

# Stable Carbocations. CLXIX.<sup>1</sup> <sup>13</sup>C-<sup>13</sup>C Spin-Spin Coupling in Carbocations

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**Abstract:** <sup>13</sup>C-<sup>13</sup>C spin-spin coupling constants in <sup>13</sup>C enriched samples of the trimethylcarbenium ion, the dihydroxyphenylcarbenium ion, and the benzoyl cation have been measured. The results are interpreted in terms of the Pople-Santry theory.

Several investigations have been directed toward elucidation of the factors affecting <sup>13</sup>C-<sup>13</sup>C coupling.<sup>2</sup> Early experimental work<sup>2a-c</sup> indicated there was a relationship between the coupling constant  $J_{AB}$  of directly bonded atoms A and B and bond hybridization parameters. Theoretical studies,<sup>2b,d,e</sup> also, assuming the dominance of the Fermi contact mechanism, predicted from VB<sup>3</sup> and MO<sup>2b,4</sup> approximations (using the average energy approximation) a proportionality between the coupling constant  $J_{AB}$  and the parameter  $P_{s_{AS} s_{B}}$ ,<sup>2</sup> where  $P_{s_{AS} s_{B}}$  is the element of the first-order density matrix between the valence-shell s orbitals of the atoms A and B involved.

Within each hybridization type (e.g., sp<sup>3</sup>-sp<sup>3</sup>, sp<sup>2</sup>-sp<sup>2</sup>, etc.), however, it was found that substituent effects were too large to be accounted for by hybridization arguments or by changes in effective nuclear charges.<sup>2d,e</sup> A more recent theoretical method to compute  $J_{AB(CC)}$  using an approximate SCF finite perturbation method<sup>5</sup> was somewhat more successful in accounting for the trends in experimental values.

To further our understanding of the factors influencing C-C coupling, and hence further their potential usefulness in structural organic chemistry, we have measured  $J_{CC}$  values in several carbocations. It was thought that the large electron deficiency in these molecules may have considerable effect on the  $J_{CC}$  values, just as charge has been shown to have very large effects on shielding constants.<sup>6</sup> The question of <sup>13</sup>C-<sup>13</sup>C coupling involving a positively charged carbon atom is therefore of particular interest.

## Results and Discussion

The stability of carbenium ions in strongly acidic solvent systems (SbF<sub>5</sub>, SbF<sub>5</sub>-SO<sub>2</sub> (SO<sub>2</sub>ClF), SbF<sub>5</sub>-FSO<sub>3</sub>H-SO<sub>2</sub> (SO<sub>2</sub>ClF)) has enabled their extensive pmr

and cmr spectroscopic investigation.<sup>6</sup> The cmr investigations have centered mainly on chemical shift data, although several direct and geminal carbon-hydrogen coupling constants were also reported.<sup>6,7</sup> As yet, no direct carbon-carbon coupling constants, apart from that of the acetyl cation,<sup>2e</sup> have been reported.

Using standard methods to generate stable carbenium ions in strongly acidic solutions, the <sup>13</sup>C-<sup>13</sup>C spin-spin coupling constants in trimethylcarbenium ion, the dihydroxyphenylcarbenium ion (protonated benzoic acid), and the benzoyl cation have been measured. Together with the result from the acetyl cation, these measurements represent the four possible combinations of hybridized carbons in carbenium ions (sp<sup>3</sup>-sp<sup>2</sup>, sp<sup>3</sup>-sp, sp<sup>2</sup>-sp<sup>2</sup>, sp<sup>2</sup>-sp).

