sealed with a gas-oxygen flame. Individual reaction tubes were marked and stored at dry ice temperature until an entire set (10-12 tubes) had been prepared and sealed. The tubes were firmly inserted into a wire cage and immersed in a Haake constant-temperature bath at 69.0 ± 0.2 °C. After 5 min, the wire cage was removed and inverted several times until each solution was thoroughly mixed. Tubes were removed at intervals, quickly frozen in a 2-propanol/dry ice bath, and labeled. Analysis of each tube was performed by GC on the opened reaction tube. A 1 m × 1/8 in. 25% DEGS on NAW Chromosorb W 60/80 column was used for analysis of the products. At a column temperature of 105 °C, retention times were 3.7 min for the propene and 5.8 min for the cyclopropane at a flow rate of 35 mL/min. Response factors were calibrated by comparing peak integration in the ^{1}H NMR spectrum with the values obtained from the GC integrator. The response factors were 4.1 for the propene and 1.7 for the cyclopropane by using the flame ionization detector. The corrected product ratios are based on averages of three to four injections.

Registry No. *trans*-CHCl=CHCl, 156-60-5; $PhHgCBr_3$, 3294-60-8; $PhNO_2$, 98-95-3; C_6H_6, 71-43-2; PhCl, 108-90-7; $PhCH_3$, 108-88-3; PhOMe, 100-66-3; *p*-$Me_2C_6H_4$, 106-42-3; Me_6C_6, 87-85-4; Ph_2Hg, 587-85-9; *p*-$MeC_6H_4HgCCl_3$, 6782-08-7; *p*-$ClC_6H_4HgCCl_3$, 96964-95-3; $PhHgCCl_3$, 3294-57-3; *p*-$Me_2NC_6H_4HgCCl_3$, 21511-17-1; *p*-$MeOC_6H_4HgCCl_3$, 89938-87-4; *p*-$NO_2C_6H_4HgCCl_3$, 89640-91-5; (*p*-$MeOC_6H_4)_2Hg$, 2097-72-5; (*p*-$MeC_6H_4)_2Hg$, 537-64-4; $(PhCH_2CH_2)_2Hg$, 956-73-0; Ph_2Zn, 1078-58-6; Ph_2CO, 119-61-9; PhHgCl, 100-56-1; PhHgBr, 1192-89-8; H_2O, 7732-18-5; Hg, 7439-97-6; $HgCl_2$, 7487-94-7; $HgBr_2$, 7789-47-1; Cu_2Cl_2, 75763-85-8; Cu_2Br_2, 63310-83-8; Cu_2I_2, 12527-63-8; Cu (bronze), 12597-70-5; $CuSO_4$, 7758-98-7; $CuCl_2$, 7447-39-4; $Hg(OAc)_2$, 1600-27-7; $SnCl_4$, 7646-78-8; $ZnCl_2$, 7646-85-7; ZnI_2, 10139-47-6; $AlCl_3$, 7446-70-0; $AlBr_3$, 7727-15-3; $FeCl_3$, 7705-08-0; mesitylene, 108-67-8; durene, 95-93-2.

Substituent Effects on One-Bond ^{13}C–^{13}C NMR Coupling Constants in Aromatic Carbonyl Compounds

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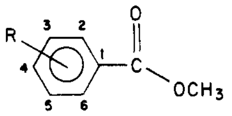
The one-bond ^{13}C–^{13}C NMR coupling constants ($^1J_{C,C}$) in a series of substituted methyl benzoates, benzoyl chlorides, and benzophenones were measured at natural abundance by using the INADEQUATE pulse sequence. These results when evaluated and compared with the $^1J_{C,C}$ values obtained from the study of substituted acetophenones, benzaldehydes, and benzoyl cations reveal their sensitivity to both mesomeric and inductive substituent effects. Within a given series, the changes in $^1J_{C_1,CO}$ values, as a function of the remote substituent on C_4 carbon, reflect the magnitude of the mesomeric interaction. The inductive effect of an α-substituent, on the other hand, is best portrayed by the consistency observed in the $\Delta J_{C_1\text{-}CO}$ ($J_{CHO} - J_{COX}$) values. Such consistency of these effects is also seen in the J_{C_3,C_4} or J_{C_4,C_5} values.

