J. Am. Chem. Soc. **1984**, *106*, 7073-7077

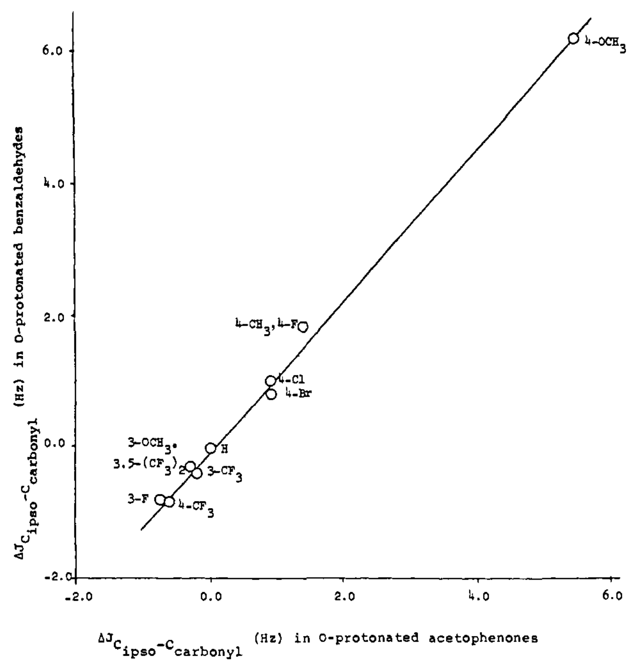

Figure 4. Plot of $\Delta J_{\mathrm{C_{ipso}-C_{carbonyl}}}$ in O-protonated benzaldehydes vs. those in O-protonated acetophenones.

that there is a linear free energy relationship between ΔJ values of two similar system. A plot of $\Delta J_{\mathrm{C_{ipso}-C_{carbonyl}}}$ values in substituted O-protonated benzaldehydes against the corresponding values in O-protonated acetophenones is also linear (Figure 4) ($r = 1.0$). These linear plots of ΔJ values indicate that the substituent effect on J_{CC} values (SCC) in systems that are closely related in their electron demand is very similar.

J_{CC} values can, as shown in the present study, be valuable in the study of carbocationic systems. We are continuing our further study on ^{13}C–^{13}C coupling in such electron-deficient systems.

Experimental Section

All acetophenones and benzaldehydes used were commercially available samples with ≥99% purity. Regular ^{13}C NMR and ^{13}C satellite spectra were recorded at 50.3 MHz with use of a Varian XL-200 superconducting NMR spectrometer equipped with a variable-temperature broad-band probe. The spectra of neutral acetophenones and benzaldehydes were obtained at room temperature in $CDCl_3$ solvent (~30% solution). The O-protonated carboxonium ions were prepared by slow addition of the corresponding acetophenone or benzaldehyde to FSO_3H at ca. -40 °C (~25% solution), and the spectra were recorded in FSO_3H at -35 °C. The pulse sequence used for the ^{13}C satellite spectra, based on Freeman et al.,[17] is $90°(x)–\tau–180°(y)–\tau–90°(x)–\Delta–90°(\phi)–\mathrm{Acq.}(\psi)$, where $\tau \simeq (2n + 1)/4J_{\mathrm{CC}}$, Δ is a very short delay (~10 μs) needed to reset the radio-frequency phase during which time double quantum coherance evolves,and ϕ and ψ are the phase of the last 90° "read" pulse and the receiver reference phase, respectively. Optimum setting of τ for direct coupling is when $n = 0$ and thus is set at 4.5 ms (corresponding to a J_{CC} value of ~55 Hz). The repetition rate of this sequence is ~10 s, and reasonable S/N was achieved in 6–8 h of acquisition. The coupling constants can be directly measured from the "satellite" spectra.[17] The accuracy of the coupling constants in a neutral compound are ±0.2 Hz while those in the protonated carboxonium ions are ±0.3 Hz. Some of the coupling constants could not be measured accurately due to overlap of peaks or due to broadening because of slow rotation around the $C_{ipso}–C_{carbonyl}$ bond (in the carboxonium ions).

Acknowledgment. Support of our work by the National Institutes of Health is gratefully acknowledged.

