TABLE II

ATOMIC COÖRDINATES, TEMPERATURE FACTORS AND STANDARD DEVIATIONS

Atom	Code number	x	σ_x[a]	y	σ_y	z	σ_z	B[b]
$^1/_8$ Ni	1	0.50000	[c]	0.25000	[c]	0.12500	[c]	3.02
$^1/_2$ N	2	.36610	0.00087	.25000	[c]	.11947	0.00154	3.47
$^1/_2$ C	3	.33126	.00155	.41874	0.00155	.12500	[c]	3.68
$^1/_2$ C	4	.11082	.00197	.37290	.00200	−.02811	0.00457	6.40
C	5	.30791	.00079	.32573	.00077	.11572	.00116	3.43
C	6	.21541	.00080	.29568	.00081	.10499	.00116	3.78
C	7	.13227	.00096	.36124	.00103	.09360	.00221	5.19

[a] Standard deviations as calculated by least squares program. [b] B is the individual isotropic temperature factor. [c] Fixed by symmetry.

TABLE III

INTRAMOLECULAR BOND LENGTHS

Bond	Length in Å.	Standard deviation
1–2	1.957	0.013
2–5	1.396	.013
3–5	1.398	.013
5–6	1.427	.016
6–6′	1.335	.023
6–7	1.554	.018
7–4	1.542	.039

TABLE IV

BOND ANGLES

Angle[a]	Angle in degrees	Standard deviation
1,2,5	127.6	0.7
2,5,6	109.6	1.0
2,5,3	126.7	1.4
3,5,6	123.6	1.3
6,7,4	108.6	1.6
5,6,7	124.0	1.1

[a] Middle number is vertex of angle.

methene atoms (3) form a plane parallel to the 001 plane at z = 0.125. We will discuss the deviation of the other atoms in the molecule from this defined plane. The pyrrole nitrogen atom (2) lies slightly out of the plane but only at the limit of significance. (We shall take three times the standard deviation as the limit of significance.) On the other hand, the carbon atoms (5) and (6) are significantly out of the above defined plane. The molecular symmetry is such that two of the pyrrole rings are bent up and two are bent down from the plane. If one defines a plane by the atoms (6) and (6′) and their mirror images, then the perpendicular distance between this plane and the reference plane is 0.25 Å. This is a considerable distortion of the molecule from planarity.

It cannot be determined if the non-planarity of the porphyrin ring is caused by the nickel atom pushing on the pyrrole nitrogens to cause a distortion. The nickel–nitrogen distance does not seem excessively small to cause this type of distortion. In order to solve the problem, a free base porphyrin structure will have to be determined.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CINCINNATI, CINCINNATI 21, OHIO]

Electronegativity. II. Bond and Orbital Electronegativities[1,2]

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A new definition for electronegativity is proposed as $\chi = \mathrm{d}E(n)/\mathrm{d}n$, where $E(n)$ is the energy of an atom in its valence state as a function of the occupation, n, of the orbital for which the electronegativity is expressed. This definition is found for singly occupied orbitals to be identical with Mulliken's definition of electronegativity. The given representation, although equivalent to previous concepts, permits in addition the computation of ***orbital electronegativities*** of vacant and doubly occupied orbitals and of groups. A new term ***bond electronegativity*** is defined, as the electronegativity of orbitals forming a bond, after charge has been exchanged between them. It is shown that this process of charge exchange will equalize the electronegativity of the two orbitals forming a bond to lower the energy of the molecule. Such a treatment leads directly to a new definition and clear understanding of ionic character in terms of charge transferred between the bond-forming orbitals.

The concept of electronegativity has had extremely wide use and considerable success in systematizing experimental chemical data. Nonetheless, it has never been quite adequately defined. Thus, in recent numerical work on electronegativities,[1] it was necessary to define the concept of orbital electronegativity to indicate that this is a property, not of the atom as such, but of an individual orbital of the atom. In addition it seemed again unreasonable that this quantity was measured in units of energy (*e.g.*, eV.). Pauling's[3] verbal definition of electronegativity: "The power of an atom in a molecule to attract electrons to itself" suggests, not the units of energy, but of potential, *i.e.*, energy/charge. This was recognized recently by Iczkowski and Margrave,[4] who redefined electronegativity as a derivative of energy with respect to charge. Their definition is not completely satisfactory; first, it ignores completely the orbital dependence of electronegativity; second, it assumes that the energy of an atom is a continuous and single-valued function of its charge. That the function is not single-valued is apparent from the fact that a variety of different valence states with different energies are readily obtained for a given element.[1] For trigonally hybridized carbon, when the charge is +1 or −1, we have reported two energies,[1] considerably different, depending on the distribution of the electrons.

We have developed a definition of electronegativity (or better orbital electronegativity) which is mathematically defensible—although based on some assumptions—and which promises to be extremely useful in all the areas in which electronegativity has generally been applied. Since this definition is capable of sen-

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(1) Paper 1 of this series, J. Hinze and H. H. Jaffé, *J. Am. Chem. Soc.*, **84**, 540 (1962).

(2) This work was supported by a contract with Materials Central, Wright Air Development Division, U. S. Air Force.

(3) L. Pauling, *J. Am. Chem. Soc.*, **54**, 3570 (1932).

(4) R. P. Iczkowski and J. L. Margrave, *ibid.*, **83**, 3547 (1961).

sitively accounting for effects due to hybridization and other orbital changes, it should attain further usefulness in the determination of semi-empirical parameters for LCAO·MO calculations and possibly even for calculations by the Pariser–Parr method. In addition, the new definition leads immediately to a further concept, the bond electronegativity, which will be effective in the estimation of ionic character and related properties, and which appears to bear a close relation to Sanderson's stability ratio.[5]

The Definition.—Following Pauling, we desire that the *orbital electronegativity* be a measure of the power of an atom, as it may exist in a molecule, to attract an electron in a given orbital to itself, thus the *orbital electronegativity* should be 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 the orbital

$$\chi_j = \partial E/\partial n_j$$

where n_j is the occupation number of the j'th orbital, the orbital electronegativity of which is χ_j.

