the products and obtain their material balances which are listed in the last two columns of Table V, where they are expressed as percentages of the initial amounts. The very small differences indicate reasonable analytical precision and no loss of material in the course of the thermal disproportionation. The differences are nevertheless sufficiently large to preclude quantitative analysis for the much less extensive concentration changes specifically due to the O atom reactions in the experiments listed in Table IVC.

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^{13}C–^{1}H Coupling Constants in Carbocations. 3.[1] Variation of ΔJ with Electron Demand in Aryldialkyl Carbocations

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Contribution from the Department of Organic Chemistry, University of Melbourne, Parkville, Victoria 3052, Australia. *Received August 4, 1980*

Abstract: One-bond ^{13}C–H coupling constants for groups adjacent to the cationic center have been measured for 3-arylnortricyclyl (**1**), 1-aryl-1-cyclopropylethyl (**2**), 2-arylnorbornyl (**3**), 1-aryl-1-methylethyl (**4**), and 1-arylcyclopentyl (**5**) carbocations. The differences ΔJ between $^1J_{CH}$ in the cations and those in neutral, model ketones are linearly dependent upon electron demand at the cationic carbon as measured by σ^+ constants. Combination of this relationship and the original ΔJ equation gives a new equation for aryldialkyl carbocations which relates ΔJ to both the dihedral angle between the C–H orbital and the vacant p orbital and the electron demand at the cationic carbon, $\Delta J = (1 + 0.6\sigma^+)(10.9 - 14.3\cos^2\theta)$.

We have previously examined the applicability of one-bond ^{13}C–^{1}H coupling constants ($^1J_{CH}$) as a criterion for structure determination in a range of alkyl carbocations.[1] In static, classical, tertiary, alkyl cations we have shown that J_{CH} of groups adjacent to the cationic carbons differ from those in appropriate, neutral model compounds (ketones) by an amount depending upon the dihedral angle θ between the C–H bond and the unoccupied p orbital.[1] This dependency is given by

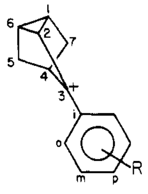
$$\Delta J = A - B\cos^2\theta \qquad (1)$$

where ΔJ is the J_{CH} value in the cation less that in a model ketone, A is the maximum inductive enhancement of J_{CH} (22.5 Hz), and B is the maximum hyperconjugative diminution of J_{CH} (33.1 Hz). Thus a maximum enhancement of J_{CH} occurs for ions where $\theta = 90°$ (+22.5 Hz) and an actual diminution of J_{CH} where $\theta = 0°$ (≤ -10Hz). For ions where $\theta = 30°$, for example, C_2–H of 1-methylcyclopentyl and C_3–H of 2-methylnorbornyl cations, no difference is observed from the values of cyclopentanone and 2-norbornanone, respectively.[1] Recent INDO-FPT calculations of Pachler and Pachter confirm the validity of the general form of our equation, although the calculated values of the constants are somewhat less than our experimental ones.[2]

Equation 1 was derived from data for static, tertiary methyl carbocations in which a "full" positive charge was considered to reside on the cationic carbon and the A term was therefore considered to be a measure of the inductive effect of a "full" charge. The obvious extension of our systematic investigation was thus to measure J_{CH} as a function of charge density at the adjacent cationic carbon. We now report the results of this investigation for cations **1–5** where the aryl group provides a controlled variation in the electron demand at the cationic center which can be quantified by the appropriate Hammett substituent constant.

Results and Discussion

The use of aryl substituents to vary the charge density at an attached cationic carbon in a controlled fashion is well documented both for solvolytic studies[3] and for NMR studies in superacids.[4-6]



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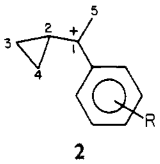

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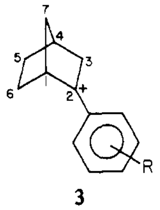

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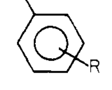

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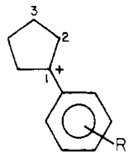

5

The choice of substituent constant to quantify this variation in charge density is critical, as has recently been demonstrated for ^{13}C shift correlations of cations in superacids.[7] For the groups adjacent to the cationic center in ions **1–5**, we have used both Brown's σ^{+8} and a substituent constant $\sigma^{\alpha C^+}$, derived from the methyl carbon shifts of a range of meta- and para-substituted 1-methyl-1-phenylethyl cations (**4**) generated in $HSO_3F/SbF_5/SO_2ClF$.[9]

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(1) Part II: Kelly, D. P.; Underwood, G. R.; Barron, P. F. *J. Am. Chem. Soc.* **1976**, *98*, 3106–3111.

(2) Pachler, K. G. R., Pachter, R. *Org. Magn. Reson.* **1979**, *12*, 183–184. $\Delta J = a_0 + a_2\cos^2\theta + a_4\cos^4\theta$, $a = 5.51$ Hz, $a_2 = 18.4$ Hz, $a_4 = 7.08$ Hz; the hyperconjugative constant is thus −11.32 Hz.

