Finally, the product was dissolved in toluene (50 mL), and this solution was washed with aqueous HCl (50 mL, 10% solution; for the amine compounds, distilled water was used in the wash). The layers were then separated, and the organic layer was dried over $MgSO_4$. The solvent was removed under vacuum, and the product, 1-phenyl-1-methyltetrachlorocyclotriphosphazene, was recrystallized from *n*-hexane. Yields and mp/bp data are listed in Table I. The NMR data (^1H, ^{19}F, ^{31}P) are listed in Table II. Ultraviolet and mass spectral data are listed in Table III. Tables II and III are available as supplementary material.

Elemental Microanalytical Data.[44] Compound I ($R = CH_3$; $X = Y = H$): Anal. Calcd for $C_7H_8N_3P_3Cl_4$: C, 22.76; H, 2.17; N, 11.38; P, 25.20; Cl, 38.48. Found: C, 22.71; H, 2.30; N, 11.03; P, 24.73; Cl, 38.31.

Compound I ($R = CH_3$; $Y = H$; $X = N(CH_3)_2$): Anal. Calcd for $C_9H_{13}N_4P_3Cl_4$: C, 26.21; H, 3.16; N, 13.58; P, 22.57; Cl, 34.47. Found: C, 26.41; H, 3.41; N, 13.46; P, 22.19; Cl, 34.51.

Compound I ($R = CH_3$; $Y = H$; $X = F$): Anal. Calcd for $C_7H_7N_3P_3Cl_4F$: C, 21.71; H, 1.81; N, 10.85; P, 24.03; Cl, 36.69. Found: C, 21.79; H, 2.13; N, 10.68; P. 24.00; Cl, 36.38.

Compound I ($R = CH_3$, $Y = H$, $X = CF_3$). Anal. Calcd for $C_8H_7N_3P_3Cl_4F_3$: C, 21.97; H, 1.60; N, 9.61; P, 21.28; Cl, 32.49. Found: C, 21.36; H, 1.63; N, 9.44; P, 21.03; Cl, 32.29.

Acknowledgment. This research was supported by a grant from Research Corp.

Registry No. I ($R = CH_3$; $X = Y = H$), 84811-29-0; I ($R = C_2H_5$; $X = Y = H$), 86709-58-2; I ($R = n\text{-}C_3H_7$; $X = Y = H$), 86711-94-6; I ($R = n\text{-}C_4H_9$; $X = Y = H$), 86709-59-3; I ($R = CH_3$; $X = N(CH_3)_2$; $Y = H$), 87048-81-5; I ($R = CH_3$; $X = H$; $Y = N(CH_3)_2$), 87921-97-9; I ($R = CH_3$; $X = N(C_2H_5)_2$; $Y = H$), 87048-82-6; I ($R = CH_3$; $X = OCH_3$; $Y = H$), 87048-79-1; I ($R = CH_3$; $X = H$; $Y = OCH_3$), 87921-98-0; I ($R = CH_3$; $X = t\text{-}C_4H_9$; $Y = H$), 87048-84-8; I ($R = CH_3$; $X = CH_3$; $Y = H$), 87048-78-0; I ($R = CH_3$; $X = C_6H_5$; $Y = H$), 87048-83-7; I ($R = CH_3$; $X = F$; $Y = H$), 87048-77-9; I ($R = CH_3$; $X = H$; $Y = F$), 87921-99-1; I ($R = CH_3$; $X = Cl$; $Y = H$), 87048-76-8; I ($R = CH_3$; $X = CF_3$; $Y = H$), 87048-80-4; methylpentachlorocyclotriphosphazene, 71332-21-3; phenyl bromide, 108-86-1.

Supplementary Material Available: NMR data (Table II) and UV and mass spectral data (Table III) of arylalkylphosphazines (17 pages). Ordering information is given on any current masthead page.

Carbon-13 Nuclear Magnetic Resonance Studies of Carbocations. 10.[1] Variation of Cationic Carbon Chemical Shifts with Increasing Electron Demand in 1,1-Diaryl-1-methyl (Benzhydryl) Carbocations

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Received June 23, 1983

A series of 28 1-X-phenyl-1-Z-phenyl-1-methyl (benzhydryl) carbocations, where the X and Z substituents have been varied over the range of electron demand (3,4-CH_2CH_2O, **11**; 4-OCH_3, **12**; 4-CH_3, **13**; 4-F, **14**; 4-H, **1**; 4-CF_3, **15**; 3,5-$(CF_3)_2$, **16**), have been prepared from the corresponding alcohols by ionization in superacids and their ^{13}C NMR spectra recorded at low temperatures (−70 to −10 °C). Plots of the substituent chemical shifts of the cationic carbons ($\Delta\delta C^+$) at −70 °C against σ^{C^+} are linear for the electron donors (Z = 3,4-CH_2CH_2O to Z = H) of **13**–**16** and **1** but deviate upward from this correlation line (relative shielding) for the electron acceptors (Z = H to Z = 3,5-$(CF_3)_2$). The plots of the highly stabilized cations **11** and **12** approximate shallow curves where groups more electron demanding than 4-CH_3 cause relative *shielding* of the cationic carbon. All these plots are interpreted in terms of competing resonance and localized inductive π-polarization effects.