This definition implies two assumptions: (a) that the occupation number n_j may have both integral and nonintegral values, and (b) that once assumption a is made, then the energy E is a continuous and differentiable function of n_j.

Strictly speaking, neither of these assumptions is valid. In formal quantum mechanics, the number of electrons is a cardinal number, and has meaning only for integral values. Nevertheless, in certain applications of quantum mechanics to valence problems, and particularly in dealing with the assignment of electrons to individual atoms, it has become quite customary, and useful, to speak of partial charges on atoms, thereby *implying* fractional values for occupation numbers. This implies possibly an over-emphasis of a population analysis, in which the electron described by a molecular orbital $a\phi_A + b\phi_B$, which is a linear combination of the atomic orbitals ϕ_A and ϕ_B of atoms A and B, is divided between the atoms A and B in the ratio of the squares of the coefficients a and b. However, n_j may be understood to represent the average charge residing in an orbital and can thus be used as a continuous variable, which ranges from 0 to 2. These limits are imposed, since it does not seem possible to assign a meaning to a negative occupation number, and exceeding the value of 2 would be a violation of the Pauli principle.

Assumption b is possibly the more drastic one. The calculation of the energy of a valence state is achieved by expansion into a series of parameters, the so-called Slater–Condon parameters, F's and G's, each of which is in itself an integral over the radial part of the wave function of the atom. Alternatively, the energy of the valence state can be obtained as a weighted average of certain spectroscopic states. Whether one prefers a completely theoretical, *a priori* calculation, or a semi-empirical procedure based on observed spectroscopic data, the calculation of the energy is feasible only for integral values of n_j, 0, 1 and 2. However, given the three values of $E(n_j)$ — $E(0)$, $E(1)$ and $E(2)$ — one can *postulate* that E is a *continuous* function of n_j. At the defined points, it is also singlevalued, so that the postulation that E be differentiable, provided one has accepted its continuity, seems perfectly reasonable.

Once one accepts the assumption b, one can still imagine an infinite number of possible functional relations; any three parameter equation can be fitted to these three points. The simplest such relation is obviously a quadratic (parabola): Fig. 1.

$$E(n_j) = a + bn_j + cn_j^2 \qquad (1)$$

This relation, eq. 1, will be chosen here as the relation of choice for two reasons: (1) because of its mathematical simplicity, and (2) particularly because, at $n_j = 1$, the slope of this curve, *i.e.*, the orbital electronegativity by our definition, is equal to $(E(2) - E(0))/2$ according to a well-known property of parabolas. But this quantity is equal to $(E(2) - E(1) + E(1) - E(0))/2$, where $E(2) - E(1)$ is the electron affinity, E_v, and $E(1) - E(0)$ is the ionization potential, I_v; in other words the orbital electronegativity as defined is equal to $(I_v + E_v)/2$, identical to Mulliken's definition.[6]

Thus, the definition given above, with the assumed energy relation of eq. 1, contains the Mulliken definition as a special case. Since the Mulliken and Pauling definitions have been shown to be substantially equivalent, it is apparent that our new definition represents a generalization of the original definitions, and will leave previous work substantially unaffected. The fact that our new definition, with the assumptions a and b above, contains the Mulliken definition as a special case may well be regarded as a justification of the assumptions.

Differentiation of eq. 1 with respect to n_j gives the orbital electronegativity of the orbital j: Fig. 1.

$$\chi_j = \partial E/\partial n_j = b + 2cn_j \qquad (2)$$

This eq. 2, together with the assumptions a and b, give a meaning to n_j for fractional values, as long as $0 \leqslant n_j \leqslant 2$, and would suggest immediately that, for a given orbital j, one can define an electronegativity as a function of n_j. This possibility, however, requires closer scrutiny.

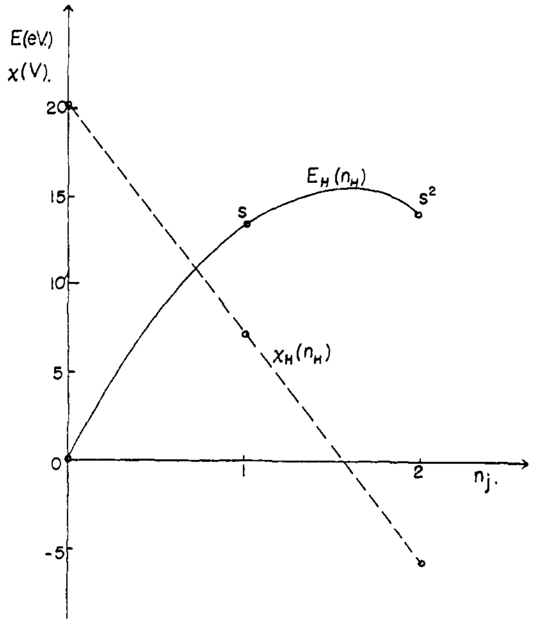

Fig. 1.—The energy and electronegativity of hydrogen as a function of the occupation number n_H of the 1s-orbital.

The entire value of the electronegativity concept, as it has been used up to now, hinges on the fact that it gives a measure of the power by which an atom, in its valence state, attracts an additional electron for bond formation. Consequently, electronegativity is a property of an atom before a bond is formed. If one assumes a coördinate covalent bond as formed from a pair of electrons on one atom, and a vacant (virtual) orbital on the other, the concept is readily extended to electron pairs and vacant orbitals. Thus the orbital electronegativity concept in the accepted sense is valid for

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[5] R. T. Sanderson, *Science*, **114**, 670 (1951).

[6] This was noted also by H. O. Pritchard and F. H. Sumner, *Proc. Roy. Soc. (London)*, **A235**, 136 (1956).

