Population Analysis with Hydrogen 2 p Polarization Functions Included in the INDO Basis Set *

J. C. Facelli ** and R. H. Contreras

Departamento de Física, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires

Z. Naturforsch. **35a**, 1350—1353 (1980); received September 3, 1980

Mulliken population analysis with 2p polarization functions included in the AO basis set of the INDO method has been performed for a set of molecules containing hydrogen as well as first row atoms. It is found that this enlargement of the basis set yields an increasing electron population in hydrogen atoms, in agreement with trends found in "ab initio" methods.

Introduction

The importance of including polarization functions in the basis set of ab initio MO calculations has received a good deal of attention during the last few years [1—8]. However, little work has been reported on the influence of the inclusion of polarization functions in the basis set of semiempirical methods. The only papers dealing with semiempirical methods that the authors are aware of are, on the one hand, those [9—12] in which polarization functions are included in the CNDO/2 [13] basis set to calculate electrical polarizabilities, and, on the orther hand, their own previous work [14] where hydrogen 2p polarization functions were included in the INDO [13] basis set in order to study their influence on the Fermi contact term of spin-spin coupling constants.

In the present paper the same INDO version of the previous work [14] has been used to perform population analysis in a set of molecules containing hydrogen as well as some of the first row atoms carbon, oxygen, nitrogen and/or fluorine.

Method

The CNINDO program [15] has been modified as indicated previously [14] to include hydrogen 2p atomic orbitals in the basis set. Semiempirical hydrogen 2p parameters were estimated according to the Slater rules [16], except the Slater exponent for which the value of Salez et al. [3] has been chosen. All other parameters were left unchanged. Population analysis has been carried out following Mulliken's formalism [17]. Results are compared with those obtained using ab initio as well as standard semiempirical methods. When available, these values were taken from the literature. Otherwise, the semiempirical ones were also calculated. In all cases geometrical structures were taken from the Pople and Gordon model [18]. Calculations were performed at the data processing center of the University of Buenos Aires ("Centro de Cómputos en Salud") using an IBM 360/50 system.

Results

In Table 1 our population analysis, for some simple hydrocarbons, calculated within the INDO approximation with hydrogen 2p polarization functions (hereafter INDO/p method), is compared with those obtained by the following methods: CNDO/2, INDO [13], ab initio STO-3G [19] and ab initio with extended basis sets [20—22]. All these results predict an increase in electron population in hydrogen atoms in the series C_2H_2, C_2H_4, C_2H_6. However, only the CNDO/2 methods yields the same polarity $C(-)-H(+)$ predicted by ab initio calculations. In all these hydrocarbons, except methane, hydrogen polarization functions increase the electron population in the hydrogen atoms. This trend was also observed by Teixeira-Dias and Murell [11] when including these polarization functions in the CNDO/2 basis set.

Net charges and the dipole moment in hydrogen fluoride are displayed in Table 2. All methods give the same bond polarity. The INDO/p electron charge on the H center is greater than that of INDO,

---

[*] Part of a PhDthesis (J.C.F.) to be presented to the University of Buenos Aires.

[**] Comisión de Investigaciones Científicas (CIC, Pcia. Bs. As.) Fellow.

Reprint requests to J. C. Facelli, Dto. de Física Fac. de Ciencias Exactas y Naturales, Pab. I, Ciudad Universitaria, 1428, Núñez, Buenos Aires, Argentina.

0340-4811 / 80 / 1200-1350 $ 01.00/0. — Please order a reprint rather than making your own copy.

Table 1. Population analysis in hydrocarbonds as calculated with different methods. Total electronic Charges in e.

		I	CNDO/2	INDO	INDO/p	STO-3G[d]
CH_4	C	6.534[a]	6.050	5.963	6.168	6.073
	H	0.867[a]	0.987	1.009	0.957	0.982
C_2H_4	C	6.278[a]	6.030	5.997	5.799	6.156
	H	0.861[a]	0.985	1.001	1.101	0.922
C_2H_6	C	6.372[a]	6.008	5.946	5.504	6.026
	H	0.876[a]	0.998	1.018	1.165	0.991
C_2H_2	C	6.188[a]	6.063	6.053	5.976	6.182
	H	0.812[a]	0.937	0.947	1.025	0.818
Cyclopropane	C	6.173[b]	5.993	5.977	5.920	6.051
	H	0.827[b]	1.007	1.023	1.080	0.949
Benzene	C	6.504[c]	6.108	5.977	5.673	—
	H	0.748[c]	0.991	1.012	1.163	—

I: ab initio calculations with extended basis set.
[a] taken from [20].
[b] taken from [21].
[c] taken from [22].
[d] taken from [19].

lowering somewhat the dipolar moment, which comes to a better agreement with the experimental value. This trend is the same as that obtained when hydrogen polarization functions are introduceded in ab initio calculations [23] of the hydrogen fluoride dipole moment.

