RESEARCH ARTICLE

DFT Investigation of Corrosion Inhibition and Nonlinear Optical Behaviour of Phenylimidazolidin-4-One Derivative

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ABSTRACT: By using Density Functional Theory (DFT/B3LYP) some quantum chemical parameters of the previously synthesized molecule were calculated to determine the relationship between molecular structure and their inhibition efficiencies as corrosion inhibitors. The results of the quantum chemical calculations their inhibition effect are closely related to E_{HOMO}, E_{LUMO}, hardness, polarizability, dipole moment, and charges. The negative sign of the E_{HOMO} values and other kinetic and thermodynamic parameters indicated that the data obtained support the physisorption mechanism. The study has also extended to calculate the thermodynamic properties of the compound. The non-linear optical behavior of the molecule was investigated by the determination of the first hyperpolarizability. From the, result in it was seen that the molecule must act as an organic light-emitting diode.

KEYWORDS: imidazolidine, nonlinear optical, corrosion, electronegativity, polarizability, DFT,

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1. INTRODUCTION

Imidazolidinone is an organic molecule containing extended *pi*-conjugated electrons and characterized by large values of molecular first hyperpolarizability showing enhanced NLO properties. As known, the origin of non-linearity in organic molecules is significantly related to the presence of a delocalized p-electron system linking donor and acceptor groups, which amplifies the required asymmetric polarizability.[1] The NLO properties magnitude of molecules is dependent on the first-order hyperpolarizability. The NLO property of molecules and their hyperpolarizability have become an important field of extensive research [2-6].

Many heterocyclic compounds containing hetero atoms like N, O, S, have been reported to be effective inhibitors for the corrosion of steel in acid media by several authors [7,8]. The inhibition property of these compounds is recognized by their molecular structure. The planarity and the lone electron pairs in the heteroatoms are important features that determine the adsorption of these molecules on the metallic surface. Generally, organic inhibitor molecules might physically or chemically adsorb on a corroding metal [9, 10].

Quantum-chemistry calculations have been widely used to study the reaction mechanisms and interpret the experimental results as well as to solve chemical ambiguities. Theoretical investigations based on quantum chemical calculations have been proposed as a powerful tool for predicting several molecular parameters directly related to the corrosion inhibiting property of any chemical compound [11,12].

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. Electronic properties (e.g., the electron density, the dipole moment, partial charges on the atoms, etc) of a molecule inform about its reactivity. The electronic properties are influenced by the type of functional groups present in the molecule. Molecules that have atoms with lone pair of electrons (e.g., heteroatoms such as N, O, S, and P), *pi*-conjugate double bond, and aromatic systems are preferred as corrosion inhibitors [13]. In our previous work, we have studied the synthesis and characterization of the titled compound [14].

Therefore, one of the objectives of the present work is to extend the study of the nonlinear optical and inhibitory properties of 5-((1*H*-indol-3-yl)methyl)-3-((2,4-dinitrophenyl) amino)-2-phenyl imidazolidine-4-one using DFT calculations to look for parameters that characterize these behaviors of the molecule.

The anticorrosive properties of organic molecules are mainly depending on their ability to get on the metal surface which consists of the replacement of water molecules at the corroding interface [15,16]. Nowadays, research and

