

Electronegativity of ionic groups. Evaluation from MNDO calculations

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Abstract. The electronegativities (χ_G) of some 78 groups/atoms (G) including some 11 ionic ones have been evaluated from the charge on the H atom in the corresponding H–G molecules. The charges are determined by the MNDO method of Dewar at the optimised geometries. For some 38 molecules/ions where *ab initio* molecular orbital calculations are available, a reasonable linearity (correlation coefficient $r = 0.900$) has been observed between the MNDO charges and the charges obtained at the 6–31G**//6–31G* level. The very good linear correlation ($r = 0.950$) obtained between the χ_G values and Inamoto's *i* scale for some 72 groups/atoms including some 8 monocationic groups shows that the method works quite well for the monocationic groups. However the anionic groups probably cannot be tackled in the present approach. The $^1J_{CC}$ (ortho-*ipso*) coupling constants in mono-substituted benzenes also correlate linearly with the χ_G values for some 33 groups/atoms to a satisfactory extent ($r = 0.917$). It is mentioned that there does not exist a proper theoretical scale for group electronegativity which can accommodate ionic and neutral groups on a uniform basis.

Keywords. MNDO calculations; group charge; group electronegativity.

1. Introduction

Electronegativity is still of much current interest (Mullay 1987; Allen 1989, 1990; Brown and Skowron 1990; Datta and Singh 1990, 1992; Pearson 1990; Datta 1991; Luo and Pacey 1991) presumably because of the elusive connection between Pauling's definition of electronegativity and his thermochemical method for its evaluation. Here we are concerned with the electronegativity of a group. As in the case of atomic electronegativity, a number of theoretical scales for group electronegativity are available. However very few of them correlate with the two presently accepted experimental scales (Datta and Singh 1990) for group electronegativity. It is curious that in the past, only Huheey (1965) and Inamoto and Masuda (1982a) have attempted to tackle ionic groups and others have dealt only with neutral groups. Elsewhere we have shown (Datta 1991) that Huheey's scale does not include the bonding features of a group and hence cannot be compared with most of the existing scales of group electronegativity. And Inamoto's approach which is essentially a modification of Wilmhurst's (1957) method has one drawback—it does not provide a single scale for all types of groups. Thus it follows there does not exist a proper theoretical scale which can describe the electronegativity of neutral and ionic groups on a uniform basis. We have attempted to develop the same and the results are reported here.

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2. Results and discussion

Earlier we have shown (Datta 1988) that it is possible to construct a reasonable theoretical scale of group electronegativity from the calculated charges on the H atom in H-G molecules where G is a chemical group. In the chosen examples, the charge calculations were done by *ab initio* molecular orbital method at the 6-31G**/6-31G* level by Marriott *et al* (1984) using Mulliken population analysis. Because of the lack of the charge calculations for ionic groups, the electronegativities of the ionic groups could not be determined earlier (Datta 1988). We have now performed the relevant charge calculations by the MNDO method of Dewar and Thiel (1977) for a number of H-G molecules at their optimised geometries. Using Sanderson's principle of equalisation of electronegativity it can be shown (Datta 1988) that χ_G , the electronegativity of a group is related to q'_H , the charge on the H atom in an H-G molecule obtained at the MNDO level via (1) with H as the reference. In the following χ_G is expressed in eV.

$$\chi_G = (7.17 + 12.84 q'_H)/(1 - 1.6 q'_H). \quad (1)$$

In order to adjust the χ value of fluorine to 4.0 in Pauling's unit it was necessary to calibrate the MNDO charges by

$$q_H = q'_H/1.8. \quad (2)$$

These calibrated charges q_H were used in (1) to determine the χ_G values of some 77 groups/atoms (table 1).

