Electronegativity and Hardness of Chemical Groups

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Received: July 10, 1992; In Final Form: October 28, 1992

Electronegativity (χ) and hardness (η) indices have been derived for a set of typical substituents, from the linear dependence between quantum chemical electronegativity and group charges. The two indices may be combined into a single-parameter description of the electronegative character of a group either by the charge transfer or by the charge-transfer affinity (CTA), derived in the framework of the density functional theory. A correlation between the charge-transfer affinity (polar bonding energy) and the field Hammett constant has been demonstrated for substituents bonded to the phenyl reference.

1. Introduction

Rationalization of the electronegativity concept for chemical groups has been an important task since the foundation of the modern theory of electronegativity.[1,2] A comprehensive review of works on group electronegativities is available.[3]

From the chemical point of view, it seems straightforward to compare the bonding effect of polyatomic groups and atoms (monoatomic groups). Substituent effects of organic chemistry are typically discussed jointly for mono- and polyatomic entities. When it comes to electronegativity, a vital difference in dealing with groups and atoms has been hampering the efforts. A bonded atom possesses its undisturbed pattern for which the electronegativity has long been known and understood. This free-atom property may be modified by the promotion energy or the bonding potential, but otherwise, it is considered an inherent property of the atom. Its linear relation to atomic charge was first proposed by Sanderson[4] and has since become a subject of extensive studies aimed at the hardness of the chemical species.[5,6]

For a polyatomic cluster, such a comfortable reference point as a free group would have no meaning for a chemist, who can only observe a group through its bonding effects. Formally, though, if the electronegativity function for a group were known, $\chi_G(q)$, it might still be interpolated to produce $\chi_G(q=0)$. The real obstacle is the need for an unequivocal definition of χ_G in terms of parameters for the component atoms. Most contemporary studies use the electronegativity equalization (EE) principle, though partial electronegativity equalization, or no EE at all, has not been uncommon in earlier studies.[7,8]

Three major trends stem from the EE principle. First is due to Sanderson himself in the form of the geometrical mean formula widely used to mimic the electronegativity of small molecules:[4]

$$\chi_{AB} = (\chi_A\chi_B)^{1/2} \quad \text{for diatomics} \quad (1)$$

Parr and Bartollotti provided theoretical support to this formula.[9]

Another approach was explored by Huheey[10] and has recently been brought to a more sophisticated level by Mortier and van Genechten.[11] It starts from the linear relation for component atoms:

$$\chi_i = a_i + b_iq_i \quad (2)$$

where a_i and b_i correspond to the electronegativity and hardness for free atoms, respectively. Electronegativity equalization in a cluster is then sought by appropriately adjusting the atomic charges q_i.

An analytical formula of considerable theoretical importance was independently obtained by several authors.[12-15] The electronegativity of a molecule (or any other cluster of interacting atoms) is expressed in terms of the electronegativities and softness of component atoms:

$$\chi = \frac{\sum \chi_i\sigma_i}{\sum \sigma_i} \quad (3)$$

The softness parameters, σ (or the inverse hardness), are available on the basis of the density functional theory (DFT).[15,16] The latter equation has rarely been used in practice, due to the ambiguities concerning the softness parameters.

Quantum chemical methods have been recognized as a possible way to electronegativities as early as 1963.[2] Of all the efforts, Ponec came closest to a working definition of the group electronegativity in his concept of the global electronegativity.[17] A review of quantum chemical works may be found in ref 3.

This present work explores the novel, quantum chemical method elaborated by Komorowski and Lipiński.[18] It produces both electronegativity and hardness (softness) for a bonded atom as well as for any given part of the molecule, without referring directly to the EE principle.

An ultimate goal of this study is to provide a hint that the language of the physical–theoretical chemistry (χ, η) can adequately describe the same properties that are typically expressed by the Hammett substituent constants used to classify the substituents in organic chemistry. The problem has been first addressed by Huheey in 1966;[19] its resolution might bring considerable progress to physical–organic chemistry.