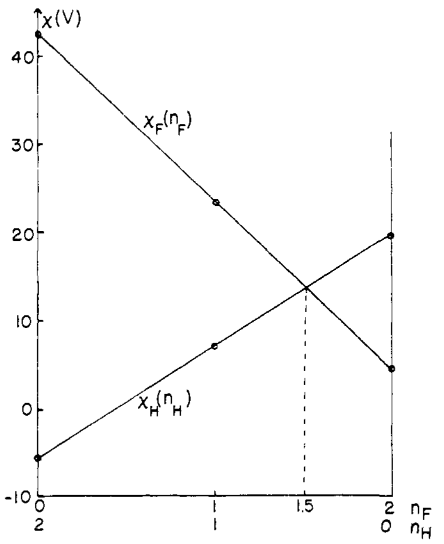

Fig. 2.—Electronegativities of A and B (using hydrogen and fluorine as examples) in an AB bond as a function of n_A and n_B.

values of $n_j = 0$, 1 and 2 only. The meaning of values obtained for fractional values of n_j will be examined in the next section.

Ionic Character and Bond Electronegativity.—Before proceeding to an examination of the meaning of $\chi(n_j)$ for non-integral values of n_j, it will be necessary to examine the concept of ionic character. This concept originated logically in the valence bond method (resonance theory) as the fraction of ionic structure in the complete wave function; thus, if the wave function of a compound was given as, $a\Psi(\mathrm{A}^-\mathrm{B}) + b\Psi(\mathrm{A}^-\mathrm{B}^+)$, b^2 is the ionic character. Similarly, using the lowest approximation of molecular orbital theory, neglecting overlap, in which a chemical bond is described by two electrons occupying an orbital $a\psi_\mathrm{A} + b\psi_\mathrm{B}$, the absolute value of $|1-2b^2|$ becomes the approximate measure of the excess charge on B, and hence the ionic character. Neither definition is completely satisfactory, because of the problems arising out of overlap populations (the electrons not readily assignable to either atom, but apparently residing in the bond); however, any more elegant definition loses simplicity.

Unfortunately, the calculations to obtain the ionic character from the above quantum mechanical definitions cannot, in general, be made, and empirically established ionic character values have frequently been used to provide a measure of the wave function. For this purpose, empirical relations have been postulated, from which ionic character may be derived. Most notable among these is the relation to dipole moment[7] which, however, is open to serious criticism.[8] The most common way of estimating ionic character, however, depends on the fact that it is related to electronegativity differences, as first observed by Pauling. Unfortunately, several different relations have been postulated, *e.g.*[7,9]

$$i = 1 - \exp {}^1/_4(\chi_\mathrm{A} - \chi_\mathrm{B})^2$$

$$i = {}^1/_2|\chi_\mathrm{A} - \chi_\mathrm{B}|$$

If we now consider the process of bond formation as starting from two atoms, A and B, each possessing one unshared electron, we may arbitrarily divide it into two steps: the pairing of the two electrons, forming a purely covalent bond, in which the occupation numbers n_A and n_B remain unity, as in the free atoms followed by a transfer of charge, changing the numbers n_A and n_B to their final values in the compound. Such charge transfer, however, will occur only if the two orbitals considered overlap strongly. We will now consider this second process in case of strong overlap from two different points of view.

If we wish to describe the two electrons forming the bond A–B as in a state of equilibrium, we must require that the potential which each electron sees on both atoms A and B be equal. This means that we obtain a restrictive condition on the equilibrium values of the occupation numbers n_A and n_B, since

$$\chi_\mathrm{eq}(n_\mathrm{A}) = \chi_\mathrm{eq}(n_\mathrm{B})$$

Furthermore the sum of n_A and n_B is 2. By plotting $\chi_\mathrm{A}(n_\mathrm{A})$ against n_A and similarly for B (n_B varies from 2 to 0 as n_A varies from 0 to 2), we obtain Fig. 2, where the intersection of the two straight lines (each of the form of eq. 2) gives the equilibrium values of n_A and n_B.

Mathematically equivalent to this procedure, but physically equally interesting, is a consideration of the energetics of the transfer of electrons from A to B (or *vice versa*). Transfer of an infinitesimal amount of charge (an infinitesimal change in n) from A to B (or *vice versa*) is accompanied by a reduction of charge on A, requiring an expenditure of energy equal to $(\mathrm{d}E_\mathrm{A}(n_\mathrm{A})/\mathrm{d}n_\mathrm{A})\mathrm{d}n_\mathrm{A}$, while at the same time an amount of energy equal to $(\mathrm{d}E_\mathrm{B}(n_\mathrm{B})/\mathrm{d}n_\mathrm{B})\mathrm{d}n_\mathrm{B}$ is released. Equilibrium is reached when the transfer involves no further change in energy, *i.e.*, since $\mathrm{d}n_\mathrm{A} = -\mathrm{d}n_\mathrm{B}$, when

$$\mathrm{d}E_\mathrm{B}(n_\mathrm{B})/\mathrm{d}n_\mathrm{B} = \mathrm{d}E_\mathrm{A}(n_\mathrm{A})/\mathrm{d}n_\mathrm{A}$$

or in other words, when the electronegativities given by eq. 2 are equal.

The electronegativities for these fractional values of n_j then have the special property that they are the same for the two atoms forming a chemical bond, or better for the orbitals of the two atoms which combine to form the bonding MO. For this reason we suggest for this electronegativity the term *bond electronegativity*, and would like to repeat that they must *not* be confused with the concept of electronegativities as defined by Pauling.

