Chemical Characterization of the Dimer 15. A solution of **15** in toluene was stirred under reflux for 2 days in the presence of a large excess of methanol. Trimethyl phosphate was identified by ^1H, ^{13}C, and ^{31}P NMR spectroscopy and by comparison of the spectroscopic data to those of an authentic sample. *N,N'*-Dimethylurea **17** and semicarbazide **18** were isolated by TLC ($CHCl_3$/EtOH 50/50, and $CHCl_3$/MeOH 66/33, respectively) and their spectra (^1H NMR, IR) compared with those of authentic samples.

Synthesis of Phosphorane Azide 4. Trimethylsilyl azide (1 g, 9 mmol) was added dropwise to a solution of 2-chloro-2,2'-spirobi[1,3,2-benzodioxaphosphole][15] in 40 mL of benzene. The solution was stirred for 2 h at room temperature. Volatile materials were removed at reduced pressure (15 mmHg). Crude **4** was obtained as highly deliquescent white crystals (1.09 g, 95%): ^{31}P NMR (C_6H_6) -27 ppm (s); ^1H NMR (C_6D_6) 6.9 [m, H (aromatic)]; IR (C_6D_6) 2140 ($P-N_3$), 1490 (P-O-C) cm^{-1}.

Photolysis of 4. A solution of **4** (289 mg, 1 mmol) in benzene (4 mL) was irradiated at 254 nm for 48 h. Removal of the solvent furnished the aminophosphorane **19** as white crystals (255 mg, 96%), mp 94-95 °C; ^{31}P NMR (C_6D_6) -27.1 ppm (s); ^1H NMR (C_6D_6) 3.0 (br d, $J(HP)$ = 15 Hz, 2 H, NH_2); 6.9 [m, 8 H, H(aromatic)]; IR (C_6D_6) 3520 and 3405 cm^{-1} (NH_2). Characterization of **19** was confirmed by comparison of its ^{31}P and IR data to those of an authentic sample prepared as indicated below.

Preparation of 2-Amino-2,2'-spirobi[1,3,2-benzodioxa-λ^5-phosphole] (19). Ammonia was bubbled into a solution of 1.1 g (3.9 mmol) of 2-chloro-2,2'-spirobi[1,3,2-benzodioxa-λ^5-phosphole] in 20 mL of dichloroethane during 30 min at O °C. The course of the reaction was monitored by ^{31}P NMR spectroscopy. The precipitate of ammonium chloride was filtered off, and the solvent was stripped off. A viscous residue remained which was washed with 10-mL portions of ether several times. The aminophosphorane **19** was finally obtained as a white powder (0.93 g, 90%). Anal. C, H, N, P. The spectroscopic properties of **19** obtained by this procedure were identical with those of the product formed in the photolysis of **4**.

Acknowledgment. Thanks are due to G. Bettermann for the preparation of phosphorane azide **1**, to the CNRS (ATP Concepts Nouveaux de l'Objectif Chimie fine) and Fonds der Chemischen Industrie, Frankfurt am Main, Germany, for financial support, and to Dr. H. J. Kleiner of Hoechst AG, Frankfurt am Main-Hochst, Germany, for generous supplies of dimethylphosphine oxide.

Registry No. 1, 66436-22-4; **2**, 89982-26-3; **3**, 89982-28-5; **4**, 72434-50-5; *cis*-**6**, 92269-73-3; *trans*-**6**, 92344-04-2; **9**, 89982-27-4; **10**, 92269-74-4; **11**, 92269-75-5; **13**, 79184-77-3; **15** (isomer 1), 92269-76-6; **15** (isomer 2), 92344-05-3; **19**, 89982-30-9; Me_3SiN_3, 4648-54-8; 1,3,5,7-tetramethyl-1,3,5,7-tetraaza-4-chloro-4λ^5-phosphaspiro[3.3]heptane-2,6-dione, 77507-70-1; 2-chloro-2,2'-spirobi[1,3,2-benzodioxaphosphole], 6857-81-4.

One-Bond $^{13}C-^{13}C$ NMR Coupling Constants in Substituted Acetophenones and Benzaldehydes and Their O-Protonated Carboxonium Ions[1]

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Abstract: One-bond $^{13}C-^{13}C$ NMR coupling constants in a series of substituted acetophenones and benzaldehydes and their O-protonated carboxonium ions were measured by natural-abundance ^{13}C NMR spectroscopy, using the INADEQUATE pulse sequence. These studies are of particular interest in regard to the effect of substituents on the nature of the electron-deficient carbonyl group. The measured $J_{C_{ipso}-C_{carbonyl}}$ values seemingly reflect the increased double bond character of the $C_{ipso}-C_{carbonyl}$ bond, and the substituent effects on these coupling constant values were analyzed in terms of inductive, resonance, and electronegativity effect of the substituent. We observed good linearity in the substituent effects on $J_{C_{ipso}-C_{carbonyl}}$ values within the acetophenone-benzaldehyde series as well as in their O-protonated carboxonium ions, indicating similarities of the closely related systems.