Registry No. MeO-C_6H_4-*p*-Ac, 100-06-1; F-C_6H_4-*p*-Ac, 403-42-9; Me-C_6H_4-*p*-Ac, 122-00-9; Cl-C_6H_4-*p*-Ac, 99-91-2; Br-C_6H_4-*p*-Ac, 99-90-1; Ph-Ac, 98-86-2; MeO-C_6H_4-*m*-Ac, 586-37-8; F-C_6H_4-*m*-Ac, 455-36-7; F_3C-C_6H_4-*m*-Ac, 349-76-8; F_3C-C_6H_4-*p*-Ac, 709-63-7; NC-C_6H_4-*p*-Ac, 1443-80-7; 3,5-$(CF_3)_2C_6H_3Ac$, 30071-93-3; Ac-C_6H_4-*p*-Ac, 1009-61-6; MeO-C_6H_4-*p*-$C(CH_3){=}OH^+$, 70205-59-3; F-C_6H_4-*p*-$C(CH)_3{=}OH^+$, 70205-60-6; Me-C_6H_4-*p*-$C(CH_3){=}OH^+$, 56485-33-7; Cl-C_6H_4-*p*-$C(CH_3){=}OH^+$, 70205-61-7; Br-C_6H_4-*p*-$C(CH_3){=}OH^+$, 70205-62-8; Ph-$C(CH_3){=}OH^+$, 39922-13-9; MeO-C_6H_4-*m*-$C(CH_3){=}OH^+$, 91842-70-5; F-C_6H_4-*m*-$C(CH_3){=}OH^+$, 91842-71-6; F_3C-C_6H_4-*m*-$C(CH_3){=}OH^+$, 86822-02-8; F_3C-C_6H_4-*p*-$C(CH_3){=}OH^+$, 70205-64-0; 3,5-$(CF_3)_2C_6H_3C(CH_3){=}OH^+$, 86803-11-4; $^+HO{=}C(CH_3)$-C_6H_4-*p*-$C(CH_3){=}OH^+$, 91842-72-7; MeO-C_6H_4-*p*-CHO, 123-11-5; F-C_6H_4-*p*-CHO, 459-57-4; Me-C_6H_4-*p*-CHO, 104-87-0; Cl-C_6H_4-*p*-CHO, 104-88-1; Br-C_6H_4-*p*-CHO, 1122-91-4; Ph-CHO, 100-52-7; MeO-C_6H_4-*m*-CHO, 591-31-1; F-C_6H_4-*m*-CHO, 456-48-4; F_3C-C_6H_4-*m*-CHO, 454-89-7; F_3C-C_6H_4-*p*-CHO, 455-19-6; NC-C_6H_4-*p*-CHO, 105-07-7; 3,5-$(CF_3)_2C_6H_3CHO$, 401-95-6; MeO-C_6H_4-*p*-$CHOH^+$, 91842-73-8; F-C_6H_4-*p*-$CHOH^+$, 36323-63-4; Me-C_6H_4-*p*-$CHOH^+$, 56485-34-8; Cl-C_6H_4-*p*-$CHOH^+$, 34256-04-7; Br-C_6H_4-*p*-$CHOH^+$, 34256-05-8; Ph-$CHOH^+$, 3441-73-4; MeO-C_6H_4-*m*-$CHOH^+$, 91842-74-9; F-C_6H_4-*m*-$CHOH^+$, 57601-03-3; F_3C-C_6H_4-*m*-$CHOH^+$, 91842-75-0; F_3C-C_6H_4-*p*-$CHOH^+$, 59356-66-0; 3,5-$(CF_3)_2C_6H_3CHOH^+$, 91842-76-1.

One-Bond ^{13}C–^{13}C NMR Coupling Constants in Substituted Benzoyl Cations[1]

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Abstract: One-bond ^{13}C–^{13}C NMR coupling constants in a series of substituted benzoyl cations were measured by natural-abundance ^{13}C NMR spectroscopy with use of the INADEQUATE pulse sequence. The $J_{\mathrm{C_1,CO^+}}$ values were qualitatively compared with the $J_{\mathrm{C_1,CN}}$ values obtained in the corresponding substituted benzonitrile series, which serve as isoelectronic models for the benzoyl cations. Evidence for the predominance of the "ketene-like" mesomer contribution to their structure is discussed in the light of these results as well as previous ^{13}C chemical shift data. A highly consistant behavior of the observed $J_{\mathrm{C_3,C_4}}$ or $J_{\mathrm{C_4,C_5}}$ values in both these series is also discussed and compared with previous results obtained in a series of similarly substituted benzenes, acetophenones, benzaldehydes, and the corresponding carboxonium ions.