2. Electronegativity and Hardness of Bonded Chemical Entities

Electronegativity of the molecule (χ_M) can be decomposed into contributions from the component atoms (χ_A)[18]

$$\chi_M = -\frac{dE_M}{dN} = -\sum\frac{\partial E_M}{\partial N_A}\frac{dN_A}{dN} = \sum \chi_A K_A \quad (4)$$

where

$$\chi_A = -\frac{\partial E_M}{\partial N_A} \quad K_A = \frac{dN_A}{dN} \quad (5)$$

χ_A are the electronegativities of bonded atoms, and K_A stands for the Fukui function indices.[20]

Equation 4 is not limited to molecules; the electronegativities of any cluster of atoms may be decomposed in the same way into a sum of contributions from its parts: orbitals, atoms, or groups.

Then, for a group of atoms (G), we have

$$K_G = \frac{dN_G}{dN} = \sum_{A \in G} \frac{dN_A}{dN} = \sum_{A \in G} K_A \quad \text{since} \quad \sum N_A = N_G \quad (6)$$

This leads to a simple definition of the group electronegativity:

$$\chi_G = \frac{\sum_{}^{G} \chi_A K_A}{\sum_{}^{G} K_A} \quad (7)$$

Equation 7 is strictly equivalent to the well-known eq (3), where Fukui indices (K_A) replaced the softness parameters via the proven relation $\sigma_A = K_A/\eta_M$;[18] η_M stands for the hardness of the molecule.

The electronegativity of molecule may be, alternatively, decomposed into a mixed representation of groups and atoms in the form

$$\chi_M = \sum_{G}^{\text{groups}} \chi_G K_G + \sum_{A \notin G}^{\text{atoms}} \chi_A K_A \quad (8)$$

Equation 7 provides the much needed and tractable formal definition for the group electronegativity. It can be directly calculated by any LCAO MO-type quantum method using results from a single SCF HF run for a molecule (for details, see ref 18). The electronegativity (χ) for a bonded atom, when calculated under the NDO approximation, may be decomposed into the standard electronegativity term (χ°) and the bonding potential (V):

$$\chi_A = \chi_A^\circ(q_A) + V(q_{B \neq A}) \quad (9)$$

The linear (statistical) relation of χ° to independently calculated Mulliken charges established for atoms leads to the average electronegativity ($\bar{\chi}$) and hardnesses ($\bar{\eta}$) that are obtained as correlation parameters:[18]

$$\chi_A^\circ = \bar{\chi}_A + \bar{\eta}_A q_A \quad (10)$$

Equations 8 and 9 are potential sources of standard electronegativity parameter for a group:

$$\chi_G^\circ(q_G) = \frac{\sum_{}^{G} \chi_A^\circ(q_A) K_A}{\sum_{A}^{G} K_A} \quad q_G = \sum_{}^{G} q_A \quad (11)$$

When a group becomes identical to the entire molecule, then $\sum K_A = 1$, $q_M = 0$, and eq 11 is identical to eq 4.

Equation 11 opens a route to straightforward calculation patterns for the standard electronegativity (χ°) of any group actually bonded to a molecular skeleton and bearing the charge q_G. SCF HF results for a molecule, on the basis of atomic orbitals, provide all the necessary data. Koopman's theorem is an essential approximation warranting equivalence of the results for molecular electronegativity to Mulliken $1/2(I + A)$.[18] Then, the χ and η parameters for a group become accessible, when $\chi^\circ(q_G)$ results are plotted for a series of molecules containing the group G, eq 10. The group charge (q_G) comes from the same SCF HF procedure; the Mulliken approximation has been tested as a reliable source of atomic charges for this purpose.

3. Results and Discussion

Details of the calculation procedure have been presented elsewhere.[18] The semiempirical, all-valence INDO method was explored in actual calculations.[21] The relation between χ° and q for a chosen group or element has been based on the result for a set of molecules, selected in order to cover a broad range of q

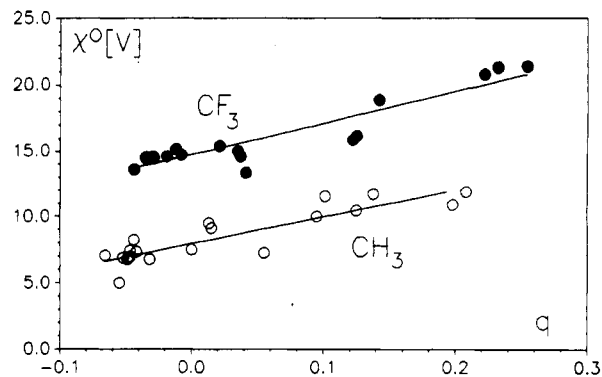**Figure 1.** Sample relationship determined between the standard electronegativity (χ°) and charge from Mulliken population analysis (q) for CF_3 and CH_3 groups.