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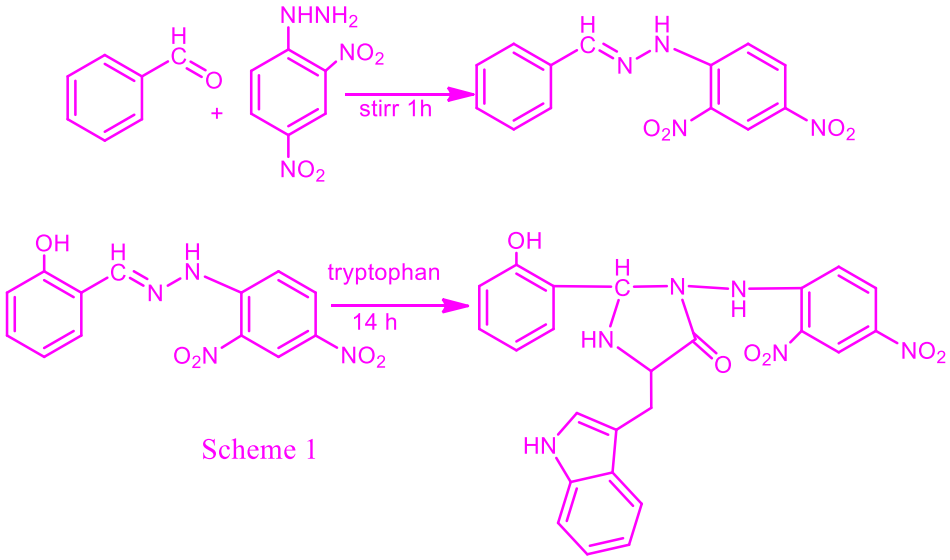
development of new and more effective organic inhibitors have been of great importance. Therefore, understanding of the electronic properties of the interaction between the inhibitor molecules and the metal surface is our next objective [17].

2. MATERIALS AND METHODS

The compound understudy was synthesized in our laboratory. Its synthetic trail and the structure confirmation were reported earlier [14].



Scheme 1

2.1. COMPUTATIONAL APPROACH

To provide complete information regarding the structural parameters of the studied molecule DFT-B3LYP with 6-31G(d,p) basis set correlation functional calculations have been carried out. The calculations of geometrical parameters in the ground state were performed using the Gaussian 09W program[18].

Three basis sets, viz., 6-31G(d,p) was utilized for the calculations. Among the molecular properties that are well reproduced by DFT/B3LYP include bond lengths and angles, the energy of the highest occupied molecular orbital (HOMO), the energy of the lowest unoccupied molecular orbital (LUMO), electronegativity, global hardness and softness, electron affinity, ionization potential, the first-order hyperpolarizability (β), dipole moment (μ), softness(*S*), electrophilicity index(*ω*), fractions of electrons transferred(ΔN) and back donation (ΔE) and the Mulliken charges, etc. These quantities are often defined following Koopmans' theorem [19,20].

Electronegativity (χ) is the measure of the power of an electron or group of atoms to attract electrons towards itself [21] and according to Koopman's theorem; it can be estimated by using the following equation:

$$\chi \cong -\tfrac{1}{2}\,(E_{HOMO} + E_{LUMO}) \qquad (1)$$

Where E_{HOMO} is the energies of the highest occupied molecular orbital (HOMO) and E_{LUMO} is the energy of the lowest unoccupied molecular orbital (LUMO).

Global hardness (η) measures the resistance of an atom to a charge transfer [22] and it is estimated using the equation:

$$\eta \cong -\tfrac{1}{2}\,(E_{HOMO} - E_{LUMO}) \qquad (2)$$

Global softness (σ) describes the capacity of an atom or group of atoms to receive electrons and it is estimated by using the equation:

$$\sigma = 1/\eta \cong -2/(E_{HOMO} - E_{LUMO}) \qquad (3)$$

where 'η' is the global hardness values

Global electrophilicity index (ω) is estimated by using the electronegativity and chemical hardness parameters through the equation:

$$\omega = \chi^2/2\eta \qquad (4)$$

A high value of electrophilicity describes a good electrophile while a small value of electrophilicity describes a good nucleophile.

Electron affinity (EA) is related to E_{LUMO} through the equation:

$$EA \cong -E_{LUMO} \qquad (5)$$

Ionization potential (IP) is related to the E_{HOMO} through the equation:

$$IP \cong -E_{HOMO} \quad (6)$$

The electronic flow will happen from the molecule with the lower electronegativity (the organic inhibitor) to higher value (the metallic surface) for a reaction of two systems with different electronegativity, until the chemical potential becomes equalized [23]. Therefore the ΔN from the inhibitor molecule to the metallic atom was calculated using Pearson electronegativity scale [24].