^{13}C NMR chemical shifts (δ_{C}) and ^{13}C–H coupling constants ($J_{\mathrm{C-H}}$) are widely used to provide detailed information about structure, bonding, and electron distribution in organic molecules, including carbocations.[2] In contrast, relatively little interest has

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Table I. One-Bond ^{13}C–^{13}C NMR Coupling Constants in Substituted Benzoyl Cations, **1R**[a]

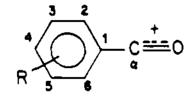
R	$J_{C_1,CO}$	J_{C_1,C_2}	J_{C_2,C_3}	J_{C_3,C_4}	others
4-OCH_3	89.8	57.6	60.5	63.7	
4-CH_3	84.0	58.1	57.2	54.1	
H	82.6	59.1	56.0	53.4	
4-Cl	85.2	59.1	57.3	59.1	
4-Br	84.4	60.6	56.1	59.1	
4-F	86.4	60.1	58.7	*b*	
3-CF_3	82.9	61.0	*b*	*b*	$J_{C_1,C_6} = 60.1$
4-CF_3	82.6	60.9	58.5	62.2	
3,5-$(CF_3)_2$	86.4	62.3	*b*	*b*	

[a] All coupling constants are in Hz and are measured in 1:1 FSO_3H:SbF_5/SO_2 solutions at ca. −65 °C (~25% solutions). [b] Could not be measured accurately due to signal overlap.

been focused on the study and utility of ^{13}C–^{13}C coupling constants, $J_{C,C}$, in structural determinations.[3,4] The one-bond coupling constants, in particular, are known to show large variations in values, ranging from −17.5 Hz (bicyclobutanes) to +185 Hz (alkynes), that arise mainly from hybridization changes in the carbons involved. Smaller variations within the series of compounds can be shown to also arise from factors such as nature and orientation of substituents, ring size, etc. However, experimental difficulties associated with measurements of such coupling constants have discouraged systematic investigations. Thus available data at present are sparse, usually involving only a limited series of compounds.

Using Freeman's INADEQUATE pulse sequence,[5] we reported one-bond ^{13}C–^{13}C coupling constants in a series of 1- and 2-substituted adamantane derivatives[6] and analyzed the substituent effect on these $^1J_{C,C}$ values (SCC) in terms of electronic and stereochemical effects. We, subsequently, extended our study to electron-deficient systems and reported[7] such results in a series of substituted acetophenones, benzaldehydes, and their corresponding O-protonated carboxonium ions. Since the primary goal of our studies was probing the transmission of electronic substituent effects, our investigation was restricted only to those systems in which the substituent and the electron-deficient carbocationic centers were well separated by a reasonably rigid molecular framework, such as an aryl ring. Ortho substituents were excluded to avoid complications arising from steric and/or other effects.

In continuation of our study of $^1J_{CC}$ constants in carbocationic systems, we herein report the results obtained in a series of 3- and 4-substituted benzoyl cations **1R**.



1R,

R = 4-OCH_3, 4-CH_3, H, 4-F, 4-Cl, 4-Br, 3-CF_3, 4-CF_3, 3,5-$(CF_3)_2$

The $^1J_{C,C}$ values obtained in this study are evaluated in conjunction with the ^{13}C chemical shift data of the ions to probe the trend of charge delocalizations as a consequence of substituent effect.

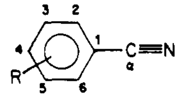
Table II. One-Bond ^{13}C–^{13}C NMR Coupling Constants in Substituted Benzonitriles, **2R**[a]

R	$J_{C_1,CN}$	J_{C_1,C_2}	J_{C_2,C_3}	J_{C_3,C_4}	others
4-OCH_3	83.7	60.5	60.0	66.5	
4-CH_3	81.5	60.3	57.3	56.2	$J_{C_4-CH_3} = 43.4$
H	80.3	60.1	56.4	54.7	
3-OCH_3	80.6	63.1	68.6	66.7	$J_{C_1,C_6} = 60.5$ $J_{C_4,C_5} = 57.4$ $J_{C_5,C_6} = 57.0$
4-Cl	84.0	61.2	57.1	64.7	
4-Br	83.1	61.0	63.4	63.0	
4-F	83.0	60.5	57.8	70.7	
3-CF_3	82.6	64.0	*b*	*b*	$J_{C_1,C_6} = 60.7$ $J_{C_5,C_6} = 56.1$
4-CF_3	80.8[c]	60.4	59.2	*b*	