Table 1. Charge on the H atom in some H-G molecules, group electronegativity χ_G and other measures of group electronegativity*

Group (G)	Charge on H		q_H	χ_G	i	${}^1J_{CC}$
	<i>ab initio</i>	MNDO				
H				7.17	2.00	0.00
Li	-0.177	-0.438	-0.243	2.91	1.15	
BeH	-0.087	-0.253	-0.140	4.38	1.51	
BH ₂	-0.041	-0.076	-0.042	6.21	1.82	
B(OH) ₂		0.020	0.011	7.44	2.01	
CH ₃	0.165	-0.018	-0.010	6.93	2.14	1.07
CH ₂ CH ₃	0.158	-0.006	-0.003	7.09	2.14	1.09
CH(CH ₃) ₂	0.153	0.004	0.002	7.23	2.15	1.5
CH(CH ₃)(C ₂ H ₅)		0.004	0.002	7.23	2.15	
C(CH ₃) ₃	0.155	0.013	0.007	7.35	2.16	1.90
<i>c</i> -C ₃ H ₅		0.037	0.020	7.68	2.15	
CHCH ₂	0.176	0.040	0.022	7.73	2.14	1.61
CHCHCH ₃		0.039	0.022	7.71	2.34	
C ₆ H ₅		0.059	0.033	8.01	2.29	
CCH	0.276	0.154	0.086	9.59	2.52	3.37
CH ₂ CN	0.228	0.021	0.012	7.46	2.20	3.07
CH ₂ NH ₂	0.155	-0.009 ^b	-0.005	7.05	2.18	1.42
CH ₂ OH	0.152	-0.026 ^b	-0.015	6.82	2.21	1.65
CH ₂ F	0.155	-0.005 ^b	-0.003	7.10	2.24	2.0
CH ₂ Cl		0.020	0.011	7.45	2.18	

(Continued)

Table 1. (Continued)

Group (G)	Charge on H			χ_G	i	${}^1J_{CC}$
	<i>ab initio</i>	MNDO	q_H			
CH ₂ Br		0.022	0.012	7.47	2.16	
CH ₂ I		0.026	0.015	7.53	2.14	
CHF ₂		0.021 ^c	0.012	7.47	2.35	
CHCl ₂		0.055	0.031	7.95	2.22	
CHBr ₂		0.056	0.031	7.97	2.18	
CF ₃	0.174	0.086	0.048	8.42	2.47	3.57
CCl ₃		0.088	0.055	8.63	2.28	
CBr ₃		0.085	0.047	8.42	2.19	
CHO	0.140	-0.001	-0.001	7.15	2.39	2.0
COCH ₃	0.145	0.013	0.007	7.34	2.39	1.9
COCF ₃		0.081	0.045	8.35	2.44	
COCN		0.130	0.072	9.15	2.46	
CONH ₂		0.028	0.012	7.46	2.30	1.89
CSNH ₂		0.032	0.018	7.62	2.18	
COOH	0.181	0.106	0.059	8.76	2.36	
COOCH ₃	0.186	0.102	0.057	8.69	2.37	2.4
COF	0.178	0.101	0.056	8.66		3.3
COCl		0.093	0.051	8.53	2.30	
CN	0.313	0.190	0.106	10.26	2.61	4.11
NH ₂	0.332	0.109	0.060	8.79	2.47	5.2
NHCH ₃	0.338	0.099	0.055	8.63	2.50	5.8
N(CH ₃) ₂	0.335	0.101	0.056	8.66	2.48	6.89
NCO	0.419	0.189	0.105	10.24	2.83	10.0
NCS		0.252	0.140	11.55	2.80	
NHCOH	0.389	0.117	0.065	8.93		6.87
NHNH ₂	0.344	0.097	0.054	8.61	2.50	5.8
NO ₂	0.396	0.189	0.105	10.24	2.74	11.43
OH	0.434	0.163	0.090	9.74	2.79	9.7
OCH ₃	0.438	0.180	0.100	10.07	2.82	11.09
OC ₂ H ₅		0.180	0.100	10.06	2.82	
OCF ₃		0.236	0.131	11.20	2.79	
OCHO		0.216	0.120	10.78	2.80	
OCOCH ₃	0.460	0.216	0.120	10.78	2.80	12.78
F	0.517	0.287	0.160	12.38	3.10	14.84
SiH ₃	-0.133	-0.151	-0.084	5.37		-6.5
Si(CH ₃) ₃		-0.175	-0.097	5.12	1.79	
SiF ₃		-0.015	-0.008	6.98	1.98	
SiCl ₃		-0.036	-0.020	6.70	1.85	
PH ₂	-0.031	-0.089	-0.049	6.06	1.91	
SH	0.109	0.043	0.024	7.78	2.17	4.2
SCH ₃	0.090	0.046	0.025	7.81	2.16	3.9
SC ₂ H ₅		0.046	0.026	7.83	2.16	
SCF ₃		0.081	0.045	8.35	2.20	
SCOCH ₃		0.051	0.028	7.88	2.18	
Cl	0.245	0.184	0.102	10.14	2.37	9.21
Br		0.108	0.060	8.78	2.32	
I		-0.053	-0.030	6.48	2.15	
CH ₂ NH ₃ ⁺		0.078	0.043	8.29	2.61	
C(CH ₃) ₃ ⁺		0.111	0.061	8.82	2.58	

