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Molecular Orbital Theory of the Electronic Structure of Organic Compounds. I. Substituent Effects and Dipole Moments

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Abstract: A recent approximate self-consistent molecular orbital theory (complete neglect of differential overlap or CNDO) is used to calculate charge distributions and electronic dipole moments of a series of simple organic molecules. The nuclear coordinates are chosen to correspond to a standard geometrical model. The calculated dipole moments are in reasonable agreement with experimental values in most cases and reproduce many of the observed trends. The associated charge distributions of dipolar molecules show widespread alternation of polarity in both saturated and unsaturated systems. These results suggest that charge alternation may be an intrinsic property of all inductive and mesomeric electronic displacements.

One of the long-term aims of quantum chemistry is to provide a critical quantitative background for simple theories of electron distribution in large molecules. Most theoretical discussions of the role of electronic structure in organic chemistry are at present based either on qualitative arguments (such as the study of resonance structures) with no clear foundation in quantum mechanics, or on postulated relationships between charge distribution and various physical and chemical properties (reactivities, acidities, nmr chemical shifts, etc.), few of which can be subjected to direct test. If quantum mechanical calculations are to lead to independent methods of studying such phenomena, they ought to satisfy the following general conditions.

(1) The methods must be simple enough to permit application to moderately large molecules without excessive computational effort. Quite accurate wave functions now exist for many diatomic and small polyatomic molecules, but it is unlikely that comparable functions will be readily available in the near future for the molecules of everyday interest to the organic chemist. To be accessible, a quantum mechanical theory has to be approximate.

(2) Even though approximations have to be introduced, these should not be so severe that they eliminate any of the primary physical forces determining structure. For example, the relative stabilities of electrons in different energy levels, the directional character of the bonding capacity of atomic orbitals, and the electrostatic repulsion between electrons are all gross features with major chemical consequences and they should all be retained in a realistic treatment.

(3) In order to be useful as an independent study, the approximate wave functions should be formulated in an unbiased manner, so that no preconceived ideas derived from conventional qualitative discussions are built in implicitly. For example, a critical theoretical study of the localization of a two-electron bond orbital ought to be based on a quantum mechanical theory which makes no reference to electron-pair bonds in its basis. Molecular orbital theories satisfy this type of condition insofar as each electron is treated as being free to move anywhere in the molecular framework.

(4) The theory should be developed in such a way that the results can be interpreted in detail and used to support or discount qualitative hypotheses. For example, it is useful if the electronic charge distribution calculated from a wave function can be easily and realistically divided into contributions on individual atoms

which may then be compared with qualitative discussions. As a rule, approximate quantum mechanical treatments are more easily interpreted in this manner than complex, accurate wave functions in cases where the latter are available.

(5) Finally, the theory should be sufficiently general to take account of all chemically effective electrons. Normally, this means all electrons in the valence shell. Extensive theories have been developed, of course, for the π electrons of conjugated planar systems, but those apply only to a limited class of molecules and even then are subject to frequent uncertainty because of lack of knowledge about the remaining σ electrons which are not treated explicitly. The extension of quantum mechanical techniques to apply to all valence electrons of a general three-dimensional molecule must be a major objective.

A number of approaches have recently been made to *approximate*, but *general*, *molecular orbital* theories for large molecules. Many of these (often referred to as extended Hückel theories) are based on an independent electron model in which the electron–electron Coulomb repulsion is not included explicitly.[1,2] These methods probably give a good description of the molecular orbital distribution in nonpolar molecules (such as neutral hydrocarbons), but are likely to have serious shortcomings in situations where polar or ionic effects play an important part, since these arise directly from the Coulomb fields of the constituent particles.

Recently, a number of new approximate molecular orbital methods based on the full many-electron Hamiltonian have been developed.[3-7] The methods developed in this laboratory[3-5] simplify the calculations by neglecting only the less important electron repulsion integrals (neglect of differential overlap). These are approximate *self-consistent* methods and are one step more sophisticated than independent electron models, but they have the advantage of taking explicit account of the electrostatic effects of polar and ionic groups. They are logical extensions of self-consistent methods previously developed for π-electron systems. The new methods are still simple enough to be applied to moderately large molecules (molecular weight $\sim$100) using very modest amounts of computer time and can be applied extensively to series of organic compounds in many configurations. Once completely specified, such a method constitutes a mathematical model which simulates chemical behavior and which can be examined in quantitative detail at any stage. The aim of this and subsequent papers will be to describe the results of applying such methods to problems involving the electronic structure of organic molecules.

The method we have developed most to date is the simplest of a series of possible approximations. This involves complete neglect of differential overlap or CNDO (neglect of the products $\varphi_\mu(1)\varphi_\nu(1)$ of different atomic orbitals φ_μ and φ_ν in all electron interaction integrals). In its second version (CNDO/2 as specified in ref 5), application to simple AB_2 and AB_3 molecules suggests that the method gives a reasonable description of stereochemistry (calculated equilibrium bond angles) and over-all electron distribution (calculated dipole moments), but total energies are not satisfactory. However, even in the absence of precise agreement with experimental data, the model should be a valuable guide for comparison of series of molecules and semiquantitative discussion of changes in electron distribution caused by substitution. In this paper we shall use the CNDO/2 method throughout.

The quantum-mechanical methods have to be based on a specified geometry for the nuclear framework. For applications to a wide range of organic molecules, this ought to be prescribed in a systematic manner. This can be done in two ways. Either the best available experimental bond lengths and angles could be used *for each individual molecule* or some *standard geometry* based on a well-defined set of rules could be applied universally. We shall normally adopt the latter approach which has a number of advantages. In the first place, we may wish to discuss the electronic structure of a molecule where there is little or no experimental data. Secondly, even in molecules where the geometry is known experimentally, a case can be made for using standard bond lengths and angles, for individual geometrical features are themselves *caused* by the electronic structure and more insight can be obtained from a standard model. For example, in the theory of alternation of bond lengths in polyenes, it is better to start with a theory of the electronic structure based on equal bond lengths and then discover the "driving force" causing alternation (alternating bond order), rather than starting with a geometrical model with the alternation already built in.

The principal aim of this paper is to use the new molecular orbital method for a critical study of the changes in the electronic structure of a hydrocarbon caused by the introduction of substituents. These effects are often discussed qualitatively in terms of inductive, mesomeric, and other shifts and often correlated with many experimental properties such as dipole moments, reactivities, acidities, and nuclear magnetic resonance chemical shifts. We shall only be concerned with the electron distribution in the unperturbed molecule, for which gas-phase dipole moments are the most directly related experimental quantities. The other correlations may well be suitable for studies by similar methods (*e.g.*, reactivities by applying the theory to postulated intermediates and transition states), but in this first paper they will not be considered in detail.

