able for stretching vibrations. Further argument suggests that this relationship probably holds also for the bending force constants.

Finally, we should like to point out the general applicability of these arguments to a wide number of phenomena. Linear relations between ΔH and ΔS are very important in organic chemistry. Taft has pointed out[15] that this condition is necessary if the Hammett sigma relations are to hold. The empirical success of these relations may well be due to the same set of curious circumstances which leads to the observed linear relation between ΔS and ΔH for iodine complexes.

(15) R. Taft, *Separation of Polar, Steric and Resonance Effects in Reactivity* in "Steric Effects in Organic Chemistry," edited by R. S. Newman, John Wiley and Sons, Inc., New York, N. Y., 1956.

Acknowledgments.—Partial financial support from the National Science Foundation is gratefully acknowledged. It is a pleasure to acknowledge helpful discussions with Professors G. C. Pimentel and R. S. Mulliken.

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Electronegativity. I. Orbital Electronegativity of Neutral Atoms

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Electronegativity is discussed on the basis of Mulliken's definition ($\chi = E_v + I_v$), which leads to the conclusion, that it is not a property of atoms in their ground state, but of atoms in the same conditions in which they are found in molecules, the valence state. Valence state promotion energies are calculated and reported for a large variety of states of the atoms and ions of the first and second period. Combining these promotion energies with ionization potentials and electron affinities yields the electronegativities of a number of valence states. It is found that electronegativity can be defined in this way only for bonding orbitals, and the term "orbital electronegativity" is suggested for the values listed. The calculated orbital electronegativities for σ orbitals are found to be higher in every case than for π orbitals, and to be linearly related to the amount of s character in the hybrid orbitals. As expected, the electronegativity increases with increasing s character of the orbital considered.

Electronegativity is a measure of the power of a chemically bonded atom to attract electrons to itself. This concept, first introduced by Pauling,[1] was rapidly accepted and many applications have been found in all fields of chemistry. Pauling set up a scale of electronegativities of the elements, by comparing the energy of the heteronuclear bond A–B with the average, arithmetic[2] or geometric,[3] of the homonuclear bond energies of the molecules A–A and B–B. With this method, no absolute values can be obtained, and because of the inherent uncertainties in thermochemical data this relative scale is somewhat indefinite. Despite these inadequacies, a wide variety of chemical phenomena have been reasonably explained by use of electronegativities.

The degree of electron transfer in the bond A–B toward the negative atom may be regarded as good measure of electronegativity difference. Unfortunately, such electron transfer is not directly observable and calculations of electron distribution for any molecule is an involved problem in itself, even for simple molecules, and not a suitable method to use as a base for an electronegativity scale. Since such exact results are not available, several alternate scales of electronegativity have been proposed, based on various observable properties of molecules which are related to the electron distribution. Such properties are dipole moments,[4] force constants[5] and nuclear quadrupole resonance frequencies.[6] The accomplishments in this field have been carefully reviewed by Pritchard and Skinner.[7]

The best theoretical definition of electronegativity is given by Mulliken,[8] based on the concept that the energy expended in going from the covalent molecule A–B to the ionic states A^+B^- and A^-B^+ is equal if A and B have the same electronegativity. Thence, he concludes[9] that the electronegativity of A is proportional to

$$\chi^A = I_v^A + E_v^A \qquad (1)$$

where I_v^A and E_v^A are the appropriate valence state ionization potential and electron affinity, respectively. Electronegativities obtained from equation 1 are, to a good approximation, proportional to Pauling's values.[10]

Pauling[1] defined electronegativity as an atomic property and believes[3] that it is virtually constant, even for different oxidation states of any one element. Thus, he quotes electronegativities of iron as, 1.8 (Fe^{2+}) or 1.9 (Fe^{3+}); of copper as 1.9 (Cu^+) or 2.0 (Cu^{2+}); and of tin as, 1.8 (Sn^{2+}) or 1.9 (Sn^{4+}).[11] This conclusion seems somewhat surprising on the basis of the Mulliken definition, since one hardly expects ionization potential and electron affinity, or even their sum, to be the same for different oxidation states, and, hence, demands closer examination, particularly because differences of electronegativities have been noted by many authors.

(1) L. Pauling and D. M. Yost, *Proc. Natl. Acad. Sci. U. S.*, **14**, 414 (1932).
(2) L. Pauling, *J. Am. Chem. Soc.*, **54**, 3570 (1932).
(3) L. Pauling, "The Nature of the Chemical Bond," 3rd Ed., Cornell University Press, Ithaca, N. Y., 1960.
(4) J. G. Malone, *J. Chem. Phys.*, **1**, 197 (1933).
(5) W. Gordy, *ibid.*, **14**, 304 (1946).
(6) W. Gordy, *ibid.*, **19**, 792 (1951).
(7) H. O. Pritchard and H. A. Skinner, *Chem. Revs.*, **55**, 745 (1955).
(8) R. S. Mulliken, *J. Chem. Phys.*, **2**, 782 (1934).
(9) R. S. Mulliken, *ibid.*, **46**, 497 (1949); W. Moffitt, *Proc. Roy. Soc.* (London), **A202**, 548 (1950).
(10) H. A. Skinner and H. O. Pritchard, *Trans. Faraday Soc.*, **49**, 1254 (1953).
(11) W. Gordy and W. J. Orville-Thomas, *J. Chem. Phys.*, **24**, 439 (1956).

Bellugue and Daudel[12] and Sanderson[13] have discussed electronegativities for different oxidation states, but their approaches were hampered by lack of data. The distinct but related problem of the dependence of electronegativities on valence states of neutral atoms has been considered by Walsh,[14] who concluded that the electronegativity of carbon increases in the order tetrahedral < trigonal < digonal. Similarly, Wilmhurst[15] inferred from n.q.r. frequencies that the electronegativity of halogens increases with increasing s character in its bonding orbital. This concept has been generalized by Bent[16] and needs careful examination, as already pointed out by Pritchard and Skinner[7]; this need has become even more urgent in view of the renewed interest in electronegativities.[15–17] A start in this direction has already been made by Mulliken[8] and Skinner,[10] but the range of the valence states considered was insufficient to permit recognition of over-all trends.

