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# QUANTUM CHEMICAL AND CORROSION INHIBITION STUDIES OF AN ORGANIC COMPOUND: 2, 5 DICHLOROANILINE

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**ABSTRACT**

Quantum chemical methods have already proven to be very useful in determining the molecular structure as well as elucidating the electronic structure and reactivity. Thus, it has become a common practice to carry out quantum chemical calculations in corrosion inhibition studies. Obvious correlations were found between corrosion inhibition efficiency and some quantum chemical parameters such as highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO) energy levels, HOMO–LUMO energy gap and electronic density etc. Once a correlation between the structure and activity or property is found, any number of compounds, including those not yet synthesized, can be readily screened employing computational methodology and a set of mathematical equations which are capable of representing accurately the chemical phenomenon under study. It is well known that organic compounds which act as inhibitors are rich in heteroatoms, such as sulphur, nitrogen, and oxygen. The present work focuses on the inhibition efficiency of 2, 5-dichloroaniline, which is a derivative of aniline. The investigation is performed using quantum chemical calculations conducted by means of the GAUSSIAN 03W and GUASSVIEW 3.0 set of programs. It is an attempt to find the correlation between the molecular structure of the compound and possible behaviour like corrosion inhibitors.

**Keywords:** Quantum chemical calculation, Corrosion inhibition, 2, 5-dichloroaniline, Molecular orbital, GAUSSIAN 03W and GUASSVIEW 3.0.



## INTRODUCTION

The study of corrosion processes and their inhibition by organic inhibitors is a very active field of research[1]. Many researchers report that the inhibition effect mainly depends on some physico-chemical and electronic properties of the organic inhibitor which relate to its functional groups, steric effects, electronic density of donor atoms, and orbital character of donating electrons, and so on[2-3]. The inhibiting mechanism is generally explained by the formation of a physically and/or chemically adsorbed film on the metal surface[4-5]. The damages by corrosion generate not only high costs for inspection, repairing and replacement, but in addition these constitute a public risk. Thus the necessity of developing novel substances that behaves like corrosion inhibitors. In general, the organic compounds have demonstrated a great effectiveness in inhibiting the watery corrosion of many metals and alloys. It has been demonstrated that the compounds that have nitrogen and sulfur in their structure provide a greater inhibition. The concept of assessing the efficiency of a corrosion inhibitor with the help of computational chemistry is to search for compounds with desired properties using chemical intuition and experience into a mathematically quantified and computerized form.

Quantum-chemistry calculations have been widely used to study the reaction mechanisms and to interpret the experimental results as well as to solve chemical ambiguities. This is an useful approach to investigate the mechanisms of reaction in the molecule and its electronic structure levels[6]. The structure and electronic parameters can be obtained by means of theoretical calculations using the computational methodologies of quantum chemistry.

The geometry of the inhibitor in its ground state, as well as the nature of their molecular orbitals, HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) are involved in the properties of activity of inhibitors.
The objective of this work is to present a theoretical study on the electronic and molecular structure of 2, 5-dichloroaniline obtained through quantum chemistry calculations carried out by the GAUSSIAN 03W program. In addition, we will attempt to find the correlation between the molecular structure of these compounds and their possible behavior as corrosion inhibitors.

**Quantum Chemical Parameters**
Quantum chemical methods and molecular modeling techniques enable the definition of a large number of molecular quantities characterizing the reactivity, shape, and binding properties of a complete molecule as well as of molecular fragments and substituents. The use of theoretical parameters presents two main advantages: firstly, the compounds and their various fragments and substituents can be directly characterized on the basis of their molecular structure only; and secondly, the proposed mechanism of action can be directly accounted for in terms of the chemical reactivity of the compounds under study[7]. Quantum chemically derived parameters are fundamentally different from experimentally measured quantities, although there is some natural overlap. Unlike experimental measurements there is no statistical error in quantum chemical calculations. There is inherent error however, associated with the assumptions required to facilitate the calculations. In most cases the direction but not the magnitude of the error is known. In using quantum chemistry-based parameters with a series of related compounds, the computational error is considered to be approximately constant throughout the series. The prominent quantum chemical parameters can be subdivided as follows:

**Atomic Charges**
All chemical interactions are either electrostatic (polar) or orbital (covalent). Electric charges in the molecule are obviously responsible for electrostatic interactions. The local electron densities or charges are important in many chemical reactions and for physico-chemical properties of compounds. Thus, charge-based parameters have been widely employed as chemical reactivity indices or as measures of weak intermolecular interactions. Despite its usefulness, the concept of a partial atomic charge is somewhat arbitrary, because it depends on the method used to delimit between one atom and the next. As a consequence, there are many methods for estimating the partial charges. Mulliken population analysis is mostly used for the calculation of the charge distribution in a molecule[8]. These numerical quantities are easy to obtain and they provide at least a qualitative understanding of the structure and reactivity of molecule[9]. Furthermore, atomic charges are used for the description of the molecular polarity of molecules.

**Molecular orbital energies**
Highest occupied molecular orbital energy ($E_{HOMO}$) and lowest unoccupied molecular orbital energy ($E_{LUMO}$) are very popular quantum chemical parameters. These orbitals, also called the frontier orbitals, determine the way the molecule interacts with other species. The HOMO is the orbital that could act as an electron donor, since it is the outermost (highest energy) orbital containing electrons. The LUMO is the orbital that could act as the electron acceptor, since it is the innermost (lowest energy) orbital that has room to accept electrons. According to the frontier molecular orbital theory, the formation of a transition state is due to an interaction between the frontier orbitals (HOMO and LUMO) of reactants[10]. The energy of the HOMO is directly related to the ionization potential and the energy of the LUMO is directly related to the electron affinity. The HOMO–LUMO gap, i.e. the difference in energy between the HOMO and LUMO, is an important stability index[11]. A large HOMO–LUMO gap implies high stability for the molecule in chemical reactions[12]. The concept of ‘‘activation hardness” has been also defined on the basis of the HOMO–LUMO energy gap. The qualitative definition of hardness is closely related to the polarizability, since a decrease of the energy gap usually leads to easier polarization of the molecule[13].

**Dipole moment (μ)**

The most widely used quantity to describe the polarity is the di-pole moment of the molecule[14]. Dipole moment is the measure of polarity of a polar covalent bond. It is defined as the product of charge on the atoms and the distance between the two bonded atoms. The total dipole moment, however, reflects only the global polarity of a molecule. For a complete molecule the total molecular dipole moment may be approximated as the vector sum of individual bond dipole moments.

**Energy**

The total energy calculated by quantum chemical methods is also a beneficial parameter. The total energy of a system is composed of the internal, potential, and kinetic energy. Hohenberg and Kohn proved that the total energy of a system including that of the many body effects of electrons (exchange and correlation) in the presence of static external potential (for example, the atomic nuclei) is a unique functional of the charge density[15]. The minimum value of the total energy functional is the ground state energy of the system. The electronic charge density which yields this minimum is then the exact single particle ground state energy.

## EXPERIMENTAL

In order to obtain the objective of this work, density functional theory (DFT) methods were used. These have become very popular in the last years. This is because they can reach exactitude similar to other methods in less time and with a smaller investment from the computational point of view. In agreement with the DFT, the energy of the fundamental state of a polielectronic system can be expressed through the total electronic density, and in fact the use of the electronic density instead of the wave function for the calculation of the energy constitutes the fundamental base of DFT[16-18]. All the calculations were done by means of the GAUSSIAN 03W program, using the B3LYP functional and a 6-31G* basis set[19-23]. The use of a small valence basis set like STO-3G* is justified on the light and spirit of a recent study on the performance of density functionals with this kind of basis sets[24].