The coupling interaction between ^{13}C nuclei have not yet been extensively examined because of experimental difficulties. The 1.1% natural abundances of ^{13}C means that the probability for two ^{13}C nuclei to be neighbors is very low (10^{-4}). Initial efforts were made in different laboratories notably by Frei and Bernstein[3] to obtain the necessary data using doubly labeled materials.[2-4] The limited number of examples of one-bond $^{13}C-^{13}C$ coupling constants of each of the six combinations of hybridized carbons (sp^3-sp^3, sp^3-sp^2, sp^3-sp, sp^2-sp^2, sp^2-sp, and sp-sp) led to the conclusion that J_{CC} values are approximately correlated to the % s character of the orbitals making up the bond. The major limitation of these studies was the difficulty in obtaining a wider variety of doubly labeled compounds.

Theoretical descriptions of coupling between nuclear spins are based on Ramsey's theory[5] that coupling via electrons originates from three types of interaction between the magnetic moments due to the nuclear and electron spins. The three types are as follows: (a) orbital interaction with the magnetic field due to the orbital motion of 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[6-12] and, as a result, would be expected to correlate with the product

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(1) Presented at the ACS National Meeting held at Seattle, March 1983, Organic Division, Abstract No. 198. Considered Stable Carbocations, Part 253. For part 252, see: Olah, G. A.; Prakash, G. K. S.; Krishnamurthy, V. V. *J. Org. Chem.* **1983**, *48*, 5116.

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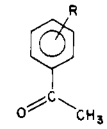
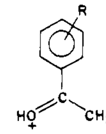
Table I. One-Bond ^{13}C–^{13}C Spin Coupling Constants[a] in Acetophenones and O-Protonated Acetophenones



in $CDCl_3$ at 20 °C



in FSO_3H at −35 °C

R	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	J_{CO,C_1}	J_{CO,CH_3}	R	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	R_{CO,C_1}	J_{CO,CH_3}
4-OCH_3	59.0	58.9	66.5	54.8	42.8	4-OCH_3	58.6	*b*	64.5	64.1	40.4
4-F	58.5	57.4	70.2	53.7	43.1	4-F	57.3	58.7	69.8	60.0	38.3
4-CH_3[c]	58.0	*b*	56.5	53.4	42.7	4-CH_3[d]	57.4	57.8	54.1	60.0	38.3
4-Cl	58.5	*b*	65.0	52.8	43.2	4-Cl	57.9	57.7	62.6	59.5	38.7
4-Br	58.7	55.7	63.6	52.7	42.9	4-Br	57.6	*b*	61.7	59.5	38.4
H	58.0	*b*	55.4	52.4	42.7	H	57.1	55.9	54.0	58.6	38.0
3-OCH_3[e]	60.7	68.3	67.0	52.3	42.9	3-OCH_3	*b*	*b*	*b*	58.3	38.7
3-F[f]	59.6	72.3	70.6	52.3	43.4	3-F	*b*	*b*	*b*	58.0	38.7
3-CF_3[g]	59.8	*b*	*b*	52.5	43.4	3-CF_3	*b*	*b*	*b*	58.4	38.4
4-CF_3	59.1	*b*	59.8	51.7	43.2	4-CF_3	58.3	56.9	*b*	57.9	38.4
4-CN	57.8	57.2	60.4	51.4	43.4						
3,5$(CF_3)_2$	59.2	61.1	59.9	52.1	44.1	3,5$(CF_3)_2$	*b*	*b*	*b*	58.3	41.8
4-C(=O)CH_3	57.7		57.7	51.5	43.0	4-$C(=OH)^+CH_3$[h]	58.7		58.7	56.0	38.4

[a] All coupling constants are in Hz. [b] Could not be measured accurately. [c] $J_{C_4-CH_3}$ = 43.4 Hz. [d] $J_{C_4-CH_3}$ = 47.4 Hz. [e] $J_{4,5}$ = 57.9 Hz, $J_{5,6}$ = 58.3 Hz, $J_{1,6}$ = 57.7 Hz. [f] $J_{4,5}$ = 56.6 Hz, $J_{5,6}$ = 56.8 Hz, $J_{1,6}$ = 59.0 Hz. [g] $J_{1,6}$ = 57.6 Hz. [h] In $FSO_3H:SbF_5$ (4:1).

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.