TABLE I: Inherent Group Electronegativities and Hardnesses

group	$\bar{\chi}$,[a] V	$\bar{\eta}$,[b] V/e	r[b]	no. of molec[c]
F	16.87	12.80	0.970	21
CF_3	14.86	17.78	0.848	21 (20)
Cl	12.73	8.15	0.949	20
Br	11.58	7.28	0.962	12
NO_2	11.31 ∓ 0.59	(<1)		10
I	10.22	6.88	0.998	7
COOH	8.93 ∓ 0.41	(1.8)	(0.964)	8 (4)
NH_2	8.65	5.84	0.846	12
OH	8.63 ∓ 0.61	(3.7)	(0.976)	24 (5)
CHO	8.45	(4.7)	(0.885)	6
CO	8.10	3.42	0.823	24
CH_3	7.95	16.52	0.860	23 (22)
2-furan	7.58	3.23	0.940	7 (6)
3-furan	7.48	0.81	0.982	7 (6)
p-pyridine	7.19 ∓ 0.43	(1.1)	(0.739)	12 (10)
H	7.18	6.40	0.999	10
2-pyrrole	7.02	2.21	0.878	8 (7)
3-pyrrole	6.83	0.72	0.975	8 (7)
m-pyridine	6.67 ∓ 0.22	(<1)		12
o-pyridine	6.63 ∓ 0.22	(<1)		12
CCH	6.55	11.03	0.844	23
CN	6.50	9.30	0.950	12 (10)
Ph	6.14	0.95	0.887	9 (7)

[a] Standard deviation is shown when χ was determined as an average of all points in the group. [b] Parentheses denote less accurate determinations. [c] A number in parentheses gives the actual number of points used in the correlation.

for a given group. This makes resulting $\bar{\chi}$ and $\bar{\eta}$ quantities more general than other commonly used group parameters, usually derived for a well-defined property but limited to a single molecule or a reaction.[3]

3.1. Group Electronegativity and Hardness. An example of the $\chi^\circ(q)$ dependence is shown in Figure 1 for CH_3 and CF_3. The results for all groups studied are collected in Table I, in the sequence of decreasing electronegativity. The results for halogens are also included in Table I. Conceptually, the resulting electronegativity and hardness parameters ($\bar{\chi}$ and $\bar{\eta}$) are closely related to Huheey's a and b constants[19] calculated for atoms as well as for groups. There are, however two remarkable differences.

(i) a and b parameters were derived for free atoms only. The valence state was arbitrarily specified; ionization energy (I) and electron affinity (A) served as attachment points for the $E(N)$ relationship. Thus, Huheey's parameters do not describe actually bonded atoms.[22]

(ii) Group parameters by Huheey were subject to another limitation, of which the author was well aware. The group charge was only an internal parameter of the method calculated on the basis of the electronegativity equalization principle. This led to identical parameters for isomeric groups.

The $\bar{\chi}$ and $\bar{\eta}$ parameters resulting from this present method for bonded atoms have been previously compared with Huheey's

TABLE II: Charge Transfer (ΔN, in Electrons) between the Substituent and the Reference Methyl (Me) and Phenyl (Ph) Calculated with Equation 12 using Data from Table I

group	ΔN(Me)	ΔN(Ph)	group	ΔN(Me)	ΔN(Ph)
F	0.152	0.390	OH	0.017	0.268
CF_3	0.101	0.233	CHO	0.009	0.193
Cl	0.097	0.362	CH_3	0	0.052
Br	0.076	0.330	H	−0.017	0.071
NO_2	0.096	1.326	CCH	−0.025	0.017
I	0.048	0.260	CN	−0.028	0.018
COOH	0.027	0.507	Ph	−0.052	0
NH_2	0.016	0.185			

historic a and b indices. No regular relation between both sets of data has been observed. They were not, however, considered as contradictory. While a and b are for free atoms, $\bar{\chi}$ and $\bar{\eta}$ are for bonded ones. In all cases, atoms appear to be considerably more softer, when bonded.

Comparison with the vast body of experimental scales for group electronegativities[7,23] should be done with caution. All chemical scales from the "best" data by Wells[24] attempt a description of the group by one single parameter, while this present study rooted in the density functional theory offers a two-parameter image. It is not surprising to see a rather poor correlation between average electronegativities in Table I and a majority of scales; reasonable correlations were found with the Sanderson[25] ($r = 0.888$) and the Bratsch scale[26] ($r = 0.836$).