Theoretical Background.—Since the electronegativity is a property of atoms in a molecule, the ionization potentials and electron affinities in equation 1 are not the values of the atoms in their ground states but of the same condition in which the atoms are in a molecule. The "atom in molecule" was defined by Van Vleck[18] as valence state. It is not a stationary state nor even a non-stationary state but a statistical average of stationary states[19] chosen so as to have as nearly as possible the same interaction of the electrons of the atom with one another, as they have when the atom is part of a molecule. The valence state can be considered as formed from a molecule by removing from one atom all the other atoms with their electrons in an adiabatic manner, *i.e.* without allowing any electronic rearrangement. This state has been discussed in many places in the literature[8,20,21] and needs no further explanation.

Two useful methods have been suggested for the calculation of valence state energies, one by Moffitt,[22] extended by Companion,[23] and the other by Van Vleck[18] and Mulliken.[8] Moffitt expresses the valence state energy as an appropriate linear combination of spectroscopic state energies. Mulliken's method is based on Slater's[24] treatment of the many electron atom, in which the energy W of any spectroscopic state is given by

$$W = \sum_i I_i + \sum_{i>j} \sum_k a_{ij}^k F_{ij}^k - \sum_{i>j} \sum_k \delta_{ij} b_{ij}^k G_{ij}^k \quad (2)$$

(12) J. Bellugue and R. Daudel, *Rev. Sci.*, **84**, 541 (1946).
(13) R. T. Sanderson, *J. Chem. Educ.*, **31**, 2, 238 (1945).
(14) A. D. Walsh, *Discussions Faraday Soc.*, **2**, 18 (1947).
(15) T. K. Wilmhurst, *J. Chem. Phys.*, **30**, 561 (1959).
(16) H. A. Bent, *Chem. Revs.*, **61**, 275 (1961).
(17) M. A. Whitehead and H. H. Jaffé, *Trans. Faraday Soc.* (in press).
(18) J. H. Van Vleck, *J. Chem. Phys.*, **2**, 20 (1934).
(19) This was pointed out by H. C. Longuet-Higgins at the 18th International Congress of Pure and Applied Chemistry, Montreal, Canada, August, 1961.
(20) H. H. Jaffé, *J. Chem. Educ.*, **33**, 25 (1955).
(21) C. A. Coulson, "Valence" Oxford University Press, 1959.
(22) W. Moffitt, *Ann. Repts. on Prog. Phys.*, **17**, 173 (1954).
(23) A. L. Companion and F. O. Ellison, *J. Chem. Phys.*, **28**, 1 (1958).
(24) J. C. Slater, *Phys. Rev.*, **34**, 1293 (1929); E. U. Condon and G. H. Shortley, "The Theory of Atomic Spectra," Cambridge University Press, 1953.

For the energy of a valence state, use of equation 2 is quite analogous to its more general application for spectroscopic states. In both cases the same integrals over the radial part of the wave function, I, F^k, and G^k, arise, while the a's and b's are easily evaluated and δ_{ij} the Kronecker δ is 0 when the spins of i and j are unequal and 1 when they are equal. Since the valence state is an average of these two alternatives, δ_{ij} is $^1/_2$. The two methods (Moffitt and Mulliken) are identical, provided just those spectroscopic states used in the Moffitt method are employed to evaluate the F's and G's in the Mulliken expression.

The Mulliken method was chosen for all our calculations for a number of reasons. (1) It lends itself much better to routine computation. (2) If one of the spectroscopic states needed to express the valence state energy is not observed, Moffitt's method fails. (3) Configuration interaction is ignored in both methods; however, use of the largest possible number of states in the determination of the F's and G's is most likely to minimize the effect of configuration interaction.[25] (4) Although the Moffitt method is reasonably straightforward for some simple valence states, it becomes very complex when hybrid orbitals are involved.

For the calculation of valence state ionization potentials I_v and valence state electron affinities E_v, we require the corresponding values for the atomic ground states, I_g and E_g, respectively. The ground state ionization potentials I_g, usually obtained by extrapolation from spectral data, are listed by Moore[26] (see Table I) and may be considered to be accurately known. Unfortunately, the ground states electron affinities, E_g, are not as readily obtainable,[27] The best values were chosen

TABLE I

GROUND STATE IONIZATION POTENTIALS I_g AND ELECTRON AFFINITIES E_g (IN eV.)

	E_g	Ref.	I_g
H	.747	28	13.595
Li	.82	28	5.390
Be	− .19	28	9.320
B	.33	28	8.296
C	1.12	29	11.256[a]
N	.05	28	14.535[a]
O	1.465	29	13.614
F	3.48	30	17.418
Ne	− .57	28	21.559
Na	.47	28	5.138
Mg	− .32	28	7.644
Al	.52	28	5.984
Si	1.46	28	8.149
P	.77	28	10.977
S	2.07	29	10.357
Cl	3.69	30	12.974[a]

[a] Private communication from Dr. Ch. E. Moore, Natl. Bureau of Standards.

(25) H. A. Skinner (Abstract of 18th International Congress of Pure and Applied Chemistry, Montreal, Canada, August, 1961) has made similar calculations including corrections for configuration interaction. Comparison of his data (private communication) with ours has shown that the differences rarely exceed 0.2 e.v.
(26) C. E. Moore, "Atomic Energy Levels," Natl. Bureau of Standards, Circular No. 467, Vol. I–III and private communications.
(27) H. O. Pritchard, *Chem. Revs.*, **52**, 529 (1953).