The change in the number of electrons transferred is estimated through the equation

$$\Delta N = \chi Fe - \chi inh / 2(\eta Fe - \eta inh) \quad (7)$$

where χ_{Fe} and χ_{inh} denote the absolute electro negativity of iron and the inhibitor molecule respectively; η_{Fe} and η_{inh} denote the absolute hardness of iron and the inhibitor molecule respectively. The values of χ_{Fe} and η_{Fe} are taken as $7eVmol^{-1}$ and $0eVmol^{-1}$ respectively [25].

An electronic back donation process might be occurring governing the interaction between the metal surface and inhibitor molecule according to the simple charge transfer model for donation and back donation of charges[26]. If both processes occur charge transfer to the molecule and back donation from the molecule, the energy change is directly related to the hardness of the molecule.

$$\Delta E_{Back\text{-}donation} = \eta/4. \quad (8)$$

The $\Delta E_{Back\text{-}donation}$ shows that when $\eta>0$ and $\Delta E_{Back\text{-}donation}<0$ the charge transfer to a molecule, followed by a back-donation from the molecule, is energetically preferred. It is possible to compare the stabilization among inhibiting molecules since there will be an interaction with the same metal. It will decrease as hardness increases.

$$\text{Electronic chemical potential } (\mu) = 1/2(ELUMO + EHOMO) \quad (9)$$

The NLO property of the material is theoretically calculated using the total static dipole moment (μ), mean polarizability (α_0) and the first order hyperpolarisability (β_0) with respect to x, y, z components using the equation given.

$$\mu = (\mu x2 + \mu y2 + \mu z2)1/2 \quad (10)$$

$$\alpha 0 = 1/3\,(\alpha XX + \alpha YY + \alpha ZZ) \quad (11)$$

$$\beta 0 = (\beta x2 + \beta y2 + \beta z2)1/2 \quad (12)$$

$$\beta x^2 = (\beta_{XXX} + \beta_{XYY} + \beta_{XZZ})^2,\ \beta y^2 = (\beta_{YYY} + \beta_{YXX} + \beta_{YZZ})^2,$$
$$\beta z^2 = (\beta_{ZZZ} + \beta_{ZXX} + \beta_{ZYY})^2 \quad (13)$$

The results obtained from the calculations were tabulated (Table 5)and the values were compared with that of urea ($0.11x10^{-30}$esu)[27] since it is one of the molecules used in the study of the NLO properties of the molecules. And the values obtained for urea were used as the threshold value for the compounds. Gaussian outputs are reported in atomic units, so the calculated values were converted to esu [α (1au= $0.1482x10^{-24}$esu) β (1au=$8.639x10^{-30}$esu)].

3. RESULTS & DISCUSSION

The compound under study is 5-((1*H*-indol-3-yl) methyl) -3-((2,4- dinitrophenyl)amino)-2-phenylimidazolidin-4-one shown in Fig 1

The geometry optimization of compound (I) was performed using the density functional theory (DFT) method with a 6-31G(d,p) basis set. The optimized structure and the scheme of numbering the atom of the compound under study are represented in figure 2.

The optimized bond lengths and angles for the thermodynamically preferred geometry were determined at B3LYP/6-31g(d,p) levels are listed in Tables 1&2 following the atom numbering scheme of the molecule shown in Figure 2. From the table, it is concluded that the molecule is which suggests that molecule is planar.

3.2. Mulliken charge analysis

The Mulliken procedure is the most common population analysis technique. In population analysis, the electrons in each molecular orbital are partitioned to each atom based on the probability that the electron is in an orbital on that atom at the end of the calculation the fractional occupation for each molecular orbital is summed to get a total atomic electron population for each atom. Mulliken charges arising from the Mulliken population analysis provide a mean of estimating partial atomic charges from calculations carried out by the methods of computational chemistry, particularly those based on the linear combination of atomic orbitals molecular orbital method [28,29]. Effective atomic charge calculations have an important role in the application of quantum chemical calculation to the molecular system because atomic charges affect dipole moment, molecular polarizability, electronic structure, acidity–basicity behavior, and a lot of properties of molecular systems.

