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# Structural Effects in Solvolytic Reactions. 40. Carbon-13 Nuclear Magnetic Resonance Studies of Carbocations. 8.[1] Anomalous Carbon-13 Chemical Shifts with Increasing Electron Demand in the 2-Aryl-2-norbornyl Cations and Related Systems. Evidence That These Anomalous Shifts Are Not Diagnostic for the Onset of Nonclassical σ Bridging

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$^{13}$C NMR spectra of an extended range of 2-aryl-2-norbornyl (**11**), 2-aryl-*exo*-5,6-trimethylene-2-norbornyl (**12**), 2-aryl-*endo*-5,6-trimethylene-2-norbornyl (**13**), 3-aryl-3-nortricyclyl (**14**), 1-aryl-1-cyclopropylethyl (**15**), 1-aryl-1-phenylethyl (**28**), and 1-aryl-1-phenylmethyl (**29**) carbocations have been obtained under standard conditions. When the cationic carbon substituent chemical shifts $\Delta\delta C^+$ are plotted against the new $\sigma^{C^+}$ constants, the points for the substituents more electron donating than H (Z = 3′,4′-$CH_2CH_2O$ to Z = H) yield excellent linear correlations, whereas those for substituents more electron demanding than H (Z = H to Z = 3′,5′-$(CF_3)_2$) curve away from this correlation line. These deviations from linearity are in contrast to the plots for a large range of static, classical acyclic (**1–4**), cyclic (**5–7**), and polycyclic (**8–10**) carbocations, which yield excellent correlations of $\Delta\delta C^+$ with $\sigma^{C^+}$. The deviations in the plots for **11** and **12** have been rationalized previously in terms of the onset of σ bridging, for **14** in terms of the onset of increased cyclopropyl conjugation and for **28** in terms of steric inhibition of resonance. However, examination of our data shows that for each of the three different molecular structures, 2-norbornyl (**11–13**), cyclopropylcarbinyl (**14**, **15**), and phenylalkyl (**28**, **29**), the same, in fact, almost identical, deviations are observed. In addition, the aryl derivatives of other cationic systems for which σ-bridged structures have been proposed, cyclobutyl (**19**), 2-bicyclo[2.1.1]hexyl (**20**), 2-bicyclo[2.2.2]octyl (**21**), and 6-bicyclo[3.2.1]octyl (**22**), fail to exhibit such deviations with the data available. Thus we conclude that the anomalous $^{13}$C shifts, which give rise to the deviations from linearity in the plots of $\Delta\delta C^+$ against $\sigma^{C^+}$ (or $\Delta\delta C^+$, cyclopentyl), are not diagnostic for the onset of nonclassical σ bridging. Possible explanations for these anomalous $C^+$ shifts are considered.

The "tool of increasing electron demand" has been used extensively to probe for σ or π participation or conjugation in the solvolytic transition states of a large number of molecular systems.[2] Only in the case of the 9-aryl-9-pentacyclo[4.3.0.0$^{2,4}$.0$^{3,8}$.0$^{5,7}$]nonyl system of Coates[3] has this tool confirmed the presence of πσ participation.[4] With this tool, the 2-aryl-2-norbornyl system failed to reveal any evidence whatsoever for σ participation.[2,4]

The concept of the "tool of increasing electron demand" has been applied to carbocationic species generated under long-life conditions in superacids. Thus Olah and coworkers plotted the $^{13}$C cationic carbon chemical shifts $\delta C^+$ of cumyl cations against $\sigma^+$ constants and noted an approximate linear correlation.[5] Farnum and Wolf plotted proton shifts $H_1$ and $H_3$ of 2-aryl-2-norbornyl cations against one another and claimed that the deviation from linearity observed for the electron-withdrawing substituents was evidence for the "onset of C(1)–C(6) σ bond delocalization or 'nonclassical' stabilization".[6] For the same system, Olah and co-workers plotted first the carbon shifts $C_1$ and $C_3$ against one another and second $\delta C_1$ against $\sigma^+$ constants. They observed similar deviations from linearity for substituents more electron withdrawing than *p*-H from which they concluded: "the so-called 'classical–nonclassical ion controversy' should be considered closed, even when considering Brown's own criterion of the tool of increasing electron demand."[7]

Subsequently, it was pointed out by Kelly and Spear that deviations in plots of carbon chemical shifts $\sigma^+$ are not necessarily due to σ bridging in the cations with electron-withdrawing substituents but rather to a failure to allow for the enhanced delocalization of the electron-donating substituents in the fully formed cations over that of the solvolytic transition states from which the $\sigma^+$ constants were derived.[8] Thus a set of "supersigma" ($\sigma^{++}$) constants was proposed for use in correlations of cationic carbon shifts of aryl carbocations.[8]

Farnum[9] and, more recently, Olah[10] and their co-workers have used the cationic shifts ($\delta C^+$) of "ordinary" ions such as 6-aryl-6-bicyclo[3.2.1]octyl[9] and 1-aryl-1-cyclopentyl[10] rather than $\sigma^+$ or $\sigma^{++}$ constants to plot against $\delta C^+$ values for 2-aryl-2-norbornyl cations. Similar deviations from linearity were observed, which they claimed confirmed the presence of nonclassical σ bridging.

We wished to compare the shifts of these norbornyl cations against a common standard and accordingly developed two new series of σ constants, $\sigma^{C^+}$ and $\sigma^{\alpha C^+}$, from an extended range of meta- and para-substituted *tert*-cu-

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[1] This is part 40 in one series and part 8 in another. For part 39, see: Brown, H. C.; Periasamy, M. *J. Org. Chem.* **1982**, *47*, 5–8. For part 7, see: Giansiracusa, J. J.; Jenkins, M. J.; Kelly, D. P., *Aust. J. Chem.* **1982**, *35*, 443–450.

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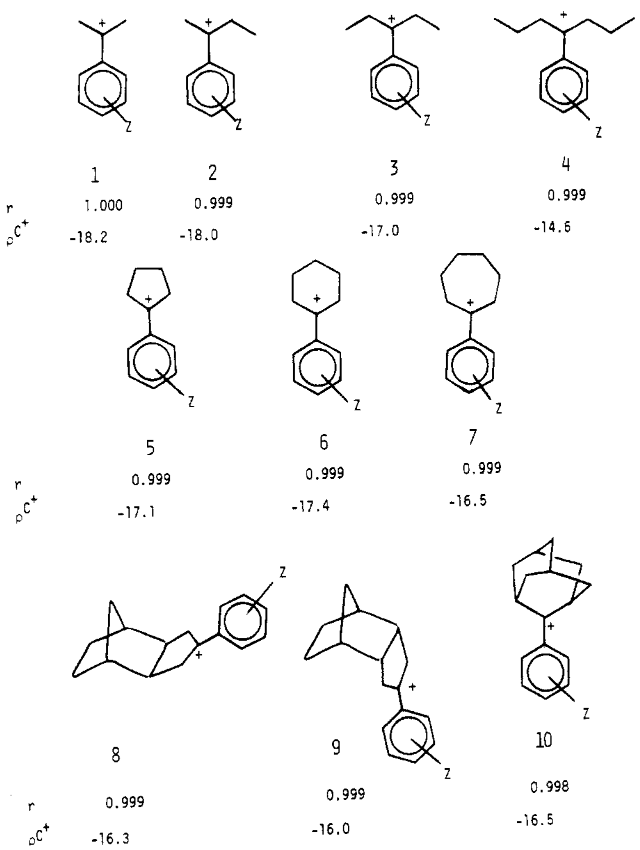
Chart I



myl cations. (Previous correlations used relatively few substituents, especially few meta substituents, to fix the slope of the line.)[7,8] These constants were derived from the modified Hammett–Brown equations (eq 1 and 2)

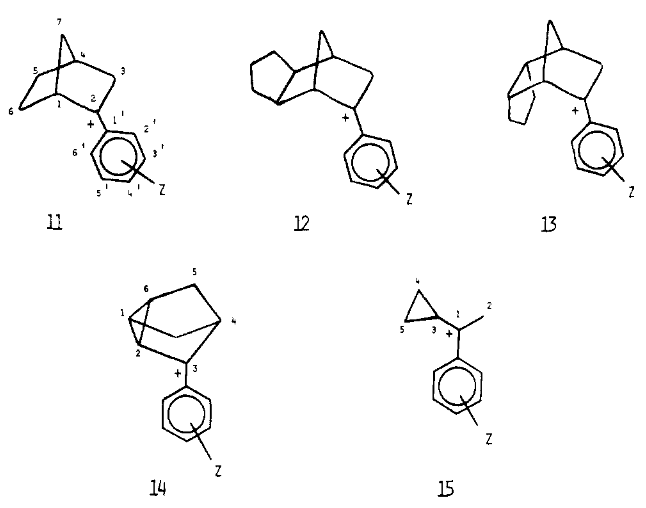
$$\Delta\delta C^+ = \rho^{C^+}\sigma^{C^+} \qquad (1)$$

$$\Delta\delta C^{\alpha C^+} = \rho^{\alpha C^+}\sigma^{\alpha C^+} \qquad (2)$$

where $\Delta\delta C^+ = [\delta(H) - \delta(Z)]$ and $\rho^{C^+} = -18.18$ for the cationic carbons[12,13] and $\Delta\delta C^{\alpha C^+} = [\delta(H) - \delta(Z)]$ and $\rho^{\alpha C^+} = -4.14$ for the $\alpha$ (methyl) carbons.[14] The new $\sigma^{C^+}$ constants have been tested in ten representative systems: acyclic[15,16] (**1–4**), cyclic[17,18] (**5–7**), and polycyclic[16,18] (**8–10**, Chart I).

Inspection of all of these plots showed that the slopes were markedly influenced by the point for *p*-methoxy ($\sigma^{C^+} = -2.02$), the only strong electron donor in the series. In order to reduce this influence and render the plots more reliable, we have determined the $\sigma^{C^+}$ value for the 5′-coumaranyl group [2,3-dihydrobenzofuran-5-yl or 3,4-(ethyleneoxy)phenyl] as −2.40 by the method outlined previously.[19] Preparation of a representative number of these new classical cations, e.g., **3**, **5**, **10** (Z = 3,4-$CH_2CH_2O$) proceeded smoothly by ionization of the corresponding alcohols in $FSO_3H/SO_2ClF$. The $\Delta\delta C^+$ values obtained from their $^{13}C$ spectra all fell on or acceptably close to the previously established correlation line with $\sigma^{C^+}$.[19] Similar results were obtained for the remainder of these classical cations in a separate study.[20] In all cases, excellent correlations with $\Delta\delta C^+$ were obtained (Chart I).[20]

Chart II



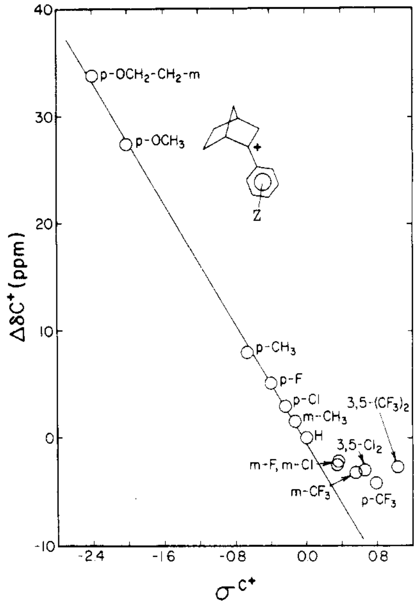


**Figure 1.** Plot of $\Delta\delta C^+$ against $\sigma^{C^+}$ for 2-aryl-2-norbornyl cations: $\rho^{C^+} = -14.03$, $r = 0.999$ (least squares analysis for electron donating substituents only).

