J. Org. Chem. 1990, 55, 5375-5386

Variation of NMR Isotope Shifts with Increasing Electron Demand in Carbocations

David A. Forsyth,*,† Chitchanun Panyachotipun,† Yi Pan,† Adel M. Moussa,‡ and Abdel-Hamid A. Youssef‡

Department of Chemistry, Northeastern University, Boston, Massachusetts 02115, and Chemistry Department, Faculty of Science, Alexandria University, Alexandria, Egypt

Received April 12, 1990

The behavior of NMR isotope shifts in various carbocations has been examined as a function of aryl substituents. This combination of the "tool of increasing electron demand" (TIED) with NMR isotope shifts has been applied to the following stable carbocation systems: 2-aryl-2-propyl-*1,1,1,3,3,3*-d_6 cations, **1**-d_6; 2-aryl-2-norbornyl-*3,3*-d_2 cations, **2**-d_2; 2-aryl-2-bicyclo[2.2.2]octyl-*3,3*-d_2 cations, **3**-d_2; 2-aryl-2-bicyclo[2.1.1]hexyl-*3,3*-d_2 cations, **4**-d_2; 2-aryl-3-methyl-2-butyl-*1,1,1*-d_3 cations, **5**-d_3; 1-aryl-1-tolylethyl-*2,2,2*-d_3 cations, **6**-d_3; acetophenone-α,α,α-d_3, **7**-d_3; 1-aryl-1-hydroxyethyl-*2,2,2*-d_3 cations, **8**-d_3; 1-aryl-1-cyclopropylethyl-*2,2,2*-d_3 cations, **9**-d_3. The two-bond isotope shifts, ${}^2\Delta C(D)$, at the cation center were plotted vs σ^{C^+} constants and compared to similar TIED plots of ^{13}C chemical shifts at C^+. The NMR isotope shifts provide an additional criterion for differentiation among stable carbocations that show similar behavior in ^{13}C chemical shifts at C^+. The onset of a rapid rearrangement is evident in the **5**-d_3 series by a large isotope shift for 4′-CF_3-**5**-d_3, which falls far from the correlation line established by the electron-donating members of the series. The nonlinear behavior in chemical shift and isotope shift TIED plots for **2**-d_2 and **9**-d_3 are considered indicative of changes in bonding or structure, probably involving σ bridging. Deviations from linearity in chemical shift and isotope shift TIED plots for **3**-d_2 and **4**-d_2 are less substantial but may also be indicative of the onset of σ bridging. Three series, **1**-d_6, **6**-d_3, and **8**-d_3, show similar linear correlations of isotope shifts with σ^{C^+}, although **6** and **8** show nonlinear behavior in chemical shift TIED plots. It is suggested that isotopic substitution in **2**–**4** and **9** affects vibrational averaging along a σ-bridging coordinate, while **6** and **8** have a π-donor group attached at C^+ and do not have a structural feature that becomes easily perturbed vibrationally as electron demand increases.

Introduction

The dependence of the ^{13}C NMR chemical shift at a cation center on the aromatic substituent has been extensively used to examine the electronic and structural characteristics of a wide variety of stable carbocations.[1] Deviations from linearity in plots of the substituent-induced changes in chemical shifts vs analogous changes observed in appropriate reference systems have been interpreted as indicating the onset of σ participation and other phenomena as electron demand increases. This "tool of increasing electron demand" (herein referred to as TIED) has provided much information, but the interpretations have often been controversial.

Another tool that has proven to be useful in examining structures of carbocations is the NMR isotope shift.[2] The distinction between isotope effects on equilibria and intrinsic isotope effects on chemical shifts was first applied to carbocations by Saunders to provide a means of distinguishing between static, bridged structures and structures undergoing rapid degenerate equilibria.[3] Since then, both intrinsic and equilibrium NMR isotope shifts have been applied to investigate various structural features in carbocations, including bonding type, hyperconjugation, rearrangements, and conformations.[2d,4]

We recently reported, in a paper with Servis, that the combination of the TIED approach with measurement of NMR isotope shifts appears to provide a highly sensitive probe of changes in bonding character in 2-aryl-2-norbornyl cations.[5] Deuteriation adjacent to a cation center induces a small change in the ^{13}C chemical shift that varies linearly with increasing electron demand in 2-aryl-2-propyl cations, but in a distinctly nonlinear fashion in 2-aryl-2-norbornyl cations.

In this paper, we report a survey of the behavior of NMR isotope shifts in various carbocations as a function of increasing electron demand. All of the carbocation systems have been examined previously for TIED correlations of ^{13}C chemical shifts. However, the apparent high sensitivity of isotope shifts to changes in structure makes it attractive to reexamine several of these series to see whether the additional tool of isotope shifts can be useful in helping to interpret nonlinear behavior in TIED correlations. The carbocation series were selected from the many possible so as to present different possible sources of nonlinear behavior. We also reexamine the original chemical shift TIED correlations, using our data, with particular emphasis on a uniform presentation of the data.

While agreement on the best interpretations is not complete, TIED correlations of chemical shifts in carbocations certainly have been successful in identifying interesting systems that respond differently to substituent effects than the standard tertiary aryldialkylcarbenium ions.[1] Deviations from linearity in chemical shift TIED plots suggest a change in bonding and/or structural character as substituents become more electron-withdrawing. However, one of the difficulties is that the deviations from linearity in TIED plots are often rather similar in appearance in various systems. In one paper,

---

† Northeastern University.
‡ Alexandria University.

[1] For comprehensive discussions, see: (a) Olah, G. A., Berrier, A. L.; Prakash, G. K. S. *Proc. Natl. Acad. Sci. U.S.A.* **1981**, *78*, 1998. (b) Brown, H. C.; Periasamy, M.; Kelly, D. P.; Giansiracusa, J. J. *J. Org. Chem.* **1982**, *47*, 2089. (c) Olah, G. A.; Prakash, G. K. S.; Farnum, D. G.; Clausen, T. P. *J. Org. Chem.* **1983**, *48*, 2146. (d) Prakash, G. K. S.; Iyer, P. S. *Rev. Chem. Intermed.* **1988**, *9*, 65.

[2] For reviews of NMR isotope shifts, see: (a) Hansen, P. E. *Annu. Rep. NMR Spectrosc.* **1983**, *15*, 105. (b) Forsyth, D. A. *Isot. Org. Chem.* **1984**, *6*, 1. (c) Hansen, P. E. *Prog. NMR Spectrosc.* **1988**, *20*, 207. (d) Siehl, H.-U. *Adv. Phys. Org. Chem.* **1987**, *23*, 63.

[3] (a) Saunders, M.; Telkowski, L.; Kates, M. R. *J. Am. Chem. Soc.* **1977**, *99*, 8070. (b) Saunders, M.; Kates, M. R. *J. Am. Chem. Soc.* **1977**, *99*, 8071. (c) Saunders, M.; Kates, M. R.; Wiberg, K. B.; Pratt, W. *J. Am. Chem. Soc.* **1977**, *99*, 8072.

[4] Recent representative papers: (a) Kirchen, R. P.; Ranganayakula, K.; Sorensen, T. S. *J. Am. Chem. Soc.* **1987**, *109*, 7811. (b) Botkin, J. H.; Forsyth, D. A.; Sardella, D. J. *J. Am. Chem. Soc.* **1986**, *108*, 2797. (c) Servis, K. L.; Domenick, R. L. *J. Am. Chem. Soc.* **1986**, *108*, 2211. (d) Siehl, H.-U.; Walter, H. *J. Chem. Soc., Chem. Commun.* **1985**, 76. (e) Jarret, R. M.; Saunders, M. *J. Am. Chem. Soc.* **1987**, *109*, 3366. (f) Saunders, M.; Jarret, R. M.; Pramanik, P. *J. Am. Chem. Soc.* **1987**, *109*, 3735.

[5] Servis, K. L.; Domenick, R. L.; Forsyth, D. A.; Pan, Y. *J. Am. Chem. Soc.* **1987**, *109*, 7263.

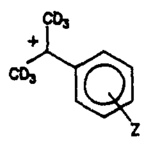
0022-3263/90/1955-5375$02.50/0

Brown noted almost identical TIED behavior for 2-norbornyl, cyclopropylcarbinyl, and diarylalkyl systems and suggested that the deviations should have a common origin;[1b] in another, it was suggested that all such deviations might have the same origin.[6] On the other hand, separate explanations have been advanced for individual systems, with Olah suggesting that "the problem of interpretation is to identify all plausible causes of the deviation in a given case and then, by careful experiment and reasoning, to eliminate those that are not significant".[1c] Proceeding in this spirit, we offer the application of an additional experimental tool, the tool of isotopic perturbation, to help distinguish between systems that behave nearly identically in chemical shift TIED correlations. In this paper, we will use the isotope shift in somewhat of a phenomenological sense, describing patterns of behavior rather than attempting a detailed analysis of each isotope shift.

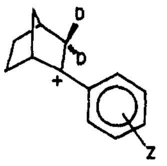
Results

NMR isotope shifts were obtained for each carbocation from ^{13}C spectra of a mixture of the deuterium-labeled and unlabeled carbocations. The isotope shift at the cation center was of particular interest, although some isotope shifts were observed for other positions. The occurrence of an isotope shift is evident by two signals near the expected chemical shift. Assignment of the signals to the unlabeled or labeled carbocation was achieved by varying the proportions of the two isotopomers in separate experiments.

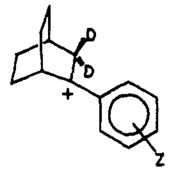
The carbocation systems examined are the following: the 2-aryl-2-propyl-*1,1,1,3,3,3*-d_6 cations, **1**-d_6; the 2-aryl-2-norbornyl-*3,3*-d_2 cations, **2**-d_2; the 2-aryl-2-bicyclo[2.2.2]octyl-*3,3*-d_2 cations, **3**-d_2; the 2-aryl-2-bicyclo[2.1.1]hexyl-*3,3*-d_2 cations, **4**-d_2; the 2-aryl-3-methyl-2-butyl-*1,1,1*-d_3 cations, **5**-d_3; the 1-aryl-1-tolylethyl-*2,2,2*-d_3 cations, **6**-d_3; the noncationic acetophenone-α,α,α-d_3 series, **7**-d_3; the 1-aryl-1-hydroxyethyl-*2,2,2*-d_3 cations, **8**-d_3, derived by protonation of the acetophenones; the 1-aryl-1-cyclopropylethyl-*2,2,2*-d_3 cations, **9**-d_3.



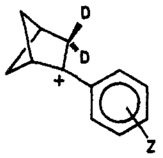
1–d6



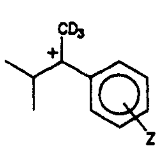
2–d2



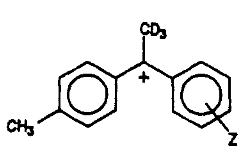
3–d2



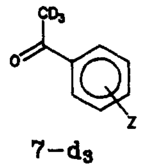
4–d2



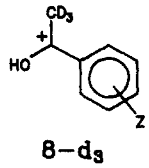
5–d3



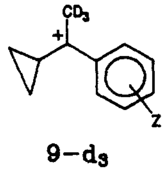
6–d3



7–d3



8–d3



9–d3

The carbocations were typically prepared from tertiary alcohol precursors by ionization in 1:1 FSO_3H-SbF_5 with SO_2ClF as solvent, usually at −78 °C (dry ice–acetone bath) unless a lower temperature was needed to prevent either structural rearrangement or scrambling of the label. The exceptions are the series of neutral acetophenones **7** observed in $CDCl_3$ solution and the carbocations **8** derived by simple protonation of the acetophenones in the FSO_3H-SbF_5/SO_2ClF medium. The unlabeled versions of the alcohol precursors were all known compounds, with a few exceptions for which data are given in the Experimental Section. The deuterium-labeled alcohols were prepared in straightforward fashion, typically by use of Grignard reagents with ketones labeled by base-catalyzed exchange in D_2O.