Results from the analysis in the isoelectronic series CH_4, NH_3 and CH_2 are shown in Table 3. Again, when including hydrogen polarization functions, ab initio and INDO methods display a similar behaviour, except in methane, in that they increase the hydrogen electron charge. However in methane the INDO net charge is of opposite sign and therefore it could be thought of as being rather unrealistic. It is interesting to observe that INDO/p values agree better with those obtained using an ab initio method with a (7,3/4,1) Gaussian basis set, [8] which includes polarization functions, than the INDO results, with the ab initio values obtained with a (7,3/4) Gaussian basis set [8]. It is also noteworthy that these trends for the water molecule are in agreement with those reported in Reference [2].

Table 2. Net charges and dipole moment in the HF molecule[a].

	F	H	Dipole moment
INDO	− 276	276	1.98
INDO/p	− 245	245	1.82
MNDO	− 287	287	1.99
STO-3G[b]	− 228	228	1.42
exp.[c]	—	—	1.83

[a] Net charges in 10^{-3} e and dipole moments in Debyes.
[b] Taken from [19]. [c] Taken from [13].

Table 3. Hydrogen electronic population in the series CH_4, NH_3 and OH_2[a].

	INDO	INDO/P	(7.3/4) basis set[b]	(7.3/4.1) basis set[b]
CH_4	1.009	0.959	0.816	0.912
NH_3	0.912	0.998	0.741	0.927
OH_2	0.669	0.874	0.656	0.860

[a] Electronic charges in e. [b] Taken from [8].

Results for fluoroethylenes are presented in Figs. 1 and 2 as net atomic charges. A comparison between INDO and INDO/p results shows that the last method decreases the net charge in the fluorine atom while it produces a charge transfer from carbon to hydrogen centers yielding both carbon atoms with positive net charge in vinyl-fluoride and leaving an alternating sign in 1,1-difluoroethylene.

The INDO/p method shows similar trends for molecules containing nitrogen and/or oxygen atoms. Hydrogen electron populations increase while those in carbon and heteroatom centers decrease when

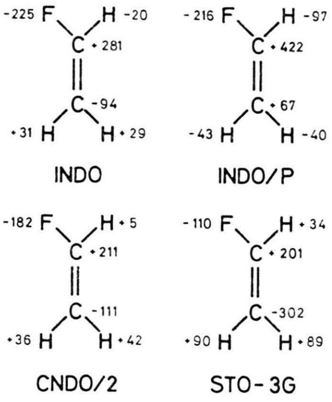

Fig. 1. Net charges in vinyl-fluoride as calculated using different methods. Charges are given in e × 10^{-3}.

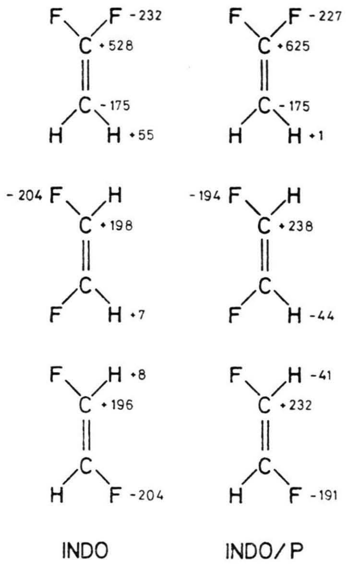

Fig. 2. Comparison between INDO and INDO/p methods in calculating atomic net charges in difluorethylenes. Charges are in e × 10^{-3}.

