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Structural Effects in Solvolytic Reactions. 45. Carbon-13 NMR Studies of Carbocations. 9. Variation of the Cationic Carbon Chemical Shifts with Increasing Electron Demand in 1,1-Diaryl-1-ethyl Carbocations. Importance of the Inductive Localized π-Polarization Effect in Causing Deviations from Linearity

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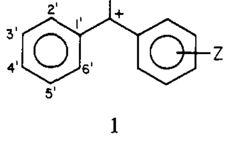
Abstract: A series of 1-aryl-1-[3′,4′-(ethyleneoxy)phenyl]-1-ethyl (or 1-aryl-1-(5′-coumaranyl)ethyl) (**9**), 1-aryl-1-(4′-methoxyphenyl)-1-ethyl (**10**), 1-aryl-1-(4′-methylphenyl)-1-ethyl (**11**), 1-aryl-1-[4′-(trifluoromethyl)phenyl]-1-ethyl (**12**), and 1-aryl-1-[3′,5′-bis(trifluoromethyl)phenyl]-1-ethyl (**13**) carbocations were prepared in either $SbF_5/FSO_3H/SO_2ClF$ or FSO_3H/SO_2ClF solutions at −78 °C and their ^{13}C NMR spectra recorded at −70 °C. The plots of the substituent chemical shifts $\Delta\delta C^+$ against σ^{C^+} are linear for the electron-donating substituents Z = 3,4-CH_2CH_2O to Z = H of **13**, **12**, **11**, and the previously reported 1-aryl-1-ethyl cations (**1**), with deshielding of the cationic carbon with increasing electron demand. However, from Z = H to Z = 3,5-$(CF_3)_2$ the cationic carbons are shielded in comparison with those predicted by the correlation line for the electron donors. The plots for the highly resonance stabilized cations **9** and **10** are in the form of shallow curves with minima at Z = *m*-CH_3 after which increasing electron demand results in shielding of the cationic carbon. This behavior is similar to that observed for the α carbon atom of substituted acetophenones and styrenes. The similarity indicates that the anomalous ^{13}C shifts that give rise to the deviations in the plots are due to substantial double-bond character between the cationic carbon and the ipso carbon ($C_{1'}$) of the phenyl group bearing the fixed substituent. Inductive π-polarization of this double bond by the Z substituent results in shielding of the cationic (C_1) carbon atom. Thus the cationic carbon chemical shifts of 1,1-diaryl-1-ethyl carbocations are determined by two competing effects, the normal resonance effect of Z (deshielding with increasing electron demand) and an inductive π-polarization effect of Z (shielding with increasing electron demand).

The tool of increasing electron demand has provided unambiguous answers regarding the structures of carbocation transition states in solvolytic processes.[2] Although this tool combined with the ^{13}C NMR method (plot of cationic carbon shifts against some measure of electron demand) should give similar unambiguous answers about the structure and bonding in "fully" formed carbocations in superacid media, often conflicting interpretations have been made. It thus appeared desirable to make a systematic study of the effect of substituents on the ^{13}C NMR shifts of aryl carbocations. Therefore we proposed new σ^{C^+} constants to correlate the cationic carbon chemical shifts (δC^+) of substituted benzylic carbocations.[3] The δC^+ values of several simple aryl dialkyl carbocations were linearly correlated against these σ^{C^+} constants.[4-7] However, the σ^{C^+} constants failed to give a linear correlation against σ^{C^+} of several other systems (**1–5**).[8,9]



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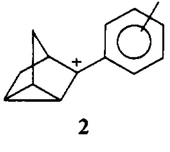

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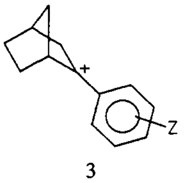

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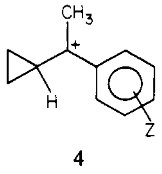

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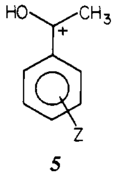

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All of these systems (**1–5**) show similar deviations in the plots of the substituent chemical shifts ($\Delta\delta C^+$) against σ^{C^+}. The deviations take the form of upward curves for the electron-withdrawing substituents with increasing electron demand; that is, the cationic carbons are shielded in comparison to that predicted by the correlation lines for the electron-donating substituents. However, different explanations have been proposed previously to account for the deviations observed for **1**, **2**, and **3**. For example, Farnum and co-workers previously observed such a deviation in the plot of δC^+ of 1-aryl-1-phenyl-1-ethyl cations (**1**) against δC^+ of 1-aryl-1-cyclopentyl cations.[10] (Since δC^+ of 1-aryl-1-cyclopentyl cations plot linearly against σC^+ this is equivalent to plotting δC^+ of 1-aryl-1-phenyl-1-ethyl cations against σ^{C^+}.) They attributed the deviation for the electron-withdrawing derivatives to the twisting of the aryl groups from coplanarity as a result of enhanced electron demand upon the unsubstituted ring. However, recently we observed that the σ^{C^+}–$\Delta\delta C^+$ plot of the substituted 9-methyl-9-anthracenium cations (**6**), where no such twisting is possible, also shows a similar deviation.[11] Consequently, such

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(1) Postdoctoral research associates on a grant provided by Exxon Research and Engineering Co.
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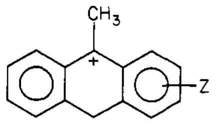

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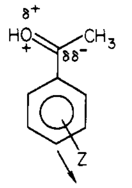
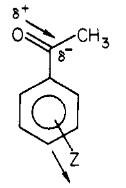
hindrance to coplanarity may not be an important factor contributing to the anomalous ^{13}C shifts in these systems.