Table I summarizes the ^{13}C chemical shifts at the cation centers or carbonyl group of the unlabeled compounds from our measurements. ^{13}C chemical shifts for nearly all of the cations have been reported previously; our data are in good agreement, always within 1.0 ppm. Most of the small differences in the chemical shifts from previous reports are systematic and can be attributed to different referencing. Our ultimate reference signal was external tetramethylsilane contained in a coaxial 2-mm capillary, although most referencing was done to the signal of internal CH_2Cl_2 (53.62 ppm in FSO_3H-SbF_5/SO_2ClF relative to capillary TMS). This referencing system results in a chemical shift that is 0.6–1.0 ppm lower than when referencing externally to a solution of TMS in acetone-d_6, which is the reference system used by Brown et al.[7] A complete set of ^{13}C data for all positions in all cations is included in the supplementary material.

NMR isotope shift data are listed in Table II for the cation center or carbonyl carbon only. Formally, these are all two-bond isotope shifts, $^2\Delta C(D)$, defined as $^2\Delta C(D) = \delta C(\text{labeled}) - \delta C(\text{unlabeled})$. By this definition, a positive value of the isotope shift indicates a signal has moved downfield due to the presence of the label. Resolution of separate signals was limited to separations of about 0.010 ppm or greater in 75-MHz ^{13}C spectra due to broad line widths (3–10 Hz) typical in spectra of carbocations. The errors in isotope shifts are also about ±0.010 ppm in most cases, and values are reported (ppb) on the basis of consideration of line widths, digital resolution, and reproducibility. In a few cases where signals were particularly broad or overlapping, fewer significant figures are reported. Other isotope shifts observed at other positions in each compound are included in tables in the supplementary material.

In the discussion of results for the individual carbocation systems that follows, we have chosen to use the σ^{C^+} constants defined by Brown et al.[7] for correlation of the data. The σ^{C^+} constants were defined from the ^{13}C chemical shifts of the cation center of substituted 2-phenyl-2-propyl cations (**1**). They account for the enhanced resonance contributions of substituents occurring in fully ionic, stable carbocations. The σ^{C^+} constants are simply a convenient form of reference data for substituent effects on chemical shifts of carbocations and correlate very well[7] in a linear relation with the ^{13}C chemical shifts of the substituted 1-phenyl-1-cyclopentyl cations that were used as reference data in the publications by Farnum et al. and Olah et al.[1,8] Simple dialkylarylcarbenium ions in which there are no extraordinary electronic interactions with the p orbital of the carbocationic center show linear behavior in TIED correlations,[9] so that the choice of the reference system is

---

(6) Brown, H. C.; Periasamy, M. *J. Org. Chem.* **1983**, *48*, 3386.

(7) Brown, H. C.; Kelly, D. P.; Periasamy, M. *Proc. Natl. Acad. Sci. U.S.A.* **1980**, *77*, 6956.

(8) Farnum, D. G.; Botto, R. E.; Chambers, W. T.; Lam, B. *J. Am. Chem. Soc.* **1978**, *100*, 3847.

Table I. ^{13}C NMR Chemical Shifts (δ)[a] at Cation Centers of 3–9[b]

Z	3	4[c]	5	6	7[d]	8	9
4'-OCH_3	237.0[e]	230.5	227.0	208.3	196.7	208.7	226.4
4'-CH_3	260.9	251.4	252.4	220.1	197.6	215.8	241.4
4'-F	265.3	255.0	256.5	220.6	196.4	216.5	243.0
4'-Cl	268.7	257.7	259.6	221.1	196.8	217.7	244.5
3'-CH_3			261.1[f]		198.1	218.6[g]	
H	272.3	261.2	264.0	223.7	198.2	219.2	247.0
3'-Cl			270.1		196.4	220.4	247.9[h]
4'-CF_3	284.1	271.3	274.5[i]	223.9	196.9	222.4	250.2
3',5'-$(CF_3)_2$		274.2			194.9	222.7	248.7

[a] Referenced (ppm) to internal CH_2Cl_2 (53.62 ppm; original reference external capillary tetramethylsilane), measured at 75.4 MHz on Varian XL-300 spectrometer. [b] All in FSO_3H–SbF_5/SO_2ClF at −78 °C unless otherwise noted. [c] Measured at −100 °C. [d] In $CDCl_3$ at 18 °C; for carbonyl carbon referenced to $CDCl_3$ (77.0 ppm). [e] In FSO_3H/SO_2ClF. [f] Second signal at 261.6 ppm for second conformer. [g] Second signal at 218.8 ppm for second conformer. [h] Additional data for 3',5'-Cl_2: 248.1 ppm. [i] Measured at 15.0 MHz.

Table II. $^2\Delta C(D)$ NMR Isotope Shifts[a] at Cation Centers of 3–9[b]

Z	3-d_2	4-d_2	5-d_3	6-d_3	7-d_3[c]	8-d_3	9-d_3
4'-OCH_3	*d*	−0.160	−0.185	−0.18	0.121	0.051	−0.121
4'-CH_3	0.00	−0.125	−0.123	−0.17	0.112	0.084	−0.144
4'-F	0.040	−0.122	−0.11	−0.17	0.099	0.095	−0.161
4'-Cl	0.062	−0.126	−0.104	−0.16	0.118	0.097	−0.167
3'-CH_3			−0.10[e,f]		0.102	0.105[e]	
H	0.098	−0.113	−0.08	−0.16	0.117	0.101	−0.167
3'-Cl			−0.08		0.116	0.115	−0.192[g]
4'-CF_3	0.190	−0.110	−1.3[h]	−0.14[f]	0.118	0.131	−0.212
3',5'-$(CF_3)_2$		−0.110			0.122	0.142	−0.231

[a] ±0.01 ppm unless otherwise noted. $^2\Delta C(D) = \delta(C(labeled)) - \delta(C(unlabeled))$. [b] Conditions as in Table I. [c] For carbonyl carbon. [d] For d_1 isotopomer, −0.05; see text. [e] Same value for both conformers. [f] ±0.02 ppm. [g] Additional data for 3',5'-Cl_2: −0.207 ppm. [h] ±0.1 ppm.

Table III. Correlations of C^+ Chemical Shifts with σ^{C+} in $\delta = \rho\sigma^{C+} + i$

cation	n[a]	ρ	i	r^2 [b]	$(CF_3)_{dev}$[c]
1[d]	5	17.8	254.9	1.000	0.3
1[d]	6	17.9	255.0	1.000	
2[d]	4	11.8	259.9	0.997	−4.7
2[d]	6	6.3	258.0	0.853	
3	5	17.6	272.5	1.000	−2.3
3	6	16.9	271.8	0.998	
4	5	15.2	261.3	1.000	−2.0
4	7	14.3	260.4	0.997	
5	7	18.2	264.0	0.999	−3.9
5	9	17.3	263.2	0.993	
6	5	7.5	223.7	0.981	−5.8
6	6	5.9	222.1	0.886	
7	6	0.5	197.6	0.187	−1.0
7	9	−0.3	196.9	0.097	
8	6	5.2	219.1	0.994	−0.7
8	9	4.7	218.7	0.988	
9	5	10.2	247.3	0.995	−5.1
9	9	7.4	244.5	0.907	

[a] Number of data points. First entry for a cation system is for electron donors and parent ion only; second entry is for all data from Table I. [b] (Correlation coefficient)^2. [c] Deviation in ppm for 4'-CF_3 point from correlation line established by electron donors, defined as $\delta(C(obsvd)) - \delta(C(pred))$. [d] Chemical shift data from ref 5.

Table IV. Correlations of C^+ Isotope Shifts with σ^{C+} in $^2\Delta C(D) = \rho\sigma^{C+} + i$

cation	n[a]	ρ	i	r^2 [b]	$(CF_3)_{dev}$[c]
1[d]	5	0.155	0.050	0.994	0.039
1[d]	6	0.166	0.061	0.991	
2[d]	4	0.064	0.054	0.981	−0.103
2[d]	6	−0.078	0.004	0.503	
3	4	0.146	0.098	1.000	−0.023
3	5	0.129	0.091	0.996	
4	5	0.022	−0.115	0.952	−0.013
4	7	0.016	−0.120	0.883	
5	6	0.048	−0.089	0.981	−1.2
5	8	−0.231	−0.327	0.208	
6	5	0.010	−0.162	0.845	0.01
6	6	0.014	−0.158	0.852	
7	6	−0.005	0.108	0.194	0.014
7	9	0.001	0.114	0.010	
8	6	0.026	0.104	0.981	0.006
8	9	0.029	0.107	0.983	
9	5	−0.024	−0.168	0.939	−0.025
9	9	−0.036	−0.180	0.924	

[a] Number of data points. First entry for a cation system is for electron donors and parent ion only; second entry is for all data from Table II. [b] (Correlation coefficient)^2. [c] Deviation in ppm for 4'-CF_3 point from correlation line established by electron donors, defined as $^2\Delta C(D)(obsd) - {}^2\Delta C(D)(pred)$. [d] Isotope shift data from ref 5.

arbitrary. The σ^{C^+} values for the substituents used in this study are as follows:[7] *p*-OCH_3, −2.02; *p*-CH_3, −0.67; *p*-F, −0.40; *p*-Cl, −0.24; *m*-CH_3, −0.13; H, 0.00; *m*-Cl, 0.36; 3,5-Cl_2, 0.66; *p*-CF_3, 0.79; 3,5-$(CF_3)_2$, 1.03.

Discussion

In the TIED plots that follow, both chemical shifts and isotope shifts are plotted vs Brown's σ^{C^+} constants. All of the chemical shift TIED plots are displayed with the same size of scale so as to make clear visually any differences in slope or magnitudes of deviations from linearity. Similarly, the isotope shift TIED plots are presented with the same scaling for all systems. In each of the TIED plots, a correlation line is shown derived from the data for electron-donating substituents only (including Z = H), even if a satisfactory correlation exists for all substituents. This approach is also intended to provide the same basis for visual comparison of deviations from linearity among the various carbocation systems.

The results of linear regressions for C^+ chemical shifts vs σ^{C^+} are presented in Table III and for isotope shifts at C^+ in Table IV. In both tables, the correlation results are given first for electron-donating substituents only and then for all substituents. To help assess the extent of deviations from linearity for electron-withdrawing substituents, the deviation is reported, $(CF_3)_{dev}$, of the observed value for

---

(9) (a) Brown, H. C.; Periasamy, M.; Liu, K.-T. *J. Org. Chem.* **1981**, *46*, 1646. (b) Kelly, D. P., Jenkins, M. H.; Mantello, R. A. *J. Org. Chem.* **1981**, *46*, 1650. (c) Brown, H. C.; Periasamy, M. *J. Org. Chem.* **1981**, *46*, 3161.