Once the enhanced electron delocalization of the para donating substituents had been catered for by the new $\sigma^{C^+}$ constants, we could turn our attention to the 2-aryl-2-norbornyl cations (**11**, Chart II) in which nonclassical $\sigma$ bridging has been proposed. We have obtained data for a set of 13 of these cations under carefully controlled conditions in two different laboratories. In addition, we have prepared and recorded the data for the related 2-aryl-*exo*-5,6-trimethylene-2-norbornyl (**12**) and 2-aryl-*endo*-5,6-trimethylene-2-norbornyl (**13**) carbocations. Finally, we have extended the study to the 3-aryl-3-nortricyclyl cations (**14**) and the 1-aryl-1-cyclopropylethyl cations (**15**) in which $\sigma$ bridging is possible in one (**15**) but not the other (**14**).[21]

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[12] The substituent chemical shifts $\Delta\delta$ are reversed from the normal presentation $[\delta(Z) - \delta(H)]$[8] in order to reproduce the form of the Hammett–Brown equation with $\rho$ negative.

[13] Brown, H. C.; Kelly, D. P.; Periasamy, M. *Proc. Natl. Acad. Sci. U.S.A.* **1980**, *77*, 6956–6960.

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[17] Brown, H. C.; Periasamy, M. *J. Org. Chem.* **1981**, *46*, 3161–3165.

[18] Brown, H. C.; Periasamy, M. *J. Org. Chem.* **1981**, *46*, 3166–3170.

[19] Giansiracusa, J. J.; Jenkins, M. J.; Kelly, D. P. *Aust. J. Chem.* **1982**, *35*, 443–450.

[20] Brown, H. C.; Periasamy, M. *J. Org. Chem.* **1982**, *47*, 5–8.

[21] (a) Brown, H. C.; Peters, E. N. *J. Am. Chem. Soc.* **1975**, *97*, 1927–1929. (b) Brown, H. C.; Peters, E. N.; Ravindranathan, M. *Ibid.* **1977**, *99*, 505–509.

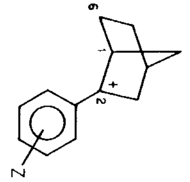
## Results and Discussion

**2-Aryl-2-norbornyl Carbocations (11).** The chemical shifts of these cations 11 at −70 °C in $SbF_5/FSO_3H/SO_2ClF$ are given in Table I. The cations have also been generated in $FSO_3H/SO_2ClF$ and their spectra recorded at −40 °C, the differences being insignificant. Some of the data have been reported previously in connection with our work on $^{13}C-^{1}H$ coupling constants[22a] and by Olah[7] and Farnum.[9] The cationic carbon substituent chemical shifts $\Delta\delta C^+$ are plotted against $\sigma^{C^+}$ in Figure 1. There are two aspects of this figure worthy of note.

First, the slope of the correlation line (−14.0) drawn through the points for the electron-donating substituents (Z = 3′,4′-$CH_2CH_2O$ to Z = H) is less negative than those observed for **1**–**10** (Chart I) and even less negative than that for the 4-aryl-4-heptyl cation, the previous extreme. Second, the points for the substituents more electron demanding than H show a marked deviation in the form of a curve away from this correlation line (toward higher shielding of the cationic carbons).

The less negative slope $\rho^{C^+}$ might indicate a lower electron demand than in the other systems **1**–**10**. However, a recent suggestion by Olah and co-workers casts doubt on this conclusion.[11] Olah and his co-workers plotted the $C^+$ shifts observed for several bicyclic systems (including 2-aryl-2-norbornyl) against the $C^+$ shifts for the 1-aryl-1-cyclopentyl cations. They observed that the slopes observed in these cases do not vary significantly in these systems. They suggested that this may be because of the similar anisotropy situations in these bicyclic systems. Consequently, if this suggestion is valid, the smaller $\rho^{C^+}$ (−14.0) observed for the 2-aryl-2-norbornyl cations (**11**, Z = 3′,4′-$CH_2CH_2O$ to Z = H) may also be due to factors other than the electron demand in the system.

The deviation similar to that observed in the $\sigma^{C^+}$–$\Delta\delta C^+$ plot (Figure 1) for the 2-aryl-2-norbornyl cations was earlier attributed to the "onset of nonclassical σ bridging" by Farnum[9] and his co-workers, as well as by Olah and his co-workers.[7,11] However, examination of the $^{13}$C shifts of the other carbons ($C_1$ and $C_6$) involved in the proposed nonclassical σ-bridging (see **16**–**18**) does not support this interpretation.



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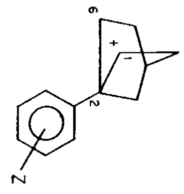

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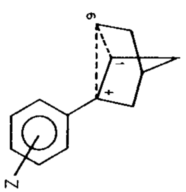

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A plot of $\Delta\delta C_1$ shifts against the $\sigma^{\alpha C^+}$ constants gives a good linear correlation with a $\rho^{\alpha C^+}$ of −5.98 and a correlation coefficient of 0.998 (Figure 2). The linear correlation observed for the $C_1$ shifts is not in accordance with the proposed "onset of σ bridging" in which increasing positive

Table I. $^{13}$C NMR Chemical Shifts of 2-Aryl-2-norbornyl Carbocations (11, 0.3–0.5 M) at −70 °C in $SbF_5/FSO_3H/SO_2ClF$[a,b]

| | chemical shift | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| substituent Z | $C_1$ | $C_2$ | $C_3$ | $C_4$ | $C_5$ | $C_6$ | $C_7$ | $C_{1'}$ | $C_{2'}$ | $C_{3'}$ | $C_{4'}$ | $C_{5'}$ | $C_{6'}$ | $C_Z$ |
| H | 59.6 | 261.0 | 50.8 | 39.9 | 25.7 | 34.5 | 41.7 | 133.9 | 141.3[d] | 132.7 | 152.4 | 132.7 | 141.3[d] | |
| 3′,4′-$CH_2CH_2O$[c] | 51.9 | 227.2 | 45.7 | 37.9 | 27.1 | 30.8 | 40.8 | 136.1 | 138.4 | 129.4 | 183.4 | 115.4 | 148.0 | 79.5, 26.6 |
| 4′-$OCH_3$ | 52.8 | 233.6 | 46.3 | 38.2 | 26.5 | 31.1 | 40.1 | 128.4 | 145.9[d] | 119.7[e] | 180.9 | 118.9[e] | 145.7[d] | 59.2 |
| 4′-$CH_3$ | 57.2 | 253.0 | 49.4 | 39.2 | 26.0 | 33.3 | 41.5 | 132.2 | 142.1[d] | 133.7[e] | 170.8 | 133.9[e] | 141.6[d] | 24.7 |
| 4′-F | 58.9 | 255.9 | 50.4 | 39.9 | 25.8 | 33.9 | 41.8 | 131.1 | 146.9 (16) | 121.1 (23) | 178.6 (287) | 121.1 (23) | 146.2 (16) | |
| 4′-Cl | 59.6 | 258.1 | 50.8 | 40.1 | 25.8 | 34.5 | 41.9 | 132.2 | 141.9[d] | 133.3 | 161.3 | 133.3 | 142.6[d] | |
| 3′-$CH_3$ | 59.2 | 259.5 | 50.6 | 39.8 | 25.9 | 34.3 | 41.8 | 134.1 | 139.6[d] | 144.0 | 153.9 | 132.5 | 141.5[d] | 20.7 |
| 3′-F | 62.2 | 263.5 (5) | 52.0 | 40.8 | 25.6 | 35.9 | 42.0 | 134.9 | 124.8 (21), 125.5 (21) | 164.1 (254) | 138.0 (17) | 139.0 | 134.6 | |
| 3′-Cl | 62.1 | 263.3 | 51.9 | 40.8 | 25.6 | 36.0 | 42.0 | 138.7 | 139.5[d] | 134.5 | 150.4 | 133.9 | 140.0[d] | |
| 3′-$CF_3$ | 63.1 | 264.3 | 52.4 | 41.1 | 25.5 | 36.6 | 42.1 | 133.0 | 143.3[d] | 136.9 (23) | 146.2 | 133.4 | 144.2[d] | 123.4 (273) |
| 3′,5′-$Cl_2$ | 64.7 | 264.1 | 52.7 | 41.3 | 25.4 | 37.5 | 41.7 | 134.5 | 137.8 | 139.3 | 148.0 | 139.3 | 136.9 | |
| 4′-$CF_3$ | 64.3 | 265.3 | 52.6 | 41.6 | 25.5 | 37.3 | 42.1 | 140.3 | 141.3[d] | 128.9 | 147.4 (34) | 128.9 | 141.0[d] | 123.0 (269) |
| 3′,5′-$(CF_3)_2$ | 66.9 | 263.8 | 53.1 | 42.4 | 25.4 | 39.0 | 42.4 | 132.6 | 139.0 | 135.3 (35) | 140.6 | 135.3 (35) | 138.3 | 122.9 (273) |

[a] Similar data obtained at −40 °C in $FSO_3H/SO_2ClF$ have been reported elsewhere.[22a] See also: Farnum, D. G., et al. ref 9; Olah, G. A., et al. ref 7. [b] Chemical shifts are ±0.1 ppm from external $Me_4Si$; couplings to $^{19}$F are given in parentheses. [c] Prepared in $FSO_3H/SO_2ClF$. [d,e] Assignments may be interchanged.

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(22) (a) Kelly, D. P.; Farquharson, D. J.; Giansiracusa, J. J.; Jensen, W. A.; Hügel, H. M.; Porter, A. P.; Rainbow, I. J.; Timewell, P. H. *J. Am. Chem. Soc.* **1981**, *103*, 3539–3543. (b) Kelly, D. P.; Underwood, G. R.; Barron, P. F. *Ibid.* **1976**, *98*, 3106–3111. (c) Kelly, D. P.; Brown, H. C. *Ibid.* **1975**, *97*, 3897–3900.

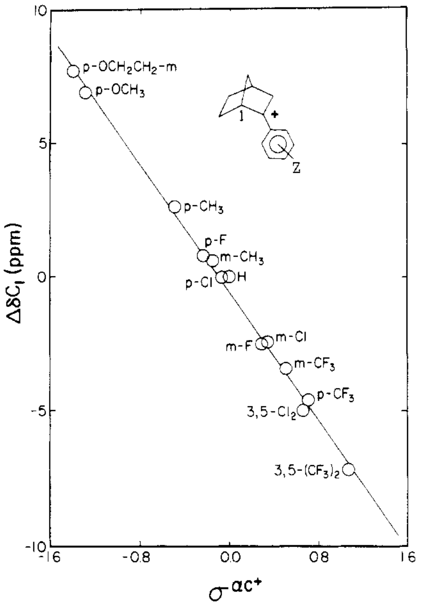


**Figure 2.** Plot of $\Delta\delta C_1$ against $\sigma^{\alpha C^+}$ for 2-aryl-2-norbornyl cations: $\rho^{\alpha C^+} = -5.98$, $r = 0.998$.

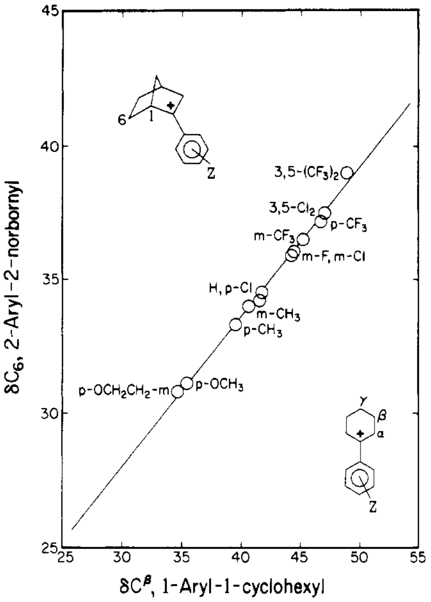


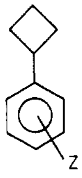
**Figure 3.** Plot of $\delta C_6$ shifts observed for 2-aryl-2-norbornyl against the $\delta C^\beta$ shifts observed for 1-aryl-1-cyclohexyl cations: slope = 0.56, $r = 0.998$.

charge would be delocalized to $C_1$.

