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PROTON CHEMICAL SHIFT-CHARGE DENSITY CORRELATIONS FOR ORTHO POSITIONS IN SUBSTITUTED BENZENES.

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The proton chemical shift of aromatic molecules has been shown to depend mainly on π-charge density at the carbon atoms.[1-3] In monosubstituted benzenes the proportionality between π-electron charge density and proton chemical shifts is satisfactory only for the para position.[1] "Ring current" contributions[4] seem to affect all the aromatic protons of substituted benzenes almost at the same extent,[5] while diamagnetic anisotropy and field effects due to substituents are considered to perturb significantly only the shift of ortho protons[6] and in any case they should be of minor importance for the remaining ring positions.[7,8] The failure of quantitative correlations between π-charge density and meta proton chemical shifts in monosubstituted benzenes is attributed to the presence of an inductive polarization of the π-electrons, concurrent with the classic mesomeric effect.[9] The situation for ortho protons is even different and the lack of any correlation of the proton chemical shift with π-charge density at the bonded carbon atom[1] is possibly due to effects which are connected with the short distance between substituents and the proton. The inductive effect of the substituent, which is mainly transmitted through σ-bond polarization, should play an important role in determining the ortho proton chemical shift. On the other hand π-electron charge distribution in aromatic derivatives should be sensitive to σ-bond polarization,[10,11] but this fact is normaly not taken in account in M.O. charge density calculations.

We have calculated electron charge densities at the proton and at the carbon atom in several substituted benzenes with a parametric M.O.L.C.A.O. method proposed by Del Re,[12] which we have already satisfactorily employed to correlate proton chemical shifts and charge densities in mono- and polysubstituted aliphatic derivatives,[13] taking in account only σ-bond polarization. These charge densities are reported in the table together with chemical shifts collected from the literature for several substituted benzenes.

It can be seen that σ-charge densities at position ortho to the substituent show significant variations both at the proton and at the carbon atom. On the contrary charge densities determined in this way for meta and para positions are scarcely affected by substituents. Plotting the charge densities obtained for ortho positions against proton chemical shifts, TABLE

Charge densities and chemical shifts (in p.p.m. from TM.S.) for *ortho* positions of substituted benzenes. In disubstituted benzenes the *ortho* positions refer to the substituent out of parentheses.

n°	Subst.	q_C^σ	q_H	δ_H
1	$N(CH_3)_2$	-0.0250	0.0314	6.589[a]
2	NH_2	-0.0233	0.0316	6.457[a]
3	$NH(CH_3)$	-0.0243	0.0315	6.434[a]
4	OCH_3	-0.0197	0.0320	6.771[a]
5	OH	-0.0182	0.0321	6.732[a]
6	F	-0.0140	0.0325	6.97 [b]
7	Cl	-0.0046	0.0334	7.27 [b]
8	Br	-0.0020	0.0336	7.43 [b]
9	SCH_3	-0.0133	0.0326	7.16 [c]
10	*o*(Cl), Cl	-0.0018	0.0337	7.365[d]
11	*o*(Br), Br	0.0011	0.0340	7.544[d]
12	*o*(Br), F	-0.0001	0.0338	7.483[d]
13	*o*(F), Br	-0.0110	0.0328	7.044[d]
14	*o*(Cl), Br	-0.0014	0.0337	7.368[d]
15	*o*(Br), Cl	0.0008	0.0340	7.537[d]
16	*o*(Cl), OH	-0.0032	0.0335	7.213[d]
17	*o*(OH), Cl	-0.0154	0.0323	6.949[d]
18	*o* tri Cl	-0.0010	0.0337	7.32 [b]
19	*p*(F), Br	-0.0002	0.0339	7.38[e]
20	*p*(Br), F	-0.0107	0.0328	6.90 [e]

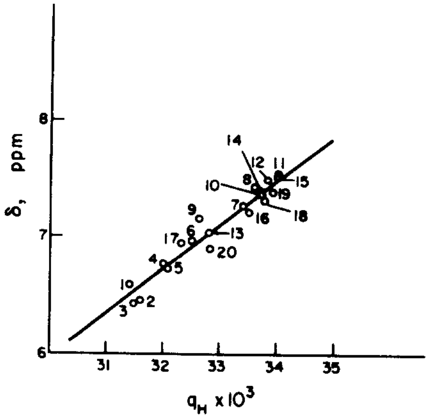
[a] Ref. 9; [b] Ref. 14; [c] Ref. 15; [d] Ref. 16; [e] Ref. 17.

fig. 1 and 2, a satisfactory linearity is observed, which is represented by eq. [1] and [2] respectively.

$$\delta_H = -385.74\, q_H + 5.61 \qquad [1]$$

$$\delta_H = -37.39\, q_C^\sigma - 7.44 \qquad [2]$$

Fig. 1 - Ortho proton chemical shifts vs. electron charge density at the proton in substituted benzenes. Numbering refers to the values reported in the table.



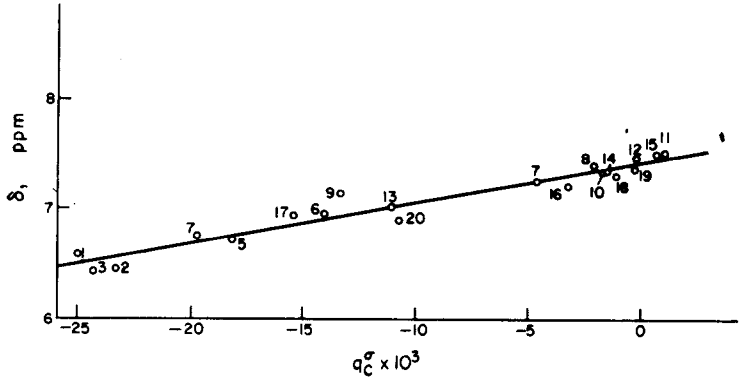


Fig. 2 - Ortho proton chemical shift vs. σ-electron charge density at the bonded carbon atom in substituted benzenes. Numbering refers to the values reported in the table.

These equations were obtained by a least square treatment of the data reported in the table. The ortho proton chemical shift seems thus to depend mainly on substituent effects transmitted through σ-bond polarization. The proportionality constant between δ_H and q_C^σ (-37.39 ± 2.15) is higher than that found in similar correlations between δ_H and q_C^π [1,2] for para protons. Taking into account the fact that the vaules of q_C^{σ} calculated for meta and para positions are almost insensitive to substituents, one can see that the proton chemical shift of aromatic molecules is very sensitive to σ-bond polarization.

Clearly the proton chemical shift of substituted benzenes is mainly a function of the electronic charge on the carbon atoms for all ring positions: ortho protons are dominated by contributions due to σ-bond polarization while for meta and para protons this effect is less important and the chemical shift is roughly reproduced by π-charge densities determined by normal M.O. methods. Attempts are to be made to determine the total electronic charge density at the carbon atoms, taking into account that π-charge distributions are also affected by σ-bond polarization. The results here reported seem to point out that no other effects than the electronic charge localized on the ring carbon atoms should be important in determining the proton chemical shift of substituted benzenes, at least for the set of substituents here examined.

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