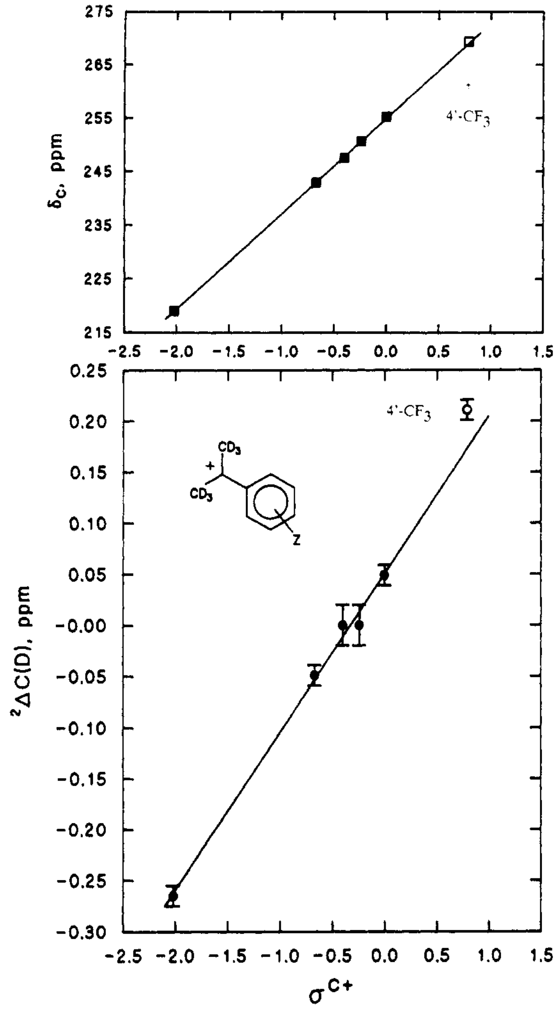


Figure 1. (a) (upper) Plot of ^{13}C chemical shifts at the cation center of 2-aryl-2-propyl cations vs σ^{C^+}. (b) (lower) Plot of isotope shifts at the cation center, $^2\Delta$C(D), in 1-d_6 vs σ^{C^+}. In each figure, a correlation line is drawn for electron-donating groups and the parent ion only (filled symbols, electron donors; open symbols, electron-withdrawing groups).

the 4′-CF$_3$ substituent from the value predicted by the correlation line for electron donors. The 4′-CF$_3$ substituent is singled out because it is common to all data sets.

Uniform presentation of all the data is vital to the process of comparing different systems. Different choices of scale can lead to quite different impressions of the same data. Likewise, choosing to plot the line from a linear correlation for only the electron-donating substituents can give a different impression than a plot showing a linear correlation for all substituents. For instance, as discussed below, the chemical shift TIED correlation for 1-aryl-1-hydroxyethyl cations (**8**) has been described by both Olah and Brown as displaying deviations from linearity for electron-withdrawing substituents.[6,10] The scale of chemical shifts in the TIED plots for **8** covered about 17 ppm in one study[10] and 20 ppm in the other,[6] and the correlation line drawn in both included only electron-donating substituents. In contrast, when the chemical shift TIED plots of **3** and **4** were examined for nonlinearity, plot scales covering 50 ppm for **4**[11] or 120 ppm for **3** and **4**[1b] were used and the correlation lines included all substituents. We find that **3**, **4**, and **8** all show deviations from linearity, as is clear when the data for all three systems are presented in the same way.

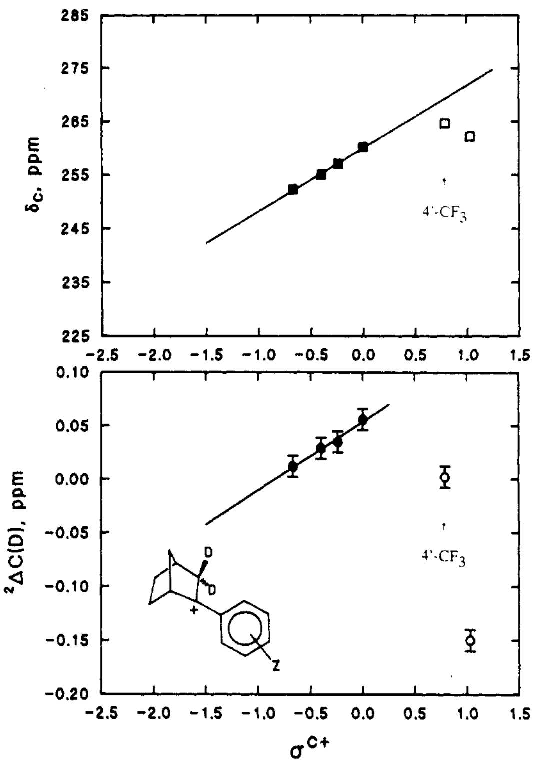


Figure 2. (a) (upper) Plot of ^{13}C chemical shifts at the cation center of 2-aryl-2-norbornyl cations vs σ^{C^+}. (b) (lower) Plot of isotope shifts at the cation center, $^2\Delta$C(D), in 2-d_2 vs σ^{C^+}. In each figure, a correlation line is drawn for electron-donating groups and the parent ion only (filled symbols, electron donors; open symbols, electron-withdrawing groups).

2-Aryl-2-propyl Cations (1). The ^{13}C chemical shifts at C2, the cation center, of 2-aryl-2-propyl cations (**1**) were used to define σ^{C^+} constants.[7] The TIED plot (Figure 1a) of our limited set of δ(C) data[5] for **1** vs σ^{C^+} shows the expected excellent correlation (see Table III). As previously described,[5] when the $^2\Delta$C(D) isotope shift data for the 1-d_6 series are plotted vs σ^{C^+} (Figure 1b), an excellent linear correlation is also found (Table IV). Thus, the σ^{C^+} constants are suitable for use in isotope shift TIED plots as well, and the linear relation for the 2-aryl-2-propyl system indicates that a linear response may be expected as normal behavior. It is necessary to note, however, that in Figure 1b, where the correlation line is drawn for only the electron-donating substituents and the parent ion, the point for 4′-CF$_3$ deviates slightly from the line in the direction of deshielding (see Table IV).

2-Aryl-2-norbornyl, 2-Aryl-2-bicyclo[2.2.2]octyl, and 2-Aryl-2-bicyclo[2.1.1]hexyl Cations (2–4). The 2-norbornyl system has historically been at the center of long-standing debate about bonding character in carbocations. Earlier studies of chemical shift TIED correlations for C2 in the 2-aryl-2-bicyclo[2.2.1]heptyl cations (**2**) show deviation from linearity for electron-withdrawing substituents, indicating more shielding than expected.[1,9,12] Our set of data[5] is plotted in Figure 2a and shows the deviation of the 4′-CF$_3$ and 3′,5′-(CF$_3$)$_2$ points from the line established by the electron-donating substituents. Much larger sets of data were presented and discussed in the earlier studies. This deviation from nonlinearity has been

---

(10) Krishnamurthy, V. V.; Prakash, G. K. S.; Iyer, P. S.; Olah, G. A. *J. Am. Chem. Soc.* **1984**, *106*, 7068.

(11) Olah, G. A.; Berrier, A. L.; Arvanaghi, M.; Prakash, G. K. S. *J. Am. Chem. Soc.* **1981**, *103*, 1122.

(12) (a) Olah, G. A.; Prakash, G. K. S.; Liang, G. *J. Am. Chem. Soc.* 1977, *99*, 5683. (b) Olah, G. A.; Berrier, A. L.; Prakash, G. K. S. *J. Org. Chem.* 1982, *47*, 3903.

interpreted by Farnum and Olah as indicating the onset of σ bridging of the C1–C6 bond. If partial bridging occurs in the tertiary aryl-substituted carbocations, it would shield C2 slightly; theoretical calculations of ^{13}C chemical shifts in carbocations clearly show that σ bridging leads to shielding.[13] Evidence indicating the involvement of partial bridging in some tertiary 2-norbornyl cations has been supplemented in recent years by isotope shift measurements[3c,14] and an X-ray crystal structure.[15] Obviously, the complete arguments about bonding in 2-norbornyl cations cannot be reviewed here; an excellent discussion of the recent evidence and additional data have recently been presented by Lenoir, Apeloig, Arad, and Schleyer.[16] In regard to the chemical shift TIED correlations, Brown challenged the σ-bridging interpretation with various arguments, including the comment that some carbocation systems showed similar behavior in TIED correlations where σ bridging is unexpected and some other systems where σ bridging might be anticipated, especially the 2-bicyclo[2.1.1]hexyl and 2-bicyclo[2.2.2]octyl cations, do not show deviations in TIED plots.[1b] Olah and Farnum have offered counterarguments to Brown's points.[1c]

We have previously presented and discussed in detail the isotope shift TIED plots for the **2**-d_2, **2**-*3-exo*-d_1, and **2**-*3-endo*-d_1 cation series.[5] The **2**-d_2 isotope shift data are replotted here in Figure 2b. When the data for the electron-donating 4'-CH_3, 4'-F, 4'-Cl, and parent ions are used to define a straight line, it is clear that the points for the electron-withdrawing 4'-CF_3 and 3',5'-$(CF_3)_2$ substituents deviate substantially from the line. The deviant isotope shifts are more upfield than expected; $(CF_3)_{dev}$ is −0.103 ppm from Table IV. Clearly, the deviations indicate a change in type of response to deuteriation as the substituents become more electron-withdrawing. The upfield direction of the deviations is consistent with the onset of σ bridging and isotopic perturbation toward enhanced σ bridging in the deuteriated isotopomers. Considering the vibrational origin of the isotope effect, we suggested that the energy barrier for bending the C2–C1–C6 angle toward bridging becomes sufficiently low with electron-withdrawing substituents that the bending vibration along the bridging coordinate occurs in a shallow potential well and isotopic substitution is then able to slightly perturb the vibrationally averaged structure toward a more bridged position.[5]

*The chemical shift TIED plots for the 2-bicyclo[2.2.2]octyl and 2-bicyclo[2.1.1]hexyl cations **3** and **4** were described previously as not showing deviations from linearity.*[1b,11] Brown suggested that the failure to show deviations from linearity in TIED plots must be considered as unexpected *if* one considers the TIED plot of the 2-norbornyl system **2** to be indicative of the onset of σ bridging.[1b] Since a σ-bridged structure has been attributed to the secondary 2-bicyclo[2.1.1]hexyl cation as well as to the 2-norbornyl cation, Brown argued that the TIED plots for **3** and **4** should also show the onset of the supposed σ bridging. *In fact, we find that the chemical shift TIED plots of **3** and **4** do show deviations from linearity as electron demand increases.*

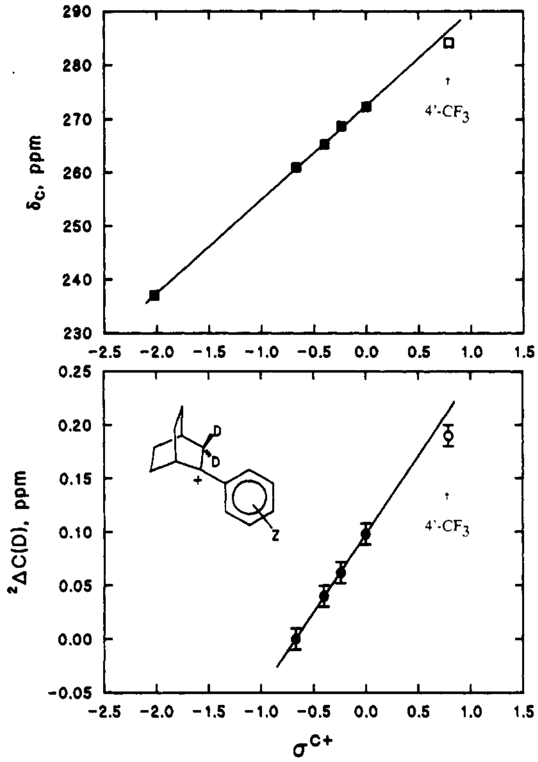


Figure 3. (a) (upper) Plot of ^{13}C chemical shifts at the cation center of 2-aryl-2-bicyclo[2.2.2]octyl cations vs σ^{C^+}. (b) (lower) Plot of isotope shifts at the cation center, $^2\Delta C(D)$, in **3**-d_2 vs σ^{C^+}. In each figure, a correlation line is drawn for electron-donating groups and the parent ion only (filled symbols, electron donors; open symbols, electron-withdrawing groups).