(Continued)

Table 1. (Continued)

Group (G)	Charge on H					
	<i>ab initio</i>	MNDO	q_H	χ_G	<i>i</i>	$^1J_{CC}$
NH ₃ ⁺	0.488	0.234	0.130	11.16	2.93	
N(CH ₃) ₃ ⁺		0.199	0.111	10.45	2.89	
N ₂ ⁺		0.428	0.238	16.50	3.71	
O(CH ₃) ₂ ⁺		0.318	0.177	13.18	3.32	
P(CH ₃) ₃ ⁺		0.139	0.077	9.31	2.26	
S(CH ₃) ₂ ⁺		0.139	0.077	9.31	2.47	
COO ⁻		-0.118	-0.065	5.73	2.33	
O ⁻	0.206	-0.003	-0.002	7.13	2.60	
S ⁻		-0.032	-0.018	6.75	2.03	

* Symbols are as defined in the text. The *ab initio* (at 6-31G*//6-31G* level) data on the charge on H are taken from Marriott *et al* (1984). The χ_G values are given in eV. The *i* values are taken from Inamoto and Masuda (1982b). The $^1J_{CC}$ values, given in Hz, are from Marriott *et al* (1984).

^b Average of the charges on the three methyl H atoms.

^c Average of the charges on two H atoms.

The two available experimental scales are based on ¹³C-NMR studies—Inamoto's "i" scale (Inamoto and Masuda 1982b) and the $^1J_{CC}$ (ortho-*ipso*) coupling constants (Marriott *et al* 1984) in the monosubstituted benzenes. For some 72 groups/atoms (table 1) our χ_G values give rise to a very good linear correlation with the *i* scale (figure 1; correlation coefficient $r = 0.950$). However two of the only three anionic groups considered (table 1), deviate very badly in figure 1. The most probable reason is as follows. In deriving (1) one of the assumptions is the proportionality between the ionisation potential (IP) and the electron affinity (EA) of the neutral groups. Such proportionality between IP and EA has been observed by various workers in case of atoms (Yang *et al* 1985; Datta 1986), molecules (Yang *et al* 1985; Datta 1986) and radicals (Datta and Singh 1991). The most interesting observation is that in all instances the proportionality constant remains more or less the same. Now, the EA in case of an anionic group may not always have any physical significance; consequently (1) may not be valid for the anionic groups. Since all the 8 monocationic groups considered (table 1) are quite in line (see figure 1), it can be stated that for the monocationic groups also IP is proportional to EA and the proportionality constant remains the same. In case of the other experimental scale, $^1J_{CC}$ values are not available for any ionic group. For some 33 neutral groups/atoms (table 1) the variation of the $^1J_{CC}$ constants with our χ_G values is found to be quite linear (figure 2; $r = 0.917$).