^{13}C NMR spectroscopy has proved to be a powerful tool in providing detailed information about structure, bonding, and electron distribution in organic molecules.[1] The focus has been predominantly on the study of chemical shifts (δ_C), together with the complimentary use of spin-spin interactions with relatively sensitive, high abundant nuclei such as ^1H, ^{19}F, ^{31}P, etc. One particular interaction which is of considerable interest is that between directly bonded ^{13}C nuclei. However, the low natural abundance of these nuclei, have, in the past, severely restricted their study and utility[2,3] generally necessitating difficult and often costly ^{13}C labeling.

Using Freeman's INADEQUATE pulse sequence,[4] we studied the one-bond ^{13}C–^{13}C coupling constants, at natural abundance, in a series of adamantane[5] and diamantane[6] derivatives 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 carbocationic systems and reported such results in a series of substituted acetophenones, benzaldehydes, their corresponding *O*-protonated carboxonium ions,[7] and benzoyl cations.[8]

Table I. One-Bond ^{13}C–^{13}C Coupling Constants[a] in Substituted Methyl Benzoates (1R)



R	J_{CO,C_1}	J_{C_1,C_2} or J_{C_1,C_6}	J_{C_2,C_3} or J_{C_5,C_6}	J_{C_3,C_4} or J_{C_4,C_5}
4-OCH_3	77.1	59.3	58.5	66.5
4-CH_3[c]	76.0	*b*	*b*	56.5
H	74.8	*b*	56.6	55.5
4-F	76.6	59.6	57.3	70.7
4-Cl	76.0	59.1	56.5	64.8
4-Br	76.1	59.6	*b*	63.4
4-CF_3	74.6	59.3	57.6	59.9

[a] All coupling constants are in hertz. [b] Could not be measured accurately. [c] J_{C_4,CH_3} = 43.6 Hz.

As an extension of this study we have determined the one-bond ^{13}C–^{13}C coupling constants in a series of sub-

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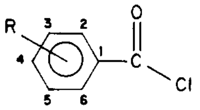
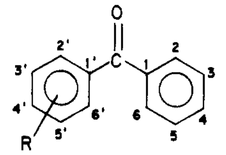
Table II. One-Bond $^{13}C-^{13}C$ Coupling Constants[a] in Substituted Benzoyl Chloride Derivatives (2R)



R	J_{CO,C_1}	J_{C_1,C_2} or J_{C_1,C_6}	J_{C_2,C_3} or J_{C_5,C_6}	J_{C_3,C_4} or J_{C_4,C_5}
4-OCH_3	77.9	60.4	58.9	66.0
4-CH_3[c]	75.6	*b*	57.0	56.1
H	74.2	60.0	56.3	55.2
4-F	75.2	60.8	57.8	70.3
4-Cl	75.7	*b*	57.5	64.6
4-CF_3	74.0	60.3	57.4	59.8
3,5-$(CF_3)_2$	76.2	61.8	*b*	*b*

[a] All coupling constants are in hertz. [b] Could not be measured accurately. [c] J_{C_4,CH_3} = 43.2 Hz.

