



Molecular orbital studies on the isomers of mono aminophenol

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Abstract: The geometry of various isomers of mono amino phenol was optimized using the DFT route B3LYP with the basis set 6-31G(p,d). The structural parameters and the SCF energy were analyzed. The output obtained was then used to run the population analysis with the "POP= REGULAR" key word. The Gross Orbital Population, Charge Distribution, HOMO-LUMO gap and the dipole moments are also analyzed.

Keywords: Amino Phenol, Gross Orbital Population, HOMO-LUMO, Dipole Moment

I. Introduction

Molecular Orbital theory is the simple and useful method of describing the electronic structure of the molecules. The MO theory of the electronic structure of molecules is a natural extension of orbital theory of atomic structure to molecules. Each electron is pictured as moving independently in an effective one - electron potential due to the nuclei and the averaged effect of the other electrons. The basic framework of the MO method was built up soon after the development of quantum mechanics, the principle contributors being Hund[1], Mulliken[2] and Lennard - Jones [3]. It enables us to interpret the nature of the ground and excited electronic states of molecules, both diatomic and polyatomic.

The stabilization of aminophenol derivatives and their radicals due to internal hydrogen bonding has been analyzed by means of density functional theory and by topological electron density analysis by JRB Gomes et al.[4] The same authors used Density Functional Theory to investigate several gas-phase thermodynamic parameters of the *o*-, *m*-, and *p*-aminophenol isomers. [5] Abraham George et al [6] have reported the structural parameters, HOMO-LUMO gap, IR and NMR spectra of amino phenol.[6]

In the present study the three isomers of amino phenol were analyzed for Orbital populations, charge density, HOMO-LUMO gap and dipole moment.

II. Results and Discussion

Gaussian-03 was used to study the molecular parameters[7]. The DFT route B3LYP with the basis set 6-31G(d,p) was used to optimise the structure of three isomers of amino phenol. The optimized parameters were used to study the orbital distributions and electronic charges. The Avagadro software [8] was used to generate the HOMO-LUMO surfaces.

Structural Parameters

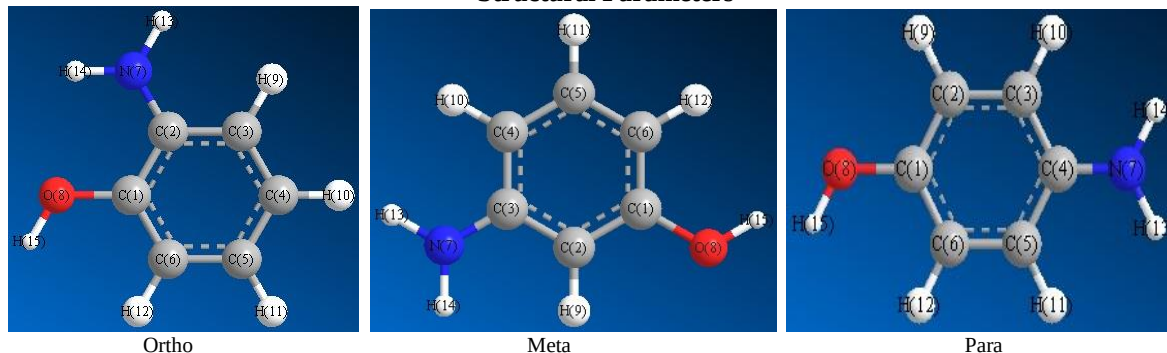


Figure 1: Isomers of mono amino phenol

When an atom in a molecule is substituted with another atom, the geometries of the interatomic bonds undergo changes. Over the years, both experimental and theoretical [9] techniques on substituent effects in phenol have been studied.

Substitution with Amine group alters the bond length and bond angle. Substitution of amine group in phenol in the ortho position overestimated the C₁C₂ bond length and more so in para substitution. Substitution at meta position underestimates the bond length value.

When Amine group is in the ortho position, the C-C bonds attached to the substituted position are considerably overestimated while the other C-C bonds have negligible variations. The same trend is also seen the meta and para substitutions.

Substitution in the ortho position overestimates the C₁C₂ bond length to a value 1.4136 Å and C₂C₃ bond length to a value 1.4015 Å. The C₂C₃ and C₃C₄ bond lengths in meta positions elongate to a value 1.4042 Å and 1.4107 Å respectively. The same bond lengths in the para positions are observed as 1.4073 Å and 1.4042 Å. All the other C-C bond lengths in the three substitutions are not affected considerably.