It has been argued[11] that plots of $\delta C_1$ against $\delta CH_3$ of *tert*-cumyl cations 1 (from which the $\sigma^{\alpha C^+}$ constants were derived) are misleading and that the good correlation observed previously[8] is "highly coincidental". However, the "coincidence" extends to a large number of cations, including **2–10**,[14] **11** (under discussion), and **12–15**, all of which provide plots revealing excellent correlations of $\Delta\delta C_\alpha$ against $\sigma^{\alpha C^+}$.

Another interesting feature in the $\sigma$-bridged ions **16–18** is the behavior of the pentacoordinated $C_6$ carbon. It has been proposed that such pentacoordinated carbon atoms in nonclassical carbocations are extremely strongly shielded and appear in the spectrum even above $Me_4Si$.[23] Accordingly, we must observe a *shielded* $C_6$ carbon when the "onset of $\sigma$ bridging" occurs. However, the spectra reveal that the $C_6$ carbon atom in **11** undergoes a regular *downfield* shift (deshielding) with increasing electron demand at the cationic center. Previously we observed such downfield shifts for the $C^\beta$ carbon atoms in 1-aryl-1-cyclohexyl[17] (**6**), 4-aryl-4-heptyl[15] (**4**), and 2-aryl-2-adamantanyl[16] (**10**) carbocations. Indeed, a plot of the $C_6$ shifts observed for the 2-aryl-2-norbornyl carbocations against the $C^\beta$ shifts for the 1-aryl-1-cyclohexyl cations gives a good linear correlation with a correlation coefficient of 0.998 and a slope of 0.56 (Figure 3). This observation suggests that the mechanism of charge attenuation in the 2-aryl-2-norbornyl cations is not different from that in the classical 1-aryl-1-cyclohexyl carbocations.

**Are Deviations Characteristic of Nonclassical Carbocations?** Nonclassical structures have been proposed for many other carbocations such as **19–22**.[2]



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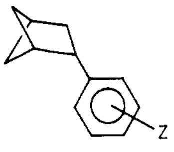

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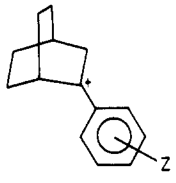

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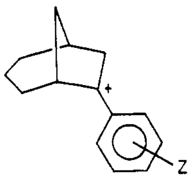
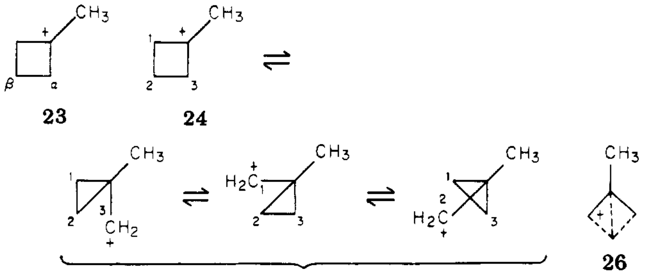


**22**

The question to be considered is whether the deviations observed for the 2-aryl-2-norbornyl cations, attributed to the onset of nonclassical participation,[7,9] will be exhibited by other systems for which nonclassical structures have been proposed. In other words, is such behavior characteristic of "nonclassical" carbocations? If so, it would be a valuable diagnostic probe for the presence of such nonclassical structures.

**Cyclobutyl System.** The interconversion of the secondary cyclobutyl cation with other $C_4H_7^+$ species, allylcarbinyl and cyclopropylcarbinyl, has been the subject of intense investigation and debate for many years. The structure of the cation in superacids has been proposed to consist of a set of equilibrating $\sigma$-bridging bicyclobutonium cations with the buckered cyclobutyl and bisected cyclopropylcarbinyl cations as higher energy intermediates,[10,24,25] although not all of the evidence is confirmatory.[22b,c]

The 1-methyl-1-cyclobutyl cation **23** has also been ex-



**23** **24** **25** **26**

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[23] Olah, G. A.; Surya Prakash, G. K.; Donovan, D. J.; Yavari, I. *J. Am. Chem. Soc.* **1978**, *100*, 7085–7086 and references cited therein.

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[25] Saunders, M.; Siehl, U.-H. *J. Am. Chem. Soc.* **1980**, *102*, 6868–6869.

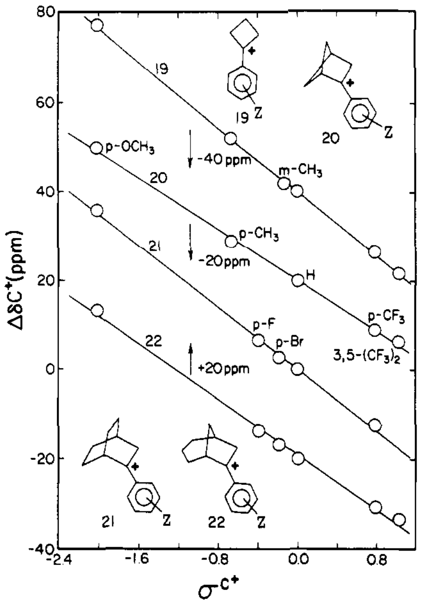


**Figure 4.** Plot of $\Delta\delta C^+$ against $\sigma^{C^+}$ for the following: **19**, $\rho^{C^+}$ −18.11, $r = 0.999$; **20**, $\rho^{C^+} = -14.37$, $r = 0.999$; **21**, $\rho^{C^+} = -17.10$, $r = 0.999$; **22**, $\rho^{C^+} = -15.40$; $r = 0.998$.

tensively investigated.[10,23,26-28] Olah and co-workers attributed the observed data (single peak for α- and β-carbon) to a very rapid equilibrium of the 1-methyl-1-cyclobutyl cation and three σ-bridged (α-methylcyclopropyl)carbinyl cations, **24** and **25**.[26]

Recently Sorensen and Kirchen reported that at −145 °C the peak due to the α- and β-carbon atoms separate into two peaks.[27] They suggested that their observation necessitated a major reinterpretation and invoked the possibility of a $sp^3$-hybridized $C^+$ center to rationalize their data.

More recently, Olah and his co-workers argued that Sorensen's data can be accounted for on the basis of a σ-bridged nonclassical structure **26**.[23] The deuterium isotopic effect ($CH_3$ vs. $CD_3$) has been proposed to support the nonclassical structure.[28] However, the ion described by these authors[28] is the equilibrating ion reported by Olah,[26] not the "frozen" ion reported by Sorensen.[27] Moreover, Sorensen earlier suggested that the deuterium isotopic effect observed for the solvolysis of methylcyclobutyl derivatives (low $k_H/k_D$, $CH_3$ vs. $CD_3$), originally attributed to σ bridging,[29] can also be explained on the basis of the $sp^3$-hybridized cation. Accordingly, the origin of these deuterium isotopic effects is not clear.

The question now is whether we can predict the behavior of the 1-aryl-1-cyclobutyl cations utilizing the large body of available data for the 1-methyl-1-cyclobutyl cation.

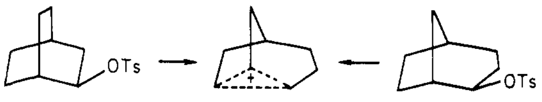
Examination of the $C^+$ shifts in some methyl tertiary dialkyl cations is of interest. The $C^+$ center in the 1-methyl-1-cyclopentyl cations appears at 336 ppm. The corresponding $C^+$ carbon atom in the 2-methyl-2-norbornyl cation appears at 271.1 ppm. Olah and co-workers rationalized this difference on the basis of "partial" σ bridging in the 2-methyl-2-norbornyl cation.[7] The $C^+$ center in 1-methyl-1-cyclobutyl cation appears at 162 ppm. Accordingly, one would anticipate that this system must be even more σ bridged. It follows that we should expect greater deviations in the $\sigma^{C^+}$–$\Delta\delta C^+$ plot for the corresponding 1-aryl-1-cyclobutyl cations. Yet the plot of the reported data[10] does not show any sign of a significant deviation (Figure 4). Either the cyclobutyl cation is not nonclassical or the deviations observed in the $\sigma^{C^+}$–$\Delta\delta C^+$ plot for the 2-aryl-2-norbornyl cations are not characteristic of the onset of nonclassical participation.

**2-Bicyclo[2.1.1]hexyl System.** A nonclassical structure has also been proposed for the intermediate in the solvolysis of 2-bicyclo[2.1.1]hexyl derivatives,[30] but application of the tool of increasing electron demand to this system failed to confirm the original proposal.[31] The structure of the parent secondary cation in superacids has been proposed as fully[32] or partially σ bridged.[33-35] Partial σ bridging has also been proposed in the structure of the tertiary 2-methyl-2-bicyclo[2.1.1]hexyl cation.[33,35,36]

Theoretical calculations of Dewar[37] indicated that the 2-bicyclo[2.1.1]hexyl system is a better candidate for σ bridging than 2-norbornyl. However, calculations by Lenoir indicated the reverse.[38]

In view of these conflicting interpretations, we would expect the $\sigma^{C^+}$–$\Delta\delta C^+$ plot to show deviation at a different point compared to that observed for 2-aryl-2-norbornyl if the latter is due to σ bridging. However, the reported data do not show any signs of a significant deviation (Figure 4). Olah[10,39] has rationalized this absence of any deviation as resulting from an insensitivity of the method for detecting only partial σ bridging. An alternative explanation may be that the deviations observed for 2-aryl-2-norbornyl may arise from some other phenomenon which may not be important in the 2-aryl-2-bicyclo[2.1.1]hexyl system.

**Other Systems.** A σ-bridged structure (**27**) has been proposed as the intermediate in the solvolysis of 2-bicyclo[2.2.2]octyl tosylate and *exo*-2-bicyclo[3.2.1]octyl tosylate, since they both yield the same mixture of products.[40,41]



**27**

Ionization of either of the corresponding 2-methyl alcohols in superacids at ≥−100 °C yields the 2-methyl-2-bicyclo[2.2.2]octyl cation,[42] the structure of which is

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[26] Olah, G. A.; Spear, R. J.; Hiberty, P. C.; Hehre, W. J. *J. Am. Chem. Soc.* **1976**, *98*, 7470–7475.

[27] Kirchen, R. P.; Sorensen, T. S. *J. Am. Chem. Soc.* **1977**, *99*, 6687–6693.

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[29] Majerski, Z.; Nikoletie, M.; Borcić, S.; Sunko, D. E. *Tetrahedron* **1967**, *23*, 640–660.

[30] Meinwald, J.; Gassman, P. G.; Hurst, J. J. *J. Am. Chem. Soc.* **1962**, *84*, 3722–3726. Meinwald, J.; Gassman, P. G. *Ibid.* **1963**, *85*, 57–59.

[31] Brown, H. C.; Ravindranathan, M.; Gundu Rao, C. *J. Am. Chem. Soc.* **1977**, *95*, 2359–2361.

[32] Seybold, G.; Vogel, P.; Saunders, M.; Wiberg, K. B. *J. Am. Chem. Soc.* **1973**, *95*, 2045–2047.

[33] Olah, G. A.; Liang, G.; Jindal, S. P. *J. Am. Chem. Soc.* **1976**, *98*, 2508–2511.

[34] Saunders, M.; Kates, M. R.; Wiberg, K. B.; Pratt, W. *J. Am. Chem. Soc.* **1977**, *99*, 8072–8073.

[35] Schmitz, L. R.; Sorensen, T. S. *J. Am. Chem. Soc.* **1980**, *102*, 1645–1648.

[36] Schleyer, P. v. R.; Lenoir, D.; Mison, P.; Liang, G.; Surya Prakash, G. K.; Olah, G. A. *J. Am. Chem. Soc.* **1980**, *102*, 683–691.

[37] Dewar, M. J. S.; Haddon, R. C.; Komornicki, A.; Rzepa, H. *J. Am. Chem. Soc.* **1977**, *99*, 377–385.

[38] Wenke, G.; Lenoir, D. *Tetrahedron* **1979**, *35*, 489–498.

[39] $\delta C^+$ values of 1-aryl-1-cyclopentyl (**5**) give an excellent correlation with $\sigma^{C^+}$ ($r = 0.999$). Plotting of the $\delta C^+$ (or $\Delta\delta C^+$) values for **11** (or any other cation) against $\delta C^+$ for **5** is equivalent to plotting against $\sigma^{C^+}$. Other workers[6,7,10] have plotted $\delta C^+$ values for the systems under investigation against $\delta C^+$ for 1-aryl-1-cyclopentyl (**5**). Since $\delta C^+$ values for 1-aryl-1-cyclopentyl plot linearly against $\sigma^{C^+}$, this is equivalent to the procedure utilized here.

