Solvent Effects in Carbon-13 Nuclear Magnetic Resonance. Electronic Perturbation of Aromatic Systems[1]

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Abstract: ^{13}C chemical shifts of phenyl ring carbons in substituted benzenes can be used to monitor changes in charge distribution at those carbons. Strong solute–solvent interactions such as hydrogen bonding to basic substituents result in significant changes in ring carbon chemical shifts. The changes in ^{13}C shifts are related to the electronic perturbation of the substituent and the ring system in a near quantitative manner. Studies of these solvation effects in relatively dilute solution are facilitated by the use of Fourier transform (FT) techniques. Dilution curves indicate that for groups such as $-OCH_3$ or $-COCH_3$ in CF_3COOH, a 10–15 mol % solute concentration effectively simulates infinite dilution insofar as electronic perturbation of the solute is concerned. By use of para ^{13}C resonances, estimates of σ^+ values can be obtained for most substituents in most media.

In contrast to the extensive investigation of solvent effects on proton chemical shifts, much less attention has been paid to the effects of solvents on ^{13}C chemical shifts. Solvent dependence of the ^{13}C chemical shifts of methyl iodide,[2] acetonitrile,[2] and chloroform[3] has been reported. Extensive solvent studies have been made on ^{13}C resonances of carbonyl carbons,[4–6] which were more easily observable by the ^{13}C instrumental methods of the early 1960's. The carbonyl carbon of acetone, for example, shows a ^{13}C chemical shift range of some 40 ppm over a variety of solvents.[4] Surprisingly little work, however, has been reported on the effect of solvents on ^{13}C chemical shifts of substituted aromatic systems. Some work relative to the effect of solvents on the ^{13}C chemical shifts of phenol,[7] benzonitrile,[8] *N,N*-dialkylanilines,[9] and acetophenones[10] has been reported. Other than for the case of phenol little regularity was observed; for that case attention was focused primarily upon the carbon of substituent attachment; a definite trend to lower field was observed as the basicity of the solvent was increased. The present work examines in detail the effect of solvent upon the electronic character of substituted aromatics.

The theoretical treatment of ^{13}C chemical shifts has been extensively discussed[11–16] particularly for aromatic systems. The total shielding constant, σ, for a particular nucleus has been approximated by a sum of three terms[17]

$$\sigma = \sigma_d + \sigma_p + \sigma'$$

where σ_d is the diamagnetic contribution, σ_p the paramagnetic contribution, and σ' the contribution from neighboring groups per nuclei. The paramagnetic term, σ_p, has been shown to dominate in the case of ^{13}C chemical shifts (>90%).[11] The principal factors affecting this term are the charge polarization, variation in bond order, and the average excitation energy. The contributions of these and other factors have received considerable coverage.[18–21]

The use of ^{13}C chemical shifts as a probe in the understanding of the electronic nature of aromatic and aromatic-like systems has been further aided by the use of Hammett σ constants. Particular success has been achieved in accounting for the chemical shifts at the para positions of monosubstituted benzenes.[22] Meta carbons *vs.* σ have shown less regularity.[23,24] Correlation of chemical shifts in 2- and 3-substituted pyridines with σ constants has been noted.[25,26] Plots of para ^{13}C chemical shifts in monosubstituted benzenes *vs.* σ and σ^+ have been used to evaluate new substituent constants in the case of PZ_n-substituted benzenes.[27]

In the present work an examination is made of the electronic nature of substituted aromatics in various solvent media. The available tools, ^{13}C nmr chemical shifts and approximate molecular orbital calculations (CNDO/2 and INDO), are used as experimental and theoretical probes.

Results and Discussion

While the ^{13}C chemical shifts for ring carbons of monosubstituted benzenes have been reported in the

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literature, measurements made on older instruments have an accuracy of +0.5-1 ppm.[28] In the present case a Varian Associates XL-100-15 nmr spectrometer equipped for both frequency sweep and Fourier transform operation yielded chemical shifts with an accuracy of ±0.04 ppm (<1 Hz) relative to internal benzene. In addition, the use of Fourier methods allowed rapid measurement in solutions at less than 10% molar dilution, for natural abundance ^{13}C measurements. Chemical shifts for the substituted benzenes of interest are shown in Table I.

