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Molecular Orbital Theory of the Electronic Structure of Organic Compounds. III. *Ab Initio* Studies of Charge Distribution Using a Minimal Slater-Type Basis

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Abstract: *Ab initio* molecular orbital studies of charge densities and electric dipole moments are reported for a series of organic molecules which have previously been studied by the semiempirical CNDO/2 technique. A minimal basis of atomic orbitals closely related to Slater-type (exponential) functions is used, each being replaced by a least-squares-fitted sum of three or four gaussian functions. The exponents (ζ values) for valence-shell atomic orbitals are chosen to minimize the total energy. Moderate overall agreement between calculated and observed dipole moments is obtained. The corresponding charge distributions have many features in common with the CNDO results, including widespread charge alternation and delocalization of lone-pair electrons.

In the first paper in this series,[1] a general semiempirical molecular orbital method was used to make a study of the distribution of electrons in a series of simple organic molecules. This method (complete neglect of differential overlap or CNDO) takes explicit account of all valence electrons in a molecule of arbitrary geometry and treats electron–electron repulsion in a simplified manner. Particular emphasis was laid on changes in electron densities brought about by substitution and the interpretation of electric dipole moments. Reasonable overall agreement with experimental dipole data was obtained and a number of regularities in charge distributions were noted. In particular, a widespread alternation was found for net charges in both saturated and unsaturated molecules with polar substituents.

The CNDO calculations are, of course, highly approximate and involve a certain amount of subjective parameterization. It is clearly desirable to undertake some more refined calculations and find the extent to which features noted at the CNDO level are retained. In the present paper we shall report some *ab initio* self-consistent molecular orbital calculations which closely parallel those of ref 1.

All studies are made with linear combination of atomic orbital (LCAO) expressions for molecular orbitals, using a minimal basis of atomic orbitals. A minimal basis includes only those atomic orbitals in shells which are populated in the ground states of the free atoms (1s for H and 1s, 2s, 2p for B–F). This is the simplest basis set that can be used for organic molecules. A similar basis set is used in the CNDO theory except that inner shell 1s orbitals are incorporated into an unpolarizable core. Using the population analysis introduced by Mulliken,[2] it is possible to break down the total density into populations of individual atomic orbitals and individual atoms, thereby leading to a quantitative description conceptually close to qualitative organic ideas.

The simplest type of atomic orbital to use in a minimal basis set is the Slater-type orbital (STO) which has a nodeless radial part of the form

$$r^{n-1} \exp(-\zeta r)$$

where n is the principal quantum number (1 or 2) and

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[1] J. A. Pople and M. S. Gordon, *J. Amer. Chem. Soc.*, **89**, 4253 (1967).

[2] R. S. Mulliken, *J. Chem. Phys.*, **23**, 1833, 1841, 2338, 2343 (1955).

ζ is a scaling constant. A number of MO wave functions using STO minimal basis sets have already been published, mostly with ζ values from Slater's well-known rules for isolated atoms.[3] However, it has recently become clear that the most appropriate ζ values for atoms in molecules, that is, values chosen to minimize the calculated total energy, may differ significantly from these rules. This has long been known for hydrogen atoms in the hydrogen molecule and it was also found for carbon in methane by Pitzer,[4] who also noted that the orbital populations were sensitive to the proper choice of ζ values. However, the undertaking of full LCAO–SCF calculations with a minimal STO basis and optimization of ζ values is hindered by the difficulty of evaluating the necessary two-electron integrals. Although efficient programs involving gaussian transformations and numerical integration are being developed for these integrals,[5] it will probably be some time before such techniques are economical enough to be applied to moderately large organic systems.

A powerful alternative, which will be followed here, is to replace the STO basis functions by least-squares-fitted linear combinations of gaussian-type orbitals, where the integrals may be evaluated more rapidly. This idea was originally proposed by Foster and Boys[6] and expounded on in some detail by Reeves and Fletcher[7] and by O-ohata, Taketa, and Huzinaga.[8] Recently it has been shown that optimized exponents, calculated atomization energies, electron populations, and electric dipole moments converge rapidly to their limiting STO values as the number of gaussians in the least-squares representation increases.[9] In particular, the three-gaussian representation (STO-3G) leads to atomic populations within 0.02 of the STO limit and electric dipole moments usually within 0.1 D. This size of gaussian representation allows us to work with organic systems of 10–20 atoms and to carry out extensive optimization of the ζ exponents. The STO-3G basis will be most used in this paper, but some results with STO-4G will also be given.