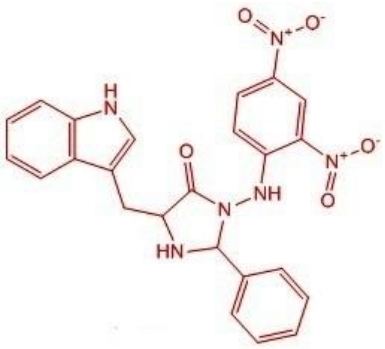


Figure 1

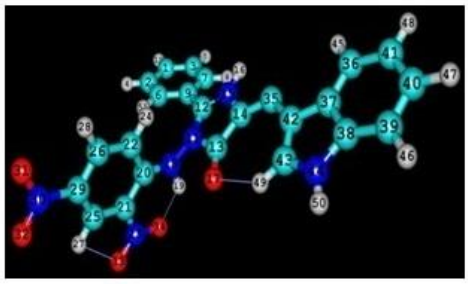


Figure 2 optimized geometry of the molecule

Table 1 The calculated bond length

atoms	bond length	atoms	bond length	atoms	bond length	atoms	bond length	atoms	bond length
C1-C2	1.396	C7-C8	1.086	C12-N15	1.322	C20-C21	1.425	C36-C41	1.399
C1-C3	1.397	C7-C9	1.408	C13-C14	1.45	C20-C22	1.415	C37-C42	1.392
C2-C6	1.392	C9-C12	1.458	C13-O17	1.225	C21-C25	1.395	C39-C40	1.463
C3-C5	1.085	N11-C12	1.375	C14-N15	1.421	C22-C26	1.082	C40-C41	1.393
C3-C7	1.391	N11-C13	1.46	C14-C35	1.391	C35-C42	1.379	C42-C43	1.407
C6-C9	1.407	N11-C18	1.379	N18-C20	1.376	C36-C37	1.42	C43-N44	1.358

Table 2 The calculated bond angle

In between	angle	In between	angle	In between	angle	In between	angle
A(2-1-3)	119.8	A(12-11-18)	124.5	A(18-20-22)	120.5	A(36-37-38)	119
A(1-2-6)	120.5	A(11-12-15)	105.5	A(21-20-22)	117.2	A(36-37-42)	132.8
A(1-3-7)	120.2	A(13-11-18)	122.4	A(20-21-23)	122.5	A(36-41-40)	121.2
A(2-6-9)	120.1	A(11-13-14)	104	A(20-21-25)	121.2	A(38-37-42)	108.1
A(3-7-9)	120.4	A(11-18-20)	119	A(20-22-26)	121.6	A(37-38-39)	122.9
A(6-9-7)	119.1	A(12-15-14)	115.1	A(21-25-29)	119.4	A(37-38-44)	106.7
A(6-9-12)	121.8	A(13-14-15)	104	A(22-26-29)	119.6	A(37-42-43)	104.7
A(7-9-12)	119.1	A(13-14-35)	139.4	A(25-29-26)	121.1	A(39-38-44)	130.4
A(9-12-11)	128.5	A(15-14-35)	116.6	A(35-42-37)	123.1	A(38-39-40)	116.9
A(9-12-15)	125.9	A(14-35-42)	122.6	A(35-42-43)	132.2	A(38-44-43)	110.3
A(12-11-13)	111.3	A(18-20-21)	122.2	A(37-36-41)	118.8	A(39-40-41)	121.1
						A(42-43-44)	110.2

The Mulliken charges of each atom for optimized Geometry of molecule under investigation were calculated and gathered in Table 3. As seen from Table 3 that C_1, C_2, C_3, C_6, C_7, N_{11},N_{15},O_{17},N18, C_{22}, C_{25}, C_{26},O_{31},O_{32},O_{33},O_{34},C_{35},C_{36}, C_{39}, C_{40}, C_{41}, C_{42} and N_{44} atoms exhibit a negative charge which is donor atoms. All the other carbon atoms exhibit a positive charge, these acts as acceptor atoms. All the H atoms have positive charges. N_{23} and O_{30} atoms also exhibit a positive charge, which accept electrons. All the other nitrogen and all the oxygen atoms in the molecule that possess negative charge were donor atoms. These atoms may also play an important role in the biological activity of the compound [30].