Table I summarizes the observed <sup>13</sup>C-<sup>13</sup>C coupling

**Table I.** <sup>13</sup>C-<sup>13</sup>C Spin-Spin Coupling Constants of Carbocations and Related Compounds

Hybridization type	Compd	$J_{13C-13C}^a$
sp <sup>3</sup> -sp <sup>2</sup>	CH <sub>3</sub> C <sup>+</sup> (CH <sub>3</sub> ) <sub>2</sub>	25.1 <sup>b</sup>
sp <sup>3</sup> -sp	CH <sub>3</sub> C <sup>+</sup> =O	46.2 <sup>2e</sup>
	CH <sub>3</sub> C≡N	56.2 <sup>2e</sup>
sp <sup>2</sup> -sp <sup>2</sup>	$\begin{array}{c} \text{OH} \\ \parallel \\ \text{C}_6\text{H}_5\text{C}^+ \end{array}$	74.0
	$\begin{array}{c} \text{OH} \\ \parallel \\ \text{C}_6\text{H}_5\text{COOH} \end{array}$	71.87 <sup>c</sup>
	$\begin{array}{c} \text{OH} \\ \parallel \\ \text{C}_6\text{H}_5\text{COO}^- \end{array}$	65.90 <sup>c</sup>
sp <sup>2</sup> -sp	$\begin{array}{c} + \\ \text{C}_6\text{H}_5\text{C}\equiv\text{O} \\ \text{C}_6\text{H}_5\text{C}\equiv\text{N} \end{array}$	81.2
		80.40 <sup>c</sup>

<sup>a</sup> Hertz, assumed to be positive 9. <sup>b</sup>  $J_{C-C}$  in the precursor, 2-chloro-2-methylpropane, is 40.0 Hz.<sup>2h</sup> <sup>c</sup> A. M. Ihrig and J. L. Marshall, *J. Amer. Chem. Soc.*, **94**, 1756 (1972).

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constants obtained from the Fourier transform cmr spectra of enriched samples. The proton decoupled cmr spectra of the benzoyl cation, and the methyl region of the trimethylcarbenium ion, are shown in Figures 1a and 1b, respectively. The most obvious trend from Table I is the approximate correlation between the magnitude of  $J_{C_1-C_2}$  and the hybridization of C<sub>1</sub> and C<sub>2</sub>. Increasing the s character of C<sub>1</sub> or C<sub>2</sub> causes  $J_{C_1-C_2}$  to increase from 25.1 Hz for the sp<sup>3</sup>-sp<sup>2</sup> system of trimethylcarbenium ion to 81.2 Hz in the sp<sup>2</sup>-sp system

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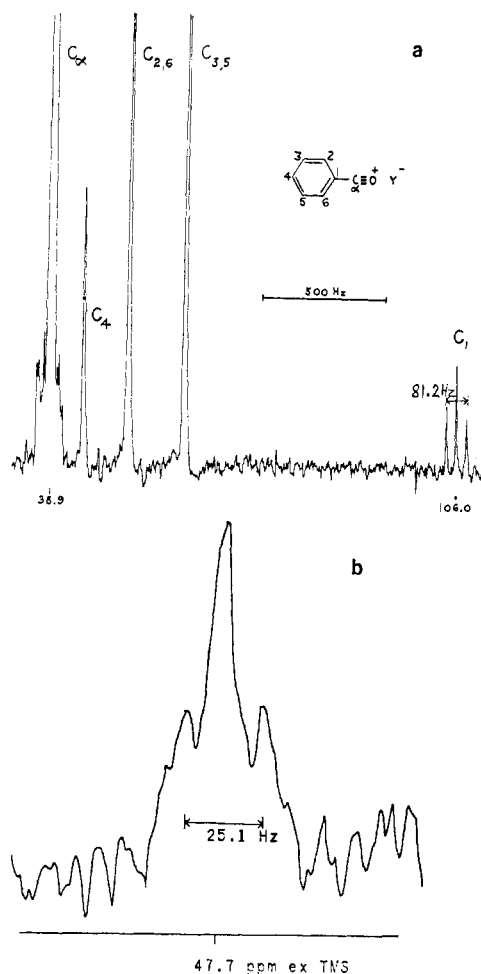


Figure 1. (a) FT- $^{13}\text{C}$  nmr spectrum of the benzoyl cation (56%  $^{13}\text{C}^{\text{O}^+}$ ) in  $\text{FSO}_3\text{H-SbF}_5\text{-SO}_2$  at ambient probe temperature ( $37^\circ$ ). (b)  $\text{CH}_3$  spectral region of the FT- $^{13}\text{C}$  nmr spectrum of the trimethylcarbenium ion (59%  $^{13}\text{C}^+$ ) in  $\text{SbF}_5\text{-SO}_2$  at  $-60^\circ$ .

of the benzoyl cation. This trend is quite consistent with the previously noted correlations between "s character" and  $J_{\text{AB}}$ .<sup>8</sup>

The effect on charge on  $J_{\text{CC}}$  is evident from a comparison of the values of charged and uncharged species, within each hybridization type.  $J_{\text{sp}^2\text{-sp}}$  values in benzonitrile and the isoelectronic benzoyl cation are almost the same despite the considerable difference in structure between these two species (we have shown<sup>9</sup> that in the benzoyl cation there is considerable charge delocalization into the benzene ring and a substantial contribution from "ketene-like" resonance forms).