[a] All coupling constants are in Hz and are measured in $CDCl_3$ (~25% solutions) containing trace amounts of $Cr(acac)_3$ as relaxing agent. [b] Could not be measured due to signal overlap. [c] Calculated value by spin simulation.[10,11]

Results and Discussion

The one-bond ^{13}C–^{13}C coupling constants[8] in substituted benzoyl cations were measured in FSO_3H:SbF_5 (1:1)/SO_2 solution at temperatures between −60 and −80 °C and are listed in Table I. For comparison, similar measurements were also made in the corresponding neutral series of benzonitriles, **2R**, whose $^1J_{C,C}$ values are summarized in Table II. These values were measured in $CDCl_3$ solution at ambient temperature in the presence of a paramagnetic relaxing agent such as chromium(III) acetylacetonate.[9] The $J_{C_1,CN}$ for 4-(trifluoromethyl)benzonitrile (80.8 Hz) had to be obtained by spin simulation technique, since only the inner peaks of the strong AB pattern (resulting from C_1 and nitrile carbon resonances) could be observed. With use of the chemical shift obtained for C_1 and nitrile carbons, the $J_{C_1,CN}$ was computed by iterative calculations employing the LAME program.[10,11] Since the calculation did not incorporate the ^{13}C-induced chemical shift shielding, the estimated error in the coupling constant is in the order of ±1 Hz. In the case of 3,5-bis(trifluoromethyl)benzonitrile, measurement of $J_{C_1,CN}$ was not possible because of the close proximity of the C_1 and nitrile ^{13}C chemical shifts resulting in a strong AB coupled pattern where overlap of inner peaks of the AB "quartet" occurs. Attempts to measure the coupling constants in the related protonated benzonitrile series within reasonable instrument time were unsuccessful due to the extremely long spin-lattice relaxation times, T_1, associated with the corresponding C_1 and protonated nitrile carbons. Use of



2R,

R = 4-OCH_3, 4-CH_3, H, 3-OCH_3, 4-F, 4-Cl, 4-Br, 3-CF_3, 4-CF_3

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(1) Stable Carbocations Part 257. For Part 256, see: Olah, G. A.; Iyer, P. S.; Prakash, G. K.; Krishnamurthy, V. V. *J. Org. Chem.*, in press.

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(8) The relative or absolute signs were not determined in this study. Signs of directly bonded coupling are assumed positive.

(9) The ^{13}C–^{13}C coupling constant values of benzonitriles in the absence of chromium(III) acetylacetonate were measured whenever possible. No difference in the values were, however, observed with those obtained in presence of this relaxation agent.

(10) The spin simulation is based on the FORTRAN program, LAME, which is LAOCOON with magnetic equivalence added.[11] LAME calculates the theoretical spectrum for spin − $^1/_2$ nuclei given the values of chemical shifts and coupling constants. It can adjust the values of the parameters to approach a given experimental spectrum.

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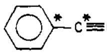
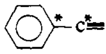
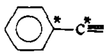
Table III. Comparison of One-Bond $^{13}C-^{13}C$ NMR Coupling Constants in Some Representative Methyl and Phenyl Derivatives[a]

compound	$^1J_{CC}$	ref
$*CH_3-*C\equiv CH$	67.4	16
$*CH_3-*C\equiv N$	56.5	16
$*CH_3-*C\equiv O^+$	45.9	16
	89.0	*b*
	80.4	*b*
	81.2	*b*

[a] Coupling constants are between the carbons indicated by an asterisk. [b] Present work.

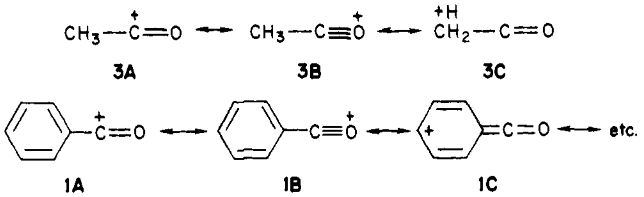
iron(III) chloride as a relaxing agent also proved futile under these conditions.