[40] Goering, H. L.; Fickes, G. N. *J. Am. Chem. Soc.* **1968**, *90*, 2848, 2856, 2862.

[41] Kirmse, W. *Top. Curr. Chem.* **1979**, *80*, 283–284.

[42] Kirchen, R. P.; Sorensen, T. S. *J. Am. Chem. Soc.* **1978**, *100*, 1487–1494.

deemed to be classical from chemical shift arguments.[36] Wolf and Farnum have reported proton NMR data for the 2-aryl cations **21**,[43] and we have plotted the cationic carbon shifts[44] against $\sigma^{C^+}$ in Figure 4. Once again an excellent linear correlation is indicated by the limited data available.[44]

A similar $\sigma$-bridged intermediate has been proposed for the solvolysis of *exo*- and *endo*-6-bicyclo[3.2.1]octyl tosylates.[41,45] Attempts to prepare the tertiary 6-methyl cation resulted in the formation of the rearranged 2-methyl-2-bicyclo[2.2.2]octyl cation.[46] Farnum and co-workers have studied the 6-aryl cations **22** in superacid and concluded that they are static classical species.[9] In fact, the cationic carbon shifts of **22** were plotted against those for **11** to illustrate the "extraordinariness" of the 2-aryl-2-norbornyl cations.[9] We have plotted the $\Delta\delta C^+$ values for **22** against $\sigma^{C^+}$ in Figure 4, which again shows an excellent linear correlation.

We are now in a position to answer the previous question. In all of the five cases, 2-norbornyl, 1-cyclobutyl, 2-bicyclo[2.1.1]hexyl, 2-bicyclo[2.2.2]octyl, and 6-bicyclo[3.2.1]octyl, $\sigma$-bridged, nonclassical cations have been proposed for the secondary cations. However, the plots of $\Delta\delta C^+$ against $\sigma^{C^+}$ for the last four aryl tertiary cations all show excellent linear correlations. Accordingly, the deviation observed for the 2-aryl-2-norbornyl case is not characteristic of systems considered to be nonclassical. In order to further understand the behavior of the 2-aryl-2-norbornyl cations, we extended our study to the related 2-aryl-*exo*-5,6-trimethylene-2-norbornyl (**12**) and 2-aryl-*endo*-5,6-trimethylene-2-norbornyl (**13**) cations.

**2-Aryl-*exo*/*endo*-5,6-trimethylene-2-norbornyl Cations 12 and 13.** The 5,6-*exo*-trimethylene-2-norbornyl system has been proposed to be classical because of the steric hindrance to $\sigma$ bridging.[47] Formation of the nonclassical structure would rotate the trimethylene bridge into the endo cavity where it would encounter strong steric repulsions. Several of the 2-aryl-*exo*-5,6-trimethylene-2-norbornyl cations have been studied previously by Farnum and his co-workers.[9] They plotted the $C^+$ shifts observed for this system against those for the "ordinary" cations **22**. They reported that the deviation observed in this case is qualitatively the same, but somewhat less pronounced, compared to that observed for the 2-aryl-2-norbornyl system. They attributed this difference to the difficulty in achieving $\sigma$ bridging because of the steric factor described above.

If the 5,6-*exo*-trimethylene bridge hinders $\sigma$ bridging, one would expect that the "onset of $\sigma$ bridging" will occur at a later point in the $\sigma^{C^+}$ scale, compared to that achieved in 2-aryl-2-norbornyl. In order to check this point, we prepared 13 2-aryl-*exo*-5,6-trimethylene-2-norbornyl cations. The data are summarized in Table II.

A plot of the observed $\Delta\delta C^+$ values against $\sigma^{C^+}$ is shown in Figure 5. The deviation is observed almost at the same point as that in the 2-aryl-2-norbornyl case, contrary to the $\sigma$-bridging proposal.

On the basis of the proposal that the *exo*-trimethylene bridge hinders $\sigma$ bridging, one would expect the *endo*-trimethylene bridge to facilitate $\sigma$ bridging. Rotation of the trimethylene moiety out of the endo cavity should facilitate formation of the nonclassical structures, decreasing the steric interactions. We should expect an increase in the deviation much greater than that observed in the 2-aryl-2-norbornyl cations. Accordingly, it was of major importance to examine the 2-aryl-*endo*-5,6-trimethylene-2-norbornyl cations (**13**). We prepared the usual 13 derivatives. The $^{13}C$ NMR data are summarized in Table III.

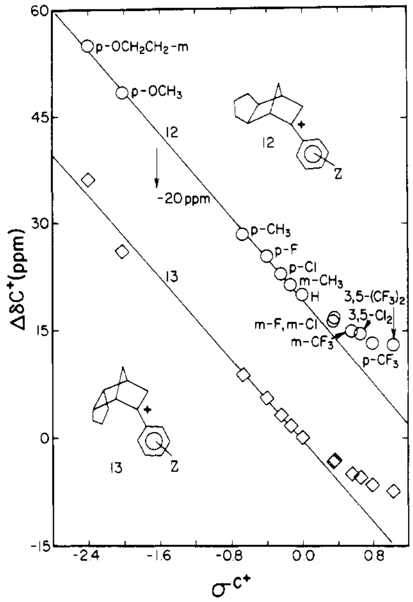

**Figure 5.** Plots of $\Delta\delta C^+$ against $\sigma^{C^+}$ for 2-aryl-*exo*-5,6-trimethylene-2-norbornyl cations ($\rho^{C^+} = -14.6$, $r = 0.999$) and 2-aryl-*endo*-5,6-trimethylene-2-norbornyl carbocations ($\rho^{C^+} = -14.3$, $r = 0.995$) (least-squares analysis for electron-donating substituents only).

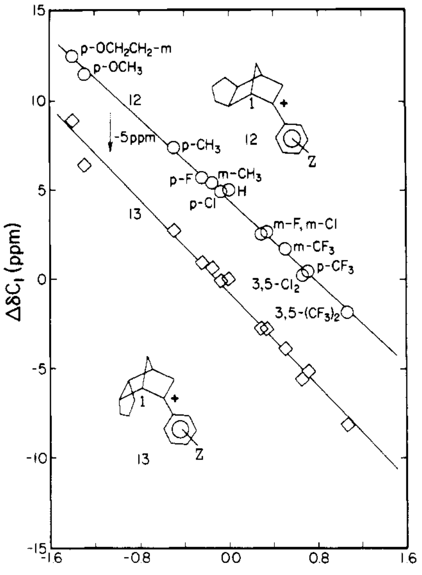

**Figure 6.** Plots of $\Delta\delta C_1$ against $\sigma^{\alpha C^+}$ for 2-aryl-*exo*-5,6-trimethylene-2-norbornyl cations and 2-aryl-*endo*-5,6-trimethylene-2-norbornyl carbocations: **12**, $\rho^{\alpha C^+} = -5.8$, $r = 0.998$; **13**, $\rho^{\alpha C^+} = -6.5$, $r = 0.994$.

A plot of the observed $\Delta\delta C^+$ values against $\sigma^{C^+}$ is shown in Figure 5. Here also a good linear correlation is observed for the electron-donating substituents with deviation from the line for the electron-withdrawing substituents. The deviation occurs almost at the same point in **11** and **12**. This observation clearly rules out the "onset of $\sigma$ bridging"

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[43] Wolf, A. D.; Farnum, D. G. *J. Am. Chem. Soc.* **1974**, *96*, 5175–5181.

[44] Botto, R. E. Ph.D. Thesis, Michigan State University, 1975.

[45] Appleton, R. A.; Fairlie, J. C.; McCrindle, R.; Parker, W. *J. Chem. Soc. C* **1968**, 1716–1721.

[46] Giansiracusa, J. J.; Kelly, D. P., unpublished results. We thank Professor T. S. Sorensen for alerting us to this rearrangement.

[47] See ref 2, Chapter 11, with comments by P. v. R. Schleyer, and references therein.

Table II. $^{13}C$ NMR Chemical Shifts of 2-Aryl-*exo*-5,6-trimethylene-2-norbornyl Carbocations (12, 0.4-0.5 M) at −80 °C in $SbF_5/FSO_3H/SO_2ClF$[a,b]

| | chemical shift | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| substituent Z | $C_1$ | $C_2$ | $C_3$ | $C_4$ | $C_5$ | $C_6$ | $C_7$ | $C_{8-10}$ | $C_{1'}$ | $C_{2'}$ | $C_{3'}$ | $C_{4'}$ | $C_{5'}$ | $C_{6'}$ | $C_Z$ |
| H | 63.0 | 261.3 | 50.8 | 42.3 | 46.1 | 52.4 | 36.2 | 33.5, 31.1, 30.1 | 134.5 | 142.5[c] | 132.8[d] | 152.9 | 132.5[d] | 141.3[c] | |
| 3',4'-$CH_2CH_2O$ | 55.5 | 226.2 | 46.8 | 41.1 | 45.2 | 48.6 | 34.8 | 32.6, 32.0, 28.9 | 136.0 | 138.7 | 129.8 | 183.4 | 115.3 | 147.7 | 79.5, 27.0 |
| 4'-$OCH_3$ | 56.5 | 232.9 | 46.6 | 41.3 | 45.9 | 49.0 | 35.0 | 32.8, 31.9, 29.0 | 129.0 | 146.4[c] | 119.8[d] | 181.1 | 119.0[d] | 145.7[c] | 59.3 |
| 4'-$CH_3$ | 60.6 | 252.9 | 49.1 | 41.9 | 46.3 | 51.1 | 35.8 | 33.2, 31.4, 29.7 | 132.9 | 142.6[c] | 133.9[d] | 171.2 | 133.9[d] | 141.6[c] | 24.7 |
| 4'-F | 62.3 | 255.9 (4) | 50.3 | 42.3 | 46.2 | 51.9 | 36.2 | 33.5, 31.3, 30.0 | 131.8 | 147.3[c] (16) | 121.3[d] (23) | 178.7 (288) | 121.0[d] (23) | 146.0[c] (16) | |
| 4'-Cl | 63.1 | 258.4 | 50.8 | 42.5 | 46.2 | 52.5 | 36.4 | 33.6, 31.2, 30.2 | 132.9 | 143.1[c] | 133.5[d] | 162.0 | 133.2[d] | 142.0[c] | |
| 3'-$CH_3$ | 62.6 | 259.9 | 50.5 | 42.2 | 46.2 | 52.1 | 36.1 | 33.5, 31.2, 30.1 | 134.9 | 141.6[c] | 144.0 | 154.3 | 132.5 | 139.7[c] | 20.6 |
| 3'-F | 65.5 | 264.9 (4) | 52.3 | 42.9 | 46.0 | 54.0 | 36.7 | 33.9, 30.0, 30.8 | 134.6 | 125.5 (21) | 164.0 (255) | 138.0 (21) | 135.7 | 134.2 | |
| 3'-Cl | 65.4 | 264.6 | 52.2 | 42.9 | 46.1 | 54.1 | 36.7 | 34.0, 30.7, 30.7 | 138.8 | 140.8[c] | 135.4 | 150.4 | 133.8 | 139.4[c] | |
| 3'-$CF_3$ | 66.3 | 266.4 | 52.8 | 43.1 | 46.0 | 54.7 | 36.9 | 34.2, 30.8, 30.8 | 134.0 | 137.6[c] | 135.5 (23) | 146.7 | 133.5 | 144.3[c] | 123.4 (273) |
| 3',5'-$Cl_2$ | 67.8 | 266.8 | 53.4 | 43.5 | 46.0 | 55.8 | 37.1 | 34.4, 31.1, 30.5 | 135.5 | 138.5 | 139.2 | 148.6 | 139.2 | 137.2 | |
| 4'-$CF_3$ | 67.6 | 268.1 | 53.3 | 43.4 | 46.0 | 55.5 | 37.0 | 34.3, 31.1, 30.5 | 135.7 | 142.1[c] | 128.9 | 147.9 (34) | 128.9 | 140.6[c] | 123.0 (274) |
| 3',5'-$(CF_3)_2$ | 69.9 | 268.3 | 54.3 | 43.9 | 45.9 | 57.1 | 37.5 | 34.8, 31.5, 30.2 | 133.8 | 140.3[c] | 135.4 (35) | 141.4 | 135.4 (35) | 138.6[c] | 122.8 (273) |

[a] Some of these data have been given previously by Farnum et al., ref 9. [b] Chemical shifts are ±0.1 ppm from external $Me_4Si$. [c,d] Assignments may be interchanged.