Previous ^{13}C NMR studies of 4-substituted benzhydryl cations **1** in (Chart I) in superacids indicated that while the chemical shifts of the para carbon in the unsubstituted ring ($\delta C_{4'}$) correlated well with Hammett–Brown σ^+ constants derived from solvolysis, those of the cationic carbons did not.[2] A subsequent investigation of 2-phenylpropyl (cumyl) cations **3** revealed a major deviation from linearity in the plot of cationic carbon substituent chemical shifts ($\Delta\delta C^+$) against σ^+.[3] This led to the development of σ^{C^+} constants[4] which have now been shown to correlate the cationic carbon shifts of a wide range of acyclic,[5,6] cyclic,[7,8] and multicyclic cations.[6,9]

However, 2-aryl-2-norbornyl (**4**),[10-12] 3-aryl-3-nortricyclyl (**5**),[10,12] 1-aryl-1-cyclopropylethyl (**6**)[10] and 1,1-diaryl-1-ethyl (**2**)[10,11] cations showed deviations in the plots of $\Delta\delta C^+$ against electron demand (either σ^{C^+} or δC^+ of 1-aryl-1-cyclopentyl cations[4,11,12]) such that the cationic carbons of those cations with substituents more electron demanding then *p*-H, were more shielded than that predicted by the correlation line for the (π) electron donors.[10] These deviations were interpreted in terms of three different effects, the onset of nonclassical σ bridging,[11-13] the onset of increased cyclopropyl conjugation,[12] and steric inhibition of resonance,[11] yet the deviations were very similar.

In the case of **2**, Farnum and co-workers attributed the deviation to the relative twisting of the two aryl groups with respect to the plane of the trigonal cationic carbon as a result of increased electron demand upon the unsubstituted phenyl ring by the Z substituent. Thus, when

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[1] For part 9 see: Brown, H. C.; Periasamy, M.; Perumal, P. T.; Kelly, D. P.; Giansiracusa, J. J. *J. Am. Chem. Soc.* **1983**, *105*, 6300–6305.

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[3] Kelly, D. P.; Spear, R. J. *Aust. J. Chem.* **1978**, *31*, 1209–1221.

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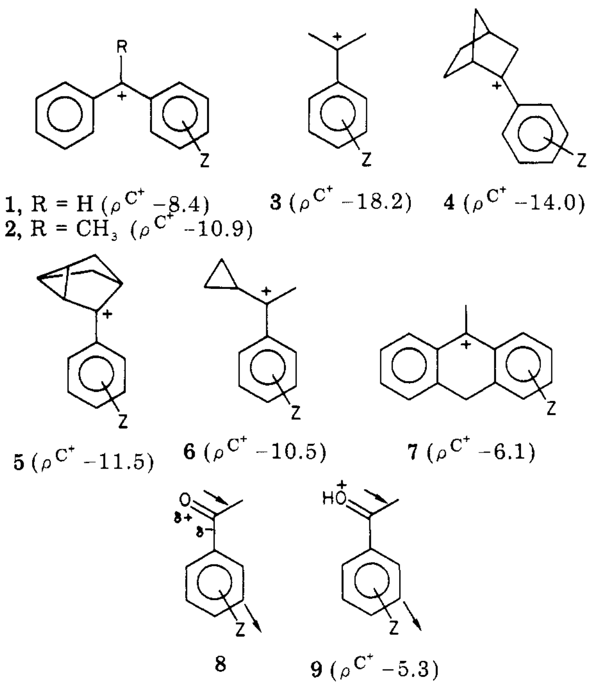
0022-3263/84/1949-0409$01.50/0

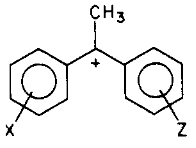
Chart I

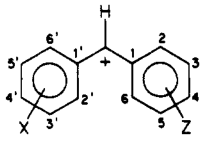

1, R = H (ρ^{C^+} −8.4)
2, R = CH_3 (ρ^{C^+} −10.9)
3 (ρ^{C^+} −18.2)
4 (ρ^{C^+} −14.0)
5 (ρ^{C^+} −11.5)
6 (ρ^{C^+} −10.5)
7 (ρ^{C^+} −6.1)
8
9 (ρ^{C^+} −5.3)