Quantum Mechanical Method

We begin with a brief resumé of the salient points of the complete neglect of differential overlap (CNDO/2) molecular orbital method described in detail elsewhere.[3-5] For a closed-shell molecule, valence electrons are assigned in pairs to molecular orbitals ψ_i which are linear combinations of valence atomic orbitals φ_μ (LCAO)

$$\psi_i = \sum_\mu c_{i\mu}\varphi_\mu \qquad (1)$$

In normalizing these molecular orbitals, overlap inte-

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(1) R. S. Mulliken, *J. Chim. Phys.*, **46**, 497, 675 (1949).
(2) R. Hoffman, *J. Chem. Phys.*, **39**, 1397 (1963).
(3) J. A. Pople, D. P. Santry, and G. A. Segal, *ibid.*, **43**, S129 (1965).
(4) J. A. Pople and G. A. Segal, *ibid.*, **43**, S136 (1965).
(5) J. A. Pople and G. A. Segal, *ibid.*, **44**, 3289 (1966).
(6) G. Klopman, *J. Am. Chem. Soc.*, **86**, 4550 (1964).
(7) M. D. Newton, F. P. Boer, and W. N. Lipscomb, *ibid.*, **88**, 2353 (1966); F. P. Boer, M. D. Newton, and W. N. Lipscomb, *ibid.*, **88**, 2361 (1966); M. D. Newton, F. P. Boer, and W. N. Lipscomb, *ibid.*, **88**, 2367 (1966).

grals $S_{\mu\nu}$ between different atomic orbitals are neglected. The total electron density (for valence electrons) may be written

$$\rho = 2\sum_{i}^{\text{occ}}\psi_i^2 = \sum_{\mu\nu}P_{\mu\nu}\varphi_\mu\varphi_\nu \qquad (2)$$

where $P_{\mu\nu}$ is the charge-density and bond-order matrix (or first-order density matrix) defined by

$$P_{\mu\nu} = 2\sum_{i}^{\text{occ}}c_{i\mu}c_{i\nu} \qquad (3)$$

the summation over i covering occupied molecular orbitals. This matrix contains the complete information obtained from the calculation about the electron density. The diagonal element $P_{\mu\mu}$ gives the total charge associated with the atomic orbital φ_μ. The total charge density assigned to an atom A is given by

$$P_{\text{AA}} = \sum_{\mu}^{\text{A}}P_{\mu\mu} \qquad (4)$$

where the sum is over all valence atomic orbitals belonging to atom A.

The molecular orbital coefficients are eigenvectors of a Fock Hamiltonian matrix given by

$$F_{\mu\mu} = -\frac{1}{2}(I_\mu + A_\mu) + [(P_{\text{AA}} - Z_{\text{A}}) - \frac{1}{2}(P_{\mu\mu} - 1)]\gamma_{\text{AA}} + \sum_{\text{B}(\neq\text{A})}(P_{\text{BB}} - Z_{\text{B}})\gamma_{\text{AB}} \qquad (5)$$

$$F_{\mu\nu} = \beta_{\text{AB}}{}^0S_{\mu\nu} - \frac{1}{2}P_{\mu\nu}\gamma_{\text{AB}} \qquad (6)$$

In eq 5 and 6, the atomic orbitals φ_μ and ϕ_ν belong to atoms A and B, respectively. I_μ and A_μ are atomic ionization potentials and electron affinities associated with φ_μ so that the first term on the right of this equation represents the Mulliken electronegativity of the orbital. Z_{A} is the core charge of atom A (equal to the nuclear charge less the number of inner shell electrons not considered explicitly). γ_{AB} is an average Coulomb repulsion energy between a valence electron on A and another on B. Thus the middle term of eq 5 gives the destabilizing effect of a net excess electronic charge on atom A (if $P_{\text{AA}} > Z_{\text{A}}$), and the final term gives the Coulomb potential at φ_μ due to the net excess charges on other atoms in the molecule. The off-diagonal elements given in (6) used a semiempirical resonance integral proportional to the overlap, the constant of proportionality $\beta_{\text{AB}}{}^0$ depending only on the nature of the atoms A and B. The final term is a correction to off-diagonal elements due to electron repulsion. Complete specification of the constants and sources of integrals are given in ref 4 and 5. The complete calculation has been formulated as a computer program, requiring only the nuclear charges, nuclear coordinates, and number of electrons as input.[8]

Electric dipole moments are calculated as the sum of two parts. The first is obtained from the net charges located at the nuclear positions, and the second measures the contribution due to the displacement of atomic electron charges away from the center. The latter effect is proportional to off-diagonal $P_{\mu\nu}$ matrix elements $P(2s_{\text{A}}, 2p_{\text{A}})$ between 2s and 2p orbitals on the same atom A. There is no contribution of this type for hydrogen atoms since only a 1s atomic orbital is used in the basis. The full formula for the x component of the dipole is (in debyes)

$$\mu_x = 2.5416\sum_{\text{A}}(Z_{\text{A}} - P_{\text{AA}})x_{\text{A}} - 14.674\sum_{\text{A}}{}^*Z_{\text{A}}'^{-1}P(2s_{\text{A}}, 2p_{x\text{A}}) \qquad (7)$$

where $\Sigma_{\text{A}}{}^*$ is a summation over nonhydrogenic atoms and Z_{A}' is the orbital exponent (Slater constant) for the 2s and 2p orbitals of atom A.

It may be noted that the product of two atomic orbitals on the same atom is used in the calculation of the electric dipole moment, even though it is neglected elsewhere in the CNDO calculations (in electron–electron repulsion integrals, for example). This means that intramolecular interactions between atomic dipoles are not properly taken into account. A more consistent but lengthier procedure would be to retain all monatomic products (neglect of diatomic differential overlap or NDDO as introduced in ref 3). Results based on this more sophisticated method will be reported later.

Standard Geometrical Models

In this section we prescribe the standard molecular geometries to be used in subsequent applications. The aim is to construct a set of Cartesian coordinates for the nuclei directly from the chemical formula.

For molecules without closed rings, the complete geometry can be defined by three types of information: (1) bond lengths for all bonds specified by the chemical formula; (2) bond angles specifying the complete stereogeometry of the neighboring atoms bonded to each atom in the molecule; and (3) dihedral angles specifying internal rotation about appropriate bonds. If rings are present, these quantities are not independent and an alternative type of specification will be needed in some cases.