Method

Each molecular orbital ψ_i (occupied by two electrons) is written in the LCAO form

$$\psi_i(\mathbf{r}) = \sum_{\mu} c_{\mu i}\phi_{\mu}(\zeta_{\mu},\mathbf{r}) \qquad (1)$$

where $\phi_{\mu}(\zeta_{\mu},\mathbf{r})$ is a least-squares gaussian representation of a Slater-type orbital with exponent ζ_{μ}. Specifically

$$\phi_{\mu}(\zeta_{\mu},\mathbf{r}) = \zeta_{\mu}^{3/2}\phi_{\mu}(1,\zeta_{\mu}\mathbf{r}) \qquad (2)$$

and

$$\phi_{1s}(1,\mathbf{r}) = \sum_{k=1}^{K} d_{1s,k}g_{1s}(\alpha_{1k},\mathbf{r})$$

$$\phi_{2s}(1,\mathbf{r}) = \sum_{k=1}^{K} d_{2s,k}g_{1s}(\alpha_{2k},\mathbf{r})$$

$$\phi_{2p}(1,\mathbf{r}) = \sum_{k=1}^{K} d_{2p,k}g_{2p}(\alpha_{2k},\mathbf{r}) \qquad (3)$$

where g_{1s} and g_{2p} are gaussian-type orbitals and the constants d and α are the coefficients and gaussian exponents in the least-squares expansion.[9] It should be noted that the 2s and 2p ϕ functions share a common set of gaussian exponents α_{2k} for computational efficiency. The basis set (2.3) is STO-KG or, in the full notation introduced previously[9]

$$\mathrm{STO}[1s\rightarrow K(1s_g)|2s\rightarrow K(1s_g),\ 2p\rightarrow K(2p_g)]$$

(Here the vertical bar separates regions with different α values.) As mentioned above, K = 3 or 4 in this paper.

The LCAO coefficients $c_{\mu i}$ are obtained by solving the Roothaan equations[10] and a first-order density matrix

$$P_{\mu\nu} = 2\sum_{i}^{\mathrm{occ}} c_{\mu i}c_{\nu i} \qquad (4)$$

is obtained. The Mulliken gross population of the atomic orbital is then given by[2]

$$q_{\mu} = P_{\mu\mu} + \sum_{\nu(\neq\mu)} P_{\mu\nu}S_{\mu\nu} \qquad (5)$$

and the net charge assigned to atom A is

$$Z_{\mathrm{A}} - \sum_{\mu}^{\mathrm{A}} q_{\mu} \qquad (6)$$

where Z_{A} is the atomic number and the sum is over all atomic orbitals on A. Finally, dipole moments are obtained from the formula

$$\boldsymbol{\mu}(\mathrm{D}) = 2.5416[\sum_{\mathrm{A}} Z_{\mathrm{A}}\mathbf{r}_{\mathrm{A}} - \sum_{\mu\nu} P_{\mu\nu}\mathbf{r}_{\mu\nu}] \qquad (7)$$

where

$$\mathbf{r}_{\mu\nu} = \int \phi_{\mu}\mathbf{r}\phi_{\nu}\mathrm{d}\tau \qquad (8)$$

All calculations were performed in single precision on a CDC 1604A computer. All one- and two-electron integrals are believed to be accurate to 2×10^{-6} hartree. The self-consistent iteration was terminated when the root-mean-square change in the density matrix elements was less than 10^{-4}. The computational or round-off error in populations and calculated dipole moments is then less than any digit quoted in this work. The full time for a single calculation on the largest system considered (toluene) is about 2 hr, two-thirds of which was devoted to the evaluation of two-electron integrals.

Inner shell ζ exponents were held fixed as the best atom values of Clementi and Raimondi[11] rounded to two decimal places (5.67, 6.67, 7.66, and 8.65 for C, N, O, and F). Valence-shell ζ exponents were varied in turn in steps of 0.01 until the total energy was minimized. Three or four cycles on the complete set of exponents usually proved necessary. To reduce the total amount of computation, the following restrictions were imposed.

(a) All hydrogen atoms attached to the same heavy atom are given the same ζ_{1s}. For example, the two methylene hydrogens of fluoroethylene are treated together.