In the case of 3-aryl-3-nortricyclyl system (**2**) such deviation has been attributed to the "onset of increased cyclopropyl conjugation"[12] and in the case of **3** to the "onset of nonclassical σ-bridging".[10,13] The observation of a similar deviation from linearity in the σ^{C^+}–$\Delta\delta C^+$ plot of the 1-aryl-1-hydroxy-1-ethyl cations (**5**) casts doubt on all of these explanations.[9] Thus we suggested that such deviations may be due to the inductive localized π-polarization shown in **7**, as a result of the partial double-bond character between oxygen and the benzylic carbon.[9]



7, Z = H to Z = 3,5-(CF$_3$)$_2$



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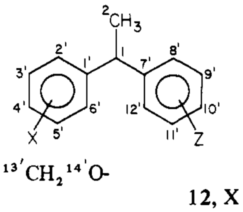
Brownlee and co-workers previously suggested such inductive localized π-polarization in substituted acetophenones (**8**) to account for the shielding of the carbonyl carbon atom observed for the electron-withdrawing derivatives.[14] The upward deviation observed for the electron-withdrawing substituents points in the σ^{C^+}–$\Delta\delta C^+$ plot of 1-aryl-1-hydroxy-1-ethyl cations (**5**) indicates that the cationic carbon atom is shielded compared to that predicted by σ^{C^+} constants.[9] Such shielding could arise in the electron-withdrawing derivatives because localized π-polarization (**7**) of the C$^+$–OH bond would be easier due to its partial double-bond character. It is not surprising that similar shielding deviations are observed in the σ^{C^+}–$\Delta\delta C^+$ plots of systems **1**, **2**, and **4**, because in these cases the cationic carbon and the first carbon atom of the conjugating phenyl or cyclopropyl groups could have double-bond character. The deviation observed in the σ^{C^+}–$\Delta\delta C^+$ plot of the 2-aryl-2-norbornyl system (**3**) may be rationalized in terms of C$_1$–C$_6$ hyperconjugation with the cationic carbon being sufficient to give partial double-bond character to the C$^+$–C$_1$ bond. (Of the three C$_\alpha$–C$_\beta$ bonds in the 2-bicyclo[2.2.1]heptyl skeleton, C$_1$–C$_6$ is aligned most favorably (<30°) with the vacant p orbital at C$_2$.)

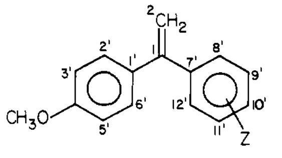
If the deviations in the σ^{C^+}–$\Delta\delta C^+$ plots are due to the double-bond character of the bond between the cationic carbon and the C$_\alpha$ carbon atom of the conjugating group, the extent of the deviation should be dependent on the conjugating ability of different stabilizing groups. Accordingly, we decided to prepare the series of 1,1-diaryl-1-ethyl cations **9**–**13** and compare the results with the available data for the 1-aryl-1-phenyl-1-ethyl cations (**1**).



9, X = 3',4'-CH$_2$$^{13'}CH_2$$^{14'}$O-
10, X = 4'-OCH$_3$
11, X = 4'-CH$_3$$^{13'}$
12, X = 4'-CF$_3$
13, X = 3',5'-(CF$_3$)$_2$

Results and Discussion

The cations **9** (Z = 9',10'-CH$_2$CH$_2$O-; 10'-OCH$_3$) and **10** (Z = 10'-OCH$_3$) were prepared from the corresponding olefins, e.g., **14** (1,1-diarylethenes) since the tertiary alcohols undergo facile dehydration during preparation. The other cations **9** and **11**–**13** were prepared by ionization of the corresponding tertiary alcohols **15**–**18** either in FSO$_3$H/SO$_2$ClF or SbF$_5$/FSO$_3$H/SO$_2$ClF.



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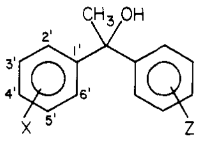
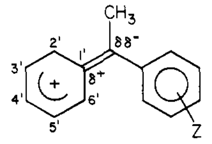


15, 3',4'-CH$_2$CH$_2$O
16, X = 4'-CH$_3$
17, X = 4'-CF$_3$
18, X = 3',5'-(CF$_3$)$_2$

Further details are given under Experimental Section. All the spectra were recorded at −70 °C and the data are summarized in Tables I–IV.

As discussed above, Farnum and co-workers proposed that the deviation in the plot of δC^+ for **1** against δC^+ for 1-aryl-1-cyclopentyl cations was due to twisting of the two aryl rings relative to one another, such that for electron-withdrawing substituents the substituted ring was forced *out of* coplanarity with the trigonal cationic carbon as the electron demand forced the unsubstituted ring *into* coplanarity in order to achieve maximum resonance stabilization of the positive charge.[10] As the substituted ring was forced further out of coplanarity the substituents influenced the chemical shift of the cationic carbon more by inductive (and therefore weak) effects than by resonance effects, resulting in shielding rather than deshielding. However, we have now shown that the substituted 9-methyl-9-anthracenium cations (**6**), in which no twisting is possible, also exhibit a similar deviation in the σ^{C^+}–$\Delta\delta C^+$ plot.[11] Consequently, this proposal of hindrance to coplanarity cannot be the major factor causing the upward deviation in the σ^{C^+}–$\Delta\delta C^+$ plot.