In setting up rules for all these quantities, it will be convenient to use a notation Xn for an atom with elemental symbol X being bonded to n neighbors. n may be referred to as the connectivity of X. For example, the carbon atoms in ethane, ethylene, and acetylene will be described as C4, C3, and C2, respectively.

Bond Length. Four principal types of bond are distinguished, single, double, triple, and aromatic, the last for use in benzene-type rings. Dative (or partially dative) bonds will also be handled in certain special groups such as nitro. In all molecules discussed in the present paper, the assignment of bond type will be unambiguous. Numerical standard values used for lengths of bonds involving H, C, N, O, and F atoms are shown in Table I. These are selected as suitable average values from available experimental data.

Bond Angles. Five types of local atomic geometry are distinguished. If the connectivity is 4, tetrahedral angles are used. For connectivity 3, the three bonds are either taken to be planar with bond angles of 120° or pyramidal with bond angles of 109.47° (the tetrahedral angle). Atoms with connectivity 2 are taken as linear (angle 180°) or bent (with a bond angle of 109.47°).

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(8) G. A. Segal, Quantum Chemistry Program Exchange, Program 91, Indiana University, 1966.

Table I. Standard Bond Lengths

Bond	Length, A	Bond	Length, A
	Single Bonds		
H-H	0.74	C3-N2	1.40
C4-H	1.09	C3-O2	1.36
C3-H	1.08	C3-F1	1.33
C2-H	1.06	C2-C2	1.38
N3-H	1.01	C2-N3	1.33
N2-H	0.99	C2-N2	1.33
O2-H	0.96	C2-O2	1.36
F1-H	0.92	C2-F1	1.30
C4-C4	1.54	N3-N3	1.45
C4-C3	1.52	N3-N2	1.45
C4-C2	1.46	N3-O2	1.36
C4-N3	1.47	N3-F1	1.36
C4-N2	1.47	N2-N2	1.45
C4-O2	1.43	N2-O2	1.41
C4-F1	1.36	N2-F1	1.36
C3-C3	1.46	O2-O2	1.48
C3-C2	1.45	O2-F1	1.42
C3-N3	1.40[a]	F1-F1	1.42
	Double Bonds		
C3-C3	1.34	C2-O1	1.16
C3-C2	1.31	N3-O1	1.24[b]
C3-N2	1.32	N2-N2	1.25
C3-O1	1.22	N2-O1	1.22
C2-C2	1.28	O1-O1	1.21
C2-N2	1.32		
Triple Bonds		Aromatic Bonds	
C2-C2	1.20	C3-C3	1.40
C2-N1	1.16	C3-N2	1.34
N1-N1	1.10	N2-N2	1.35

[a] 1.32 used in N—C=O group. [b] Partial double bonds in NO_2 and NO_3 groups.

The nature of the local atomic geometry frequently depends on the presence of unsaturation in a neighboring group. While this cannot always be handled satisfactorily, some account can be taken by considering the total excess valence of the neighboring atoms (the excess valence being the normal valence minus the connectivity). In allene, for example, the excess valence of the outer carbons is one and the total excess valence of the neighbors of the central atom is two.

The rules adopted for selecting the atomic local geometry are given in Table II. Inevitably, the model will give the incorrect type of geometry in some cases. For example, the equilibrium structure of the CF_3 radical is probably nonplanar,[9] although taken as planar in the standard model. However, the rules given provide a broadly correct picture of the dependence of local geometry on the atomic arrangement.

Table II. Standard Atomic Geometry and Bond Angles

Atom	Total excess valence of neighbors	Examples	Geometry	Bond angle, deg
C4	All values	CH_4	Tetrahedral	109.47
C3	All values	C_2H_4	Planar	120
C2	0, 1	CH_2, CHO	Bent	109.47
	2, 3, 4	CO_2, HCN	Linear	180
N4	All values	NH_4^+	Tetrahedral	109.47
N3	0	NH_3	Pyramidal	109.47
	1, 2, 3, 4	H_2N-CHO	Planar	120
N2	0, 1, 2	H_2CNH	Bent	109.47
	3, 4	HNC	Linear	180
O3	0	H_3O^+	Pyramidal	109.47
	1, 2, 3, 4		Planar	120
O2	All values	O_3, H_2O	Bent	109.47

These models as defined can only be used for cyclic compounds if no strain is involved. This will be true only if the bond lengths and angles are consistent with the cyclic structure. Benzene and chair cyclohexane rings belong to this category.

Dihedral Angles. In an open-chain molecule, dihedral angles have to be specified for each bond joining atoms with connectivity greater than one (unless they are linear). Values of 0, 60, and 180° will be used for *cis*, *gauche*, and *trans* arrangements in accordance with usual nomenclature.

Rules used for dihedral angles are as follows: (1) staggered configurations are used for bonds connecting atoms with tetrahedral angles; (2) for bonds between tetrahedral and trigonal atoms, as in propene, one of the other bonds on the tetrahedral atom is in the trigonal plane, single bonds being *trans* where appropriate; (3) neighboring trigonal atoms are taken to be coplanar. These rules conform closely to most known data on equilibrium configurations.

Results and Discussion

The quantum-mechanical procedure described in the Quantum Mechanical Method section has been used to calculate LCAO molecular orbitals, charge distributions, and electric dipole moments for a series of simple organic molecules. The dipole moment results are compared with available experimental values in Tables III and IV, using microwave data where possible. For directions, comparison is made for the angle between the dipolar axis and a particular bond. This involves some arbitrary selection, since the standard bond angles used in the calculation will differ from experimental bond angles determined by microwave spectral data. Figures 1–4 show the calculated net atomic charge densities for a selection of these molecules in units of 10^{-3} electron charges. (Owing to rounding errors and limitations of the method of computation, these numbers are subject to some uncertainty in the last figure.)

The general level of agreement between calculated and observed dipole moments is evidently good, few molecules being seriously in error. In Table IV, some calculated dipole directions are compared with the directions that would follow from a simple bond dipole additivity model. In almost all cases the deviation from the bond additive direction is calculated in the right sense. This over-all level of agreement provides some general support for the validity of the calculated charge densities. In this section we shall discuss some of these in detail and the bearing they have on theories of electron displacement.

a. Hydrocarbons. The three simple nonpolar hydrocarbons ethane, ethylene, and acetylene show increasingly positive hydrogen atoms in line with the usual qualitative picture of more C^-–H^+ character as the s character of the bond increases. If the hydrogen atoms in any of these are replaced by substituents,

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(9) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, 43, 2704 (1965).