## RESULTS AND DISCUSSION

The optimized molecular structure and HOMO–LUMO of the 2, 5-dichloroaniline are shown in Figures-1(a), 1(b) and 1(c).

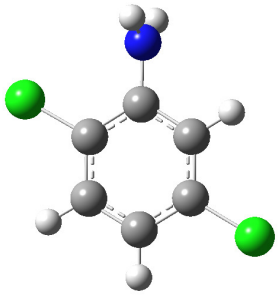

Fig.-1(a): The optimized molecular structure 2, 5-dichloroaniline

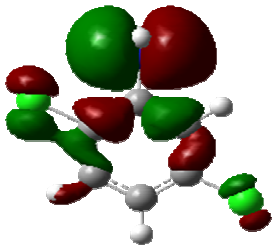

Fig.-1(b): HOMO of 2, 5-dichloroaniline

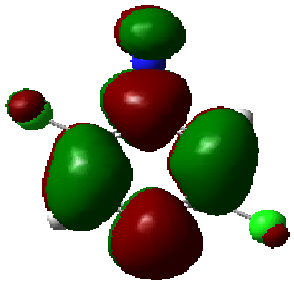

Fig.-1(c): LUMO of 2, 5-dichloroaniline

The dipole moment μ is another way to obtain data on the electronic distribution in a molecule and is one of the properties more used traditionally to discuss and to rationalize the structure and reactivity of many chemical systems[25]. The results are shown in Table-1.

Calculations of the HOMO–LUMO gap $(\Delta E = E_{LUMO} - E_{HOMO})$ were done as well as the global hardness h that is approximated as $\Delta E / 2$, and can be defined under the principle of chemical hardness and softness[26]. The parameters also provide information about the reactive behavior of molecules. In Table 1 the calculated total energies, the energies for orbitals HOMO and LUMO, $\Delta E$, η, and μ are reported for 2, 5-dichloroaniline. All these computational calculations have been performed in the gas phase.

Table-1: Molecular properties of 2, 5-dichloroaniline calculated with B3LYP/6-31G* chemistry model

| Total energy(a.u) | HOMO(eV) | LUMO(eV) | ΔE(eV) | η=ΔE/2(eV) | μ (debyes) |
|---|---|---|---|---|---|
| -1206.7880 | -0.238 | -0.024 | 0.262 | 0.131 | 0.9790 |

Moreover, MO level is the gap between the HOMO and LUMO energy levels for the studied molecule. As was reported, some atoms such as N have unoccupied d orbitals and so exhibit a tendency to obtain electrons; the electrons in the d orbitals can easily be offered because the applied force they affect is small[27-29]. Excellent corrosion inhibitors are considered to be such organic compounds which not only offer electrons to unoccupied d orbitals of metal surface to form coordinate covalent bond, but also can accept the free electrons from the surface of metal as well, by using their antibond orbital to form feedback bonds in turn.

Quantum chemistry calculation reveals that the substitution of (-$NH_2$) results in a great increase of HOMO energy level (and a great decrease of energy difference, i.e. LUMO–HOMO) obviously. The great increase of inhibition efficiency due to $NH_2$ substitution should arise from the great increase of HOMO level, implying the ability of organic molecule to offer free electrons to the metal surface. The lower the LUMO energy, the easier the acceptance of electrons from metal surface, which decreases HOMO–LUMO energy gap and improves the efficiency of inhibitor.

## CONCLUSION

Quantum chemistry calculation reveals that the substitution of $NH_2$ in 2, 5-dichloroaniline results in an increase of HOMO energy level. The great increase of inhibition efficiency due increase of HOMO level, implying the ability of organic molecule to offer free electrons to the metal surface. Efficiency of inhibitor compounds cannot be directly correlated to individual molecular parameters. A composite index of more than one descriptor quantum parameter should be considered to characterize the inhibition performance of the molecule. The correlation coefficient r between experimental and calculated inhibition efficiencies may be improved significantly if a systematic change in the structure of the compounds is considered to avoid overlapping of structural effects.