(b) For toluene and fluorobenzene, the *meta* and *para* carbons and hydrogens are varied together. ζ optimization for these molecules was terminated

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(4) R. M. Pitzer, *J. Chem. Phys.*, **47**, 965 (1967).

(5) I. Shavitt and M. Karplus, *ibid.*, **36**, 550 (1962); **43**, 398 (1965).

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Table I. Optimum Exponents for Molecules

Molecule	Atom	STO-3G	STO-4G
Hydrocarbons			
Methane	C	1.76	1.76
	H	1.18	1.17
Ethane	C	1.76	1.75
	H	1.18	1.17
Ethylene	C	1.70	1.70
	H	1.23	1.22
Acetylene	C	1.68	1.67
	H	1.31	1.31
Propane	C_1	1.76	
	C_2	1.75	
	(C_1)–H	1.18	
	(C_2)–H	1.18	
Propene	C_1	1.70	
	C_2	1.71	
	C_3	1.78	
	(C_1)–H	1.22	
	(C_2)–H	1.22	
	(C_3)–H	1.17	
Propyne	C_1	1.66	1.66
	C_2	1.70	1.69
	C_3	1.79	1.79
	(C_1)–H	1.31	1.31
	(C_3)–H	1.19	1.17
Benzene	C	1.72	1.71
	H	1.21	1.21
Toluene	C_1	1.72	
	C_2, C_6	1.71	
	C_3, C_4, C_5	1.72	
	C_{Me}	1.77	
	(C_2)–H	1.22	
	(C_3,C_4)–H	1.21	
	(C_{Me})–H	1.18	
Fluorine Compounds			
Hydrogen fluoride	F	2.55	2.55
	H	1.33	1.31
Methyl fluoride	C	1.79	1.79
	F	2.56	2.55
	H	1.19	1.18
Methylene fluoride	C	1.82	1.81
	F	2.56	2.55
	H	1.20	1.20
Fluoroform	C	1.83	1.83
	F	2.56	2.55
	H	1.20	1.21
Tetrafluoromethane	C	1.84	1.83
	F	2.56	2.56
Fluoroethane	C_1	1.79	1.79
	C_2	1.76	1.75
	F	2.56	2.55
	(C_1)–H	1.19	1.18
	(C_2)–H	1.18	1.17
1,1,1-Trifluoroethane	C_1	1.82	
	C_2	1.76	
	F	2.56	
	H	1.18	
Fluoroethylene	C_1	1.76	1.75
	C_2	1.68	1.68
	F	2.57	2.56
	(C_1)–H	1.21	1.21
	(C_2)–H	1.23	1.22
Fluoroacetylene	C_1	1.74	1.75
	C_2	1.64	1.63
	F	2.59	2.58
	H	1.33	1.34
3,3,3-Trifluoropropyne	C_1	1.68	
	C_2	1.70	
	C_3	1.85	
	F	2.56	
	H	1.31	
Fluorobenzene	C_1	1.77	
	C_2, C_6	1.70	
	C_2, C_4, C_5	1.72	
	F	2.57	
	(C_2)–H	1.21	
	(C_3,C_4)–H	1.21	
Oxygen Compounds			
Water	O	2.24	2.23
	H	1.28	1.26
Methanol	C	1.78	
	O	2.24	
	(C)–H	1.19	
	(O)–H	1.29	
Dimethyl ether	C	1.79	
	O	2.24	
	H	1.18	
Formaldehyde	C	1.76	1.75
	O	2.25	2.24
	H	1.21	1.21
Acetaldehyde	C_1	1.76	
	C_{Me}	1.76	
	O	2.25	
	(C_1)–H	1.20	
	(C_{Me})–H	1.18	
Acetone	C_1, C_3	1.76	
	C_2	1.76	
	O	2.24	
	H	1.18	
Ketene	C_1–(H_2)	1.65	
	C_2	1.78	
	O	2.27	
	H	1.25	
Formic acid	C	1.79	
	O_1	2.23	
	O_2	2.25	
	(C)–H	1.22	
	(O_2)–H	1.30	
Carbon dioxide	C	1.82	
	O	2.25	
Nitrogen Compounds			
Ammonia	N	1.95	1.95
	H	1.25	1.23
Methylamine	C	1.78	
	N	1.96	
	(C)–H	1.18	
	(N)–H	1.25	
Dimethylamine	C	1.78	
	N	1.96	
	(C)–H	1.18	
	(N)–H	1.26	
Trimethylamine	C	1.78	
	N	1.96	
	H	1.18	
Hydrogen cyanide	C	1.70	
	N	1.96	
	H	1.31	
Methyl cyanide	C_1	1.71	
	C_{Me}	1.79	
	N	1.95	
	H	1.19	
Mixed Compounds			
Nitrogen trifluoride	N	2.01	
	F	2.58	
Formyl fluoride	C	1.79	
	O	2.24	
	F	2.57	
	H	1.21	
Carbonyl fluoride	C	1.81	
	O	2.23	
	F	2.57	
Formamide	C	1.81	
	N	1.98	
	O	2.22	
	(C)–H	1.19	
	(N)–H	1.26	
Nitromethane	C	1.77	
	N	2.11	
	O	2.22	
	H	1.21	