Table I. ^{13}C Chemical Shifts[a] of Substituted Benzenes in CCl_4

Substituent	Position C_1	 Ortho	 Meta	 Para
Br	−5.5	+3.4	+1.7	−1.6
CF_3	−9.0	−2.2	+0.3	+3.2
CH_3	+8.9	+0.7	−0.1	−2.9
CN	−15.4	+3.6	+0.6	+3.9
CN, 4-Cl[b]	−16.6	+5.1	+1.3	+10.8
CN, 4-F[b]	−19.0	+6.1	−11.5	+36.1
C≡C—H	−6.1	+3.8	+0.4	−0.2
1,4-Di-C≡C—H	−5.6	+3.8		
$COCF_3$	−5.6	+1.8	+0.7	+6.7
$COCH_3$	+9.1	+0.1[c]	+0.0[c]	+4.2
COCl	+4.6	+2.4	0.0	+6.2
CHO	+8.6	+1.3[c]	+0.6[c]	+5.5
COOH	+2.1	+1.5	0.0	+5.1
CO—C_6H_5	+9.4	+1.7	−0.2	+3.6
Cl	+6.2	+0.4	+1.3	−1.9
F	+34.8	−12.9	+1.4	−4.5
H	0.0			
NCO	+5.7	−3.6	+1.2	−2.8
NH_2	+18.0	−13.3	+0.9	−9.8
NO_2	+20.0	−4.8	+0.9	+5.8
OCH_3	+31.4	−14.4	+1.0	−7.7
OH	+26.9	−12.7	+1.4	−7.3

[a] Parts per million relative to internal benzene standard positive shifts downfield (based on TMS convention); [solute] *ca.* 10% in carbon tetrachloride. [b] C_1 = CN. [c] Ortho and meta assignments unconfirmed.

As discussed, previous workers have correlated ^{13}C chemical shifts of carbons para to substituents in monosubstituted benzenes with Hammett type σ parameters and with electron densities obtained from molecular orbital calculations.[22,23,28] However, the inaccuracy of chemical-shift measurements made on older instruments coupled with the use in early work of low order molecular orbital calculations, while not invalidating such correlations, places constraints on their utility.

Table II. CNDO/2 Calculated Total Charge Densities of Substituted Benzenes (× 10^3)

Substituent	Position C_1	 Ortho	 Meta	 Para
CF_3	−28	+33	+1	+16
CH_3	+39	−14	+14	0
CN	+13	+5	+13	+19
CN, 4-F	+48	+35	−58	+224
CN, 4-Cl	+19	+4	+22	+97
C≡C—H	+35	0	+13	+12
1,4-Di-C≡C—H	+41	+6		
$COCF_3$	−37	+17	+11	+36
$COCH_3$	−44	+15	+7	+26
CHO	−13	+23	−1	+18
CO—C_6H_5	−36	+12	+7	+28
Cl	+91	+16	+4	+9
F	+231	−59	+33	−9
H	+6			
NH_2	+159	−53	+28	−33
NO_2	+67	+7	+10	+20
OH	+176	−55	+31	−14
NH_3^+	+62	−2	+39	+44