(3) For example, H. C. Brown's "Tool of Increasing Electron Demand": Brown, H. C. "The Nonclassical Ion Problem"; Plenum Press: New York, 1977; Chapter 10. This technique has been applied to the systems under consideration here. 3-Nortricyclyl (**1**): Brown, H. C.; Peters, E. N. *J. Am. Chem. Soc.* **1975**, *97*, 1927–1929. 1-Cyclopropylethyl (**2**): Brown, H. C.; Peters, E. N.; Ravindranathan, M. *Ibid.* **1977**, *99*, 505–509. 2-Norbornyl (**3**): Brown, H. C.; Ravindranathan, M.; Takeuchi, K.; Peters, E. N. *Ibid.* **1977**, *99*, 2684–2690. 1-Cyclopentyl (**5**): Brown, H. C.; Peters, E. N. *Ibid.* **1975**, *97*, 7454–7457.

(4) (a) Farnum, D. G.; Wolf, H. D. *J. Am. Chem. Soc.* **1974**, *96*, 5166–5175. (b) Farnum, D. G.; Botto, R. E.; Chambers, W. I.; Lam, B. *J. Am. Chem. Soc.* **1978**, *100*, 3847–3855.

(5) Olah, G. A.; Prakash, G. K. S.; Liang, G. *J. Am. Chem. Soc.* **1977**, *99*, 5683–5687.

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

(7) Kelly, D. P.; Spear, R. J. *Aust. J. Chem.* **1978**, *31*, 1209–1221.

(8) The values of σ_p^+ are MeO −0.78, Me −0.31, F −0.07, Cl 0.11, and CF_3 0.61; σ_m^+ CF_3 0.52: Stock, L. M.; Brown, H. C. *Adv. Phys. Org. Chem.* **1963**, *1*, 35.

(9) The values of $\sigma_p^{\alpha C^+}$ are MeO −1.29, Me −0.49, F −0.24, Cl −0.07, Br −0.1, and CF_3 0.70; $\sigma_m^{\alpha C^+}$ CF_3 0.51, derived from the least-squares analysis of meta and para cations **4** ($\Delta\delta(CH_3) = 4.12\sigma^{\alpha C^+}$ r 0.990, SD 0.22). Brown, H. C.; Kelly, D. P.; Periasamy, M. *J. Org. Chem.*, in press.

0002-7863/81/1503-3539$01.25/0

Table I. ^{13}NMR Parameters for Ayldialkyl Carbocations and Model Compounds[a]

