

Chemical Activity Studies with Density Functional Theory

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Presentation/Paper Type: Oral / Tam Metin

Abstract – Density functional theory (DFT) is a computational quantum mechanical modelling method used in physics, chemistry and materials science to investigate the electronic structure (principally the ground state) of many-body systems, in particular atoms, molecules, and the condensed phases. DFT has been very popular for survey the electrophilic and nucleophilic nature of the molecules. The local and global chemical descriptions are identify the electrophilic and nucleophilic nature of the studied molecule well. The global chemical descriptors which are the HOMO-LUMO energy, energy gap (ΔE), ionization potential (I), the electron affinity (A), absolute electronegativity (χ), electrophilicity index (w), the absolute hardness (η) and softness (s) determine the chemical reactivity, kinetic stability, softness and hardness stability of the studied molecule. Also, local chemical activity parameters are determined with Fukui function analysis and molecular electrostatic potential. This study includes theoretical studies with DFT method which was given a complete description of the molecular and chemical activity of electrophilic and nucleophilic nature with local & global chemical activity calculations which which cannot be examined by experimental ways.

Keywords – Electrophilic & Nucleophilic Nature, hardness & softness parameters, local & global chemical activity

I. INTRODUCTION

The name of density functional theory (DFT) comes from the use of functionals of the electron density. DFT is among the most popular and versatile methods available in condensed-matter physics, computational physics, and computational chemistry. Firstly, the structure is optimized by DFT/B3LYP with selected bases set (6-311++G(d,p) which is presumed to be suitable for studied molecule by drawing the shape of the this molecule. The aim of theoretical calculations is obtaining chemical activity properties that cannot be obtained by experimental ways. Chemical activity calculations (electrophilic and nucleophilic regions) were determined by hardness/softness calculations, Fukui function (FFA) and molecular electrostatic potential (MEP) analyses. All theoretical calculations (chemical activity studies) were investigated by DFT/B3LYP/6-311++G(d,p) for compound of (E)-4-bromo-5-methoxy-2-((o-tolylimino)methyl)phenol I.

II. MATERIALS AND METHOD

The entire calculations for title compound I was performed at B3LYP levels included in the Gaussian 09W [1] package program together with 6-311++G(d,p) basis set function of the density functional theory (DFT) utilizing gradient geometry optimization. We have utilized the gradient corrected density functional theory with the three parameter hybrid functional (B3) for the exchange part and the Lee-Yang-Parr (LYP) correlation function, accepted as a cost effective approach for the computation of molecular structure, fukui function analysis, MEP and chemical activity descriptors (softness and hardness parameters) of optimized structure.

III. DISCUSSION

A. Molecular Electrostatic Potential (MEP)

The molecular electrostatic potential is related to the electronic density and is a very useful descriptor for determining the regions for electrophilic and nucleophilic reactions as well as hydrogen bonding interactions [2]. The different values of the electrostatic potential at the surface are represented by different colors (Fig. 1). Most electronegative and positive regions are represented by red and blue color respectively. Zero potential regions are represented by green color. In color grading scheme, the blue represents most electropositive (electron poor region), whereas the red corresponds to the most electronegative region (electron-rich region). From the MEP, that is evident that the negative charge covers the N, Br and O atoms and the positive region is over the methoxy and benzene ring groups. The more electronegativity in the hydroxyl group makes it the most reactive part of the molecule.

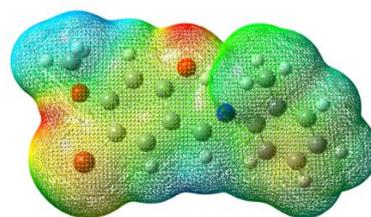


Fig. 1 Molecular electrostatic map (MEP) calculated with DFT/B3LYP/6-311++G(d,p) for compound I.