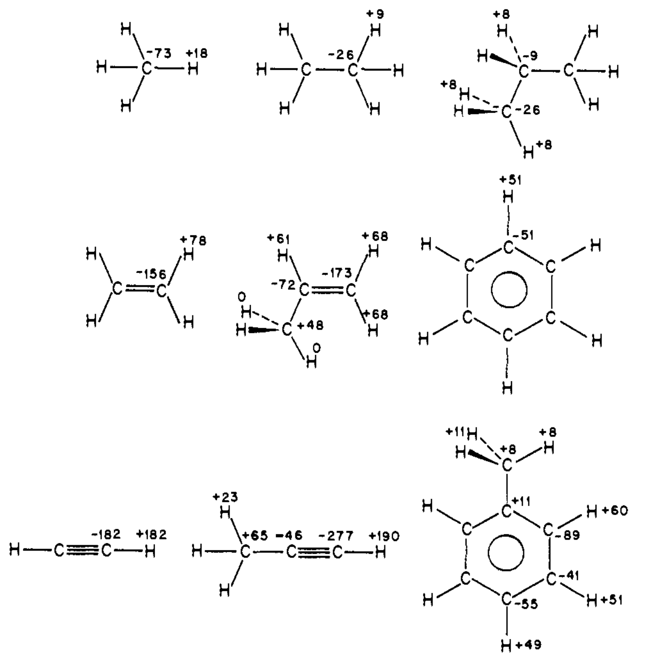


Figure 1. Electron populations for hydrocarbons (10^{-3} electron).

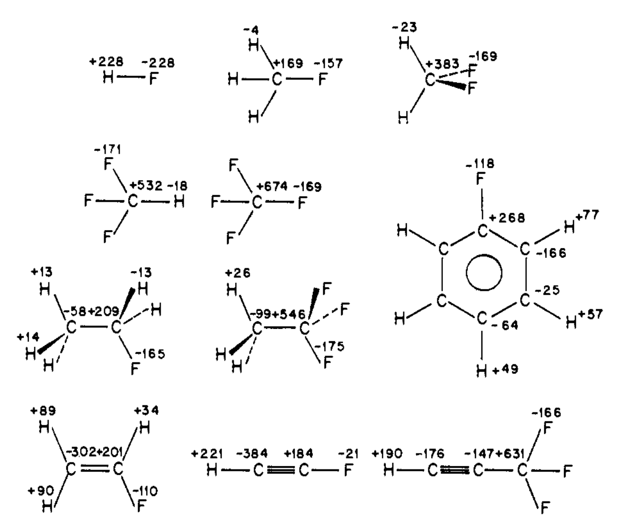


Figure 2. Electron populations for fluorine compounds (10^{-3} electron).

before a stationary point was reached. The values quoted are probably within 0.02 of the correct numbers.

Molecular geometries were chosen according to the standard model used previously.[1] Staggered configurations are chosen for appropriate single bonds. For propene, acetaldehyde, and acetone, X=C—C—H (X = C, O) is *cis*. For formic acid, O=C—O—H is *cis*. For toluene and nitromethane, one C—H bond is the plane of the phenyl and nitro groups, respectively.

Results and Discussion

Table I gives the optimized valence ζ values for the molecules considered. For those molecules for which STO-4G calculations were also made, both sets of numbers are reported. These show that the deviations between the ζ values is never greater than 0.02, so that the use of only three gaussians per STO is not likely to modify any of the qualitative conclusions in a significant manner. The calculated dipole moments are presented in Table II, together with the CNDO/2 results[1] and experimental values. Corresponding results for dipole directions are given in Table III. Figures 1–4 show the calculated atomic charges (for STO-3G) in units of 10^{-3} electrons. These are obtained from the Mulliken gross populations as indicated in the previous section.

