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Ab Initio Determination of Substituent Constants in a Density Functional Theory Formalism: Calculation of Intrinsic Group Electronegativity, Hardness, and Softness

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Three intrinsic group properties, the group electronegativity, hardness, and softness, were obtained for 30 organic groups in a nonempirical way starting from the definitions within the framework of density functional theory and applying limited configuration interaction (CISD). The calculated group electronegativities correlated well with most scales introduced for this quantity. The values were compared with the field factor F and with the ^{13}C $^1J_{CC}$ (ipso-ortho) coupling constant in monosubstituted benzenes, the most important experimental quantity known to reflect substituent electronegativities. The trends for the group hardnesses and softnesses were interpreted in terms of the hardness (or softness) values for the corresponding central atoms. The correlation with the experimental hardness values for the corresponding radicals was examined and was found to be satisfactory.

Introduction

Group quantities such as group electronegativity, hardness, and softness are important tools in structural and reactivity studies in inorganic and organic chemistry. In the past, group electronegativity has by far recieved the most attention and a variety of scales have been proposed. Among the most important ones are the following: Wells' scale,[1] which is largely based on bond vibrational data; the inductive parameter ι introduced by Inamoto and Masuda,[2] derived from electronegativities based on Gordy's covalent boundary potentials;[3] scales by Huheey,[4] Sanderson,[5] and Bratsch,[6] who used complete electronegativity equalization[7] schemes and scales by Mullay[8] and Hinze and Bergmann,[9] based on a partial electronegativity equalization scheme. The scales introduced by Marriott, Reynolds, Taft, and Topsom[10] and by Boyd and Edgecombe[11] find their origin in quantum chemical calculations. The substituent constants given by Marriott et al.[10] are based on a Mulliken population analysis of compounds of the HG type, i.e., a group G bonded to hydrogen; Boyd and Edgecombe[11] evaluated group electronegativities from topological properties of electron density distributions; the number of groups considered was extended in a very recent publication,[12] when the present work was already terminated. Sen, Böhm, and Schmidt[13] calculated molecular orbital based electronegativities within the semiempirical CNDO LCAO MO theory, using the transition operator method.

Reed and Allen[14] reported values for substituent electronegativities by calculating the so-called bond polarity index, BPI_{AB}, a quantum mechanical measure of the one-electron energy difference between adjacent atoms A and B in a molecule. On the basis of a correlation analysis with the above-mentioned scales and relevant experimental data, they argued that their scale is the "most quantitatively useful".

Quite recently, Korchowiec and Nalewajski obtained group electronegativities for molecular fragments,[15] based on an NDO calculation scheme, which included contributions due to the molecular environment. Together with the calculated Fukui function indices, these group electronegativities were seen to provide adequate reactivity criteria to reproduce known substituent effects.

For the group hardness and softness, very few values have been published until now. Pearson has published a series of experimental hardness values for atoms and radicals, based on

experimental values for the electron affinity and the ionization energy.[16] Bergmann and Hinze[9] obtained values for the group hardness, based on the calculation of the charge density in the group and using Sanderson's electronegativity equalization[7] principle.

The whole of the situation indicates that a uniform, nonempirical calculation scheme for the series of the above-mentioned group properties was not presented hitherto, although its importance has been recognized, e.g., by Bartolotti,[17] claiming that "calculation of electronegativities of molecules and molecular fragments is very important and should be performed".

In this paper, a density functional theory[18] based computational scheme for obtaining these three important quantities of molecular systems is presented and applied to a series of 30 groups, frequently encountered in organic molecules. We will refer to the group properties obtained in this way as to "intrinsic" properties, as indicated by the title, since they do not explicitly take into account the contributions of the group molecular environment. Unless stated otherwise, our calculated group properties will always be intrinsic group properties, which can be considered as the theoretical counterparts of the substituent constants.[19]

Theory and Computational Details

Density functional theory, based on the two famous theorems by Hohenberg and Kohn,[20] considers the electron density $\rho(r)$ as the basic information for atomic and molecular systems instead of the wave function Ψ. By application of the variational principle to the functional $E_{el}[\rho(r)]$[18] (with E_{el} the electronic energy of the system), taking into account that the electron density should at all times integrate to the total number of electrons, one obtains the density functional analogue to the Schrödinger equation:

$$v(r) + \frac{\partial F_E(r)}{\partial \rho(r)} = \mu \qquad (1)$$

where $v(r)$ is the external (i.e., due to the nuclei) potential at position r and $\rho(r)$ the ground-state electron density. $F_E(r)$ yields upon integration the electronic kinetic energy and the electron-electron repulsion energy and μ is the Lagrange multiplier.