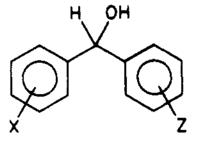
the latter were electron withdrawing, e.g., Z = 4′-CF_3 and 3′,5′-$(CF_3)_2$, the unsubstituted ring would be brought closer (from 25° to 30°[11]) to coplanarity with the trigonal cationic carbon in order to provide stabilization. This would result in the twisting of the substituted aryl ring further out of coplanarity such that the influence of Z upon C^+ would be via (weak) inductive/field effects rather than the (strong) resonance effect. However, the recent observation of a similar deviation in the $\Delta\delta C^+$–σ^{C^+} plot for 9-methyl-9-anthracenium cation 7, in which no such twisting is possible, indicates that steric hindrance to coplanarity may not be the major factor responsible for these deviations.[14]

Of the other alternative explanations for the deviations advanced so far, (a) problems associated with using a single substituent parameter,[10] (b) equilibration,[15] (c) enhanced electron supply of the substrate,[10] and (d) localized inductive π polarization,[1,16,17] the last is most reasonable. Localized inductive π polarization was proposed by Brownlee[17] and Reynolds[18] to account for *increases* in shielding of the benzylic carbons of acetophenones and styrenes with increasing electron demand. Thus the electron-withdrawing substituent Z sets up a dipole which polarizes the C═O bond of acetophenones 8, resulting in relative shielding of the benzylic carbon.[17] Protonated acetophenones 9 in SbF_5/FSO_3H also exhibit a deviation from linearity in the $\Delta\delta C^+$–σ^{C^+} plot, similar to those observed for 1–7.[16] This suggests that partial double bond character remains after protonation in superacid when Z is more electron demanding than *p*-H.[19] Inductive π polarization of this bond results in relative shielding of the benzylic carbon compared to that predicted for the correlation line for the electron-donating substituents, the deviation produced taking the form of an upward curve away from the correlation line.

If this interpretation of the deviations is correct, then the extent of the deviation should be dependent upon the π-donor ability of the different substrates. Thus for 1,1-diaryl-1-ethyl cations 10, the deviation should be greater for X = 4′-OCH_3 than for X = 4′-CF_3. We have recently shown this to be true, with the deviations from linearity in the plots becoming increasingly severe as X is changed from 4′-CF_3 to 3′,4′-CH_2CH_2O (5-coumaranyl).[1] In the latter case there is relatively little change in $\Delta\delta C^+$, and the plot approximates a shallow curve.[20]


10


11, X = 3′,4′-CH_2CH_2O
12, X = 4′-OCH_3
13, X = 4′-CH_3
14, X = 4′-F
1, X = H
15, X = 4′-CF_3
16, X = 3′,5′-$(CF_3)_2$


17, X = 3′,4′-CH_2CH_2O
18, X = 4′-OCH_3
19, X = 4′-CH_3
20, X = 4′-F
21, X = 4′-CF_3
22, X = 3′,5′-$(CF_3)_2$

A similar effect was observed in the solvolyses of disubstituted benzhydryl chlorides by Nishida, where the slope of the modified Hammett plot decreased with the ability of X to supply electron density to the transition state.[21]

We report here the results for the series of 1,1-diaryl-1-methyl cations 11–16.

Results and Discussion

The cations 11–16 were generated from the corresponding alcohols 17–22 by ionization in either $SbF_5/FSO_3H/SO_2ClF$ or FSO_3H/SO_2ClF. Data for 1 were available from earlier studies[2] and are included with selected ^{13}C NMR data, measured at −70 °C, in Table I. The alcohols were prepared by standard Grignard reactions of the appropriate bromides and benzaldehydes or ethyl formate and the physical constants are reported in Table II. Complete ^{13}C NMR data for both the cations and the alcohols are available as supplementary material.

The assignments of the spectra were based on previous results for benzhydryl cations,[2] diarylalkyl cations,[1,22] and dialkylaryl cations[3,10] and on known substituent effects.[23-25]

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[16] Brown, H. C.; Periasamy, M. *J. Org. Chem.*, in press.

[17] Bromilow, J.; Brownlee, R. T. C.; Craik, D. J.; Fiske, P. R.; Rowe, J. E.; Sadek, M. *J. Chem. Soc. Perkin Trans. 2*, 1981, 753–759. Brownlee, R. T. C.; Craik, D. J. *Ibid.* **1981**, 761–764.

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[19] In H_2SO_4, acetophenones do not show "reverse" substituent chemical shifts, which is consistent with the view that protonation on oxygen destroys the C═O π-bond character.[17] However, in "magic acid", a larger range of acetophenones do show a reversal of shielding consistent with partial π-bond character.

[20] It was suggested by one referee of that paper that the relationship may not be a curve and that dual substituent parameter (DSP) analysis may yield additional information. In the case of parent cations 2, DSP analysis was considered not likely to improve the correlation.[10] See also ref 31.