	C_1	C_2	C_3	C_4	C_5	C_6	C_7	R	C_{aryl}[f]
1, R = *p*-OCH$_3$	43.1 (d, 186)	33.6 (d, 191)	234.6 (s)	38.8 (d, 157)	38.4 (t, 139)	43.1 (d, 186)	38.4 (t, 139)	58.9 (q, 150)	128.1 (s, C_i), 118.3, 120.3 (d, C_m), 144.5 (d, C_o), 179.8 (d, C_p)
R = *p*-CH$_3$	54.4 (d, 185)	41.9 (d, 194)	250.8 (s)	39.9 (d, 158)	39.9 (t, 140)	54.4 (d, 185)	39.9 (t, 140)	24.1 (q, 129)	132.1 (s, C_i), 133.0, 133.7 (d, C_m), 140.1 (d, C_o), 167.3 (d, C_p)
R = *p*-H	61.1 (d, 189)	46.9 (d, 196)	257.1 (s)	40.8 (d, 156)	40.8 (t, 140)	61.1 (d, 189)	40.8 (t, 140)		134.1 (s, C_i), 132.1, 132.6 (d, C_m), 139.5 (d, C_o), 148.9 (d, C_p)
R = *p*-F	58.9 (d, 189)	45.1 (d, 195)	252.9 (s)	40.5 (d, 158)	40.5 (t, 137)	58.9 (d, 189)	40.5 (t, 137)		131.2 (s, C_i), 144.1 (d, 16,[b] C_o), 120.6 (d, 22,[b] C_m), 176.4 (d, 288,[b] C_p)
R = *p*-CF$_3$	73.6 (d, 187)	56.1 (d, 200)	260.2 (s)	41.6 (d, 160)	42.3 (t, 141)	73.6 (d, 187)	42.3 (t, 141)	125.6 (q, 270)[b]	135.8 (s, C_i), 128.4, 129.6 (d, C_m), 138.3 (d, C_o), 144.4 (q, 35,[b] C_p)
R = 3,5-(CF$_3$)$_2$	80.4 (d, 186)	61.1 (d, 202)	258.5 (s)	41.9 (d, 158)	43.0 (t, 138)	80.4 (d, 186)	43.0 (t, 138)	123.0 (q, 270)[b]	135.9 (s, C_i), (C_o, C_p),[c] 136.4 (q, C_m)
2, R = *p*-OCH$_3$	227.8 (s)	33.9 (d, 174)	30.9 (t, 172)	30.9 (t, 172)	20.1 (q, 131)			58.7 (q, 148)	134.3 (s, C_i), 141.4 (d, C_o), 118.4 (d, C_m), 177.4 (s, C_p)
R = *p*-CH$_3$	242.4 (s)	41.0 (d, 177)	39.5 (t, 173)	39.5 (t, 173)	21.7 (q, 131)			23.4 (q, 131)	138.1 (s, C_i), 135.9 (d, C_o), 132.6 (d, C_m), 162.7 (s, C_p)
R = *p*-H	247.6 (s)	45.2 (d, 179)	44.1 (t, 174)	44.1 (t, 174)	22.7 (q, 131)				140.0 (s, C_i), 135.0 (d, C_o), 131.4 (d, C_m), 145.9 (s, C_p)
R = *p*-Cl	245.1 (s)	45.4 (d, 179)	44.5 (t, 174)	44.5 (t, 174)	22.8 (q, 132)				138.2 (s, C_i), 136.0 (d, C_o), 130.9 (d, C_m), 153.7 (s, C_p)
R = *p*-CF$_3$	251.1 (s)	52.3 (d, 183)	52.3 (t, 175)	52.3 (t, 175)	24.0 (q, 132)			123.7 (q, 273)[b]	142.4 (s, C_i), 134.2 (d, C_o), 128.0 (m, C_m), 142.4 (q, 34,[b] C_p)
R = 3,5-(CF$_3$)$_2$	249.4 (s)	55.6 (d, 185)	56.7 (t, 176)	56.7 (t, 176)	24.3 (q, 132)			123.2 (q, 272)[b]	140.7 (s, C_i), 132.7 (d, C_o), 134.4 (q, 35,[b] C_m), 135.1 (m, C_p)
3,[d] R = *p*-OCH$_3$	52.9 (d, 153)	233.5 (s)	46.5 (t, 133)	38.2 (d, 151)	26.5 (t, 135)	31.3 (t, 141)	41.1 (t, 141)	59.3 (q, 150)	128.7 (s, C_i), 145.7, 146.0 (d, C_o), 119.1, 119.8 (d, C_m), 181.5 (s, C_p)
R = *p*-CH$_3$	57.2 (d, 156)	253.0 (s)	49.4 (t, 133)	39.2 (d, 153)	26.0 (t, 139)	33.3 (t, 141)	41.5 (t, 140)	24.6 (q, 130)	132.3 (s, C_i), 141.6, 142.1 (d, C_o), 133.7, 133.9 (d, C_m), 171.0 (s, C_p)
R = *p*-H	59.6 (d, 158)	260.7 (s)	50.8 (t, 133)	39.9 (d, 153)	25.7 (t, 137)	34.5 (t, 142)	41.7 (t, 137)		133.8 (s, C_i), 141.0, 141.8 (d, C_o), 132.7 (d, C_m), 152.5 (d, C_p)
R = *p*-Cl	59.6 (d, 158)	257.7 (s)	50.8 (t, 133)	40.1 (d, 152)	25.8 (t, 136)	34.5 (t, 142)	41.9 (t, 140)		132.3 (s, C_i), 141.9, 142.5 (d, C_o), 133.3 (d, C_m), 161.8 (s, C_p)
R = *p*-CF$_3$	64.3 (d, 162)	265.0 (s)	52.6 (t, 133)	41.4 (d, 152)	25.3 (t, 138)	37.5 (t, 146)	42.0 (t, 140)	123.3 (q, 274)[b]	134.7 (s, C_i), 140.7 (d, C_o), 128.8 (d, C_m), 147.5 (q, 34,[b] C_p)
R = 3,5-(CF$_3$)$_2$	67.4 (d, 164)	263.1 (s)	53.1 (t, 133)	42.2 (d, 154)	25.1 (t, 136)	38.8 (t, 147)[e]	42.2 (t, 138)	122.7 (q, 272)[b]	132.7 (s, C_i), 138.6 (d, C_o), 135.3 (q, 35,[b] C_m), 140.2 (d, C_p)
4, R = *p*-OCH$_3$	218.7 (s)	29.6 (q, 130)	29.6 (q, 130)					61.4 (q, 152)	134.9 (s, C_i), 145.9 (d, C_o), 119.7 (d, C_m), 180.5 (s, C_p)
R = *p*-CH$_3$	243.6 (s)	31.9 (q, 131)	31.9 (q, 131)					25.1 (q, 130)	138.7 (s, C_i), 142.4 (d, C_o), 134.7 (d, C_m), 175.2 (s, C_p)
R = *p*-F	248.4 (s)	32.9 (q, 131)	32.9 (q, 131)						137.6 (s, C_i), 147.5 (d, C_o), 121.8 (d, C_m), 181.0 (d, 296,[b] C_p)
R = *p*-H	255.7 (s)	33.9 (q, 131)	33.9 (q, 131)						140.7 (s, C_i), 142.4 (d, C_o), 133.2 (d, C_m), 156.4 (d, C_p)
R = *p*-CF$_3$	270.0 (s)	36.8 (q, 131)	36.8 (q, 131)					122.4 (q, 276)[b]	142.7 (s, C_i), 142.7 (d, C_o), 129.6 (d, C_m), 150.8 (q, 35,[b] C_p)
R = 3,5-(CF$_3$)$_2$	274.4 (s)	38.3 (q, 132)	38.3 (q, 132)					122.5 (q, 274)[b]	140.6 (s, C_i), 139.9 (d, C_o), 135.9 (q, 37,[b] C_m), 145.5 (d, C_p)