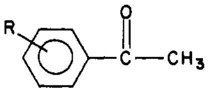
Recently, Contreras et al.[13] carried out molecular orbital calculations using the SCPT-INDO method in order to separate σ- and π-transmitted components of the Fermi contact, spin–dipolar, and orbital terms of ^{13}C–^{13}C coupling constants in several unsaturated hydrocarbons. It was observed that the Fermi contact interaction is mostly transmitted through the σ system, although there is also a π-transmitted component whose magnitude is similar to the average value of noncontact terms. On the other hand, the spin–orbital interaction requires the π system for transmitting the information, the component along the molecular axis being directly transmitted, i.e., originated in and carried by the π-electron system. Components of the spin–dipolar interaction show behavior similar to those of the spin–orbital components, but for some of them there is also a small σ component. These authors also observed that for one-bond couplings the π component of the Fermi contact term increases from a formal single bond to a formal double bond. While the σ component of the spin–dipolar term (for one-bond couplings) depends on the type of the bond and is larger for the formal single bond, the π component is smaller for the formal single bond. For spin–orbital term, however, while the σ component depends only slightly on the type of bond the π component is smaller for a single than for a double bond. Thus, it is clear that although the σ component is far more important, the contribution of the π component is definitely non-negligible, particularly in the substituent effect on ^{13}C–^{13}C coupling constants (SCC).

Although this method with the INDO level of approximation may not achieve quantitative agreement with the experimental values, many qualitative trends have been correctly reproduced. The use of ab initio methods with extended basis sets is limited to small molecular systems only. Earlier Gray et al.[14] also noted that neither simple hybridization theory nor effective nuclear charge densities are adequate by themselves to account for observed trends of J_{CC} values in some selected series of compounds. Thus, there has been considerable effort to provide experimental values of J_{CC}[15,16] and to find empirical correlations with other molecular properties which are dependent on the same electronic characteristics of the molecules.

The basic problem in observing the ^{13}C–^{13}C coupling constants in the NMR spectra of compounds with natural abundance ^{13}C is that of identifying the appropriate weak satellite signals on the sides of strong ^{13}C lines. The INADEQUATE pulse sequence technique developed by Freeman et al.[17] enables one to investigate one-bond and long-range carbon–carbon couplings by suppressing the strong signals from molecules with isolated ^{13}C nucleus.

Recently using the INADEQUATE pulse sequence we reported[18] a study of substituent effect on the one-bond ^{13}C–^{13}C NMR coupling constants (SCC) in 1- and 2-substituted adamantane derivatives and showed that this technique can be used to study the substituent and stereochemical effects on J_{CC} values. Moreover, ^{13}C–^{13}C coupling constants can be routinely used as a tool in ^{13}C NMR peak assignment in addition to the more commonly used ^{13}C–^{1}H coupling constants and ^{13}C chemical shifts.

In continuation of our interest in the substituent effects on the nature of electron-deficient carbon centers,[19-21] we undertook a study of ^{13}C–^{13}C coupling constants in a series of substituted acetophenones, **1**, and benzaldehydes, **2**, and their corresponding O-protonated carboxonium ions, **3** and **4**.



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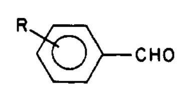

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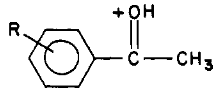

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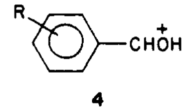

4

Results and Discussion

The ^{13}C–^{13}C NMR coupling constants in all the neutral compounds were measured in $CDCl_3$ at room temperature, and those in the O-protonated carboxonium ions were measured in FSO_3H solution at −35 °C. The coupling constants are listed in Tables I and II.

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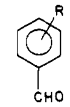
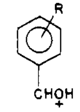
Table II. One-Bond $^{13}C-^{13}C$ Spin Coupling Constants[a] in Benzaldehydes and O-Protonated Benzaldehydes



in $CDCl_3$ at 20 °C

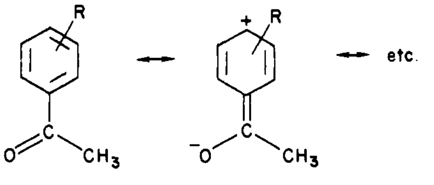


in FSO_3H at −35 °C

R	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	J_{CO,C_1}	R	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	J_{CO,C_1}
4-OCH_3	58.1	59.1	66.4	55.5	4-OCH_3	54.9	55.3	61.5	65.5
4-F	57.9	57.9	70.5	54.3	4-F	58.4	*b*	69.0	61.1
4-CH_3[c]	58.0	*b*	56.1	54.0	4-CH_3[d]	56.7	*b*	53.7	61.1
4-Cl	58.5	54.2	64.8	53.9	4-Cl	*b*	*b*	62.2	60.3
4-Br	58.6	56.7	63.1	53.8	4-Br	*b*	58.3	60.1	60.1
H	59.0	*b*	55.4	53.0	H	*b*	*b*	54.0	59.3
3-OCH_3[e]	60.4	69.4	67.0	52.9	3-OCH_3	*b*	*b*	*b*	59.0
3-F[f]	59.5	72.7	70.6	53.0	3-F	*b*	*b*	*b*	58.5
3-CF_3[g]	61.0	*b*	*b*	53.1	3-CF_3	*b*	*b*	*b*	58.9
4-CF_3	58.3	57.7	*b*	52.4	4-CF_3	*b*	59.2	*b*	58.5
4-CN	58.1	57.7	60.4	52.7					
3,5-$(CF_3)_2$	59.8	60.1	61.1	52.9	3,5-$(CF_3)_2$	*b*	*b*	*b*	59.0