This Lagrange multiplier is called the electronic chemical potential and is identified as the partial derivative of the energy of the system, E, with respect to the number of electrons, N, at a constant external potential $v(r)$:

$$\mu = (\partial E/\partial N)_{v(r)} \qquad (2)$$

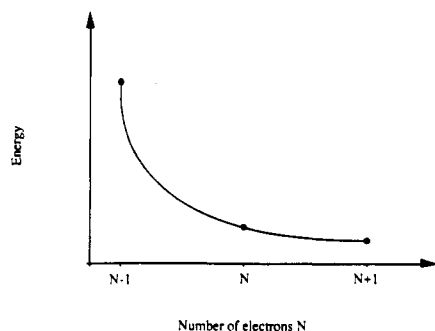This electronic chemical potential was identified by Parr et al.[21]

Figure 1. $E = E[N]$ curve governing the group properties χ, η, and S.

as the opposite of the electronegativity, as defined by Iczkowski and Margrave:[22]

$$\chi = -(\partial E/\partial N)_{v(r)} = -\mu \tag{3}$$

Assuming a quadratic relationship between the energy and the number of electrons and using a finite difference approximation, one obtains from (3) Mulliken's formula[23] for the electronegativity:

$$\chi = \frac{I + A}{2} \tag{4}$$

with I and A the ionization energy and the electron affinity of the system, respectively. A functional relationship is seen to exist between μ on one hand and N and $v(r)$ on the other hand. Explicitly written, one obtains

$$d\mu = (\partial^2 E/\partial N^2)_{v(r)}\, dN + \int (\delta\mu/\delta v(r))_N \delta v(r)\, dr \tag{5}$$

where

$$f(r) = (\delta\mu/\delta v(r))_N = (\partial\rho(r)/\partial N)_{v(r)} \tag{6}$$

is the Fukui function, defined by Parr and Yang[24] and

$$\eta = \frac{1}{2}\left(\frac{\partial^2 E}{\partial N^2}\right)_{v(r)} \tag{7}$$

is the hardness, defined by Parr and Pearson.[25]

Again assuming that the energy varies quadratically with the number of electrons and using a finite difference approximation, one obtains

$$\eta = \frac{I - A}{2} \tag{8}$$

Finally, the global softness is defined as[26]

$$S = 1/2\eta \tag{9}$$

which, in the above-mentioned assumptions, can be written as

$$S = \frac{1}{I - A} \tag{10}$$

We now propose to use the expressions (4), (8), (10) as working equations to calculate the group electronegativity, group hardness, and softness, all governed by the $E = E[N]$ curve, depicted in Figure 1.

For a group G (e.g., the CH_3 group), the corresponding (neutral) radical was considered in the geometry the group usually adopts when being a part of a molecule and not in the equilibrium geometry of the isolated radical. The $CH_3^\bullet$ radical, for example, is therefore considered in a pyramidal geometry and not in the planar geometry it adopts as an individual molecule.[27] Within this option, standard bond angles and distances[28] were used throughout this work.

By calculating the energies of the radical (N electron system), the cation ($N - 1$ electron system), and the anion ($N + 1$ electron system) of the group G (cf. Figure 1), all at the same geometry (cf. the requirement of a constant external potential $v(r)$), one

TABLE I: Calculated Group Properties at the SCF Level

group	χ, eV	η, eV	S, 10^{-2} eV^{-1}
1. CH_3	4.41	5.64	8.86
2. CH_2CH_3	3.75	5.34	9.36
3. $CH{=}CH_2$	4.74	5.59	8.95
4. $C{\equiv}CH$	8.05	6.57	7.61
5. CHO	4.65	5.48	9.13
6. $COCH_3$	4.18	4.96	10.09
7. $COOH$	5.91	5.47	9.14
8. $COCl$	5.89	4.99	10.02
9. $COOCH_3{}^a$	5.50	5.32	9.41
10. $CONH_2$	4.63	5.14	9.73
11. $C{\equiv}N$	9.54	6.63	7.54
12. NH_2	5.33	6.45	7.75
13. CH_2NH_2	3.05	5.04	9.92
14. NO_2	8.61	5.62	8.89
15. OH^b	5.59	5.84	8.56
16. CH_2OH	3.80	5.45	9.17
17. $OCH_3{}^b$	4.57	5.12	9.76
18. F^b	8.52	7.24	6.91
19. CH_2F	4.57	5.85	8.55
20. CHF_2	5.08	6.09	8.21
21. CF_3	6.24	6.30	7.93
22. SiH_3	4.22	4.36	11.46
23. PH_2	4.71	4.61	10.85
24. SH^b	5.14	3.99	12.52
25. CH_2SH	4.01	4.86	10.28
26. $SCH_3{}^b$	4.40	3.76	13.31
27. Cl^b	7.13	4.65	10.74
28. CH_2Cl	4.68	5.32	9.40
29. $CHCl_2$	5.10	5.01	9.99
30. CCl_3	5.58	4.71	10.63

^{a} The geometry used for the $COOCH_3$ group was taken from the s-cis, syn conformer of methyl acrylate.[37] ^{b} See text.

can determine the ionization energy and electron affinity of G and thus the group quantities.

Calculations were performed at two levels, the first one (the Hartree–Fock level) serving merely as a reference point. It is indeed highly advisable to go beyond the Hartree–Fock level and include electron correlation to give an adequate description of the electron affinity[29] (or, more generally, to compare situations with different numbers of electron pairs[30]). Therefore, correlation effects were partly incorporated by the CISD[31] (configuration interaction with single and double substitutions) technique, using the frozen core approximation and including a size-consistency correction.[31,32] A possible alternative for including correlation effects, Møller–Plesset perturbation theory,[33] was not used due to the fact that in some cases the perturbation series lacks convergence, which has been associated with spin contamination in the underlying UHF wave function.[34]

The basis set used for all calculations was the 6-31++G(d,p) basis set:[35] the 6-31G* basis set is usually considered as the smallest basis set, useful to describe correlation effects;[35] diffuse functions were added to give a better description of the anionic systems.