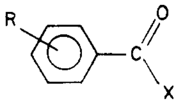
Table III. One-Bond $^{13}C-^{13}C$ Coupling Constants[a] in Substituted Benzophenones (3R)



R	J_{CO,C_1}	J_{C_1,C_2} or J_{C_1,C_6}	J_{C_2,C_3} or J_{C_5,C_6}	J_{C_3,C_4} or J_{C_4,C_5}
4-OCH_3	56.8	57.0	58.9	66.4
4-CH_3[c]	55.1	57.7	*b*	56.4
H	54.6	57.7	56.3	55.5
4-F	56.0	*b*	57.6	70.7
4-Cl	56.5	58.1	56.8	65.0

[a] All coupling constants are in hertz and measured in $CDCl_3$ solution containing trace amounts of $Cr(acac)_3$ at ambient temperatures. [b] Could not be measured accurately. [c] J_{C_4,CH_3} = 43.5 Hz.

stituted aromatic carbonyl compounds such as methyl benzoates **1R**, benzoyl chlorides **2R**, and benzophenones **3R**. The results are evaluated and compared with the $^1J_{C,C}$ values obtained in our previous studies.[7,8]



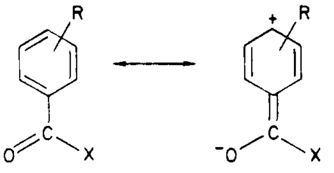
1, X = OCH_3; 2, X = Cl; 3, X = C_6H_5
R = 4-OCH_3, 4-CH_3, 4-F, 4-Cl, 4-Br, 4-CF_3

Results and Discussion

The one-bond $^{13}C-^{13}C$ coupling constants[9] of all the carbonyl compounds in this study were measured in $CDCl_3$ solution at ambient temperature. The $^1J_{C,C}$ values obtained for substituted methyl benzoates and benzoyl chlorides are listed in Tables I and II. Due to poor solubility of the benzophenones, trace amounts of chromium(III) acetylacetonate as relaxing agent were used in order to increase the repetition rate and achieve adequate signal to noise ratio in a reasonable time.[10] The values obtained are listed in Table III.

As in the previous studies[7,8] the coupling constants of major interest are those involving the carbonyl and the C_1 carbon atoms. In general, the $^1J_{C_1,CO}$ values are higher with electron-donating substituents (such as 4-OCH_3) in the aryl ring while they are less with electron-withdrawing substituents (such as 4-CF_3). This observation, in the present study, is in line with our earlier observation of the substituent effect on $J_{C_1,CO}$ coupling constants in substituted acetophenones, benzaldehydes, their protonated carboxonium ions,[7] and substituted benzoyl cations.[8]

We attribute such differences in the $C_{ipso}-C_{carbonyl}$ coupling constants to the changes in the π-bond order between these two carbon centers, due to changes in the relative contribution of the two canonical structures, A and B.



A B

Thus, electron-donating groups (such as R = 4-OCH_3), due to their ability in stabilizing a positive charge in the aryl ring, increase the π-bond order between the ipso and the carbonyl carbon and is thereby reflected in the greater $^1J_{C1,CO}$ value. Similarly electron-withdrawing groups (such as R = 4-CF_3) decrease the π-bond order between the ipso and the carbonyl carbon and thus the $^1J_{C,CO}$ values are less.

The $C_{ipso}-C_{carbonyl}$ coupling constants measured in aromatic carbonyl compounds (those of the present study as well as those reported earlier[7,8]) are compared with each other in Table IV. Two clear and distinct trends emerge from the analysis of these $^{13}C-^{13}C$ coupling constant values. An almost consistent range (within the limited number of substituents used) of ~ 3 Hz in the $^1J_{C_1,CO}$ values is observed within any given series of neutral aromatic carbonyl compounds. This range almost doubles in the case of more electron-deficient systems such as protonated acetophenones, protonated benzaldehydes, and benzoyl cations. Such an increase in the range of $^1J_{C_1,CO}$ within a given series of electron-deficient systems can be attributed to the higher electron demand of the carbonyl group in these positively charged systems compared to that in the neutral systems. In other words, a change in the π-bond order (and thus $^{13}C-^{13}C$ coupling constant) between the ipso and the carbonyl carbon, brought about by a change in the electron-donating or -withdrawing ability of the substituent in the aryl ring, is much more significant in electron-deficient systems compared to that in neutral systems.