5, R = p-OCH_3	234.8 (s)	41.3 (t, 130)	26.1 (t, 134)	26.1 (t, 134)	41.3 (t, 130)		59.6 (q, 150)	131.1 (s, C_i), 146.4 (d, C_o), 119.4 (d, C_m), 182.1 (s, C_p)
R = p-CH_3	258.8 (s)	45.3 (t, 130)	26.4 (t, 136)	26.4 (t, 136)	45.3 (t, 130)		25.0 (q, 130)	135.4 (s, C_i), 142.6 (d, C_o), 134.0 (d, C_m), 173.2 (s, C_p)
R = p-H	270.1 (s)	47.8 (t, 131)	26.4 (t, 136)	26.4 (t, 136)	47.8 (t, 131)			131.5 (s, C_i), 142.4 (d, C_o), 128.7 (d, C_m), 154.5 (d, C_p)
R = p-Cl	266.5 (s)	47.4 (t, 130)	26.8 (t, 137)	26.8 (t, 137)	47.4 (t, 130)			135.2 (s, C_i), 142.0 (d, C_o), 133.6 (d, C_m), 163.8 (s, C_p)
R = p-CF_3	282.5 (s)	51.2 (t, 131)	26.7 (t, 138)	26.7 (t, 138)	51.2 (t, 131)		c	(C_i),[c] 142.3 (d, C_o), 129.0 (d, m, C_m), (C_p)[c]
R = 3,5-$(CF_3)_2$	286.2 (s)	52.8 (t, 130)	27.0 (t, 140)[e]	27.0 (t, 140)[e]	52.8 (t, 130)		c	c
6	199.3 (s)	16.2 (d, 167)	10.8 (t, 167)					137.1 (s, C_i), 132.0 (d, C_o), 127.8 (d, C_m), 127.2 (d, C_p)
7	196.2 (s)	25.9 (q, 128)					55.1 (q, 146)	130.2 (s, C_i), 130.2 (d, C_o), 113.3 (d, C_m), 163.1 (s, C_p)
8	197.0 (s)	26.7 (q, 128)					123.9 (q, 262)	139.9 (s, C_i), 128.8 (d, C_o), 125.8 (q, 3,[b] C_m), 134.6 (q, 33,[b] C_p)
9	49.8 (d, 148)	215.3 (s)	45.2 (t, 133)	35.4 (d, 144)	27.3 (t, 132)	24.2 (t, 134)	36.7 (t, 135)	

[a] Chemical shifts are ±0.1 ppm from internal Me_4Si (6-9) or external Me_4Si (1-5). Coupling constants are ±1 Hz unless otherwise specified, s = singlet, d = doublet, t = triplet, q = quartet. For concentrations and temperatures of measurement, see Experimental Section. [b] J_{CF}. [c] Peaks too weak to measure. [d] Chemical shifts have been reported previously by Olah et al.[5] and Farnum et al.[4b] [e] ±3 Hz. [f] C_i is C_{ipso}.

Consideration of eq 1 applied to the aryl cations **1**-**5** provides us with the following expectations. First, substitution at the cationic carbon by aryl groups (rather than methyl[1]) should result in lower values of A and B due to delocalization of charge. Second, for a series of ions with the same stereochemistry, the greatest variation of ΔJ with electron demand should occur for those with $\theta = 90°$. From the data collected in Table I, we obtain values of ΔJ for ions where the dihedral angles are expected to be 90° (**1**, C_2-H; **2**, C_2-H), 80° (**3**, C_1-H), 45° (**2**, **4**, C-H_3), and 30° (**3**, C_3-H; **5**, C_2-H).

$\theta \simeq 90°$. 3-Arylnortricyclyl (1), 1-Aryl-1-cyclopropylethyl (2), and 2-Arylnorbornyl (3). The C_2 doublets of **1** in some cases were obscured by other multiplets in the normal coupled spectrum, but selective excitation of C_2 allowed accurate measurement of J_{C_2H} (see Experimental Section). In these rigid ions the dihedral angle of C_2-H is unambiguous ($\theta = 90°$) and gives rise to large values of ΔJ (based on the J_{CH} value of nortricyclnanone, 186 Hz[1]) which vary from 5 Hz for p-OCH_3 to 16 Hz for 3,5-$(CF_3)_2$. Satisfactory linear correlations are obtained with both σ^+ and $\sigma^{\alpha C^+}$ (r 0.997, 0.994, respectively.). Since $\sigma^{\alpha C^+}$ has been shown to yield more accurate correlations than σ^+ with α-carbon chemical shifts[9] it is surprising that such little difference is observed in the correlations with J_{CH}. This may be due to the fact that we cannot measure $J_{C_\alpha H}$ with the same relative accuracy as we can measure chemical shifts in these cations.