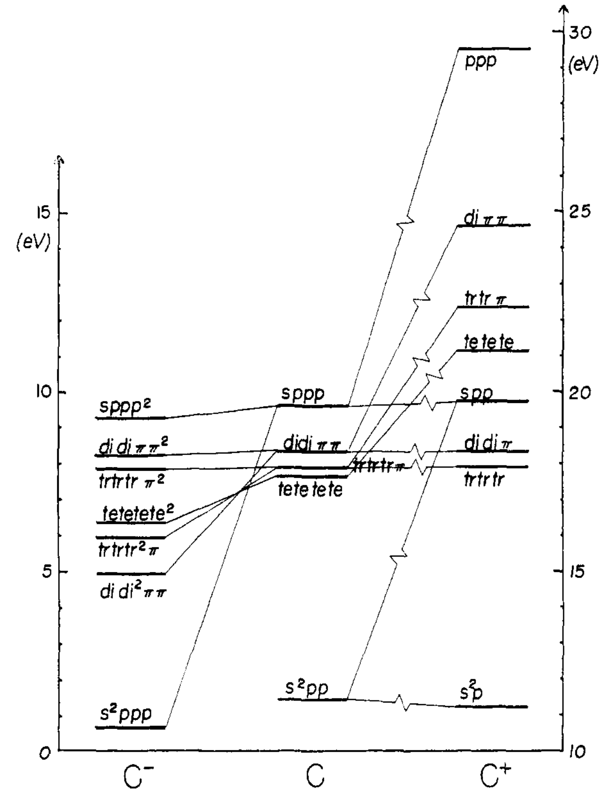

Fig. 1.—Valence state term system of C, C^- and C^+ with possible connections.

from papers by Edlen,[28] Branscomb[29] and Cubicciotti[30] (see Table I). These electron affinities probably represent the most important source of inaccuracy in our calculations ($\approx$ 0.3 eV.). Such absolute errors, however, do not affect the valence state *dependence* of the calculated electronegativities.

The valence state ionization potentials and electron affinities are obtained by combining the valence state promotion energies of the atom, P_0, and of the positive and negative ion P^+ and P^-, respectively, with the ground state potentials

$$I_v = I_g + P^+ - P_0$$
$$E_v = E_g + P_0 - P^-$$

Since I_v is the energy necessary to remove an electron from the valence state, and E_v the energy released by addition of an electron to this state, while the remaining electrons are not permitted to rearrange, the following transitions must be considered, using carbon as an example[31]

$$C^-(te^5) \xleftrightarrow{E_{te}{}^\sigma} C(te^4) \xleftrightarrow{I_{te}{}^\sigma} C^+(te^3)\text{: } \chi_{te}{}^\sigma$$
$$C^-(te^4\pi) \xleftrightarrow{E_{tr}{}^\sigma} C(tr^3\pi) \xleftrightarrow{I_{tr}{}^\sigma} C^+(tr^2\pi)\text{: } \chi_{tr}{}^\sigma$$
$$C^-(tr^3\pi^2) \xleftrightarrow{E_{tr}{}^\pi} C(tr^3\pi) \xleftrightarrow{I_{tr}{}^\pi} C^+(tr^3)\text{: } \chi_{tr}{}^\pi \text{ etc.}$$

(28) B. Edlén, *J. Chem. Phys.*, **33**, 98 (1960).

(29) L. M. Branscomb, D. S. Burch, J. S. Smith and S. Geltman, *Phys. Revs.*, **111**, 504 (1958); L. M. Branscomb and S. J. Smith, *J. Chem. Phys.*, **25**, 598 (1956).

(30) D. Cubicciotti, *ibid.*, **31**, 1646 (1959).

(31) To prevent confusion of hybrids with pure s and p orbitals, the notation introduced by Mulliken[32] will be used throughout this paper; *i.e.*, *te* tetrahedral = (sp^3), *tr* = trigonal = (sp^2), *di* = digonal = (sp).

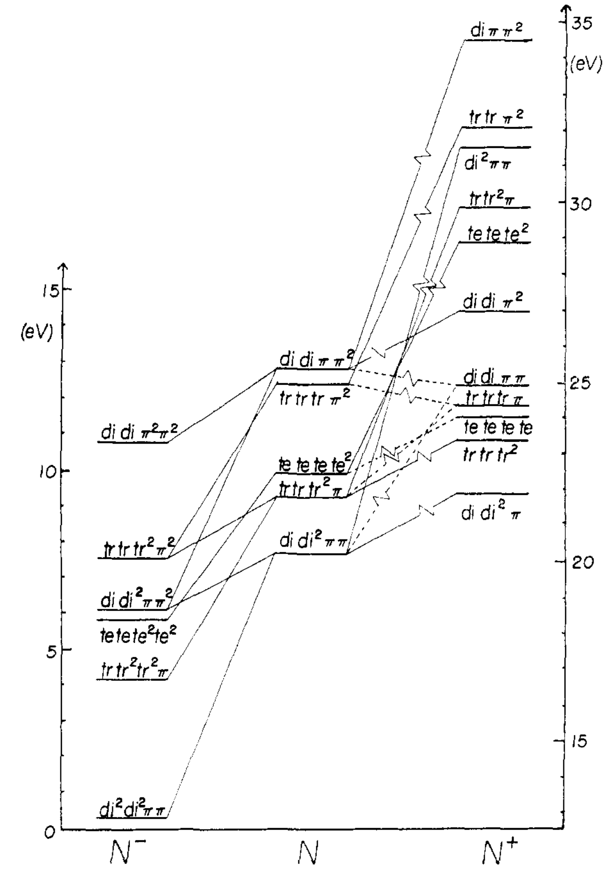

Fig. 2.—Valence state term system of N, N^- and N^+ with possible connections. Ionization of lone pair electrons indicated with dotted line.

All combinations needed are shown in Fig. 1. The possibilities are considerably more varied and complex for many other elements, such as nitrogen, as shown in Fig. 2.

Procedure

Determination of the Slater–Condon Parameters.—In principle it is possible to evaluate the Slater–Condon parameter from equation 2 by integration. This calculation is very time consuming and cumbersome, especially since good Hartree–Fock functions are frequently not available. An alternate method was used to obtain the parameters semiempirically by fitting this equation to spectroscopic energy levels.