The chemical reactions or intermolecular interactions for chemical active moieties of title compound can play important roles. The MEP surfaces (global chemical descriptors), and local chemical descriptors (softness and hardness parameters) results are supported each other for identifying the electrophilic and nucleophilic attacks.

B. Fukui Function Analysis

The Fukui function (FF) is among the most basic and commonly used reactivity indicators. The FF for a molecule has been defined as the derivative of electron density with respect to the change of numbers of electrons, keeping the positions of nuclei unchanged [3]. The FF gives us information about a highly electrophilic/nucleophilic center in a molecule. The FF $f_k^+(r)$ for nucleophilic attack (r), $f_k^-(r)$ for electrophilic attack (r) and $f_k^0(r)$ for free radical attack (r) can be expressed as;

$$f_k^+(r) = q_k(r)(N + 1) - q_k(r)(N) \quad (1)$$

$$f_k^-(r) = q_k(r)(N) - q_k(r)(N - 1) \quad (2)$$

$$f_k^0(r) = \frac{1}{2}[q_k(r)(N + 1) - q_k(r)(N - 1)] \quad (3)$$

In these equations, q_k is the atomic charge (evaluated from NPA, electrostatic derived charge, etc.) at the k th atomic site is the neutral (N), anionic ($N + 1$) or cationic ($N - 1$) chemical species. Morell et al. [4] have recently proposed a dual descriptor $[\Delta f_k(r)]$, which is defined as the difference between the nucleophilic and electrophilic FF and is given by;

$$\Delta f_k(r) = [f_k^+(r) - f_k^-(r)]. \quad (4)$$

If $\Delta f_k(r) > 0$, then the site is favored for a nucleophilic, whereas if $\Delta f_k(r) < 0$, then the site may be favored for an electrophilic attack. In this situation, the dual descriptors $\Delta f_k(r)$ provide a clear difference between nucleophilic and electrophilic attack at a particular region with their sign and it provides positive value for site prone for nucleophilic attack and a negative value prone for electrophilic attack. From the calculated values, the reactivity order for the electrophilic case atoms (negative value *i.e.* $\Delta f_k(r) < 0$) was O1 > C7 > O2 > N1 > C13 > C15 > C8 > C3 > C5 > C9 > C4 > C10 > C6 > Br. On the other hand, for nucleophilic attack (positive value *i.e.* $\Delta f_k(r) > 0$) we can observe H1 > C14 > C12 > H13 > H10 > Br > H7B > H3 > H7C > H5 > H7A > H4 > H15A > H2 > H8 > H15C > H15B > C1 > C6 > C9 > C8 > C11 (Fig. 2).

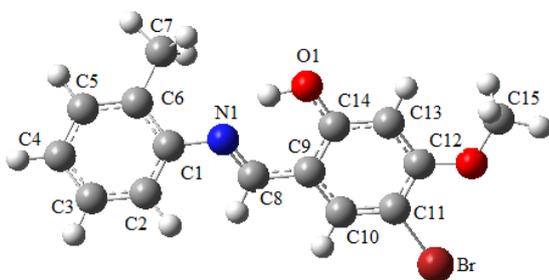


Fig. 2. Optimized structure of compound I with DFT/ B3LYP/6-311++G(d,p).

Position of reactive electrophilic sites and nucleophilic sites are accordance with the total electron density surface and chemical behavior. The behavior of molecules as electrophiles/nucleophiles during a reaction depends on the local behavior of molecules. The title compound was more electrophilic attack than nucleophilic attack and radical attack. Position of reactive electrophilic sites and

nucleophilic sites are well accordance with the total electron density surface and chemical behavior. Also, the same results of dominant electrophilic regions on O, N and Br atoms were obtained in all other chemical activity calculations.