A different substituent effect (SCC) on the $C_{ipso}-C_{carbonyl}$ coupling constants is observed when the role of neighboring substituent X is analyzed. The changes in $^1J_{C1,CO}$ brought about by substituents directly attached to the carbonyl carbon is best represented when $\Delta J_{CHO\ vs.\ COX}$ (the difference between the $^1J_{C_1,CO}$ values of substituted benzaldehyde and similar R substituted carbonyl compound) is analyzed. A remarkably consistent ΔJ value is obtained which is characteristic of the nature of the α-substituent, X. Considering the experimental error of ±0.3 Hz, the small standard deviation, σ, seen in all the neutral series strongly suggests that the mean ΔJ values are independent of the electronic effect of the remote R substituents. These values instead give a measure of the "electronegative" effect of an α-substituent. While substitution by OMe or Cl on the carbonyl gives a mean ΔJ value of −22.0 and −21.6, respectively, a methyl substituent gives a value of +0.8. The large negative values in the former cases clearly reflect the greater *inductive* electron-withdrawing ability of these substituents. A methyl group (as in the acetophenone series) on a sp^2 carbon, on the other hand, being an inductive electron-donating substituent, gives a positive ΔJ

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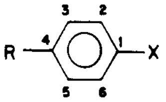
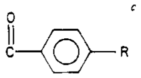
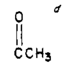
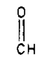
[9] The relative or absolute signs were not determined in this study. Signs of directly bonded couplings are assumed positive.

[10] The $J_{C,C}$ values of benzophenones were measured in the absence of chromium(III) acetylacetonate, whenever possible. No differences were, however, observed with those obtained in the presence of this relaxing agent.

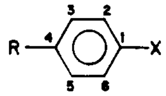
Table IV. Comparison of $^1J_{C_1,CO}$ Values[a] in Aromatic Carbonyl Compounds

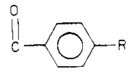


	X =							
R	$COOCH_3$[c]	COCl[c]	 $C(=O)C_6H_4R$[c]	CHO[d]	$COCH_3$[d]	 $\overset{O}{\overset{\|}{C}}CH_3$[d]	 $\overset{O}{\overset{\|}{C}}H$[d]	CO^+[e]
OCH_3	77.1	77.9	56.8	55.5	54.8	64.1	65.5	89.8
CH_3	76.0	75.6	55.1	54.0	53.4	60.0	61.1	84.0
H	74.8	74.2	54.6	53.0	52.4	58.6	59.3	82.6
F	76.6	75.2	56.0	54.3	53.7	60.0	61.1	86.4
Cl	76.0	75.7	56.5	53.9	52.8	59.5	60.3	85.2
Br	76.1	*b*	*b*	53.8	52.7	59.5	60.1	84.4
CF_3	74.6	74.0	*b*	52.4	51.7	57.9	58.5	82.6
range	2.5	3.7		3.1	3.1	6.2	7.0	7.2
$\Delta J^f = J_{CHO} - J_{COX}$	−22.0 (0.2)	−21.6 (0.5)	−1.66 (0.5)	0	+0.8 (0.2)	−6.1 (1.0)	−7.0 (1.3)	−31.2 (1.5)

[a] All coupling constants values in hertz. [b] Data not available. [c] Present study. [d] Reference 7. [e] Reference 8. [f] Values in parenthesis denote, σ, the standard deviation.