In the present study, CNDO/2 (both Pople and Wiberg parameters)[29,30] and INDO SCF-MO calculations were performed and plots of charge density at each position made *vs.* observed ^{13}C chemical shifts. Experimental geometries were used in the calculations where available;[31] in other cases, reasonable geometries were assumed. For some cases several geometries were tried. CNDO/2 using Pople parameters gave the best overall correlation, although CNDO/2 (Wiberg parameters) and INDO gave nearly comparable results. Table II lists the CNDO/2 total charge densities calculated for the compounds of interest. Total charge densities were found to give better overall correlation than π charge densities do, although both are equivalent for consideration of the para position only. The σ electronic distribution is undoubtedly important. Figure 1 shows a plot of total charge density *vs.* chemical shift for the para positions of 14 substituted aromatics (correlation coefficients (r) = 0.95). Reasonable correlation is obtained. A plot of total charge density *vs.* observed ^{13}C chemical shifts for *all aromatic carbons* is shown in Figure 2 (correlation coefficient (r) = 0.93). A correction has been applied to the calculated total charge densities for carbons of attachment of conjugated double and triple bonded functional groups in the amount of +0.105 and −0.050 charge unit, respectively. Prior to such correction a correlation coefficient, r = 0.78, was obtained. The corrections were derived as follows. From a plot of total charge density *vs.* ^{13}C chemical shifts for the aromatic carbon atoms in substituted acetophenones (p-NO_2, p-F, p-OH, p-OMe, p-Me, and m-OH) it was found that the line determined by the carbons bearing the acetyl function was parallel to the line determined by the other ring carbons but shifted 0.105 charge unit to higher electron density. A similar correction of 0.050 unit (to lower electron density) was made for the carbons of attachment in cyano- and ethynylbenzenes. CNDO/2 calculated total charge densities incorrectly predict the magnetic environment at the carbons of attachment bearing conjugated double and triple bonds.[12] The shifts appear regular; thus the application of correction factor seems reasonable and correlation is greatly enhanced.[32]

CNDO/2 charge densities have been previously reported[33,34] for a number of monosubstituted benzenes. A comparison of these data with the present results indicates that geometry is critical.[35] Where geometries

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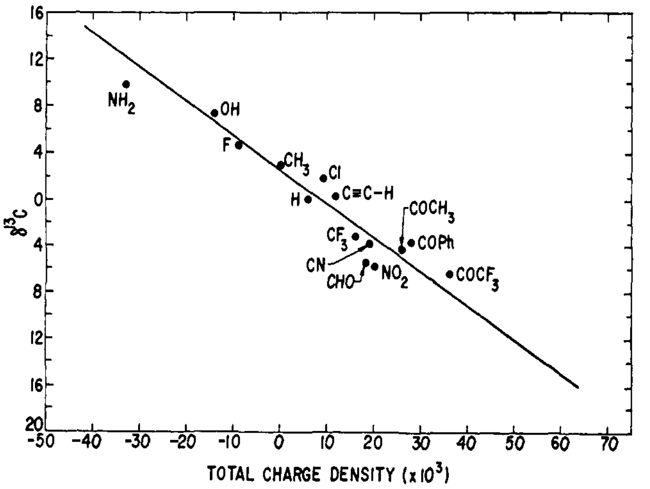

Figure 1. Plot of ^{13}C chemical shifts *vs.* total charge densities (CNDO/2) for the para position of monosubstituted benzenes.

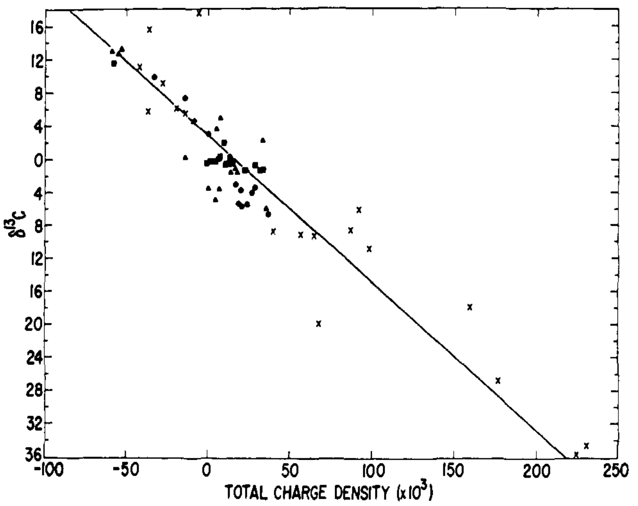

Figure 2. Plot of ^{13}C chemical shifts *vs.* total charge densities at all aromatic carbons for 17 mono- and disubstituted benzenes: ×, point of attachment; ○, ortho; △, para; □, meta positions.