Table III. Dipole Moments

Compound	Dipole moment, D. Calcd	Dipole moment, D. Obsd
Hydrocarbons		
Propane	0.00	0.083[a]
Propene	0.36	0.364[b]
Propyne	0.43	0.75[c,d]
2-Methylpropane	0.00	0.132[e]
2-Methylpropene	0.65	0.503[f]
2-Methyl-1,3-butadiene	0.25	0.292[g]
Toluene	0.21	0.43[h]
Fluorine compounds		
Hydrogen fluoride	1.85	1.8195[i]
Methyl fluoride	1.66	1.855[j]
Methylene fluoride	1.90	1.96[k]
Fluoroform	1.66	1.645[l]
Ethyl fluoride	1.83	1.96[m]
1,1-Difluoroethane	2.23	2.30[n]
1,1,1-Trifluoroethane	2.18	2.32[o]
Fluoroethylene	1.51	1.427[p]
1,1-Difluoroethylene	1.02	1.37[q]
cis-1,2-Difluoroethylene	2.83	2.42[r]
Fluoroacetylene	1.04	0.75[s]
n-Propyl fluoride (*trans*)	1.84	2.05[t]
trans-1-Fluoropropene	1.67	1.85[u]
cis-1-Fluoropropene	1.59	1.46[v]
2-Fluoropropene	1.69	1.60[w]
3-Fluoropropene (*s-cis*)	1.83	1.765[x]
3,3,3-Trifluoropropene	2.34	2.45[y]
3,3,3-Trifluoropropyne	2.48	2.36[z]
2-Fluoro-1,3-butadiene	1.65	1.417[aa]
Fluorobenzene	1.66	1.66[bb]
Oxygen compounds		
Water	2.10	1.846[cc]
Methanol	1.94	1.69[dd]
Dimethyl ether	1.83	1.30[ee]
Oxygen compounds		
Formaldehyde	1.98	2.339[l]
Acetaldehyde	2.53	2.68[ff]
Propionaldehyde	2.46	2.52[gg]
Acetylacetylene	2.85	2.4[hh]
Acetone	2.90	2.90[ii]
Acrolein (*s-trans*)	2.63	3.11[jj]
Methyl vinyl ketone	2.92	3.16[kk]
Ketene	1.30	1.414[ll]
Methylketene	1.35	1.79[mm]
Formic acid	0.87	1.415[nn]
Phenol	1.73	1.55[h]
Nitrogen compounds		
Ammonia	1.97	1.468[oo]
Methylamine	1.86	1.326[pp]
Dimethylamine	1.76	1.03[qq]
Trimethylamine	1.68	0.612[rr]
Hydrogen cyanide	2.48	2.986[ss]
Methyl cyanide	3.05	3.92[c,d]
Mixed compounds		
Nitrogen trifluoride	0.43	0.235[tt]
Difluoramine	2.13	1.93[uu]
Nitrous acid	2.27	1.85[vv]
Nitric acid	2.24	2.16[ww]
Cyano fluoride	1.55	1.68[xx]
Formyl fluoride	2.16	2.02[yy]
Carbonyl fluoride	1.42	0.951[zz]
Acetyl fluoride	2.84	2.96[aaa]
Acetyl cyanide	2.80	3.45[bbb]
Isocyanic acid	1.88	1.59[ccc]
Methyl isocyanate	1.80	2.81[ddd]
Formamide	3.79	3.71[eee]
Nitromethane	4.38	3.46[fff]
Nitrobenzene	5.33	4.28[ggg]