In the flexible 1-cyclopropylethyl cations (**2**) there is the possibility of distortion of θ from the most favorable bisected arrangement. ΔJ values for the apical methine carbon (C_2-H) based on the value for cyclopropyl phenyl ketone (**6**, 167 Hz) increase from 7 Hz for p-OCH_3 to 18 Hz for 3,5-$(CF_3)_2$ with an excellent linear correlation (σ^+ r 0.997) and an identical gradient to that for **1**.[10] The latter indicates that there has been *no* deviation in the dihedral angle from that in **1**. This is confirmed by consideration of the change in chemical shifts of cyclopropyl carbons in **1** and **2**.

In **1** the cyclopropyl group is locked into the favored bisected arrangement with the cationic center. σ-Π delocalization of positive charge into the cyclopropyl ring is most favored in this orientation,[11] as evidenced by the substantial change in δC_2 and $\delta C_{1,6}$ from R = p-OCH_3 to R = 3,5-$(CF_3)_2$; C_2 33.6 → 61.1 (27.5 ppm) and $C_{1,6}$ 43.1 → 80.4 (37.3 ppm) (Table I). For the nonrigid cyclopropyl cations **2** the values are 21.7 ppm (C_2) and 25.8 ppm ($C_{3,4}$), somewhat less than for **1** but still much greater than for C_α and C_β carbons in other cations, for example, **3**, C_1 11.8 and C_6 7.5 ppm.[12] In addition the para carbon shift (R = p-H), which is the most reliable criterion for charge density at the cationic carbon,[7] is slightly *less* for **2** (145.9) than for **1** (148.9). Significant deviation of the dihedral angle from 90° would result in higher charge at C_1 and a greater para shift.

We are now left with one anomaly. The ΔJ values for **2** are consistently 2 Hz greater than those for **1** and **3** (Figure 1A). Initially this suggests a higher positive charge at the cationic carbon, brought about either by rotation of the aryl substituent

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(10) The ΔJ values would be significantly higher (4 Hz) if cyclopropyl methyl ketone (163 Hz) had been used as the neutral model compound.

(11) Brown, H. C. "The Nonclassical Ion Problem"; Plenum Press: New York, 1977; Chapter 5.

(12) The greater chemical shift range ($\Delta\delta$C ppm) of C_β over C_α observed for **1** and **2** requires some comment. In some aryl cations such as 1-aryl-1-cyclopentyl,[a] 1-aryl-1-cycloheptyl,[b] and 3-aryl-3-pentyl[c] δC_β varies very little and is close to zero ($\Delta\delta C_\alpha \simeq$ 8-12, $\Delta\delta C_\beta \simeq$ 0.1-3), in others such as 2-aryl-2-adamantyl[c] and **3**, $\Delta\delta C_\beta$ is significant (7-9) but still less than $\Delta\delta C_\alpha$ (12-14), while in **1** and **2** it is large and greater than $\Delta\delta C_\alpha$. This is probably due in part to the ability of C_β to delocalize the charge and may be dependent upon C_α-C_β hyperconjugation. Changes in the hybridization of C_β are not indicated in **1** as $J_{C_{1,6}H}$ is constant. In **2**, $J_{C_{3,4}H}$ varies a small amount (4 Hz) which may indicate some change in hybridization or structure. However, excellent linear correlations of $\Delta\delta C_\beta$ or $\Delta\delta C_\alpha$ with $\sigma^{\alpha C^+}$ constants for both **1** and **2**[d] do not support such changes. The factors influencing both J and δ are complex and cannot be elaborated further at this stage. (a) Brown, H. C.; Kelly, D. P.; Periasamy, M. *Proc. Natl. Acad. Sci. U.S.A.* **1980**, *77*, 6956-6960. (b) Brown, H. C.; Periasamy, M. *J. Org. Chem.*, in press. (c) Kelly, D. P.; Jenkins, M. J.; Mantello, R. A. *J. Org. Chem.*, in press. (d) Brown, H. C.; Giansiracusa, J. J.; Kelly, D. P.; Periasamy, M., unpublished results.