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Table I. Selected ^{13}C NMR Parameters for 1,1-Diaryl-1-methyl Carbocations at −70 °C[a]

substituent			
ion[b]	Z	C^+	C_4
1	H[c]	199.8	149.9
11	3,4-CH_2CH_2O	176.8	
	4-OCH_3	177.8	172.1
	4-CH_3	179.2, 179.5	155.0
	4-F	178.9	171.0 (270)
	4-H	179.3, 179.5	139.7
	4-CF_3	175.5	137.1[d]
	3,5-$(CF_3)_2$	172.0	129.2[d]
12	4-OCH_3	179.5	
	4-CH_3	183.3	157.8
	4-F	181.6	171.5 (272)
	4-H[c]	183.5	141.5
	4-CF_3	180.0	138.1 (33)
	3,5-$(CH_3)_2$	176.4	128.7
13	4-CH_3	192.8	
	4-F	193.3	175.7 (283)
	4-H[c]	196.1	147.9
	4-CF_3	195.7	142.5 (34)
	3,5-$(CF_3)_2$	193.4	134.7[e]
14	4-F	193.8	
	4-H[c]	197.1 (5)	
15	4-F	198.0	181.3 (297)
	4-H[c]	202.2	155.9
	4-CF_3	207.3	
	3,5-$(CF_3)_2$	208.0	142.0
16	4-F	196.3	183.2 (303)
	4-H[c]	201.2	158.8
	3,5-$(CF_3)_2$	209.1	

[a] Chemical shifts are ±0.1 ppm from external (capillary) Me_4Si. $^{13}C-^{19}F$ coupling constants (in hertz) are in parentheses. The complete table of all ^{13}C NMR data is available as supplementary material. [b] For purposes of economy, data for the same ions which would appear twice have not been included; for example, **1** 4-CH_3 is **13** 4-H, **12** 3,4-CH_2CH_2O is **11** 4-OCH_3, etc. [c] Data for monosubstituted cations have been taken from ref 2 and 10. [d] Estimated position; overlapping peaks. [e] Broad signals at −70 °C; chemical shifts (and coupling constants) taken from spectrum at −30 °C.

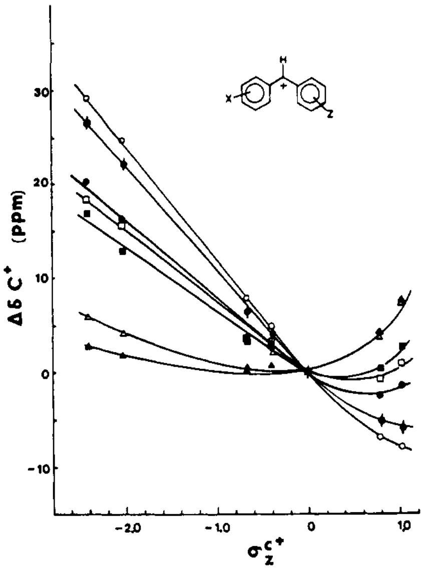


Figure 1. Plots of substituent chemical shifts[22] ($\Delta\delta C^+ = \delta C^+$ (Z = H) − δC^+ (Z ≠ H) against σ^{C^+} for **1** (●), **11** (▲), **12** (△), **13** (■), **14** (□), **15** (solid circle with vertical bar), **16** (○). Least-squares analysis for electron donors only (σ^{C^+} from 0 to −2.4): **1**, $r = 0.996$, $\rho^{C^+} = -8.6$; **11**, $r = 0.957$, $\rho^{C^+} = -1.0$; **12**, $r = 0.936$, $\rho^{C^+} = -2.2$; **13**, $r = 0.995$, $\rho^{C^+} = -6.9$; **14**, $r = 0.997$, $\rho^{C^+} = -7.7$; **15** $r = 0.999$, $\rho^{C^+} = -11.2$; **16**, $r = 0.9999$, $\rho^{C^+} = -12.2$. σ^{C^+} values are from ref 4 and 9. Least-squares analysis of the data for the seven symmetrically substituted compounds (X = Z) yields $r = 0.998$ and $\rho^{C^+} = -9.84$.

The ipso carbon (C_1, $C_{1'}$) resonances are recognized by their characteristically sharp lines,[2] but their individual assignments are equivocal. They have been tentatively assigned on the basis of the substituent effects of X and Z in the above related cations. The resonances due to the quaternary carbons in **11** ($C_{3'}$) were assigned on the basis of their larger line width due to incomplete coalescence of two (almost equal) shifts or on the observation of separate resonances of two different rotamers. Assignments of the various resonances to ortho and meta carbons, $C_{2'}$, $C_{6'}$, $C_{3'}$, $C_{5'}$, etc., were based on the expected γ-effect shielding between the two rings;[2] thus $C_{2'}$ amd C_6 will be shielded compared to $C_{6'}$ and C_2, and $C_{3'}$ and C_5 will be shielded compared to $C_{5'}$ and C_3, respectively. Nonequivalence of ortho and meta carbons is exhibited by the phenyl ring which supplies most electron density to the charged carbon due to hindered rotation about the ipso–C^+ bond. Within any one series of cations **11**, **12**, etc., the temperature at which coalescence of the nonequivalent peaks occurs (in the X ring) increases with increasing electron demand from the other (Z) ring, as expected for increasing barriers to rotation about the $C_{1'}$–C^+ bond. Where resonances were broad at −70 °C, the chemical shifts (and $^{13}C-^{19}F$ coupling constants) were taken from spectra recorded at higher temperatures.