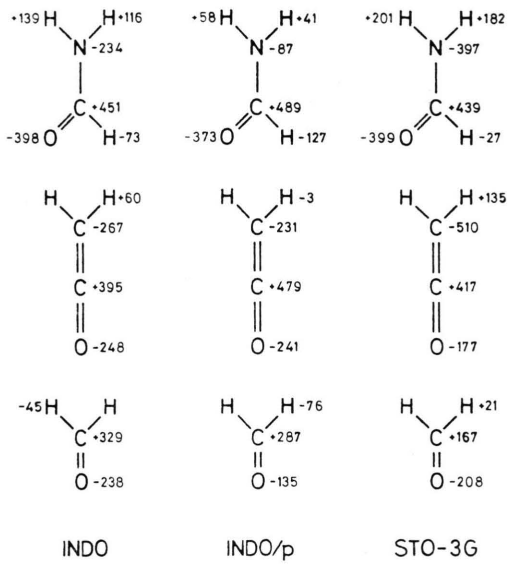

Fig. 3. Influence of polarization functions on the net charges of some molecules containing heteroatoms. Charges are in e × 10^{-3}.

compared with those of INDO. Values for formamide, ketene and formaldehyde are given in Figure 3.

σ, π and total net atomic charges in pyridine according to different semiempirical and "ab initio" methods with [26] and without [24], [25] hydrogen polarization functions in the basis set, are compared in Table 4. It should be pointed out that in the previous paper [14] it was found that the inclusion of hydrogen 2p orbitals in pyridine has

Table 4. Net charges in Pyridine according to several ab initio and semiempirical methods[a].

N	CNDO/2	INDO	INDO/p	EC[b]	PGF[c]	ARWJ[d]
σ	− 0.0860	− 0.1163	− 0.0991	− 0.2159	− 0.2419	− 0.52
π	− 0.0572	− 0.0717	− 0.0446	− 0.0102	0.0067	− 0.11
tot.	− 0.1432	− 0.1880	− 0.1437	− 0.2262	− 0.2352	− 0.63
C(α)						
σ	0.0645	0.1111	0.0735	− 0.1049	− 0.0851	0.40
π	0.0330	0.0407	0.0962	− 0.0048	− 0.0094	0.05
tot.	0.0975	0.1518	0.1697	− 0.1097	− 0.0945	0.25
$C(\beta)$						
σ	− 0.0034	0.0028	− 0.0763	− 0.2198	− 0.2268	− 0.14
π	− 0.0267	− 0.0285	0.1077	− 0.0024	0.0016	− 0.04
tot.	− 0.0301	− 0.0257	0.0314	− 0.2222	− 0.2252	− 0.18
$C(\gamma)$						
σ	− 0.0030	0.0227	− 0.0657	− 0.2269	− 0.2258	− 0.11
π	0.0445	0.0472	0.2183	0.0245	0.0089	0.07
tot.	0.0415	0.0699	0.1526	− 0.2024	− 0.2169	− 0.04
$H(\alpha)$						
tot.	− 0.0164	− 0.0417	− 0.0873	0.2217	0.2187	0.11
$H(\beta)$						
tot.	0.0027	− 0.0122	− 0.0721	0.2171	0.2179	0.11
$H(\gamma)$						
tot.	− 0.0055	− 0.0257	− 0.0920	0.2203	0.2182	0.11

[a] Net charges in e. [b] Taken from [24]. [c] taken from [25]. [d] Taken from [26].

markedly improved the calculated spin-spin coupling constants. Hydrogen net charges increase in the sequence CNDO/2, INDO and INDO/p and have the opposite sign of the ab initio values, except for β protons in CNDO/2 calculations. It is observed that carbon and nitrogen atoms become more electropositive and hydrogen more electronegative within the INDO/p method as compared with INDO.

The magnification of the back donation effect of electronegative groups when these polarization functions are included, is shown in Table 5, where π charge distributions in fluoroacetylene, formaldehyde and cyanhydric acid are presented as examples. This back donation effect diminishes the dipolar moments as it may also be observed for hydrogen fluoride in Table 2.

Table 5. Comparison between INDO and INDO/p π charges in fluoroacetylene, formaldehyde and cyanhydic acid[a].