Table 3. The calculated Mulliken charge values

atom	charge	atom	charge	atom	charge	atom	charge	atom	charge	atom	charge
C1	-0.0732	H10	0.1052	H19	0.3241	H28	0.1519	C37	0.0850	H46	0.0767
C2	-0.0946	N11	-0.4738	C20	0.3664	C29	0.2350	C38	0.2653	H47	0.0783
C3	-0.0896	C12	0.5374	C21	0.2162	N30	0.3859	C39	-0.0978	H48	0.0763
H4	0.1066	C13	0.5358	C22	-0.1168	O31	-0.3977	C40	-0.1058	H49	0.1617
H5	0.1065	C14	0.1568	N23	0.3854	O32	-0.3954	C41	-0.0958	H50	0.2660
C6	-0.0887	N15	-0.5586	H24	0.1272	O33	-0.3806	C42	-0.0525	H51	0.1030
C7	-0.1153	H16	0.2765	C25	-0.1058	O34	-0.4342	C43	0.0960		
3H8	0.1037	O17	-0.5436	C26	-0.0791	C35	-0.2221	N44	-0.6055		
C9	0.1016	N18	-0.4477	H27	0.1843	C36	-0.1333	H45	0.0925		

3.3. Frontier molecular orbital analysis

FMO analysis is a physical property used to determine, ability to absorb light, electronic as well as optical properties of organic compounds[31]. In molecular interaction, the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) play the key role. HOMO is the orbital that can donate electrons and its energy corresponds to ionization potential (I. P.), while LUMO has electrons accepting ability, and its energy corresponds to an electron affinity (E. A.). HOMO-LUMO surfaces of molecules shown in Figure 3.

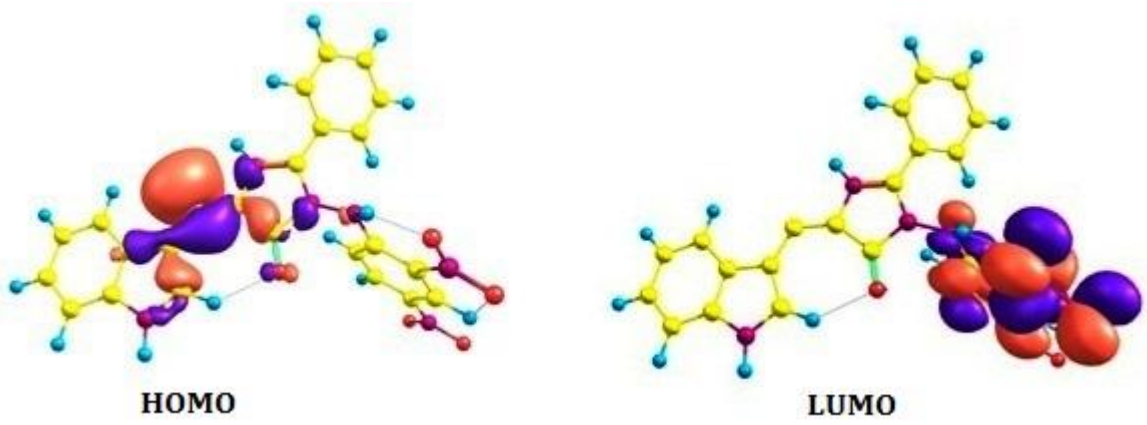


Figure 3

The calculated parameters that can be expressed through HOMO and LUMO orbital energy are listed in Table 4.

3.4. Thermodynamic parameters

The dipole moment is (μ in Debye) is another important electronic parameter that provides information on the polarity and the reactivity indicator of the molecule. The calculated dipole moment of the compound is 5.9254.The high value of dipole moment results from stronger intermolecular interactions and high reactivity.