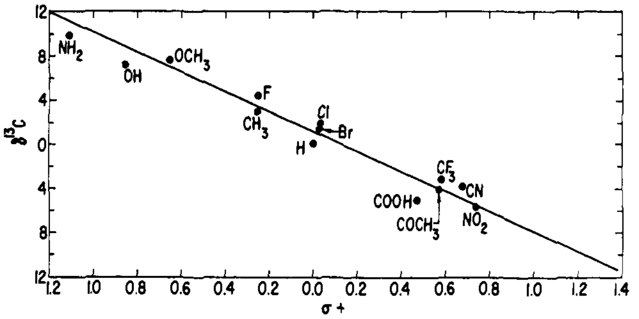

Figure 3. Plot of ^{13}C chemical shifts at the para positions for monosubstituted benzenes *vs.* σ^+.

are known, charge density discrepancies on the order of 0.025 charge unit at the point of attachment, 0.015 charge unit at the ortho and para positions, and 0.005 charge unit at the meta positions are observed relative to reasonable assumed geometries (geometrical differences *ca.* 0.02 Å). Such charge discrepancies are, in some cases, comparable to the calculated charge densities. This is particularly true for substituents like nitro which are known[31] to induced considerable distortion of the benzene ring, or in those cases such as acetophenone where the rotational angle of the conjugated substituent is important.

With this uncertainty in the charge densities based solely on the geometries used, errors and limitations in the CNDO/2 method itself notwithstanding, it seemed of limited value to include other factors in direct calculation of the ^{13}C chemical shifts; thus Figures 1 and 2 serve only as a first approximation to correlation.

Performing CNDO calculations on monosubstituted benzenes is both expensive and time consuming. The correlation obtained (Figure 1) of para ^{13}C chemical shifts *vs.* total charge density is reasonably good. Using Figure 1 it is possible to estimate the total charge density at the para carbon atom for a substituted benzene to ±0.005 charge unit simply by measuring the ^{13}C nmr spectrum, determining the para carbon resonance, and reading the appropriate total charge density from the graph.

While plots of ^{13}C chemical shifts against total charge density provide considerable predictive ability, most chemists find Hammett σ parameters more meaningful. Considerable use is made of various σ constants in much of the organic chemistry literature. Studies of rates of reactions, equilibria, and organic mechanistic studies all have involved the use of σ parameters of various kinds. Figure 3 shows a plot of ^{13}C chemical shifts *vs.* σ^+,[36] correlation coefficient, $r = 0.98$ ($r = 0.91$ was obtained for a similar plot against σ). By using Figure 3, σ^+ values for any substituent can be found simply by measuring the para carbon ^{13}C chemical shift for the appropriate monosubstituted benzene and reading off the corresponding σ^+. Table III gives five examples.

Table III. Estimates of σ^+ Values Based upon ^{13}C Nmr Chemical Shifts at Para Positions of Monosubstituted Benzenes

Substituent	σ^+
NCO	−0.19
$CH{=}CH_2$	+0.10
$CO{-}C_6H_5$	0.51
CHO	0.73
COCl	0.79
$COCF_3$	0.85
$C{\equiv}C{-}H$	0.10

Solvent Effects. There is little reason to believe that σ^+ values for a series of substituents should remain constant in strongly interacting solvent media. In various solvents an individual substituent may behave quite differently; this should be reflected in the nature of the substituent's electronic effect on the attached aromatic ring. Some groups would be expected to interact strongly in hydrogen bonding media, for example.