In the use of equation 2 to express the energies of spectroscopic states some integrals, I, F_0(ss) F_0(sp) and F_0(pp) always appear with the same factors for all states arising out of any one configuration. Hence, it is impossible to obtain values for these integrals separately. By combining all these into one constant term, W_0, which is characteristic for each configuration and noting that: $F_2(\text{pp}) = G_2(\text{pp})$, equation 2 simplifies to

$$W = W_0 + \sum_l c^l M^l \qquad (3)$$

The factors c^l have been calculated for all spectroscopic states, which arise from the different combinations of s and p electrons.[33,34] The M's in equation 3 are integrals over the radial part of the wave function and dependent on n and l only. The Slater functions depend on l only through the

(32) R. S. Mulliken, *Tetrahedron*, **6**, 68 (1959).

(33) The notation is that used in Condon and Shortly, ref. 24.

(34) For most of the cumbersome calculations extensive use was made of an IBM 650 electronic computer and programs written by I. Goldfarb; Ph.D. Dissertation, Univ. of Cincinnati, 1959.

effective nuclear charge (Z_{eff}) which does not differ, according to Slater's recipe, for configurations involving only s and p electrons. But, it has been shown that the Slater–Condon parameter are different for different configurations of the same atom. These differences must be ignored here, since it is not possible to obtain enough information from one configuration to calculate all the Slater–Condon parameters necessary to express a valence state energy. Thus, in configuration sp the spectroscopic state depends only on F_{sp}^k and G_{sp}^k, but the energy of the valence state di^2 involves also the integrals F_{ss}^k, F_{pp}^k and G_{pp}^k. Therefore, it was necessary to consider together the configurations s^2p^n, sp^{n+1} and p^{n+2} for the evaluation of the Slater–Condon parameters of one atom or ion. It was found, however, that this procedure does not increase appreciably the uncertainties in the Slater treatment.[35] Under these considerations equation 3 changes to:

$$W = W_0 + n\Delta W_{sp} + m\Delta W_{p^2} + \sum_l c^l M^l \qquad (4)$$

where W_0 is the constant term for configuration s^2p^n, $(W_0 + \Delta W_{sp})$ and $(W_0 + \Delta W_{p^2})$ are the constant terms for the configurations sp^{n+1} and p^{n+2}, respectively. Thus, $n = 1$ if data of configuration sp^{n+1} are fitted and $m = 1$ if data of configuration p^{n+2} are fitted, otherwise, n and m are zero.

In Slater's treatment many approximations are made, especially all configuration interaction is neglected. Consequently, equation 4 is not expected to represent the observed energy levels exactly. Since, in most cases, more multiplet levels are known than are needed to estimate the unknowns in equation 4, a least squares multiple regression method was used to obtain the best average values for the Slater parameters. For these elaborate calculations an IBM 650 was used. The energy levels to be fitted in this way have been obtained from Moore's[26] tables. Some of the data not tabulated have been obtained by extrapolation, using the straight line relation of corresponding states in an isoelectronic sequence noted by Rohrlich.[36]

The calculations described have been made for the elements of the first and second period up to their triply positive ions. For some of these elements no multiplet levels for the configuration p^{n+2} have been observed, and consequently ΔW_{p^2} could not be obtained by the method described. The evaluation of these ΔW_{p^2} was done by the following procedure. With the known ΔW_{p^2} and the corresponding ΔW_{sp} a factor k was determined, so that

$$k\Delta W_{sp} = \Delta W_{p^2} \qquad (5)$$

This factor k shows little but steady variation in any one period. This permits a reliable extrapolation of the k's corresponding to the unknown ΔW_{p^2} values. Having determined the k's, the ΔW_{p^2}'s for the configuration $2p^6$; $3p^4$; $3p^5$ and $3p^6$ have been estimated by equation 5.

Evaluation of the Valence State Energy.—For the expression of the valence state energy equation 3 was used. The rather cumbersome evaluation of the factors c^l for the valence states was performed using an IBM 650.[37] The F_0's appearing in the valence state equation cannot be obtained explicitly, as shown above. It is, however, always possible to eliminate these F_0's in terms of the W's described. The evaluation of the promotion energies involving these eliminations and substitution of the Slater–Condon parameters into the valence state equation was also performed with the IBM 650.[37]

Two methods appear feasible for the treatment of negative ions, for which calculations as described above cannot be done, since no spectroscopic data are available. One method is to extrapolate along a series of *ionization potentials* of equivalent valence states of an isoelectronic sequence, using one of the procedures described.[28,38] The other method involves extrapolation of *promotion energies* along a series of equivalent valence states of an isoelectronic sequence and combination of the resultant promotion energy of the negative ion with the ground state electron affinity. Rohrlich[36] has shown that the extrapolation involved in the second method is linear and hence the values obtained are more reliable, than those calculated by the first method in which the functional relation is open to considerable doubt. Consequently, P^- values were obtained by a least squares fit to the corresponding valence states P^0, P^+, P^{++} and P^{+++}.

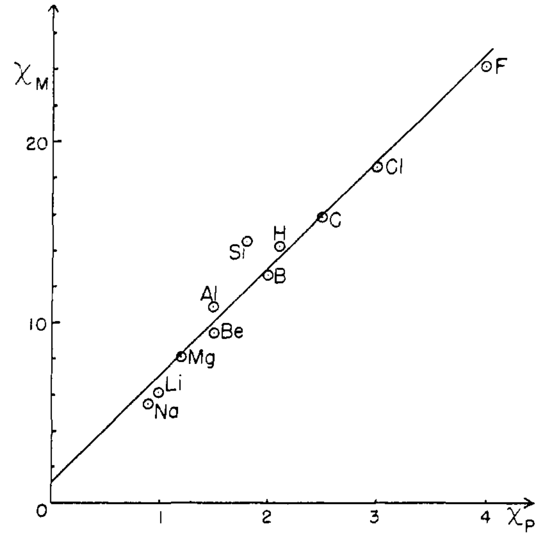

Fig. 3.—Correlation between Mulliken's and Pauling's electronegativity scale with the values used for the evaluation of the correlation coefficients. The equation found is $0.168(\chi_M - 1.23) = \chi_P$.