Table V. Comparison of J_{C_3,C_4} or $^1J_{C_4,C_5}$ Values in Substituted Benzenes



	X =								
R	H[c]	CHO[d]	$COCH_3$[d]	CHO^+H[d]	$C(O^+H)CH_3$[d]	$C{=}O^+$[e]	COOMe[f]	COCl[f]	 $C(=O)C_6H_4R$
OCH_3	67.0	66.4	66.5	61.5	64.5	63.7	66.5	66.0	66.4
CH_3	57.0	56.1	56.5	53.7	54.1	54.1	56.5	56.1	56.4
H	56.0	55.4	55.4	54.0	54.0	53.4	55.5	55.2	55.5
Cl	65.2	64.8	65.0	62.2	62.6	59.1	64.8	64.6	65.0
Br	63.7	63.1	63.6	60.1	61.7	59.1	63.4	*b*	*a*
F	70.8	70.5	70.6	69.0	69.8	*a*	70.7	70.3	70.7

[a] Could not be measured accurately due to signal overlap. [b] Data not available. [c] Reference 11. [d] Reference 7. [e] Reference 8. [f] Present study.

value. While a similar comparison with the benzophenone series may not be completely justified, a ΔJ value of −1.5 Hz is reasonable and in line with an aryl group being an inductive electron-withdrawing substituent. The largest ΔJ value of −31.2 Hz is observed for benzoyl cations where the substituent X can now be envisaged as a strongly electron withdrawing empty p orbital. This "electronegativity" effect is in line with our earlier observation in the study of substituted adamantanes[5] and diamantanes.[6] In our earlier studies we have shown that the C_α–C_β coupling constant is sensitive to the C_α substituent and increases with increase in the electronegativity.

The deviations (σ) in ΔJ values in the protonated carbonyl compounds and carbocation series is much larger. This may be due to the fact that ΔJ values now represent comparison of the values of $^1J_{C_1,CO}$ in neutral and cationic species where the electronic effect of the remote R group may not be entirely cancelled out. Nevertheless, such comparisons still allow for simple and useful insights into the behavior of ^{13}C–^{13}C coupling constants.

Similar α-effects are also observed in the $^1J_{C_3,C_4}$ or $^1J_{C_4,C_5}$ values. These values have been collected in Table V for comparison. Wray et al.[11] have earlier reported $^1J_{C,C}$ values in a series of monosubstituted benzenes. The remarkable constancy in these values is once again observed both in the present study of substituted methyl benzoates, benzoyl chlorides and benzophenones as well as in our earlier studies on acetophenones, benzaldehydes, and their protonated carboxonium ions[7] and benzoyl cations.[8]. This consistent behavior, therefore, makes it an attractive compliment to chemical shifts (δ_C) measurement for the determination of substition pattern in aromatic systems.

Theoretical descriptions of coupling between nuclear spins are based on Ramsey's theory[12] that coupling via electrons originates from three types of interaction between the magnetic moments due to the nuclear spin and the electrons. The three types are (a) orbital interaction with the magnetic field due to the orbital motion of the electrons, (b) dipolar interaction with the electron spin, and (c) Fermi contact interaction with the electron spin. While these three contributions may vary in sign as well as in magnitude, calculations indicate that coupling between the majority of first-row elements is dominated by the Fermi contact[13-19] and, as a result, would be expected to correlate

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with the product of the s electron densities at the coupled nuclei. However, the noncontact contributions are also expected to be important especially in unsaturated compounds where a π-electronic system is well defined.[20] It is generally accepted that while calculations are able to qualitatively reproduce some of the observed trends, they are still of limited reliability at the present time.

In our present study, we have attempted to demonstrate the scope and utility of measuring one-bond carbon coupling constants and believe that these results will help understand the mechanism of ^{13}C spin interactions. We hope that, perhaps, the experimental data provided in our study will also stimulate theoretical interest to gain a more quantitative understanding of the effect of substituents on one bond ^{13}C–^{13}C coupling constants.

Experimental Section

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

All the benzophenones used were either commercially available with 99% purity or prepared from the correspondig 4-substituted bromobenzene by standard literature procedures. The benzoyl chlorides and methyl benzoates were prepared from the corresponding, commercially available, acid precursors. The former was freshly distilled before use. All compounds used gave satisfactory spectral characteristics.

