

Effect of Solvent Media on the Electronic Character of Substituted Aromatic Systems

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Summary Correlation of phenyl ring ^{13}C n m r chemical shifts with SCF-MO charge densities and Hammett type σ -parameters can be used to determine interaction between ring substituents and solvent

NATURAL abundance ^{13}C chemical shifts of carbon atoms *para* to substituents in monosubstituted benzenes have

p p m) made previously limit accuracy of such correlations and reduce their utility Earlier observations of solvent-induced ^{13}C shifts for ring carbon atoms *para* to various substituents have revealed no quantitatively useful effects ²

^{13}C Chemical shifts in this work, relative to an internal benzene standard, have errors < 0.05 p p m (1 Hz) (Varian Associates XL-100-15 spectrometer) CNDO/2 (both Wiberg and Pople parameters) and INDO SCF-MO

TABLE *para* ^{13}C Chemical shifts for mono substituted benzenes in various solvents

Substituent	^{13}C Shifts ^a					
	Neat	MeCOMe ^b	MeOH ^b	MeCO ₂ H ^b	CF ₃ CO ₂ H ^b	MeSO ₃ H ^b
Me	-2.97	-3.10	-2.97	-3.09	-3.16	-3.07
OMe	-7.93	-8.02	-7.90	-7.83	-5.56	
COMe	+4.54	+4.52	+5.01	+5.06	+7.21	
NO ₂	+6.32	+6.51	+6.43	+6.21	+7.46	+6.88
CHO	+5.88	+5.99	+6.34	+6.34	+8.63	

^a P p m relative to internal benzene standard, reproducibility ≤ 0.05 p p m (1 Hz), positive numbers indicate downfield shifts.

^b [Solute] ca 10 mol %

been correlated with Hammett type σ -parameters and π -electron densities obtained from MO calculations¹ The inaccuracy of chemical shift measurements (± 0.5 —1

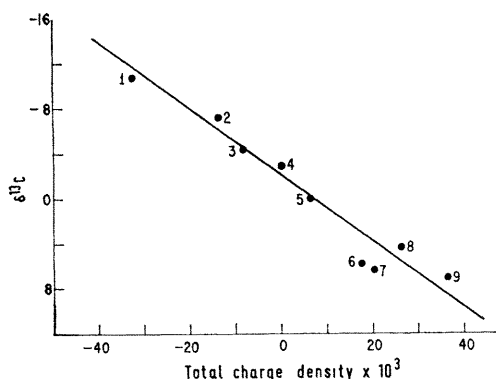


FIGURE 1 Total charge densities versus ^{13}C chemical shifts for the *para* carbon atoms of substituted benzenes Substituents 1 = NH₂, 2 = OH, 3 = F, 4 = CH₃, 5 = H, 6 = CHO, 7 = NO₂, 8 = COCH₃, 9 = COCF₃

calculations³ were performed CNDO/2 using Pople parameters gave the best overall correlation of chemical shift with charge density A plot of chemical shift *versus* total charge density at the *para* carbon (correlation coefficient $[r] = 0.98$) is shown in Figure 1 A plot of the total charge density at all carbon atoms including carbon of attachment *versus* ^{13}C chemical shifts gave a minimum acceptable correlation coefficient ($[r] = 0.91$) †

In the present study, complete ¹H decoupling at 100 MHz with simultaneous ^{13}C observation at 25.2 MHz allows easy ^{13}C measurements for substituted benzenes at less than 10 mol % dilution In cases where significant solute-solvent interactions are expected, we found that the ^{13}C chemical shifts of *para* carbons are strongly affected No large solvent-induced shifts are observed when there is no strong solute-solvent interaction The solvent-induced shift at *para* carbon appears to arise from a change in electron density at that carbon ‡ Dilution curves indicate that the *para* carbon chemical shifts are constant in solutions containing less than 15—20 mol % solute The Table shows results for several solvents

The chemical shifts for the carbon *para* to OMe, COMe, CHO, and NO₂ groups are strongly affected in the relatively

† Preliminary results indicate that di- and tri-substituted benzenes exhibit regular behaviour

‡ The size of these shifts precludes over-riding contributions from solvent anisotropies due to local ordering of solvent molecules around the functional groups

§ A comparable plot versus σ_p is not as precise, $[r] = 0.95$

strong acid, $\text{CF}_3\text{CO}_2\text{H}$. For acetophenone and benzaldehyde even MeOH and MeCO_2H appear to induce appreciable shifts of the *para* resonance. In contrast, the *para* carbon chemical shift for toluene remains nearly constant in all media.

An approximate charge density for the solute species can be obtained from Figure 1 by reading the charge density corresponding to a particular observed chemical shift. A more practical correlation in terms of chemical reactivity, however, might be found with σ_p^+ values. Figure 2 shows a plot of σ_p^+ versus ^{13}C chemical shift ($[r] = 0.99$). Using *para* ^{13}C shifts and Figure 2 σ^+ constants can be estimated for the OMe , COMe , NO_2 , and CHO groups in $\text{CF}_3\text{CO}_2\text{H}$ solution (-0.6 , $+0.9$, $+0.9$, and $+1.1$ respectively). Such estimates may be used to determine the reactivity of aromatic systems with strongly solvated functional groups in the reaction medium of interest.

Solution studies of the ^{13}C chemical shift *para* to an individual functional group provide insight into strong solute-solvent effects such as hydrogen bonding. For example, nitrobenzene [$pK(\text{BH}^+) = -12.33$]⁴ appears to interact (Table) more strongly with $\text{CF}_3\text{CO}_2\text{H}$ ($H_0 = -3.3$) than with the stronger acid MeSO_3H ($H_0 \approx -8$).

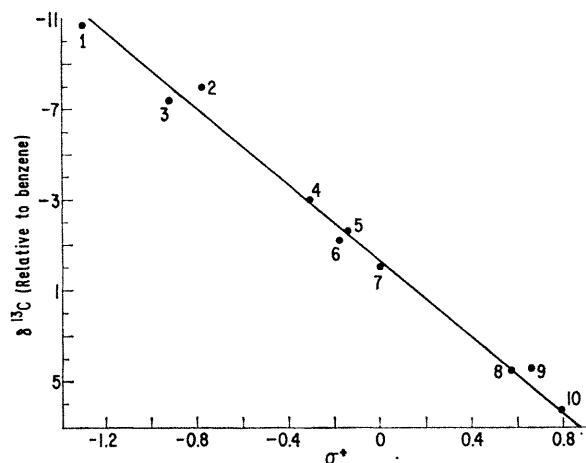


FIGURE 2. σ^+ Reactivity parameters versus ^{13}C chemical shifts for substituted benzenes. Substituents 1 = NH_2 , 2 = OCH_3 , 3 = OH , 4 = CH_3 , 5 = Br , 6 = Ph , 7 = H , 8 = COCH_3 , 9 = CN , 10 = NO_2 .

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