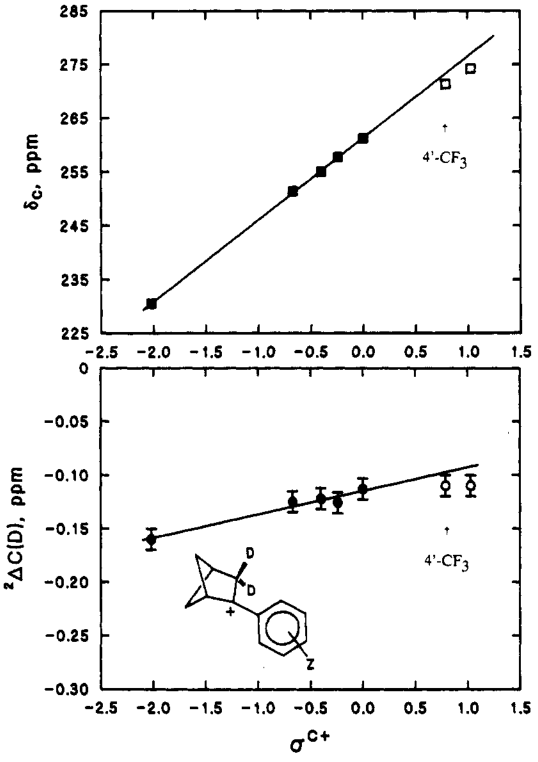


Figure 4. (a) (upper) Plot of ^{13}C chemical shifts at the cation center of 2-aryl-2-bicyclo[2.1.1]hexyl cations vs σ^{C^+}. (b) (lower) Plot of isotope shifts at the cation center, $^2\Delta C(D)$, in **4**-d_2 vs σ^{C^+}. In each figure, a correlation line is drawn for electron-donating groups and the parent ion only (filled symbols, electron donors; open symbols, electron-withdrawing groups).

Our data for **3** and **4** from Table I are plotted vs σ^{C^+} constants in Figures 3a and 4a. The points for 4'-CF_3 in

---

[13] (a) Schindler, M. *J. Am. Chem. Soc.* **1987**, *109*, 1020. (b) Schleyer, P. v. R.; Laidig, K.; Wiberg, K. B.; Saunders, M.; Schindler, M. *J. Am. Chem. Soc.* **1988**, *110*, 300. (c) Schleyer, P. v. R.; Carneiro, J. W. de M.; Koch, W.; Raghavachari, K. *J. Am. Chem. Soc.* **1989**, *111*, 5475.

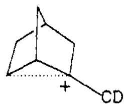
[14] (a) Servis, K. L.; Shue, F.-F. *J. Am. Chem. Soc.* **1980**, *102*, 7233. (b) Forsyth, D. A.; Botkin, J. H.; Puckace, J. S.; Servis, K. L.; Domenick, R. L. *J. Am. Chem. Soc.* **1987**, *109*, 7270. (c) Forsyth, D. A.; Panyachotipun, C. *J. Chem. Soc., Chem. Commun.* **1988**, 1564.

[15] Laube, T. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 561.

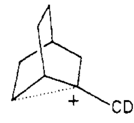
[16] Lenoir, D.; Apeloig, Y.; Arad, D.; Schleyer, P. v. R. *J. Org. Chem.* **1988**, *53*, 661.

Figures 3a and 4a and the point for 3′,5′-$(CF_3)_2$ in Figure 4a deviate in the direction of shielding from the correlation line for electron donors. The $(CF_3)_{dev}$ of −2.3 ppm for **3** and −2.0 ppm for **4** are smaller than the −4.7 ppm for **2** (see Table III) but are actually larger than the −0.7 ppm for 1-aryl-1-hydroxyethyl cations (**8**) for which deviation from linearity has previously been noted.[6,10]

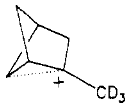
In initiating this study, we thought there was a reasonable possibility that the isotope shift TIED plots for **3**-d_2 and **4**-d_2 would show deviation from linearity where the chemical shift TIED plots did not (although, as described above, we have now found deviations in the chemical shift TIED plot). This anticipation was based on analogy to the chemical shift and isotope shift behavior of the 2-methyl-2-norbornyl cation (**10**), 2-methyl-2-bicyclo[2.2.2]octyl cation (**11**), and 2-methyl-2-bicyclo[2.1.1]hexyl cation (**12**). The C2 chemical shift of **10** is unusually shielded at δ 269 ppm, compared to the δ 322 ppm for both **11** and **12**. However, the patterns of isotope shifts are similar for **10**–**12**, including upfield shifts at C^+ and unusually large magnitude isotope shifts at C^+ for **10** and **11**.[14b,17] The $^2\Delta C(D)$ for **10** is largest at −2.26 ppm, followed by **11** at −1.49 ppm and **12** at −0.22 ppm. The similarities between isotope shifts for **10** and **11** were interpreted as indicating a similarly shallow energy surface for bending motion along the bridging coordinate, even though the vibrationally averaged structure of **10** is probably more bridged than **11**. It was considered possible that the isotope shift TIED plots for **3**-d_2 and **4**-d_2 might indicate the onset of a shallow energy surface for vibration along the direction of bridging even if the extent of bridging was not sufficient to be detected in the chemical shift TIED plots. The onset was expected to occur first in **2**, then in **3**, and last in **4**, based on the results for **10**–**12**.



10



11



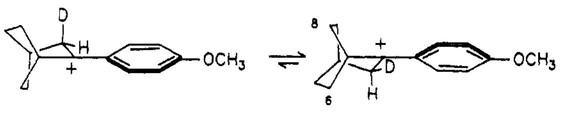
12

The isotope shift TIED plots for **3**-d_2 and **4**-d_2, based on data in Table II, are shown in Figures 3b and 4b. The points for the electron-withdrawing substituents deviate slightly in the direction of shielding from the correlation line for electron donors. The deviations toward shielding of the 4′-CF_3 points are in the opposite direction of the deviation seen in the reference system, **1**-d_6, and are in the same direction as for **2**-d_2, but much smaller (see Table IV). Unfortunately, the more electron-demanding 3′5′-$(CF_3)_2$-**3** cation cannot be prepared because it rearranges to bicyclo[3.2.1]octyl cations.[18] The electron-withdrawing substituents may have created just enough electron demand to reach that point in **3** and **4** where the barrier for bending along the bridging coordinate is lowered sufficiently for isotopic perturbation to alter the vibrationally averaged position on this coordinate.

The order of the magnitude of the deviations of the 4′-CF_3 points from the correlation lines for electron donors in both the chemical shift and isotope shift TIED plots is **2** > **3** > **4**. The order indicates that if the onset of σ bridging is the explanation for **2**, then a lesser degree of σ bridging could account for the behavior of **3** and **4**. Certainly the previous failure to see nonlinearity in the TIED behavior of **3** and **4** can no longer be cited as an argument against a σ-bridging explanation for **2**. We suggest that the structures of all three types of bicyclic cations are best represented as having some degree of nonclassical σ bridging, as shown for **10**–**12**, for the more electron-demanding members of the series.

Why were deviations in linearity of the chemical shift TIED plots of **3** and **4** not noted previously? In addition to the most important factor of the choices made in previous presentations of the data, as described in the beginning of this Discussion, other factors are involved. In the case of **4**, our data differ from the previous in two respects. First, only two electron-donating substituents (4′-OCH_3, 4′-CH_3) were examined previously.[11] Our data in Table I and Figure 4a include two additional points (4′-F, 4′-Cl), which allows the line for the electron donors plus parent to be defined by five points instead of three. Second, the C^+ chemical shifts for 4′-OCH_3, 4′-CH_3, 4′-CF_3, and 3′,5′-$(CF_3)_2$ are shifted systematically from the previous data by −0.8 to −1.0 ppm due to different referencing, but the shifts for the parent ion differ by only −0.1 ppm. These two differences give a slightly different slope to the correlation line for electron donors for **4**. In the case of **3**, one more electron-donating substituent (4′-CH_3) than in the previous study is included.

Supportive evidence for another postulated structural feature of 2-bicyclo[2.2.2]octyl cations was also found. Sorensen suggested that the 2-bicyclo[2.2.2]octyl framework may oscillate between twisted conformations on either side of the symmetrical form.[19] If so, such a degenerate equilibrium should be subject to equilibrium isotope effects if the degeneracy is lifted by appropriate isotopic labeling. In all our attempts to prepare the alcohol precursor to cation 4′-OCH_3-**3**-d_2, the elimination product 2-(4′-methoxyphenyl)bicyclo[2.2.2]oct-2-ene-*3*-d_1 was obtained instead.[18a] Protonation of this alkene in superacid gave the monolabeled 2-(4′-methoxyphenyl)bicyclo[2.2.2]octyl-*3*-d_1 cation (**13**). Evidence for an equilibrium between the twisted forms **13a** and **13b** was found in the ^{13}C spectrum, which shows splitting of 0.306 ppm between the C6 and C8 signals, with the splitting occurring nearly symmetrically about the position of the C6,8 signal of the unlabeled cation. The average position of C6 and C8 is 0.007 ppm downfield of the C6,8 signal of the unlabeled cation. This slight downfield shift represents the average intrinsic $^4\Delta C(D)$ for C6 and C8. This type of signal splitting where one signal moves upfield and the other downfield by an equal amount is characteristic of equilibrium isotope shifts when a degenerate equilibrium has been perturbed.[3] The equilibrium should be perturbed in the direction of placing the C–D bond in the more tightly bound, nonhyperconjugating position in **13b**. It is then reasonable to assign the upfield signal as the signal for the less hyperconjugating position C6 and the downfield signal for the more hyperconjugating position C8.



13a 13b

The existence of the conformational equilibrium isotope effect for **13** means that the observed intrinsic isotope shift of −0.05 ppm (Table II) at C^+ in **13** cannot be used to estimate the intrinsic shift at C^+ for the d_2 isotopomer, 4′-OCH_3-**3**-*2,2*-d_2. The apparent intrinsic shifts are ex-

---

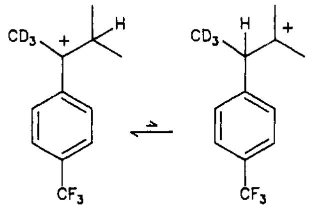
(17) Panyachotipun, C. Ph.D. Thesis, Northeastern University, 1989.

(18) (a) Farnum, D. G.; Wolf, A. D. *J. Am. Chem. Soc.* **1974**, *96*, 5166. (b) Wolf, A. D.; Farnum, D. G. *J. Am. Chem. Soc.* **1974**, *96*, 5175.

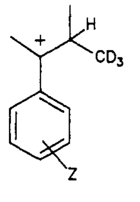
(19) Brown, H. C.; Periasamy, M. *J. Am. Chem. Soc.* **1983**, *105*, 529.

pected to be nonadditive when a system is conformationally mobile and the conformational equilibrium is perturbed by the isotope.[4b] Thus, unfortunately, the 4'-OCH_3-**3**-2,2-d_2 point could not be included in Figure 3b, which might have strengthened the evidence for onset of σ bridging by establishing more firmly the correlation line for electron donors. However, the existence of the twisted structure does suggest an optimal geometry for the onset of σ bridging by one C–C bond as electron demand increases.

2-Aryl-3-methyl-2-butyl Cations (5). The series **5** cations represent a system in which a rapid equilibration process ensues as electron demand increases. A hydride shift from the methine carbon (C3) of the isopropyl group converts the ion from a tertiary benzylic cation to a tertiary alkyl cation. Brown and Periasamy demonstrated that the tertiary alkyl form reaches a significant concentration in a rapid equilibrium with the tertiary benzylic form when substituents on the aryl ring are sufficiently electron-withdrawing, for example, 4'-CF_3-**5** in equilibrium with **14**.[19] In a chemical shift TIED plot for C2, the deviations of the 4'-CF_3-**5** and 3',5'-Cl_2-**5** points from the correlation line provided by electron-donating substituents were found to be temperature-dependent. The greater deviation at higher temperature was accounted for on the basis of a greater population of the tertiary alkyl cation at higher temperature. Further, in 3',5'-$(CF_3)_2$-**5**, the hydride shift was slow enough at −80 °C that dynamic line broadening in the 20-MHz ^{13}C spectrum obscurred several of the signals, including C2 and C3.