All calculations were performed by using the GAUSSIAN 90[36] program on the CRAY-YMP of the Brussels Free University computing centre.

Results and Discussion

General Considerations. In Tables I and II the SCF and CISD values for the group properties are given. A difference in sensitivity to correlation effects between χ on one hand and η and S on the other hand shows up when comparing these tables. The inclusion of correlation effects in the energy calculations seems to have a larger influence on the values for the group hardnesses and softnesses than on those for the group electronegativities. The correlation coefficient r between the group electronegativities calculated at the SCF level and those calculated at the CI level equals 0.943. The correlation between the group electronegativities calculated at these two levels is shown in Figure 2. The correlation between the two computational levels for the group

TABLE II: Calculated Group Properties at the CISD Level

group	χ, eV	η, eV	S, 10^{-2} eV^{-1}
1. CH$_3$	5.12	5.34	9.36
2. CH$_2$CH$_3$	4.42	4.96	10.07
3. CH=CH$_2$	5.18	4.96	10.07
4. C≡CH	8.21	5.77	8.67
5. CHO	4.55	4.88	10.25
6. COCH$_3$	4.29	4.34	11.51
7. COOH	5.86	4.71	10.61
8. COCl	5.73	4.39	11.38
9. COOCH$_3$^{a}	5.48	b	b
10. CONH$_2$	4.67	4.42	11.32
11. C≡N	8.63	5.07	9.86
12. NH$_2$	6.16	6.04	8.28
13. CH$_2$NH$_2$	3.39	4.42	11.32
14. NO$_2$	7.84	4.89	10.22
15. OH	6.95	5.69	8.79
16. CH$_2$OH	4.14	4.85	10.31
17. OCH$_3$	5.73	4.86	10.28
18. F	10.01	7.00	7.14
19. CH$_2$F	4.97	5.31	9.41
20. CHF$_2$	5.25	5.42	9.22
21. CF$_3$	6.30	5.53	9.05
22. SiH$_3$	4.61	4.12	12.14
23. PH$_2$	5.05	4.38	11.41
24. SH	5.69	3.96	12.62
25. CH$_2$SH	4.15	4.18	11.95
26. SCH$_3$	4.99	3.71	13.49
27. Cl	7.65	4.59	10.89
28. CH$_2$Cl	4.89	4.71	10.61
29. CHCl$_2$	5.12	4.38	11.42
30. CCl$_3$	5.53	4.10	12.21

^{a} The geometry used for the COOCH$_3$ group was taken from the s-cis, syn conformer of methyl acrylate.[37] ^{b} Not calculated due to computational limits.
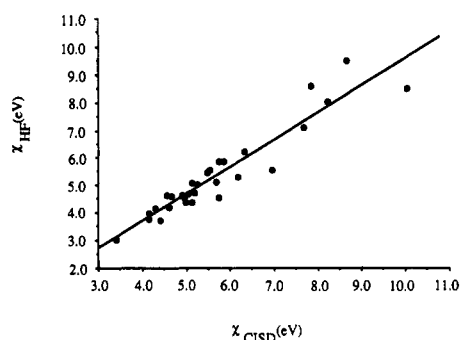

Figure 2. Correlation of the group electronegativities calculated at the SCF level with those calculated at the CISD level.
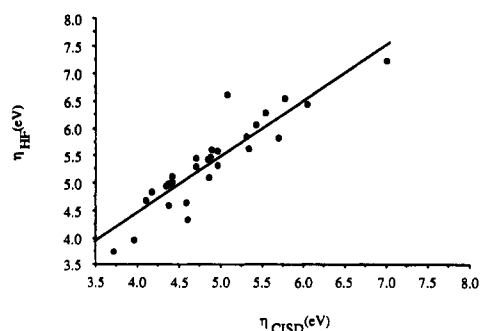

Figure 3. Correlation of the group hardnesses (softnesses) calculated at the SCF level with those calculated at the CISD level.

hardnesses (and softnesses) on the other hand equals 0.906: this correlation is shown in Figure 3. The reason for this sensitivity difference is probably the cancellation of the energy of the neutral radical in χ (cf. eq 4, calculated as the energy difference between two closed-shell systems, as opposed to η and S (eqs 8 and 10), where a combination of the energy of two closed- and one open-shell system is found. In the following discussions, the

values for the group quantities obtained with limited configuration interaction were used; even the calculation of group electronegativities should be performed at the highest possible level and with a large basis set, a fact again recently stated in a paper by Boyd and Boyd.[12]

Before turning to this discussion, a technical point should be mentioned. The UHF wave function for the cases indicated by a superscript b in Table I was found to have lost the full molecular symmetry, thus recovering Löwdin's Hartree–Fock symmetry dilemma.[38] In the OH· and the SH· systems, the Mulliken population analysis reveals that the population in the p$_x$ orbital differs from the population in the p$_y$ orbital, the z-axis being the molecular symmetry axis. The symmetry around the z-axis, which should be reflected in the symmetry of the orbitals and the electronic population, is therefore lost. This effect is clearly due to the fact that the HOMO for these two systems shows a twofold degeneracy and that no averaging of the population of the three electrons, occupying the two orbitals, is carried out during the SCF procedure in the GAUSSIAN 90 package (cf. the study of the OH radical by Cook[39]).