The measured scalar coupling constant values basically represent the energy of interaction between the two ^{13}C nuclei under observation. The mechanism contributing to this interaction has been described by Ramsey[12] with three terms—Fermi contact, spin-dipolar, and orbital dipolar, the last two being non-contact terms. Fermi contact mechanism has been generally regarded as the major contributor to the observed one-bond $^{13}C-^{13}C$ coupling constants and is believed to operate predominantly via the σ-molecular framework.[13] Recently, however, the relative importance of both σ- and π-transmitted components of all three terms in substituted benzenes has been evaluated by Contreras, et al.[14] They concluded that in aryl systems, (a) the π-component contributions of all three terms (contact and non-contact) are larger in the case of a formal double bond than in a single bond and (b) that they represent non-negligible contribution to the observed one-bond $^{13}C-^{13}C$ coupling constant values, even though the σ-component is still the dominant contributor.

It is therefore of substantial interest to study J_{C_1,C_α} in benzoyl cations and related benzonitriles. The basis for comparing the J_{C_1,C_α} values of the benzoyl cations with neutral benzonitriles stems from the fact that the carbons of interest in both cases are approximately in the sp^2–sp hybridized state. Moreover, a plot of the ^{13}C chemical shift of C_1 of the substituted benzoyl cations vs. the corresponding C_1 shifts in benzonitriles yields a good correlation, $r = 0.97$.[15] A reasonable correlation of $r = 0.89$ was also obtained in a similar plot of the C_α ^{13}C chemical shifts from both series.[15] Hence replacing the positively charged oxygen atom with the isoelectronic nitrogen seems to induce similar changes in the $\delta^{13}C$ values. No correlation was, however, obtained when the C_α ^{13}C chemical shifts of benzoyl cations are plotted vs. those of similarly substituted thiobenzoyl cations.[16]

Theoretical studies have previously compared the $^1J_{C,C}$ values in the related series of propyne, acetonitrile, and the acetyl cation, where the carbons of interest are in approximately the sp^3–sp hybridized state. A list of these representative experimental $^1J_{C,C}$ values is summarized in Table III. The observed trend for these three systems has been correctly rationalized by CNDO molecular orbital calculations by Gray et al.[17] and by Pople[18] and are found to be in opposite trend as dictated by ρ_{SASA}, the bond order/charge density matrix term.

Scheme I



A similar, qualitative comparison of J_{C_1,C_α} values between phenyl acetylene, benzonitrile, and the benzoyl cation shows, however, an interesting deviation (Table III). The difference in the coupling constant, ΔJ, between propyne and acetonitrile is approximately of the same magnitude as the ΔJ between the related phenyl acetylene and benzonitrile, roughly 10 Hz. In view of this, the J_{C_1,C_α} of the benzoyl cation would be predicted to have a value ~10 Hz lower than benzonitrile (since $^1J_{C,C_\alpha}$ of the acylium cation is approximately 10 Hz lower than that of acetonitrile). However, the observed $^1J_{C,C_\alpha}$ value of the benzoyl cation is actually very close to that of benzonitrile. This relative increase in the coupling constant of the benzoyl cation clearly must have its origin in the mesomeric interaction of the phenyl ring with an electron-deficient cationic center.

The acylium ions can be described in terms of the resonance hybrid contributions as depicted in Scheme I. This is strongly supportive of the fact that whereas the oxocarbenium ion **3A** and carboxonium ion **3B** mesomers are dominant contributors to the electronic description of the structure of the acetyl ion,[19,20] the "ketene-like" mesomer **1C** contributes to a greater extent in the benzoyl cation. The resulting increased "double bond" character between C_1 and C_α is in turn reflected in the relative increase observed in J_{C_1,C_α}. This is in agreement with the conclusions drawn earlier from ^{13}C chemical shift studies[21] which indicated a substantial deshielding of the $C_{2,6}$ and C_4 carbons (approximately 21 ppm for the C_4 carbon of the parent benzoyl cations with repect to benzene) implying considerable charge delocalization into the aryl ring. Support for the importance of "ketene-like" mesomer also comes from other methods of investigation such as UV measurements,[22] X-ray crystallography,[20] ^1H NMR[23] and X-ray electron spectroscopy.[24]