The INADEQUATE spectra were all recorded at ambient temperatures in $CDCl_3$ solutions. Concentration of solutions were typically in the order of ~30% for the methyl benzoates and benzoyl chlorides. In the case of benzophenones they varied from 8% to 15% and needed the presence of trace amounts of $Cr(acac)_3$.

The pulse sequences used for the ^{13}C satellite spectra, based on Freeman et al.[4], is $90°(x)–\tau–180°(\pm y)–\tau–90°(x)–\Delta–90°(\phi)–$Acq.($\psi$), where $\tau = (2n + 1)/4J_{CC}$, 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. Optimum setting for direct coupling is when $n = 0$ and thus set at 3.5 ms for benzoyl chlorides and methyl benzoates, and at 4.5 ms for the benzophenones. Repetition rate of this sequence is 15 s for the former and 2 s for the latter which contained $Cr(acac)_3$. Reasonable signal to noise ratio was achieved in 12–20 h of acquisition. Errors in the $^1J_{C,C}$ measurements are estimated to be ±0.3 Hz.

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Registry No. 1 (R = 4-OCH_3), 121-98-2; 1 (R = 4-CH_3), 99-75-2; 1 (R = H), 93-58-3; 1 (R = 4-F), 403-33-8; 1 (R = 4-Cl), 1126-46-1; 1 (R = 4-Br), 619-42-1; 1 (R = 4-CF_3), 2967-66-0; 2 (R = 4-OCH_3), 100-07-2; 2 (R = 4-CH_3), 874-60-2; 2 (R = H), 98-88-4; 2 (R = 4-F), 403-43-0; 2 (R = 4-Cl), 122-01-0; 2 (R = 4-CF_3), 329-15-7; 2 (R = 3,5-$(CF_3)_2$), 785-56-8; 3 (R = 4-OCH_3), 90-96-0; 3 (R = 4-CH_3), 611-97-2; 3 (R = H), 119-61-9; 3 (R = 4-F), 345-92-6; 3 (R = 4-Cl), 90-98-2.

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Solvolysis of Allyl Arenesulfonates. Cautionary Comments concerning the N_{OTs} Scale of Solvent Nucleophilicities

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The rates of solvolysis of five allyl arenesulfonates are analyzed in terms of the extended Grunwald–Winstein equation. The l values are constant but the m values decrease slightly as the nucleofugality of the leaving group increases. The solvent nucleophilicity (N_{OTs}) values presently available in the literature are based upon a m value for methyl p-toluenesulfonate (tosylate) solvolysis of 0.3; it is demonstrated that a value of 0.55 is more appropriate. The previously reported l values and correlation coefficients for tosylate ester solvolyses are accurate and the "apparent" sensitivities to solvent ionizing power (m values) are easily corrected. However, for use in conjunction with solvent ionizing power scales for other leaving groups, N_{OTs} values based on the appropriate m value or, alternatively, $N_{Et_3O^+}$ values (based on triethyloxonium ion solvolysis) are required.

Recently, we used[1] the extended Grunwald–Winstein equation[2–4] (eq 1) to analyze the kinetic data of Sendega and co-workers for the solvolyses of allyl arenesulfonates[5–7] (eq 2). In eq 1, k and k_0 are the specific rates of solvolysis

$$\log (k/k_0) = lN + mY \qquad (1)$$

$$CH_2{=}CHCH_2OSO_2Ar + SOH \rightarrow CH_2{=}CHCH_2OS + ArSO_3H \qquad (2)$$

in the solvent under consideration, and in the standard (80% ethanol) solvent, l represents the sensitivity to solvent nucleophilicity values (N) and m represents the sensitivity to solvent ionizing power values (Y). The specific rates of solvolysis were correlated for a combination of ethanol, aqueous methanol, aqueous dioxane, and aqueous acetone systems.

Using N_{KL} values based on triethyloxonium ion solvolysis[8] and Y values based on *tert*-butyl chloride solvolysis,[9] it was found that as the nucleofugality of the arene-

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