Table III. $^{13}C$ NMR Chemical Shifts of 2-Aryl-*endo*-5,6-trimethylene-2-norbornyl Carbocations (13, 0.4-0.5 M) at −80 °C in $SbF_5/FSO_3H/SO_2ClF$[a]

| | chemical shift | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| substituent Z | $C_1$ | $C_2$ | $C_3$ | $C_4$ | $C_5$ | $C_6$ | $C_7$ | $C_{8-10}$ | $C_{1'}$ | $C_{2'}$ | $C_{3'}$ | $C_{4'}$ | $C_{5'}$ | $C_{6'}$ | $C_Z$ |
| H | 67.6 | 262.7 | 47.8 | 42.2 | 45.9 | 64.4 | 43.2 | 28.7, 27.0, 27.0 | 136.8 | 142.2[b] | 132.8 | 152.8 | 132.8 | 140.3[b] | |
| 3',4'-$CH_2CH_2O$ | 58.7 | 226.6 | 44.3 | 42.5 | 42.9 | 55.3 | 41.5 | 28.3, 27.0, 27.0 | 136.0 | 137.9 | 132.0 | 183.4 | 115.6 | 147.6 | 79.6, 27.5 |
| 4'-$OCH_3$ | 61.2 | 236.7 | 44.8 | 42.7 | 43.1 | 57.9 | 42.1 | 28.5, 27.3, 27.3 | 131.6 | 146.1[b] | 119.9[c] | 179.4 | 119.0[c] | 144.3[b] | 60.4 |
| 4'-$CH_3$ | 64.9 | 253.9 | 45.9 | 42.4 | 45.5 | 61.5 | 42.6 | 28.6, 27.1, 27.1 | 135.1 | 142.4[b] | 133.9 | 171.1 | 133.9 | 140.5[b] | 24.7 |
| 4'-F | 66.7 | 257.1 (5) | 47.1 | 42.3 | 45.9 | 63.3 | 43.1 | 28.7, 27.1, 27.1 | 134.0 | 146.9[b] (16) | 121.5[c] (22) | 178.7 (288) | 121.3[c] (22) | 145.1[b] (16) | |
| 4'-Cl | 67.7 | 259.5 | 47.6 | 42.3 | 46.1 | 64.6 | 43.4 | 28.8, 27.1, 27.1 | 135.2 | 142.7[b] | 133.6 | 162.1 | 133.6 | 140.9[b] | |
| 3'-$CH_3$ | 67.0 | 261.0 | 47.4 | 42.2 | 45.8 | 63.8 | 43.1 | 28.7, 27.1, 27.1 | 137.0 | 143.0[b] | 137.9 | 154.1 | 132.7 | 139.9[b] | 20.7 |
| 3'-F | 70.4 | 266.0 | 49.2 | 42.2 | 46.4 | 67.7 | 44.0 | 28.9, 27.0, 27.0 | 134.5 | 125.5 (21) | 164.0 (255) | 138.0 (21) | 136.8 | 134.6 | |
| 3'-Cl | 70.4 | 265.9 | 49.1 | 42.2 | 46.4 | 67.8 | 44.0 | 29.0, 27.0, 27.0 | 139.0 | 140.0[b] | 137.5 | 150.8 | 134.0 | 138.1[b] | |
| 3'-$CF_3$ | 71.5 | 267.8 | 49.8 | 42.2 | 46.7 | 69.3 | 44.3 | 29.0, 26.9, 26.9 | 136.1 | *d* | *d* | 146.7 | 133.8 | 135.7 | *d* |
| 3',5'-$Cl_2$ | 73.1 | 268.2 | 50.5 | 42.3 | 46.4 | 71.4 | 44.9 | 29.0, 27.0, 27.0 | 137.7 | 138.1 | 139.7 | 148.7 | 139.7 | 136.3 | |
| 4'-$CF_3$ | 72.8 | 269.3 | 50.3 | 42.1 | 46.7 | 70.8 | 44.7 | 29.0, 26.9, 26.9 | 137.7 | 141.5 | 129.2 | 147.8 (34) | 129.2 | 139.8 | 123 (274) |
| 3',5'-$(CF_3)_2$[e] | 75.8 | 270.1 | | | | 74.8 | | | | | | | | | |

[a] Chemical shifts are ±0.1 ppm from external $Me_4Si$. [b,c] Assignments may be interchanged. [d] Signals are very weak and were not assigned. [e] Ion decomposes during data acquisition, giving additional peaks in other regions.

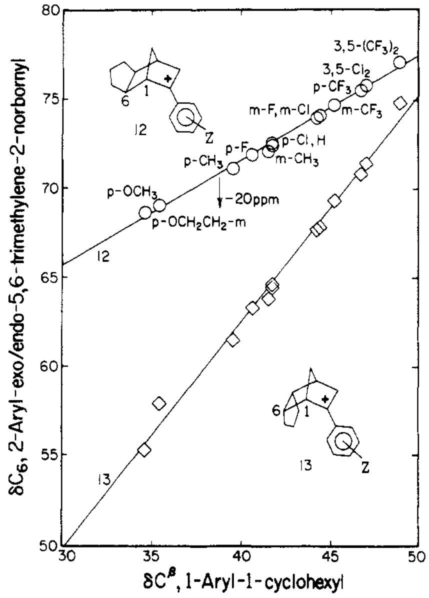

**Figure 7.** Plots of $\delta C_6$ shifts for the ions **12** and **13** against the $\delta C^{\beta}$ shifts observed for 1-aryl-1-cyclohexyl cations: **12**, slope = 0.59, $r$ = 0.998; **13**, slope = 1.23, $r$ = 0.995.

as the cause for the deviation.

If these deviations are due to the "onset of $\sigma$ bridging", it should be possible to observe the corresponding changes in the other carbons ($C_1$ and $C_6$) involved in such $\sigma$ bridging. The $\Delta\delta C_1$ shifts observed in these cases correlate nicely against the $\sigma^{\alpha C^+}$ constants (Figure 6). The $C_6$ carbon atom would be pentacoordinated in the case of $\sigma$ bridging and should undergo an upfield (shielding) shift with an onset of $\sigma$ bridging. However, the $C_6$ shifts in these cases undergo a regular downfield shift with increasing electron demand. Indeed, the chemical shifts are nicely correlated (Figure 7) against the corresponding shifts observed for the $\beta$-carbon atoms in 1-aryl-1-cyclohexyl cations, indicating that the mechanism of attenuation of charge to the $C^{\beta}$ carbon atom in these cases is not different from that in the classical 1-aryl-1-cyclohexyl cations. These observations further indicate that the electron release to the cationic center occurs in a regular manner even when the cationic carbon shifts are deviating from linearity with $\sigma^{C^+}$.

It is evident from the above discussion that the deviation observed for the 2-aryl-2-norbornyl cations (Figure 1) cannot be attributed to the "onset of $\sigma$ bridging". In order to understand the phenomenon (deviation) further, we extended our examination to the systems **14** and **15**.

**3-Aryl-3-nortricyclyl Cations (14).** Application of the "tool of increasing electron demand" to the solvolysis of 3-aryl-3-nortricyclyl derivatives has shown a major enhancement of rate with increasing electron demand over that for the 7-aryl-7-norbornyl derivatives. However, this enhancement is due to $\sigma$ conjugation, not $\sigma$ participation, since the bisected orientation of the cyclopropyl ring with the developing cationic center militates against $\sigma$ participation (bridging).[2,21,48] Both the parent secondary and tertiary 3-alkylnortricyclyl cations generated in superacid are static classical cations.[22,36,48] In our study of $^{13}C-^{1}H$ coupling constants, we prepared a number of 3-aryl-3-nortricyclyl cations (**14**),[22a] the cationic carbon shifts of which did not appear to be linear with electron demand. We have therefore prepared an extended range of these cations in order to define this anomaly more clearly. The chemical shifts are summarized in Table IV.

Table IV. $^{13}C$ NMR Chemical Shifts of 3-Aryl-3-nortricyclyl Carbocations (**14**, 0.3–0.5 M) at −65 °C in $SbF_5/FSO_3H/SO_2ClF$[a,b]

| | chemical shift | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| substituent Z | $C_{1,6}$ | $C_2$ | $C_3$ | $C_4$ | $C_{5,7}$ | $C_{1'}$ | $C_{2'}$ | $C_{3'}$ | $C_{4'}$ | $C_{5'}$ | $C_{6'}$ | $C_Z$ |
| H | 61.1 | 46.9 | 257.1 | 40.8 | 40.8 | 134.1 | 139.5 | 132.1[c] | 148.9 | 132.6[c] | 139.5 | |
| 3′,4′-$CH_2CH_2O$[d] | 40.3 | 31.5 | 229.8 | 38.0 | 38.0 | 136.2, 134.6 | 138.2 | 128.9 | 182.1 | 114.6, 116.0 | 146.3, 147.6 | 78.9, 27.0 |
| 4′-$OCH_3$[d] | 43.1 | 33.6 | 234.6 | 38.4 | 38.4 | 128.0 | 144.6 | 118.1[c] | 179.5 | 120.0[c] | 144.6 | 58.9 |
| 4′-$CH_3$ | 54.7 | 42.1 | 251.0 | 40.1 | 40.1 | 132.1 | 140.1 | 130.0[c] | 167.3 | 133.7[c] | 140.1 | 24.3 |
| 4′-F | 58.9 | 45.1 | 252.9 | 40.5 | 40.5 | 131.2 | 144.1 (16) | 120.6 (22) | 176.4 (288) | 120.6 (22) | 144.1 (16) | |
| 4′-Cl | 61.7 | 47.4 | 254.5 | 40.6 | 41.0 | 132.6 | 133.3 | 132.5 | 158.2 | 132.5 | 133.3 | |
| 3′-$CH_3$ | 59.7 | 45.8 | 256.4 | 40.6 | 40.6 | 134.5 | 137.3[c] | 143.5 | 151.2 | 132.4 | 139.6 | 20.8 |
| 3′-Cl | 68.1 | 52.1 | 258.4 | 41.2 | 41.8 | 138.7 | 135.1[c] | 138.1 | 147.5 | 133.4 | 137.2[c] | |
| 3′-$CF_3$ | 70.9 | 54.1 | 259.3 | 41.3 | 42.1 | 141.4 | 133.8[c] | 134.5 (34) | 143.4 | 133.2 | 134.4[c] | 123.7 (273) |
| 4′-$CF_3$ | 73.5 | 56.1 | 260.1 | 41.5 | 42.3 | 135.8 | 138.3 | 128.4[c] | 144.4 (35) | 129.6[c] | 138.3 | 125.6 (270) |
| 3′,5′-$(CF_3)_2$ | 80.4 | 61.1 | 258.5 | 41.9 | 43.0 | 135.9 | e | 136.4 | e | 136.4 | e | 123.0 (270) |

[a] Some of these data have been reported elsewhere.[10,22a] [b] Chemical shifts are ±0.1 ppm from external $Me_4Si$. Couplings to $^{19}F$ are given in parentheses. [c] Assignments may be interchanged. [d] From $FSO_3H/SO_2ClF$ at −70 °C. [e] Peaks too weak to measure.

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(48) Olah, G. A.; Liang, G. *J. Am. Chem. Soc.* 1975, *97*, 1920–1927.