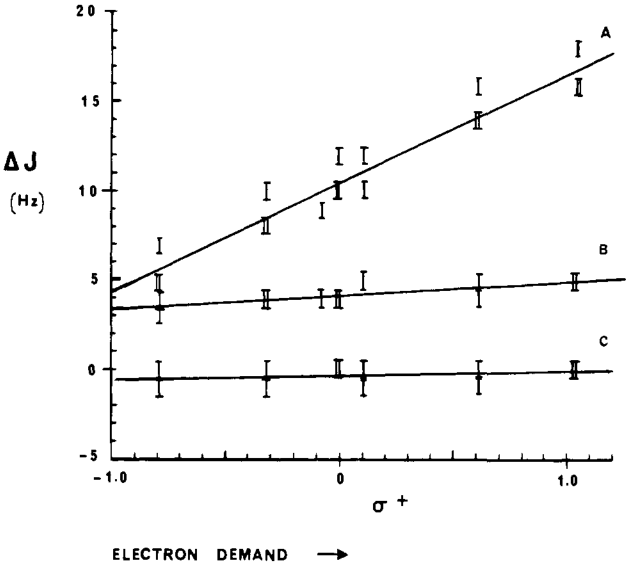

Figure 1. Correlations of $\Delta J_{C_\alpha H}$ with electron demand in 1-aryldialkyl carbocations where the dihedral angles are A, 90°; B, 45°; and C, 30°. Error bars are 1 Hz.

out of orthogonality with the vacant p orbital (which would have to be the same in all the aryl substituents since the plot is linear and of the same gradient as for **1**) or by decreased ability of the alicyclic moiety in **2** to stabilize the charge.[13] From the above discussion of chemical shifts this does not appear to be the case and we can only conclude that there are factors other than dihedral angle and charge density affecting ΔJ still to be delineated.

In the case of 2-arylnorbornyl cations **3**, the C_1–H bond makes an angle of approximately 80° with the adjacent p orbital,[1] from which we may expect a reduction in the ΔJ values and/or the slope of the correlation line. However, the values are almost coincidental with those for **1** (σ^+ r 0.997) which is in fact reasonable, since a change of 10° results in an insignificant change in ΔJ (<0.5 Hz) as determined by eq 2 derived from data for the 1-phenyl cations **1**–**5**, R = p-H (see below). Application of the para carbon shift criterion to **3** (152.5, R = p-H) indicates that there may be greater positive charge at C_2 than at the cationic carbons in **1** and **2**, the effect of which would be to offset any decrease in ΔJ due to changes in θ.

For clarity of presentation the ΔJ values for **1**, **2**, and **3** are plotted together against σ^+ in Figure 1A, the overall linear correlation with σ^+ being inferior to that of each individual series **1**, **2**, and **3** (σ^+, $\sigma^{\alpha C^+}$ r 0.966, 0.962).

θ = 45°. 1-Aryl-1-cyclopropylethyl (2) and 2-Aryl-2-propyl (4). In freely rotating methyl groups, the dihedral angle between the C–H orbital and the adjacent p orbital is effectively 45°, that is $\langle\cos^2\theta\rangle = 0.5$.[14] Thus the ΔJ values of the methyl groups of **2** and **4** are expected to be lower than those of groups where θ = 90°. This is observed, as seen in Figure 1B. The small positive slope (0.78) shows the much reduced dependence of ΔJ on electron demand as θ decreases and as a consequence the correlation coefficient of the line decreases.

In order to show that the variation in ΔJ is a result of variation in $J_{C_\alpha H}$ of the cation and not the model compound, we have measured $J_{C_\alpha H}$ of the methyl groups of p-methoxy (**7**) and p-(trifluoromethyl)acetophenones (**8**) where the methyl quartets are sharp (absence of long-range coupling) and the couplings can be measured to <±1 Hz. The values are identical (128 Hz, Table I).

θ = 30°. 2-Aryl-2-norbornyl (3) and 1-Arylcyclopentyl (5). From eq 1, when θ = 30° the hyperconjugative diminution of ΔJ ($-B\cos^2\theta$) exactly cancels the inductive enhancement (A) by the positive charge so that *no change occurs* for J_{CH} of the group between that of the neutral ketone and that of the carbocation. Thus for C_3–H of **3** and C_2H of **5**, ΔJ is expected to be constant (zero), independent of electron demand of the cationic center. This is indeed the case as is shown in Figure 1C. The ΔJ values for **3** were based on J_{C_3H} for 2-norbornanone (**9**) measured at 67 MHz (previously measured at 18 MHz[1]) to reduce the experimental error. The C_3 multiplets of **3** could all be measured at 25 MHz without recourse to selective excitation techniques, as at least two adjacent lines of the triplet were always visible. This is not the case for C_6 and C_7 where substantial overlap of the multiplets occurs. Selective excitation of each multiplet in turn provided the data in Table I.