[a] D. R. Lide, *J. Chem. Phys.*, **33**, 1514 (1960). [b] D. R. Lide and D. E. Mann, *ibid.*, **27**, 868 (1957). [c] S. N. Ghosh, R. Trambarulo, and W. Gordy, *Phys. Rev.*, **87**, 172 (1952). [d] S. N. Ghosh, R. Trambarulo, and W. Gordy, *J. Chem. Phys.*, **21**, 308 (1953). [e] D. R. Lide and D. E. Mann, *ibid.*, **29**, 914 (1958). [f] V. W. Laurie, *ibid.*, **34**, 1516 (1961). [g] D. R. Lide and M. Jen, *ibid.*, **40**, 252 (1964). [h] A. L. McClellan, "Tables of Experimental Dipole Moments," W. H. Freeman and Co., San Francisco, Calif., 1963, p 251. [i] R. Weiss, *Phys. Rev.*, **131**, 659 (1963). [j] M. Larkin and W. Gordy, *J. Chem. Phys.*, **38**, 2329 (1963). [k] D. R. Lide, *J. Am. Chem. Soc.*, **74**, 3548 (1952). [l] J. N. Shoolery and A. H. Sharbaugh, *Phys. Rev.*, **82**, 95 (1951). [m] J. Kraitchman and B. P. Dailey, *J. Chem. Phys.*, **23**, 184 (1955). [n] G. H. Kwei and D. R. Hershbach, *ibid.*, **32**, 1270 (1960). [o] R. G. Shulman, B. P. Dailey, and C. H. Townes, *Phys. Rev.*, **78**, 145 (1950). [p] A. M. Mirri, A. Guanieri, and P. Favero, *Nuovo Cimento*, **19**, 1189 (1961). [q] A. Roberts and W. F. Edgell, *J. Chem. Phys.*, **17**, 742 (1949). [r] V. W. Laurie, *ibid.*, **34**, 291 (1961). [s] J. K. Tyler, and J. Sheridan, *Proc. Chem. Soc.*, 119 (1960). [t] E. Hirota, *J. Chem. Phys.*, **37**, 283 (1962). [u] S. Siegel, *ibid.*, **27**, 989 (1957). [v] R. A. Beaudet and E. B. Wilson, *ibid.*, **37**, 1133 (1962). [w] L. Pierce and J. M. O'Reilly, *J. Mol. Spectry.*, **3**, 536 (1959). [x] E. Hirota, *J. Chem. Phys.*, **42**, 2071 (1965). [y] J. J. Conradi and N. C. Li, *J. Am. Chem. Soc.*, **75**, 1705 (1953). [z] J. N. Shoolery, R. G. Shulman, W. F. Sheehan, Jr., V. Schomaker, and D. M. Yost, *J. Chem. Phys.*, **19**, 1364 (1951). [aa] D. R. Lide, *ibid.*, **37**, 2074 (1962). [bb] D. G. deKowalski, P. Koheritz, and H. Selen, *ibid.*, **31**, 1438 (1959). [cc] G. Birnbaum and S. K. Chatterjie, *J. Appl. Phys.*, **23**, 220 (1952). [dd] D. G. Burkhard and D. M. Dennison, *Phys. Rev.*, **84**, 408 (1951). [ee] L. G Groves and S. Sugden, *J. Chem. Soc.*, 1779 (1937). [ff] R. W. Kilb, C. C. Lin, and E. B. Wilson, Jr., *J. Chem. Phys.*, **31**, 882 (1959). [gg] S. S. Butcher and E. B. Wilson, Jr., *ibid.*, **40**, 1671 (1964). [hh] O. L. Streifvater and J. Sheridan, *Proc. Chem. Soc.*, 368 (1963). [ii] J. D. Swalen and C. C. Costain, *J. Chem. Phys.*, **31**, 1562 (1959). [jj] R. J. Wagner, J. Fine, J. W. Simmons, and J. H. Goldstein, *ibid.*, **26**, 634 (1957). [kk] P. D. Foster, V. M. Rao, and R. F. Curl, Jr., *ibid.*, **43**, 1064 (1965). [ll] H. R. Johnson and M. W. P. Strandberg, *ibid.*, **20**, 687 (1952). [mm] B. Bak, J. J. Christiansen, K. Kunstmann, L. Nygaard, and J. Rastrup-Andersen, *ibid.*, **45**, 883 (1966). [nn] H. Kim, R. Keller, and W. D. Gwinn, *ibid.*, **37**, 2748 (1962). [oo] D. K. Coles, W. E. Good, J. K. Bragg, and A. H. Sharbaugh, *Phys. Rev.*, **82**, 877 (1951). [pp] D. R. Lide, *J. Chem. Phys.*, **27**, 343 (1957). [qq] R. J. W. LeFevre and P. Russell, *Trans. Faraday Soc.*, **43**, 374 (1947). [rr] D. R. Lide, Jr., and D. E. Mann, *J. Chem. Phys.*, **28**, 572 (1958). [ss] B. N. Bhattacharya and W. Gordy, *Phys. Rev.*, **119**, 144 (1960). [tt] P. Kisliuk, *J. Chem. Phys.*, **22**, 86 (1954). [uu] D. R. Lide, Jr., *ibid.*, **38**, 456 (1963). [vv] A. P. Cox and R. L. Kuczkowski, *J. Am. Chem. Soc.*, **88**, 5071 (1966). [ww] D. J. Millen and J. R. Morton, *J. Chem. Soc.*, 1523 (1960). [xx] J. Sheridan, J. K. Tyler, E. E. Aynsley, R. E. Dodd, and R. Little, *Nature*, **185**, 96 (1960). [yy] O. H. LeBlanc, V. W. Laurie, and W. D. Gwinn, *J. Chem. Phys.*, **33**, 598 (1960). [zz] V. W. Laurie and D. T. Pense, *ibid.*, **37**, 2995 (1962). [aaa] L. Pierce and L. C. Krisher, *ibid.*, **31**, 875 (1959). [bbb] L. C. Krisher and E. B. Wilson, Jr., *ibid.*, **31**, 882 (1959). [ccc] J. N. Shoolery, R. G. Shulman, and D. M. Yost, *ibid.*, **19**, 250 (1951). [ddd] R. F. Curl, Jr., V. M. Rao, K. V. L. N. Sastry, and J. A. Hodgeson, *ibid.*, **39**, 3335 (1963). [eee] R. J. Kurland and E. B. Wilson, Jr., *ibid.*, **27**, 585 (1957). [fff] E. Tannenbaum, R. J. Myers, and W. D. Gwinn, *ibid.*, **25**, 42 (1956). [ggg] R. J. W. LeFevre and P. Russell, *J. Chem. Soc.*, 491 (1936).

we need to consider changes in charge relative to the parent molecule.

The paraffins propane and 2-methylpropane show small experimental dipole moments, but these are not interpreted by the theory (using the standard model) which gives vanishingly small calculated values.

Propene has a calculated dipole in good agreement with experiment and it is clear from Figure 1 that this arises from a considerable rearrangement of charge. However, if we consider the process of replacing one of the hydrogens in ethylene by a methyl group, the rearrangement of charge is mainly a "polarization" within the vinyl group rather than a net transfer of charge from methyl to vinyl. Thus the total vinyl charge in ethylene is −0.015, and this only changes to −0.012 in propene. The most significant change, however,

Table IV. Dipole Moment Orientations

Molecule	Angle[a]	Calcd[b]	Obsd[c]
Propene	From C═C toward C—C	−8.4 (0)	−22[b]
Ethyl fluoride	From C—F toward C—C	−5.4 (0)	−7[m]
1,1-Difluoroethane	From C—Me toward C—H	−131.9 (−125.3)	−133.7[n]
Fluoroethylene	From C—F toward C═C	+8.8 (0)	∼0[p]
n-Propyl fluoride (*trans*)	From C—F toward C—Et	−5.6 (0)	−10.6[t]
cis-1-Fluoropropene	From C—F toward C═C	−2.5 (0)	−15.3[v]
2-Fluoropropene	From C—F toward C═C	+24.5 (0)	+6.2[w]
3-Fluoropropene (*s-cis*)	From C—F toward C—C	−0.8 (0)	±1.5[x]
2-Fluoro-1,3-butadiene	From C—F toward C═C	+20.8 (0)	±10–15[aa]
Acetaldehyde	From C═O toward C—C	−7.0 (0)	−14.2[ff]
Propionaldehyde (*s-cis*)	From C═O toward C—C	−7.4 (0)	−17[gg]
Acrolein (*s-trans*)	From C═O toward C—C	−7.8 (0)	±14[ii]
Methylketene	From C═C toward C—C	+5.6 (0)	−8[mm]
Formic acid	From C═O toward C—O	−21.5	−42.4[nn]
Difluoramine	From N—H toward bisector of N—F bonds	+7.2	−18.6[uu]
Nitrous acid (*trans*)	From N═O toward N—O	+10.3	+0.8[vv]
Formyl fluoride	From C═O toward C—F	+38.2	+41.0[yy]
Acetyl fluoride	From C═O toward C—F	+39.9	+43[aaa]
Acetyl cyanide	From C═O toward C—CN	+59.3	+71[bbb]
Formamide	From C═O toward C—N	−16.8	−17.5[eee]
Methylamine	From C—N toward C—H	−65.0	−73.2[pp]

[a] The convention used for direction is specification of an angle with a bond C–A in the sense of a rotation toward another bond C–B from the same atom C. If the angle is *positive* (and less than the ABC bond angle), the resulting direction lies *between* the bonds C–A and C–B. [b] Values in parentheses correspond to a vector additive bond moment model with zero moments for all C–C and C–H bonds. [c] Superscripts in this column refer to Table III.

is the redistribution of charge between the two carbon atoms in vinyl, the methyl group "driving" electrons away from the atom to which it is attached onto the β position. A further breakdown can be effected into charge distributions in π and σ atomic orbitals. The π-electron charges on the vinyl carbons are