Table V. $^{13}C$ NMR Chemical Shifts of 1-Aryl-1-cyclopropylethyl Carbocations (15, 0.5-0.9 M) at −60 °C in $FSO_3H/SO_2ClF$[a,b]

| | chemical shift | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| substituent Z | $C_1$ | $C_2$ | $C_3$ | $C_{4,5}$ | $C_{1'}$ | $C_{2'}$ | $C_{3'}$ | $C_{4'}$ | $C_{5'}$ | $C_{6'}$ | $C_Z$ |
| H | 248.0 | 22.8 | 45.1 | 44.3 | 140.3 | 135.3 | 131.7 | 146.2 | 131.7 | 135.3 | |
| 3′,4′-$CH_2CH_2O$ | 222.0 | 19.2 | 31.3 | 27.5 | 137.3 | 134.8 | 134.8 | 179.4 | 114.2 | 143.8 | 78.3, 27.5 |
| 4′-$OCH_3$ | 227.8 | 19.9 | 33.5 | 30.3 | 134.3 | 141.4 | 118.1 | 177.6 | 118.8 | 141.4 | 58.7 |
| 4′-$CH_3$ | 242.4 | 21.6 | 40.8 | 39.2 | 138.2 | 136.1 | 132.7 | 162.9 | 132.7 | 136.1 | 23.4 |
| 4′-F | 243.8 | 22.4 | 43.9 | 42.8 | 137.0 | 139.8 (15) | 119.7 (22) | 174.5 (278) | 119.7 (22) | 139.8 (15) | |
| 4′-Cl | 245.4 | 22.7 | 45.5 | 44.7 | 138.5 | 136.3 | 132.1 | 154.2 | 132.1 | 136.3 | |
| 3′-$CH_3$ | 247.4 | 22.7 | 44.3 | 43.1 | 140.5 | 132.9[c] | 142.5 | 147.5 | 131.5 | 135.5[c] | 21.0 |
| 3′-Cl[d] | 248.9 | 23.5 | 49.0 | 49.0 | 141.4 | 133.0[c] | 137.8 | 144.2 | 133.0 | 133.5[c] | |
| 3′-$CF_3$[d] | 249.7 | 23.6 | 50.7 | 50.7 | e | | | | | | |
| 4′-$CF_3$[d] | 251.1 | 24.0 | 52.3 | 52.3 | 142.4 | 134.2 | 128.0 | 142.4 (34) | 128.0 | 134.2 | 123.7 (273) |
| 3′,5′-$(CF_3)_2$[d] | 249.4 | 24.3 | 55.6 | 56.7 | 140.7 | 132.7 | 134.4 (35) | 135.1 | 134.4 (35) | 132.7 | 123.2 (272) |

[a] Some of these data have been reported elsewhere.[22a] See also Olah, G. A., et al., ref 11, 46. [b] Chemical shifts are ±0.1 ppm from external $Me_4Si$. Couplings to $^{19}F$ are given in parentheses. [c] Assignments may be interchanged. [d] From $FSO_3H/SbF_5/SO_2ClF$ at −70 °C. [e] Peaks too weak to measure.

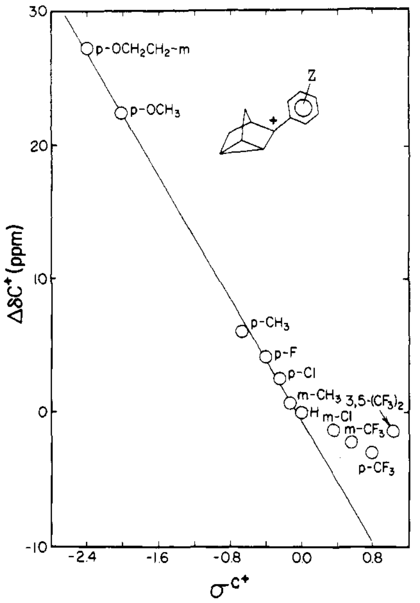


Figure 8. Plot of $\Delta\delta C^+$ against $\sigma^{C^+}$ for 3-aryl-3-nortricyclyl cations: $\rho^{C^+} = -11.46$, $r = 0.999$ (least-squares analysis for electron-donating substituents only).

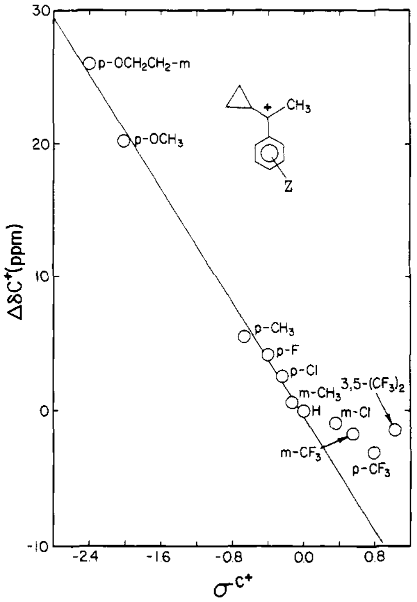


Figure 9. Plot of $\Delta\delta C^+$ against $\rho^{C^+}$ for 1-aryl-1-cyclopropylethyl cations: $\rho^{C^+} = -10.54$, $r = 0.997$ (least-squares analysis for electron-donating substituents only).

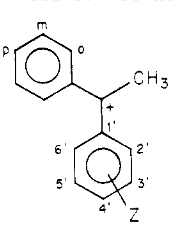
When the $\Delta\delta C^+$ values are plotted against $\sigma^{C^+}$ (Figure 8), one feature is strikingly apparent: the plot is almost identical with that for the 2-norbornyl cations! The linear correlation for the electron donors (Z = 3′,4′-$CH_2CH_2O$ to Z = H) is excellent ($r = 0.999$), with the points for the electron-withdrawing substituents curving upward. Thus we have a static classical cationic system exhibiting the same behavior as the supposedly σ-bridged cationic system 11. The deviation in the correlation for the 3-aryl-3-nortricyclyl cations was also observed by Olah et al., who rationalized the behavior as due to the "onset of increased cyclopropyl conjugation" with electron-demanding substituents.[10] This concept was not further defined. Why should the electron release from the cyclopropyl moiety suddenly increase in a nonlinear fashion at Z = H? Examination of the α ($C_2$) and β ($C_{1,6}$) carbon shifts in Table IV shows that they increase regularly with increasing electron demand. In fact, the substituent chemical shifts give excellent linear correlations with the α substituent constants $\sigma^{\alpha C^+}$: $\Delta\delta C_2$, $r = 0.998$, $\rho^{\alpha C^+} = -11.90$; $\Delta\delta C_{1,6}$, $r = 0.998$, $\rho^{\alpha C^+} = -16.09$. In addition, the value of $^1J_{C_2H}$ has recently been shown to increase regularly with increasing electron demand in these cations.[22a] Comparison of the slope of Figure 8, $\rho^{C^+} = -11.46$, with those for all of the cations discussed so far indicates that substantial delocalization is occurring in 14, that is, there is a much lower electron demand in 14 than in 1–13 and 19–22. This must arise from enhanced electron supply from the cyclopropyl group, as has been observed in the case of the solvolyses of the corresponding p-nitrobenzoates.[21] The large range of chemical shifts of $C_2$ and $C_{1,6}$, compared to those in other acyclic and alicyclic ions, is consistent with the facile electron-releasing ability of the cyclopropyl group. However, the electron release to the cationic center appears to occur in a regular (linear) manner, and we must look elsewhere for reasons for the deviations in the plots.

**1-Aryl-1-cyclopropylethyl Carbocations (15).** Under solvolytic conditions, 1-aryl-1-cyclopropylethyl p-nitrobenzoates exhibit rate accelerations similar to those of the 3-nortricyclyl derivatives, indicating similar electron release to the cationic center.[21] However, in this system, 15 there is the possibility of conformations of the cyclopropyl moiety other than the bisected one. From the analysis of $^{13}C$ chemical shifts and $^1J_{C_2H}$ values in a range of these cations 15 generated in superacids, Kelly and co-workers have concluded that the cyclopropyl group does maintain the favored bisected orientation.[22] We have prepared an extended range of these cations in order to investigate the linearity of $\Delta\delta C^+$ with $\sigma^{C^+}$, and the chemical shifts are summarized in Table V.[49] When the values for $\Delta\delta C^+$ are plotted against $\sigma^{C^+}$ (Figure 9), a result similar to that for **14** is obtained.

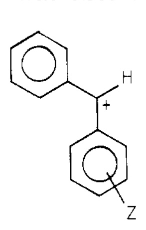
The enhanced electron supply is again shown in these cations by the low $\rho^{C^+}$ value of −10.54, the large range of shifts for the α ($C_3$) and β ($C_{4,5}$) carbons, and the linearity of electron supply by the excellent correlations of the shifts with $\sigma^{\alpha C^+}$ ($\Delta\delta C_3$, $r = 0.999$, $\rho^{\alpha C^+} = -9.86$; $\Delta\delta C_{4,5}$, $r = 0.998$, $\rho^{\alpha C^+} = -11.70$).

Thus, cations **11**, **14**, and **15** (and, to a lesser extent, **12** and **13**) all show similar, in fact almost identical, behavior, yet they have been interpreted in terms of quite different concepts, one of which, "the onset of increased cyclopropyl conjugation", remains obscure. This does not seem reasonable. Finally, we can ask if there are any further cationic systems which show deviations in their plots of $\Delta\delta C^+$ against $\sigma^{C^+}$ (or against $\delta C^+$ for **5**).[39]

**1-Aryl-1-phenylalkyl Carbocations 28 and 29.** Following up the observation that the solvolysis data for benzhydryl derivatives[50] were best correlated for by two constants, $\sigma^+$ for electron-donating substituents and $\sigma$ for electron-withdrawing substituents, Farnum and co-workers investigated the correlation of $\delta C^+$ for the tertiary cations **28** with $\delta C^+$ for **5**.[9] A deviation was observed, as they expected from the solvolysis results, such that the electron donors were correlated by one straight line and the electron acceptors by another. This was interpreted by Farnum in terms of steric inhibition of resonance, whereby in symmetrically substituted diaryl cations, the two phenyl rings are twisted equally out of the plane of the unoccupied p orbital by 25–30°. When electron-withdrawing substituents are placed on one ring, the unsubstituted ring is forced further into coplanarity to stabilize the cationic center and thus force the substituted ring further out of coplanarity. More electron-demanding substituents will have less and less effect on the cationic carbon as the substituted phenyl ring is twisted well out of the plane. Thus the substituent becomes effectively unconjugated with the cationic carbon and influences the cationic $^{13}C$ shift only to a very limited extent, presumably by inductive and/or field effects. An analogous argument was applied for electron-donating substituents which force the unsubstituted ring out of the plane.



**28**



**29**

However, when Farnum's data for **28** are supplemented with $\delta C^+$ for **28** (Z = 3′,4′-$CH_2CH_2O$)[19] and plotted against $\sigma^{C^+}$ on the same scale as the other figures, the graph obtained (Figure 10) is almost superimposable on those for **11**, **14**, and **15**! Once again we have a molecular system in which σ bridging is impossible but which shows the same deviation in the plot of $\Delta\delta C^+$ vs. $\sigma^{C^+}$ as that for 2-aryl-2-norbornyl cations.

Since we had data available for the benzyhydryl cations **29** from previous studies,[51] it was of interest to see if a deviation occurred here also. Indeed, when we augmented the data with those for **29** [Z = 3′,4′-$CH_2CH_2O$,[19] 3′-$CF_3$, and 3′,5′-$(CF_3)_2$] a plot was obtained almost identical with those for **11**, **14**, **15**, and **28** (Figure 10).