A similar situation with regard to the HOMO shows up in the ·OCH$_3$ and ·SCH$_3$ radicals, where the Mulliken population analysis shows three nonequivalent hydrogen atoms. These two systems also show a twofold degenerate HOMO containing three electrons (cf. the recent study of the OCH$_3$ radical by Carter and Cook[40] and references therein).

Finally, F· and Cl· also show an electron distribution having lost its (spherical) symmetry. The Mulliken population analysis for the atomic orbitals yields, for example, electronic populations in the p$_x$, p$_y$, and p$_z$ orbitals that are not equal. The HOMO of these two systems, containing five electrons, is found to have a threefold degeneracy. An analogous problem still shows up in the cations F$^+$ and Cl$^+$, where now four electrons have to be distributed among the three degenerate components of the HOMO.

All these symmetry problems can be solved by performing a GVB/ROHF[41] calculation. As in the present work, it was necessary to include electron correlation effects, and, since the ROHF/GVB orbitals could not be used for the CISD calculation, the UHF orbitals were used as the basis for the CISD calculation, because we were only interested in the energy of the systems considered. Of course, this procedure would not be justified when studying, for example, the Fukui function (eq 6), for which two of the present authors recently published contour plots that are free from this disadvantage[42] and other related density functional based local properties.

Group Electronegativity. The overall trend of the group electronegativities shows a fair correlation with chemical intuition. Among the most important trends, we mention χCH$_3$ < χNH$_2$ < χOH < χF; χSiH$_3$ < χPH$_2$ < χSH < χCl; and χCH$_3$ > χSiH$_3$, χNH$_2$ > χPH$_2$, χOH > χSH; and χF > χCl. This sequence shows the same trend along the periodic table as the atomic electronegativities of the central atoms of the group; the only difference is the fact that, in these groups, the atoms are now "saturated" with hydrogen atoms (except of course for the halogen atoms F and Cl). These results are in agreement with the fact that the electronegativity of a group is largely determined by the electronegativity of the atom linking the group to the other part of the molecule.

The effect of increasing s character of the central atom of the group is shown in the three following series: χCH$_2$CH$_3$ < χCH=CH$_2$ < χC≡CH (sp^3, sp^2, and sp hybridization of the central carbon atom); χCH$_2$NH$_2$ < χC≡N (sp^3 and sp hybridization); χCH$_2$OH < χCHO (sp^3 and sp^2 hybridization). It is clear from this sequence that the electronegativity of a group increases when the percent s character of the central atom is increased.

For the "carbonyl derivative" groups, the following sequence is found: χCOCH$_3$ < χCHO < χCONH$_2$ < χCOOCH$_3$ <

TABLE III: Correlation of the CISD Calculated Group Electronegativity Values (Table II) with the Scales Listed in the Introduction

scale	no. of groups compared	correlation coefficient r	"problem" groups[c]
Wells [1]	16	0.824	OH, OCH₃
Inamoto [2]	19[a]	0.919	OH, OCH₃, CCH, CN, CH₃
	4[b]	0.946	SCH₃
Marriott [10]	15[a]	0.918	OH, OCH₃, CCH, CN
	4[b]	0.963	SCH₃
Mullay [8]	15[a]	0.913	OH, OCH₃, CCH, CN
	3[b]	0.720	
Boyd [11]	10[a]	0.964	OH, OCH₃, CCH, CN
	4[b]	0.956	
Reed [14]	19[a]	0.907	SiH₃, CCH
Boyd [12]	21[a]	0.911	OH, OCH₃, CCH, CN
	4[b]	0.950	SCH₃

[a] Groups with a first-row central atom. [b] Groups with a second-row central atom. [c] The "problem" groups are excluded from the correlation analysis and are not counted in "number of groups compared".

χCOCl < χCOOH. Substituting the hydrogen atom in the formyl group by an electron-donating (+I) group (here the methyl group) lowers the electronegativity of the resulting group. The substitution by an electron-withdrawing (–I) group (NH₂, OCH₃, Cl, or OH), however, has the opposite effect.

Substituting a hydrogen atom in the methyl group by a more electronegative halogen atom (F or Cl) results in the following series: χCH₂F < χCHF₂ < χCF₃ and χCH₂Cl < χCHCl₂ < χCCl₃. Although the electronegativity of a group is primarily determined by the electronegativity of the central atom, there is a "secondary" effect: the electronegativities of the atoms bonded to the central atom have a clear effect on the electronegativity of the group. A problem seems to exist with the methyl group: its electronegativity appears to be abnormally high, although it is generally recognized as an electron-donating (+I) substituent. Examples are available, however, in which alkyl substituents act as electron-withdrawing substituents, when being placed on an electron-rich center.[43] Mariott et al.[10] have encountered a similar result with this group, also obtaining a χCH₃ > χCH₂F sequence.