Hardnesses for the chemical groups can hardly be compared, as no data (except by Huheey) are available for groups. The intuitive expectations are confirmed. The hardest groups in this collection are CH_3 and CF_3 followed by CCH, CN, and the halogens in the proper order. Π-Systems are the softest, which is expected, since η provides a measure for the HOMO–LUMO energy gap.[27] An intriguing feature was discovered for furanes and pyrroles: the position vicinal to the heteroatom is remarkably harder than the other. No correlation was found between group hardnesses and group refraction data. Such a relation has long been anticipated, on the basis of the chemical approximation, an electrodynamical model for an atom.[15]

3.2. Charge Transfer. A meaningful comparison between the results presented in Table I and other measures of electronegativity is possible only after conversion of $\bar{\chi}$, $\bar{\eta}$) into a single-parameter representation. (The importance of such a conversion has recently been stressed by R. Drago in a related field.[28]) Since electronegativity ex definitio represents a measure of electrostatic (ionic) interaction, the charge transfer (ionicity) may serve as the first reference point for all scales, very much in the spirit of the original Pauling definition. The direct measure of electronegativity by charge transfer was once proposed by Taft et al.[23] and then pursued by Datta.[29]

Parr and Pearson's formula may be used to convert $\bar{\chi}$ and $\bar{\eta}$ into the charge transfer:[30]

$$\Delta N(\text{X–R}) = \frac{1}{4}\frac{\chi_R - \chi_X}{\eta_R + \eta_X} \quad (12)$$

where R stands for a reference. Methyl and phenyl have been chosen as two limiting references for this study, hard and soft, respectively. Charge transfers between each group and the reference were calculated (Table II). Charge transfer to the hard methyl group was in all cases lower than to soft phenyl. The HSAB principle is well illustrated in Table II: ΔN to hard methyl is highest for hard F and CF_3, while the soft NO_2 group gives its largest ΔN to soft phenyl.

Correlation of the charge transfer (ΔN) with a handful of theoretical and experimental electronegativity scales was tested. The resulting correlation coefficients were markedly improved for some scales (Huheey,[10] Mullay[7]). However, the significance of all correlations was low, $r < 0.9$. The lack of correlation between ΔN and the weighted scale of Wells was striking, as this scale
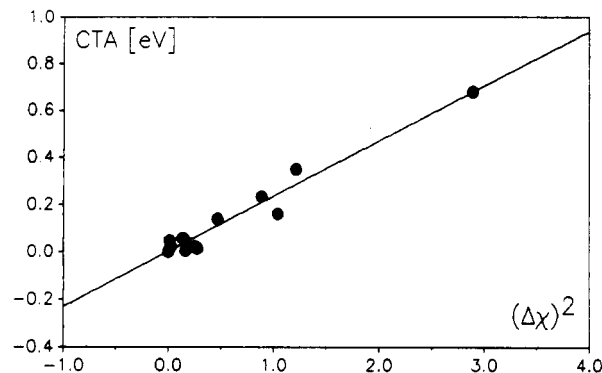
Figure 2. Charge-transfer affinity (CTA) for the charge transfer between a group and the methyl reference, determined by eq 13, using electronegativities and hardness parameters from Table I. $\Delta\chi$ on the abscissa stands for the electronegativity difference between a given group and methyl, on the Bratsch scale [ref 26] in Pauling units.

has been shown to correlate very well with atomic charges on hydrogen in the H–X pair (ab initio calculations).[23,29,31]

3.3. Charge-Transfer Affinity. The predictive power of the electronegativity concept suggested by Pauling had been limited to the bond polarity between two bonded atoms or, more rigorously, to the polar energy contribution to this bond. This energy has been recently discussed in terms of electronegativity and hardness and identified as the charge-transfer affinity (CTA).[32] An analysis has been presented as to how the polar energy fraction (CTA) may be expressed by electronegativity and hardness indices. The commonly used formula given by Parr and Pearson[30] is a convenient first approximation:

$$CTA = \frac{1}{2}\frac{(\chi_R - \chi_X)^2}{\eta_R + \eta_X} \quad (13)$$

Extension of this equation to include the polarization terms was also proposed.[32] Pauling's original formula may be considered a zeroth-order approximation to eq 13, by neglecting the hardness effect, CTA $\sim (\chi_R - \chi_X)^2$.