If the deviation previously observed in the $\Delta\delta C^+$–σ^{C^+} plot for **1**[10] is due to shielding of the cationic carbon by inductive π polarization of the $C_+ - C_{1'}$ bond, then it follows that replacement of 4′-H of **1** by *less* stabilizing substituents (weaker π donors) such as 4′-CF_3 and 3′,5′-$(CF_3)_2$ should result in *less* π-bond character in this bond, and the plots for these cationic systems **15** and **16**, respectively, should show less deviation than for **1**. This is indeed the case as can be seen from Figure 1. The plot for **16** is very close to being linear over the entire range of electron de-

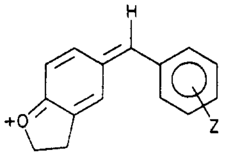
Table II. Physical Constants for 1,1-Diaryl-1-methanols

	mp or bp (mm), °C					
Z	**17**	**18**	**19**	**20**	**21**	**22**
3,4-CH_2CH_2O	154–156					
4-OCH_3	*a*	*a*, *b*				
4-CH_3	*a*	96–98[c]	67.5–70[d]			
4-F	*a*	181 (0.5)[e]	51–53.5[f]	110 (0.01)[g]	77–80[h]	69–70
4-CF_3	94.5–95.5	76–77	88–90[i]		78–80	
3,5-$(CF_3)_2$	67–69	99.5–100	124.5–125.5		81–82	148–149

[a] Viscous oil which was purified by chromatography. [b] Lit. mp 72 °C: Schnackenberg, H; Scholl, R. *Ber.* **1903**, *36*, 655. [c] Lit. mp 64.0–64.2 °C: Ogata, F.; Nagura, K. *J. Org. Chem.* **1974**, *39*, 3680–3683. [d] Lit.[21] mp 71 °C. [e] Lit. bp 145 °C (0.4 mm): Dayal, S. K.; Ehrenson, S.; Taft, R. W. *J. Am. Chem. Soc.* **1972**, *94*, 9113. [f] Lit. mp 51.5–52.5 °C: Eckstein, Z.; Fluksik, B.; Sobótka, W. *Bull. Acad. Polon. Sci., Cl. 3* **1959**, 7, 803–809. [g] Lit. bp 125–130 °C (0.1 mm): Riemschneider, R. *Pharmazie* **1947**, *1* (2), 99–157. Lit. bp 150–154 °C (5 mm): Gunther, F. A.; Blinn, R. C. *J. Am. Chem. Soc.* **1950**, *72*, 4282. [h] Lit. mp 65–66 °C, reference as for e. [i] Lit. mp 84–86 °C: De Roos, A. M.; Rekker, R. F. *Nauta W. Th. Arzneim Forsch.* **1971**, *21*, 818–820.

mand, and the cationic carbons of **15** and **16**, Z = 3,5-$(CF_3)_2$, are deshielded ($\Delta\delta C^+$ more negative[26]) compared to those for Z = 4-CF_3, unlike that for **1**. Our interpretation predicts that even greater electron-withdrawing groups (π acceptors) should eventually result in completely linear plots as observed for **3** and many other cations.[27]

Replacement of 4′-H of **1** by *more* stabilizing substituents (π donors) should result in greater π-bond character between $C_{1'}$ and C^+ and greater deviations from linearity. This is also observed as shown in Figure 1, with the deviations increasing from X = 4′-CH_3 (**13**) to X = 4′-OCH_3 (**12**) to X = 3′,4-CH_2CH_2O (**11**). The latter two cationic systems give plots which approximate shallow curves and only cover a range of approximately 7 ppm compared to 37 ppm for **16**. Thus in **11** and **12**, the normal resonance effect of the Z substituents, which results in deshielding of C^+ with increasing electron demand, is almost completely nulled by the inductive π-polarization effect, facilitated by substantial π-bond character ($C_{1'}{=}C^+$) as shown in **23** and **24**. Thus **11** and **12** behave like neutral conjugated side-chain benzene derivatives such as styrenes.[18] The π-bond character in these cations is evidenced by duplication of resonances of the X ring of **11** and by separate resonances for the ortho and meta carbons of the other cations as a result of restricted rotation about the $C_{1'}$–C^+ bond (Table I).