A final remark should be made about the nature of the values obtained for the group electronegativities. We recall that our "intrinsic" values are obtained by considering very simple model systems and do not need extensive calculations on larger molecules containing the groups considered. Dependency of the molecular surroundings can be obtained, when, e.g., AIM (atoms in molecules) electronegativities are calculated.[44]

Comparison with Other Group Electronegativity Scales. The correlation of our scale with the other group electronegativity scales, listed in the Introduction, is shown in Table III. No meaningful correlation exists with the scales introduced by Sanderson,[5] Huheey,[4] and Bratsch.[6]

From this comparison, two important conclusions can be drawn. In the first place, it appears that the calculated electronegativities for the two groups containing a triple bond (the cyano and the ethynyl group) are rather high in comparison with the other scales. A still inadequate treatment of the electron correlation on these systems might be invoked for this failure.

In the second place, there seems to be a problem with the values derived for the hydroxyl and the methoxy group and with their sulfur analogues: the sequence we predict is the following: χOH > χOCH₃ and χSH > χSCH₃ but χOH > χSH and χOCH₃ > χSCH₃. This sequence is in accordance with the methyl group being an electron-donating group (although according to our results, it has a rather high electronegativity): the electron-withdrawing effect of the oxygen atom in the methoxy group (or the electronegativity of the sulfur atom in the sulfur analogue of this group) is lowered due to an electron transfer from the methyl group attached to it.
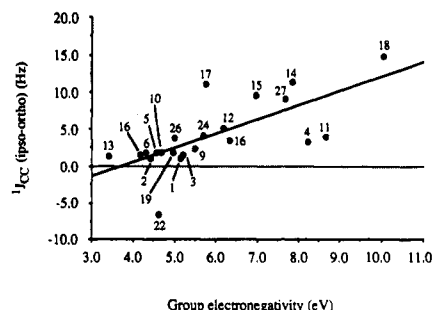
Figure 4. Correlation between experimental ¹³C ¹J_{CC} (ipso-ortho) coupling constants in monosubstituted benzenes and CISD calculated group electronegativities. The values for the ¹³C ¹J_{CC} for monosubstituted benzenes were taken from ref 10 and were determined as 80% solutions in (CD₃)₂CO, relative to unsubstituted benzene. The numbering of the points refers to Table II.

When looking at the other group electronegativity scales, there is no clear agreement about what the sequence should be. Some scales (Marriott,[10] Inamoto,[2] Mullay,[8] and Boyd and Edgecombe[11]) predict the electronegativity of the methoxy group to be higher than that of the hydroxyl group. A remark should be made concerning the scales by Marriott and co-workers on one hand and Inamoto's scale on the other: these scales all predict the inverse sequence for the sulfur analogues of the hydroxyl and the methoxy group.

Our sequence for the methoxy group and the hydroxyl group is confirmed by the scales from Huheey,[4] Sanderson,[5] and Bratsch[6] and also by the recently published scale from Boyd and Boyd.[12]

Comparison to Experimental Data. Several experimentally measured quantities have been postulated to correlate with substituent electronegativities.

A great deal of values arise from NMR data. The ¹³C ¹J_{CC} (ipso-ortho) coupling constants in monosubstituted benzenes[45] for which many experimental values are available in literature, were recently considered to be the best experimental measures of group electronegativities available at the moment.[46] The overall correlation equals 0.705 for 22 values compared and is depicted in Figure 4. (The values obtained for the group electronegativities, obtained at the SCF level, show a correlation coefficient of 0.571.)

As can be seen from the graph, the correlation fails badly for the SiH₃ and the OCH₃ groups and for the groups containing a triple bond. Leaving these groups out of the correlation analysis yields a correlation coefficient of 0.941 for 18 groups. It is important to note that the SiH₃, the cyano, and the ethynyl groups are also found to fail the correlation with the ¹³C ¹J_{CC} coupling constants in the work of Marriott et al.[10]

Finally, a correlation analysis of our group electronegativity values with the F-factor (field constant), introduced by Swain and Lupton,[47] was performed. These values are obtained by assuming that the Hammett substituent constants are fitted by the expression

$$fF + rR + h \qquad (11)$$

where F is the nonresonance or field constant and R the resonance constant, both depending on the substituent only, and f, r, and h depend on the reaction series but not on the substituent. Values for 43 substituents, obtained by applying (11), have been tabulated.

For 15 substituents, the correlation coefficient was 0.631 (with the values from ref 47b). Swain et al. predict in their work the following sequence for the field constant F, NO₂ > CN > Cl ≈ F > OH > NH₂ > CH₃, where our sequence for the group electronegativity χ is the following: F > CN > NO₂ > Cl > OH > NH₂ > CH₃. Again, a wrong sequence for the hydroxyl and the methoxy group seems to exist: F_{OH} < F_{OCH_3}, while we predict χOH > χOCH₃. Taking all these things into account, no clear correlation seems to exist between our scale and the F-factor.