The concept of bond electronegativity lends itself particularly well to a definition of ionic character. According to the bond electronegativity concept, the ionic character is the amount of charge transfer necessary to make the bond electronegativities of the bonded atoms equal: In other words, the ionic character, $|n_j - 1|$ (where it is immaterial which of the n_j's of the two atoms is taken, since their sum is equal to 2) is obtained by equating $\chi_{\mathrm{A}}^{\mathrm{bond}}{}_j$ and $\chi_{\mathrm{B}}^{\mathrm{bond}}{}_j$, *i.e.*

$$b_\mathrm{A} + 2c_\mathrm{A}n_{\mathrm{A}i} = b_\mathrm{B} + 2c_\mathrm{B}n_{\mathrm{B}i} = b_\mathrm{B} + 2c_\mathrm{B}(2 - n_{\mathrm{A}i})$$

thus

$$i = |n_{\mathrm{A}i} - 1| = \left|\frac{b_\mathrm{B} - b_\mathrm{A} + 2(c_\mathrm{B} - c_\mathrm{A})}{2(c_\mathrm{A} + c_\mathrm{B})}\right| = \left|\frac{\Delta\chi}{2(c_\mathrm{A} + c_\mathrm{B})}\right| \qquad (3)$$

The numerator of eq. 3 is the electronegativity difference (*i.e.*, the difference in *orbital* electronegativities). The denominator, however, is a function not directly expressible in terms of the electronegativity difference, and consequently no simple relation between ionic character and electronegativity is possible. However, Gordy's relation,[9] which postulates the ionic character as linear in the electronegativity difference, seems to be most nearly obeyed.

Group Orbital Electronegativities.—The definition of orbital electronegativity introduced above permits further the determination of the orbital electronegativities of groups. Thus it has long been considered desirable to obtain electronegativities, not only of a tetrahedral carbon atom, but of the group $\mathrm{X_3C}$ with

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(7) L. Pauling, "The Nature of the Chemical Bond," 3rd ed., Cornell University Press, Ithaca, N. Y., 1960.

(8) D. Z. Robinson, *J. Chem. Phys.*, **17**, 1022 (1949).

(9) W. Gordy, *ibid.*, **19**, 792 (1951).

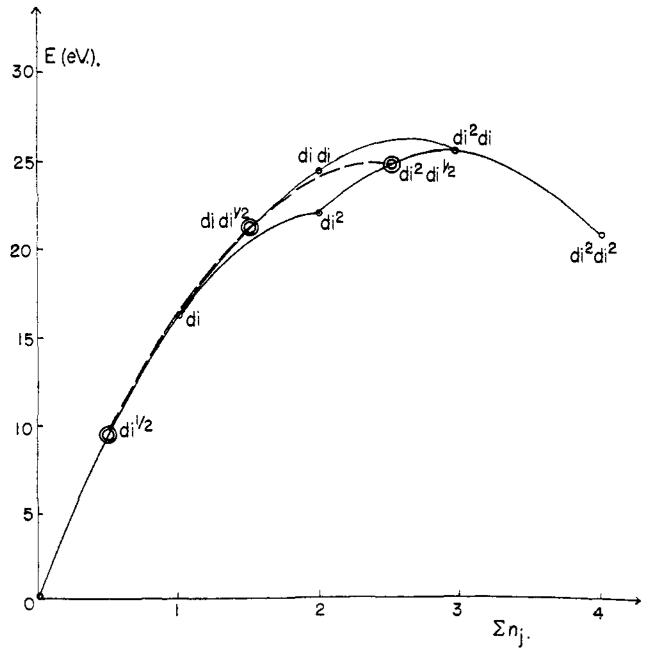

Fig. 3.—The various energy parabolas for diagonally hybridized beryllium.

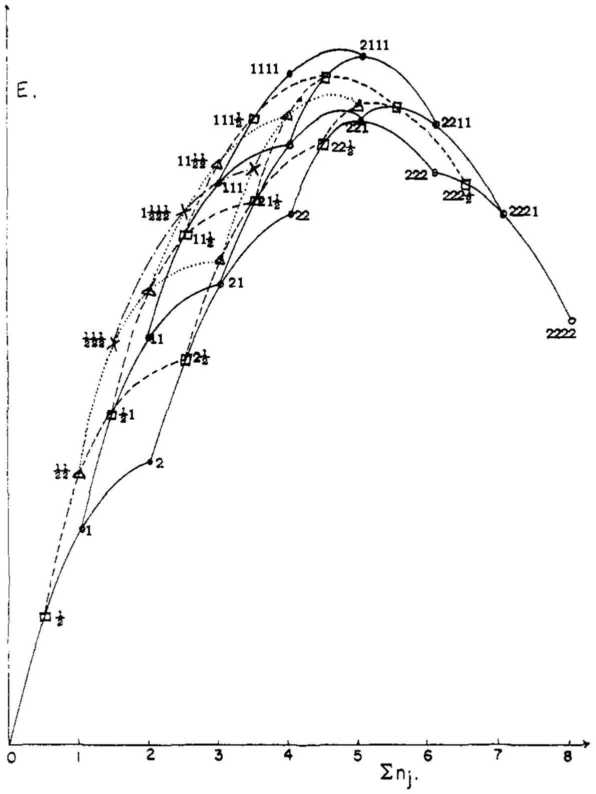

Fig. 4.—The various energy parabolas for tetrahedrally hybridized carbon.

respect to an atom Y with which it forms a bond in the compound X_3CY. Considerable purely empirical work has been done on such group electronegativities[10]; however, no reasonably fundamental procedure seems to have been developed.