4'-CF_3-**5**-d_3 14-d_3



15

Our less extensive data set of C2 chemical shifts (see Table I) for **5** is plotted vs σ^{C^+} in Figure 5a. The 4'-CF_3-**5** point deviates downward from the correlation line, consistent with shielding due to a contribution of the hydride shifted form. The C2 chemical shifts of 4'-CF_3-**5** were obtained in a 15-MHz ^{13}C spectrum instead of the usual 75.4-MHz spectra because C2 and C3 in both 4'-CF_3-**5** and 3',5'-Cl_2-**5** could not be observed in high-field spectra at −80 °C. The hydride shift occurs at an intermediate rate on the NMR time scale at 75.4 MHz, giving very broad signals for C2 and C3. Spectra were also measured at −120 °C in an attempt to slow the process, but broad signals were still observed. Substantial decomposition of the cations is seen at −50 °C.

A dramatic deviation from linearity for the 4'-CF_3-**5**-d_3 cation occurs in the isotope shift TIED plot. The isotope shifts (see Table II) at C2 for **5** are plotted vs σ^{C^+} in Figure 5b. The correlation line has a positive slope; i.e., the C2 isotope shifts tend toward a less upfield shift with increasing electron demand, until the 4'-CF_3 substituent is reached. The isotope shift for 4'-CF_3-**5**-d_3 is −1.3 ppm upfield. This deviation from the correlation line is 1 order of magnitude larger than the deviation of the 4'-CF_3-**2** point in the 2-norbornyl series (Table IV). The large deviation reflects the changeover from a small, intrinsic NMR isotope shift to an isotope effect on a rapid equilibrium. Here, the 4'-CF_3-**5**-d_3 cation is in equilibrium with the 3-[4'-(trifluoromethyl)phenyl]-2-methyl-2-butyl-4,4,4-d_3 cation (**14**-d_3). The position of the existing rapid equilibrium, which overall favors 4'-CF_3-**5**-d_3, is shifted slightly toward **14**-d_3 by the isotope effect, resulting in the shielding of the time-averaged C2 environment. We have previously commented[20] on the large magnitude of this isotope shift, which is particularly evident in the context of the TIED plot of Figure 5b.

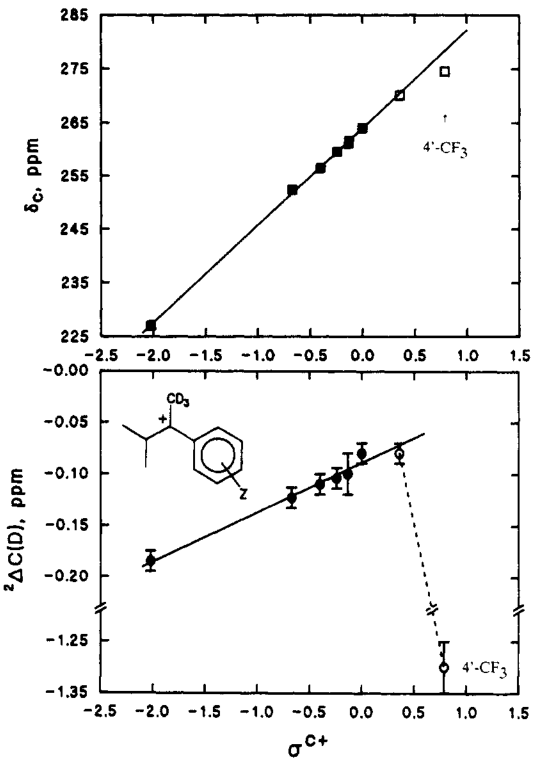


Figure 5. (a) (upper) Plot of ^{13}C chemical shifts at the cation center of 2-aryl-3-methyl-2-butyl cations vs σ^{C^+}. (b) (lower) Plot of isotope shifts at the cation center, $^2\Delta C(D)$, in **5**-d_3 vs σ^{C^+}. In each figure, a correlation line is drawn for electron-donating groups and the parent ion only (filled symbols, electron donors; open symbols, electron-withdrawing groups).

The isotopic perturbation of equilibrium in 4'-CF_3-**5**-d_3 also results in a large isotope shift at C3. The C3 isotope shift is 1.45 ppm,[20] a downfield shift reflecting the increased contribution of cation **14**-d_3 to the time-averaged signal. No isotope shift was detected at C3 in the other series **5** cations.

It is also possible to examine isotope shifts for 2-aryl-3-butyl-2-butyl-4,4,4-d_3 cations (**15**), several of which are available due to a slow rearrangement of methyl groups occurring in the **5**-d_3 cations. The isotope shift at C2 is nearly the same, 0.12 ± 0.02 ppm, for the 3'-CH_3, 4'-F, 4'-Cl, 4'-H, and 3'-Cl substituted cations in the **15** series but is 1.3 ppm upfield in 4'-CF_3-**15**. In other words, placement of the label at C4 instead of C1 shifts the equilibrium in the opposite direction by about the same amount.

The chemical shift TIED plot for this system, **5**, showing the onset of a rapid equilibrium with increasing electron demand, appears very similar to other chemical shift TIED plots, which show deviation for other reasons, for example, in the 2-norbornyl cations **2**. The distinction can only be made by comparing TIED plots determined at different temperatures. In contrast, the isotope shift TIED plots are dramatically different, because the isotope effect on the equilibrium produces a 1 order of magnitude larger change in chemical shift. Of course, the isotope shift for

---

[20] Forsyth, D. A.; Pan, Y. *Tetrahedron Lett.* **1985**, *26*, 4997.

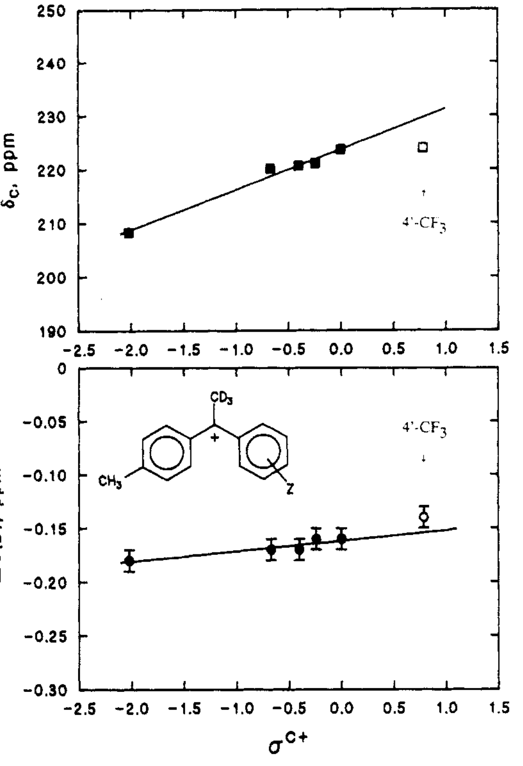


Figure 6. (a) (upper) Plot of ^{13}C chemical shifts at the cation center of 1-aryl-1-tolylethyl cations vs σ^{C^+}. (b) (lower) Plot of isotope shifts at the cation center, $^2\Delta$C(D), in **6**-d_3 vs σ^{C^+}. In each figure, a correlation line is drawn for electron-donating groups and the parent ion only (filled symbols, electron donors; open symbols, electron-withdrawing groups).

an equilibrating system should also be temperature-dependent, as has been shown many times in other studies of isotope shifts arising from perturbation of rapid equilibria.[2d]

1-Aryl-1-tolylethyl Cations (6). Several series of unlabeled diarylcarbenium ions have been previously prepared and examined in separate studies by several research groups.[1,8,21,22] Plots of the chemical shifts of the cationic carbons against σ^{C^+} are distinctly curved for several of the systems.[21] In the case of the 1-aryl-1-tolylethyl cations **6**, an approximately linear relation to σ^{C^+} can be drawn for the electron-donating substituents in a chemical shift TIED plot, but points for electron-withdrawing substituents deviate substantially from this line. Our set of data (see Table I), which includes 4'-CF$_3$ as the only example of an electron-withdrawing group, is plotted in Figure 6a, and the linear regression results are found in Table III.

The isotope shifts at the cation center are listed in Table II for deuteriation at the adjacent methyl group in **6**-d_3 cations. The change in isotope shifts with electron demand is small; all values are upfield shifts of -0.14 to -0.18 ppm. The data are shown in a TIED plot in Figure 6b. A correlation line is drawn for the electron donors, but the small slope, or ρ value of nearly 0, means that only a fair correlation with σ^{C^+} is observed (see Table IV). The point for 4'-CF$_3$-**6**-d_3 falls slightly above this line, a deviation in the same direction as seen in the reference system **1**. This behavior is suggestive that there is no structural feature in **6** other than features also present in **1** that lends itself to perturbation of its vibrationally averaged character due to deuterium substitution.

Olah concluded that there are no unusual changes in bonding or structure nor any need to invoke localized inductive π polarization at the cationic carbon in the diarylcarbenium ion systems.[23] They showed that if the total of chemical shifts at all of the ortho, para, and cationic carbons (i.e., those that receive charge in simple resonance structures) were used in the chemical shift TIED correlation, instead of just the C$^+$ chemical shift, then a straight-line correlation could be obtained. In other words, the diarylcarbenium ions behave normally if the whole π-delocalized structure is considered. In essence, the explanation of Olah and Farnum is that the nonlinear TIED behavior of C$^+$ shifts is due to enhanced resonance involvement of the second aryl group (or other π donor) as substituents in the first aryl ring create more electron demand. Earlier, Farnum had suggested that the nonlinear TIED correlation for C$^+$ alone could be explained by a change in which of the two aryl rings was most coplanar with the cation center as the substituents in one ring were changed from electron-donating to -withdrawing.[8] The coplanarity explanation was ruled out by Brown's observation of a similar TIED plot for anthracenium ions, which are constrained to planarity.[21a] Instead, Brown suggested that the curvature in TIED plots for C$^+$ shifts occurred because of the π-bond character between C$^+$ and C(ipso) of the more donating aromatic ring. Electron-withdrawing substituents in the second ring could then inductively polarize the π bond toward C$^+$, resulting in relative shielding of C$^+$, in analogy to the postulated inductive polarization of the carbonyl π bond in acetophenones (see below) and related structures.

Acetophenones (7). The carbonyl ^{13}C chemical shifts of the substituted acetophenones (Table I) show little variation with substituents compared to the variation seen in most carbocation series. Brownlee et al. reported a comprehensive study of ^{13}C chemical shifts in acetophenones and the side chains of many other groups conjugated with the aryl ring.[24] For acetophenones, they found that the inductive effects of substituents were dominant and proposed localized inductive π polarization as the mechanism of influence. Thus, a TIED plot using σ^{C^+} constants emphasizing resonance effects is not likely to be successful. As indicated in Table III and in Figure 7a, the correlation with σ^{C^+} is nonexistent, with both electron-withdrawing and electron-donating (by resonance) substituents having small shielding effects on the carbonyl carbon.

The isotope shifts (see Table II) at the carbonyl carbon in the **7**-d_3 series also show little variation. The measured $^2\Delta$C(D) values occur between 0.10 and 0.13 ppm, and the variation that does occur does not appear to be systematically related either to the variations in chemical shifts or to the σ^{C^+} constants, as seen in the isotope shift TIED plot of Figure 7b and Table IV.