F-C1≡C2–H	INDO	INDO/p	Exp.[b]
H	–	0.050	
C2	1.045	1.065	
C1	0.980	0.951	
F	1.955	1.955	
Dipole moment[c]	1.074	0.369	0.75
CH_2O			
H	–	0.068	
C	0.811	0.817	
O	3.102	2.968	
Dipole moment[c]	1.999	0.451	2.339
HCN			
H	–	0.042	
C	0.937	0.928	
N	2.126	2.060	
Dipole moment[c]	2.455	1.861	2.986

[a] Charges in e. [b] Taken from [13]. [c] In Debyes.

Conclusions

To increase the atomic orbitals basis set to include hydrogen polarization functions has a similar influence on the semiempirical INDO method as others with an ab initio base, at least as far as population analysis in concerned.

The magnification of electronic charge in hydrogen atoms and its decrease in hetero- and carbon atoms may be a consequence of employing an unbalanced basis set [8]. Teixeira-Dias and Murell [11], though using only hydrogen polarization functions in the CNDO/2 basis set, suggested the necessity of including also polarization d functions for first row atoms in order to overcome this lack of equilibrium.

It is thought that the use of a more balanced basis set with an adequate reparametrization, may correct the anomalous results while preserving the improvements already achieved [14]. Work along this line is in progress.

Acknowledgements

Grants from the Argentine Research Council (CONICET) and from the Argentine Science and Technology Secretariat (SECYT) are gratefully acknowledged. The authors thank Dr. H. Grinberg for his keen interest in this work.

[1] R. Krishnan, J. S. Binkley, R. Seeger, and J. A. Pople, J. Chem. Phys. **72**, 650 (1980).
[2] W. J. Janis, P. Kaijser, J. R. Sabin, and V. H. Smith, Mol. Phys. **37**, 463 (1979).
[3] C. Salez and A. Veillar, Theor. Chim. Acta **11**, 441 (1968).
[4] E. Clementi and H. Popkie, J. Chem. Phys. **57**, 1077 (1972).
[5] T. H. Dunning, J. Chem. Phys. **55**, 3958 (1971).
[6] P. C. Hariharan and J. A. Pople, Theor. Chim. Acta **28**, 213 (1973).
[7] P. C. Hariharan and J. A. Pople, Chem. Phys. Lett. **16**, 217 (1972).
[8] B. Roos and P. Siegbahn, Theor. Chim. Acta **17**, 199 (1970).
[9] E. Nørby Svendsen and T. Stroyer-Hansen, Int. J. Quantum Chem. **13**, 235 (1978).
[10] D. W. Davies, Mol. Phys. **17**, 473 (1969).
[11] J. J. C. Teixeira-Dias and J. N. Murrel, Mol. Phys. **19**, 329 (1970).
[12] J. J. C. Teixeira-Dias and P. J. Sarre, J. C. S. Faraday II, **71**, 906 (1975).
[13] J. A. Pople and D. L. Beveridge, Approximate Molecular Orbital Theory, McGraw-Hill, New York 1970.
[14] J. C. Facelli and R. H. Contreras, Int. J. Quantum Chem. (in press).
[15] P. A. Dobosh, Quantum Chemistry Program Exchange, Indiana University.X, 141 (1974).
[16] J. C. Slater, Phys. Rev. **36**, 57 (1930).
[17] R. S. Mulliken, J. Chem. Phys. **23**, 1833; 1841 (1955) and **36**, 3428 (1962).
[18] J. A. Pople and M. S. Gordon, J. Amer. Chem. Soc. **89**, 4253 (1967).
[19] W. J. Hehre and J. A. Pople, J. Amer. Chem. Soc. **92**, 2181 (1970).
[20] W. E. Palke and W. H. Lipscomb, J. Amer. Chem. Soc. **88**, 2384 (1966).
[21] W. C. Ermler, R. S. Mulliken, and E. Clementi, J. Amer. Chem. Soc. **98**, 388 (1976).
[22] A. Skancke, J. Mol. Structure **30**, 95 (1978).
[23] T. H. Dunning and P. J. Hay, in Methods of Electronic Structure, H. F. Schaefer III, Ed., Plenum Press, New York 1977, Vol. 3.
[24] E. Clementi, Chem. Rev. **68**, 341 (1968).
[25] M. H. Palmer, A. J. Gaskell, and R. R. Findlay, J. C. S. Perkin II, **7**, 778 (1974)
[26] J. Almofb, B. Roos, V. Wahlgren, and H. Johansen, J. Electron Spectrosc. **2**, 51 (1973).