Equation 13 leads to an important suggestion: the electronegativity difference alone is insufficient to determine the bond polarity. The CTA energy provides an opportunity to include the hardness effect in the interaction of chemical species.

There are two limitations in exploring the CTA as a measure of interaction. (i) Its meaning is purely electrostatic;[32,33] hence, only polar effects will be reflected by CTA. (ii) A set of transferable χ and η parameters for atoms and groups is needed.

Group electronegativity and hardness parameters derived in this work conform to the transferability requirement. Conceptually and formally, they are identical to corresponding atomic parameters presented elsewhere.[18]

It was possible to calculate the CTA energies for a collection of 15 substituents (including halogens) using again methyl and phenyl as standard references. They were correlated with the square of the electronegativity difference. The best fits obtained in this group were for the Bratsch scale[26] (methyl) and Mullay scale[7] (phenyl), Figure 2.

$$CTA(\text{X–Me}) = 0.233(\Delta\chi_{\text{Bratsch}})^2 \quad (r = 0.977) \quad (14)$$

$$CTA(\text{X–Ph}) = 3.158\Delta(\chi_{\text{Mullay}})^2 + 0.646 \quad (r = 0.946) \quad (15)$$

A similar correlation with the Wells scale was found at $r = 0.791$.

The two scales with the best observed correlation are in fact modern mutations of old electronegativity scales, adopted to the group concept. The Bratsch scale contains generalized Mulliken electronegativities, while the Mullay scale is based on the concept of Gordy[34] as well as Allred and Rochow.[35] Both Bratsch and Mullay included the valence-state analysis into their electrone-

gativity indices, which brings their concepts more closely to bonded atoms. Finding the newly derived indices $\bar{\chi}$ and $\bar{\eta}$ for bonded groups (Table I) properly related to these two realistic scales is very encouraging. It does suggest that the CTA energy may indeed be a common ground for all scales of electronegativity. The Bratsch and Mullay scales appear to have the hardness effect indirectly built in. A similar effect has been observed for the Pauling scale of atomic electronegativities.[32]

3.4. Substituent Effect. Common descriptions of substituents by means of the Hammet-type constants (σ) have been an early alternative to the electronegativity concept. It is also based on an energy analysis. Experimental parameters (log k, log K), directly related to ΔG_r for a chosen standard reaction, are expressed as linear functions of the parameter σ for a substituent distant from the reaction site. The complexicity of σ is a well-known fact and much research has been done in order to find the "best" σ values.[36] One of the most easily interpreted contributions to the σ parameter is the field constant (σ_F). Its meaning is purely electrostatic, and its value has been experimentally established for situations where substituents affect the reaction site by pure through-space electrostatic interactions. Then

$$\Delta G_r = \rho_r \sigma_F(X) \qquad (16)$$

where only σ_F varies with the substituent (X). Such a linear relation between the energy (ΔG_r) and σ_F parameter suggests, at the level of pure electrostatics, that σ_F may have the meaning of a potential. This conclusion has been proven for a set of monosubstituted benzene derivatives.[18] When substitution takes place at a fixed position, the change in distance to the reactive site of the molecule is insignificant. The substitution effect may be reduced to changing the charge (q) formally assigned to the attached group or atom (X):

$$\Delta G_r = \rho_r' q(X) \qquad (17)$$

The ρ_r' constant is formally also modified by the substitution, due to the countercharge ($-q$) transferred to and from the substituent group from and to the separating molecular skeleton. Nearly constant reaction constants (ρ), which are typically observed for a given type of molecule and reaction, may be understood when the countercharge is diffused over many atoms of the skeleton. In such a case, only the field constant (σ_F) would approximately reflect the variation of charge transferred to and from the reference by substituent X:

$$\sigma_F(X) \sim q(X) \qquad (18)$$

At this point, a relationship between the charge-transfer affinity, the substituent (X), and the molecular skeleton (R, usually the phenyl ring) is expected:

$$CTA(R-X) \sim q(X)^2 \sim \sigma_F(X)^2 \qquad (19)$$

A linear relation has indeed been found between the CTA energy (eq 13), calculated with the electronegativity and hardness parameters in Table I, and the squared substituent constants, σ_F (Figure 3), when the phenyl ring has been chosen as a reference:

$$CTA(Ph-X) = 3.086\sigma_F(X)^2 - 0.734 \quad (r = 0.953) \quad (20)$$

The non-zero intercept arises from arbitrarily setting $\sigma_F = 0$ for hydrogen, while the CTA correctly predicts a small polar energy contribution to the H–Ph bond. A slightly less satisfactory relation with F^2 developed by Swain and Lupton[36] has also been found:

$$CTA(Ph-X) = 1.072F^2 - 0.205$$
$$(r = 0.932, \text{ CN group ommited}) \quad (21)$$

