we confirm the conclusion that a set of new substituent constants (σ^+_{s}) can be used for comparing the relative stability of π - and π -participating

cation systems, but more studies of the utility for these new constants are in progress in our Lab.

Experimental Section

NMR Spectra. The ^{13}C NMR spectra were recorded between -90°C and -100°C on a Bruker AC-80 NMR spectrometer operating at 20.1 MHz in the FT mode in 10 mm tube. Data was accumulated by using 32768 data point, spectral widths of 5000 or 6000 Hz, and pulse angles of 60° . Chemical shifts reported in ppm from internal TMS and CD_2Cl_2 for cation solution. Assignment was based on DEPT pulse program.

Carbocations. Each cation was prepared by slow addition of solution of corresponding alcohol in dichloromethane- d_2 to a rapidly stirred solution of $\text{FSO}_3\text{H}/\text{SO}_2\text{ClF}$ at -120°C using an ion generating apparatus. The concentration of the ion based on the precursor added was in the range 0.3-0.5 mM and were generally colored yellow-brown.

Synthesis of Alcohols. A substituted 7-aryl norbornen-7-ol and 9-aryl-norsnoutanon was synthesized by reaction of ketone precursor with the *Grignard* reagent prepared from the corresponding bromobenzenes, and was purified by column chromatography. All of the alcohols gave satisfactory ^1H and ^{13}C NMR, IR, and mass spectra.

Synthesis of Ketone. Bicyclo[2.2.1]hepten-7-one was prepared by *Diels-Alder* reaction from hexachlorocyclopentadiene and ethylene over 4 reaction steps.⁸ ^1H NMR (CDCl_3); δ 1.03 (m, 2H), 1.82 (m, 2H), 2.85 (m, 2H), 5.82 (t, 2H). Pentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]nona-9-on (Norsnoutanon) was prepared from α,β -dibromosuccinic acid over 10 reaction steps.⁹ ^1H NMR (CDCl_3); δ 1.20 (m, 4H), 2.33 (m, 2H), 2.43 (m, 2H). ^{13}C NMR (CDCl_3); δ 29.15, 33.14, 41.39, 204.58. IR (CCl_4 , film) cm^{-1} ; 3055 (w), 3017 (m), 1170 (s).

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