There are not many variations in all the C-H bond lengths due to the substitutions in all three positions. When we come to the C-N bond length it has the highest value in the para position followed by meta and then the ortho position.

The N-H bond length for all the three substitutions have more or less the same value with meta position having comparatively highest bond length. Again this is comparable to those proposed by A. George *et al* [6]. O-H bond length exhibits more or less the same value for all substitutions with meta position having comparatively highest bond length. But it is slightly lesser than the unsubstituted phenol. Hence there is a slight decrease in the OH bond length due to the substitution which may be attributed to the second activating group that is substituted in the aromatic ring. The value of C-O bond length is around 1.36 to 1.38 which is close agreement with that proposed by Fahmi Himo *et al* in their work on substituted Phenols [10]. But underestimated to that proposed by A. George *et al* [6]. The amine substitution in all positions narrows the CCC angle where the NH₂ is substituted. The endocyclic angle opposite to this CCC angle also narrows. All the other CCC angles widen. This establishes that phenolic ring is not a regular hexagon endorsing the finding by Bretholon *et al* [11]. From the values of the C-C-O angles it is observed that when the amine group is substituted in the ortho position it bends more towards the substituted position and this bending becomes less pronounced when the substitution is in the meta and para positions. Angle C-C-N bends towards the OH group more in the ortho position than in meta and para because of the proximity of the OH group. Angle C-C-H in ortho position nearer to the amine bends towards the amine substitution presumably due to the hydrogen bonding. Similarly the angle C-C-H near the OH group in meta and para also bends towards the OH group but bending is less. From the Table 1 it is shown that there is not much difference in the bond angles of angle C-N-H, H-N-H and C₁-O-H in the substituted molecule in all the three positions. The details of the bond lengths are listed in the **Table- 1**.

BOND LENGTH AND BOND ANGLE	Substituted Positions		
	Ortho	Meta	Para
C ₁ -C ₂	1.4136	1.3941	1.3971
C ₁ -C ₆	1.3884	1.3995	1.3958
C ₂ -C ₃	1.4015	1.4042	1.3909
C ₃ -C ₄	1.3968	1.4102	1.4073
C ₄ -C ₅	1.3922	1.39	1.4042
C ₅ -C ₆	1.4001	1.3956	1.3948
C-O	1.3798	1.3698	1.3761
O-H	1.0872	1.0864	1.0852
C-N	1.3761	1.3773	1.3839
∠C ₁ C ₂ C ₃	117.8798	120.137	120.4415
∠C ₂ C ₃ C ₄	121.0542	119.0867	121.1483
∠C ₃ C ₄ C ₅	120.4546	119.774	117.874
∠C ₁ C ₆ C ₃	120.4825	118.4707	120.5978
∠C ₄ C ₅ C ₆	119.1918	121.5213	120.9115
∠C-C-O	115.3897	116.751	117.783
∠COH	108.9179	108.5988	108.6602
∠C-C-N	118.9601	120.3759	120.9682
∠C-N-H	121.0552	120.9042	121.0224
∠C-N-H	119.5861	121.0243	120.9656
∠H-N-H	119.3587	118.0715	118.012

All bond lengths are in angstrom units and bond angles are in degrees

Table 1: Optimized Parameters of Amine Substitution in Phenol

During the process of optimization, the self Consistent Field (SCF) energy is analyzed and on optimization of the molecule the minimum value of SCF energy is reached for that particular conformer. Though the energy is minimum in meta position, both hydroxyl and Amine groups being activating groups, the possible stable isomer could either by para or ortho amino phenol. The variation is represented in fig.. 2.

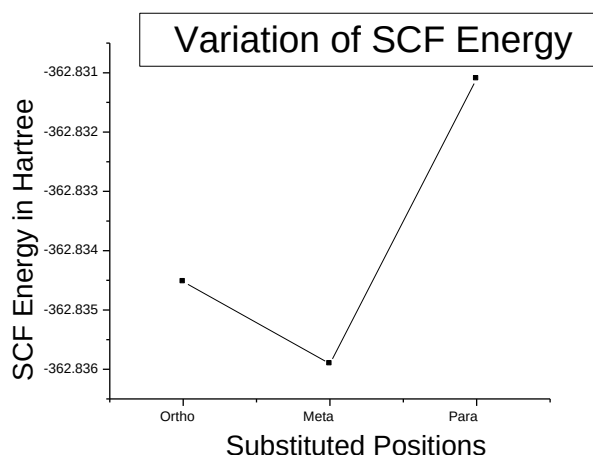


Figure 2

Gross orbital population

The molecular orbitals contribute in building the total wavefunction of the system providing invaluable insight that give rise to bonding.