Results

The procedure described was used to calculate the orbital electronegativities for a wide variety of valence states of the elements of the first two rows of the periodic system. The promotion energies obtained for the states of the highest valence are given in Table II.[39] The resulting orbital electronegativities with the corresponding valence state ionization potentials and electron affinities are given in Table III.

In the last column of this table the orbital electronegativities are transformed to values comparable with Pauling's. Since the zero point of Pauling's scale is arbitrary, there is no compelling reason to anticipate the previously reported direct proportionality between the Mulliken and Pauling scales[10]; however, a linear relation must hold, if both definitions represent the same property. The correlation between the two scales was consequently obtained by fitting, by least squares, the best straight line to the selected electronegativities shown in Fig. 3. Values for those valence states were applied, which most probably correspond to the compounds used for the evaluation of Pauling's electronegativities; these values are designated by asterisks in Table III. As seen in Fig. 3, the correlation is highly satisfactory and can be represented by

$$0.168(\chi_M - 1.23) = \chi_P \qquad (6)$$

Based on the considerations outlined, it is possible to define electronegativity as a property only of bonding orbitals or other singly occupied orbitals.

(35) V. T. Zung, Ph.D. Dissertation, Univ. of Cincinnati, 1960.

(36) F. Rohrlich. *Phys. Revs.*, **101**, 69 (1956).

(37) The program for this evaluation was written by Zung.[35]

(38) H. R. Johnson and F. Rohrlich, *J. Chem. Phys.*, **30**, 1608 (1959).

(39) The Slater–Condon parameters obtained, promotion energies, ionization potentials, electron affinities and electronegativities for states of lower valence, ionization potentials of lone pairs and electron affinities of vacant orbitals were obtained but are not reported here, owing to space limitations. These data are contained in an Air Force report, copies of which are available for distribution.

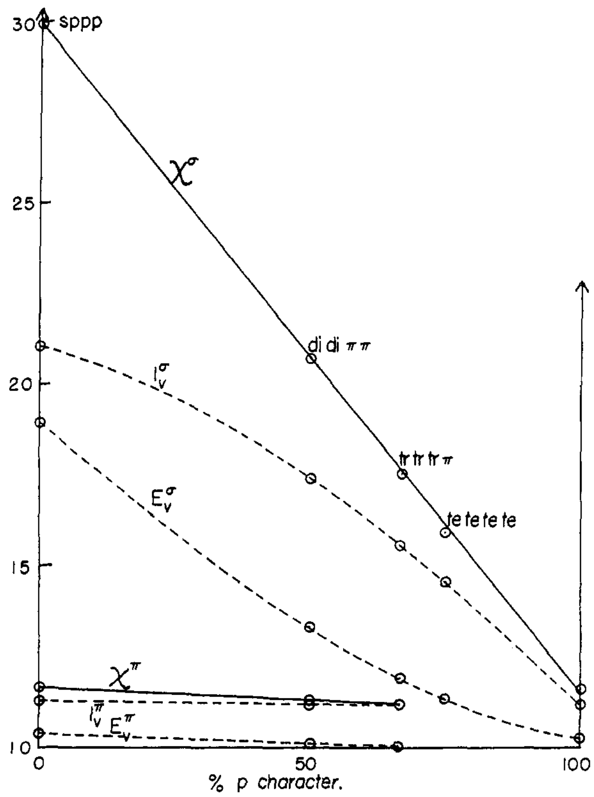

Fig. 4.—Electronegativity of carbon as a function of s character of the hybrid orbital. Dotted lines give electron affinity and ionization potential as function of s character of the hybrid orbital.

Lone pairs and electron holes (vacant orbitals) cannot be treated in the same manner, since here electron affinity and ionization potential, respectively, lose their meaning.

TABLE II

PROMOTION ENERGIES (IN eV.)