C. Frontier Molecular Orbitals (FMOs) and Softness & Hardness Parameters

The frontier molecular orbitals (Highest Occupied Molecular Orbital HOMO and Lowest Unoccupied Molecular Orbital LUMO) determine the way how the molecule interacts with other species and support to characterize the chemical activity and kinetic stability of the molecule. They play an important role in the electrical, chemical and optical properties as well as in the UV-Vis spectra [5]. The HOMO is the orbital that primarily acts as an electron donor while the LUMO is the orbital that largely acts as the electron acceptor. The energy gap $\Delta(E)$ between the HOMO and LUMO is a very useful factor in determining the chemical reactivity of the molecule. The chemical reactivity and the hardness of molecules were derived from the HOMO and LUMO $\Delta(E)$ energy gap. The chemical reactivity descriptions of MO such as ionization potential (I), the electron affinity (A), the absolute electronegativity (χ), the absolute hardness (η) and softness (s) are defined as follows :

$$\chi = \frac{I+A}{2} \quad (5)$$

$$\mu = -\frac{I+A}{2} \quad (6)$$

$$\eta = \frac{I-A}{2} \quad (7)$$

$$s = \frac{1}{2\eta} \quad (8)$$

$$w = \frac{\mu^2}{2\eta} \quad (9)$$

Where I and A are ionization potential and electron affinity; $I = -E_{\text{HOMO}}$ and $A = -E_{\text{LUMO}}$ respectively. The (HOMO), (LUMO) and $\Delta(E)$ energies are -6.578 eV, -1.320 eV and 5.258 eV, respectively. If the molecule is hard, the $\Delta(E)$ is large and is usually connected with a lower chemical reactivity and high kinetic stability. Contrary to this if the molecule is soft, the $\Delta(E)$ is small and is usually connected with a high chemical reactivity and low kinetic stability. The soft molecule electron density can easily alter than the hard molecule. The electronegativity, chemical potential, chemical hardness, chemical softness and electrophilicity values are calculated with 3.949 eV, -3.949 eV, 3.258 eV, 0.153 eV and 2.393 eV, respectively. The large $\Delta(E)$ =5.258 showed that the compound I has high kinetic stability and low chemical reactivity. According to chemical reactivity descriptions results, high hardness (3.258 eV) and low softness (0.153 eV) values display lower intramolecular charge transfer.

IV. RESULTS

The theoretical chemical activity calculations which were not obtained by experimental ways, were discussed with DFT/B3LYP/6-311++G(d,p). The very high ΔE gap (hard molecule), result of global reactivity descriptors, chemical potential, chemical hardness and electrophilicity index show that the studied molecule has high kinetic stability and low chemical reactivity. Fukui function method, MEP, chemical activity parameters could be used for interpreting and predicting the reactive behavior of a wide variety of chemical systems and also their results were supporting each other about chemical active regions (electrophilic/nucleophilic attack). The compound I was more electrophilic attack than

nucleophilic attack and radical attack. Position of reactive electrophilic sites and nucleophilic sites are well accordance with the total electron density surface and chemical behavior. Also, the same results of dominant electrophilic regions on Br, O and N atoms were obtained in MEP result.

V. CONCLUSION

After a successful optimization with DFT/B3LYP/6-311++G(d,p) level basis set, the aim of computational method was obtained molecular and chemical properties that are not obtained by experimentally ways. The chemical reactions or intermolecular interactions for chemical active moieties of compound can play important roles. The compound I has high kinetic stability and low chemical reactivity with values of electronegativity (3.949 eV), chemical potential (-3.949 eV), chemical hardness (3.258 eV), chemical softness (0.153 eV) and electrophilicity (2.393 eV). The molecular MEP map showed that the negative potential sites (electrophilic attack) are on the electronegative atoms of Br, O and N atoms (intra molecular hydrogen bond sites) as well as the positive potential (nucleophilic attack) sites are around the inter molecular bond sites, methoxy group and hydrogen atoms. The MEP surface and chemical descriptors are supported each other for identifying the electrophilic and nucleophilic attacks.

ACKNOWLEDGMENT

Special thanks to Çiğdem Albayrak Kaştaş for his worthy contributions during the synthesis process.

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