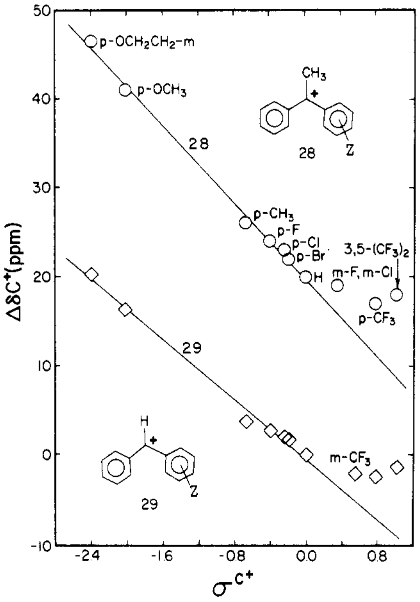


**Figure 10.** Plots of $\Delta\delta C^+$ against $\sigma^{C^+}$ for 1-aryl-1-phenylethyl cations and 1-aryl-1-phenylmethyl cations: **28**, $\rho^{C^+} = -10.89$, $r = 0.998$ and **29**, $\rho^{C^+} = -8.4$, $r = 0.996$ (least-squares analysis for electron-donating substituents only).

Thus there are three different molecular systems, 2-norbornyl (**11–13**), cyclopropylcarbinyl (**14**, **15**), and diarylalkyl (**28**, **29**), which all show similar (in some cases, almost identical) deviations in the plots of $\Delta\delta C^+$ against $\sigma^{C^+}$. In each of the three cases, three different reasons have been proposed previously for these deviations: onset of σ bridging in **11** and **12**, onset of cyclopropyl conjugation (ill-defined) in **14** and **15**, and steric inhibition of resonance in **28** and **29**. In addition, a variety of other alicyclic cationic systems which have been suggested to have nonclassical, σ-bridged, secondary, cationic structures do not show deviations in the plots of their aryl derivatives **19–22**.

Accordingly, we conclude that the anomaly in the plots of the cationic carbon chemical shifts against $\sigma^{C^+}$ (or $\delta C^+$ for cyclopentyl[39]) is not diagnostic for the onset of nonclassical σ bridging in 2-aryl-2-norbornyl cations.

It is now appropriate to consider possible reasons for the deviations in the plots for these three different carbocationic systems.

**Possible Reasons for Deviations from Linearity. (1) Single Substituent Parameter.** The problem of using a single Hammett substituent constant in any correlation is that it does not allow for different polar and resonance contributions of the substituents. This may be overcome by use of the dual substituent parameter (DSP) treatment of Ehrenson, Brownlee, and Taft by which the data are fitted to eq 3, where $\rho_I$ and $\rho_R$ are the polar and resonance

$$\Delta\delta = \rho_I\sigma_I + \rho_R\sigma_R \qquad (3)$$

transmission coefficients, respectively.[52] In the case of 1-aryl-1-phenylmethyl cations **29**, it has been shown previously that the use of the single constant $\sigma^+$ to correlate the para carbon chemical shifts is justified since $\rho_I = \rho_R$.[51] However, in the case of the cationic carbon shifts $\rho_I \neq \rho_R$,

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(49) Some of the data have been reported previously and the cationic carbon shifts correlated with $\sigma^+$. The relatively poor correlation ($r = 0.934$) was improved by the use of the DSP equation which gave values of the inductive and resonance transmission coefficients: $\rho_I = 6.3$, $\rho_R = 11.0$; sd/rms = 0.13. Olah, G. A.; Surya Prakash, G. K.; Liang, G. *J. Org. Chem.* **1977**, *42*, 2666–2671.

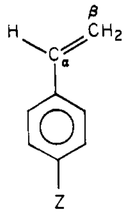
(50) Nishida, S. *J. Org. Chem.* **1967**, *32*, 2697–2701.

(51) Kelly, D. P.; Spear, R. J. *Aust. J. Chem.* **1977**, *30*, 1993–2004.

(52) Ehrenson, S.; Brownlee, R. T. C.; Taft, R. W. *Prog. Phys. Org. Chem.* **1973**, *10*, 1–80.

and use of $\sigma^+$ is not valid.[51] Examination of the reported correlations of $\delta C^+$ with $\sigma^+$ for the *tert*-cumyl cations **1** showed that there was a significant deviation from linearity. This was considered to be due to the failure to allow for the extra electron demand of the fully formed carbocation over that of the solvolytic transition state and leads to the development of enhanced substituent constants.[8,13] Application of the enhanced constant $\sigma^{C^+}$ to a wide range of carbocations (**1**–**10**) results in nearly perfect correlations against $\sigma\delta C^+$; thus the DSP treatment using $\sigma_R{}^+$ is not likely to yield better correlations. Nor is the treatment likely to substantially improve the correlations for the cations **28** and **29** by using $\sigma^{C^+}$ since the deviations from linearity are of the form of curves at one end of the $\sigma$ scale rather than a general poor fit over the entire range.[53] This curve is a result of a change in chemical shifts such that the cationic carbons become shielded with increasing electron demand of the substituent. Such reversal of chemical shifts (from deshielding with increased electron demand) has been observed before in "side-chain" carbons of a variety of benzene derivatives.[54]

For example, in the case of para-substituted styrenes (**30**) the chemical shift of the olefinic carbon adjacent to the aryl ring ($\alpha$-carbon) undergoes a downfield shift (deshielding) from Z = $p$-$OCH_3$ to Z = H and then an upfield shift (shielding) from Z = $p$-H to Z = $p$-$CF_3$.[54] However, the $\beta$-carbon undergoes a regular downfield shift (deshielding) from $p$-$OCH_3$ to $p$-$CF_3$ approximately in the same order as the variation in the Hammett $\sigma$ constants. The reversal of chemical shifts observed for the $\alpha$-carbon atom in styrenes and other substrates is considered to be due to the side-chain carbon (adjacent to the phenyl ring) becoming less conjugated with the substituent and the polar (inductive and/or field) effect of the substituent becoming more important (decreasing $\rho_R/\rho_I$) than the resonance effect.[55] In the case of the carbocations under consideration, decreased electron demand by the cation and/or steric hindrance to coplanarity would create a similar situation and could produce the shielding effect observed for the carbon adjacent to the aryl ring ($C^+$ center).



**30**

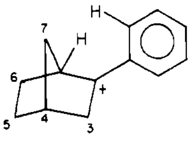
**(2) Decreased Electron Demand by the Carbocations.** The relative rates of solvolysis of the tertiary $p$-nitrobenzoates $RC(CH_3)_2OPNB$ increase in the order shown, indicating the cation stabilizng ability order of these groups.[56]

| R | $CH_3$ | Ph | c-Pr |
|---|---|---|---|
| $k_{rel}$ | 1 | 969 | 503 000 |

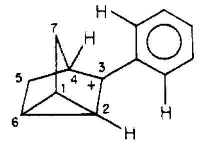
Accordingly, the carbocations (**14**, **15**, **28**, **29**) incorporating the stabilizing groups would be less electron demanding. Consequently, the polar effects (inductive and/or field) of the substituent would become more important for aryl rings containing electron-withdrawing substituents. As a result, instead of becoming deshielded, the carbocationic center chemical shift becomes more shielded, similar to the effect observed for substituted styrenes.

The $\rho^{C^+}$ values ($\sim$−14.0) observed for the electron-donating substituents (Z = 3′,4′-$CH_2CH_2O$ to Z = H) of the cations **11**–**13** are relatively less negative compared to those observed for simple aryldialkyl carbocations **1**–**10**. This may be because of the ability of the norbornyl skeleton to stabilize the charge at $C_2$ better than the simple dialkyl carbocations **1**–**10**. Consequently, in these cases also the polar (inductive and/or field) effect may become more important for the electron withdrawing substituents and could result in the reversal of the chemical shifts. In addition, steric hindrance to coplanarity (see below) also could make the polar (inductive and/or field) effect more important for the ions.

**(3) Steric Hindrance to Coplanarity.** From an examination of molecular models, Olah concluded that there was a nonbonded (van der Waals) interaction between an ortho proton and $H_1$ in 2-phenyl-2-norbornyl cation **31** and between the ortho protons and both $H_2$ and $H_4$ in 3-phenyl-3-nortricyclyl cation **32**.[48]



**31**
$\delta C^+$ 257.3 ppm



**32**
$\delta C^+$ 275.8 ppm

Olah and Liang primarily suggested these interactions to account for the relatively more deshielding (downfield) shift (275.8 ppm) observed for the $C^+$ center in 3-phenyl-3-nortricyclyl cation compared to 257.3 ppm observed for the $C^+$ center in 2-phenyl-2-norbornyl cation.[48] However, recently Olah and co-workers reported that the $C^+$ centers in **31** and **32** appear at 261.0 and 257.1 ppm, respectively.[10,11] Evidently, no special explanation is now needed to account for the observed chemical shift difference. However, the van der Waals interaction may still be present. Such steric hindrance to coplanarity would make the polar (inductive and/or field) effect of the substituent more important compared to the resonance effect for the electron-withdrawing aryl groups. Consequently, it could produce the shielding effect at the $C^+$ center similar to the effect observed for substituted styrenes and other side-chain benzene derivatives, as previously discussed.

Examination of Drieding models shows a similar interaction of the ortho protons with $H_3$ of **15** in the bisected conformation and also with the other ortho proton in the opposite phenyl ring of **28**. As indicated above, Farnum proposed that for the parent ion **28** (Z = H), the two phenyl rings are twisted equally out of coplanarity. Sub-

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(53) In order for the DSP equation to correlate this data, the $\rho_R/\rho_I$ ratio ($\lambda$) would have to change within any one series of cations.[52] Correlation of the para cations by the DSP equation using $\sigma_R{}^+$ gives reasonable correlations as there is only one para substituent more electron demanding than H (4′-$CF_3$). ion, $\rho_I$, $\rho_R$, sd/rms: **11**, 13.2, 27.7, 0.26; **12**, 16.3, 29.9, 0.20; **13**, 15.0, 28.0, 0.19; **14**, 10.0, 22.3, 0.29; **15**, 9.5, 20.0, 0.24. We thank Dr. R. T. C. Brownlee of La Trobe University, Melbourne, for the DSP analyses of our data.

(54) Bromilow, J.; Brownlee, R. T. C. *Tetrahedron Lett.* **1975**, 2113–2114. Robinson, C. N.; Slater, C. D.; Covington, J. S.; Chang, C. R.; Dewey, L. S.; Franceschini, J. M.; Fritzsche, J. L.; Hamilton, J. E.; Irving, C. C.; Morris, J. M.; Norris, D. W.; Rodman, L. E.; Smith, V. I.; Stablein, G. E.; Ward, F. C. *J. Magn. Reson.* **1980**, *41*, 293–301. Hamer, G. K.; Peat, I. R.; Reynolds, W. F. *Can. J. Chem.* **1973**, *51*, 897–914; **1973**, *51*, 915–927. Frahm, A. W.; Hambloch, H. D. *Org. Magn. Reson.* **1980**, *14*, 444–446.

(55) Bromilow, J.; Brownlee, R. T. C.; Craik, D. J.; Fiske, P. R.; Rowe, J. L., Sadek, M. *J. Chem. Soc., Perkin Trans. 2* **1981**, 753–759.

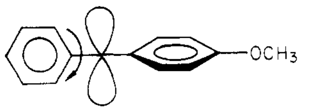
(56) Brown, H. C., in ref. 2, p 70.