Finally, it should be remarked that the group electronegativities can be correlated with a lot of other properties, available through experimental measurements. A description of the major part of data available can be found in the review by Wells[1] and in the recent paper by Reed and Allen.[14]

Group Hardness and Softness. In the following discussion, only the main trends for the group hardnesses will be considered. The results for the group softnesses are completely analogous, since the group softness is simply the inverse of the group hardness divided by two. The evolution of the group hardnesses when going from left to right in a period of the periodic table for the central atom is the following: $\eta CH_3 < \eta NH_2$ but $\eta NH_2 > \eta OH$ and $\eta OH < \eta F$; $\eta SiH_3 < \eta PH_2$ but $\eta PH_2 > \eta SH$ and $\eta SH < \eta Cl$. These trends are the same as for the corresponding central atoms without "hydrogen saturation". The sequence there is[48] $\eta C < \eta N$ but $\eta N > \eta O$ and $\eta O < \eta F$ and also $\eta Si < \eta P$ but $\eta P > \eta S$ and $\eta S < \eta Cl$. This could mean that the group hardnesses and softnesses are largely determined by the hardnesses (or softnesses) of the central atoms.

Vinayagam and Sen, however, consider the above depicted trends for the atomic hardnesses as "anomalies", resulting from the application of the finite difference approximation.[49]

Surprisingly, this sequence of calculated group hardnesses is not reproduced by the experimental hardnesses of the corresponding radicals, published by Pearson,[16] showing a uniform increase in hardness from left to right in the periodic table: $\eta CH_3 < \eta NH_2 < \eta OH < \eta F$ at least for groups with a first row central atom. On the contrary, for groups with a second row central atom an inversion between ηPH_2 and ηSH is to be noticed.

The following sequence for the group hardnesses is obtained when going from a first-row to a second-row central atom in the group: $\eta F > \eta Cl$, $\eta OH > \eta SH$, $\eta NH_2 > \eta PH_2$, and $\eta CH_3 > \eta SiH_3$. This sequence is also found for the corresponding free central atoms[48] and for the experimental hardness values for the radicals.[16]

For the double bond groups containing the carbonyl group, the sequence is the following: $\eta COCH_3 < \eta COCl < \eta CONH_2 < \eta COOH < \eta CHO$. Substituting the hydrogen atom in a methyl group by a halogen atom (F or Cl) has the following effect on the group hardness: $\eta CH_2F < \eta CHF_2 < \eta CF_3$ but $\eta CH_3 > \eta CH_2Cl > \eta CHCl_2 > \eta CCl_3$. These results are in accordance with the fact that the experimental hardness of fluorine is higher than that of hydrogen; so the substitution of H by F in the group results in an increase in the group hardness. When hydrogen is substituted by a softer atom, e.g. chlorine, the group hardness decreases. These results lead to the conclusion that the hardnesses of atoms bonded to the central atom also influence the group hardness. The hardness of the methyl group seems overestimated: its value is higher than the value for the CH_2F group. This is in accordance with problems with this group in discussing the group electronegativity.

Another intriguing result is found when looking at the effect of hybridization of the central atom in a group on the group hardness. The results are the following: $\eta CH_2CH_3 = \eta CH=CH_2$ and $\eta CH=CH_2 < \eta C=CH$, $\eta CH_2OH < \eta CHO$, and $\eta CH_2NH_2 < \eta C=N$. These sequences are in accordance with the fact that the absolute hardness should increase with the percent s character of the hybridized orbitals, due to the fact that, with a decrease of the p character, the polarizability decreases.[50] On the other hand, adding a certain number of π bonds in the group should increase the group polarizability and, as a consequence, lower the group hardness.[16b]

A correlation analysis of the calculated hardness values with the experimental values for free radicals published by Pearson[16] was performed. This correlation is shown in Figure 5.

A correlation coefficient of 0.834 was obtained for 15 values. The CF_3 group was found to be an outlier, probably due to the
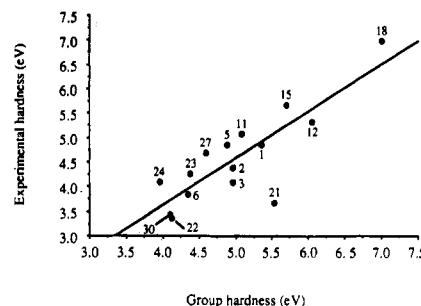
Figure 5. Correlation between Pearson's experimental hardnesses for radicals[16] and calculated group hardnesses. The numbering refers to Table II.

presence of three hard fluorine atoms in this group. Leaving out this group, the correlation coefficient was improved to 0.926, which can be considered as satisfactory. It must be stressed again, however, that the values published by Pearson are experimental values for the free radicals whose geometries can differ considerably from the standard geometry of the groups in the molecule, used in our calculations, especially for groups with C_{3v} symmetry.