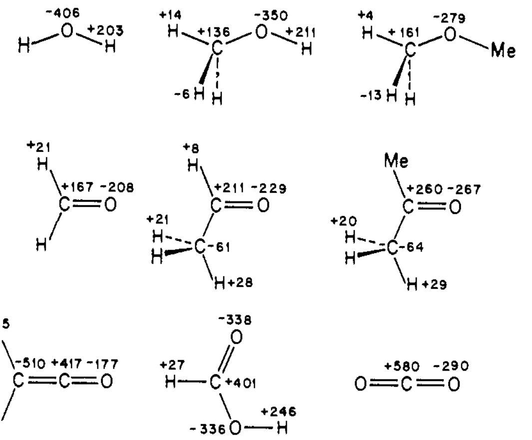


Figure 3. Electron populations for oxygen compounds (10^{-3} electron).

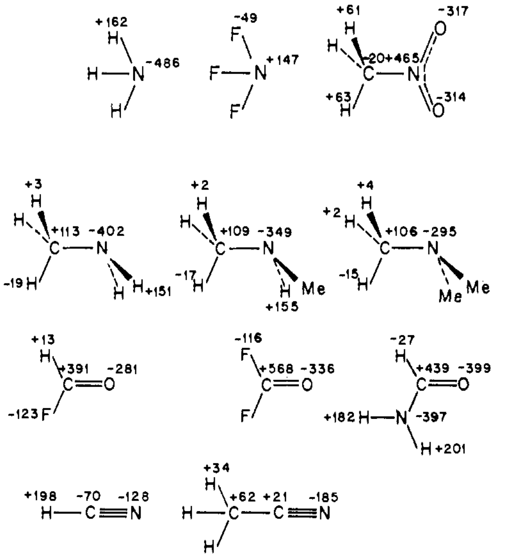


Figure 4. Electron populations for nitrogen and mixed compounds (10^{-3} electron).

The overall agreement between calculated STO-3G and experimental dipole moments is moderately good, but somewhat inferior to that for the semiempirical CNDO/2 method. CNDO appears to be much more successful for fluorocarbons, but for other molecules there is no such clear conclusion. We shall discuss the detailed ζ values (measuring valence orbital size) and charge distribution for each class of compound in turn.

a. Hydrocarbons. The ζ values for both carbon and hydrogen show significant variations. For carbon, largest values are obtained for paraffins (1.75–1.76) and smallest for triple bonds (1.66–1.70). All values are considerably larger than that for an isolated carbon atom (1.59). The hydrogen exponent varies in the opposite direction from 1.18 in methane to 1.31 in acetylene.

Table II. Dipole Moments

Molecule	STO-3G	STO-4G	CNDO/2[a]	Exptl[b]
Hydrocarbons				
Propane	0.03		0.00	0.083
Propene	0.24		0.36	0.364
Propyne	0.50	0.43	0.43	0.75
Toluene	0.17		0.21	0.43
Fluorine Compounds				
Hydrogen fluoride	1.41	1.42	1.85	1.8195
Methyl fluoride	0.96	1.06	1.66	1.855
Methylene fluoride	1.10	1.24	1.90	1.96
Fluoroform	0.96	1.05	1.66	1.645
Fluoroethane	0.97	1.07	1.83	1.96
1,1,1-Trifluoroethane	1.05		2.18	2.32
Fluoroethylene	0.71	0.79	1.51	1.427
Fluoroacetylene	−0.01	0.07	1.04	0.75
3,3,3-Trifluoropropyne	1.25		2.48	2.36
Fluorobenzene	0.59		1.66	1.66
Oxygen Compounds				
Water	1.78	1.83	2.10	1.846
Methanol	1.51		1.94	1.69
Dimethyl ether	1.18		1.83	1.30
Formaldehyde	1.53	1.65	1.98	2.339
Acetaldehyde	1.66		2.53	2.68
Acetone	1.87		2.90	2.90
Ketene	0.11		1.30	1.414
Formic acid	0.97		0.87	1.415
Nitrogen Compounds				
Ammonia	1.66	1.66	1.97	1.468
Methylamine	1.41		1.86	1.326
Dimethylamine	1.19		1.76	1.03
Trimethylamine	0.95		1.68	0.612
Hydrogen cyanide	2.43		2.48	2.986
Methyl cyanide	2.92		3.05	3.92
Mixed Compounds				
Nitrogen trifluoride	0.62		0.43	0.235
Formyl fluoride	1.75		2.16	2.02
Carbonyl fluoride	1.67		1.42	0.951
Formamide	3.34		3.79	3.71
Nitromethane	3.58		4.38	3.46

[a] Reference 1. [b] For references to experimental dipole moments see Table III of paper I.

