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SUBSTITUENT ELECTRONEGATIVITIES

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Summary: It is shown that theoretical calculations (ab initio 6-31G* basis) of the charge on the hydrogen in molecules HX and experimental values for J_{CC} (ipso-ortho) in monosubstituted benzenes both provide measures of substituent electronegativity.

Pauling[1] introduced the term electronegativity to describe "the power of an atom to attract electrons to itself". Since that time many workers have attempted to extend electronegativity scales to groups of atoms (substituents) as well as to improve the derivation of such values both theoretically and experimentally. The work up to 1966 was extensively reviewed by Wells[2] who proposed a series of mutually consistent group electronegativities. He further showed their approximate relationship to various properties such as proton shifts, J_{HH} and J_{CH} values in methanes and ethanes.

Interest has continued since that time including a proposed[3] 'inductive' substituent parameter (i, iota) which was shown to be related to various series of C-13 chemical shifts with some substantial limitations. A number of recent publications[4-9] attest to the current importance of concepts and scales of electronegativity.

A related subject is the mode of transmission of polar effects in the absence of resonance effects. There is some continued controversy[10,11,12] as to the primacy of direct transmission through space, the so-called field effects (F), or alternatively by progressive relay through bonds, the so-called sigma-inductive effect. Reynolds[4] has pointed out that field effects should depend on the substituent dipole while sigma-inductive effects should, by contrast, depend on the group electronegativity of the substituent. These scales are quite different; for example, electronegativity values are quite similar for NH_2 and NO_2 but the latter has a far higher group dipole. In an examination of various properties Reynolds[4] found that most polar effects were primarily of field origin with only very limited indication of any dependence on substituent electronegativity. A major problem in such an analysis is having a reliable scale of electronegativity values to compare with the field effects values, σ_I (the dependence of inductive constants, σ_I, on field transmission now seems well established[4,10,12]).

Various theoretical approaches have been used to estimate substituent electronegativities. It seemed to us that the charge on the hydrogen atom, q_H, in the compounds HX was the only satisfactory measure since the hydrogen charge is free from the effects of hyperconjugation found, for example, in compounds CH_3X if the total charge on the methyl group is used.[8] It has[13] been shown that q_H values for a series of HX obtained at various levels of basis set using ab initio methods are approximately linearly related. We use here figures obtained at the 6-31G* level including geometry optimization. The (1.000-q_H) figures are listed in the Table and plotted against Well's group electronegativities (χ) in Figure 1. The theoretical values are clearly reasonably linear against χ for most substituents and, in our opinion, provide a better scale of electronegativity in having a clear definition and easy derivation for most common substituents. The χ values are not well established for many substituents. For example, for the methyl group, various methods give[4] values ranging from 2.27 to 2.63, the latter value being in reasonable agreement with the (1-q_H) value.

We have also been seeking a satisfactory experimental basis for an electronegativity scale. The J_{CC} values for CH_3CH_2X and CH_3COX both seem to follow electronegativity but values for J_{CC} between the ipso and ortho carbons in monosubstituted benzenes give a scale of greater magnitude and the compounds are readily available. Values are given in the Table and are plotted versus χ values in Figure 2. These coupling constants show an approximate[8] but non-linear relationship to χ and to (1-q_H). They also may contain field or resonance components, but an empirical relationship with the theoretical figures is found according to the equation below.

$$\Delta J_{CC} = 56(1-q_H)^2$$

The work is being extended to other substituents.