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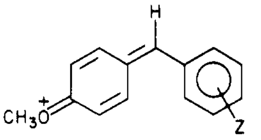

24

The increasing stabilization of the charge by the X-substituent is shown by the slopes of the linear part of the plots (*Z* = π donors). Least-squares analyses for each of the systems **1** and **11**–**16** yields of ρ^{C^+} values of −12.2 (3′,5′-$(CF_3)_2$), −11.2 (4′-CF_3), −8.6 (H), −7.7 (4′-F), −6.9 (4′-CH_3), −2.2 (4′-OCH_3), and −1.0 (3′,4′-CH_2CH_2O),[28] the order corresponding to the order of π-donor ability of these groups, as also observed by Nishida in the solvolyses of the benzhydryl chlorides.[21]

Since para carbon shifts are a reliable measure of charge density in benzylic cations,[2] the above order of stability should be reflected in the shifts of C_4 (Z = H, or $\delta C_{4'}$ of **1**). This is observed, the shifts decreasing in the order 158.8 (3,5-$(CF_3)_2$), 155.9 (4-CF_3), 149.9 (H), 147.9 (4-CH_3), 141.5 (4-OCH_3), and 139.7 (3,4-CH_2CH_2O) ppm.[2,10] (Least-squares analysis of δC_4 against σ^+ yields $r = 0.995$ and a slope of 9.6.)

It is obvious from Figure 1 that the decrease in the slopes (ρ^{C^+} less negative) of the correlation lines for the electron donors (which are a quantitative measure of the electron supply to the cationic center) from X = 3′,5′-$(CF)_2$ (**16**) to X = 3′,4′-CH_2CH_2O (**11**) is accompanied by increasing deviations from these lines for the electron acceptors. Therefore, in this series of cations (and also in **10**)[1] ρ^{C^+} gives some quantitative measure of the deviation from linearity and therefore of the effectiveness of the inductive π-polarization mechanism. However, extrapolation of this concept to obtain a measure of the extent of deviations in cations of widely varing structure, e.g., **4**–**7**, is not straightforward.

A criticism of the use of using this single substituent parameter approach rather than the dual substituent parameter (DSP) approach[29] to the analysis of the chemical shifts is that it restricts the inductive and resonance transmission coefficients (ρ_I, ρ_R) of the latter to the same value (i.e., ρ^{C^+}).[2] We have argued previously that for normal systems the excellent fit of the data by using σ^{C^+} constants renders the use of the DSP equation redundant[10] as agreed by the authors.[30] In the case of "deviant" systems such as **1**, **2**, and **4**–**6**, we have argued that the failure to use the DSP equation is not the reason for the deviations, since these deviations take the form of a sudden curve at one end of the correlation rather than an overall poor fit.[10] However, the highly stabilized cations **11** and **12**, show poor overall correlations (Figure 1), and thus the complete series of compounds **16**–**11** were subjected to DSP analysis.[31] For **16** → **11**, the ρ_I value decreased from 15.1 to −6.0 and the ρ_R value from 26.7 to −2.5 with a concomitant increase in the error (*f* value 0.18 → 0.69[29]). While the most appropriate, available σ_R scale was σ_{R^+} for **16**, σ_{R^0} was more appropriate for **11**. These results support the proposal of increased π polarization in the series **16** → **11** more negative ρ_I) as the molecules become more neutral, styrene like, at the benzylic center (decreasing ρ_R).[30,32]

Conclusion

The competition between the normal (strong) π-resonance effect and a (weaker) localized, inductive π-polarization (through space) effect provides an alternative[11] rationalization of the deviations in the $\Delta\delta C^+$–σ^{C^+} plots of **1**, **2**, and **10**–**16**. Within a closely related series of cations, **10**[1] or **11**–**16**, this rationalization is also quantitative in that the extent of the deviation is approximately proportional to the value of ρ^{C^+} (slope) of the linear portion of the correlation. This proposal may also provide a unifying, qualitative rationalization for the deviations observed in the plots of all the cations **1**, **2**, **4**–**7**, and **9**–**16**, which previously have been interpreted in terms of three different concepts, although the deviations are all much the same.

A consequence of our interpretation of the deviations is that carbocations in which a formal double bond exists between the cationic carbon and the substrate should show a linear "reverse" substituent chemical shift correlation as the inductive π-polarization mechanism dominates the shielding of the benzylic carbon atom. This is indeed observed for benzoyl cations[23,33] where the linear correlation ($r = 0.992$, $\rho^{C^+} = 3.5$) is of modest (positive) slope,

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[26] The substituent chemical shifts $\Delta\delta$ are reversed from the normal presentation $[\delta(Z) - \delta(H)]^2$ in order to reproduce the form of the Hammett–Brown equation with ρ negative.