[a] All coupling constants are in Hz. [b] Could not be measured accurately. [c] $J_{C_4,CH_3} = 43.3$ Hz. [d] $J_{C_4-CH_3} = 47.2$ Hz. [e] $J_{4,5} = 57.9$ Hz, $J_{5,6} = 56.7$ Hz, $J_{1,6} = 59.0$ Hz. [f] $J_{4,5} = 56.8$ Hz, $J_{5,6} = 56.9$ Hz, $J_{1,6} = 58.7$ Hz. [g] $J_{1,6} = 56.3$ Hz.

The substituent effect on the $^1J_{CC}$ values in monosubstituted benzene derivatives has been reported and discussed earlier by Wray and Ernst.[22] The coupling constant of major interest in the present study is $J_{C_{ipso}-C_{carbonyl}}$. In neutral substituted acetophenones its value ranges from 51.4 to 54.8 Hz, with that of parent acetophenone being 52.4 Hz. Electron-donating substituents such as *p*-OCH_3, *p*-F, *p*-CH_3, etc., which can stabilize a positive charge in the aromatic ring, as in the resonance structure **5**, increase the double bond character between the ipso and the carbonyl carbon.



1 **5**

This is reflected in the $^{13}C-^{13}C$ coupling constant between them. Thus, substituted acetophenones with electron-donating substituents show a higher $^{13}C-^{13}C$ coupling constant between the ipso and the carbonyl carbon compared to the parent acetophenone. Moreover, the higher the electron-donating ability of the substituents the higher is the $J_{C_{ipso}-C_{carbonyl}}$ value. Similarly, electron-withdrawing substituents in the ring decrease the contribution of the cannonical form **5** to the total structure and thus decrease the double bond character between the ipso and the carbonyl carbon as compared to the parent system. Thus substituted acetophenones with strongly electron-withdrawing substituents, such as *p*-CF_3, *p*-CN, and *p*-$COCH_3$, show less $^{13}C-^{13}C$ coupling constant values. The fluoro and methoxy substituents at the meta position are also weak inductively electron withdrawers and thus the $J_{C_{ipso}-C_{carbonyl}}$ values are slightly less, almost within the experimental error, than that of acetophenone. Thus the $J_{C_{ipso}-C_{carbonyl}}$ values in substituted acetophenones reflect the extent of conjugation between the carbonyl group and the aromatic ring (in other words, the extent of double bond character between the ipso and the carbonyl carbon) and thus in turn reflect the electron-withdrawing or -donating ability of the substituent.

The effect of the substituents on $J_{C_{ipso}-C_{carbonyl}}$ is even more significant in the case of the corresponding O-protonated acetophenones where the electron demand of the carbonyl carbon is increased. Whereas the change in the $J_{C_{ipso}-C_{carbonyl}}$ value, in neutral acetophenones, covers only a range of 3.1 Hz (from 51.7 to 54.8 Hz) on going from the electron-withdrawing (*p*-CF_3) to most electron-donating (*p*-OCH_3) substituents, $J_{C_{ipso}-C_{carbonyl}}$ in the O-protonated acetophenones changes by 6.2 Hz (from 57.9 to 64.1 Hz), reflecting the increased electron demand by the carbonyl carbon in the case of protonated acetophenones. The increase in $J_{C_{ipso}-C_{carbonyl}}$ of 6.2 Hz (from 51.7 to 57.9 Hz) upon protonation of *p*-(trifluoromethyl)acetophenone indicates that even with this strongly electron-withdrawing substituent the deactivated aryl group is still capable of contributing to the stabilization of the electron-deficient center by its resonance effect.

Similar analysis of the $J_{C_{ipso}-C_{carbonyl}}$ value in benzaldehydes and O-protonated benzaldehydes reveals that these values show the same trend as those in acetophenones and O-protonated acetophenones.