The comparison of the deviation observed in the σ^{C^+}–$\Delta\delta C^+$ plot observed for the 1-aryl-1-hydroxy-1-ethyl cations (**5**) with that observed for the 1-aryl-1-phenyl-1-ethyl cations (**1**) indicates that the origin of the deviation in these cases may be similar. The deviation observed in the former case was attributed to the inductive π-polarization of the stabilizing hydroxyl group (**7**). Such inductive π-polarization (**19**) is also possible in the case of the 1-aryl-1-phenyl-1-ethyl system (**1**) for the electron-withdrawing derivatives. This polarization would result in a net buildup of electron density at the formal cationic center. Consequently, the cationic carbon is shielded, and δC^+ is less than that predicted by the σ^{C^+} constants and results in the observed upward deviation in the σ^{C^+}–$\Delta\delta C^+$ plot.



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If the deviation in the plot is due to the inductive π-polarization shown in **19**, the extent of the deviation should be dependent on the conjugating ability of the aryl groups. Thus replacement of 4'-H by *less* stabilizing substituents such as 4'-CF$_3$ and 3',5'-(CF$_3$)$_2$ should result in less π-bond character between C$_{1'}$ and C$^+$ and the plots for these systems, **12** and **13**, respectively, should show less deviation than that for **1**. This is indeed the case as can be seen from Figure 1. Unlike the plot of **1**, which shows the cationic carbon for 3',5'-(CF$_3$)$_2$ (σ^{C^+} 1.03) more shielded than for 4'-CF$_3$ (σ^{C^+} 0.79) thus resulting in an upward curve, the plots of **12** and **13** show continuous deshielding of the cationic carbon ($\Delta\delta C^+$ more negative) with both 4'-CF$_3$ and 3',5'-(CF$_3$)$_2$ substituents. These plots are still not linear for the electron-withdrawing substituents, but we can predict that the substitution of a substitutent X more

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Table I. ^{13}C NMR Shifts of 1-Aryl-1-[3',4'-(ethyleneoxy)phenyl]-1-ethyl Cations (9) in FSO_3H/SO_2ClF at −70 °C

	chemical shift, δ[a]															
Z	C^+	CH_3	C_{13}'	C_{14}'	C_Z	C_1'	C_2'	C_3'	C_4'	C_5'	C_6'	C_7'	C_8'	C_9'	C_{10}'	C_{11}'	C_{12}'
3,4-CH_2CH_2O[b]	201.8	27.0	28.1	78.1		136.0	136.0	133.4	172.8	113.5	144.6						
p-OCH_3	202.8	26.9	27.8	78.4	58.6	135.7	137.2	135.3	176.2	114.2	146.7	134.5	141.3	117.2	169.4	117.2	141.3
p-CH_3	204.1	27.0	27.5	79.0	22.3	136.4	136.4, 142.1	135.4	180.7	114.6, 115.6	146.0, 151.7	138.3	136.4	131.4	152.7	131.4	136.4
p-F	201.4	27.2	27.2	79.6		137.0	136.9, 142.0	135.3, 135.5	182.5	115.2, 116.4	147.0, 152.1	135.8	138.1 (9)	118.0 (22)	169.4 (264)	118.0 (22)	138.1 (9)
p-Cl	200.8	27.1	27.1	80.0		137.2	137.4, 142.0	135.4, 135.6	183.1	115.5, 116.7	147.4, 152.2	139.0	136.1	130.6	144.4, 144.7	130.6	136.1
m-CH_3	204.1	27.2	27.2	79.5	21.1	136.8	137.2, 142.5	135.3, 135.4	182.2	115.0, 116.3	146.9, 152.4	140.9	132.9	140.9	139.0	130.1	135.4
H	203.5	27.2	27.2	79.7		136.9	137.4, 142.5	135.3, 135.5	182.6	115.2, 116.5	147.2, 152.7	140.7	134.7[c]	130.3	137.9	130.3	135.1[c]
m-Cl	199.8	27.1	27.1	80.5		137.7	137.8, 141.9	135.4, 135.6	184.2	116.0, 117.1	148.2, 152.8	141.8	132.7	136.2	136.2	131.5	132.7
m-CF_3	199.3	27.2	27.2	80.8	124.4 (272)	137.9	137.9, 142.1	135.5, 135.7	184.6	116.2, 117.4	148.5, 152.5	136.8	130.9	136.2 (31)	136.8	129.2	132.2
p-CF_3	199.1	27.2	27.2	81.0	124.4 (272)	138.1	138.1, 142.2	135.4, 135.5	185.0	116.3, 117.5	148.6, 153.0	143.4	133.1[c]	126.8	136.1 (35)	126.8	133.5[c]
3,5-$(CF_3)_2$	195.2	27.1	27.1	81.7	123.7 (273)	137.7	137.7, 141.6	135.3, 135.7	186.1	117.0, 118.2	149.3, 152.8	141.6	127.9	133.3[c] (33)	131.6	135.3[c] (33)	127.9

[a] Chemical shifts are ±0.1 ppm from external Me_4Si (capillary). ^{13}C–^{19}F coupling constants (hertz) are in parentheses. [b] The positions of the substituents have been labeled 3,4, *m*, *p*, and 3,5 for convenience; they correspond to 9'10', 9', 10', and 9', 11', respectively in structure 9. [c] Nonequivalence due to restricted rotation.