Using our definition of orbital electronegativity and our supplementary assumptions a and b, it is now possible to derive group orbital electronegativities in a manner exactly analogous to atomic orbital electronegativities. Take as an example the simple case of a molecule XBeY in which we desire the group electronegativity of the group XBe, in order to discuss the bond with Y. In the terminology of the chemist, in general, the bond XBe has some ionic character, so that the charge on the Be atom, or better the occupation number of the Be orbital forming the BeX bond, is not exactly 1, but n. Assuming the two bonds of Be to be formed by diagonal hybrid orbitals, the Be atom in the group is $di_1{}^n di_2{}^1$, and the orbital electronegativity of the XBe group is the derivative of the energy of the Be atom with this electronic structure with respect to the occupation number n_2 of the orbital di_2. The assumption of the continuity of the energy of the atom with respect to the occupation numbers permits us to construct the diagram shown in Fig. 3, in which we have three separate quadratic curves of the type described by eq. 1, corresponding to variation of one of the occupation numbers, while the other is held constant at 0, 1 or 2, respectively. Interpolation on each of these three quadratics permits us to find three points corresponding to $di^n di^0$, $di^n di^1$ and $di^n di^2$, which are indicated in Fig. 3 by open circles, and which, *together* define another quadratic curve of the type of eq. 1, which is indicated on Fig. 3 by a heavy dashed curve, assuming $n_1 = {}^1/_2$. The slope of this curve at the point $di^n di^1$ is the group orbital electronegativity of the XBe group.

The same arguments and logic can be extended to any arbitrary system. Thus, in the case of a radical X_3C, or even XYZC, with electronic structures $te_1{}^{n_X} te_2{}^{n_X} te_3{}^{n_X} te_4$, or $te_1{}^{n_X} te_2{}^{n_Y} te_3{}^{n_Z} te_4$, the process, as illustrated in Fig. 4, involves successive construction of a set of quadratics from which will be interpolated the points for n_X; from the quadratics formed by these will be interpolated points with n_Y, and from the quadratics formed from these will finally be interpolated three points with n_Z, giving rise to the single parabola which gives the electronegativity of the group. Although the process is long, it is fundamentally straightforward. The special problems involved, which arise out the necessity of evaluating the energy of valence states which are not readily available, will be discussed below.

This procedure, then, provides a route toward the group orbital electronegativity of any group, provided only that the various n within this group are either available, or may be estimated. Such estimation might be made empirically, but a completely self-consistent procedure is possible, which will be outlined in the next section.

Self-consistent Group Orbital and Bond Electronegativities.—The procedure to obtain group orbital electronegativities outlined in the preceding paragraph requires the occupation numbers for the bonds within the group. On the other hand, the occupation numbers were derived above from bond electronegativities. A combination of the two approaches, in conjunction with either an iterative method or an analytical solution, will provide a means of calculating ionic characters, bond electronegativities, etc., throughout a molecule. Take as an example, the molecule X_3CY. Assume that we have some reason to believe that the CX bond is about 10% ionic. Using $n_X = 0.9$, we can now obtain the electronegativity curve for the X_3C group as a function of n_Y. We can use the bond electronegativity concept (together with the electronegativity curve for Y), to calculate n_Y. Using this value of n_Y we can get an electronegativity curve in terms of n_X, from which, in conjunction with the electronegativity of X, we obtain a corrected curve for electronegativity as a function of n_Y. Provided we have started with a reasonable assumption, this procedure should yield a

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[10] R. E. Kagarise, *J. Am. Chem. Soc.*, **77**, 1377 (1955).

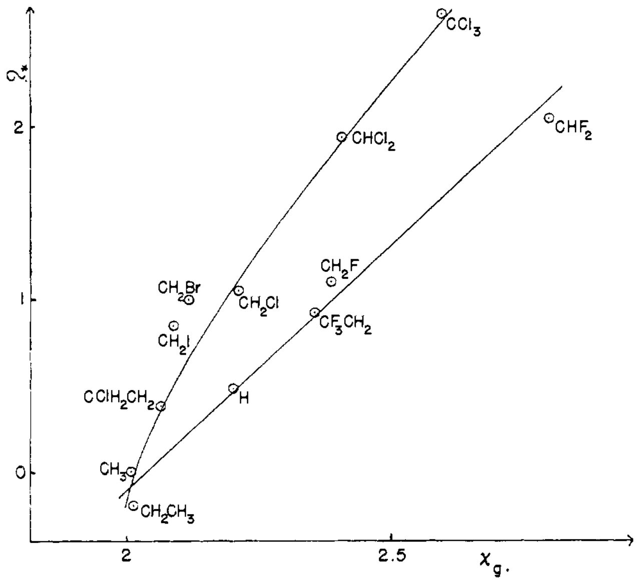

Fig. 5.—Group electronegativities for groups bonded to a carboxo group plotted *versus* Taft's σ^*-values.

self-consistent set of n-values quite rapidly, from which the charge distribution in the molecule become apparent.

In order to test whether electronegativities obtained by use of the new definition, the bond electronegativity concept and the ionic character obtained thereby have meaning, we have calculated the electronegativities of a series of groups for which previous literature values were available. The results of these calculations are shown in Table I. In the case of NH_2, PH_2, OH and SH, the calculations required of the hybridization of the central atoms. These were obtained from the bond angles. Although this procedure may be questionable, it is the best presently available. The group electronegativities obtained are in reasonable agreement with the rather widely divergent literature values. More important, trends obtained are exactly those anticipated from chemical information and intuition, and all expected regularities obtain.

TABLE I

GROUP ELECTRONEGATIVITIES

Group	% S[a]	$\chi_g{}^1$	[b]	[c]	χ_g (Lit.)
CH_3		2.30	1.93	2.33	2.63,[d] 2.34[f]
CH_2Cl		2.47	2.13	2.55	2.74,[d] 2.48,[f] 3.22[g]
$CHCl_2$		2.63	2.32	2.77	2.88,[d] 2.62,[f] 3.22[g]
CCl_3		2.79	2.50	2.98	3.03,[d] 2.76,[f] 3.25,[g] 2.99[g]
H_2N	22.5	2.82	2.61	2.96	3.40,[d] 2.99,[e] 3.63,[g] 3.36,[g] 1.70[h]
H_2P	5	2.06	1.76	2.04	2.20,[d] 2.29[g]
HO	20	3.53	3.45	3.82	3.89,[d] 3.51,[e] 3.86,[g] 3.79,[g] 2.30[h]
HS	5	2.35	2.11	2.38	2.61,[d] 2.45,[e] 2.92,[g] 2.54[g]

[a] Estimated from bond angles. [b] Group electronegativity in the fluoride. [c] Group electronegativity in the hydride. [d] J, K. Wilmhurst, *J. Chem. Phys.*, **27**, 1129 (1957). [e] B. P. Daley and J. N. Schoolery, *J. Am. Chem. Soc.*, **77**, 3977 (1955). [f] Ref. 10. [g] J. K. Wilmhurst, *J. Chem. Phys.*, **28**, 733 (1958). [h] J. V. Bell, J. Heisler, H. Tannenbaum and J. Goldenson, *J. Am. Chem. Soc.*, **76**, 5185 (1954).