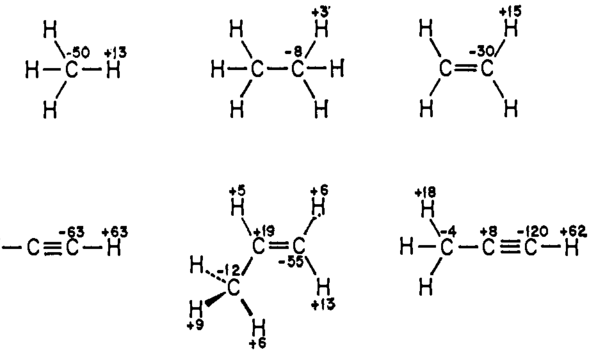
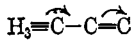


Figure 1. Electron distribution in hydrocarbons (10^{-3} electron unit).

$$\mathrm{Me}\text{——}\overset{0.972}{C_\alpha}\text{═══}\overset{1.043}{C_\beta}$$

The corresponding figures are unity in ethylene, so that there is a small donation of π electrons from methyl to vinyl, but again the main effect is a redistribution within the vinyl group, the β position acquiring the greater electron density. In fact, most of the total redistribution between C_α and C_β occurs in the π system.

These theoretical results have some bearing on discussions of the role of hyperconjugation in determining the polarity of propene by means of a charge displacement of the type



Recently, Dewar[10] has argued that the dipole moment may alternatively be due to the polarity of the C(sp^3)–C(sp^2) bond, this being more sensitive to hybridization changes than C-H bonds. The present calculations favor the hyperconjugative explanation insofar as the origin of the calculated moment lies mainly in the π orbitals. However, the polarity occurs without major charge migration into the double bond.

The origin of the dipole moment in methylacetylene (the methyl end of the molecule being positive) can be interpreted in a similar manner. There is little over-all charge transfer into the ethynyl group when hydrogen is replaced by methyl, but there is again a large redistribution between the α and β carbons. The π-electron charges are

$$\mathrm{Me}\text{——}\overset{1.968}{C_\alpha}\equiv\equiv\overset{2.066}{C_\beta}$$

so the redistribution is again mainly associated with the π orbitals.

b. Fluorine Compounds. The agreement between experimental dipole moments of fluorocarbons and those calculated by this model is very good, all the main effects being well reproduced. An examination of the atomic charge densities, however, reveals surprising features (Figure 2). In methyl fluoride the main effect is a transfer of electrons from carbon to the more electronegative fluorine, but a secondary feature is that the hydrogens are slightly more negative than in methane. This negative character of atoms separated by two bonds from the substituting fluorine is also apparent in fluoroform and becomes more evident for β-carbon atoms as in ethyl fluoride and 1,1,1-trifluoroethane.

These results challenge the common interpretation of fluorine as an inductive-type substituent leading to positive character in a saturated hydrocarbon which

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(10) M. J. S. Dewar, "Hyperconjugation," The Ronald Press Co., New York, N. Y., 1962.

diminishes steadily with the distance down the chain[11]

$$\begin{array}{cccc} \delta- & \delta+ & \delta\delta+ & \delta\delta\delta+ \\ \mathrm{F} \longleftarrow & \mathrm{C} \longleftarrow & \mathrm{C} \longleftarrow & \mathrm{C} \cdots \end{array}$$

The calculations rather suggest that the induced charges *alternate* in a decaying manner, so that the β position is normally negative

$$\begin{array}{cccc} \delta- & \delta+ & \delta\delta- & \delta\delta+ \\ \mathrm{F} \longleftarrow & \mathrm{C} \longleftarrow & \mathrm{C} \longleftarrow & \mathrm{C} \cdots \end{array}$$

Experimental dipole moments do not, of course, provide a direct test of these two charge distributions. However, certain trends evident in the data are consistent with the alternating hypothesis. According to this, a fluorine substituent leads to a polarization of the hydrocarbon in which the atom two removed from the fluorine is relatively negative

$$[(\mathrm{C\ or\ H})^-\text{—}\mathrm{C}^+]\text{—}\mathrm{F}$$

This corresponds to a dipolar distribution in the hydrocarbon which is *opposed* to the primary dipole of the bond to fluorine. For a CF_3 substituent, on the other hand, the alternating hypothesis predicts a charge distribution

$$[(\mathrm{C\ or\ H})^+\text{—}\mathrm{C}^-]\text{—}\mathrm{CF_3}$$

leading to a hydrocarbon dipole which *reinforces* the primary moment. If we now compare the experimental dipole moments of HX and CH_3X, where X is F or CF_3, we find that CF_3 does have a considerably larger dipole when attached to CH_3 compared to H, but the two compounds with X fluorine have very similar moments, in spite of the fact that methyl is a larger polarizable group.

Another piece of evidence supporting the CNDO charge distributions of Figure 2 is the fact that the experimental and calculated dipole directions in ethyl fluoride are *external* to the F–C–C angle (Table IV). This is consistent with the alternating hypothesis which leads to an additional polarization in the methyl group H_3^+–C^-.

Some insight into the origin of the calculated charge alternation in fluoroparaffins may be obtained by breaking down the electron distribution of methyl fluoride into σ and π parts relative to the C–F bond. If this is the z axis, the population of the $2p_x$ atomic orbitals on carbon and fluorine and the corresponding hydrogen group orbital are

$$\overset{1.035}{\mathrm{H_3}}\equiv\overset{0.986}{\mathrm{C}}\text{—}\overset{1.979}{\mathrm{F}}$$

The bond order between the carbon and fluorine π orbitals is 0.147. The fact that the fluorine figure is less than 2 implies a "back-donation" effect by the fluorine π lone pairs which could be represented by a valence structure

$$\mathrm{H_3^-{=}C{=}F^+}$$

This leads to additional charge in the hydrogen π-type group orbital. In fact, this group orbital contains more electrons than in methane where the corresponding population is 1.002. In summary, fluorine behaves as a strong σ-electron attractor, removing electrons from the carbon to which it is bonded, but it is also a weak π-electron donor and these electrons go to the hydrogens in methyl fluoride (or the β position in larger molecules). This type of back-donation has also been proposed in a theory of geminal proton–proton spin coupling constants.[12]

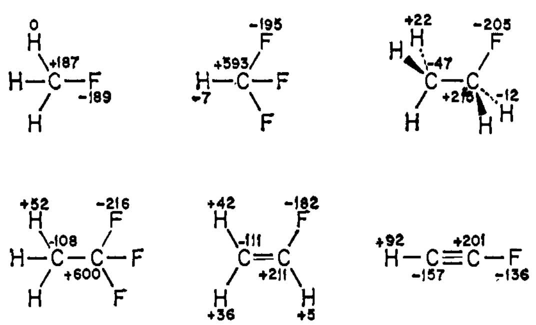
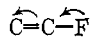


Figure 2. Electron distribution in fluorocarbons (10^{-3} electron unit).