Table II. ^{13}C NMR Shifts of 1-Aryl-1-(4'-methoxyphenyl)-1-ethyl Cations (10) in $SbF_5/FSO_3H/SO_2ClF$ at −70 °C

	chemical shift, δ[a]															
Z	C^+	CH_3	OCH_3	C_Z	C_1'	C_2'	C_3'	C_4'	C_5'	C_6'	C_7'	C_8'	C_9'	C_{10}'	C_{11}'	C_{12}'
p-OCH_3[d]	204.8	26.6	58.1	58.1	134.4	143.0	117.7	173.2	117.7	143.0	134.4	143.0	117.7	173.2	117.7	143.0
p-CH_3	208.7	27.2	58.7	22.4	134.5	146.3[b]	118.9	178.0	118.9	146.0[b]	138.3	137.5	131.7	154.8	131.7	137.5
p-F	206.8	27.4	59.1		134.6	149.7[b]	119.6[c]	179.6	118.4[c]	144.1[b]	136.8 (2)	139.5 (11)	118.3 (23)	170.4 (266)	118.3 (23)	139.5 (11)
p-Cl	206.4	27.3	59.3		134.7	149.9[b]	121.0[c]	180.3	118.5[c]	144.4[b]	138.7	136.9	130.8	146.5	130.8	136.9
m-CH_3	209.3	27.5	59.0	21.0	134.7	150.3[b]	120.6[c]	179.5	118.0[c]	143.9[b]	140.5	134.0	141.2	140.8	130.3	136.1
H	208.9	27.5	59.2		134.7	150.4[b]	120.7[c]	179.9	118.3[c]	144.3[b]	140.3	135.9	130.5	139.3	130.5	135.9
m-F	205.8	27.5	59.7		134.8	150.7[b]	121.2[c]	181.5	119.0[c]	145.2[b]	141.9 (8)	120.6 (26)	163.5 (250)	124.7 (21)	132.2 (8)	131.5 (2)
m-Cl	205.6	27.5	59.8		134.8	150.6[b]	121.4[c]	181.6	119.0[c]	145.2[b]	141.7	133.4	136.5	137.3	131.6	133.4
m-CF_3	205.4	27.6	59.9	124.5 (280)	134.8	150.6[b]	121.6[c]	182.1	119.3[c]	145.5[b]	140.5	130.2 (3)	132.5 (34)	137.8	131.0	133.3
3,5-Cl_2	202.5	27.5	60.3		134.8	150.6[b]	121.9[c]	183.0	119.7[c]	145.9[b]	142.3	131.4	137.0	135.5	137.0	131.4
p-CF_3	205.1	27.6	60.1	123.4 (274)	134.8	150.8[b]	121.7[c]	182.6	119.3[c]	145.7[b]	143.1	134.1	126.9 (4)	136.6 (35)	126.9 (4)	134.1
3,5-$(CF_3)_2$	201.2	27.6	60.6	123.5 (272)	135.0	150.4[b]	122.1[c]	183.8	120.4[c]	146.5[b]	141.3	132.6	133.5 (34)	128.8	133.5 (34)	132.6

[a] Chemical shifts are ±0.1 ppm from external Me_4Si (capillary). The assignments are based on off-resonance experiments and comparison with the data reported for other aryl cationic systems. ^{13}C–^{19}F coupling constants (hertz) are in parentheses. [b,c] Assignments may be interchanged. [d] The positions of the substituents have been labeled *p*, *m*, and 3,5 for convenience; they correspond to 10',9', and 9',11', respectively, in structure 10.

Table III. ^{13}C NMR Shifts of 1-Aryl-1-(4'-methylphenyl)-1-ethyl Cations (11) in FSO$_3$H/SO$_2$ClF at −70 °C

	chemical shift, δ^a															
Z	C$^+$	CH$_3$	C_{13}'	C_Z	C_1'	C_2'	C_3'	C_4'	C_5'	C_6'	C_7'	C_8'	C_9'	C_{10}'	C_{11}'	C_{12}'
3,4-CH$_2$CH$_2$O^b	204.1	27.0	22.3	27.5, 79.0	138.3	136.4	131.4	152.7	131.4	136.4	136.4	136.4, 142.1	135.4	180.7	114.6, 115.6	146.0, 151.7
p-OCH$_3$	208.7	27.2	22.4	58.7	138.2	137.4	131.7	154.8	131.7	137.4	134.5	146.0	118.7	178.0	118.9	146.0
p-CH$_3$	220.7	29.0	23.5	23.5	139.2	141.4	132.8	162.0	132.8	141.4	139.2	141.4	132.8	162.0	132.8	141.4
p-F	221.4	29.6	23.8		139.4	142.2	133.3	164.7	133.3	142.2	137.9	144.3 (12)	119.6 (23)	174.2 (273)	119.6 (23)	144.3 (12)
p-Cl	222.1	29.6	24.1		139.6	140.9	133.5	166.2	133.5	140.9	139.6	140.9	131.9	153.0	131.9	140.9
m-CH$_3$	224.1	29.6	23.8	21.0	139.6	142.4	133.2	164.8	133.2	142.4	139.9	138.5	141.7	146.0	131.2	139.6
H	224.5	29.8	23.9		139.5	141.4	133.3	165.7	133.3	141.4	141.4	140.0	131.9	144.6	131.9	140.0
m-Cl	223.8	30.1	24.5		139.7	142.2^c	133.4^d	169.2	134.4^d	147.1^c	141.0	136.8	137.5	142.2	132.3	137.9
m-CF$_3$	224.5	30.3	24.6	123.9 (273)	139.9	141.6^c	133.8^d	170.5	134.6^d	147.4^c	141.1	133.8	133.2 (33)	141.6	131.9	137.9
p-CF$_3$	224.8	30.5	24.9	124.0 (273)	140.0	142.0^{c,e}	133.9^{d,e}	171.8	134.7^{d,e}	147.3^{c,e}	143.5	138.1	127.4	140.7 (34)	127.4	138.1
3,4-(CF$_3$)$_2$	222.9		25.3	123.3 (272)	140.1	143.1^{c,e}	134.6^{d,e}	174.7	135.3^{d,e}	147.8^{c,e}	141.5	136.0	133.8 (34)	132.6	133.8 (34)	136.0

[a] Chemical shifts are ±0.1 ppm from external Me$_4$Si (capillary). The assignments are based on off-resonance experiments and comparison with the data reported for other aryl cationic systems. ^{13}C–^{19}F coupling constants (hertz) are in parentheses. [b] The positions of the substituents have been labled 3,4, *p*, *m*, and 3,5 for convenience; they correspond to 9',10', 10', 9', and 9',11', respectively, in structure 11. [c,d] Assignments may be interchanged. [e] Nonequivalence due to restricted rotation.

