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Gross orbital charges of aniline and its reaction products

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Abstract

We have calculated gross orbital charges of aniline and its reaction products like diphenyl urea, acetanilide and Benzanilide by semi-empirical molecular orbital technique MINDO/3 which is an improved version of MINDO. The results obtained for above mentioned molecules are summarsied.

Keywords: MINDO/3, FORCE,GEO-OK

Introduction

The molecular orbital studies on the electronic structure of molecules gives a deeper insight in understanding the chemical reactivity and spectral properties. The development of self consistent field method for molecules, it has been held a common and widely belief that the non-relativistic Schrodinger equation provides the necessary framework for the consideration of all aspects of molecular structure. The study of electronic structures has received very much attention at every stage at the development of molecular orbital theory. The π electron structure of aniline and its derivatives have been investigated using different refinements of the simple molecular orbitals starting with Huckel and continuing with the SCF based π molecular orbitals developed by Pariser-Paar and Pople (PPP). This (PPP) method provides very satisfactory results of (both) the ground and excited state properties in which they performed an extensive application of the method in its original fixed parameter formalism as well as in the variable electro-negativity approximation (VE-PPP). Although different features of the electronic structure can be studied with the help of these calculations, but many important aspects could not be satisfactory explained.

Later, these aspects include contributions from inductive effect of the substituents and correspond to the changes in σ electron framework of compounds and therefore attempts were made to develop semi-emperical procedures involving all valence electrons of the molecules in early sixties. The extension of Huckel theory and Haffmann were the first such attempts. During this period Pople and coworkers developed a series of approximation (People and Beveridge) based on neglect of differential overlap. In this approximation they tried to retain the symmetry invariance by the neglected integrals. The simplest approximation of this type is called the complete neglect of differential overlap (CNDO). This approximation was very little successful in explaining spectral properties of molecule. A modification of procedure was suggested by Del, Bene and Jaffee and these various versions of the CNDO method, with appropriate parameterization were used to study the electronic structure and spectra of molecules by several workers (Yadav *et al*., Pople and Gordon, Baird and Dewar, Bloor and Breen, and Klopman and O'Leary), leading to a moderately successful description of the polarity of substituted benzene (aniline). The general agreement between the π-electron methods and the all valence electron approximation was encouraging. However, all valence electron method discussed so far also did not reproduce all the experimental results. Since the parameters suitable for some properties were not exactly suitable for the other indices. Also different set of parameters were often suggested in the same approximation by different workers (Del, Bene and Jaffee). Furthermore, different approximate methods were used to evaluate similar integrals by different authors making it difficult to draw general calculations (People and Beveridge). A feeling that the semi-rigorous procedures are no longer suitable (adequate) for molecular electronic structure calculations, also grew up steadily (Kaufman).

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The availability of fast and powerful computers made it practical to use rigorous ab-initio quantum chemical methods for the molecules starting in mid 1970's with minimal basis set. Recently many researchers (Binning and Sando; Boggs *et al*.) have studied the electronic structure of some molecules at ab-initio level with minimal and double zeta contracted basis sets. The use of this method to all electrons of the conjugated system appears very attractive since in principle they may help in a better description of all the σ-electrons which are completely or partially neglected in the π-electrons or all valence electron calculations, respectively. However, it is found that such calculations are very expensive and time consuming. Furthermore, Bingham *et al*. showed that the failings of earlier semi-empirical treatments were in fact due to only insufficient or inappropriate parameterization or to the use of procedures too crude to be rescued even by the introduction of the parameters. They developed successively a series of better treatments. In this treatment a single set of parameters allowed the calculation of varied properties of wide range of molecules. One of the such treatments (MINDO/3) reported by them has so far survived every test without serious failure and proved to be an extraordinary versatile procedure, giving good results for every ground state property studied so far (Bingham *et al*., Dewar and Thiel) and apparently offering hope of equally successful extension to excited state and photochemistry. Thus available evidence would seem to suggest the MINDO/3 may provide a better overall qualitative guide to chemical behavior than even good Roothan-Hall calculations. In this chapter we have applied MINDO/3 method to aniline and its reaction product such as dipheny1 urea, acetanilide and benzanilide, formed with certain reactants for calculating gross orbital charges.

Method of Calculation

Gross orbital charges of aniline and its reaction products diphenyl urea, acetanilide and benzanilide are calculated by molecular orbital package (MOPAC) software. A semi-empirical SCF MO method MINDO/3 is used for calculating gross orbital charges.

Results and Discussion

Gross Orbital Charges: The MINDO/3 gross orbital charges of aniline and its reaction products have been presented in the Table. Some of the interesting features regarding these charges are discussed below:

1. The neglect of inner most IS orbital of all the non-hydrogenic atoms (carbon, oxygen and nitrogen) in the present all valence MINDO/3 calculation is justified because of the fact that the ab-initio 4-31G (spilt valence) and 6-31G* (spilt valence + polarized) populations (Singh and Yadav) on these orbitals on several molecules are almost equal to 2. This shows that their innermost IS orbital is not significantly involved in the chemical bonds.

