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SIGNIFICANCE OF THE RESONANCE EFFECT IN DETERMINING RING PROTON MAGNETIC SHIELDING IN SUBSTITUTED BENZENES AND PYRIDINES

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From the theory of chemical shifts, substituent-induced ring proton shifts should depend primarily on the π-electron charge density of the carbon atom to which the proton is bound assuming substituent-independence of the ring current effect and minimal long range substituent effects for meta and para protons. Although large variations in α-proton shielding accompanying β-substitution of ethylene are (qualitatively) those expected from the resonance effects of the substituents[1], attempts to establish the relative importance of resonance and field effects on ring proton shifts in substituted aromatic and heterocyclic systems have led to some confusion. In one report[2] a linear correlation between $\Delta\delta_p$ (the change in chemical shift, relative to benzene, of the proton para to the substituent) and the Hammett constant σ_p was interpreted as evidence that mesomeric effects largely govern the proton shieldings in monosubstituted benzenes. In another report[3] inductive effects were considered more important. Our purpose here is to show that the confusion arises from the former absence of reliable parameters which measure these effects separately and to make use of recently-derived[4] pure field *(F)* and resonance *(R)* parameters to establish the relative importance of the resonance effect.

Previously reported data on ring proton shifts of monosubstituted benzenes and 2-substituted pyridines, supplemented by that newly reported here for 3- and 4-substituted pyridines, is assembled in Table 1. The recent separation of Hammett parameters (σ) into their field and resonance components[4] establishes that σ_p comprises approximately equal contributions from *F* (47%) and *R* (53%) while σ_m (78%*F*, 22%*R*) cannot be assumed free from a resonance contribution. Clearly the composition of σ_p and σ_m must largely invalidate earlier conclusions (made on the basis of the nature of $\Delta\delta/\sigma$ correlations) as to the relative importance of field and resonance effects.

TABLE 1

Proton chemical shifts ($\Delta\delta \times 10^2$; p.p.m.) of substituted benzenes and pyridines

	Meta protons				σ_m	R	F	σ_p	Para protons			
Substituent	Benzenes[a]		Pyridines[b]		$\times 10^2$	$\times 10^2$	$\times 10^2$	$\times 10^2$	Benzenes[a]		Pyridines[c]	
CN	-30		-22	-21	+68	+18	+85	+63	-30		-22	-36
$COCH_3$	-27		-17		+31	+20	+53	+52	-27		-19	-16
$CO_2C_2H_5$			-15	-13	+40	+14	+55	+52			-14	
C_6H_5			-2		+22	-9	+14	+1				
H	0	0	0	0	0	0	0	0	0	0	0	0
Cl	0	+2		+1	+37	-16	+69	+23	0	+12	+11	+6
Br	0	+8		+9	+39	-18	+73	+23	0	+3	+12	-4
I	+17	+25		+15	+35	-20	+67	+28	+10	+3	+5	
F					+34	-34	+71	+6		+22		+17
$t\text{-}C_4H_9$			+12		-10	-14	-10	-20				
C_2H_5	+7		+13	+4	-4	-11	-6	-15	+7		+17	+20
CH_3	+10		+20	+7	-7	-14	-5	-17	+10		+20	+22
OH					0	-64	+49	-36	+37		+53	
NH_2	+13	+20	+42	+28	-16	-68	+4	-66	+40	+63	+69	+62

[a] First column : ref. 3, in cyclohexane; second column: ref. 2, in cyclohexane.

[b] First column: 4-substituted pyridines in deuterochloroform (this work); second column: 3-substituted pyridines in deuterochloroform (this work).

[c] First column: 3-substituted pyridines in deuterochloroform (this work); second column: 2-substituted pyridines in cyclohexane, ref. 6.

Correlations between $\Delta\delta_m$ and the parameters σ_m, *F* and *R* (Fig. 1) demonstrate the superiority of the pure resonance parameter, *R*. Similar conclusion obtain for $\Delta\delta_m$ in 4-substituted pyridines and monosubstituted benzenes. Reference to Table 1 shows that poor correlations between $\Delta\delta$ and σ stem largely from the anomalous shifts of the proton resonances in halogen-substituted molecules in relation to the σ values whereas the shifts are roughly those expected from the order of *R* values. The halogens exhibit maximum divergence of direction (sign) and magnitude of field and resonance components.