Table IV. ^{13}C NMR Shifts of 1-Aryl-1-[4'-(trifluoromethyl)phenyl]-1-ethyl Cations (12) in SbF$_5$/FSO$_3$H/SO$_2$ClF at −70 °C

	chemical shift, δ^a															
Z	C$^+$	CH$_3$	4'-CF$_3$	C_Z	C_1'	C_2'	C_3'	C_4'	C_5'	C_6'	C_7'	C_8'	C_9'	C_{10}'	C_{11}'	C_{12}'
p-OCH$_3$^{d}	205.1	27.6	123.4 (274)	60.1	143.1	134.1	126.9 (4)	136.6 (35)	126.9 (4)	134.1	134.8	150.8^b	121.7^c	182.6	119.3^c	145.7^b
p-CH$_3$	224.5	30.1	123.9 (273)	24.7	143.5	138.0	127.4	140.6 (34)	127.4	130.8	139.9	147.8^b	134.7^c	171.9	133.9^c	141.9^b
p-F	227.7 (3)	31.1	123.7 (272)		143.5	138.8	127.8	141.9 (34)	127.8	138.8	139.9	152.1^b (15)	130.0^c (21)	179.0 (290)	122.0^c (22)	146.2^b (16)
p-Cl	229.4	31.3	123.7 (273)		143.7	139.5	128.0	142.5 (34)	128.0	139.5	140.3	147.6^b	133.6^c	162.8	133.5^c	142.5^b
m-CH$_3$	231.3	31.4	123.7 (273)	20.8	143.8	139.6	127.6	142.1 (34)	127.6	139.6	142.6	144.2	143.0	153.6	132.5	140.5
H	232.8	31.6	123.7 (272)		143.7	140.0	127.7	142.7 (34)	127.7	140.0	142.7	147.0^b	132.8	152.0	132.8	141.3^b
m-F	235.5	32.7	123.5 (274)		143.9	141.4	128.2	144.2 (34)	128.2	141.4	143.6	127.0 (23)	164.3 (255)	137.4 (22)	134.2 (7)	141.9
m-Cl	235.5	32.6	123.5 (272)		143.9	141.4	128.3	144.5 (33)	128.3	141.4	143.3	142.9	139.1	149.3	133.6	140.7
m-CF$_3$	237.9	33.0	123.4 (272)	123.4 (272)	144.0	142.0	128.5	145.5 (33)	128.5	142.0	142.0	144.4	134.4 (35)	146.1	133.3	138.3
3,5-Cl$_2$	237.6	33.4	123.3 (274)		144.0	142.6	128.8	146.3 (34)	128.8	142.6	143.6	139.3	139.1	146.4	139.1	139.3
4'-CF$_3$	239.5	33.3	123.4 (274)	123.4 (274)	144.1	142.9	128.6	146.0 (34)	128.6	142.9	144.1	142.9	128.6	146.0 (34)	128.6	142.9
3,5-(CF$_3$)$_2$	240.6	34.2	123.1 (274)	122.9 (273)	144.3	143.9	129.5	147.9 (35)	129.5	143.9	142.2	140.1 (2)	135.3 (36)	138.8 (5)	135.3 (36)	140.1 (2)

[a] Chemical shifts are ±0.1 ppm from external Me$_4$Si (capillary). The assignments are based on off resonance experiments and comparison with the data reported for other cationic systems. ^{13}C–^{19}F coupling constants (hertz) are in parentheses. [b,c] Assignments may be interchanged. Nonequivalence due to restricted rotation. [d] The positions of the substituent have been labeled *p*, *m*, and 3,5 for convenience; they correspond to 10', 9', and 9',11' in structure 12.

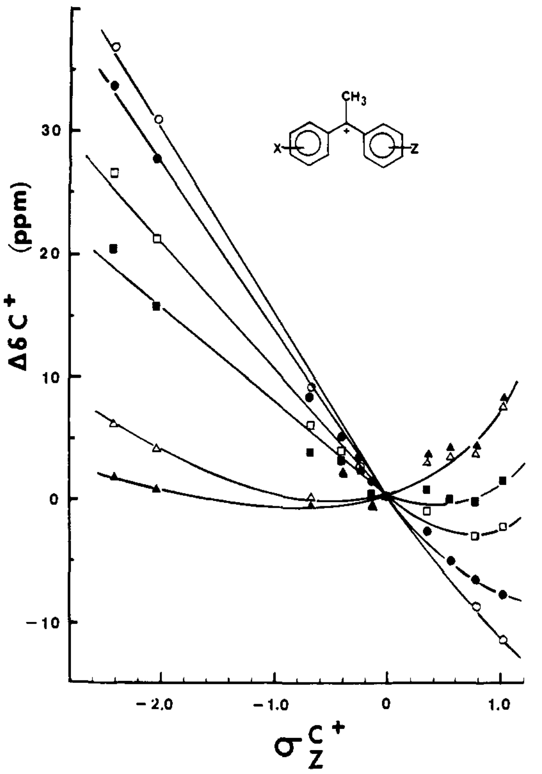
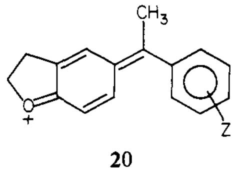