Substitution with Amine group shows a re-distribution of electrons in the orbitals. The 1s orbital exhibits a marginal difference in the occupancy and stands around 1.99. It is the 2s orbital which has a population of only 0.7 as against the required 2. This population is distributed among the 3s orbital and the 3pz orbital with negligible distributions on the rest of the orbitals ranging till 4yz. 2p shows a total population ranging from 1.8 to 2 depending on the substituted positions. Mild anti bonding character is displayed by 4zz in all substitutions. As for the nitrogen atom, both 2s and 2p show a deficiency in the population. 2s stands at around 0.7 and 2px, 2py and 2pz total to around 2.4 as against 3. This is distributed in 3s and 3p. 4zz and 4yy show mild anti bonding properties. Identical to Nitrogen, Oxygen atoms also show a shift of 2s and 2p population towards 3s and 3p. The ortho substitution induces anti bonding properties in 4xx and 4zz which turns out to the 4yy and 4zz in the other two substitutions. All the hydrogen atoms appear to be only half populated in the 1s orbital. This lost population is mostly shifted to the 2s orbital for all the hydrogen atoms in the aromatic ring. The hydrogen atoms in the amine group and the hydroxyl group show a lesser population in 2s. The comparative populations of the Carbon, Nitrogen, Oxygen and Hydrogen of the ortho substitution is presented in Fig. 3. This trend is almost identical in the meta and para substitutions.

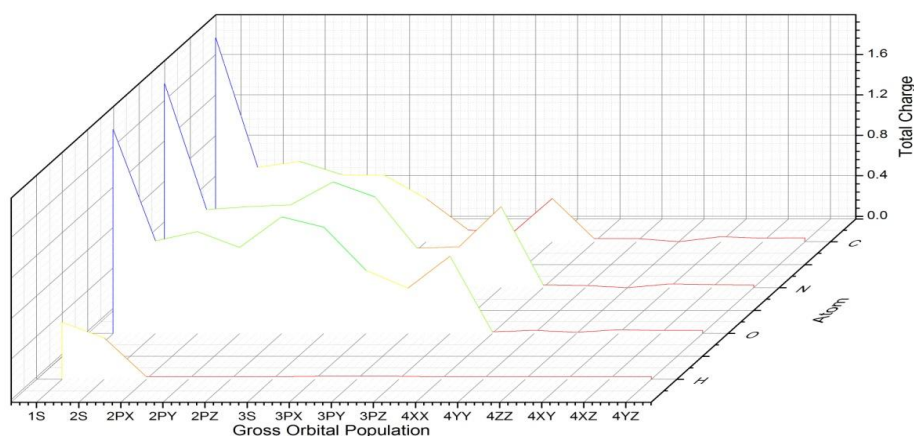


Figure 3

Charge Distribution

Mulliken population analysis assigns half the overlap population to each contributing orbital giving the total population of each atomic orbital. It is observed that the carbon atoms lose out around 1.5 of the charge to the overlap population. Each carbon appears to share 0.5 each of its charge to the bonding carbon atom. Nitrogen atom maintains most of the charge to itself displaying a total charge of around 6.8. Hydrogen atoms lose half the charge to the overlap populations. The more electronegative nature of the oxygen atom is evident in that it displays an individual charge of more than 8.

Analysing the partial charges, the carbon atoms attached to the amine group and the hydroxyl group display a net positive charge as against the other carbon atoms. The nitrogen atom and the oxygen atoms also display a negative charge while the hydrogen atoms show a positive charge.