Similar, but stronger alternation effects are shown in the calculations on vinyl fluoride and ethynyl fluoride. In both cases, the β carbon acquires considerable negative charge, leading to a relatively small dipole moment. CF_3 substituents, on the other hand, lead to large dipoles (3,3,3-trifluoropropene and 3,3,3-trifluoropropyne). The small dipoles of vinyl fluoride and ethynyl fluoride are often attributed to π-electron donation from a fluorine lone pair into the unsaturated group leading to a structure



$$\mathrm{C{=}C{-}F}$$

This suggestion is supported by the CNDO/2 calculations on vinyl fluoride which give π densities

$$\overset{1.076}{\mathrm{C}}{=\!=}\overset{0.973}{\mathrm{C}}\text{—}\overset{1.951}{\mathrm{F}}$$

Clearly, most of the increase in electron density on the β carbon (Figure 2) is due to π-electron donation from the fluorine. On the other hand, a CF_3 group polarizes the C=C in the opposite direction, leading to the large moment of 3,3,3-trifluoropropene.

c. Oxygen Compounds. There is less satisfactory agreement between experimental and calculated dipole moments for the oxygen compounds listed in Table III, but the theory does reproduce a number of significant trends.

The calculated values for water, alcohols, and ethers are too high but the observed ordering, $\mu(H_2O) > \mu(MeOH) > \mu(Me_2O)$, is correctly reproduced. According to the CNDO/2 charge distribution shown in Figure 3, the reason why methyl alcohol has a lower moment than water is again charge alternation, two of the methyl hydrogens having a negative charge. This is also a result of "back-donation" from the π-type lone pair of the oxygen, for the population of the $2p\pi$ atomic orbital on oxygen (with a node in the oxygen valence plane) is 2.000, 1.976, and 1.951 for the series water, methyl alcohol, and methyl ether.

The observed decrease of moment along this series is rather larger than calculated. Part of the decrease may be due to the opening out of the bond angle in ethers. However, this does not seem to be very important, for CNDO/2 calculations with experimental

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[11] C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Bell and Sons, London, 1953.

[12] J. A. Pople and A. A. Bothner-By, *J. Chem. Phys.*, **42**, 1339 (1965).

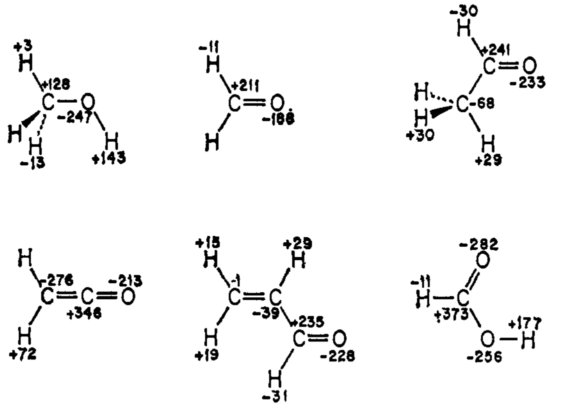
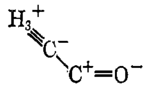


Figure 3. Electron distribution in oxygen compounds (10^{-3} electron unit).

(rather than standard) bond angles give $\mu = 2.14$ D. for water (angle 104.5°) and $\mu = 1.80$ D. for methyl ether (angle 111.6°).

A corresponding series for the carbonyl group shows the opposite ordering of dipoles, $\mu(H_2CO) < \mu((CH_3)HCO) < \mu((CH_3)_2CO)$, and this is also reproduced by the calculations. However, the theory incorrectly gives a dipole moment for formaldehyde less than that of water. The increase in dipole moment of a carbonyl compound with methyl substitutions is again consistent with an alternating charge effect



$$H_3^{+}C^{-}\!-\!C^{+}{=}O^{-}$$

and this is reflected in the CNDO/2 atomic densities (Figure 3). The direction of the dipole in acetaldehyde is also consistent with this. The total charge on the oxygen increases from 6.188 in formaldehyde to 6.233 in acetaldehyde and 6.266 in acetone. The population of the 2pπ oxygen atomic orbital has values 1.160, 1.208, and 1.241 along the same series, so these changes are again mainly associated with the π system. The corresponding charges on the 2pπ atomic orbital of the carbonyl carbon are 0.840, 0.828, and 0.823. These decrease less than the oxygen π charge increases, so there is transfer of π electrons from CH_3 into the carbonyl group by hyperconjugation in this theory. A similar π-electron transfer is also noted in acrolein, although the calculated dipole moment for this molecule is rather too small.

The theory also predicts the observed low dipole moment of ketene compared to formaldehyde. The CNDO/2 charge distribution in ketene (Figure 3) clearly shows alternation due primarily to back-donation of the oxygen n electrons into the π-atomic orbital of the methylene carbon atom. (It should be noted that in ketene the oxygen lone pair is in a π-type orbital with a node in the molecular plane.)

d. Nitrogen Compounds. The comparison between calculated and experimental dipoles for compounds containing nitrogen shows similar trends. The experimental moments for ammonia and methylamines have the order $\mu(NH_3) > \mu(MeNH_2) > \mu(Me_2NH) > \mu(Me_3N)$, and this progression is reproduced by the theory. As with corresponding oxygen compounds, the theory does not give the full magnitude of the decrease along the series. There is a slight opening of the angle in trimethylamine (from 107.1° in ammonia to 108.7°), but this is not sufficient to account completely for the very low dipole moment of this molecule.

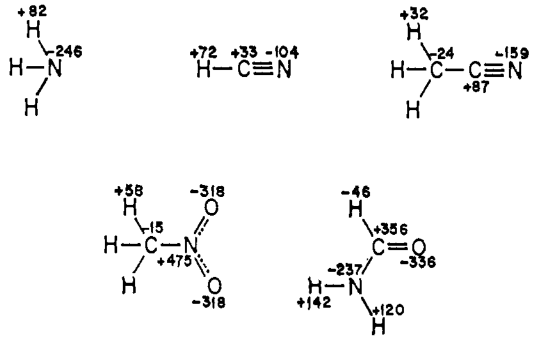


Figure 4. Electron distribution in nitrogen and mixed compounds (10^{-3} electron unit).