Figure 1. Plots of substituent chemical shifts ($\Delta\delta C^+ = \delta C^+(Z = H) - \delta C^+(Z \neq H)$) against $\sigma^{C^+}{}_Z$ for **1** (□), **9** (▲), **10** (△), **11** (■), **12** (●), and **13** (○). Least-squares analysis for electron donors only (σ^{C^+} 0 to −2.4): **1**, $r = 0.998$, $\rho^{C^+} = -10.9$; **9**, $r = 0.19$, $\rho^{C^+} = -0.3$; **10**, $r = 0.879$, $\rho^{C^+} = -2.2$; **11**, $r = 0.995$, $\rho^{C^+} = -8.3$; **12**, $r = 0.999$, ρ^{C^+} −14.0; **13**, $r = 0.999$, $\rho^{C^+} = -15.5$. δ^{C^+} values[3]: 3,4-CH_2CH_2O, −2.4;[15] *p*-OCH_3, −2.02; *p*-CH_3, −0.67; *p*-F, −0.4; *p*-Cl, −0.24; *m*-CH_3 −0.13; *m*-Cl, 0.36; *m*-CF_3, 0.56; 3,5-Cl_2, 0.66; *p*-CF_3, 0.79; 3,5-$(CF_3)_2$, 1.03.

electron withdrawing than 3′,5′-$(CF_3)_2$ should eventually lead to a linear correlation over the whole range of Z substituents. At this stage there would be no π-bond character between $C_{1'}$ and C^+ according to our interpretation. Such destabilization may be provided by the 4′-methylsulfonium group ($SHCH_3^+$, σ^{C^+} 1.54) although there is some doubt as to its reliability.[15]

Replacement of 4′-H (**1**) by *more* electron-donating (resonance stabilizing) substituents should lead to greater deviations from linearity of the plots of $\Delta\delta C^+$ vs. σ^{C^+} as the amount of π-bond character between $C_{1'}$ and C^+ increases. Figure 1 shows that this is also observed; the deviations from linearity becoming greater in the order X = H < 4′-CH_3 < 4′-OCH_3 < 3′,4′-CH_2CH_2O-. With the latter two highly stabilizing groups,[15] the plots are in the form of shallow curves with minima at the points for Z = *m*-CH_3 and poor correlation coefficients. The substantial π-bond character between $C_{1'}$ and C^+ is confirmed by the observation of separate resonances for $C_{2',6'}$ and $C_{3',5'}$ of **10** and **11** and for $C_{8',12'}$ and $C_{9',11'}$ of **12** and duplication of resonances of **9** consistent with restricted rotation about the $C_{1'}$–C^+ bond (Tables I and II). In addition, the resonance of the methyl carbon (C_2) is constant throughout the series (27.0 ± 0.2 ppm) indicative of no significant variation in charge density at C_1 and consistent with substantial contributions of the oxonium ion structures **20** and **21** to cations **9** and **10**, respectively. Thus these two series of cations behave like neutral conjugated side-chain benzene derivatives such as styrenes[16] where the α-carbon shielding is dominated by the inductive localized π-polarization effect and not by resonance effects of the substituent Z. It should be also pointed out that the *p*-F and *p*-Cl substituents, which are normally electron donors in highly electron-demanding carbocations, are electron acceptors in these less electron-demanding systems **9** and **10**.



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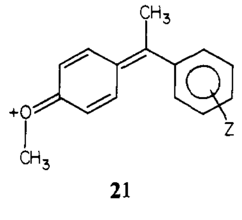

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The increasing stabilization of the positive charge at C^+ by X in these diaryl systems is also demonstrated by the ρ^{C^+} values for the electron donors (Z). Least-squares analyses for each of the systems **1** and **9**–**13** yields ρ^{C^+} values of −15.5 (3′,5′-$(CF_3)_2$), −14.0 (4′-CF_3), −10.9 (H), −8.3 (4′-CH_3), −2.2 (4′-OCH_3), and −0.3 (3′,4′-CH_2CH_2O-), the order corresponding to the order of stability of these groups.

Since the para carbon chemical shift of monosubstituted benzenes is a reliable probe of charge density at the α carbon atom,[17] the above order of stability should also be reflected by the values of $\delta C_{10'}$ (Z = H). Increasing resonance stabilization of the cationic carbon by X should be accompanied by shielding of $C_{10'}$ (decrease in $\delta C_{10'}$) as less electron demand is placed upon the unsubstituted ring. This is indeed observed, the chemical shifts decreasing in the order 152.0 (X = 4′-CF_3), 149 (X = H)[10], 144.6 (X = 4′-CH_3), 139.3 (X = 4′-OCH_3), and 137.9 ppm (X = 3′,4′-CH_2CH_2O-). (Least-squares analysis of $\delta C_{10'}$ against σ^+ yields $r = 0.984$ and slope = 9.4. More accurate data than those available for X = H[10] may give a better correlation.)

Conclusions

The deviations from linearity in the plots of $\Delta\delta C^+$ vs. σ^{C^+} for these 1,1-diaryl-1-ethyl carbocations increase in the order X = 3′,5′-$(CF_3)_2$ (**13**) < 4′-CF_3 (**12**) < H (**1**) < 4′-CH_3 (**11**) < 4′-OCH_3 (**10**) < 3′,4′-CH_2CH_2O (**9**) (Figure 1), the order of increasing resonance donor ability of these groups and thus the order of increasing $C_{1'}$–C^+ π-bond character. Thus these plots show two competing effects on the cationic carbon shielding (a) the normal resonance effect of the Z substituents leading to deshielding with increasing electron demand when there is little or no $C_{1'}$–C^+ π-bond character and (b) the inductive localized π-polarization effect of the Z substituent, leading to shielding of the cationic carbon with increasing electron demand when there is substantial $C_{1'}$–C^+ π-bond character. It follows from this proposal that 1,1-diaryl-1-ethyl cations with X substituents less stabilizing than 3′,5′-$(CF_3)_2$ will give plots with less deviation from linearity (eventually they should yield linear plots with negative ρ^{C^+} values like the dialkylaryl cations[4–7]) and with X substituents more stabilizing than 3′,4′-CH_2CH_2O- will give plots that are linear but with small positive slope (ρ^{C^+} positive) as observed for styrenes and other neutral benzyl derivatives. Rationalization of the deviations in the plots of the dialkylaryl systems **2**–**4** may now be possible.