Another important evidence in support of the contribution of ketene-like structure (**1C**) for benzoyl cations comes from the analysis of the substituent effect on the carbonyl carbon chemical shift.[21] Electron-donating substituents such as 4-OCH$_3$ and 4-CH$_3$ deshield the carbonyl carbon (with respect to the parent benzoyl cation) while electron-withdrawing substituents shield it. Hence, a plot of the carbonyl carbon chemical shift against σ^{C^+} values[25] gives a straight line ($r = 0.99$) with positive ρ^{C^+} (+3.5). This trend in the substituent effect is opposite to what one would predict on the basis of only charge delocalization (due to inductive and/or resonance effects) into the aryl ring. However, as a consequence of increased charge delocalization into the aryl ring (with electron-donating groups), the contribution of the mesomeric ketene-like structure, **1C**, increases. Such an increase in the mesomer (**1C**) contribution is expected to deshield the carbonyl carbon and in fact more than offsets the shielding expected on the basis of

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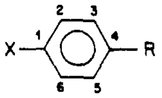
Table IV. Comparison of J_{C_3,C_4} Values in Substituted Benzenes



	X						
R	H[c]	CHO[d]	$COCH_3$[d]	CN[e]	CH^+OH[d]	$C(^+OH)CH_3$[d]	$C{\equiv}O^+$[e]
OCH_3	67.0	66.4	66.5	66.5	61.5	64.5	63.7
CH_3	57.0	56.1	56.5	56.2	53.7	54.1	54.1
H	56.0	55.4	55.4	54.7	54.0	54.0	53.4
Cl	65.2	64.8	65.0	64.7	62.2	62.6	59.1
Br	63.7	63.1	63.6	63.0	60.1	61.7	59.1
F	70.8	70.5	70.6	70.7	69.0	69.8	*a*
CN	60.1	60.4	60.4	*b*	*b*	*b*	*b*

[a] Could not be measured accurately due to signal overlap. [b] Data not available. [c] Reference 29. [d] Reference 7. [e] Present study.

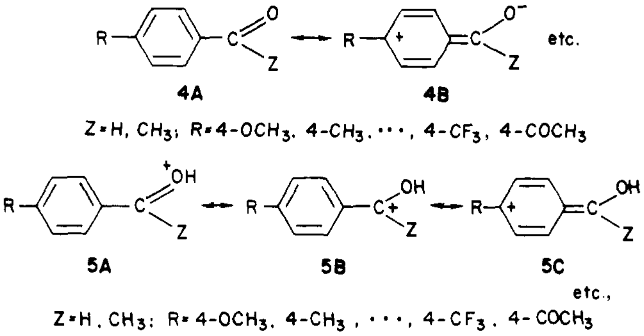
charge delocalization. Similar argument will explain the shielding observed with an electron-withdrawing group.

Some confusion was introduced recently by Kelly et al.,[26] who interpreted the positive ρ^{C^+} in the benzoyl cation (in comparison to the positive ρ_I observed[27] in acetophenone, styrene, etc. by DSP analyis) as due to the dominance of the inductive π-polarization mechanism. While a positive ρ_I[28] in DSP analysis is indeed indicative of "reverse" substituent effect on chemical shift which can be interpreted as due to π-polarization, a comparison of such ρ_I values to ρ^{C^+} is highly misleading. ρ^{C^+} is the slope in the SSP analysis and is thus a combination of *both* inductive and resonance transmission coefficients (ρ_I and ρ_R), while ρ_I (from DSP analysis) reflects only the inductive component. Moreover, in the case of the benzoyl cation (and other systems with a conjugated triple bond such as phenylacetylenes, benzonitriles, etc.) the large deshielding in the carbonyl carbon (C_α) due to an increase in the mesomeric contribution of the ketene-like structure (in general, allenyl structure) is also reflected in the ρ^{C^+} value. Thus one must use caution in using the sign and magnitude of ρ^{C^+}, in systems with conjugated triple bond as a probe for the presence of chemical shift shielding "mechanisms" other than inductive and resonance effects.

In our previous report related to the study of acetophenones, benzaldehydes, and their corresponding carboxonium ions,[7] we also described the substituent-induced behavior of the $J_{C_1,CO}$ values in terms of inductive and resonance effects. For example, in all of these systems, the coupling constants increased (with respect to the $J_{C_1,CO}$ value of the corresponding parent compounds) with electron-donating groups such as 4-OCH_3 and 4-CH_3 and decreased with electron-withdrawing groups like 4-CF_3 and 4-$COCH_3$.