The effect of substituent on the ^{13}C chemical shift in a series of substituted aromatic carbonyl compounds,[23] benzonitriles,[24] and styrenes[25,26] has been studied earlier. The carbonyl, cyano, and α-styryl carbon chemical shifts in these systems, respectively, show interesting substituent effects. Both electron-donating and electron-withdrawing substituents shield the carbon in question (for example, the carbonyl carbon in acetophenones). The substituent effect on the ^{13}C chemical shift (SCS) has been analyzed by a dual substituent parameter (DSP), eq 1,[27] where the SCS values are treated as a combination of inductive ($\rho_I\sigma_I$ term) and resonance ($\rho_R\sigma_R$ term) term) components. The ρ_I values for the

$$SCS = \Delta\delta = \rho_I\sigma_I + \rho_R\sigma_R \qquad (1)$$

acetophenone and benzaldehyde series are −2.6 and −3.0, respectively, whereas for the protonated acetophenones it is +5.3. The ρ_R values for the acetophenone, benzaldehyde, and protonated acetophenones are +0.8, +1.0, and +10.9, respectively. The negative ρ_I value in the neutral series is indicative of "reverse" SCS effect, i.e., electron-withdrawing groups cause an upfield shift. This has been explained as due to localized inductive π-polarization effect. When the substituent is an inductive electron-withdrawing group (R), a dipole on R or near the C–R bond is set up. The interaction of this dipole through the space of the molecular cavity (partially transmitted via molecular lines of force)[28] results in the π polarization as shown (**7**). The net result is that the inductive withdrawing substituent increases the electron density around the carbonyl carbon and hence causes shielding. Whereas, elec-

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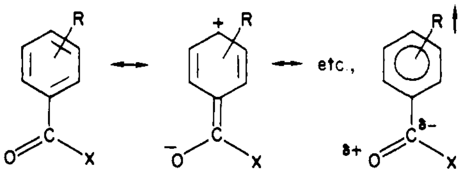


5 **6** **7**

X = H or CH_3

resonance effect

localized inductive π-polarization effect

tron-donating substituents, as expected, due to their ability to stabilize a positive charge in the ring, cause shielding of the carbonyl carbon. Thus, both electron-donating and -withdrawing substituents cause shielding of the carbonyl carbon in substituted acetophenones and benzaldehydes.[23]

The positive ρ_I value of 5.3 for the protonated acetophenone indicates a "normal" SCS effect, i.e., electron-withdrawing group deshields the carbonyl carbon. This is understandable because the carbonyl π-bond order is substantially decreased (though not completely diminished) upon protonation and thus π polarization (if any) is only a minor contributor to the SCS value. It must be pointed out that the most electron-withdrawing substituent studied by Brownlee et al.[23] is 4-CF_3 for the protonated acetophenone series. The normal SCS effect (as predicted from resonance and inductive effects alone) was observed up to this point. However, a stronger electron-withdrawing group such as 3,5-$(CF_3)_2$ has been used in the present work (cf. Table III). The carbonyl carbon in O-protonated 3,5-bis(trifluoromethyl)acetophenone, contrary to the expected deshielding, resonates at the same chemical shift as that in O-protonated 4-(trifluoromethyl)acetophenone (221.9 ppm), although it is still deshielded from that in O-protonated acetophenone (219.0 ppm). The carbonyl carbon in O-protonated benzaldehydes also behave similarly.

Recently, Brown and Periasamy[29] analyzed the carbonyl chemical shift of protonated acetophenones by the single substituent parameter (SSP) method using σ^{C^+} substituent constants, which is essentially the application of the Gassman–Fentiman tool of increasing electron demand to the carbonyl chemical shift. The σ^{C^+} substituent constants were developed by Brown et al.[30] which are considered to take into account the true electron demand of a carbocationic center in the superacid media. Since the σ^{C^+} constants were defined by linear relationship with the ^{13}C NMR chemical shifts of the cationic carbon of 1-aryl-1-cyclopentyl cations, its use in the present study is essentially similar to the previously employed method of Farnum[31] and Olah[19] in the application of the Gassman–Fentiman tool of increasing electron demand. The $\Delta\delta_{\text{carbonyl}}$[32] in protonated acetophenones and protonated benzaldehydes are plotted against σ^{C^+}, Figures 1 and 2. It can be seen that in both cases linearity was observed with electron-donating substituents and the values for electron-withdrawing substituents deviate from linearity.

The general principle basic to the application of the Gassman–Fentiman tool of increasing electron demand is simply this: if a parameter for a number of structurally related systems shows a linear correlation with all of them and another apparently structurally related system is found in which this parameter deviates from linearity, then there must be some mechanism operating in the new system which is not common to all the others to account for the deviation. Note that the principle does not state that if a deviation is not found the mechanism is not operating. Nor does it state that if two systems show the same or similar deviations the same mechanism must be operating in both cases. Application of this method with the understanding of the above principle has proved to be of considerable use[33] in determining the onset of π, πσ, or σ delocalizations in various carbocationic systems. The deviation observed in the σ^{C^+}–$\Delta\delta_{\text{carbonyl}}$ plot for the O-protonated acetophenones has been interpreted[29] as due to π polarization. As pointed out earlier the carbonyl π-bond order is substantially decreased, but not completely diminished, upon protonation. In other words, the protonated acetophenones has substantial contribution from the carboxonium ion structure, **8**, along with the α-hydroxycarbenium ion structure **9**. Thus, the polarization of the carbonyl π bond in protonated acetophenones becomes noticeable only with electron-withdrawing groups.