One compound which would be expected to show large changes in behavior depending upon solvent is acetophenone. Figure 4 shows that the para carbon ^{13}C chemical shift of acetophenone on dilution in tri-

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Table IV. Para ^{13}C Chemical Shifts for Monosubstituted Benzenes in Various Solvents

Substituent solvent[b]	^{13}C Shifts[a]						
	CCl_4	C_6H_{12}	CH_3COCH_3	CH_3OH	CH_3COOH	CF_3COOH	CH_3SO_3H
CH_3	−2.9	−2.9	−3.1	−3.0	−3.1	−3.2	−3.1
CHO	5.5	5.4	6.0	6.3	6.3	8.6	
$COCH_3$	4.2	4.0	4.5	5.0	5.1	7.2	
NH_2	−9.8	−10.0	−11.5	−10.0	−1.1	2.1	1.7
NO_2	5.8	5.7	6.5	6.4	6.2	7.5	6.9
OCH_3	−7.7	−7.7	−8.0	−7.9	−7.8	−5.7	

[a] Parts per million relative to internal benzene standard; reproducibility ≤ 0.04 ppm (1 H_2); positive numbers indicate downfield shifts.
[b] Solute concentration = *ca.* 10 mol %.

fluoroacetic acid undergoes a pronounced downfield shift. This results from an increase in the positive character of the aromatic ring due to hydrogen bonding at the carbonyl group. Two moles of TFA per mole of acetophenone cause a dramatic chemical-shift change; two additional moles of trifluoroacetic acid cause a smaller change. Before 10 mol % dilution, a constant plateau has been reached. Figures 1 and 3 indicate that para ^{13}C chemical shifts are responsive to real changes in the electronic nature of the ring. It is thus clear that the electron withdrawing nature of the acetyl group is increased considerably in trifluoroacetic acid, the strongly hydrogen-bonded acetyl being similar to an unsolvated trifluoroacetyl group.

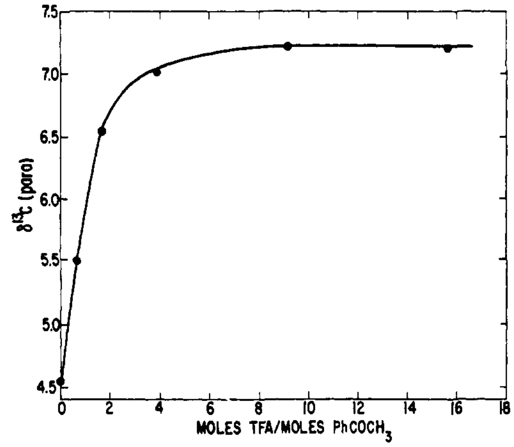

Figure 4. Dilution curve for acetophenone in CF_3COOH (TFA); $\delta^{13}C$ (para) relative to benzene (positive values downfield).

For methoxy a similar effect is observed. A dilution curve for anisole in trifluoroacetic acid is shown in Figure 5. The methoxy group in trifluoroacetic acid has its electron-donating power reduced considerably; reference to Figure 1 or 3 indicates that a methoxy group in trifluoroacetic acid is similar in para electron donating ability to a fluoro substituent.

Clearly, the para ^{13}C chemical shifts of anisole and acetophenone are sensitive to solvent and at less than 15–20 mol % dilution the medium effect has reached a plateau. The chemical-shift plateau found in both Figures 4 and 5 corresponds to completion of the "primary" solvation of the functional groups. Thus, at this plateau "infinite dilution" is *simulated* insofar as the electronic perturbation of the substituent and aromatic ring is concerned. From the shape of dilution curves such as these it may be possible to gain some insight into the solvation behavior of various functional groups.

For a substituent such as methyl, on the other hand, little solvent–solute interaction would be expected in most solvent systems. Indeed, the para ^{13}C chemical shift in toluene remains constant (±0.1 ppm, as shown in Table IV) relative to an internal benzene standard over a wide range of solvents from carbon tetrachloride to methanesulfonic acid. Table V shows the variation of the ^{13}C chemical shift of benzene relative to TMS in a series of solvents. The benzene standard appears to be a reasonable choice for the present work since only a range of ±0.2 ppm is observed in the various solvents. Thus, the large ^{13}C chemical-shift changes observed for the substituted aromatics are real measures of solvent–solute interactions. The solvent-induced shift at the para carbon appears to arise primarily from a change in the electronic environment at that carbon. The size of these shift differences precludes overriding contributions from solvent anisotropies due to local ordering of solvent molecules around the functional groups.