Table III. Dipole Moment Orientation

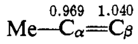
Molecule	Angle[a]	STO-3G	CNDO/2[b]	Obsd[c]
Propene	From C=C toward C—C	+1.1	−8.4	−22
Ethyl fluoride	From C—F toward C—C	−1.7	−5.4	−7
Fluoroethylene	From C—F toward C=C	+46.6	+8.8	~0
Acetaldehyde	From C=O toward C—C	−4.3	−7.0	−14.2
Formic acid	From C=O toward C—O	−29.5	−21.5	−42.4
Formyl fluoride	From C=O toward C—F	+23.2	+38.2	+41.0
Formamide	From C=O toward C—N	−20.0	−16.8	−17.5
Methylamine	From C—N toward C—H	−79.3	−65.0	−73.2

[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 ACB bond angle), the resulting direction lies between the bonds CA and CB. [b] Reference 1. [c] For reference to experimental dipole moment orientations see Table IV of paper I.

As in the CNDO/2 theory, the paraffins have atomic charges close to zero, while the series ethane, ethylene, and acetylene shows increasingly positive hydrogen atoms corresponding to more C^{-}–H^{+} character. It has been pointed out previously that this qualitative trend is only given by the *ab initio* calculations if the ζ values are optimized.[12]

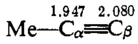
Unlike CNDO/2, this treatment does give a small calculated electric dipole moment for propane. This is in the sense C_1^{-}–C_2^{+}–C_3^{-}. The direction of the dipole has not been determined unequivocally, but evidence from deuteration does suggest that the methyl groups are at the negative end.[13] It may be noted from Figure 1 that this polarity is partly attributed to a larger negative charge on the methyl carbon atoms.

The molecules propene and propyne show electric dipole moments characteristic of the interaction of a methyl group with an unsaturated system. The interpretation of the origin of these polarities is much the same as in the CNDO theory.[1] Replacement of a hydrogen in ethylene by a methyl group leads to a substantial redistribution of charge within the vinyl group. In particular, there is a "polarization" of the π electrons leading to the π electron charges



$$\mathrm{Me}\text{—}\overset{0.969}{C_\alpha}=\overset{1.040}{C_\beta}$$

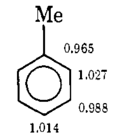
in the double bond. This redistribution leads to an increase in the negative character of the β carbon. The charge distribution in propyne shows similar effects, the π-electron charges in the triple bond being



$$\mathrm{Me}\text{—}\overset{1.947}{C_\alpha}\equiv\overset{2.080}{C_\beta}$$

There is some π-electron transfer from the methyl groups, but the polarization effect is greater. These results are similar to those of a previous study by Newton and Lipscomb[14] using a minimal STO basis without ζ optimization. The amount of π-electron polarization is increased by this refinement. The direction of the dipole moment of propene is poorly reproduced by the theory, which fails to give an adequate component perpendicular to the C=C bond.

The interaction of methyl and phenyl groups in toluene shows similar features. The π-electron charges in the phenyl ring are



The total π-electron charge of the ring is only 6.009, so again the π charge transfer from methyl is small and the main effect is alternating polarization within the ring. This leads to negative π charges at the *ortho* and *para* positions. The total atomic charges (Figure 1) show similar changes from *ortho* to *meta* to *para*.

b. Fluorine Compounds. The fluorine ζ values vary only slightly among the compounds considered (2.55–2.59) and are close to the value for a free atom (2.56). The carbon values increase with fluorine substitution. Thus ζ_C goes from 1.76 in CH_4 to 1.84 in CF_4, indicating a contraction of the valence shell as the carbon loses electrons. This is associated with and

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(12) W. J. Hehre and J. A. Pople, *Chem. Phys. Lett.*, **2**, 379 (1968).

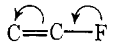
(13) J. S. Muenter and V. W. Laurie, *J. Chem. Phys.*, **45**, 855 (1966).

