

GROUP ELECTRONEGATIVITIES OF A FEW RING RADICALS FROM MICROWAVE SPECTROSCOPY

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THE group electronegativity of a radical X_nC derived from the molecule X_nC-A (the radical X_nC always bonded through C) can be regarded as the electronegativity of an atom C perturbed by its chemical bonding to A. Group electronegativities of the group have been estimated from various methods like Infra red, solubility, basicity and coupling potential and NMR data. Hinze *et al.*¹ and Gordy² have developed methods of calculating group electronegativities.

Hinze and co-workers¹ introduced the idea of orbital electronegativity which is defined as the derivative of the energy of the atom with respect to the charge in the orbital, *i.e.*, the number of electrons in that orbital ($0 \leq n_j \leq 2$). They have expressed the energy E of the atom

$$E(n_j) = a + bn_j + cn_j^2$$

where a , b and c are constants and n_j is the occupation number of the j^{th} orbital. Then the j^{th} orbital electronegativity is

$$\chi_j = \frac{\partial E}{\partial n_j} = b + 2cn_j \quad (1)$$

Gordy's² approach, subsequently modified by Wilmschurst³ consists in relating the electronegativity of an atom with the energy of a valence-state electron arising from its interaction with the unscreened nucleus at a distance corresponding to covalent-bond formation. Hence for a radical $X_nC\cdot$, the electronegativity can be written as

$$\chi = 0.31 \frac{n^* + 1}{r} + 0.50 \quad (2)$$

where r is the covalent radius of atom C. n^* , a modified valence electron number, can be considered to be composed of three terms: (i) non-bonded electrons, (ii) bonded electrons and (iii) resonance electrons and can be written as

$$n^* = (n - p) + \frac{2m\chi_c}{(\chi_c + \chi_x)} + \frac{s\chi_c}{(\chi_c + \chi_x)}$$

where n is the number of valence electrons on the free atom C, p is the number of electrons taking part in the bonding to A, m the number of two electron bonds between C and A and s the number of resonance contributors.

Different relations relating ionic character to the electronegativity differences have been postulated.

However, Gordy's² relation that ionic character i for a bond A-B

$$i = \frac{(\chi_A - \chi_B)}{2} \quad (3)$$

seems to be most generally followed. χ_A and χ_B refer to the electronegativities of atoms A and B respectively. From the theory of nuclear quadrupole coupling constants, it is possible to estimate the ionic character in a bond and it is given by

$$i = \left(1 - s + d - \frac{\pi}{2}\right) - U_p \quad (4)$$

where the amount of s and d hybridization are indicated by s and d and π refers to the double bond character and

$$U_p = - \frac{(eQq)_{mol}}{(eQq)_{at}}$$

represents the number of unbalanced p electrons. $(eQq)_{mol}$ is the quadrupole coupling constant of the atom in a molecule determined by microwave spectroscopy and $(eQq)_{at}$ that of the free atom. In most cases d character is negligible and hence can be ignored. Regarding the contribution due to hybridization, Gordy⁴ prefers to put s always equal to zero, while Townes and Dailey⁵ have assigned a value of 0.15 for s if the electronegativity of the halogen is 0.25 units more than that of its partner. The π -character in the bond is given by

$$\pi = \frac{2}{3} \frac{(\chi_{xx} - \chi_{yy})}{(eQq)_{at}} \quad (5)$$

when χ_{xx} and χ_{yy} are the components of the quadrupole constant along the x and y axes respectively. Using Gordy's approach, the eqn. (4) can then be written as⁴

$$i = 1 - \frac{\pi}{2} + \frac{(eQq)_{mol}}{(eQq)_{at}} \quad (6)$$

Recently a number of halogen substituted benzene, pyridine and thiophene compounds have been studied by microwave spectroscopy. Hence if the halogen is considered as atom A and the group to be B, then combining eqns. (3) and (6) we get

$$\chi_B = \chi_{hal} - 2 \left[1 - \frac{\pi}{2} + \frac{(eQq)_{mol}}{(eQq)_{at}} \right] \quad (7)$$

Using the quantities listed in Table I, the electronegativities of various groups have been evaluated from the quadrupole coupling constants determined from microwave spectroscopy. These are given in

Table II through V. However, if we include the s character as per the prescription of Townes and Dailey⁵ the group electronegativity increases by 10% of its quoted value.

TABLE I
Quadrupole coupling constants and electronegativity of halogens⁴

Atom	$(eQq)_{\text{at}}$ (MHz)	χ_{at}
³⁵ Cl	109.74	3.0
³⁷ Cl	86.51	3.0
⁷⁹ Br	-769.76	2.8
⁸¹ Br	-643.03	2.8
I	2292.71	2.55

TABLE II
Group electronegativity of Phenyl radical

Molecule	$(eQq)_{\text{mol}}$ (MHz)	π	χ_g	$(\chi_g)_{\text{av}}$	χ_g from other methods ⁶	Ref.
Chlorobenzene- ³⁵ Cl	-71.09	0.0326	2.36			6
Bromobenzene- ⁷⁹ Br	558.9	0.0226	2.30			6
				2.30	3.13	
Bromobenzene- ⁸¹ Br	464.1	0.0221	2.27			6
Iodobenzene	-1892.1	0.0175	2.27			7

TABLE III
Group electronegativity of Pyridyl radical

Molecule	$(eQq)_{\text{mol}}$ (MHz)	π	χ_g	$(\chi_g)_{\text{av}}$	Ref.
2 Chloropyridine- ³⁵ Cl	-74.29	0.045	2.44		9-10
" ³⁷ Cl	-58.24	0.044	2.43		9
3 Chloropyridine- ³⁵ Cl	-68.77	0.035	2.36		11,12
				2.34	
2 Bromopyridine- ⁷⁹ Br	552.2	0.049	2.28		13
" ⁸¹ Br	460.4	0.046	2.28		13
4 Bromopyridine- ⁷⁹ Br	557.5	0.0377	2.24		13
" ⁸¹ Br	475.4	0.0339	2.31		13

TABLE IV

Group electronegativity of monofluorophenyl radical

Molecule	$(eQq)_{\text{mol}}$ (MHz)	π	χ_g	Ref.
<i>m</i> fluorochlorobenzene- ³⁵ Cl	-76.00	0.044	2.43	14

TABLE V

Group electronegativity of Thiophene radical

Molecule	$(eQq)_{\text{mol}}$ (MHz)	π	χ_g	$(\chi_g)_{\text{av}}$	Ref.
2 Chlorothiophene- ³⁵ Cl	-76.15	0.011	2.40		15
	-75.54	0.010		2.40	
" ³⁷ Cl	-60.07	0.008	2.40		
	-59.59				

It may be noted from Tables I and II that the group electronegativity decreases as the bonding of the radical changes from chlorine to iodine. Because these are conjugated systems, the uncertainty in the evaluation of the group electronegativity is likely to be large. Nevertheless it is interesting to note that the group electronegativities for these widely varying radicals are very nearly equal to 2.35.

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