These changes were rationalized as being a reflection of changes in the double bond character caused by the relative contributions of mesomers such as **4B** or **5C** (in Scheme II). In addition, the relative increase in the magnitude as well as span of values obtained in the protonated series further indicates the increased mesomeric interaction of the aryl ring. A similar comparison of the range of J_{C_1,C_α} values obtained in the present study, indeed, also reveals a spread of 3.7 Hz in the neutral benzonitriles while exhibiting a relatively larger span of 7.2 Hz in the electron-deficient benzoyl cation series. The largest J_{C_1,C_α} value of 89.8 Hz was observed in the 4-methoxybenzoyl cation while a relatively lower coupling constant of 82.6 Hz was obtained in the 4-(trifluoromethyl)benzoyl cation. In the corresponding benzonitriles, the 4-methoxy substituent induces a J_{C_1,C_α} value of 83.7 Hz while the 4-(trifluoromethyl) renders a value of 80.8 Hz.[29] However, an attempt to explain the SCC values in either of these two systems simply on the basis of mesomeric interactions alone fails since *all* the substituents cause the J_{C_1,C_α} values to be greater than that of the corresponding parents, benzoyl cation or benzonitrile.

Scheme II



Analysis of the J_{C_3,C_4} or J_{C_4,C_5} values in substituted benzonitriles and benzoyl cations reveals a more consistant behavior when compared with those obtained in the corresponding acetophenones, benzaldehydes, and their O-protonated analogues. The data are collected in Table IV. The coupling constants in the neutral series of acetophenones, benzaldehydes, and benzonitriles are almost identical (within ±1 Hz) and seem to be characteristic of the substituent attached to the C_4 carbon atom. Furthermore, these values compare just as well with J_{C_1,C_2} values obtained for the corresponding series of monosubstituted benzenes reported earlier by Wray et al.[30] Hence, the magnitude of the substituent effect in neutral systems seems to depend critically upon the proximity of the substituent to the carbons involved in coupling and sharply attenuates at distances greater than one bond. The J_{C_3,C_4} or J_{C_4,C_5} and J_{C_1,C_2} or J_{C_1,C_6} therefore exhibit values which are mutually exclusive to the presence of another substituent three bonds away. The general trend is that inductively electron withdrawing groups increase the coupling constant while electron donating groups decrease it.

Comparison of these coupling constant with the J_{C_3,C_4} or J_{C_4,C_5} values obtained in the corresponding carbocationic series of compounds, namely the O-protonated acetophenones, benzaldehydes, and benzoyl cations, shows that while the overall trend still persists, the magnitudes are generally lower. These results may be rationalized, if one considers (in addition to the electronegative effect of the directly attached substituent) the bond localization effects brought about by a relative increase in the contribution of mesomer **5C** and **1C** (see Schemes I and II) in protonated acetophenones, benzaldehydes, and benzoyl cations, respectively. We are well aware that such a simplified explanation ignores the possible effect of the positive charge residing on the C_4 carbons in either of the two mesomers **5C** and **1C**. However, until detailed theoretical investigations critically evaluate such effects, the proposed qualitative explanation based on simple inductive and resonance effects seems reasonable.

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(28) The sign of the ρ value is defined by following the convention[24] that $\Delta\delta$ ($\delta_H - \delta_X$) is positive for shielding and negative for deshielding.

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J. Am. Chem. Soc. 1984, 106, 7077-7082

Experimental Section

Regular ^{13}C and ^{13}C satellite spectra were recorded at 50.3 MHz on a Varian XL-200 superconducting NMR spectrometer equipped with a variable-temperature broad-band probe.

All the benzonitriles used were commercially available with >99.0% purity and were used as such. Aroyl chloride precursors for benzoyl cation were either commercially available or made by thionyl chloride reaction from the corresponding acids. The acid chlorides were freshly distilled before ionization.

All the benzoyl cations were prepared with use of 1:1 $FSO_3H:SbF_5$ in SO_2 solutions at temperatures of −10 to −20 °C. Solution concentration for the natural abundance coupling constant studies were typically in the order of ~25%.

Similarly ~30% $CDCl_3$ solutions of substituted benzonitriles containing a trace amount of $Cr(acac)_3$ were used at ambient tempeatures for the coupling constant measurements.