TABLE 2

Proton chemical shifts ($\Delta\delta \times 10^2$; p.p.m.) for halogen-substituted benzenes and pyridines

Substituent	Meta protons		Para protons		
	Benzenes[a]	Pyridines[b]	Benzenes[a]	Pyridines[c]	
F	+2.3	-	+22	-	+17
Cl	+2.5	+1	+12	+11	+6
Br	+8.0	+9	+3.0	+12	-4
I	+25	+15	+3.3	+5	-

[a] Ref. 2, in cyclohexane.

[b] 3-substituted pyridines in deuterochloroform (this work).

[c] First column: 3-substituted pyridines in deuterochloroform (this work);
Second column: 2-substituted pyridines in cyclohexane, ref. 6.

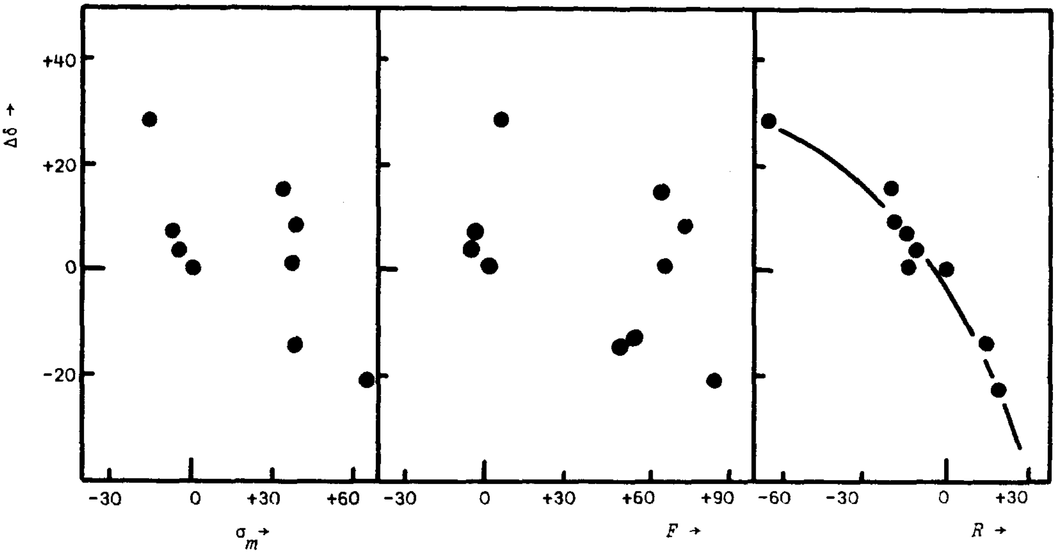

Fig. 1. Relationship between σ_m, F, R and $\Delta\delta$ for meta protons in 3-substituted pyridines.

F is a pure non-resonance parameter in which the (spatial) field effect and the inductive effect on the σ-electrons (I_σ) are lumped together. *R* represents the total ortho-para directing effect comprising the mesomeric effect (*M*) and the inductive effect on the π-electrons (I_π). The $-I_\sigma$ effect of the halogens would be expected to deshield the meta and para protons while their combined $+(M + I_\pi)$ effect would shield the para proton and deshield the meta proton. If (as Fig. 1 implies) the $-I_\sigma$ effect on proton shielding is small, the halogen with maximum $+(M + I_\pi)$ effect (fluorine) should exhibit maximum para proton shielding and minimum meta proton shielding. The most precise available results for halogen substituents indicate that this is observed (Table 2). The order of mesomeric effects of the halogens,[5] F < Cl < Br < I, revealed by π-π^* shifts in the electronic spectra of halogen-substituted aromatic systems, is that expected from their ionization potentials. The total ortho-para directing effects are in the reverse order and this order is revealed by ground state properties. That the values of Δδ imply the latter order of resonance effects is therefore entirely consistent with the dependence of shielding on π-electron density distribution rather than energy changes.

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