(14) M. D. Newton and W. N. Lipscomb, *J. Amer. Chem. Soc.*, **89**, 4261 (1967).

is a contributory cause of the observed shortening of the C–F bond from H_3C–F (1.385 Å) to F_3C–F (1.317 Å).[15]

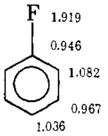
The agreement between calculated and experimental dipole moments is much less satisfactory than with the CNDO/2 theory. All values are too small, and in the case of fluoroacetylene the calculated moment is close to zero. The direction of the dipole in fluoroethylene is very poorly reproduced. The distribution of charge shows many features similar to the CNDO/2 results. Thus the hydrogens in methyl fluoride are slightly more *negative* than those in methane, in spite of the fact that the carbon is much more positive. This corresponds to the alternating charge distribution effect noted previously.[1] The same effect shows in ethyl fluoride and 1,1,1-trifluoroethane where the β carbon is more negative than in ethane.

The alternating charge distribution shows up very strongly for unsaturated fluorocarbons. As in CNDO/2, this arises primarily from back donation from fluorine 2pπ lone pairs, represented by the structure



For fluoroacetylene, this leads to a very large negative charge on the β carbon. However, the poor agreement with the experimental dipole moment suggests that the effect may be exaggerated by the method of calculation.

The π-electron distribution in fluorobenzene is



This shows some π-electron transfer from fluorine to phenyl and a considerable alternating polarization within the ring. However, this may again be exaggerated since the calculated dipole moment is too small. The CNDO/2 calculations show a similar, but less accentuated, distribution (1.953, 0.969, 1.048, 0.978, and 1.026 on F, C_1, C_2, C_3, and C_4) and a dipole moment in good agreement with experiment.

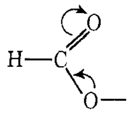
c. Oxygen Compounds. The ζ values among this set of compounds show similar variations to the fluorocarbons. The oxygen values vary little (2.23–2.27) while carbon values are increased by proximity to oxygen (most notably for carbon dioxide).

The calculated charge distributions and dipole moments have many features in common with the CNDO/2 results. For the series water, methanol, methyl ether, the agreement with experiment is good (better than CNDO) and the decrease in polarity with methyl substitution is well reproduced. According to charge distributions shown in Figure 3, the oxygen in methyl ether is substantially less negative than in water. This is primarily associated with back donation of charge from the π-type lone pair of oxygen into the antibonding orbitals of the methyl group. The gross orbital populations of this atomic orbital are 2.000, 1.977, and 1.950 for water, methanol, and methyl ether, respectively. This electron density shows up on the hydrogens not lying in the oxygen valence plane which become negative in methanol and methyl ether.

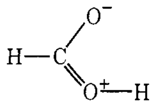
The carbonyl series formaldehyde, acetaldehyde, and acetone also shows the correct trend of increasing polarity with methyl substitution. However, in this case, the calculated dipole moments are all about 1 D less than the experimental values. The high dipole moment of acetone compared with that of formaldehyde is associated with a more negative oxygen and a more positive carbonyl carbon. Thus the C=O bond is polarized in the sense C^+—O^- by the methyl substituents in the same manner as the C=C bond in propene. The gross populations of the oxygen 2pπ atomic orbital are 1.095, 1.125, and 1.162 for the series formaldehyde, acetaldehyde, and acetone, and the corresponding values for the carbonyl carbon 2p orbital are 0.905, 0.889, and 0.864. Thus the hyperconjugative interaction between the carbonyl and methyl groups leads to increased polarization C^+—O^- in the π electrons, together with some charge transfer from Me to CO.

The calculated dipole moment of ketene is very small primarily because of the large back donation of electrons from oxygen into the π atomic orbital of the methylene carbon. Experimentally there is an observed reduction of dipole moment (from 2.34 to 1.41) from formaldehyde to ketene, but the effect is apparently exaggerated by this treatment. This is analogous to the excessively small calculated dipole moment for fluoroacetylene.

The calculated charge distribution in formic acid shows greater C^+—O^- polarization of the C=O bond than for the other compounds. This corresponds to electron transfer of the type



Again this is associated mainly with the π electrons, the 2pπ gross atomic orbital populations being 1.875 (OH), 0.858 (C), and 1.267 (O) compared with 0.905 (C) and 1.095 (O) for formaldehyde. This charge transfer or resonance with the structure



leads to some confluence of the nature of the two C—O bonds.