1-Aryl-1-hydroxyethyl Cations (8). Brown and coworkers prepared a series of meta- and para-substituted cations **8** in FSO$_3$H-SbF$_5$/SO$_2$ClF.[6] The chemical shift TIED plot for **8** obtained by Brown displayed a linear correlation with σ^{C^+} as observed for the electron-donating substituents, but the points for the electron-withdrawing groups were more shielded than expected. Olah et al. also reported similar deviations in a TIED plot based on their

---

(21) (a) Brown, H. C.; Periasamy, M. *J. Org. Chem.* **1982**, *47*, 4742. (b) Brown, H. C.; Periasamy, M.; Perumal, P. T.; Kelly, D. P.; Giansiracusa, J. J. *J. Am. Chem. Soc.* **1983**, *105*, 6300.

(22) (a) Ancian, B.; Membrey, F.; Doucet, J. P. *J. Org. Chem.* **1978**, *43*, 1509. (b) Membrey, F.; Ancian, B.; Doucet, J. P. *Org. Magn. Reson.* **1978**, *11*, 580.

(23) Prakash, G. K. S.; Krishnamurthy, V. V.; Olah, G. A.; Farnum, D. G. *J. Am. Chem. Soc.* **1985**, *107*, 3928.

(24) Bromilow, J. Brownlee, R. T. C.; Craik, D. J.; Fiske, P. R.; Rowe, J. E.; Sadek, M. *J. Chem. Soc., Perkin Trans. 2* **1981**, 753.

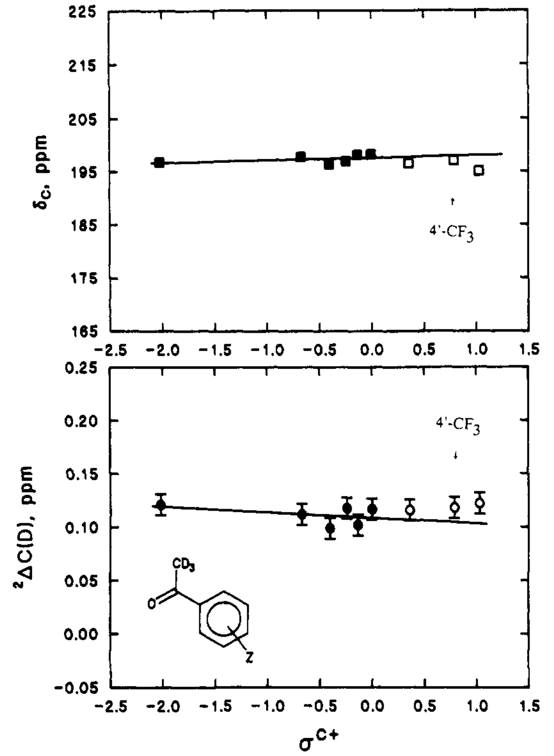


Figure 7. (a) (upper) Plot of ^{13}C chemical shifts at the carbonyl carbon of acetophenones vs σ^{C^+}. (b) (lower) Plot of isotope shifts at the carbonyl carbon, $^2\Delta C(D)$, in 7-d_3 vs σ^{C^+}. In each figure, a correlation line is drawn for electron-donating groups and the parent ion only (filled symbols, electron donors; open symbols, electron-withdrawing groups).

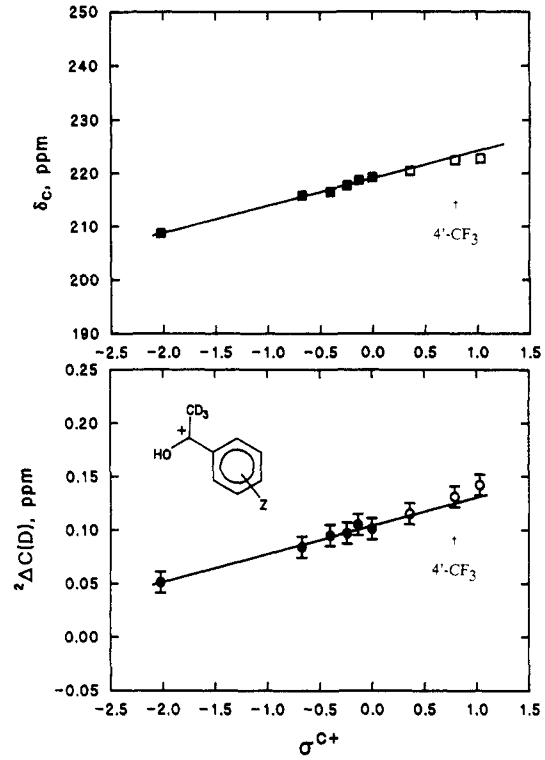


Figure 8. (a) (upper) Plot of ^{13}C chemical shifts at the cation center of 1-aryl-1-hydroxyethyl cations vs σ^{C^+}. (b) (lower) Plot of isotope shifts at the cation center, $^2\Delta C(D)$, in 8-d_3 vs σ^{C^+}. In each figure, a correlation line is drawn for electron-donating groups and the parent ion only (filled symbols, electron donors; open symbols, electron-withdrawing groups).

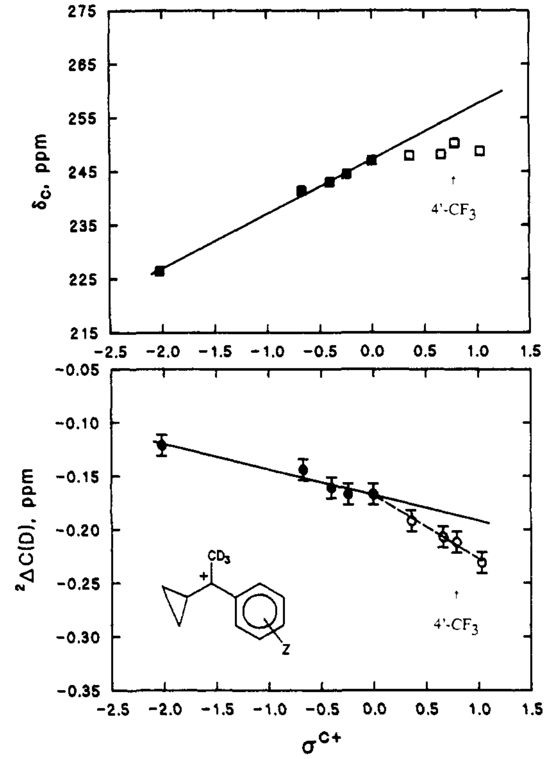


Figure 9. (a) (upper) Plot of ^{13}C chemical shifts at the cation center of 1-aryl-1-cyclopropylethyl cations vs σ^{C^+}. (b) (lower) Plot of isotope shifts at the cation center, $^2\Delta C(D)$, in 9-d_3 vs σ^{C^+}. In each figure, a correlation line is drawn for electron-donating groups and the parent ion only (filled symbols, electron donors; open symbols, electron-withdrawing groups).

own data for 8.[10] Our data for 8 from Table I are shown in a TIED plot in Figure 8a. In our plot also, the points for 4'-CF$_3$ and 3',5'-(CF$_3$)$_2$ deviate from the line established by the electron-donating substituents. *It is important to note that the existence of the nonlinear behavior is accepted as significant even though the deviations from linearity are small* compared to those for other systems such as 2 and 9. Also, note again that the $(CF_3)_{dev}$ for 8 is only −0.7 ppm, compared to −2.3 ppm for 3 and −2.0 ppm for 4.

Brown's explanation for the chemical shift TIED behavior of 8 was localized inductive π polarization of the partial π bond between the hydroxyl group and C$^+$.[6] Olah suggested that π polarization could be partly responsible but that increased resonance participation of the oxygen could explain the behavior.[10] On both sides of the discussion, the analogy to the diaryl-substituted cations, such as 6, was noted.

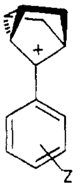
The isotope shifts at the cationic center for 8-d_3 are listed in Table II. All are downfield isotope shifts that increase in magnitude with increasing electron demand. The TIED plot for 8-d_3 is shown in Figure 8b. A good linear relation is seen not only for the electron-donating substituents but for all substituents (Table IV). However, if the line is drawn for electron donors only, as in Figure 8b, the points for 4'-CF$_3$ and 3',5'-(CF$_3$)$_2$ deviate slightly upward from this line. The small deviation from this line in the deshielding direction resembles the slight upward deviation of the 4'-CF$_3$-1 point in Figure 1b for the reference system. Thus, the isotope shift behavior for 8 is comparable to that of the reference system 1 and the diarylcarbenium ion system 6.

1-Aryl-1-cyclopropylethyl Cations (9). In a previous TIED study of the C$^+$ chemical shifts of 9, distinctly nonlinear behavior was found.[1b] Our chemical shift data for C$^+$ of 9 from Table I are plotted vs σ^{C^+} in Figure 9a. The points for electron-withdrawing substituents clearly deviate toward more shielded values than predicted by the correlation line for electron donors, as found previously. Kelly et al. conducted from their study of $^{13}C-^{1}H$ coupling in **9** that the cyclopropyl ring maintains the favored bisected orientation throughout the series.[25]

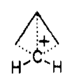
Upfield isotope shifts are found at C^+ for all cations in the **9** series, as listed in Table II. Variation in the $^2\Delta C(D)$ with increasing electron demand is seen in the TIED plot for **9** in Figure 9b. Two aspects of Figure 9b stand out. First, the slope of the plot is negative, while all the other plots for cations in this paper have been positive. There is one precedent for this in the 3-endo-d_1 isotopomers of the 2-aryl-2-norbornyl cations. Second, the variation is clearly nonlinear in Figure 9b and could be considered as being curved or as having two linear segments as shown in the figure. The isotope shifts associated with the electron-withdrawing substituents are more upfield than expected from the correlation line drawn for electron donors, but these points appear to correlate linearly with σ^{C^+} also. The slope for the electron-withdrawing cases (including Z = H) is steeper; $\rho = -0.060$ ($i = -0.168$; $r^2 = 0.991$) instead of $\rho = -0.024$ for the electron donors (see Table IV).

Cyclopropyl-substituted carbenium ions have provided a considerable challenge to the ability of chemists to understand and describe structure and bonding.[26] At one extreme, the parent "cyclopropylcarbinyl/bicyclobutonium cation" or "$C_4H_7^+$" and the related methylbicyclobutonium ion appear to have a σ-delocalized bicyclobutonium framework as the lowest energy form, although the exact description is made difficult by rapid rearrangements.[27] At the other extreme, the cyclopropyl group can act simply as a good hyperconjugative electron donor to an electron-deficient center, with a preference for the bisected geometry in which both C1–C2 and C1–C3 bonds of the ring interact equally.

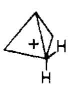
Olah et al. examined the related 3-aryl-3-nortricyclyl cations **16** and rationalized the deviation from linearity in the chemical shift TIED plot as being due to the "onset of increased cyclopropyl conjugation".[11] They reasoned that the cyclopropyl ring in **16** is fixed in the bisected orientation, which is ideally oriented for conjugation, but, according to Olah, not suited for σ participation. Thus, in Olah's view, the nonlinear TIED behavior could not signal the onset of nonclassical bonding because of the geometrical constraint.



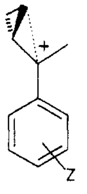
16



17



18



19

On the other hand, the concept of the "onset of increased cyclopropyl conjugation" is rather vague and ill-defined, as noted by both Brown and Olah,[1] and conveys no information about a change in structure or bonding character or why the extent of conjugation should not change smoothly in response to increased electron demand. Brown suggested instead that localized inductive π polarization might explain the nonlinear TIED behavior of **9** and be the common denominator in the behavior of **6–9**,[1b] and possibly all cases of nonlinear TIED behavior.[6] In the case of **9**, the π-type bond between C^+ and the cyclopropyl ring would be polarized toward C^+ by the electron-withdrawing substituents. However, in view of the isotope shift TIED plots, it no longer appears that **6–9** behave similarly. Only **9**-d_3 shows a clear change in response to isotope effects with increasing electron demand. Thus, the postulate of a common origin for nonlinear TIED behavior is neither necessary nor desirable. Furthermore, the concept of *inductive π* polarization, as introduced by Brownlee,[24] implies that the inductive withdrawing effects of resonance donors such as the methoxy group should lead to deviation of these points also in a TIED plot.