We finally correlated our values for the group hardnesses with values obtained by Bergmann and Hinze,[9] on the basis of the calculation of the charge density in the group. An overall correlation coefficient of 0.582 was found for 24 values. A remarkable difference in hardnesses of the halogen atoms F and Cl shows up between the two scales. Here, however, it should be remarked that the molecular environmental contributions were explicitly taken into account by Bergmann and Hinze when obtaining their values (Sanderson electronegativity equalization scheme), while we did not. The poor correlation is probably due to the fact that the second-order derivatives of the energy such as η and S are expected to be much more dependent on the group environment than the group electronegativities.[15]

Conclusion

Values for three important "intrinsic" group quantities were obtained for 30 groups, frequently occurring in organic molecules. The sequences for the group electronegativity values were found to be in good agreement with chemical intuition. They were also found to correlate well with most group electronegativity scales proposed in the past. A problem exists with three of the groups. The electronegativity value of the CH_3 group, generally recognized as an electron-donating (+I) group, was high in comparison to the other groups. The second problem is encountered in the groups containing a triple bond: as compared to the other group electronegativity scales, our scale apparantly overestimates their electronegativity.

A correlation was made with experimental values, known to be a reflection of the group electronegativity. Our values seem to correlate well with the most important of them, the ^{13}C $^1J_{CC}$ (ipso-ortho) coupling constant in monosubstituted benzenes. A correlation coefficient of 0.941 was found for 18 groups.

For the group hardnesses and softnesses, the results were rationalized on the basis of atomic hardnesses. A satisfying correlation was found with the "experimental" values by Pearson on isolated radicals. No clear correlation seems to exist with the group hardness values listed by Bergmann and Hinze.

References and Notes

(1) Wells, P. R. *Prog. Phys. Org. Chem.* **1968**, *6*, 111.

(2) (a) Inamoto, N.; Masuda, S. *Tetrahedron Lett.* **1977**, *37*, 3287. (b) Inamoto, N.; Masuda, S.; Tori, K.; Yoshimura, Y. *Tetrahedron Lett.* **1978**, *46*, 4547. (c) Inamoto, N.; Masuda, S. *Chem. Lett.* **1982**, *1003*, 1007.

(3) Gordy, W. *Phys. Rev.* **1946**, *69*, 604.

(4) (a) Huheey, J. E. *J. Phys. Chem.* **1965**, *69*, 3284. (b) Huheey, J. E. *J. Phys. Chem.* **1966**, *70*, 2086.

(5) Sanderson, R. T. *Polar Covalence*; Academic Press: New York, 1983.

(6) Bratsch, S. G. *J. Chem. Educ.* **1985**, *62*, 101.

(7) Sanderson, R. T. *Chemical Bonds and Bond Energy*; Academic Press: London, 1976.

(8) Mullay, J. *J. Am. Chem. Soc.* **1985**, *107*, 7271.

(9) Bergmann, D.; Hinze, J. In *Electronegativity*; Sen, K. D., Jørgenson, C. K., Eds.; Springer Verlag: Berlin, Heidelberg, 1987; p 145.

(10) Marriott, S.; Reynolds, W. F.; Taft, R. W.; Topsom, R. D. *J. Org. Chem.* **1984**, *49*, 959.

(11) Boyd, R. J.; Edgecombe, K. E. *J. Am. Chem. Soc.* **1988**, *110*, 4182.

(12) Boyd, R. J.; Boyd, S. L. *J. Am. Chem. Soc.* **1992**, *114*, 1652.

(13) Sen, K. D.; Böhm, M. C.; Schmidt, P. C. In *Electronegativity*; Sen, K. D., Jørgenson, C. K., Eds.; Springer Verlag: Berlin, Heidelberg, 1987; p 100.

(14) Reed, L. H.; Allen, L. C. *J. Phys. Chem.* **1992**, *96*, 157.

(15) Korchowiec, J.; Nalewajski, R. F. *Int. J. Quantum Chem.*, in press.

(16) (a) Pearson, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 7684. (b) Pearson, R. G. *Inorg. Chem.* **1988**, *27*, 734. (c) Pearson, R. G. *J. Org. Chem.* **1989**, *54*, 1423.

(17) Bartolotti, L. J. In *Electronegativity*; Sen, K. D., Jørgenson, C. K., Eds.; Springer Verlag: Berlin, Heidelberg, 1987; p 39.

(18) Parr, R. G.; Yang, W. *Density-functional theory of atoms and molecules*; Oxford University Press: New York; Clarendon Press: Oxford, 1989.

(19) Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165.

(20) Hohenberg, P.; Kohn, W. *Phys. Rev.* **1964**, *136* (Ser. B), 864.

(21) Parr, R. G.; Donnelly, R. A.; Levy, M.; Palke, W. E. *J. Chem. Phys.* **1978**, *68*, 380.

(22) Iczkowski, R. P.; Margrave, J. L. *J. Am. Chem. Soc.* **1961**, *83*, 3547.

(23) Mulliken, R. S. *J. Chem. Phys.* **1934**, *2*, 782.

(24) Parr, R. G.; Yang, W. *J. Am. Chem. Soc.* **1984**, *106*, 4049.

(25) Parr, R. G.; Pearson, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 7512.

(26) Yang, W.; Parr, R. G. *Proc. Natl. Acad. Sci. U.S.A.* **1985**, *82*, 6723.