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A consistent trend for  $J_{\text{sp}^2\text{-sp}^{\text{O}^+(\text{COOH})}}$  values in protonated benzoic acid, benzoic acid, and the benzoate anion is apparent, as the electron density at the carboxylic carbon atom increases.

An interpretation in terms of the Pople-Santry theory,<sup>10</sup> based on a localized model of the CC  $\sigma$  bond, was presented by Maciel, *et al.*,<sup>2d,3</sup> to rationalize the large difference between  $J_{\text{C}_{\text{sp}^3\text{-sp}}}$  values in acetonitrile and the acetyl cation. A larger difference between  $J_{\text{C}_{\text{sp}^3\text{-sp}^2}}$  in the trimethylcarbenium ion (Table I) and neutral compounds (*e.g.*, 39.4 Hz for  $\text{C}^*\text{H}_3\text{C}^*\text{H} = 0$  and 40.6 Hz for  $\text{C}^*\text{H}_3\text{C}^*\text{H} = 0$ )<sup>11</sup> is also observed and may be rationalized in a similar manner. If the MO energy levels for a CC  $\sigma$  bond are denoted by  $\psi_1$ ,  $\psi_2$ ,  $\psi_3$ , and  $\psi_4$ , then the "bonding" contribution<sup>2d</sup> ( $\psi_3$ ) shows a greater per cent increase in going from  $\text{CH}_3\text{COR}$  to  $\text{CH}_3\text{C}^+(\text{CH}_3)_2$  than the corresponding "antibonding" contributions ( $\psi_2$ ,  $\psi_4$ ). Thus, there is a larger increase in the magnitude of the negative ( $\psi_1$ ,  $\psi_3$ ) contribution to the computed mutual polarizability,<sup>2d,e</sup>  $\pi_{\text{SA}^{\text{SB}}}$ , in going from  $\text{CH}_3\text{COR}$  to  $\text{CH}_3\text{C}^+(\text{CH}_3)_2$ , with a consequent decrease in  $\pi_{\text{SA}^{\text{SB}}}$  and  $J_{\text{CC}}$ .

### Experimental Section

**Preparation of Ions.** The trimethylcarbenium ion was generated from 59%  $^{13}\text{C}$ -enriched 2-chloro-2-methylpropane in  $\text{SbF}_5\text{-SO}_2$  at  $-60^\circ$ . Protonated benzoic acid was prepared from benzoic acid (56%  $^{13}\text{COOH}$ ; Merck, Sharp and Dohme, Ltd., Montreal, Canada) and  $\text{FSO}_3\text{H-SbF}_5\text{-SO}_2$  at  $-60^\circ$ , and the benzoyl cation, by raising the solution of protonated benzoic acid to room temperature for several minutes.<sup>12,13</sup> In each case the pmr spectrum of the ion generated was identical with the reported spectrum.<sup>13,14</sup>

**Carbon-13 Nuclear Magnetic Resonance Spectra.** A Varian Associates Model XL 100 spectrometer equipped with a broad-band decoupler and variable-temperature probe was used. The instrument operates at 25.2 MHz for  $^{13}\text{C}$ , and is interfaced with a Varian 620 L computer. The combined system was operated in the pulse-Fourier transform mode, employing a Varian Fourier transform accessory. Typically 3000–5000 pulses, each of width 20–30  $\mu\text{sec}$ , needed to be accumulated in order to give a satisfactory signal-to-noise ratio for all signals of interest. Field-frequency stabilization was maintained by locking on the  $^{19}\text{F}$  signal of an external sample of fluorobenzene. Chemical shifts were measured from the  $^{13}\text{C}$  signal of 5%  $^{13}\text{C}$ -enriched tetramethylsilane in a 1.75-mm capillary held concentrically inside the standard 12-mm sample tube.

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