Experimental Section

Precursors. The 1-aryl-1-[3′,4′-(ethyleneoxy)phenyl]ethanols (**15**) were prepared from 5-acetoxy-2,3-dihydrobenzofuran via Grignard reactions with the appropriate bromobenzenes. In the case of two alcohols, **15** X = Z = 3′,4′-CH_2CH_2O- and X = 3′,4′-CH_2CH_2O-, Z = 10′-OCH_3, dehydration occurred, and the data are given in Table V is for the olefins. Similarly, 1-aryl-1-(4′-methoxyphenyl)ethanols also undergo dehydration on distillation to yield the olefins **14** reported in Table V. The 1-aryl-1-(4′-methylphenyl)ethanols (**16**) were all prepared by Grignard reactions with p-methylacetophenone. The 1-aryl-1-[4′-(trifluoromethyl)phenyl]ethanols (**17**) were synthesized either by the addition of *p*-(trifluoromethyl)acetophenone to the corresponding Grignard reagent or by the addition of the corresponding substituted acetophenone to *p*-(trifluoromethyl)phenylmagnesium bromide. The 1-aryl-1-[3′,5′-bis(trifluoromethyl)phenyl]ethanols were prepared as in the above series of alcohols except for **18**, X = Z = 3′,5′-$(CF_3)_2$, which was prepared by the addition of 2 mol of 3,5-bis(trifluoromethyl)phenylmagnesium bromide to ethyl acetate, mp 108–109 °C. All of the above alcohols gave ^{13}C NMR

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Table V. Physical Constant Data for the Precursors[a]

Z	mp or bp, °C/mm			
	14	15	16	17
9′,10′-CH$_2$CH$_2$O	102–104	115–118[c]	87–88	82–84
10′-OCH$_3$	141	102–104[c]	73–74	72–73[c]
10′-CH$_3$	73–74	87–88	108/0.3[d]	116/0.2
10′-F	72–73	86–88	99/0.3[e]	108–109/0.2
10′-Cl	78	74–76	119/0.3	118/0.15
9′-CH$_3$	119/0.1	67–70	111/0.3	112/0.2
10′-H	75–76[b]	80–82	107/0.3[f]	110/0.15[g]
9′-F	104/0.1			108/0.2
9′-Cl	125/0.1	89–90	120/0.3	122/0.2
9′,11′-Cl$_2$	140/0.1			132/0.2
9′-CF$_3$	95/0.1	55–57	99/0.3	106/0.15
10′-CF$_3$	72–73	82–84	101/0.3	110/0.2[h]
9′,11′-(CF$_3$)$_2$	86/0.1	74–76	95–97	102/0.2

[a] Satisfactory analytical data (C (±0.3%), H, Cl, F (±0.2%)) have been obtained for all new compounds. [b] Lit.[10] mp 74–75 °C. [c] Olefins. [d] Lit.[19] bp 125–130 °C/5 mm. [e] Lit.[20] bp 120 °C/0.4 mm. [f] Lit.[10] bp 112 °C/0.4 mm. [g] Lit.[10] bp 110 °C/0.1 mm. [h] Lit.[10] bp 112 °C/0.2 mm.

spectra in accordance with the assigned structures. Satisfactory elemental analyses (C, H, F, and Cl ± 0.3%) were obtained for all new compounds. The physical constants are summarized in Table V.

Carbocations. The ions were prepared by slow addition of the appropriate precursor as a solution in SO_2ClF at −78 °C or as a powder in cases in which the precursors are insoluble in SO_2ClF to a solution of FSO_3H/SbF_5(1:1 mol/mol)/SO_2ClF or HSO_3F/SO_2ClF (**9**, **11**) cooled to −78 °C with rapid vortex mixing. The "magic acid", SbF_5/FSO_3H (1:1 mol/mol), concentration in the solution was 3 M. The concentration of the ion based on the precursor added was ~0.5 M. Transfer of the solutions under nitrogen to an 8- (CFT 20) or 10-mm (FX 100) NMR tube was achieved via a cooled double-ended syringe needle as described previously.[18]

NMR Spectra. ^{13}C NMR spectra were recorded at −70 °C on either a Varian CFT-20 or JEOL FX-100 spectrometer operating at 20 or 25 MHz, respectively. Field stabilization was provided by a 3-mm (o.d.) capillary of acetone-d_6 containing Me_4Si. Spectral widths of 6000 (CFT-20) or 8000 Hz (FX-100), 8192 data points, and pulse angles of 45° were employed. Chemical shifts are ±0.1 ppm from external Me_4Si. Assignments were made on the basis of off-resonance proton-decoupled spectra, ^{13}C–^{19}F coupling constants and previously reported assignments for benzylic cations. ^{13}C data for cation from **18**, X = Z = 3′,5′-$(CF_3)_2$, not given in tables: δ 243.4 (C_1), 142.5 ($C_{1'}$), 141.4 ($C_{2'6'}$ and $C_{4'}$, overlapping peaks), 135.6 ($C_{3'5'}$, J_{CF} = 35 Hz), 122.8 (CF_3, J_{CF} = 273 Hz), 35.3 (CH_3).