The partial charges on various atoms for various substitutions is presented in Fig.. 4

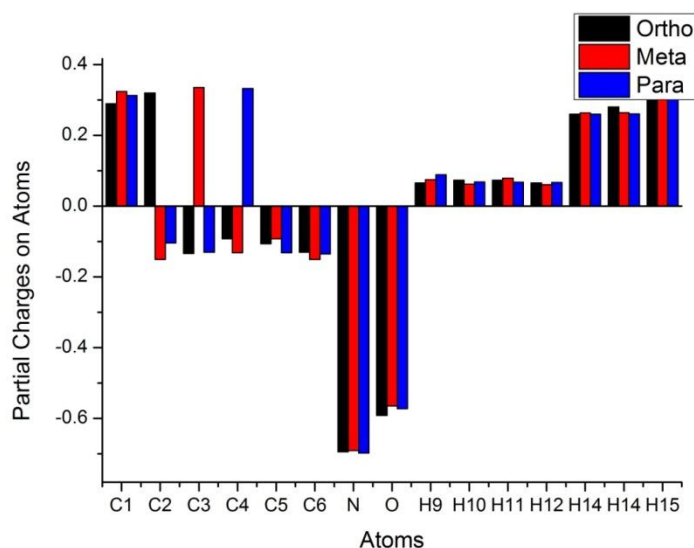


Figure 4

Dipole Moment

Ortho substitution has a net dipole moment of 1.18 debye with both the x and y directions showing an almost equal dipole. The meta substitution possesses a net dipole marginally lesser than the ortho with the major contribution from the x axis while y shows a negative dipole moment. The Para shows a maximum dipole of over 2. The disturbance is more along the y and significantly high along the x direction too indicating a high level distortion of the ring. The values are listed in Table 2

	X	Y	Z	TOTAL
Ortho	0.7643	0.9083	0.0000	1.1871
Meta	1.0422	-0.1892	0.0000	1.0592
Para	1.0055	2.0712	0.0000	2.3024

Table 2 : Dipole Moment in Debye

HOMO-LUMO

A. Geroge *et al.* [6] all have calculated the HOMO-LUMO energies giving a graphical representation of the HOMO and the LUMO. Here the HOMO-LUMO gap for the various isomers were calculated. The HOMO-LUMO gap for various isomers were as follows. Ortho -0.19942 Hartrees meta -0.20745 Hartrees para -0.18202 Hartrees. The graphical representation of the HOMO and LUMO are given below. The electronic state for all substitutions in A' and the HOMO values show antibonding characters. The graphical representation of HOMO for all substitutions is given in Fig.. 5 and that of LUMO in Fig.. 6

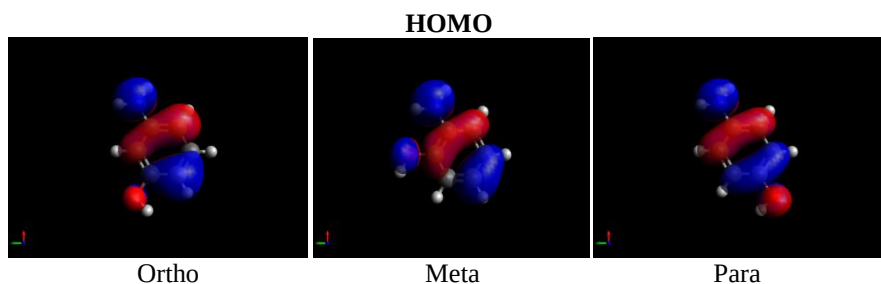


Figure 5

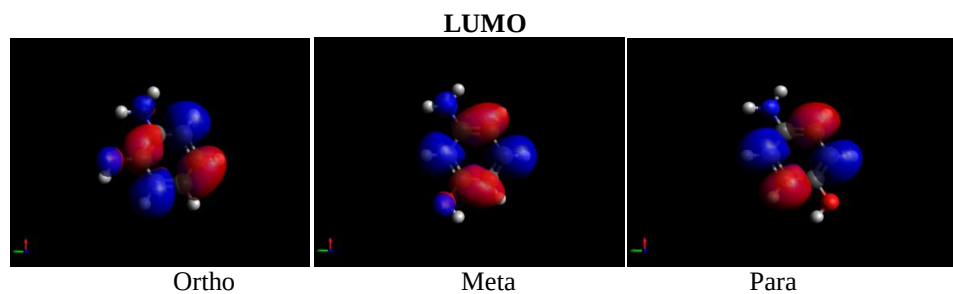


Figure 6

III. Conclusion

The present study is aimed at shedding light on the structural alterations, charge distribution and the orbital distribution of electrons which would raise out of the amine substitution at various position in the amine ring. Further studies on the thermal chemistry and the differences arising on further amine substitutions is proposed to be carried out.

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