No. of val. electrons	Valence state					
			Li	Be^{+}	B^{++}	C^{+++}
(1)	s		0.0	0.0	0.0	0.0
	p		1.847	3.958	5.997	8.002
		Li^{-a}	Be	B^{+}	C^{++}	N^{+++}
(2)	sp	1.083	3.362	5.746	8.040	10.304
	pp	2.284	7.168	12.237	17.139	22.004
	didi	0.809	2.720	4.674	6.595	8.496
	diπ	1.684	5.265	8.992	12.590	16.154
	trtr	1.362	4.345	7.433	10.431	13.400
	trπ	1.884	5.899	10.073	14.106	18.104
	tete	1.616	5.105	8.724	12.228	15.702
		Be^{-a}	B	C^{+}	N^{++}	O^{+++}
(3)	spp	2.889	5.621	8.492	11.228	13.956
	ppp	6.040	12.129	18.231	24.377	30.409
	didiπ	2.365	4.738	7.124	9.505	11.870
	di$\pi\pi$	4.464	8.875	13.362	17.803	22.183
	trtrtr	2.190	4.443	6.668	8.930	11.175
	trtrπ	3.706	7.398	11.130	14.845	18.513
	tetete	3.284	6.586	9.901	13.223	16.505
		B^{-a}	C	N^{+}	O^{++}	F^{+++}
(4)	sppp	5.059	8.479	12.130	15.533	18.970
	didi$\pi\pi$	4.048	7.193	10.393	13.523	16.682
	trtrtrπ	3.712	6.764	9.814	12.854	15.919
	tetetete	3.542	6.549	9.524	12.519	15.538
		C^{-a}	N	O^{+}	F^{++}	Ne^{+++}
(3)	s^{2}ppp	0.682	1.082	1.536	1.941	2.335
	sp^{2}pp	9.254	14.292	19.224	24.291	29.301
	di^{2}di$\pi\pi$	4.968	7.687	10.380	13.116	15.818
	didi$\pi^2\pi$	8.208	12.867	17.476	22.151	26.795
	tr^{2}trtrπ	5.931	9.255	12.551	15.890	19.199
	trtrtrπ^2	7.858	12.392	16.893	21.437	25.960
	te^{2}tetete	6.326	9.920	13.491	17.098	20.680
		N^{-a}	O	F^{+}	Ne^{++}	Na^{+++}
(2)	s^{2}p^{2}pp	0.290	0.537	0.708	0.885	1.081
	sp^{2}p^{2}p	11.799	16.969	21.988	27.112	32.328
	di^{2}di$^2\pi\pi$	0.290	0.537	0.708	0.885	1.081
	di^{2}di$\pi^2\pi$	6.074	8.753	11.348	13.998	16.705
	didi$\pi^2\pi^2$	10.772	15.558	20.210	24.967	29.782
	tr^{2}tr^{2}trπ	4.166	6.014	7.801	9.627	11.497
	tr^{2}trtrπ^2	7.526	10.864	14.104	17.416	20.781
	te^{2}te^{2}tete	5.818	8.400	10.903	13.462	16.068
		O^{-a}	F	Ne^{+}	Na^{++}	Mg^{+++}
(1)	p	−0.011	0.017	0.036	0.056	0.092
	s	15.036	20.892	26.903	32.778	38.614
			Na	Mg^{+}	Al^{++}	Si^{+++}
(1)	s		0.0	0.0	0.0	0.0
	p		2.103	4.429	6.673	8.874
		Na^{-a}	Mg	Al^{+}	Si^{++}	P^{+++}
(2)	sp	0.984	3.121	5.342	7.485	9.616
	pp	1.822	6.422	11.146	15.596	20.347
	didi	0.820	2.757	4.691	6.598	8.566
	diπ	1.404	4.772	8.244	11.527	14.981
	trtr	1.191	4.060	6.988	9.786	12.726
	trπ	1.543	5.322	9.212	12.876	16.770
	tete	1.362	4.681	8.081	11.306	14.719
		Mg^{-a}	Al	Si^{+}	P^{++}	S^{+++}
(3)	spp	2.594	4.856	7.263	9.464	11.786
	ppp	5.947	10.628	15.380	19.977	24.742
	didiπ	2.278	4.320	6.443	8.399	10.527
	di$\pi\pi$	4.271	7.742	11.322	14.721	18.264
	trtrtr	2.173	4.142	6.170	8.044	10.108
	trtrπ	3.572	6.542	9.604	12.495	15.545
	tetete	3.195	5.897	8.677	11.293	14.081
		Al^{-a}	Si	P^{+}	S^{++}	Cl^{+++}
(4)	sppp	3.866	6.223	8.463	10.806	13.176
	didi$\pi\pi$	3.245	5.415	7.427	9.545	11.767
	trtrtrπ	3.038	5.145	7.082	9.125	11.297
	tetetete	2.935	5.011	6.910	8.915	11.062
		Si^{-a}	P	S^{+}	Cl^{++}	Ar^{+++}
(3)	s^{2}ppp	0.745	0.831	1.002	1.126	1.174
	sp^{2}pp	4.867	7.891	11.084	13.942	17.131
	di^{2}di$\pi\pi$	2.806	4.361	6.043	7.534	9.152
	didi$\pi^2\pi$	4.674	7.450	10.313	12.959	15.864
	tr^{2}trtrπ	3.408	5.342	7.381	9.233	11.249
	trtrtrπ^2	4.610	7.303	10.057	12.631	15.442
	te^{2}tetete	3.692	5.795	7.986	10.001	12.192
		P^{-a}	S	Cl^{+}	Ar^{++}	K^{+++}
(2)	s^{2}p^{2}pp	0.180	0.309	0.397	0.491	0.591
	sp^{2}p^{2}p	6.686	9.462	12.293	15.089	17.846
	di^{2}di$^2\pi\pi$	0.180	0.309	0.397	0.491	0.591
	di^{2}di$\pi^2\pi$	3.449	4.886	6.345	7.790	9.219
	didi$\pi^2\pi^2$	6.203	8.747	11.358	13.914	16.446
	tr^{2}tr^{2}trπ	2.370	3.360	4.363	5.357	6.343
	tr^{2}trtrπ^2	4.313	6.093	7.912	9.701	11.472
	te^{2}te^{2}tete	3.328	4.707	6.111	7.496	8.869
		S^{-a}	Cl	Ar^{+}	K^{++}	Ca^{+++}
(1)	p	−0.003	0.036	0.057	0.089	0.129
	s	8.027	10.761	13.426	16.189	18.894

[a] Extrapolated values.

It is interesting to note the extent to which the electronegativities obtained in this work depend on the character of the orbital. As may have been expected, the electronegativities for σ orbitals are considerably larger than those for the π orbitals. Also, the electronegativity increase with increasing s character anticipated by Walsh[14] and Bent[16] is borne out of the data observed.

An important feature is the linear relation observed between s character of the σ orbital and its electronegativity, which is shown in Figs. 4 and 5, where the electronegativities of the orbitals of the form

$$\psi = \cos \alpha \, (s) + \sin \alpha \, (p)$$

are plotted against $\cos^2 \alpha$ for C and N. This aspect

TABLE III

VALENCE STATE IONIZATION POTENTIALS I_v, VALENCE STATE ELECTRON AFFINITIES E_v AND ORBITAL ELECTRONEGATIVITIES[a]