2. The sp^2 hybridization on a carbon atom requires an orbital charge description of the type $2S^1$, $2p^1x$, $2p^1y$ and $2p^1z$. This expected behaviour is followed closely in our computed results. The 2S orbitals of all the unsubstituted carbons show a population of approximately 1.23 e in aniline so that, there is a deficit of about 0.77 e from the $2S^2$ configuration. This deficit represents promotion from a 2S to a 2P orbital is explained as being due to the energy gain in molecular formation from SP^2 hybridized orbitals. However, this deficit is slightly larger (approximately 0.80 e) for the carbon atoms attached to the substituent. Similar results have been found in earlier ab initio calculations (Singh and Yadav).

3. The population on P^2 orbitals of nitrogen in aniline is approximately two. And also the population on P^2 orbitals of nitrogen and oxygen in dipheny1 urea, acetanilide and benzanilide is approximately 2. This shows that the π orbitals of these atoms are occupying the lowest enery state and thus has privilege to be filled on priority basis by the electron as per Aufbau principle.

4. A close inspection of charges at various orbital in aniline and its reaction products shows the following results:
   a. In aniline, a charge is seen to migrate from the 2py orbital of C_5 to 2S orbital of N_7.
   b. In dipheny1 urea, the migration of a large number of charges takes place from 2Px orbital of C_{10} to 2S orbital of N_1, from 2px orbital of C_4 to the 2S orbital of N_3 and from the 2Px orbital of C_2 to 2Px orbital of O_{22}.
   c. In acentanilide, the migration of charges takes place from the 2Px orbital of C_4 to the 2S orbital on N_1 and from the 2Py (2Pz) orbital of C_2 to the 2Px orbital of O_{16}.
   d. In benezanilide, a large number of charges are seen to migrate from the 2Px orbital of C_1 to 2S orbital of N_1 and from the 2Px orbital of C_2 to 2Px orbital of O_{22}.

   The above results show that the migration of charges takes place from the σ orbitals of the ring carbons to the σ orbitals of the substituent atoms to which they are attached. In general, the IS and the 2Pz orbitals of both the atoms do not take part in such migrations. This results prepares a basis to assume SP^2 hybridization among the σ orbitals 2S, 2Px and 2Py of the ring carbons for applying similarity transformation to evaluate the bond orders and bond lengths of the atoms.

5. The (π) charges on carbon atoms attached to the substituents (C_5) in aniline are found smaller than π charges on the other ring carbon atoms.

6. A comparison of the charges flowing into the Py orbitals of the subsituents (N, C or O) from carbon atom attached to them in aniline, dipheny1 urea, acetanilide and benzanilide shows that they are in order of O Py>NPy>CPyWhichis in the order of electronegativities of the three atoms.

7. The electronic charges on the IS orbitals of the hydrogen atoms attached to ring carbons reveal that there is a little exchange of charges from hydrogen to ring carbon attached to it or vice-versa. However, if we look upon the charges on such orbitals in ab initio 4-31G method (Singh and Yadav), was find greater exchange. Furthermore the IS orbitals of hydrogen atoms of NH_2 in aniline contains less charges than the orbitals of hydrogen atoms attached to the ring carbon contrary to this observation, the IS orbital of hydrogen atoms attached of CH_3 in acetanilide have greater charges than the IS orbitals of the hydrogen atoms attached to ring carbons. However, the tow hydrogen atoms of $-CH_3$ in acetanilide are slightly less populated

than the IS orbital of the hydrogen atom lying in the plane of the ring.

8. The all valence electronic distribution on the nitrogen atom in aniline without hybridization is assumed as $2S^2$, $2P^1y$, $2P^1y$, $2P^1z$. The present study shows that the electron distribution on various orbitals of atom N in aniline is $2S^{1.32}$, $2Px^{1.007}$, $2Py^{1.005}$ and $2Pz^{1.83}$. Similar distribution of charges are also found in the ab-initio 4-31G method.

9. In aniline σ orbital population of the nitrogen atoms are approximately $2S^{1.322}$, $2Px^{1.007}$ and $2Py^{1.005}$ which allows the flow of charges from 2Py orbitals of the carbon C_5 take place towards the 2S orbitals of the nitrogen atom. This increases the population of 2S orbitals. This result agreed with the other semi-empirical CNDO/2and INDO calculations (Yadav *et al*.).

10. In the reaction products of aniline, i.e. in the diphenyl urea and acetanilide, the population of nitrogen atom show that the flow of charges from 2Px orbital of carbon C_{10} takes place towards the 2S orbitals of the nitrogen atom. This increase the population of nitrogen atom.

11. If we compare the charges on 2S orbital of nitrogen and oxygen in all reaction products of aniline we find that

inacetanilide	$2S^{1.969}$ (O)> $2S^{1.894}$ (N)
in diphenyl urea	$2S^{1.865}$ (O)>$2S^{1.377}$ (N)
and in benzanilide	$2S^{1.861}$(O)>$2S^{1.388}$(N)

Hence we can say that 2S (O) > 2S (N). Thus the predicted charge distribution are generally similar to those given by ab initio SCF 4-31G calculations. In short MINDO/3 seems to give quite realistic electron distribution.