It should be noted that Olah's description of the nonclassical geometry of cyclopropylcarbinyl/bicyclobutonium cations differs from that of some other researchers. Olah depicts the nonclassical, rapidly equilibrating structures of the most stable bicyclobutonium form as shown for **17**,[28] which implies two equivalent hydrogens at the bridging atom and incompatibility with a bisected geometry as proposed for **16**. In contrast, Roberts, Siehl, and Saunders feel the evidence from isotopic perturbation studies favors two different hydrogens at the bridging carbon, as in **18**.[29] Furthermore, both theoretical calculations and experiment show a very shallow energy surface for interconversion of the parent bicyclobutonium and cyclopropylcarbinyl structures.[27] If one considers it possible for nonclassical bonding to evolve out of a bisected structure with relatively little geometric distortion, given sufficient electron demand, then it is possible that the deviations from linearity in the chemical shift and isotope shift TIED plots signal the onset of σ bridging. In this explanation, the bonding in 4′-CF_3-**9** would have to involve partial σ bridging in two equilibrating, equivalent structures as shown for **19**, rather than the equal hyperconjugative involvement of two cyclopropyl bonds expected in the precisely bisected structure.

The onset of σ bridging, i.e., a change from simple C–C hyperconjugation without bridging to partial bridging, could provide a common explanation for the TIED plots for **2** and **9** and for the less pronounced deviations in TIED plots for **3** and **4**. However, the isotope shift TIED plot for **9**-d_3 does not have the same appearance as the isotope shift TIED plot for **2**-d_2. The TIED plot in Figure 9b appears to mildly change slope, while the plot in Figure 2b shows a dramatic deviation toward shielding. Thus, if the onset of σ bridging is the explanation for nonlinear behavior in both systems, then while the chemical shift TIED plots indicate a similar extent of shielding due to development of σ bridging, the isotope shift TIED plots may indicate a shallower surface for bending along the bridging coordinate in the case of the 2-norbornyl system.

Summary and General Comments. The isotope shift TIED plots for carbocations can be grouped into three types: (i) A very large deviation from the correlation line for electron donors is seen for 4′-CF_3-**5**-d_3 in the 2-aryl-3-methyl-2-butyl cation series. This is clearly due to the onset of a rapid rearrangement and need not be discussed further. (ii) Four systems show deviations from the correlation line toward isotope effects that are more shielding

---

[25] Kelly, D. P.; Farquharson, G. J.; Giansiracusa, J. J.; Jensen, W. A.; Hugel, H. M.; Porter, A. P.; Rainbow, I. J.; Timewell, P. H. *J. Am. Chem. Soc.* **1981**, *103*, 3539.

[26] Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*, 3rd ed.; Harper & Row: New York, 1987; pp 454–463.

[27] For the most recent theoretical work and a leading reference to the extensive literature, see: Saunders, M.; Laidig, K. E.; Wiberg, K. B.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1988**, *110*, 7652.

[28] Prakash, G. K. S.; Arvanaghi, M.; Olah, G. A. *J. Am. Chem. Soc.* **1985**, *107*, 6017.

[29] (a) Saunders, M.; Siehl, H.-U. *J. Am. Chem. Soc.* **1980**, *102*, 6868. (b) Brittain, W. J.; Squillacote, M. E.; Roberts, J. D. *J. Am. Chem. Soc.* **1984**, *106*, 7280. (c) Siehl, H.-U. *J. Am. Chem. Soc.* **1985**, *107*, 3390. (d) Saunders, M.; Krause, N. *J. Am. Chem. Soc.* **1988**, *110*, 8050.

than expected as electron demand increases: 2-aryl-2-norbornyl cations, **2**-d_3; 2-aryl-2-bicyclo[2.2.2]octyl cations, **3**-d_2; 2-aryl-2-bicyclo[2.1.1]hexyl cations, **4**-d_2; 1-aryl-1-cyclopropylethyl cations, **9**-d_3. (iii) Three systems show very similar linear correlations with σ^{C^+} in isotope shift TIED plots: 2-aryl-2-propyl cations, **1**-d_6; 1-aryl-1-tolylethyl cations, **6**-d_3; 1-arylhydroxyethyl cations, **8**-d_3. Each of these three shows a deviation in the direction of an isotope effect for the 4'-CF_3 point that is more deshielding than predicted from the line established by electron donors (and excellent correlations exist among these three sets of data).

Structural features common to cations displaying each of the latter two types of isotope shift TIED behavior are readily apparent. The cation centers of **2**–**4** and **9** are each substituted by the aryl group, an alkyl group bearing the C–D (or C–H) bonds, and a third alkyl group that has C–C bonds available for hyperconjugation and/or σ bridging. It is obvious that the C–C hyperconjugation would increase as electron demand increases; possibly increased C–C hyperconjugation alone could account for a nonlinear chemical shift TIED plot if C–C hyperconjugation responds differently than C–H hyperconjugation in the reference system **1**. However, to explain the isotope shift results, we propose that as electron demand increases, the potential energy surface for motion of nuclei toward bridging by the C–C bond is lowered sufficiently that the vibrationally averaged structure becomes slightly bridged. If the more electron-deficient cations have a more shallow, broad surface along the bridging coordinate, isotopic substitution could slightly alter the vibrationally averaged extent of bridging, leading to nonlinear isotope shift TIED plots for **2**-d_2, **3**-d_2, **4**-d_2, and **9**-d_3.

Another type of isotope shift TIED response is found for **1**-d_6, **6**-d_3, and **8**-d_3. The cation centers of these cations are substituted by the aryl group, an alkyl group with only C–D bonds available for interaction, and either a second such alkyl group (**1**-d_6) or a π-type donor. Presumably, the third group as a π donor provides no vibration that becomes easily perturbable with increasing electron demand. Hence, even if inductive π polarization or increased π-resonance participation leads to a nonlinear chemical shift TIED plot as for **6** and **8**, the behavior in the isotope shift TIED plot will be essentially the same as in the reference system **1**.

Winstein was the first to suggest that hyperconjugation and bridging by σ bonds are different degrees of a single delocalization phenomenon, and, over the intervening years, the possibility of a whole spectrum of structural types has been suggested frequently.[30] A recent study by le Noble concludes that σ delocalization is not swamped by donating substituents at the cation center in tertiary cumyl cations and that some geometric distortion likely accompanies σ delocalization.[31] As noted by Schleyer,[13c] very few carbocations may be fully "classical" either by geometry or in terms of electronic structure, in the sense of being "adequately represented by a single Lewis structure involving two-electron-two-center bonds".[32] His recent high-level ab initio calculations on the cyclopentyl cation, which has two C–H bonds positioned for hyperconjugation, indicate that strong hyperconjugative interactions are accompanied by geometric distortion not only of bond lengths but also of bond angles, leading to a partially bridged structure.[13c] We conclude that the combination of the "tool of increasing electron demand" with NMR isotope shifts permits examination of the subtle transition from simple hyperconjugation to a point at which geometric distortion toward bridging has observable physical consequences. Intrinsic NMR isotope shift evidence indicates that vibrationally averaged geometries can be altered sufficiently by isotopic substitution to affect hyperconjugation and bridging, either directly by deuterium substitution for protium in a C–H bond involved in hyperconjugation[4b,33] or indirectly, when electron demand is high and a C–C bond is well aligned for hyperconjugation and bridging.[5,14] The direct effect for a hyperconjugating C–H bond is a deshielding contribution to the isotope shift at the electron-deficient center;[4b,33] the indirect effect for a hyperconjugating C–C bond can either be shielding (as seen in **2**–**4** and **9**–**12**) or deshielding, depending on the location of the deuterium.[5,14]

Experimental Section

NMR Spectroscopy. ^{13}C NMR spectra of cations were acquired at 75.4 MHz with a Varian XL-300 spectrometer. Initial spectra were acquired within 1000 transients by using a 30–60° pulse, 2.5–3.5-s repetition rate, 30K data points, 25000-Hz spectral width. Narrower spectral widths, e.g., 1000 Hz, and resolution-enhancing weighting functions were used where necessary to resolve isotope shifts in the C^+ region. Spectra were run unlocked, and chemical shifts were referenced to internal CH_2Cl_2 (53.62 ppm).

Cation Preparation. The general procedure was to add in small portions ca. 2 mmol of the appropriate cation precursor in SO_2ClF (1.0 mL) at −78 °C to a Vortex-stirred solution of ca. 10 mmol of 1:1 FSO_3H–SbF_5 in SO_2ClF (2.0 mL) at −78 °C. Some cations were prepared directly in NMR tubes; for others, the cation solution was transferred by precooled pipet to a precooled 8-mm NMR tube. In most cases, separate solutions were prepared with different ratios (e.g., 1:2 and 2:1) of labeled and unlabeled isotopomers.

Cation Precursors. Precursors to the **1**, **1**-d_3, **2**, and **2**-d_2 cations were described previously,[5] as were the acetophenone precursors to the **8** series.[6,10]

Alcohol or olefin precursors to the **3** and **3**-d_2 series were prepared by standard reactions of Grignard reagents from aryl bromides or iodides with 2-bicyclo[2.2.2]octanone or 2-bicyclo[2.2.2]octanone-*3,3*-d_2[34] in anhydrous ether. Purification by flash column chromatography on silica gel with 3% ethyl acetate in pentane as eluent gave the 2-aryl-2-bicyclo[2.2.2]octanol or -*3,3*-d_2 isotopomer in all cases except 2-(4'-chlorophenyl)- and 2-(4'-methoxyphenyl)-2-bicyclo[2.2.2]octene and 2-(4'-methoxyphenyl)-2-bicyclo[2.2.2]octene-*3*-d_1. Preparations of alcohol or olefin precursors to all series **3** ions have been previously reported, but few NMR data were given.[18] In similar fashion, the 2-aryl-2-bicyclo[2.1.1]hexanols and -*3,3*-d_2 isotopomers were prepared as precursors to the **4** and **4**-d_2 cations from 2-bicyclo[2.1.1]hexanone[35] or its -*3,3*-d_2 isotopomer. Four repetitions of vigorous stirring of a solution of 2-bicyclo[2.1.1]hexanone in ether over D_2O/NaOD at reflux for 12 h led to 2-bicyclo[2.1.1]hexanone-*3,3*-d_2 with >99% dideuteriation at C3. Although several of the series **4** ions were reported previously,[11] no details of the alcohol precursors appears to be available. Therefore, ^1H and ^{13}C NMR data for precursors to **3** and **4** cations are listed in the supplementary material.

The 2-aryl-3-methyl-2-butanol and -*1,1,1*-d_3 precursors to **5** and **5**-d_3 cations, and the 1-*p*-tolyl-1-arylethanol and -α,α,α-d_3 precursors to **6** and **6**-d_3 cations were prepared by addition of isopropylmagnesium iodide to 4'-substituted acetophenones or their -α,α,α-d_3 isotopomers and addition of aryl Grignard reagents to

---

[30] (a) Winstein, S.; Morse, B. K.; Grunwald, E.; Schreiber, K. C.; Corse, J. *J. Am. Chem. Soc.* **1952**, *74*, 1113. (b) Olah, G. A. *Carbocations and Electrophilic Reactions*; Verlag Chemie: Weinheim, 1974.

[31] Lin, M.-H.; Cheung, C. K.; le Noble, W. J. *J. Am. Chem. Soc.* **1988**, *110*, 6562.