We have observed a reasonable linearity (figure 3; $r = 0.900$) between the charges computed at the *ab initio* molecular orbital 6-31G*//6-31G* level using Mulliken population analysis and MNDO charges. Of the 38 molecules/ions used for this purpose (table 1), LiH seems to be the only significant deviant (figure 3). Thus the gross features of our earlier scale (Datta 1988) based on the 6-31G*//6-31G* calculations are expected to be reflected here which is true with some differences. Dewar himself has found (Dewar and Thiel 1977) that the MNDO charges are usually similar to those obtained at the STO-3G level. It is obvious that the usual

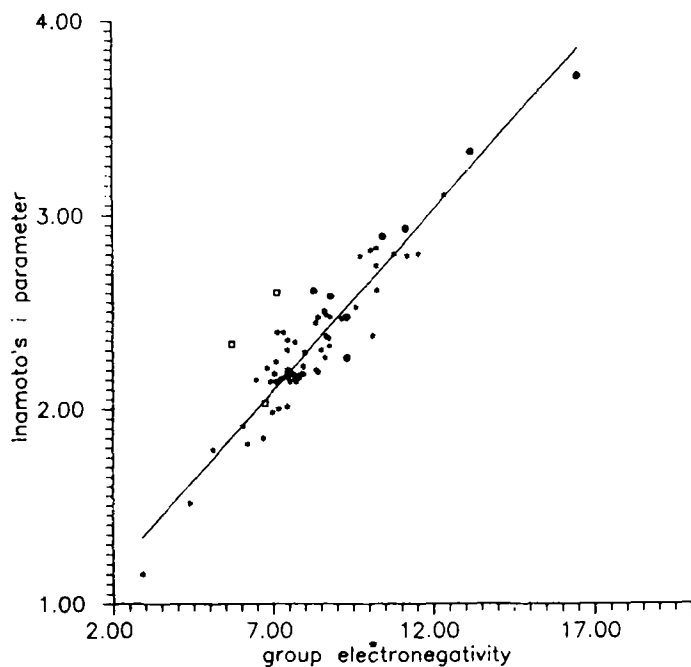


Figure 1. Correlation between the calculated group electronegativities (in eV) and Inamoto's *i* scale; for data, see table 1. $r = 0.950$; the anionic groups marked by the squares are not used for the least squares fit (see text); the cationic groups are marked by the full circles.

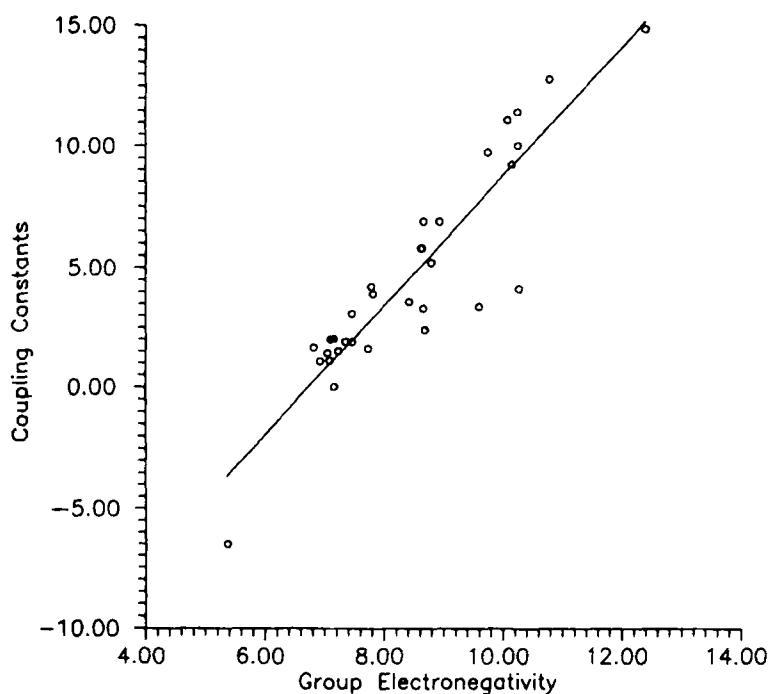


Figure 2. Variation in the $^1J_{CC}$ (ortho-*ipso*) coupling constants (in Hz) in some mono-substituted benzenes with group electronegativity (in eV); for data, see table 1. $r = 0.917$.