[27] More highly electron-withdrawing substituents than 3,5-$(CF_3)_2$ ($\sigma^{C^+} = 1.03$) have been reported: 4–$SHCH_3^+$ $\sigma^{C^+} = 1.54$[9]; 4-$C(OH)CH_3^+$ $\sigma^{C^+} = 1.60$: Olah, G. A.; Berrier, A. L.; Surya Prakash, G. K. *J. Org. Chem.* **1982**, *47*, 3903–3909.

[28] See footnote in Figure 1 for correlation coefficients.

[29] Ehrenson, S.; Brownlee, R. T. C.; Taft, R. W. *Prog. Phys. Org. Chem.* **1973**, *10*, 1–80.

[30] Craik, D. J.; Brownlee, R. T. C.; Sadek, M. *J. Org. Chem.* **1982**, *47*, 657–661.

[31] Results of the DSP analysis[29] are as follows [ρ_I, ρ_R σ type, standard deviation (ppm), *f* (SD/rms[29])]: **16**, 15.1, 26.7, R^+, 2.2, 0.18; **15**, 12.2, 23.2, R^+, 2.4, 0.22; **1**, 7.1, 16.0, R^+, 2.3, 0.31; **14**, 4.2, 14.5, R^+, 2.3, 0.31; **13**, 1.9, 11.4, R^+, 2.3, 0.37; **12**, −5.3, 1.5, R^+/R^0, 1.3, 0.50; **11**, −6.0, −2.5, R^0, 1.4, 0.69. These results can only be used qualitatively as there are not enough data to give a "basis set" of substituents.[29] This is an inherent problem when working in superacid solutions.

[32] A referee has suggested that the major deviations observed in the case of the monosubstituted alkoxy compounds may be due to small quantities of dications which may profoundly effect the average chemical shift of C^+. This can be discounted from the facts that the shifts are not temperature sensitive and that even when there is *no* electron demand upon a *p*-methoxy residue (as in anisole), protonation occurs on carbon rather than oxygen at these low temperatures: Olah, G. A.; Mo, Y. K. *J. Org. Chem.* **1973**, *38*, 353–366.

[33] Olah, G. A.; Westerman, P. W. *J. Am. Chem. Soc.* **1973**, *95*, 3506–3535. Larsen, J. W.; Bouis, P. A. *Ibid.* **1975**, *97*, 4418–4419.

similar to those observed in neutral compounds.[17,34]

Experimental Section

NMR Spectra. ^{13}C NMR spectra were recorded at −70° to −10 °C on a JEOL FX-100 spectrometer with a 6000-Hz spectral width, 8192 data points, and a 45° pulse angle. In the case of solutions of cations, field stabilization was provided by acetone-d_6 held in a 3-mm (o.d.) capillary together with Me_4Si as a reference. Chemical shifts are ±0.1 ppm from external Me_4Si. Assignments were made on the basis of fully coupled and off-resonance decoupled spectra, $^{13}C-^{19}F$ coupling constants, and previously reported assignments for benzylic[2,10] and 1,1-diaryl-1-ethyl cations (see above). Equivocal assignments have been indicated in Table I (supplementary material).

Carbocations. The ions were prepared by the slow addition of the appropriate alcohol, either as a solution in SO_2ClF or as a solid to a solution of FSO_3H/SbF_5 (1 mol/1 mol)/SO_2ClF or FSO_3H/SO_2ClF (11, Z = 3,4-CH_2CH_2O, Z = 4-OCH_3, Z = 4-CH_3; Z = H; 12) at −78 °C with rapid vortex mixing. The resulting highly colored (orange to brown) solutions (∼0.5 M) were transferred under nitrogen to 10-mm NMR tubes.

Alcohols. The aryl(3,4-ethyleneoxyphenyl)methanols **17** were prepared by Grignard reactions by using the appropriate reactants, including 5-lithio-2,3-dihydrobenzo[*b*]furan[35] and 5-formyl-2,3-dihydrobenzo[*b*]furan.[36] Alcohols **18–22** were prepared in a similar fashion by using the appropriate benzaldehydes and bromobenzenes. In the case of the symmetrically substituted compounds **18** (4-OCH_3), **20** (4-F), **21** (4-CF_3), and **22** (3,5-$(CF_3)_2$), two mol of Grignard reagent were treated with ethyl formate. All of the above alcohols gave ^{13}C spectra and mass spectra in accordance with the assigned structures. All new compounds also gave satisfactory elemental (C, H ±0.3% F ±0.4%) or high-resolution mass spectral analysis.