General Conclusions

Within the experimental error, ΔJ is linearly dependent upon electron demand at the adjacent cationic carbon for all the aryl cations **1**–**5**. From the data for the parent phenyl cations (**1**–**5**, R = p-H) we obtain an equation

$$\Delta J = 10.9 - 14.3\cos^2\theta \qquad (2)$$

where the magnitudes of the constants reflect the decrease in charge density at the cationic center from that in the corresponding methyl cations. For each series of ions **1**–**5** with the same substituent, similar equations are obtained but with different values of the constants. From the ratios of each constant $A_{R\neq H}/A_{R=H}$ and $B_{R\neq H}/B_{R=H}$ we derive an empirical relationship relating ΔJ to both dihedral angle and the electron demand at the cationic center

$$\Delta J = (1 + 0.6\sigma^+)(10.9 - 14.3\cos^2\theta) \qquad (3)$$

where the electron demand (charge density) is measured by σ^+.

The excellent linear correlations of ΔJ with electron demand as given by both the solvolytic constant σ^+ and the superacidic constant $\sigma^{\alpha C^+}$ indicate that ΔJ is a reliable probe for charge density at adjacent cationic carbon. Use of this equation constitutes the first quantitative experimental method for determining stereochemistry of carbocations in superacids.

Experimental Section

NMR Spectra. ^{13}C spectra of the model compounds in $CDCl_3$ were recorded at probe temperature on either a Bruker HX-270 (**9**) or a JEOL FX-100 instrument (**6**–**8**). Spectra of the ions were recorded at various temperatures between −25 and −70 °C (see below) on either or both a hybrid Varian HA-60/Digilab/PDP-15 spectrometer operating at 15.08 MHz in the FT mode or a JEOL FX-100 spectrometer operating at 25.00 MHz. Field stabilization was provided by a concentric capillary (3 mm o.d.) of acetone-d_6 containing Me_4Si. Chemical shifts are ± 0.1 ppm from external Me_4Si. The proton-coupled spectra were obtained by the normal gated decoupling technique with a minimum 50% duty cycle, using spectral widths of 3128 Hz and 8K data points (HA-60) or 5000 Hz and 16K data points (FX-100). Coupling constants were measured by hand from multiplets plotted over 500 Hz chart width and are accurate to ±1 Hz. In some cases, e.g., **1** and **3** R = p-H, p-F, 3,5-$(CF_3)_2$, selective excitation of a single ^{13}C multiplet was employed to obtain accurate values of J_{CH}. This excitation was achieved by using a DANTE sequence of 50 pulses of 2 μs duration with a repetition period calculated for the first sideband.[15] The decoupler was gated off during acquisition only.

Assignments of the carbon resonances were straightforward, based on (a) previous assignments for 1-methyldialkyl[1], 3-nortricyclyl, 2-norbornyl[4b] 1-cyclopropyl,[16] and 1-methylethyl[7] carbocations, (b) C–H and C–F coupling constants, and (c) known substituent effects in disubstituted phenyl cations.[17]

Least-squares analyses were performed on ΔJ for each series of cations with both σ^+ and $\sigma^{\alpha C^+}$. For $\Delta J = a\sigma + b$ (σ type, a, standard deviation (SD), b, SD, correlation coefficient (r)): **1**, σ^+, 6.17, 0.22, 9.83, 0.13, 0.997; **1**, $\sigma^{\alpha C^+}$, 4.37, 0.26, 10.53, 0.20, 0.994; **2**, σ^+, 6.14, 0.25. 11.81, 0.15,

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0.997; **2** $\sigma^{\alpha C+}$, 4.71, 0.25, 12.56, 0.19, 0.994; **3**, σ^+, 6.14, 0.25, 9.81, 0.15, 0.997; **3**, $\sigma^{\alpha C+}$, 4.71, 0.25, 10.56, 0.19, 0.994. For the combined series of ions: **1–3**, σ^+, 6.17, 0.41, 10.48, 0.25, 0.966; **1–3**, $\sigma^{\alpha C+}$, 4.73, 0.33, 11.22, 0.26, 0.962; **2, 4** (45°), σ^+, 0.78, 0.20, 4.17, 0.12, 0.777; **2, 4**, $\sigma^{\alpha C+}$, 0.58, 0.16, 4.27, 0.12, 0.752; **3, 5** (30°), σ^+, 0.19, 0.24, −0.36, 0.15, 0.244; **3, 5**, $\sigma^{\alpha C+}$, 0.15, 0.19, −0.33, 0.14, 0.252.

Ion Precursors. The tertiary alcohol precursors for **1–3** and **5** were all prepared by standard Grignard procedures from the corresponding alkanones or were available from a previous study.[7] Physical constants of these materials are available in the literature (H. C. Brown et al.[3]) and we have measured their ^{13}C spectra.