Table III. Carbonyl Chemical Shifts in O-Protonated Acetophenones and Benzaldehydes

R	σ^{C+} [b]	O-protonated acetophenones		O-protonated benzaldehydes	
		$\delta_{C}O$	$\Delta\delta_{CO}$(SCS)[c]	δ_{CO}	$\Delta\delta_{CO}$(SCS)[c]
4-OCH_3	−2.02	208.2	−10.8	191.5	−12.6
4-CH_3	−0.67	215.5	−3.5	200.2	−3.9
4-F	−0.40	216.3	−2.7	201.3	−2.8
4-Cl	−0.24	217.7	−1.3	202.5	−1.6
4-Br	−0.19	218.2	−0.8	203.0	−1.1
H	0.00	219.0	0.0	204.1	0.0
3-OCH_3		220.0	+1.0	204.7	+0.6
3-F	+0.35	220.1	+1.1	205.4	+1.3
3-CF_3	+0.56	220.9	+1.9	206.3	+2.2
4-CF_3	+0.79	221.9	+2.9	207.3	+3.2
3,5-$(CF_3)_2$	+1.03	221.9	+2.9	207.3	+3.2

[a] All chemical shifts are measured in FSO_3H (10% w/v solutions) at −35 °C and are reported in ppm with reference to external Me_4Si. [b] Reference 30. [c] Substituent effect on ^{13}C chemical shift reported in ppm ($\Delta\delta_{CO} = \delta_{CO}(R) - \delta_{CO}(H)$).

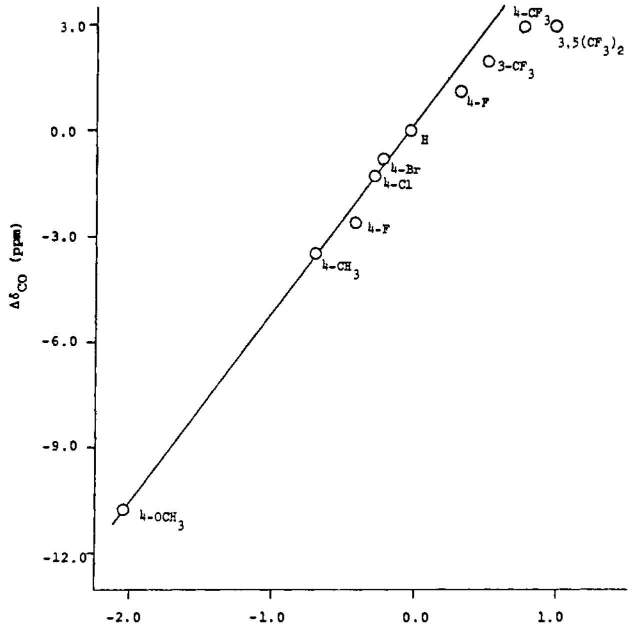
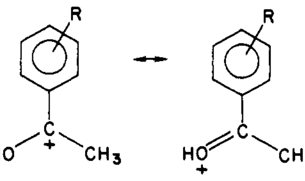


Figure 1. Plot of $\Delta\delta_{CO}$ in O-protonated acetophenones vs. σ^{C^+}



9 **8**

However, on the basis of a recent study on the tool of increasing electron demand in allyl and propargyl cation systems,[34] we have

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[29] Brown, H. C.; Periasamy, M. *J. Org. Chem.* **1983**, *48*, 3386.

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[32] $\Delta\delta_{\text{carbonyl}}$ is the difference in carbonyl chemical shift between the parent and the substituted derivatives.

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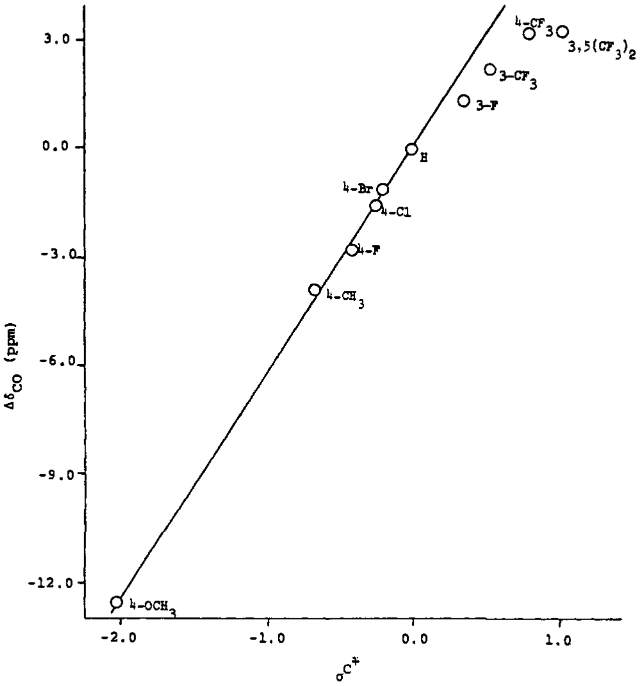