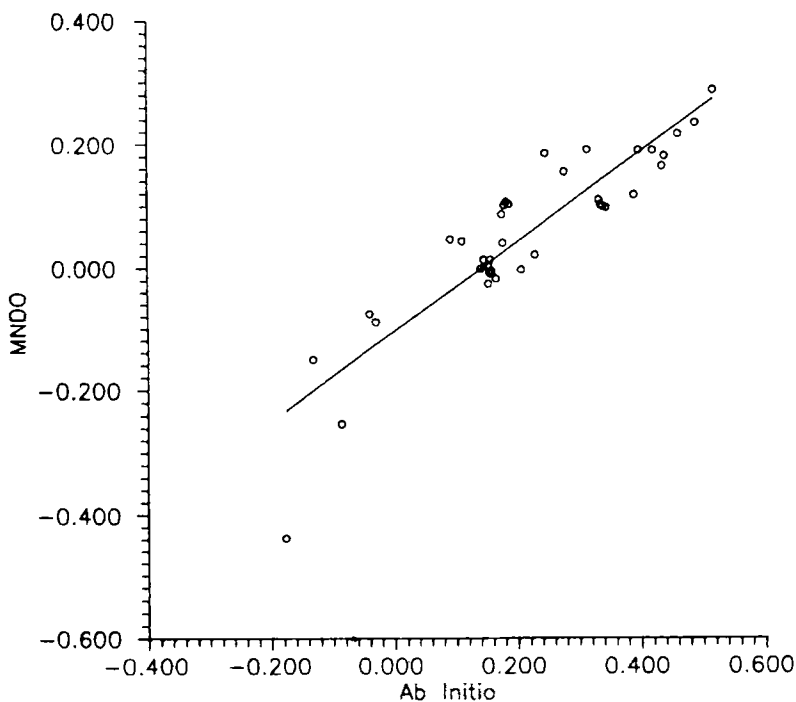


Figure 3. Correspondence between the charges on H in some 38 H-G molecules/ions calculated at the *ab initio* molecular orbital 6-31G**/6-31G* level within the framework of Mulliken population analysis and those obtained by the MNDO method; for data, see table 1. $r = 0.900$.

improvement in the charge calculations by the *ab initio* method using higher order basis sets is lacking in the MNDO results.

3. Conclusions

The main conclusion of our present work is that (1) can be used to evaluate the electronegativity of a monocationic group on the same basis as that for a neutral group. However in view of the semiempirical nature of our charge calculations, for obtaining more reliable numerical values of χ_G , *ab initio* molecular orbital calculations at the 6-31G**/6-31G* level are desirable. In our earlier work (Datta 1988) and here we have used Mulliken population analysis (Mulliken 1955). Since our χ_G values are calculated from the charge densities, these will depend markedly on the nature of the model used for the population analysis. There are other models for calculating atomic charge densities (Huzinaga and Narita 1980; Cioslowski 1989). A particularly interesting approach is that of Bader *et al* (1971, 1980) where the atoms and bonds in a molecule are defined uniquely from the topological properties of the electron distribution. It is generally believed that compared to Mulliken's approach, Bader's method yields atomic charges which are more satisfactory from a chemist's point of view (Wiberg and Breneman 1990). Thus it would be interesting to work out group electronegativity by (1) using the atomic charges obtained by Bader's theory of atoms in molecules. Work in this line is in progress.

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