		I_v	E_v	χ_M	χ_p
H (1)		13.60	0.75	14.34	2.21*
Li (1)	s	5.39	.82	6.21	0.84*
	p	3.54	.56	4.10	0.47
Be (2)	sp	σ 9.92	3.18	13.10	2.15
		π 5.96	0.11	6.07	0.82
	pp	6.11	.76	6.87	0.95
	didi	8.58	.99	9.57	1.40*
	$di\pi$	σ 8.02	.92	8.94	1.29
		π 6.04	.43	6.47	0.88
	trtr	7.61	.59	8.20	1.17
	$tr\pi$	σ 7.38	.63	8.01	1.13
		π 6.06	.54	6.60	0.90
	tete	7.18	.51	7.69	1.09
B (3)	spp	s14.91	5.70	20.61	3.25
		p 8.42	0.32	8.74	1.26
	ppp	8.40	3.46	11.86	1.79
	$didi\pi$	σ12.55	2.12	14.68	2.27
		π 8.23	0.44	8.68	1.26
	$di\pi\pi$	σ11.66	2.56	14.21	2.19
		π 8.41	1.89	10.30	1.53
	trtrtr	11.29	1.38	12.67	1.93*
	$trtr\pi$	σ10.97	1.87	12.84	1.96
		π 8.33	1.42	9.75	1.44
	tetete	10.43	1.53	11.97	1.81
C (4)	sppp	s21.01	8.91	29.92	4.84
		p11.27	0.34	11.61	1.75
	$didi\pi\pi$	σ17.42	3.34	20.77	3.29
		π11.19	0.10	11.29	1.69
	$trtrtr\pi$	σ15.62	1.95	17.58	2.75
		π11.16	0.03	11.19	1.68
	tetetete	14.61	1.34	15.95	2.48*
N (3)	s^2ppp	13.94	0.84	14.78	2.28
	sp^2pp	s26.92	14.05	40.98	6.70
		p14.42	2.54	16.96	2.65
	$di^2di\pi\pi$	σ23.91	7.45	31.35	5.07
		π14.18	1.66	15.84	2.46
	$didi\pi^2\pi$	σ22.10	6.84	28.94	4.67
		π14.11	2.14	16.25	2.53
	$tr^2trtr\pi$	σ20.60	5.14	25.74	4.13
		π14.12	1.78	15.90	2.47
	$trtrtr\pi^2$	19.72	4.92	24.63	3.94
	$te^2tetete$	18.93	4.15	23.08	3.68
O (2)	s^2p^2pp	17.28	2.01	19.29	3.04
	sp^2p^2p	s36.07	18.44	54.51	8.98
		p18.53	3.40	21.93	3.49
	$di^2di^2\pi\pi$	17.28	2.01	19.29	3.04
	$di^2di\pi^2\pi$	σ30.17	10.23	40.40	6.60
		π17.91	2.71	20.61	3.26
	$didi\pi^2\pi^2$	28.71	9.51	38.22	6.23
	$tr^2tr^2tr\pi$	σ26.65	7.49	34.14	5.54
		π17.70	2.47	20.17	3.19
	$tr^2trtr\pi^2$	26.14	7.32	33.47	5.43
	te^2te^2tete	24.39	6.11	30.50	5.93
F (1)	$s^2p^2p^2p$	20.86	3.50	24.36	3.90*
	$sp^2p^2p^2$	38.24	24.37	62.61	10.31
Na (1)	s	5.14	0.47	5.61	0.74*
	p	3.04	0.09	3.13	0.32
Mg (2)	sp	s 8.95	2.80	11.75	1.77
		p 4.52	0.06	4.58	0.56
	pp	5.65	0.01	5.66	0.75
	didi	7.10	1.08	8.18	1.17*
	$di\pi$	σ 7.30	0.78	8.08	1.15
		π 5.09	.03	5.12	0.65
	trtr	6.54	.52	7.06	.98
	$tr\pi$	σ 6.75	.38	7.13	.99
		π 5.27	.02	5.30	.69
	tete	6.28	.32	6.60	.90
Al (3)	spp	s12.27	4.92	17.19	2.69
		p 6.47	1.37	7.84	1.11
	ppp	6.50	4.89	11.39	1.71
	$didi\pi$	σ 9.91	2.61	12.51	1.90
		π 6.36	1.45	7.81	1.11
	$di\pi\pi$	σ 9.39	3.66	13.05	1.99
		π 6.49	3.13	9.61	1.41
	trtrtr	8.83	2.11	10.94	1.64*
	$trtr\pi$	σ 8.65	2.94	11.59	1.74
		π 6.43	2.58	9.01	1.31
	tetete	8.17	2.58	10.75	1.59
Si (4)	sppp	s17.31	6.94	24.24	3.88
		p 9.19	2.82	12.01	1.82
	$didi\pi\pi$	σ14.06	4.07	18.12	2.85
		π 9.18	2.20	11.38	1.71
	$trtrtr\pi$	σ12.61	3.20	15.80	2.33
		π 9.17	2.00	11.17	1.67
	tetetete	11.82	2.78	14.59	2.25*
P (3)	s^2ppp	10.73	1.42	12.15	1.84
	sp^2pp	s20.20	8.48	28.68	4.62
		p12.49	1.98	14.46	2.23
	$di^2di\pi\pi$	σ17.53	4.95	22.49	3.58
		π11.61	1.68	13.29	2.03
	$didi\pi^2\pi$	σ16.78	4.77	21.55	3.42
		π11.89	2.02	13.91	2.14
	$tr^2trtr\pi$	σ15.59	3.74	19.33	3.05
		π11.64	1.80	13.44	2.06
	$trtrtr\pi^2$	15.18	3.76	18.94	2.98
	$te^2tetete$	14.57	3.24	17.80	2.79
S (2)	s^2p^2pp	12.39	2.38	14.77	2.28
	sp^2p^2p	s20.08	11.54	31.62	5.12
		p13.32	3.50	16.83	2.63
	$di^2di^2\pi\pi$	12.39	2.38	14.78	2.28
	$di^2di\pi^2\pi$	σ17.78	6.96	24.74	3.96
		π12.86	2.94	15.80	2.45
	$didi\pi^2\pi^2$	17.42	6.80	24.22	3.87
	$tr^2tr^2tr\pi$	σ16.33	5.43	21.76	3.46
		π12.70	2.76	15.46	2.40
	$tr^2trtr\pi^2$	16.27	5.49	21.76	3.46
	te^2te^2tete	15.50	4.77	20.27	3.21
Cl (1)	$s^2p^2p^2p$	15.03	3.73	18.76	2.95*
	$sp^2p^2p^2$	24.02	14.45	38.47	6.26

[a] The orbital electronegativities in Mulliken's scale χ_M in (eV.) and in Pauling's scale χ_p. The values with * have been used to obtain the correlation parameter in equation 6. For nomenclature see footnote 31. The numbers in parentheses after the elements indicate how many bonding electrons the element has in the particular valence state .C(4) carbon four bonding.

makes electronegativities of intermediately hybridized orbitals available by linear interpolation. Such intermediate hybrids are undoubtedly needed in compounds of N and O, probably of the halogens, where some hybridization is likely, and even in carbon.[40]

Calculations for d orbital hybrids of second row elements have not been possible because of lack of spectroscopic data. These results would be of considerable interest, especially for the elements Si to Cl, where use of d orbitals has frequently been

(40) H. H. Jaffé, *J. Chem. Educ.* (in press).