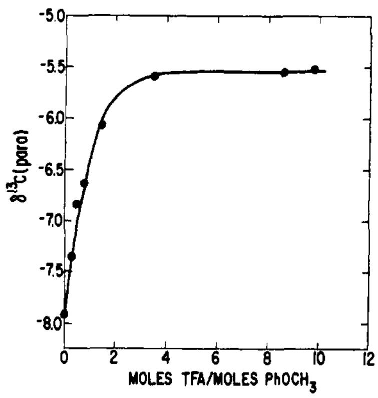

Figure 5. Dilution curve for anisole in CF_3COOH (TFA); $\delta^{13}C$ (para) relative to benzene (negative values upfield).

Table V. Chemical Shift of Benzene in Various Solvent Media[a]

Solvent	Shift
None (35% TMS)	128.35[b]
CCl_4	128.46
$CDCl_3$	128.58
CH_3COCH_3	128.74
CH_3OH	128.50
CF_3COOH	128.59
CH_3COOH	128.65

[a] Internal cyclohexane standard. Benzene and cyclohexane concentrations both 10% (v/v). [b] ±0.02 ppm; reported relative to TMS, based upon cyclohexane = +27.42 ppm.

Table IV summarizes results for several monosubstituted benzenes in a series of solvents. The chemical shifts for the carbon para to the OCH_3, $COCH_3$, CHO, NO_2, and NH_2 groups are strongly affected in the relatively strong acid trifluoroacetic acid. For acetophenone and benzaldehyde, even methanol and acetic acid appear to induce appreciable shifts of the para resonance.

From Figures 1 or 3 the appropriate "charge density" or σ^+ value can be obtained for a substituent in each solvent. Table VI compares the σ^+ values for several substituents in carbon tetrachloride and trifluoroacetic acid solution. Estimates such as these may be used to predict the relative reactivity of aromatic systems with strongly solvated functional groups in the reaction medium of interest. In addition, solution studies of the ^{13}C chemical shift para to an individual functional group provide insight into strong solute–solvent effects with various media. For example, nitrobenzene ($pK_{BH^+} = -12.33$)[38] appears to interact (Table IV) more strongly with trifluoroacetic acid (Hammett acidity, $H_0 = -3.3$) than with the stronger acid methanesulfonic acid ($H_0 \sim -8$).

Table VI. Estimates of σ^+ Values of Substituents in TFA

	Solvent		
Substituent	Ref 37	CCl_4	TFA
CH_3	−0.26	−0.20	−0.26
CHO		+0.73	+1.1
$COCH_3$	+0.57	+0.57	+0.90
NH_2	−1.1	−0.99	+0.35
NO_2	+0.74	+0.75	+0.92
OCH_3	−0.65	−0.73	−0.49

So far, only hydrogen bonding situations have been considered. (Acetophenone, $pK \sim -6.4$, is not significantly protonated in TFA [$H_0 = -3.3$].) The procedures described above can be applied in cases of protonation or ionization as well. Table VII shows the solvent dependence of the ^{13}C nmr of aniline. The ^{13}C nmr of aniline on protonation in methanesulfonic acid changes significantly when compared with that of aniline in carbon tetrachloride. The ortho and para positions move downfield considerably, the meta position to a lesser extent (8.1, 11.4, and 1.0 ppm, respectively). On the other hand, the carbon of attachment moves upfield strongly, 17.6 ppm. The qualitative features of these changes are also strongly apparent in acetic acid where aniline is largely protonated.