In a previous section we have pointed out that the electronegativity of an element is a property of the element in its valence state, independent of the bond it will form. This is no longer true for a group electronegativity. A group electronegativity must depend on the bond that the group will form because, by definition, it is a property of the group obtained by an adiabatic breaking of this bond. Thus, the entire electron distribution in the group is assumed to be identical to that in the final compound. This is a limitation which applies to all group electronegativities and suggests that any empirical values must depend on the compound from which they are obtained. To demonstrate the importance of this effect, we have calculated the group electronegativities of the groups in Table I not only for the free group but also for the group as it exists in the hydride and in the fluoride. It is seen that the differences are significant, although the trends have remained the same.

As an another example of the use of the new definition, we have calculated the group electronegativities of a series of groups for which Taft σ^*-values are available. It has long been postulated that these σ^*-values are a function of electronegativity.[11] The data obtained are shown in Table II. If these group electronegativities are plotted against the σ^*-values, a single smooth curve is obtained for the various fluorinated methyls and another smooth curve for the various chlorinated methyls. However, neither hydrogen nor the monobromo- or monoiodomethyls fall on either of these curves.

TABLE II

GROUP ELECTRONEGATIVITIES AND σ^*-VALUES

Groups	σ^{*a}	$\chi_g{}^b$	$\chi_g{}^c$
H	0.49	2.20	2.20
CH_3	0.00	2.30	2.00
CH_2F	1.10	2.61	2.39
CHF_2	2.05	2.94	2.81
CF_3		3.29	3.27
CH_2Cl	1.05	2.47	2.21
$CHCl_2$	1.94	2.63	2.41
CCl_3	2.65	2.79	2.60
CH_2Br	1.00	2.40	2.12
$CHBr_2$		2.49	2.22
CBr_3		2.57	2.31
CH_2I	0.85	2.38	2.08
CHI_2		2.44	2.16
CI_3		2.50	2.22
CF_3CH_2	0.92		2.36
CH_2ClCH_2	.38		2.07
CH_3CH_2	− .10		2.01

[a] Tafts σ^*-values from M. S. Newman, "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956. [b] Group electronegativity, if orbital considered is singly occupied. [c] Group electronegativity, if group is bonded to carboxo group.

As was pointed out in the preceding paragraph, group electronegativities must depend to some extent on the molecule in which the group finds itself. Consequently, it seemed of interest to repeat the calculations of the group electronegativities of the same groups in an environment at least similar to that from which σ^*-values were obtained; that is, bonded through a carboxo group. These values are also listed in Table I and are graphed in Fig. 5. It is immediately seen that the values for the fluorinated methyls, together with that for hydrogen, methyl and ethyl, fall on a straight line. The same line includes the point for 1,1,1-trifluoroethyl. The chloromethyls and 1-chloroethyl fall on a separate line and if methyl itself is to be included, this line shows a distinct curvature and does not comprise hydrogen. Bromo- and iodomethyl fall on neither of these lines.

The calculations have been made on the assumption that none of the halogens are hybridized. This is very likely an incorrect assumption, especially since recent calculations based on NQR data have indicated considerable s-character in chlorine, bromine and iodine

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(11) R. W. Taft, Jr., *J. Am. Chem. Soc.*, **74**, 2729, 3120 (1952).

organic compounds. It seems further very likely that the s-character in chlorine exceeds considerably that in fluorine because the promotion energy is much higher and because energy matching makes hybridization in fluorine particularly unlikely. If we assume fluorine to be unhybridized, repetition of all the calculations for the chloromethyls with somewhere between 15 and 20% s-character brings the points on to the line of the fluoromethyls. Similarly, the two points for bromo- and iodomethyl would fall onto the curve for the fluoro compounds if one assumes between 20 and 25% s-character. These amounts of s-character appear reasonable. It is also possible that the carbon atom rehybridizes somewhat and such rehybridization might well tend to equalize these curves. This effect, however, cannot be adequately treated at this time.

Calculations

The atomic orbital electronegativities are quite readily obtained. In order to obtain the quadratic curve of the form of eq. 1 we require, for any given element X, the energies of three valence states $E(0)$, $E(1)$ and $E(2)$. If we arbitrarily define the energy scale such that

$$E(0) = 0,\ \text{then}$$
$$E(1) = +I_v,\ \text{and}$$
$$E(2) = +I_v + E_v$$

and therefore

$$E(n) = {}^1/_2(I_v - E_v)n^2 + {}^1/_2(3I_v - E_v)n \qquad (4)$$

and the derivative

$$\chi(n) = \mathrm{d}E(n)/\mathrm{d}n = (I_v - E_v)n + {}^1/_2(3I_v - E_v) \qquad (5)$$

where the constant a of eq. 1 has become equal to zero due to the arbitrary choice of the zero of the energy scale. Consequently, the three orbital electronegativities of interest are

$$\chi(0) = {}^1/_2(3I_v - E_v)$$
$$\chi(1) = {}^1/_2(I_v + E_v)$$
$$\chi(2) = {}^1/_2(3E_v - I_v)$$

Since the three points above describe necessarily a straight line, the bond electronegativities are simultaneously completely defined. The quantities I_v and E_v for the elements of the first two rows of the periodic system have been reported previously,[1] and for the transition series they are in process of publication. The magnitude of the previously reported orbital electronegativities remains unchanged by the new definition.[12] The orbital electronegativities of vacant orbitals and lone pairs, up to now unobtainable, are given in Tables III and IV for the elements of interest of the first two rows of the periodic system.