Acknowledgment. This work was supported in part by a grant from Exxon Research and Engineering Co. We are grateful to M. J. Jenkins for preparation and recording the spectrum of cation from **18**, X = Z = 3′,5′-$CF_3)_2$.

Registry No. 9 (Z = 3,4-CH_2CH_2O), 86766-78-1; **9** (Z = *p*-OCH_3), 86766-79-2; **9** (Z = *p*-CH_3), 86766-80-5; **9** (Z = *p*-F), 86766-81-6; **9** (Z = *p*-Cl), 86766-82-7; **9** (Z = *m*-CH_3), 86766-83-8; **9** (Z = H), 81390-57-0; **9** (Z = *m*-Cl), 86766-84-9; **9** (Z = *m*-CF_3), 86766-85-0; **9** (Z = *p*-CF_3), 86766-86-1; **9** (Z = 3,5-$(CF_3)_2$), 86766-87-2; **10** (Z = *p*-OCH_3), 25836-80-0; **10** (Z = *p*-CH_3), 60665-82-9; **10** (Z = *p*-F), 39769-48-7; **10** (Z = *p*-Cl), 86766-88-3; **10** (Z = *m*-CH_3), 86766-89-4; **10** (Z = H), 60665-78-3; **10** (Z = *m*-F), 86784-86-3; **10** (Z = *m*-Cl), 86766-90-7; **10** (Z = *m*-CF_3), 86766-91-8; **10** (Z = 3,5-Cl_2), 86766-92-9; **10** (Z = *p*-CF_3), 64999-88-8; **10** (Z = 3,5-$(CF_3)_2$), 86766-93-0; 11 (Z = 3,4-CH_2CH_2O), 86766-94-1; 11 (Z = *p*-OCH_3), 60665-82-9; 11 (Z = *p*-CH_3), 41912-36-1; 11 (Z = *p*-F), 39769-51-2; 11 (Z = *p*-Cl), 86766-95-2; 11 (Z = *m*-CH_3), 86766-96-3; 11 (Z = H), 41912-34-9; 11 (Z = *m*-Cl), 86766-97-4; 11 (Z = *m*-CF_3), 86766-98-5; **11** (Z = *p*-CF_3), 86766-99-6; 11 (Z = 3,4-$(CF_3)_2$), 86767-00-2; **12** (Z = *p*-OCH_3), 64999-88-8; **12** (Z = *p*-F), 39769-52-3; **12** (Z = *p*-Cl), 86767-01-3; **12** (Z = *m*-CH_3), 86767-02-4; **12** (Z = H), 60665-79-4; **12** (Z = *m*-F), 86767-03-5; **12** (Z = *m*-Cl), 86767-04-6; **12** (Z = *m*-CF_3), 86767-05-7; **12** (Z = 3,5-Cl_2), 86767-06-8; **12** (Z = *p*-CF_3), 60665-81-8; **12** (Z = 3,5-$(CF_3)_2$), 86767-07-9; **14** (Z = 9′,10′-CH_2CH_2O), 86767-08-0; **14** (Z = 10′-OCH_3), 4356-69-8; **14** (Z = 10′-CH_3), 13392-76-2; **14** (Z = 10′-F), 38695-33-9; **14** (Z = 10′-Cl), 13392-79-5; **14** (Z = 9′-CH_3), 13392-77-3; **14** (Z = 10′-H), 4333-75-9; **14** (Z = 9′-F), 86767-09-1; **14** (Z = 9′-Cl), 34564-84-6; **14** (Z = 9′,11′-Cl_2), 86767-10-4; **14** (Z = 10′-CF_3), 68036-77-1; **14** (Z = 9′,11′-$(CF_3)_2$), 86767-11-5; **15** (Z = 9′,10′-CH_2CH_2O), 86767-12-6; **15** (Z = 10′-OCH_3), 86767-13-7; **15** (Z = 10′-CH_3), 86767-14-8; **15** (Z = 10′-F), 86767-15-9; **15** (Z = 10′-Cl), 86767-16-0; **15** (Z = 9′-CH_3), 86767-17-1; **15** (Z = 10′-H), 81390-91-2; **15** (Z = 9′-Cl), 86767-18-2; **15** (Z = 9′-CF_6), 86767-19-3; **15** (Z = 10′-CF_3), 86767-20-6; **15** (Z = 9′,11′-$(CF_3)_2$), 86767-21-7; **16** (Z = 10′-OCH_3), 86767-22-8; **16** (Z = 10′-CH_3), 17138-82-8; **16** (Z = 10′-F), 39768-91-7; **16** (Z = 10′-Cl), 86767-23-9; **16** (Z = 9′-CH_3), 86767-24-0; **16** (Z = 10′-H), 86767-25-1; **16** (Z = 9′-Cl), 86767-26-2; **16** (Z = 9′-CF_3), 86767-27-3; **16** (Z = 10′-CF_3), 86767-28-4; **16** (Z = 9′,11′-$(CF_3)_2$), 86767-29-5; **17** (Z = 10′-OCH_3), 86767-30-8; **17** (Z = 10′-F), 39769-39-6; **17** (Z = 10′-Cl), 86767-31-9; **17** (Z = 9′-CH_3), 86767-32-0; **17** (Z = 10′-H), 86767-33-1; **17** (Z = 9′-F), 86767-34-2; **17** (Z = 9′-Cl), 86767-35-3; **17** (Z = 9′,11′-Cl_2), 86767-36-4; **17** (Z = 10′-CF_3), 86767-37-5; **17** (Z = 9′,11′-$(CF_3)_2$), 86767-38-6.

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