[32] Brown, H. C. (with comments by Schleyer, P. v. R.). *The Nonclassical Ion Problem*; Plenum Press: New York, 1977; pp 49–50.

[33] Arrowsmith, C. H.; Kresge, A. J. *J. Am. Chem. Soc.* **1986**, *108*, 7918, and references therein.

[34] Forsyth, D. A.; Botkin, J. H.; Osterman, V. M. *J. Am. Chem. Soc.* **1984**, *106*, 7603.

[35] Della, E. W.; Pigou, P. E. *Aust. J. Chem.* **1983**, *36*, 2261.

4′-methylacetophenone or its -α,α,α-d_3 isotopomer. The 1-aryl-1-cylopropylethanol and -*2,2,2*-d_3 precursors to **9** and **9**-d_3 cations were similarly prepared by addition of aryl Grignard reagents to cyclopropyl methyl ketone or its -α,α,α-d_3 isotopomer. All of the unlabeled precursors have been previously reported,[1b,19,21] with the exception of 1-(3′,5′-dichlorophenyl)-1-cyclopropylethanol: bp 109 °C (1 mm); ^{1}H NMR (CDCl$_3$) δ 0.3–0.6 (m, 4 H), 1.1–1.3 (m, 1 H), 1.4 (s, 3 H), 2.8 (s, 1 H), 7.2 (s, 1 H), 7.4 (s, 2 H); ^{13}C NMR (CDCl$_3$) δ 0.9 (C5), 2.1 (C4), 22.4 (C3), 27.7 (C2), 72.8 (C1), 123.7 (C2′,6′), 126.5 (C4′), 134.3 (C3′,5′), 151.6 (C1′).

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research, and also to the National Science Foundation (Grant CHE-8211125).

Registry No. **3**, 25954-80-7; **3** (4′-OCH$_3$), 53600-78-5; **3** (4′-CH$_3$), 53600-80-9; **3** (4′-F), 51804-52-5; **3** (4′-Cl), 53600-81-0; **3** (4′-CF$_3$), 53272-70-1; **3**-d_2, 128631-30-1; **3**-d_2 (4′-CH$_3$), 128631-28-7; **3**-d_2 (4′-F), 92720-90-6; **3**-d_2 (4′-Cl), 128631-29-8; **3**-d_2 (4′-CF$_3$), 128631-31-2; **4**, 59856-44-9; **4** (4′-OCH$_3$), 77938-38-6; **4** (4′-CH$_3$), 77938-39-7; **4** (4′-F), 128631-26-5; **4** (4′-Cl), 128631-27-6; **4** (4′-CF$_3$), 77938-40-0; **4** [3′,5-(CF$_3$)$_2$], 77938-41-1; **4**-d_2, 59856-44-9; **4**-d_2 (4′-OCH$_3$), 128631-32-3; **4**-d_2 (4′-CH$_3$), 128631-33-4; **4**-d_2 (4′-F), 128631-34-5; **4**-d_2 (4′-Cl), 128599-40-6; **4**-d_2 (4′-CF$_3$), 128631-35-6; **4**-d_2 [3′,5′-(CF$_3$)$_2$], 128631-36-7; **5**, 36043-29-5; **5** (4′-OCH$_3$), 35144-47-9; **5** (4′-CH$_3$), 36043-28-4; **5** (4′-F), 51804-42-3; **5** (4′-Cl), 41912-30-5; **5** (3′-CH$_3$), 84074-03-3; **5** (3′-Cl), 84074-05-5; **5** (4′-CF$_3$), 84074-08-8; **5**-d_3, 128599-45-1; **5**-d_3 (4′-OCH$_3$), 128631-37-8; **5**-d_3 (4′-CH$_3$), 128599-41-7; **5**-d_3 (4′-F), 128599-42-8; **5**-d_3 (4′-Cl), 128599-43-9; **5**-d_3 (3′-CH$_3$), 128599-44-0; **5**-d_3 (3′-Cl), 128599-46-2; **5**-d_3 (4′-CF$_3$), 128599-47-3; **6**, 41912-34-9; **6** (4′-OCH$_3$), 60665-82-9; **6** (4′-CH$_3$), 41912-36-1; **6** (4′-F), 39769-51-2; **6** (4′-Cl), 86766-95-2; **6** (4′-CF$_3$), 86766-99-6; **6**-d_3, 128599-51-9; **6**-d_3 (4′-OCH$_3$), 128599-48-4; **6**-d_3 (4′-CH$_3$), 128599-49-5; **6**-d_3 (4′-F), 128599-50-8; **6**-d_3 (4′-Cl), 128631-38-9; **6**-d_3 (4′-CF$_3$), 128599-52-0; **7**, 98-86-2; **7** (4′-OCH$_3$), 100-06-1; **7** (4′-CH$_3$), 122-00-9; **7** (4′-F), 403-42-9; **7** (4′-Cl), 99-91-2; **7** (3′-CH$_3$), 585-74-0; **7** (3′-Cl), 99-02-5; **7** (4′-CF$_3$), 709-63-7; **7** [3′,5′-(CF$_3$)$_2$], 30071-93-3; **7**-d_3, 17537-31-4; **7**-d_3 (4′-OCH$_3$), 29268-64-2; **7**-d_3 (4′-CH$_3$), 128599-53-1; **&**-d_3 (4′-F), 101493-81-6; **7**-d_3 (4′-Cl), 128599-54-2; **7**-d_3 (3′-CH$_3$), 128599-55-3; **7**-d_3 (3′-Cl), 128599-56-4; **7**-d_3 (4′-CF$_3$), 128599-57-5; **7**-d_3 [3′,5′-(CF$_3$)$_2$], 128599-58-6; **8**, 3441-74-5; **8** (4′-OCH$_3$), 53909-70-9; **8** (4′-CH$_3$), 56083-69-3; **8** (4′-F), 31067-67-1; **8** (4′-Cl), 56683-70-6; **8** (3′-CH$_3$), 128599-36-0; **8** (3′-Cl), 128599-37-1; **8** (4′-CF$_3$), 128599-38-2; **8** [3′,5′-(CF$_3$)$_2$], 128599-39-3; **8**-d_3, 128599-63-3; **8**-d_3 (4′-OCH$_3$), 128599-59-7; **8**-d_3 (4′-CH$_3$), 128599-60-0; **8**-d_3 (4′-F), 101493-83-8; **8**-d_3 (4′-Cl), 128599-61-1; **8**-d_3 (3′-CH$_3$), 128599-62-2; **8**-d_3 (3′-Cl), 128599-64-4; **8**-d_3 (4′-CF$_3$), 128599-65-5; **8**-d_3 [3′,5′-(CF$_3$)$_2$], 128599-66-6; **9**, 41912-19-0; **9** (4′-OCH$_3$), 15810-35-2; **9** (4′-CH$_3$), 15810-34-1; **9** (4′-F), 56519-31-4; **9** (4′-Cl), 15876-04-7; **9** (3′-Cl), 81390-54-7; **9** (4′-CF$_3$), 62586-66-7; **9** [3′,5′-(CF$_3$)$_2$], 78195-83-2; **9**-d_3, 128599-71-3; **9**-d_3 (4′-OCH$_3$), 128599-67-7; **9**-d_3 (4′-CH$_3$), 128599-68-8; **9**-d_3 (4′-F), 128599-69-9; **9**-d_3 (4′-Cl), 128599-70-2; **9**-d_3 (3′-Cl), 128631-39-0; **9**-d_3 (4′-CF$_3$), 128599-72-4; **9**-d_3 [3′,5′-(CF$_3$)$_2$], 128599-73-5; 2-phenylbicyclo[2.2.2]octanol, 53601-08-4; 2-(4′-trifluorophenyl)-2-bicyclo[2.2.2]octanol, 53272-75-6; 2-(4′-fluorophenyl)-2-bicyclo[2.2.2]octanol, 53272-74-5; 2-(4′-methylphenyl)-2-bicyclo[2.2.2]octanol, 128599-74-6; 2-(4′-chlorophenyl)-2-bicyclo[2.2.2]octanol-*3,3*-d_2, 128599-75-7; 2-(4′-chlorophenyl)-2-bicyclo[2.2.2]octene, 128599-76-8; 2-(4′-methoxyphenyl)-2-bicyclo[2.2.2]octene, 53601-00-6; 2-phenyl-2-bicyclo[2.1.1]hexanol, 125642-76-4; 2-[3′,5′-bis(trifluoromethyl)-phenyl]2-bicyclo[2.1.1]hexanol, 128599-77-9; 2-(4′-chlorophenyl)-2-bicyclo[2.1.1]hexanol, 128599-78-0; 2-[4′-(trifluoromethyl)phenyl]-2-bicyclo[2.1.1]hexanol, 128599-79-1; 2-(4′-fluorophenyl)-2-bicyclo[2.1.1]hexanol, 128599-80-4; 2-(4′-methylphenyl)-2-bicyclo[2.1.1]hexanol, 128599-81-5; 2-(4′-methoxyphenyl)-2-bicyclo[2.1.1]hexanol, 128599-82-6.

Supplementary Material Available: Listings of additional ^{13}C chemical shifts and isotope shifts for cations **3–9** and NMR data for the 2-aryl-2-bicyclo[2.1.1]hexanols and 2-aryl-2-bicyclo[2.2.2]octanols (10 pages). Ordering information is given on any current masthead page.

Regioselective Reductive Electrophilic Substitution of 1,2,3-Trimethoxybenzene and Its 5-Alkyl-Substituted Homologues

Ugo Azzena,* Teresa Denurra, Giovanni Melloni, and Anna Maria Piroddi

Dipartimento di Chimica, Università di Sassari, via Vienna 2, I-07100 Sassari, Italy

Received February 23, 1990

The methoxy group in the 2-position of 1,2,3-trimethoxybenzene (**1**) can be regioselectively removed by electron transfer from alkali metals and replaced with a variety of electrophiles in a one-pot procedure, affording 2-substituted resorcinol dimethyl ethers. The usefulness of this synthetic method is illustrated by numerous examples. This reaction procedure has been successfully extended to the 5-methyl-substituted homologue (**2**), but limitations occur with the higher homologue 1-pentyl-3,4,5-trimethoxybenzene (**3**). Investigations on the mechanism of demethoxylation, with the aid of labeling experiments, provided clear evidence for the intermediacy of aryl radicals and explained the low yields obtained in the reductive electrophilic substitutions of compound **3**.

Aromatic methoxy groups are considered, from a synthetic point of view, as stable linkages not suitable for transformation purposes; indeed, such groups are almost always regarded as masked phenols,[1] not as versatile synthetic functionalities. However, replacement of the methoxy group with a hydrogen atom (reductive demethoxylation) can be achieved under electron-transfer conditions; under such conditions, cleavage of the alkyl–oxygen bond (reductive demethylation) usually occurs as a competitive reaction.[2]

1,2,3-Trimethoxybenzene (**1**) is particular in that its reduction with alkali metals, in solvents of low polarity, leads to 100% regioselective demethoxylation in the 2-position in almost quantitative yields.[2-4] Such uncommon regioselectivity in the cleavage of an aryl–oxygen bond has

---

(1) Bhatt, M. V.; Kulkarni, S. U. *Synthesis* **1983**, 249.

(2) Maerker, A. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 972.

(3) Azzena, U.; Denurra, T.; Fenude, E.; Melloni, G.; Rassu, G. *Synthesis* **1989**, 28.

(4) On the contrary, reaction of **1** with sodium metal in hexamethylphosphoric triamide affords 2,3- and 2,6-dimethoxyphenol in 1:1 ratio and 60% overall yield: Testaferri, L.; Tiecco, M.; Tingoli, M.; Chianelli, D.; Montanucci, M. *Tetrahedron* **1982**, *38*, 3687.

0022-3263/90/1955-5386$02.50/0 © 1990 American Chemical Society