Table 1: Gross orbital charges Orbitals

Atoms	Orbitals				
	1S	2S	2P$_x$	2P$_y$	2P$_z$
Aniline					
C_1	-	1.233	0.879	0.862	0.946
C_2	-	1.232	0.881	0.874	1.093
C_3	-	1.233	0.858	0.882	0.946
C_4	-	1.238	0.863	0.885	1.139
C_5	-	1.219	0.862	0.803	0.893
C_6	-	1.239	0.875	0.873	1.138
N_7	-	1.322	1.007	1.005	1.837
H_8	0.997	-	-	-	-
H_9	1.018	-	-	-	-
H_{10}	0.997	-	-	-	-
H_{11}	1.018	-	-	-	-
H_{12}	0.997	-	-	-	-
H_{13}	0.919	-	-	-	-
H_{14}	0.919	-	-	-	-
Reaction Products					
(i)Dipheny1 urea					
N1	-	1.377	1.026	1.035	1.758
C2	-	1.227	0.716	0729	0.646
N3	-	1.374	1.045	1.027	1.757
C_4	-	1.225	0.785	0.898	0.913
C_5	-	1.245	0.902	0.947	0.980
C_6	-	1.237	0.886	0.901	0.928
C_7	-	1.238	0.886	0.941	0.971
C_8	-	1.236	0.882	0.910	0.924
C_9	-	1.240	0.901	0.958	0.960
C_{10}	-	1.228	0.815	0834	0.938
C_{11}	-	1.245	0.874	0.879	1.090
C_{12}	-	1.240	0.904	0.862	1.069
C_{13}	-	1.235	0.882	0.867	0.962
C_{14}	-	1.232	0.880	0.882	1.047
C_{15}	-	1.232	0.863	0.883	0.966
H_{16}	0.997	-	-	-	-
H_{17}	1.012	-	-	-	-
H_{18}	1.003	-	-	-	-
H_{19}	0.966	-	-	-	-
H_{20}	1.009	-	-	-	-
H_{21}	0.940	-	-	-	-
O_{22}	-	1.865	1.666	1.393	1.662
H_{23}	0.938	-	-	-	-
H_{24}	1.001	-	-	-	-
H_{25}	1.011	-	-	-	-
H_{26}	0.993	-	-	-	-
H_{27}	1.009	-	-	-	-
H_{28}	0.979	-	-	-	-

(ii)Acetanilide					
N_1	-	1.894	0.638	0.905	1.794
C_2	-	1.686	0.814	0.790	0.309
C_3	-	1.322	0.873	0.884	0.918
C_4	-	1.075	0.906	0.970	1.050
C_5	-	1.329	0.848	0.865	1.087
C_6	-	1.198	0.851	0.914	1.041
C_7	-	1.243	0.848	0.884	0.969
C_8	-	1.278	0.853	0.901	1.004
C_9	-	1.335	0.849	0.850	0.930
H_{10}	0.925	-	-	-	-
H_{11}	1.015	-	-	-	-
H_{12}	0.953	-	-	-	-
H_{13}	0.991	-	-	-	-
H_{14}	1.028	-	-	-	-
H_{15}	0.638	-	-	-	-
O_{16}	-	1.969	1.698	1.031	1.831
H_{17}	1.042	-	-	-	-
H_{18}	0.976	-	-	-	-
H_{19}	0.976	-	-	-	-
(iii) Benzanilide:					
N_1	-	1.388	1.026	1.062	1.724
C_2	-	1.234	0.727	0.781	0.630
C_3	-	1.234	1.002	0.938	0.918
C_4	-	1.240	0.944	0.907	0.868
C_5	-	1.241	0.934	0.909	0.870
C_6	-	1.236	0.963	0.919	0.883
C_7	-	1.238	0.936	0.901	0.894
C_8	-	1.236	0.959	0.922	0.884
C_9	-	1.231	0.826	0.867	0.920
C_{10}	-	1.242	0.900	0.927	1.007
C_{11}	-	1.246	0.893	0.927	1.005
C_{12}	-	1.235	0.875	0.900	0.938
C_{13}	-	1.234	0.888	0.918	0.995
C_{14}	-	1.235	0.888	0.888	0.937
H_{15}	0.994	-	-	-	-
H_{16}	1.009				
H_{17}	1.005	-	-	-	-
H_{18}	0.993	-	-	-	-
H_{19}	1.010	-	-	-	-
H_{20}	0.908	-	-	-	-
O_{21}	-	1.861	1.711	1.406	1.583
H_{22}	1.014	-	-	-	-
H_{23}	0.997	-	-	-	-
H_{24}	1.003	-	-	-	-
H_{25}	0.998	-	-	-	-
H_{26}	1.006	-	-	-	-

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