The pulse sequence used for the ^{13}C satellite spectra, based on Freeman et al.,[5] is $90°(x)–\tau–180°(\pm y)–\tau–90°(x)–\Delta–90°(\phi)–$Acq.$(\psi)$, where $\tau = (2n + 1)/4J_{C,C}$, Δ is a very short delay (~10 μs) needed to reset the radiofrequency phase during which time double quantum coherence evolves, and ϕ and ψ are the phase of the last 90° "read" pulse and the receiver reference phase, respectively. The optimum setting for direct coupling is when $n = 0$ and thus set at 3.1 ms (corresponding to a $^1J_{C,C}$ value of ~80 Hz). The repetition rate of this sequence is 2 and 15 s respectively for benzonitriles [with $Cr(acac)_3$] and benzoyl cations. Reasonable signal to noise was achieved in 6–8 h for the former and in 24–36 h for the latter.

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Registry No. 1R (R = 4-OCH_3), 41868-76-2; **1R** (R = 4-CH_3), 20122-40-1; **1R** (R = H), 19270-10-1; **1R** (R = 4-Cl), 20122-41-2; **1R** (R = 4-Br), 45709-42-0; **1R** (R = 4-F), 39981-36-7; **1R** (R = 3-CF_3), 46060-47-3; **1R** (R = 4-CF_3), 46061-29-4; **1R** (R = 3,5-$(CF_3)_2$), 92270-09-2; **2R** (R = 4-OCH_3), 874-90-8; **2R** (R = 4-CH_3), 104-85-8; **2R** (R = H), 100-47-0; **2R** (R = 3-OCH_3), 1527-89-5; **2R** (R = 4-Cl), 623-03-0; **2R** (R = 4-Br), 623-00-7; **2R** (R = 4-F), 1194-02-1; **2R** (R = 3-CF_3), 368-77-4; **2R** (R = 4-CF_3), 455-18-5; $C_6H_5C{\equiv}CH$, 536-74-3.

Benzidine Rearrangements. 19. The Concerted Nature of the One-Proton Rearrangement of 2,2′-Dimethoxyhydrazobenzene[1,2]

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Abstract: Kinetic isotope effects (KIE) in the acid-catalyzed, one-proton rearrangement of 2,2′-dimethoxyhydrazobenzene (**1**) into 3,3′-dimethoxybenzidine (**2**) have been measured. Nitrogen KIE were determined on the bis(trifluoroacetyl) derivative of **2** which was isolated from low and 100% conversions of mixtures of **1** and $[^{15}N,^{15}N']$**1** under kinetic conditions. The ratio of masses M(438)/M(436) as determined by whole-ion mass spectrometric techniques led to the result $k(^{14}N)/k(^{15}N) = 1.0289$ (for two nitrogens). Similar measurements on the derivative of **2** isolated from conversions of mixtures of **1** and $[4,4'\text{-}^{13}C_2]$**1** led to the result $k(^{12}C)/k(^{13}C) = 1.0286$ (for two carbons). These results show that the formation of **2** is a concerted process and, thus, that the acid-catalyzed rearrangement of **1** is a 5,5-sigmatropic shift. Rearrangement via a π-complex intermediate or a solvent-caged, radical/radical-ion pair is excluded. That bonding in the 4,4′ positions of **1** is part of the rate-determining step in this rearrangement was confirmed by measurement of an inverse secondary deuterium KIE ($k_H/k_D = 0.929$ for two deuteriums). This result was obtained from ratios of M(244)/M(242) which were measured on 2,2′-dimethoxyazobenzene (**3**), obtained by oxidizing the hydrazo substrate remaining after high conversions of mixtures of **1** and $[4,4'\text{-}^2H_2]$**1**.

Acid-catalyzed rearrangement of hydrazoarenes into benzidines, diphenylines, and semidines are called, collectively, benzidine rearrangements. In spite of the very large amount of information which has been gathered about these intramolecular rearrangements,[5-15] questions on their mechanisms still remain. A major mechanistic uncertainty concerns concertedness, that is, whether or not the rearrangements are concerted processes, as described in the polar-transition-state theory of Ingold, Hughes, and Banthorpe,[16] or go through intermediates such as π-complexes[8,9] or solvent-caged radical/radical-ion pairs. Recently we have shown with measurements of kinetic isotope effects (KIE) that the rearrangement of hydrazobenzene into benzidine is a concerted process while the accompanying rearrangement into diphenyline is not.[17] Also, the *p*-semidine rearrangement of 4-methoxy-

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