5-Formyl-2,3-dihydrobenzo[*b*]furan. 2,3-Dihydrobenzo[*b*]furan (10.8 g) was formylated with dichloromethyl ether (8.63 g) and $TiCl_4$ (16.5 cm^3) according to the method of Rieche et al.[37] Distillation afforded 6.1 g (55%) of 5-formyl-2,3-dihydrobenzo[*b*]furan: bp 110–112 °C (1.5 mm) [lit.[35] bp 140–142 °C (8 mm)]; IR $\nu_{C=O}$ 1680 cm^{-1}; ^{13}C NMR δ ($CDCl_3$) 190.5, 165.6, 132.9, 130.4, 128.5, 125.9, 109.5, 72.4, 28.7.

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Registry No. **11** (Z = 3,4-CH_2CH_2O), 87901-52-8; **11** (Z = 4-OCH_3), 87901-53-9; **11** (Z = 4-CH_3), 87901-54-0; **11** (Z = 4-F), 87901-55-1; **11** (Z = 4-H), 81390-58-1; **11** (Z = 4-CF_3), 87901-64-2; **11** (Z = 3,5-$(CF_3)_2$), 87901-65-3; **12** (Z = 4-OCH_3), 13948-07-7; **12** (Z = 4-CH_3), 42289-58-7; **12** (Z = 4-F), 39769-54-5; **12** (Z = 4-CF_3), 87901-56-2; **12** (Z = 3,5-$(CH_3)_2$), 87901-57-3; **13** (Z = 4-CH_3), 58493-75-7; **13** (Z = 4-F), 39769-57-8; **13** (Z = 4-CF_3), 87901-58-4; **13** (Z = 3,5-$(CF_3)_2$), 87901-59-5; **14** (Z = 4-F), 39769-55-6; **15** (Z = 4-F), 39769-58-9; **15** (Z = 4-CF_3), 87901-60-8; **15** (Z = 3,5-$(CF_3)_2$), 87901-61-9; **16** (Z = 4-F), 87901-62-0; **16** (Z = 3,5-$(CF_3)_2$), 87901-63-1; **17** (Z = 3,4-CH_2CH_2O), 87901-66-4; **17** (Z = 4-OCH_3), 87901-67-5; **17** (Z = 4-CH_3), 87901-68-6; **17** (Z = 4-F), 87921-90-2; **17** (Z = 4-H), 81390-92-3; **17** (Z = 4-CF_3), 87901-69-7; **17** (Z = 3,5-$(CF_3)_2$), 87901-70-0; **18** (Z = 4-OCH_3), 728-87-0; **18** (Z = 4-CH_3), 838-22-2; **18** (Z = 4-F), 1426-55-7; **18** (Z = 4-CF_3), 87901-71-1; **18** (Z = 3,5-$(CH_3)_2$), 87901-72-2; **19** (Z = 4-CH_3), 885-77-8; **19** (Z = 4-F), 345-91-5; **19** (Z = 4-CF_3), 33757-36-7; **19** (Z = 3,5-$(CF_3)_2$), 87901-73-3; **20** (Z = 4-F), 365-24-2; **21** (Z = 4-F), 39768-86-0; **21** (Z = 4-CF_3), 22543-52-8; **21** (Z = 3,5-$(CF_3)_2$), 87901-74-4; **22** (Z = 4-F), 87901-75-5; **22** (Z = 3,5-$(CF_3)_2$), 87901-76-6; 5-lithio-2,3-dihydrobenzo[*b*]furan, 68151-00-8; 5-formyl-2,3-dihydrobenzo[*b*]furan, 55745-70-5; 2,3-dihydrobenzo[*b*]furan, 496-16-2; dichloromethyl ether, 542-88-1.

Supplementary Material Available: Tables of ^{13}C NMR data of carbocations **1** and **11–16** and of precursor alcohols **17–22** (4 pages). Ordering information is given on any current masthead page.

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A Spectrophotometric Study of 4-Nitro-, 2,4-Dinitro- and 2,4,6-Trinitrobenzyl Carbanions. Decarboxylation of (Nitrophenyl)acetate Anions[1]

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A spectrophotometric study of the reactions of the potassium salts of (2,4,6-trinitrophenyl)acetic acid (**3**), (2,4-dinitrophenyl)acetic acid (**4**), and (4-nitrophenyl)acetic acid (**5**) in Me_2SO, THF, and DME is reported, including the effect of catalysis by crown ether **1**. These processes are believed to give rise to the corresponding carbanions resulting from decarboxylation. The UV–visible spectrum of the species obtained from reaction of **3** agrees well with literature data for the expected carbanion **6**, but there is some discrepancy regarding the species derived from **4** and **5**. From the decay of the absorption spectra with time, the stabilities of the benzyl carbanions in these systems correspond to 2,4,6-trinitrobenzyl > 2,4-dinitrobenzyl > 4-nitrobenzyl.

Decarboxylation reactions are important in a variety of biological processes as well as in synthesis.[2,3] Mechanistic studies of decarboxylation have proceeded in parallel and various criteria have been used to shed light on transi-