It is well-known that σ_F constants are purely field indices, while F contains also an inductive increment, which could explain the decreased correlation between CTA and F^2 and especially the strong deviation for the CN group.
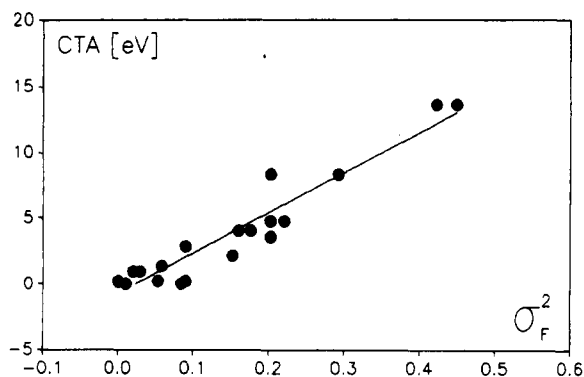

Figure 3. Charge-transfer affinity (CTA) for the charge transfer between a group and the phenyl reference, determined by eq 13, using electronegativities and hardness parameters from Table I. σ_F on the abscissa stands for the field Hammett constant, as given by Taft et al. [ref 23]. Two sets of σ_F reported by the authors were used.

The relationship involving a square of the Hammett constant has already been observed for another energy parameter. Taft et al. have determined a linear function for $J_{CC}(\sigma_X{}^2)$, where J_{CC} is the ipso–ortho, carbon–carbon NMR coupling constant in a series of Ph–X molecules, and σ_X is the inductive Hammett constant for substituent X.[23] Taft et al.'s results and the finding of this present study suggest that the substituent effect on the energy of the molecular system may be more adequately given by σ^2, at least for charge-related interactions: field and inductive. The most important resonance effects have not yet been the subject of similar analysis.

4. Conclusions

The primary result of this work, electronegativity and hardness for a set of common substituents, should not be taken just as an alternative measure of electronegativity for chemical groups. The role of hardness has been clearly exposed. A coherent description of chemical groups can no longer escape the definition of group hardness, which is equally as important a parameter as electronegativity. While numerical values of χ and η need further studies that would unveil the role of valence states and possible symbiotic effects, the need for a two-parameter description of chemical groups can hardly be questioned. Also important is the observed relation to existing scales of group electronegativity. Conceptually, they all may be unified by the polar energy parameter CTA, even though rigorous correlation was found only for a handful of modern scales. It is suggested that the various scales of group electronegativity indirectly contain the hardness effect.

A technique for avoiding the hardness analysis is exemplified by the latest paper by Reed and Allen.[37] These authors take the bond polarity index (BPI, equivalent to the CTA energy in this work) for the direct measure of the electronegativity difference. This in itself contradicts the original Pauling definition and its theoretical support by the density functional theory.[18,32,33] The hardness effect remains hidden in BPI energies; its role is further minimized by derivation of $\Delta\chi$ for selected references only. Challenged with substantial differences in ordering of groups by means of BPI for various references, Reed and Allen argue for choosing CH_3 as the standard reference. This introduces an arbitrary element to the resultant scale of group electronegativity which may be found attractive for practical purposes but does not bring understanding into the complex mosaic of electronegativity scales.

An intriguing result of this work, the direct relationship between polar bonding energy CTA and the square of the polar substituent constant (σ_F), finds interesting context in other works in the area. Contrary to an early suggestion,[22] group electronegativities could not be directly related to Hammett substituent constants, unless the hardness effect is taken into account. Charge-transfer affinity

was found to describe adequately the substituent effect. Relationships exist between CTA and σ_F, as well as between CTA and $\Delta\chi$ for other scales, which strongly suggest that the languages of inorganic chemistry (χ, η) and organic chemistry (σ), may eventually provide equivalent descriptions of chemical observations.

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