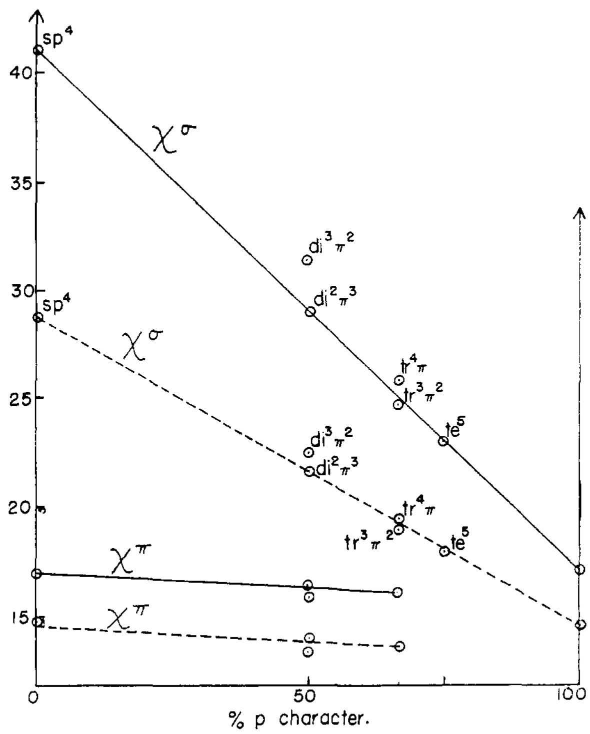

Fig. 5.—Electronegativities of nitrogen and phosphorous as a function of s character of the hybrid orbital. Solid line, nitrogen; broken line, phosphorus.

postulated. Computations of electronegativities of positive ions are now in progress, and it is hoped that values for partially charged atoms may also be obtained.[41] It was found in this Laboratory that these values are urgently required in order to get explanations[10] for hybrid and ionic character of chemical bonds consistent with n.q.r. frequency changes and other molecular properties.

(41) NOTE ADDED IN PROOF.—Such values have been obtained and are in the process of publication.

These subjects have been studied in a recent review article by Bent.[16] By considering compounds of the type X–A–Y, he has examined qualitatively the influence of the more electronegative group Y on the character of the bond X–A. He has attempted to explain the observed changes in the X–A bond, when going from X–A–X to X–A–Y by considering only rehybridization of atom A, combined with the postulate that the electronegativity of an orbital of A increases when its s character increases. The first conclusion, that A becomes more electronegative in its bond to X is reasonable. But, the second conclusion drawn, that this is only due to increased s character in the bonding orbital of A toward X, appears dubious. As Coulson[42] has shown, the bond strength is not only governed by the overlap, but also by the energy match of the bonding orbitals; *e.g.* the bond is stronger, the better the energies match. If this concept is applied in Bent's picture, it is easily seen that increasing the s character of the A orbital toward X upsets the energy match of A with X, and also a corresponding increase of p character in the orbital toward Y makes the energy mismatch larger. But, if we consider, in addition to rehybridization, partial charges on the atoms, all the examples presented can be explained, and the energy match will be found to improve.

Thus, it must be pointed out that the picture given by Bent is questionable, since for simplicity's sake he has chosen not to introduce partial charges which is a serious approximation in a valence bond treatment. In order to make a more complete study possible, it is necessary to examine thoroughly the dependence of the orbital electronegativities on partial charges on the atoms.

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(42) C. A. Coulson, *Proc. Phil. Soc.*, **33**, 111 (1937).

[CONTRIBUTION FROM THE DIVISION OF PHYSICAL CHEMISTRY, INSTITUTE OF TECHNOLOGY, UNIVERSITY OF MINNESOTA, MINNEAPOLIS, MINNESOTA]

Some Flash-photolytic and Photochemical Studies of Retinene and Related Compounds[1a]

BY KARL-HEINZ GRELLMANN, RUDIGER MEMMING[1b] AND ROBERT LIVINGSTON

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Flash illumination of air-free solutions of retinene produces a transient spectral response. The labile species, presumably the lowest triplet state of retinene, has a strong absorption band with a peak at 450 mμ. It disappears by a first order process. The value of the rate constant depends on the solvent, being, at room temperature, 9.6×10^4 for hexane and 4.3×10^4 sec.$^{-1}$ for glycerol. The rate decreases with temperature. The energies of activation are 0.9, 0.7 and 2.4 kcal. for hexane, toluene and glycerol, respectively. No spectral transients were observed when anaerobic solutions of a Schiff's base, a protonated Schiff's base or a hemiacetal of retinene were illuminated. Both the all-*trans* and the all-*cis* forms of the protonated Schiff's base of retinene and propylamine undergo rapid *cis–trans* isomerization when they are exposed in methanolic solution to white light.

Introduction

Abrahamson, *et al.*, report[2] that flash illumination of all-*trans* retinene, in anaerobic tetrahydrofuran or methyl cyclohexane, produces a short-lived transient species, which disappears by a first order process. Neither vitamin A nor a protonated

(1) (a) This research was supported by the Division of Biology and Medicine of U. S. A. E. C. under Contract AT (11-1) 718. (b) Phillips Zentrallaboratorium GMBH, Hamburg-Stellingen.

(2) E. Abrahamson, R. Adams and V. Wulff, *J. Phys. Chem.*, **63**, 441 (1959); E. Abrahamson, J. Marquisee, P. Gavuzzi and J. Roubie, *Z. Elektrochem.*, **64**, 177 (1960).