Carbon dioxide is expected to have considerable polar character $O^-C^+O^-$ even though it has no dipole moment. The calculated charge distribution does show this with a very positive carbon atom. This distribution is reflected quantitatively in the electric quadrupole moment. The wave function found in this paper leads to a value of −6.11 buckinghams,[16] which may be compared with the experimental value of −4.3.[17]

d. Nitrogen Compounds. The nitrogen compounds dealt with in this paper show very similar trends to the oxygen compounds. The decreasing electric dipole moments of the amine series NH_3, $MeNH_2$, Me_2NH, Me_3N is well reproduced by the theory. The charge

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(16) The authors are indebted to Dr. R. Ditchfield for the calculation of the CO_2 quadrupole moment.

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densities show that this is associated with decreasing electron density on the nitrogen and increasing electron density on the hydrogens *trans* to the direction of the nitrogen lone pair. Thus there is a predicted back donation of electrons from N to Me.

It is interesting to note that the methylamines are stronger bases than ammonia.[18] Thus it appears that, for this series of molecules at least, increasing base strength is *not* associated with increasing electron density on the nitrogen atom.

The description of HCN and MeCN by this method is very similar to the CNDO treatment. The methyl compound has a larger dipole moment in agreement with experiment. This is associated with increased polarity in the π part of the C≡N bonds. The total atomic π densities in this bond are

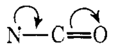
$$\text{H—}\overset{1.968}{\text{C}}\equiv\overset{2.032}{\text{N}} \qquad \text{Me—}\overset{1.938}{\text{C}}\equiv\overset{2.093}{\text{N}}$$

These show increasing polarization C^+—N^- in the triple bond, together with some electron transfer from the methyl group.

e. Mixed Compounds. Charge distributions and dipole moments for a number of mixed compounds are included in Figure 4 and Table II. These lend support to suggestions about the structure of these molecules that have previously been put forward on qualitative grounds.

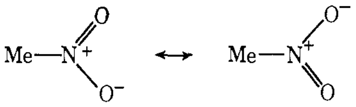
Nitrogen trifluoride has a relatively small calculated dipole moment because of the competing polar effects of the polar N–F bond and the nitrogen directed lone pair. The negative charge on the fluorine is relatively small.

As in the CNDO/2 theory, the observed large dipole moment of formamide is well reproduced. It is associated with high polarization of the C═O bond due to the neighboring nitrogen atom. There is π-electron donation from the (planar) nitrogen lone pair to the carbonyl group. The $2p\pi$ nitrogen population drops from 2.000 in planar NH_3 to 1.817 in formamide. The corresponding change in the oxygen $2p\pi$ population is from 1.095 in formaldehyde to 1.340 in formamide. Thus strong electron transfer of the type



is predicted. The direction of the dipole moment of the molecule is well reproduced.

The large dipole moment of nitromethane is also well reproduced by the theory. The charge distribution shown in Figure 4 indicates that this is primarily due to a positive nitrogen and negative oxygen atoms in agreement with the usual qualitative picture



The π charge densities are 1.117 on nitrogen and an average of 1.446 on each oxygen.

Conclusions

From this survey of theoretical charge distributions and dipole moments for a fairly broad range of organic molecules, the following general conclusions emerge.

1. The overall agreement between experimental and theoretical electric dipole moments is moderate, there being a series of compounds such as fluorocarbons where the description is considerably in error. These deficiencies are presumably due to the limited nature of the STO basis set, since more extensive studies on small molecules using larger bases generally give improved agreement.[19–30] Nevertheless most trends of dipole data along series of related molecules are well reproduced and these lend some support to the more detailed features of charge distribution predicted by the theory.

2. The atomic populations obtained in these *ab initio* calculations parallel those obtained by the semiempirical CNDO/2 procedure quite closely. One feature that persists is the widespread alternation in both saturated and unsaturated systems with polar substituents.

3. Another marked property of the calculated distributions is the way in which electron density from lone-pair atomic orbitals on nitrogen, oxygen, and fluorine delocalize or "back-donate" into neighboring hydrocarbon groups. This feature of charge distribution, long appreciated for substituted unsaturated hydrocarbons, is predicted to occur also for saturated groups and to be the primary cause of the low dipole moments of alkyl amines and ethers.

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