Computation of the energy of group electronegativities is considerably more difficult. Thus examination of Fig. 3 shows that, in addition to the valence states of Be^+, Be^0 and Be^-, valence states of Be^{2+} and Be^{2-} are required. Be^{2+} produces no problems, and the energies have actually been calculated and reported.[1] But we already had a problem of obtaining values for Be^-, since we required extrapolations. The situation becomes much more serious in the case of multiply negative ions, since no observations are available, and consequently no reasonable extrapolation schemes appear available.

For the case of $Be(\mathrm{di}_1{}^n\mathrm{di}_2{}^1)$ illustrated in Fig. 3 a very reasonable approximation method is available, which depends on the following consideration: The energy of the state $\mathrm{di}_1{}^n\mathrm{di}_2{}^2$, which can, according to Fig. 3, be obtained only by an interpolation of a curve, which requires $\mathrm{di}_1{}^2\mathrm{di}_2{}^2$ *i.e.*, Be^{2-}, is given by

$$E(\mathrm{di}_1{}^n, \mathrm{di}_2{}^2) = (2 + n)I + J_{11} + 2nJ_{12} - nK_{12}$$

where the I, J and K are the usual integrals involved in the calculations of atomic energies. Similarly, the energy of the state $\mathrm{di}_1{}^{n+1}\mathrm{di}_2$ is given by

$$E(\mathrm{di}_1{}^{n+1}\mathrm{di}_2{}^1) = (2 + n)I + nJ_{11} + (n + 1)J_{12} - {}^1/_2(1 + n)K_{12}$$

Hence the energy difference between these two states, ΔE, is given by

$$\begin{aligned}\Delta E &= (1 - n)J_{11} - (1 - n)J_{12} + {}^1/_2(1 - n)K_{12} \\ &= (1 - n)L\end{aligned}$$

where $L = J_{11} - J_{12} + K_{12}/2$. Since each of the integrals J_{ij} and K_{ij} is a function of configuration, total number of electrons and nuclear charge, the function L just defined is a function of these quantities. Since it has long been shown that the different Slater–Condon parameters and hence the electron interaction

TABLE III

ELECTRONEGATIVITY OF VACANT ORBITALS

Occupied orbitals	χ_σ^0	χ_π^0	χ_σ^0	χ_π^0
	Be		Mg	
sp	..	0.10	..	0.24
pp	1.81	− .30	1.75	− .43
didi	..	.02	..	.20
di π	1.30	− .10	1.21	− .10
$\pi\pi$	0.97	..	0.79	..
trtr	.94	−0.07	.91	0.00
tr π	.79	..	.67	..
tete	.64	..	.58	..
	B		Al	
spp	..	1.06	..	0.82
ppp	3.67	..	3.52	..
didi π	..	1.18	..	0.98
di $\pi\pi$	3.05	..	2.59	..
trtrtr	..	1.22	..	1.03
trtr π	2.59	..	2.16	..
tetete	2.32	..	1.93	..

TABLE IV

ELECTRONEGATIVITIES OF LONE PAIRS

Occupied orbitals	χ_σ^2	χ_π^2	χ_σ^2	χ_π^2
	N		P	
s^2ppp	5.66	..	3.68	..
sp^2pp	..	1.21	..	1.88
$\mathrm{di}^2\mathrm{di}\pi\pi$	2.26	..	2.08	..
$\mathrm{didi}\pi^2\pi$	..	1.05	..	1.59
$\mathrm{tr}^2\mathrm{trtr}\pi$	1.58	..	1.73	..
$\mathrm{trtrtr}\pi^2$	..	0.99	..	1.49
$\mathrm{te}^2\mathrm{tetete}$	1.32	..	1.59	..
	O		S	
spp^2p^2	..	2.04	..	1.71
s^2p^2pp	7.44	1.42	4.52	1.50
$\mathrm{didi}\pi^2\pi^2$	..	1.92	..	1.76
$\mathrm{di}^2\mathrm{di}\pi^2\pi$	3.56	1.73	2.60	1.60
$\mathrm{di}^2\mathrm{di}^2\pi\pi$	3.75	..	2.59	..
$\mathrm{trtrtr}^2\pi^2$	2.74	1.78	2.21	1.66
$\mathrm{tr}^2\mathrm{tr}^2\mathrm{tr}\pi$	2.81	..	2.16	..
$\mathrm{te}^2\mathrm{te}^2\mathrm{tete}$	2.45	..	2.01	..
	F		Cl	
$sp^2p^2p^2$	..	2.28	..	2.54
$s^2p^2p^2p$	9.10	2.26	6.52	2.10
$\mathrm{didi}^2\pi^2\pi^2$	4.50	2.27	3.90	2.32
$\mathrm{di}^2\mathrm{di}^2\pi^2\pi^2$	4.96	2.26	3.98	2.10
$\mathrm{trtr}^2\mathrm{tr}\pi^2$	3.70	2.28	3.30	2.25
$\mathrm{tr}^2\mathrm{tr}^2\mathrm{tr}^2\pi$	3.90	..	3.28	..
$\mathrm{te}^2\mathrm{te}^2\mathrm{te}^2\mathrm{te}$	3.32	..	3.00	..

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(12) The χ_M values of (1) should be divided by 2, since reported for χ_M is $I_v + E_v$ and not $(I_v + E_v)/2$.

integrals J and K can be reasonably extrapolated within an isoelectronic sequence,[13] it follows that the same is true for L. But the L's for the isoelectronic sequence B^-, C, N^+ and O^{2+} can be obtained as the energy difference of the equivalent two states.