(27) (a) Herzberg, G. *Molecular Spectra and Molecular Structure: III. Electronic Spectra and Electronic Structure of Polyatomic Molecules*; Van Nostrand Reinhold Co.: New York, 1966; p 609. (b) Foster, S. C.; Miller, T. A. *J. Phys. Chem.* **1989**, *93*, 5986.

(28) Pople, J. A.; Gordon, M. *J. Am. Chem. Soc.* **1967**, *89*, 4253.

(29) (a) Baker, J.; Nobes, R. H.; Radom, L. *J. Comp. Chem.* **1986**, *7*, 349. (b) Simons, J.; Jordan, K. D. *Chem. Rev.* **1987**, *87*, 535.

(30) Čársky, P.; Urban, M. *Ab initio Calculations* (*Lecture Notes in Chemistry 16*); Springer Verlag: Berlin, 1980; p 74.

(31) Pople, J. A.; Seeger, R.; Krishnan, R. *Int. J. Quantum Chem.* **1977**, *S XI*, 149.

(32) (a) Langhoff, S. R.; Davidson, E. R. *Int. J. Quantum Chem.* **1974**, *VIII*, 61. (b) Davidson, E. R.; Silver, D. W. *Chem. Phys. Lett.* **1978**, *52*, 403.

(33) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618.

(34) (a) Nobes, R. H.; Pople, J. A.; Radom, L.; Handy, N. C.; Knowles, P. J. *Chem. Phys. Lett.* **1987**, *138*, 481. (b) Gill, P. M. W.; Pople, J. A.; Radom, L.; Nobes, R. H. *J. Chem. Phys.* **1988**, *89*, 7307. (c) Andrews, J. S.; Jayatilaka, D.; Bone, R. G. A.; Handy, N. C.; Amos, R. D. *Chem. Phys. Lett.* **1991**, *183*, 423.

(35) For an detailed account of this type of basis sets, see: Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986; p 65.

(36) Frisch, M. J.; Head-Gordon, M.; Trucks, G. W.; Foresman, J. B.; Schlegel, H. B.; Raghavachari, K.; Robb, M.; Binkley, J. S.; Gonzalez, C.; Defrees, D. J.; Fox, D. J.; Whiteside, R. A.; Seeger, R.; Melius, C. F.; Baker, J.; Martin, R. L.; Kahn, L. R.; Stewart, J. J. P.; Topiol, S.; Pople, J. A. *Gaussian 90*; Gaussian, Inc.: Pittsburgh, PA, 1990.

(37) Loncharich, R. J.; Schwartz, T. R.; Houk, K. N. *J. Am. Chem. Soc.* **1987**, *109*, 14.

(38) Löwdin, P. O. *Rev. Mod. Phys.* **1963**, *35*, 496.

(39) Cook, D. B.; *Int. J. Quantum Chem.* **1987**, *XXXI*, 251.

(40) Carter, J. T.; Cook, D. B. *J. Mol. Struct.* (*THEOCHEM*) **1991**, *251*, 111.

(41) Bobrowicz, F. W.; Goddard, W. A., III. In *Modern Theoretical Chemistry 3: Methods of Electronic Structure Theory*; Schaefer, H. F., III, Ed.; Plenum Press: New York, 1977; p 79.

(42) (a) Langenaeker, W.; De Decker, M.; Raeymaekers, P.; Geerlings, P. *J. Mol. Struct.* (*THEOCHEM*) **1990**, *207*, 115. (b) Langenaeker, W.; Demel, K.; Geerlings, P. *J. Mol. Struct.* (*THEOCHEM*) **1991**, *234*, 329. (c) Langenaeker, W.; Demel, K.; Geerlings, P. *J. Mol. Struct.* (*THEOCHEM*) **1992**, *259*, 317. (d) Tielemans, M.; Areschka, V.; Colomer, J.; Promel, R.; Langenaeker, W.; Geerlings, P. *Tetrahedron*, in press.

(43) (a) Hehre, W. J.; Pople, J. A. *Tetrahedron Lett.* **1970**, *34*, 2959. (b) March, J. *Advanced Organic Chemistry*, 3rd ed.; John Wiley: New York, 1985; pp 17–18. (c) Vanermen, G.; Toppet, S.; Van Beylen, M.; Geerlings, P. *J. Chem. Soc., Perkin Trans 2* **1986**, 699.

(44) Nalewajski, R. F. *Int. J. Quantum Chem.* **1991**, *XL*, 265.

(45) Wray, V.; Ernst, L.; Lund, T.; Jakobsen, H. J. *J. Magn. Reson.* **1980**, *40*, 55.

(46) Datta, D.; Nabakishwar, S. S. *J. Phys. Chem.* **1990**, *94*, 2187.

(47) (a) Swain, C. G.; Lupton, E. C., Jr., *J. Am. Chem. Soc.* **1968**, *90*, 4328. (b) Swain, C. G.; Unger, S. H.; Rosenquist, N. R.; Swain, M. S. *J. Am. Chem. Soc.* **1983**, *105*, 492.

(48) See ref 18, p 276.

(49) Vinayagam, S. C.; Sen, K. D. *Chem. Phys. Lett.* **1988**, *144*, 178.

(50) Sen, K. D.; Schmidt, P. C.; Böhm, M. C. *J. Phys. B.* **1985**, *18*, L35.