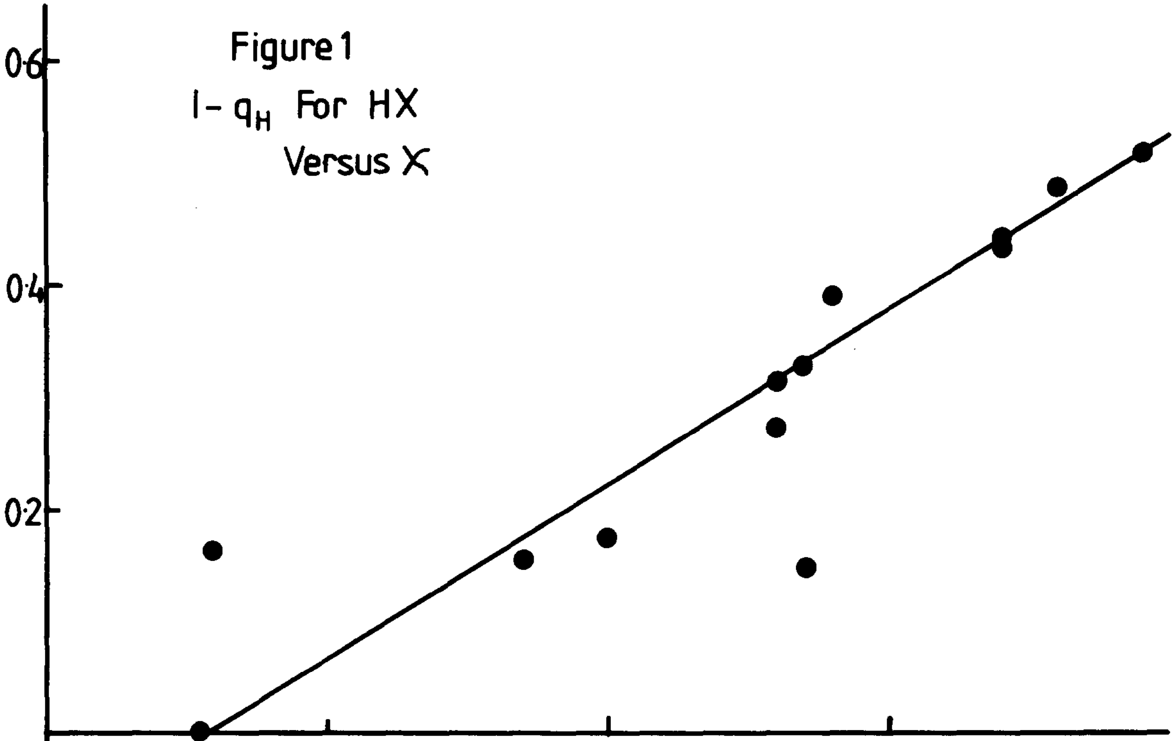

Figure 1
$1 - q_H$ For HX
Versus χ

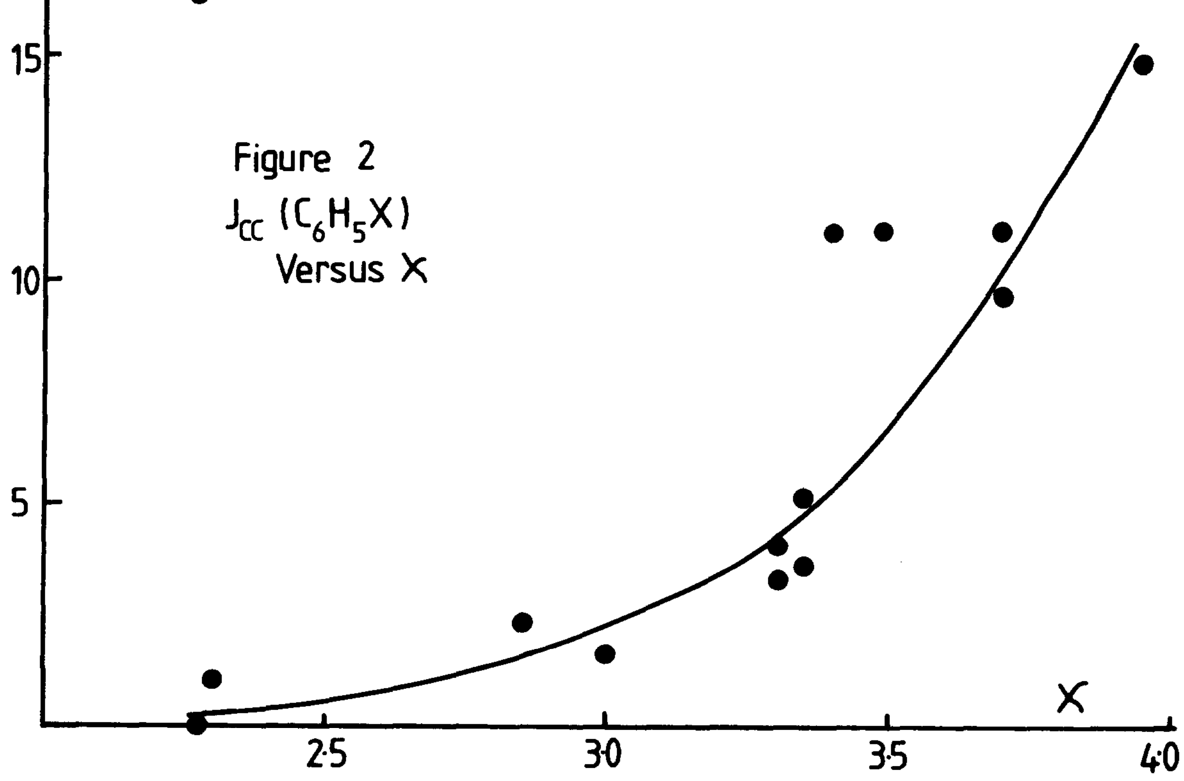

Figure 2
J_{CC} (C_6H_5X)
Versus χ

Table 1. Electronegativity Parameters for Some Common Substituents

X	$1-q_H$	ΔJ_{CC}[b]	χ[4]
	HX $(6\text{-}31G^*//6\text{-}31G^*)$	C_6H_5X	
H	0.000	0.00	2.28
Me	.165	1.07	2.3,(2.63)
$CHCH_2$	.176	1.61[c]	3.0
CCH	.276	3.37[c]	3.3
CF_3	.174[a]	3.57[c]	3.35
CN	.313	4.11	3.3
CO_2H	.181	2.4[d]	2.85
NH_2	.332	5.2	3.35
NO_2	.396	11.43	3.4
OH	.434	9.7	3.7
OMe	.438	11.1	3.7
NH_3^+	.488		3.8
F	.517	14.84	3.95

[a] $6\text{-}31G^*//4\text{-}31G$

[b] From ref. 8 except those specified

[c] This work, 80% sample - 20% $(CD_3)_2CO$

[d] CO_2Me

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