## REFERENCES

1. M. Bouayed, H. Rabaa, A. Srhiri, J.Y. Saillard and A. Ben Bachir, *Corros. Sci.,* **41**, 501 (1999).
2. M.A. Quraishi and R. Sardar, *Mater. Chem. Phys.,* **78**, 425(2002).
3. E. Stupnisek-Lisac, S. Podbrscek and T. Soric , *J. Appl. Electrochem.,* **24**, 779(1994).
4. F. Touhami, A. Aouniti, Y. Abed, B. Hammouti, S. Kertit, A. Ramdani and K.Elkacemi, *Corros. Sci.,* **42**, 929(2000).
5. L. Tang, X. Li, L. Li, G. Mu and G. Liu, *Surf. Coat. Technol*., **201**, 384(2006).
6. D. Wang, S. Li, Y. Ying, M. Wang, H. Xiao and Z. Chen, *Corros. Sci*., **41**, 191, (1999).
7. I.N. Levine, *Quantum Chemistry, Prentice Hall International, New Jersey,* (1991).
8. J.N. Murrell, S.F. Kettle and J.M. Tedder, *The Chemical Bond, John Wiley & Sons, Chichester,* (1985).
9. C. Grüber and V. Buss, *Chemosphere,* **19**, 1595(1989).
10. K. Fukui, *Theory of Orientation and Stereo selection, Springer-Verlag, New York,* (1975).
11. D.F.V. Lewis, C. Ioannides and D.V. Parke, *Xenobiotica*, **24**, 401(1994).
12. Z. Zhou and R.G. Parr, *J. Am. Chem. Soc.,* **112**, 5720(1990).
13. R.G. Pearson, *J.Org. Chem.,* **54**, 1423(1989).
14. O. Kikuchi, *Quant. Struct.-Act. Relat*., **6**, 179(1987).
15. P. Hohenberg and W. Kohn, *Phys. Rev.,* **136**, B864(1964).
16. J. Andres and J. Beltran, *Quantum Theory of Computational Chemistry, University press, Castellon delana, Espana,* (2000).
17. W. Yang and W.J. Mortier, *J. Am. Chem. Soc*., **108**, 5708(1986).
18. F. Mendez, M. Galvan, A. Garritz, A. Vela and J. Gazquez, *J. Mol. Struct*., **277**, 1981(1992).
19. M.J. Frisch, G.W. Trucks and H.B. Schlegel, G*AUSSIAN 03 Revision, B.05,Gaussian, Inc., Pittsburgh PA,* (2003).
20. C. Lee, W. Yang and R.G. Parr, *Phys. Rev*., **37**,785(1988).
21. A.D. Becke, *J. Chem. Phys*., **98**, 5648(1993).
22. W.J. Hehre, R.F. Stewart and J.A. Pople, *J. Phys. Chem.,* **51,** 2657(1969).
23. J.B. Collins, P.V.R. Schleyer, J.S. Binkley and J.A. Pople, *J. Chem. Phys*., **64**, 5142(1976).
24. E.N. Brothers and K.M. Merz Jr., *J. Phys. Chem.*, **A108**, 2904(2004).
25. V.S. Sastri, *Corrosion Inhibitors-Principles and Applications, Wiley, Chichester, England,* (1998)
26. J. Foresman, *Exploring Chemistry with Electronic Structure Methods, Gaussian, Inc., Pitssburgh, Pa,* (1996).
27. J.Cruz, L.M.Martınez-Aguilera, R.Salcedo and M.Castro, *Int. J.Quant.Chem.*, **85**, 546(2001).
28. I. Fleming, *Frontier Orbitals and Organic Chemical Reactions, Wiley, Chichester,* (1987).
29. S.L.Li, Y.G.Wang, S.H.Chen, R.Yu, S.B. Lei, H.Y.Ma and De X. Liu, *Corros. Sci*.,**41**, 1769 (1999).

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