Table VII. Solvent Dependence of the ^{13}C Chemical Shifts of Aniline[a]

Solvent	C_1	Ortho	Meta	Para
CCl_4	+18.0	−13.2	+0.9	−9.7
CH_3COOH	+5.5	−6.0	+1.4	−1.1
CH_3SO_3H	+0.4	−5.1	+1.9	+1.7
DMSO-d_6	+20.7	−14.3	+0.5	−12.5
Acetone-d_6	+20.1	−13.8	+0.6	−11.5

[a] Parts per million relative to internal benzene.

CNDO/2 calculations were performed on aniline and protonated aniline. The calculated *changes* in total charge densities for all positions of the phenyl ring were determined (Table VIII). A slope of 5.5×10^{-3} e/ppm is obtained from the plot given in Figure 2. By multiplying this value by the observed change in ^{13}C chemical shift for each ring position, an "experimental" change in charge density is obtained as shown in Table VIII. The agreement is quite remarkable between the ^{13}C nmr "experimental" estimates and the CNDO/2 calculated values. Considering the uncertainties involved in geometries and the inherent inconsistencies in comparing solution measurements with gas-phase predictions, the observed agreement is indeed quite good.

Table VIII. Comparison of the CNDO/2 and ^{13}C Nmr Calculated Changes in Total Charge Density ($\times 10^3$)[a]

	CNDO/2	^{13}C
C_1	−97	−97
Ortho	+51	+45
Meta	+11	+6
Para	+77	+63

[a] Protonation of aniline.

An increase in the positive character of the substituent induces an increase in the (*negative*) electron density at the point of attachment while an increase in positive character is taking place at the ortho and para positions. Within the uncertainty of the calculations the meta position remains unchanged.

As expected the total amount of positive charge in the ring increases upon protonation of the amino group. This can be seen by *adding together* either the various changes in charges or the changes in ^{13}C chemical shifts. In doing this, the changes in ortho and meta chemical shifts must be added twice to account for the two equivalent positions for each. The result for $C_6H_5NH_3^+$ is +12 ppm, corresponding to +0.068 charge unit. CNDO/2 calculations yield the value +0.104 charge unit net change for anilinium ion relative to aniline.

Acetophenone exhibits similar ^{13}C nmr behavior. A comparison of the ^{13}C nmr of acetophenone in carbon tetrachloride and trifluoromethanesulfonic acid ($H_0 = 13.7$)[39] is made in Table IX. The ortho and para positions become more positive while the carbon of attachment becomes more negative: +6.8, +12.2, and −8.0 ppm, respectively. On the basis of the para chemical shift, the σ^+ for the protonated acetyl group is estimated to be +1.9.

Table IX. ^{13}C Chemical Shifts for Acetophenone[a]

	CCl_4	CF_3SO_3H	$\Delta\delta^{13}C$
C_1	+9.1	+1.1	−8.0
Ortho	+0.1	+6.9	+6.8
Meta	+0.0	+2.5	+2.5
Para	+4.2	+16.4	+12.2

[a] Parts per million relative to internal benzene.

Analogous but opposite behavior has been observed for phenol by Maciel and James.[7] In ethanol–sodium ethoxide solution the para position moves upfield 6.7 ppm while the carbon of attachment moves downfield 12.6 ppm, as compared with phenol in carbon tetra-

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[38] R. J. Gillespie and T. E. Peel, *Advan. Phys. Org. Chem.*, **9**, 1 (1971).

[39] G. C. Levy, J. D. Cargioli, and W. Racela, *J. Amer. Chem. Soc.*, **92**, 6238 (1970).

chloride. As expected, the para position becomes more negative. As might be anticipated from aniline and acetophenone the carbon of attachment becomes more positive. The same qualitative result is obtained for phenol as a hydrogen bond donor in dimethyl sulfoxide.