Table VI. Physical Constant Data for Alcohol Precursors[a]

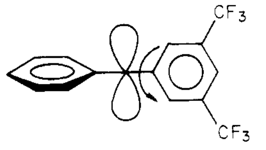
| | alcohol A | | alcohol B | | alcohol C, mp, °C | alcohol D | | alcohol E | |
|---|---|---|---|---|---|---|---|---|---|
| substituent | mp, °C | lit. mp, °C | mp, °C | lit. mp, °C | | mp, °C | lit. mp, °C | bp, °C (mm) | lit. bp, °C (mm) |
| 3',4'-$CH_2CH_2O$ | 71-74 | 75-76[b] | 119-120[d] | | 129 | 92-93 | | 133-134 (0.6) | |
| 4'-$OCH_3$ | 47-48 | 47[c] | 56-57 | 56-56.5[e] | 96-97 | 85-86 | 87.5-88.5[h] | 100-101 (0.2) | 103-104 (0.5)[j] |
| 4'-$CH_3$ | 45-46 | 46-47[c] | 87-88 | 88-89[e] | 62-63 | 64-65 | | 84-85 (1) | |
| 4'-F | 63-64 | 63-64[c] | 58-59 | 58-60[f] | 95-96 | 52-53 | | 65-67 (0.5) | |
| 4'-Cl | 85-87 | 85-87[c] | 86-87 | | 76-77 | 87-88 | | 94 (1) | 131-132 (13)[k] |
| 3'-$CH_3$ | 57-58 | | 48-49 | | 54-55 | 50-51 | | 76-78 (0.5) | |
| H | 40-42 | 41-42[c] | 69-70 | 69-70[f] | 95[g] | 60-61[i] | | 85-86 (2) | 69 (0.6)[j] |
| 3'-F | 37-38 | | 65-66 | | 63-64 | | | | |
| 3'-Cl | 39-41 | 42-44[c] | 65-66 | | 59-60 | 95-96 | | 89-90 (0.5) | |
| 3'-$CF_3$ | 47-48 | | 74 | 75-76[e] | 59-60 | 77-78 | | 64-65 (0.5) | |
| 3',5'-$Cl_2$ | 96-97 | | 151-152 | | 61-62 | | | | |
| 4'-$CF_3$ | 65-66 | 64-66[c] | 76 | 75-76[e] | 87-88 | 84-86 | 87.5-88.5[h] | 79-80 (1) | 74 (0.6)[j] |
| 3',5'-$(CF_3)_2$ | 74-76 | 75-77[c] | 120 | 121-122[e] | 60-61 | 103-105 | 104-105[h] | 68 (1) | 66 (0.6)[j] |

[a] Alcohol A, 2-aryl-2-*endo*-norbornanol; alcohol B, 2-aryl-*exo*-5,6-trimethylene-2-*endo*-norbornanol; alcohol C, 2-aryl-*endo*-5,6-trimethylene-2-*endo*-norbornanol; alcohol D, 3-aryl-3-nortricyclanols; alcohol E, 1-aryl-1-cyclopropyl-1-ethanol. Physical constant data for some other alcohol precursors used in this work: 1-[(3,4-ethyleneoxy)phenyl]-1-phenyl-1-ethanol, mp 80-82 °C; 1-[(3,4-ethyleneoxy)phenyl]-1-phenylmethanol, mp 58-59 °C; 1-[3-(trifluoromethyl)phenyl]-1-phenylmethanol, mp 58-60 °C (lit.[62] mp 61-62 °C); 1-[3,5-bis(trifluoromethyl)phenyl]-1-phenylmethanol, mp 78-80 °C. All of the new compounds gave satisfactory analytical data (C, H, Cl, and F, $\leqslant \pm 0.3\%$). [b] Reference 58. [c] Reference 6. [d] This compound was available from earlier work in our laboratories.[60] [e] Reference 59. [f] Reference 9. [g] This compound was available from earlier work in our laboratories.[61] [h] Reference 21a. [i] Lit.[21a] bp 100 °C (0.1 mm). [j] Reference 21b. [k] Reference 49.

stitution by an electron donor forces that ring into coplanarity (and the unsubstituted ring out of coplanarity, A), and substitution by an electron acceptor forces that ring further out of coplanarity (and the unsubstituted ring into coplanarity, B). As the substituted ring is twisted out of coplanarity with the vacant 2p orbital, the resonance interaction decreases, and the substituent exerts its polar effect on the cationic carbon shielding by inductive and/or field effects.



A



B

## Conclusion

Our observation of almost identical behavior for 2-norbornyl (**11–13**), cyclopropylcarbinyl (**14**, **15**), and diarylalkyl (**28**, **29**) systems suggesting that the deviations in the plots of $\Delta\delta C^+$ against $\sigma^{C^+}$ should all have a common origin. While $\sigma$ bridging has been proposed previously to account for the deviations of **11** and **12**, it cannot be seriously considered for those of the other cations. "Onset of enhanced cyclopropyl conjugation" (whatever that may be) has been proposed previously to account for the deviation of **14**. It cannot account for **11–13**, **28**, or **29**. Steric inhibition of resonance has been proposed to account for different shielding of the cationic carbons of **11** and **14** and for deviation in the plot of **28**.

One possible explanation for the unusual deviations observed in the $\sigma^{C^+}$–$\Delta\delta C^+$ plots for certain cations (**11–15**, **28**, and **29**) is that steric inhibition of resonance can affect the observed shifts. Another possible explanation is that structural features make certain cations more stable, so that the $^{13}C$ shift fails to follow the usual behavior of "normal" systems (**1–10**). However, the similarities in the unusual upfield shifts observed for the "exceptional" cationic systems with the unusual upfield shifts recently observed for conjugated side-chain benzene derivatives[55] suggest that both phenomena may be related. Brownlee and co-workers[55] suggested that the unusual upfield shifts that they observed in their benzene derivatives were the result of a $\pi$ polarization of the side chain by strongly electron-withdrawing substituents. Consequently, we must also consider this as a possible explanation of the phenomenon. This will require an understanding of why the phenomenon appears in certain systems (**11–15**, **28**, and **29**) and not in others (**1–10**). We are exploring the cause of this phenomenon experimentally.

Many criteria have been proposed for nonclassical structures of carbocations, but few have withstood critical examination. Recently, the deviations from linearity of plots of $\delta C^+$ against $\delta C^+$ for **5** (or $\sigma^{C^+}$)[39] have been cited quite frequently. We have now shown that such deviations are not diagnostic of nonclassical $\sigma$ bridging. Thus this criterion must join the huge graveyard of disproved criteria for nonclassical structures.

## Experimental Section

$^{13}C$ NMR spectra were recorded of solutions in 10-mm tubes on either a JEOL FX-100 spectrometer operating at 25.00 MHz or in 8-mm tubes on a Varian CFT-20 spectrometer operating at 20 MHz. $^{13}C$ chemical shifts (±0.1 ppm) were measured from external $Me_4Si$ held in a 3-mm-o.d. capillary tube containing acetone-$d_6$ for field stabilization. The spectra were recorded with spectra widths of 10 000 (FX-100) or 8000 Hz (CFT-20), 8192 data points, and a 45° pulse angle. Assignments were made on the basis of multiplicities in off-resonance decoupled spectra, $^{13}C$–$^1H$ and $^{13}C$–$^{19}F$ coupling constants, known substituent effects, and previously assigned spectra. Satisfactory analyses (≤0.3%) and spectral data were obtained for all new compounds.

**Preparation of Ion Solutions.** The ion solutions were prepared as described previously.[8,13,22,48,57] Solid alcohols which would not dissolve in $SO_2ClF$ at −78 °C were added in small amounts to the precooled (−78 °C) acid solutions (1:1 molar ratio) of $SbF_5/FSO_3H$ in $SO_2ClF$ or $FSO_3H/SO_2ClF$ (1:1 pbv) under nitrogen with vigorous vortex mixing. The resulting highly colored ion solutions varied between 0.3 and 0.9 M (see tables) and were transferred to the NMR tubes via a precooled double-ended syringe.[57] The 3',4'-ethyleneoxy substituted cations were best prepared in (1:1 pbv) solutions of $FSO_3H/SO_2ClF$.[19] They all showed additional aromatic carbon resonances indicative of hindered rotation about the C1'–$C^+$ bond. $^{13}C$ NMR data for cations not appearing in the tables are as follows (assignments

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(57) Kelly, D. P.; Brown, H. C. *Aust. J. Chem.* **1976**, *29*, 957–965.

of some of the phenyl resonances may be ambiguous). For **28** (Z = 3′,4′-$CH_2CH_2O$): $\delta$ 203.5 (s, $C^+$), 182.6 (s, C4′), 152.7, 147.2 (d, C6′), 142.5, 137.4 (d, C2′), 140.7 (s, $PhC_i$), 137.9 (d, $PhC_p$), 136.9 (s, C1′), 135.5, 135.3 (s, C3′), 135.1 (d, $PhC_o$), 134.7 (d, $PhC_o$), 130.3 (d, $PhC_m$), 116.5, 115.2 (d, C5′), 79.7 (t, $CH_2O$), 27.2 (t, $CH_2$–C), 27.2 (q, $CH_3$). For **29** (Z = 3′,4′-$CH_2CH_2O$): $\delta$ 183.9 (s, C4′), 179.5 (d, $C1^+$), 156.7, 149.2 (d, C6′), 141.1, 139.1 (d, C2′), 138.3 (s, C1′), 135.4 (s, C3′), 118.4, 116.8 (d, C5′), 80.9 (t, $CH_2O$), 27.3 (t, $CH_2$), 139.9, 137.7, 134.2, 131.6 (Ph). For **29** (Z = 3′-$CF_3$): $\delta$ 201.9 (d, $C1^+$), 146.3 (m, C4′), 144.7 (d, C6′), 139.9 (m, C2′), 138.8 (s, C1′), 135.0 (q, *J* = 36 Hz, C3′), 133.9 (d, C5′), 123.6 (q, *J* = 273 Hz, $CF_3$), 154.8, 151.8, 143.4, 134.6, 133.9, 137.1 (s, Ph). For **29** (Z = 3′,5′-$(CF_3)_2$): $\delta$ 201.2 (d, $C1^+$), 141.3 (d, C2′,6′), 139.8 (s, C1′), 135.6 (q, *J* = 35 Hz, C3′,5′), 123.1 (q, *J* = 274 Hz, $CF_3$), (C4′ not observed), 158.8, 154.5, 146.3, 135.5, 134.9, 137.0 (s, Ph).

**Preparation of Alcohol Precursors.** The alcohol precursors were prepared by standard Grignard reactions of the corresponding ketone with the appropriate bromo- or iodobenzene. The 3′,4′-(ethylenoxy)phenyl (3′,4′-$CH_2CH_2O$) derivatives were prepared by the method of Brown and Gundu Rao from the corresponding ketone and 5-lithio-2,3-dihydrobenzofuran.[58] The physical constant data for these precursors are summarized in Table VI. All new compounds gave satisfactory analytical data (±≤0.3%). The $^{13}C$ NMR spectral data for all of the precursors were in accordance with the assigned structures. All of the parent ketones used for the Grignard reactions are commercially available except for nortricyclanone and *endo*-5,6-trimethylene-2-norbornanone. These ketones were prepared by following the procedures developed in our laboratories.[21a,63]

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# Regioselective Metalation Reactions of Some Substituted (Methoxymethoxy)arenes

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The methoxymethoxy substituent acts as a relatively strong ortho-directing group in hydrogen–metal exchange reactions. However, the directing effects are influenced by the metalation medium, thus permitting an unusual degree of control of the site of metalation. In conjunction with weak ortho-directing groups, the metalation ortho to the methoxymethoxy group can be directed to either of the ortho positions by controlling the electron-donating capacity of the metalating solvent. In strongly donating solvents the 1,2,4-substitution pattern will arise from a meta-substituted methoxymethoxy arene, while in nondonating solvents the 1,2,3-substitution is favored. In addition, the methoxymethoxy group serves also to enhance the rate of metalation and to stabilize the aryl-metalated products so that some competing addition reactions are suppressed.

The wide variety of transformations possible via organolithium intermediates make them crucially important in synthetic chemistry.[1] In the elaboration of aromatic systems they are becoming increasingly more prevalent due to the development of substituents capable of directing the introduction of the metal in a predictable manner.[2-8] For example, treatment of an arene bearing an ortho-directing group with an alkyllithium reagent results in metalation regioselectively in the ortho positions. A number of ortho-directing groups have been investigated, their directing capability frequently being compared to the methoxy group which is considered to be of intermediate ortho-directing capacity.[9] Strong directing groups are $SO_2NR_2$,[9] SONHR,[9] $CONR_2$,[10] CONHR,[9] $CH_2NR_2$,[9] $OCH_2OCH_3$,[11] NHCOR,[12] $NHCO_2R$,[13] CSNHR,[14] and oxazolines.[15,16] Weaker ortho-directing groups include $NR_2$, $CF_3$, F,[9] SR,[17] and some other groups which have shown ortho-directing capabilities such as $CH_2OH$,[18] $CH(OR)_2$,[19] and imidazolidines.[20]

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