Preparation of Ions. The ions were prepared in known concentration from the tertiary alcohols either by direct addition to the precooled (−78 °C) acid solution or by addition of a solution (−10 to −70 °C) of the alcohol to the precooled acid solution. Ion, concentration, superacid, temperature of ^{13}C measurement: **1** (R = *p*-OCH_3) 0.46 M, HSO_3F, −25 °C, (R = *p*-CH_3) 0.78, HSO_3F, −70 °C, (R = *p*-H) 0.34, HSO_3F/SbF_5, −65 °C, (R = *p*-F) 0.35, HSO_3F/SbF_5, −65 °C, (R = *p*-CF_3) 0.60, HSO_3F/SbF_5, −40 °C, (R = 3,5-$(CF_3)_2$) 0.33, HSO_3F/SbF_5, −65 °C; **2** (R = *p*-OCH_3) 0.77, HSO_3F, −60 °C, (R = *p*-CH_3) 0.89, HSO_3F, −60 °C, (R = *p*-H) 0.85, HSO_3F, −60 °C, (R = *p*-Cl) 0.75, HSO_3F, −60 °C, (R : *p*-CF_3) 0.54, HSO_3F/SbF_5, −70 °C, (R = 3,5-$(CF_3)_2$) 0.45, HSO_3F/SbF_5, −70 °C; **3** (R = *p*-OCH_3) 0.46, HSO_3F, −25 °C, (R = *p*-CH_3) 0.56, HSO_3F, −25 °C, (R = *p*-H) 0.64, HSO_3F, −25 °C, (R = *p*-Cl) 0.54, HSO_3F, −25 °C, (R = *p*-CF_3) 0.47, HSO_3F, −30 °C, (R = 3,5-$(CF_3)_2$) 0.38, HSO_3F, −30 °C; **4** (all HSO_3F/SbF_5, −40 °C)[7] (R = *p*-OCH_3) 0.44, (R = *p*-CH_3) 0.48, (R = *p*-H) 0.51, (R = *p*-F) 0.51, (R = *p*-CF_3) 0.38, (R = 3,5-$(CF_3)_2$ 0.33; **5** (R = *p*-OCH_3) 0.77, HSO_3F, −60 °C, (R = *p*-CH_3) 0.84, HSO_3F, −60 °C, (R = *p*-H) 0.91, HSO_3F, −60 °C, (R = *p*-Cl) 0.75, HSO_3F, −60 °C, (R = *p*-CF_3) 0.53, HSO_3F/SbF_5, −60 °C, (R = 3,5-$(CF_3)_2$) 0.35, HSO_3F/SbF_5, −60 °C.

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Transport of Photoproduced Ions in Water in Oil Microemulsions: Movement of Ions from One Water Pool to Another[1]

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Abstract: Pulsed laser photolysis techniques were used to study the following reactions in reversed micelles of AOT/alkane/water:

$$\mathrm{Ru^{II}(bpy)_3{}^* + Fe(CN)_6{}^{3-} \rightarrow Ru^{III}(bpy)_3 + Fe(CN)_6{}^{4-}}$$

$$\mathrm{Ru^{II}(bpy)_3{}^* + MV^{2+} \rightarrow Ru^{III}(bpy)_3 + MV^{+}}$$

$$\mathrm{PTS^{T} + FS \rightarrow PTS}$$

$$\mathrm{PTS^{T} + Cu^{2+} \rightarrow PTS}$$

where $\mathrm{Ru^{II}(bpy)_3}$ and $\mathrm{MV^{2+}}$ represent ruthenium tris(bipyridyl) and methyl viologen, respectively, while $\mathrm{PTS^T}$ and FS represent the triplet excited state of pyrenetetrasulfonic acid and Fremy's salt, respectively. These ionic reactants are associated only with the water pools of the reversed micelle systems, a situation which introduces unusual features into the kinetics. Analysis of the kinetics shows that the reactants distribute themselves among the micelles according to a Poisson rather than a geometric distribution. Analysis of the decay kinetics under various conditions enables the measurement of the exchange rate of ions among micelles to be measured. This ion exchange occurs only on collision of water pools, and the effectiveness of exchange is 1% or less in a simple AOT system for both $\mathrm{Cu^{2+}}$ and the anionic Fremy's salt. Various additives such as benzyl alcohol markedly increase the efficiency of ion exchange, while solutes such as benzene decrease it. These data are discussed in terms of the interactions of the additives with the micellar head groups.

The last few years have seen considerable activity in the area of micellar catalysis. In particular, catalysis in reversed micelles or microemulsions has received detailed attention[2,3] as these systems strongly catalyze many reactions. Much is known about the structure of specific systems,[4-6] and a reasonable description of reaction sites can be put forward with some confidence. Basically, these systems consist of pools of water (radii 15–150 Å) stabilized in a bulk hydrocarbon by a suitable surfactant, e.g., disodium diisooctylsulfosuccinate (AOT), or a surfactant-cosurfactant pair, e.g., potassium oleate/hexanol or cetyltrimethylammonium bromide (CTAB)/hexanol. The surfactants are located at the water–hydrocarbon boundary. The nature of the water has received some attention,[7] and it is found that many physical measurements indicate that the properties reminiscent of bulk water are only approached in larger water bubbles.

Micellar systems are of general interest as suitable vehicles for promotion of photochemical studies.[8] The correct selection of a system can lead to large yields of photoproduced ions which are stabilized by the micelle system.[9,10] Some work in reversed micelles or microemulsions[11-13] suggests that these systems may

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