3.5. Anti-corrosive analysis

The higher values of E_{HOMO} indicate an increase for the electron donor and this means a better inhibitory activity with increasing adsorption of the inhibitor on a metal surface, whereas E_{LUMO} indicates the ability to accept electron of the molecule. The adsorption ability of the inhibitor to the metal surface increases with increasing of E_{HOMO} and decreasing of E_{LUMO}. The HOMO and LUMO orbital energies and relationships between HOMO-LUMO orbital energies of the molecule were calculated. Here it is very clear that the

inhibition efficiency has a good correlation with EHOMO and ELUMO.

The dipole moment (μ) of a molecule is another important electronic parameter which provides the information on the polarity and the reactivity indicator. The calculated results show that the high value of dipole moment 5.9254 Debye were found. From here, it can assume that the adsorption of inhibitor onto the metallic surface will be stronger, and thus the corresponding inhibition efficiencies.

The number of electrons transferred (ΔN) indicates the tendency of a molecule to donate electrons. The higher the value of ΔN, the greater is the tendency of a molecule to donate electrons to the electron poor species. In the case of corrosion inhibitors the higher value of ΔN implies a greater tendency to interact with the metal surface [32].

Values of Δ*N* 2.0513 show that the inhibition efficiency resulting from electron donation agrees with Lukovit's study [33]. If Δ*N* < 3.6, the inhibition efficiency increases by increasing the electron-donating ability of these inhibitors to donate electrons to the metal surface. The results indicate that Δ*N* values are in good agreement with Lukovit's study. So in the experimental studies also the molecule may act as a good anti-corrosive agent.

This result implies good disposition of studied molecule to donate their electrons leading to increase their adsorption on the metal surface and to increase their inhibition efficiencies.

Table 4 The FMO parameters

Molecular Property	B3LYP/6-31G(d,p)
E_{HOMO}	-4.5672eV
E_{LUMO}	-2.9990eV
Energy gap	1.5682 eV
Ionization potential (IP)	4.5672
Electron affinity(EA)	2.9990
Global hardness(η)	0.7841
Chemical softness(s)	1.2753
Chemical potential(μ)	-3.7831
Global electrophilicity(ω)	9.1263
Total energy E	-1628.5568
$\Delta E_{Back\ donation}$	0.1960
Electronegativity χ	3.7831
The fraction of electrons transferred (ΔN)	2.0513

Table 5 NLO parameters

μ(Dipole moment)	α_0 (esu)	β (esu)	μ(Dipole moment)	βurea (esu)
5.9254Debye	$29.7855X10^{-2}$	$2.4410X10^{-27}$	1.3732 Debye	0.3728×10^{-30}

3.6. Non-linear optical effects

The interactions of electromagnetic radiation in some molecules can give a non-linear optical (NLO) effect. To study the NLO properties of a molecule the value of a urea molecule which is a prototypical molecule is used as a threshold value for comparison. The Mean polarizability α_0 *is* $29.7855X10^{-24}$esu and the first hyperpolarizability of the title molecule is found to be $2.4410X10^{-27}$ esu. It greater than the urea [μ and β of urea are 1.3732 Debye and $0.3728\times10^{-30}cm^5$/esu] and from the resultant values, we identified that 5-((1*H*-indol-3-yl)methyl)-3-((2,4-dinitrophenyl)amino)-2-phenyl imidazolidine-4-one possess comparatively good NLO property indicating that this might a good OLED material.

4. CONCLUSION

The optimized geometry parameters such as bond angle, bond length, of the previously synthesized 5-((1*H*-indol-3-yl)methyl)-3-((2,4-dinitrophenyl)amino)-2-phenyl imidazolidine-4-one were calculated using Gaussian 09 software by DFT method. Various quantum chemical

parameters such as dipole moment (μ), energy difference (ΔE), softness (S) and global hardness (η), highest occupied molecular orbital (EHOMO), and lowest occupied molecular orbital (ELUMO) has been calculated to elucidate the adsorption and corrosion inhibition behavior of the molecules. The anticorrosive ability of the molecule was established. The Nonlinear optical character of the same was determined from dipole moment and hyperpolarizability values.

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