Figure 2. Plot of $\Delta\delta_{CO}$ in O-protonated benzaldehydes vs. σ^{C^+}.

shown the unimportance of π polarization in carbocations. Thus, the deviation observed in the σ^{C^+}–$\Delta\delta$ carbonyl plots (Figures 1 and 2) for the O-protonated acetophenones and benzladehydes can also be explained as due to an increased oxygen participation (i.e., increased contribution of the mesomeric structure **8**) with increasingly electron-withdrawing substituents. Alternatively, the deviation could be due to a combination of both the π-polarization effect and increased oxygen participation.

One can analyze the ^{13}C–^{13}C NMR coupling constant between the ipso and the carbonyl in acetophenone and O-protonated acetophenones in light of the resonance, inductive, and inductive π-polarization effects. As pointed out earlier, in neutral as well as in protonated acetophenones electron-donating substituents increased the C_{ipso}–$C_{carbonyl}$ coupling constant and electron-withdrawing substituents decrease the coupling constant in relation to the parent system. This trend can simply be explained qualitatively on the basis of a combination of inductive and resonance effects alone. Only 3,5-bis(trifluoromethyl)- (which is stronger electron-withdrawing group than 4-trifluoromethyl) substituted system deviates from the expected trend. The C_{ipso}–$C_{carbonyl}$ coupling constant in 3,5-bis(trifluoromethyl)acetophenone and the O-protonated 3,5-bis(trifluoromethyl)acetophenone is slightly higher than those in the corresponding 4-(trifluoromethyl)-substituted system. However, the coupling constant in 3,5-bis(trifluoromethyl)-substituted systems is still less than that in the parent system. Another item to be noted in this context is the C_{ipso}–$C_{carbonyl}$ coupling constant in 3-(trifluoromethyl)-substituted systems. According to the σ,[35] σ^+,[36] or σ^{C+} [30] substituent constants, a CF_3 group at the meta position is only slightly less electron withdrawing than the one in the para position. In light of this one would expect the C_{ipso}–$C_{carbonyl}$ coupling constant in 3-(trifluoromethyl)acetophenone to be very close to that in 4-(trifluoromethyl)acetophenone. However, its value is practically the same as that of acetophenone. This difference in coupling constant between 3-(trifluoromethyl)- and 4-(trifluoromethyl)acetophenones has to be the effect of moving a strongly electronegative CF_3 group one bond closer to the bond in question. It is known that electronegative atoms increases C_α–C_β and C_β–C_γ coupling constants in aliphatic systems.[18] Thus, one can argue that any decrease in the C_{ipso}–$C_{carbonyl}$ coupling constant in 3-(trifluoromethyl)acetophenone due to a decrease in the π-bond order is probably compensated by an increase in the coupling constant due to the "electronegativity" effect. If we extend the same argument to the 3,5-bis(trifluoromethyl) system, it is not surprising that the C_{ipso}–$C_{carbonyl}$ coupling constant in 3,5-bis(trifluoromethyl)acetophenone is higher than that in 4-(trifluoromethyl)acetophenone in spite of the fact that 3,5-$(CF_3)_2$ is a stronger electron-withdrawing group than 4-CF_3.

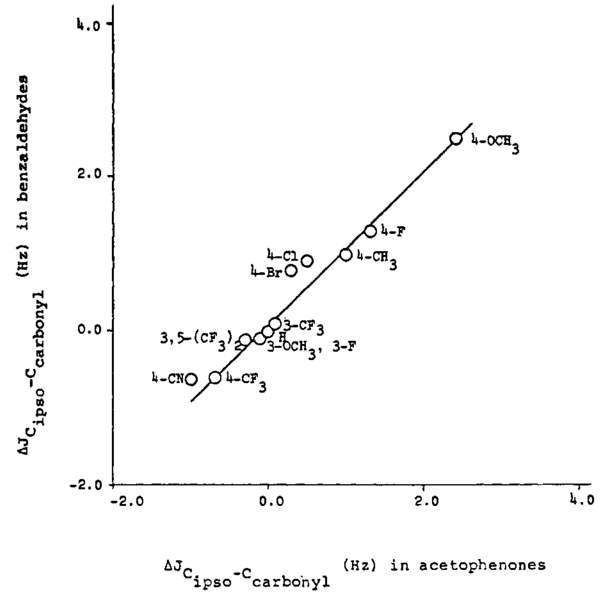

Figure 3. Plot of $\Delta J_{C_{ipso}-C_{carbonyl}}$ in benzaldehydes vs. those in acetophenones.