The cyanide group C≡N behaves in the opposite manner, having a *larger* dipole when attached to methyl instead of hydrogen. This effect is also reproduced by the theory, and the CNDO/2 densities shown in Figure 4 suggest that this is associated with charge alternation. The total π densities on the carbon and nitrogen atoms in HCN and MeCN are

$$\mathrm{H}-\overset{1.898}{\mathrm{C}}\equiv\overset{2.102}{\mathrm{N}} \qquad \mathrm{Me}-\overset{1.882}{\mathrm{C}}\equiv\overset{2.170}{\mathrm{N}}$$

A comparison with the total atom densities (Figure 4) again indicates that most of the rearrangement on methyl substitution is in the π system and that there is considerable hyperconjugation.

e. Mixed Compounds. Dipole moments for a number of mixed compounds with nitrogen, oxygen, and fluorine are also given in Tables III and IV, including some that contain two groups already considered. Both magnitudes and directions are given fairly satisfactorily by the theory.

The high dipole moment of formamide is clearly due to the increased polarity of the carbonyl group when conjugated with the neighboring nitrogen. The charge in the π-lone pair of nitrogen (the bonds to this atom being coplanar according to model A) is reduced from 2.00 in planar NH_3 to 1.82 in this molecule. The corresponding π-bond order of the C–N single bond is 0.47 indicating a large amount of double bond character.

Conclusions

The most important conclusion to be drawn from these calculations is that current qualitative theories of inductive charge displacement may need modification. The general pattern of charge distributions calculated by the molecular orbital method of this paper suggests a classification of substituents (attached to hydrocarbon fragments) in terms of the following two characteristic features.

1. Electrons may be withdrawn from or donated to the hydrocarbon fragment as a whole. According to the usual nomenclature, such substituents would be described as inductive −I and +I types, respectively.

2. The distribution of electrons remaining in the hydrocarbon fragments may be polarized so that electrons are drawn to or from the site of substitution. These

two possibilities could be denoted by − and + superscripts, respectively, leading to four types of substituent, $-I^-$, $-I^+$, $+I^-$, and $+I^+$. The double classification based on these criteria is illustrated schematically in Figure 5.

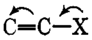
The substituents dealt with in this paper are of the −I type, with the further subdivision

$-I^+$ type: F, OR, NR_2

$-I^-$ type: CF_3, RC═O, C≡N, NO_2, COOR

In all these cases, the $-I^+$ substituents are those with the most electronegative atom directly attached to the hydrocarbon, while the $-I^-$ types have the electronegative atom one position removed. This is a consequence of the widespread charge alternation noted in Figures 1–4.

It may be noted that the ± superscript of this classification corresponds to the label used for a "mesomeric displacement" if the substituent is attached to an unsaturated system. Thus the usual charge displacement diagram



$C{=}C{-}X$

for a +M mesomeric substituent leads to a high electron density on the β carbon as shown for a $-I^+$ group in Figure 5. The CNDO calculations confirm this behavior, but also suggest that this feature of the $-I^+$ substituent and the consequent charge alternation apply even in saturated molecules. In both cases the alternation is associated with "back-donation" of lone-pair electrons in molecular orbitals of π-type relative to the C–X bond (that is, with a nodal plane through the C–X bond).

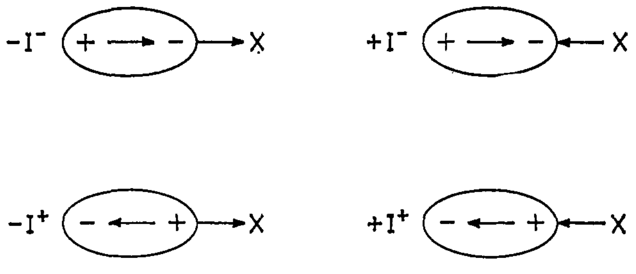


Figure 5. Schematic representation of types of inductive substituent.

More refined calculations to test the theory of electron distribution presented in this paper are clearly needed as well as studies of other related physical properties. In the meantime, the satisfactory reproduction of so many details of electric dipole data does constitute evidence in its favor.

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Interaction of a Methyl Group with a Triple Bond. Molecular Self-Consistent Field Calculation on Methylacetylene

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Contribution from the Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138. *Received February 6, 1967*

Abstract: An accurate molecular orbital calculation for a minimum basis set of Slater orbitals (H exponent, 1.2) has yielded an analysis of the methyl–triple bond interaction in methylacetylene. The calculated dipole moment of 0.70 D. (microwave value, 0.75 D.) is mostly due to a π-system polarization (0.88 D.) in the direction $HC^-(1)$-$C^+(2)C^-(3)H_3^+$, reduced by an opposite σ polarization of the molecule. The methyl group, which shows a negligible π-inductive effect on the acetylenic group, donates 0.056 and 0.026 electron respectively to the σ and π system of the acetylene residue. The suggestion by Dewar that the dipole moment may arise primarily from σ polarization is not in agreement with these results. Assumption of suitable localized MO's yields calculated π-electron delocalization energies of 3.26 kcal in C_2H_6 and 7.62 kcal in $HCCCH_3$. The existence of negligible π-electron overlap populations across the C–C single bonds in methylacetylene and ethane is discussed. The first (vertical) ionization potential is calculated (by Koopmans' theorem) at 10.24 ev (experimental value, 10.36 ev) in $HCCCH_3$. Results are also compared with those for $HCCCH_3$ obtained earlier by parameterization from acetylene and ethane.

The dipole moment (0.72–0.77 D.)[2] of the small hydrocarbon methylacetylene is a simple example of a large electronic interaction between an alkyl group and an unsaturated hydrocarbon to which it is bonded. In many approximate molecular orbital studies of such molecules, the methyl group is treated as a pseudo-π-electron system ($C{\equiv}H_3$), and it has been suggested[3a] that π-electron resonance accounts for the charge-transfer effects. On the other hand, an inductive model for the π-electron system has been proposed,[3b] in which the alkyl group polarizes the unsaturated system by changing the electronegativity of the unsaturated carbon atom to which it is bonded; in the extreme form of this theory, neither resonance nor charge transfer is invoked between the alkyl group and the unsaturated group.

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[1] National Science Foundation Postdoctoral Fellow, 1966–1967.

[2] A. L. McClellan, "Tables of Experimental Dipole Moments," W. H. Freeman and Co., San Francisco, Calif., 1963, p 77.

[3] (a) See A. Lofthus, *J. Am. Chem. Soc.*, 79, 24 (1957), and references quoted therein; (b) see, *e.g.*, A. Streitwieser, Jr., and P. M. Nair, *Tetrahedron*, **5**, 149 (1959).