When the amino group is not protonated but is instead acting as a hydrogen bond donor, a situation similar to that of phenol in dimethyl sulfoxide is observed. Hydrogen bonded complexes in which aromatic amines act as proton donors have been studied extensively in recent years.[40] Acetone and dimethyl sulfoxide are two such proton acceptions. In both cases the ortho and para carbons of aniline move upfield as the point of attachment moves downfield (see Table VII). This result is to be anticipated from the results for acetophenone and aniline reported above. Indeed, the electronic changes experienced at the carbon of attachment appear to be in opposition to those experienced by the ortho and para positions.

Conclusions

The ^{13}C nmr resonances of substituted aromatic hydrocarbons are strongly dependent not only on the nature of the substituent but on the nature of the solvent. Changes due to strong solvent interactions, particularly hydrogen bonding and protonation, appear to be regular and predictable on the basis of electronic considerations. While the correlation of ^{13}C chemical shifts with calculated total charge densities from semiempirical MO methods is not always quantitative, these shifts, and particularly their changes in different solvent media, are strong probes into the changes in the electronic nature of the aromatic ring that result from solute–solvent interactions. From the results of these techniques it would appear that the electronic perturbation experienced at the carbon of attachment to a strongly solvated substituent is opposite in direction to that experienced by the ortho and para positions. Finally some insight into the nature of solvent shells becomes possible based on studies of dilution curves in interacting media.

Experimental Section

Nmr Analyses. ^{13}C nmr spectra were obtained at 25.2 MHz on a Varian XL-100-15 spectrometer equipped for both CW (continuous wave–frequency sweep) and FT (pulsed Fourier transform) operations. In most cases, pulse operation was utilized. Computer-controlled time averaging of between 100 and several thousand transient responses was used depending on sample concentration. Specific and wide band proton decoupling (100.1 MHz) was generated from the system Gyrocode decoupler. Pseudonoise modulation was used to achieve complete ^1H decoupling in the wide band experiments. Field-frequency control (lock) was effected by means of a solvent deuterium resonance or by utilization of a coaxial inner tube (5 mm) of acetone-d_6. The accumulated free induction decays were processed, *e.g.*, scaling of data, apodization, and exponential weighting of the free induction decay if required for sensitivity improvement, and transformed on the system computer (Varian 620-i). In each case 4096 data points were acquired, yielding 2048 output points in the phase corrected real spectrum. Partial spectra (500-2500 Hz) were obtained in cases where chemical-shift accuracy better than *ca.* 2.5 Hz (5120 Hz/2048 output points) was required.

For the purposes of this study, chemical shifts are reported in parts per million relative to internal benzene. Positive shifts are downfield, in accord with the ^{13}C TMS convention (benzene = 128.5 ppm). Unless otherwise noted, chemical shifts can be considered accurate to better than ±0.1 ppm. Spectral reproducibility was >0.04 for individual solutions.

Chemicals. In most cases reagent grade materials were used without further purification. Benzaldehyde was distilled immediately prior to use. Other substituted aromatics were recrystallized or distilled where necessary.

Solutions. Aromatic substrates were mixed or dissolved in solvents at room temperature, except for solutions of CF_3SO_3H which were prepared to 0°. Probe temperature for all experiments was *ca.* 40°. The benzene standard concentration was kept below 2% (v/v).

Molecular Orbital Calculations. CNDO/2 calculations were carried out using the QCPE program written by G. A. Segal[41a] as modified and described by Professor K. B. Wiberg.[41b]

INDO and some CNDO/2 calculations were carried out using the QCPE program written by Dobosh[42] as modified by Dr. R. P. Messmer and Dr. B. McCarroll of these laboratories. Modifications involved considerable saving of time and storage. Calculations were performed on a GE-605 computer.

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(40) C. Madec, J. Lauransan, and P. Saumagne, *J. Phys. Chem.*, **75**, 1157 (1971).

(41) (a) G. A. Segal, Quantum Chemistry Program Exchange, Indiana University, Bloomington, Ind., Program No. 91; (b) K. B. Wiberg, *Tetrahedron*, **24**, 1083 (1968).

(42) P. A. Dobosh, Quantum Chemistry Program Exchange, Indiana University, Bloomington, Ind., Program No. 141.