Alternatively, one can explain the deviation of the C_{ipso}–$C_{carbonyl}$ coupling constant in 3,5-bis(trifluoromethyl)acetophenone from the expected trend as due to the "π-polarization" effect. One can argue that the effect of π polarization on the ^{13}C–^{13}C NMR coupling constant is small and comes into picture only with strongly electron-withdrawing substituents such as 3,5-$(CF_3)_2$. Since the π-polarization effect with electron-withdrawing groups works against the usual resonance and inductive effect, the C_{ipso}–$C_{carbonyl}$ coupling constant in 3,5-bis(trifluoromethyl)acetophenone is more than that expected from resonance and inductive effects alone. However, such an agreement will not explain the anomalous behavior of the *m*-CF_3 group. Thus, the explanation on the basis of "electronegativity effect" seems to be better than the π-polarization effect for the anomalous behavior of 3,5-$(CF_3)_2$ and the *m*-CF_3 groups.

Another item of importance in this context is that observed in di-O-protonated *p*-diacetylbenzene (cf. Table I). The $J_{C_{ipso}-C_{carbonyl}}$ for this ion is 56.0 Hz, considerably less than that in protonated 4-(trifluoromethyl)acetophenone. The protonated acetyl group in the para position is a strongly electron-withdrawing group [σ^{C^+} = 1.60[20] as compared to 1.03 for 3,5-$(CF_3)_2$ and 0.79 for 4-CF_3] and as expected decreases the $J_{C_{ipso}-C_{carbonyl}}$ value. If the π-polarization effect were the reason for the anomalous effect of the 3,5-$(CF_3)_2$ group, then the $J_{C_{ipso}-C_{carbonyl}}$ value in diprotonated *p*-diacetylbenzene should be expected to be even more anomalous. However, the fact that the *p*-O-protonated acetyl group exhibits a "normal" substituent effect is a strong support for the explanation based on the "electronegativity effect".

An attempted plot of the $\Delta J_{C_{ipso}-C_{carbonyl}}$ (difference between the C_{ipso}–$C_{carbonyl}$ coupling constant in substituted system and that in the parent) with any of the known Hammett substituent parameter (σ, σ^+, σ^{C^+}) does not show any linear correlation. This is understandable because the ΔJ values represent the change in the electronic environment around *both* the ipso and the carbonyl carbons caused by the substituent. An excellent linear correlation (r = 0.98) is indeed observed when the $\Delta J_{C_{ipso}-C_{carbonyl}}$ values in substituted benzaldehyde are plotted against the corresponding values in substituted acetophenone (Figure 3). This indicates

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(34) Prakash, G. K. S.; Krishnamurthy, V. V.; Olah, G. A.; Farnum, D. G. *J. Am. Chem. Soc.*, submitted for publication.

(35) Hammett, L. P. *Chemical Rev.* **1953**, *17*, 125.

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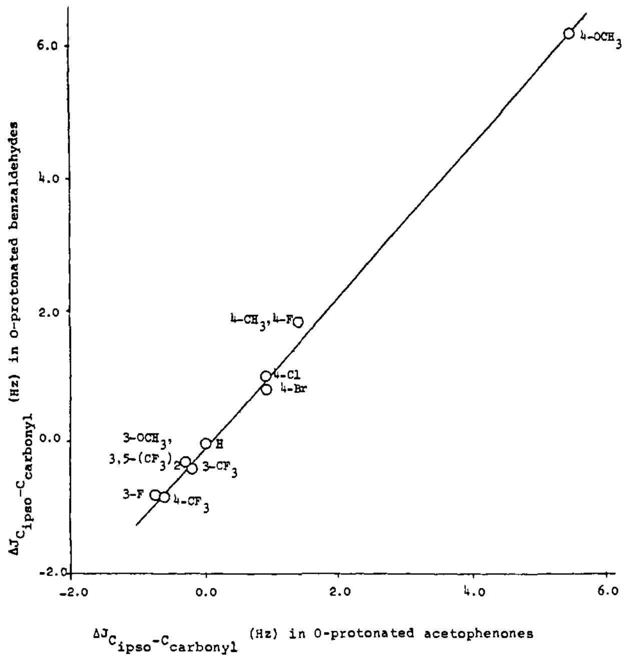

Figure 4. Plot of $\Delta J_{C_{ipso}-C_{carbonyl}}$ in O-protonated benzaldehydes vs. those in O-protonated acetophenones.

that there is a linear free energy relationship between ΔJ values of two similar system. A plot of $\Delta J_{C_{ipso}-C_{carbonyl}}$ 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 $\tau \simeq (2n + 1)/4J_{CC}$, 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-$(CF_3)_2C_6H_3$Ac, 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-$(CF_3)_2C_6H_3$CHO, 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_{C_1,CO^+} values were qualitatively compared with the $J_{C_1,CN}$ 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_{C_3,C_4} or J_{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_{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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