There is one flaw in the above derivation: if $n > 1$, the second state, $Be(di_1^{n+1}di_2)$, is a state violating the Pauli principle, and cannot be dealt with. For cases of this type, another procedure is possible. In order to establish the desired quadratic equations, any three points are sufficient. When, as is the case for $Be(di_1^2di_2^2)$, the energy value cannot be obtained, one may well establish the curve by use of three points, $n = 0$, $n = 1$, and an intermediate value, which is obtained by the method described in the preceding paragraph. Although this procedure is liable to greater uncertainties, it appears satisfactory.

[13] F. Rohrlich, *Phys. Rev.*, **101**, 69 (1956).

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The Effect of Coördination on the Reactivity of Aromatic Ligands. V. Diazo Coupling

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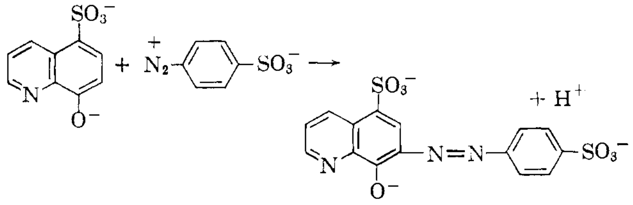
A kinetic study of the coupling reaction of both free and coördinated 8-hydroxyquinoline-5-sulfonic acid with diazotized sulfanilic acid shows the rate to be strongly affected by coördination. The coördination of the phenolate anion to zinc(II) reduces the rate of coupling by a factor of 10^4, but does not change the position at which the electrophilic reagent attacks the ligand. The zinc(II) chelate is much more reactive than the phenol itself, however, by a factor of approximately 10^6. The deactivation of the ligand occurs through an enormous decrease in the frequency factor; much of the change must be attributed to the change in the *charge* on the reactants. The activation energy for substitution on the complex is *less* than that for the phenolate anion.

Coördination does not drastically alter the relative reactivity of positions in alternant aromatic systems toward electrophilic reagents. This has been clearly established in several specific cases in the previous papers in this series.[1-3] It should alter the rates of such reactions, however, either by changes of a steric nature which aid or hinder the reaction or by changes in the electronic density at the reaction site or by both. For aromatic systems there are no quantitative data available which indicate how large such rate differences might be. The present work had the acquisition of such quantitative data as its principal goal. The chief justification for such an empirical approach lies in the uncertainty of the magnitude of the theoretically anticipated changes in electronic densities which should accompany the coördination act. Calculations using a number of different procedures[4-6] all give different estimates of this change. Since the variation in chemical reactivity is extremely dependent on the variation of electronic charge density,[7] experimental data are needed as guideposts if further theoretical work is to be fruitful.

In order to determine the nature of such changes in rates, a kinetic study has been carried out on the diazo coupling of 8-hydroxyquinoline-5-sulfonic acid and its zinc(II) chelate with diazotized sulfanilic acid. The reaction proceeds *via* an electrophilic attack on the 7-position of the phenolate ion derived from the ligand. The electrophilic reagent is the diazonium ion. This reaction is



The products of the reaction of the free ligand and its zinc complex were shown to be identical by means of absorption spectra and analyses. For the free ligand, this type of coupling reaction has been studied by Phillips and Price[8] and by Matsumura.[9] When the 5-position is blocked, as in the present case, the coupling occurs at the 7-position. The mechanism of the diazo coupling reaction has been thoroughly reviewed[10] and is sufficiently well delineated that the interpretation of the kinetic data is unambiguous.

Experimental

8-Hydroxyquinoline-5-sulfonic Acid.—The preparative method described by Liu and Bailar[11] was employed. The compound does not have a sharp melting point, but decomposes at 300°. The S-benzylisothiourea derivative of the compound melts at 199°, lit.[12] 197°. *Anal.* (after drying at 120°): Calcd. for $C_9H_7O_4NS$: C, 47.99; H, 3.13; N, 6.22; S, 14.23. Found: C, 47.87; H, 3.26; N, 6.01; S, 14.00.

***p*-Diazobenzenesulfonate** was prepared using the method recommended by Fierz-David and Blangey.[13]

The dried product may be stored in a caged vacuum desiccator prior to use for no longer than one week, and in quantities not exceeding one gram. This solid, when dissolved in sodium acetate–acetic acid buffer solution of *p*H 5, gave a clear water-white solution. If the temperature of the solution was maintained below 15° the solution remained free from discoloration and nitrogen evolution for approximately 8 hours. This material exists as an inner salt or zwitterion.

7-(4-Sulfobenzeneazo)-5-sulfo-8-hydroxyquinoline is the red, water-soluble azo dye formed when diazo-sulfanilic acid is coupled with oxine-5-sulfonic acid. It will be called the "red azo dye" in the rest of this paper.

Sulfanilic acid (17.3 g., 0.1 mole) is dissolved in 2 *M* ammonia solution (60 ml.) and diluted to approximately 250 ml. with water. This solution is then cooled to 0–5° with an ice-bath, and acidified with concentrated hydrochloric acid (10 ml.). The suspension of sulfanilic acid produced is then diazotized by the addition of sodium nitrite (7 g., 0.1 mole) dissolved in water (100 ml.). The addition of sodium nitrite is continued until an immediate dark blue color is produced when a piece of starch-iodide paper is spotted with the reaction mixture.

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[5] A. Goudot, *Compt. rend.*, **252**, 125 (1961).

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[7] Examples may be seen in R. Daudel, R. Lefebvre and C. Moser, "Quantum Chemistry," Interscience Publishers, Inc., New York, N. Y., 1959, Chs. XI, XII.

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[10] H. Zollinger, "Diazo and Azo Chemistry, Aliphatic and Aromatic Compounds," Interscience Publishers, Inc., New York, N. Y., 1961, Ch. X.

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[13] H. E. Fierz-David and L. Blangey, "Fundamental Processes of Dye Chemistry," trans. by P. W. Vittum, Interscience Publishers, Inc., New York, N. Y., 1949, pp. 248 and 261.