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MATHEMATICS

PREDICTION OF CORROSION INHIBITION AND NONLINEAR OPTICAL BEHAVIOUR OF 5-((1H-INDOL-3-YL) METHYL) -3-((2,4- DINITROPHENYL)AMINO)-2-PHENYLIMIDAZOLIDIN-4-ONE USING DFT METHOD

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ABSTRACT

By using Density Functional Theory (DFT/B3LYP) some quantum chemical parameters of the previously synthesised molecule was 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 EHOMO, ELUMO, hardness, polarizability, dipole moment and charges. The negative sign of the EHOMO values and other kinetic and thermodynamic parameters indicated that the data obtained support physisorption mechanism. The study has also extended to calculate the thermodynamic properties of the compound. Non linear optical behavior of the molecule was investigated by the determination of first hyperpolarizability. From the result it was seen that the molecule must act as organic light emitting diode.

KEYWORDS: Imidazolidine, Nonlinear Optical, Corrosion, Electronegativity, Polarizability

INTRODUCTION

Imidazolidinone is an organic molecule containing extended □-conjugated electrons and characterized by large values of molecular first hyperpolarisability showing enhanced NLO properties. As known, the origin of non-linearity in organic molecules is significantly related to the presence of delocalized p-electron system linking donor and acceptor groups, which amplify the required asymmetric polarizability.[1] The NLO properties magnitude of molecules is dependent on the first-order hyperpolarisability. The NLO property of molecules and their hyperpolarisability 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. The inhibition property of these compounds is recognized to their molecular structure. The planarity and the lone electron pairs in the hetero atoms 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. [7,8]

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. Theoretical investigations based on quantum chemical calculations have been proposed as a powerful tool for predicting a number of molecular parameters directly related to the corrosion inhibiting property of any chemical compound.[9,10]

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 informs about its reactivity. The electronic properties are influenced by the type of the functional groups present in the molecule. Molecules that have atoms with lone pair of electrons (e.g., hetero atoms such as N, O, S and P), □ conjugate double bond and aromatic systems are preferred as corrosion inhibitors11. In our previous work, we have studied synthesis and characterization of the titled compound[18].

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

EXPERIMENTAL

The compound under study was synthesised in our laboratory. Its synthetic trail and the structure confirmation were reported earlier[24].

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[17].

Threebasisset,viz., 6-31G(d,p) wasutilizedfor thecalculations.Among

themolecularpropertiesthatarewellreproduced by DFT/B3LYPincludebond lengths and angles, the energy ofthehighestoccupiedmolecularorbital(HOMO),energy ofthelowestunoccupiedmolecular orbital (LUMO),electronegativity,global hardnessand softness,electronaffinity, ionisation potential, the first-order hyperpolarisability (β), dipole moment (μ), ,softness(*S*) ,electrophilicity index(*ω)*,fractions of electrons transferred(ΔN) and back donation (ΔE) and the Mulliken charges, etc.ThesequantitiesareoftendefinedfollowingKoopmans't heorem[12,13].

Electronegativity(χ)is themeasureofthepowerofanelectronorgroupofatomstoattr actelectronstowardsitself[14]and accordingtoKoopman'stheorem; it can beestimated byusingthe followingequation:

$\chi \cong -\frac{1}{2}(E_{HOMO}+E_{LUMO})$ (1)

WhereE_{HOMO}istheenergiesofthehighestoccupiedmolecu larorbital(HOMO)andE_{LUMO} is the energyof thelowest unoccupied molecularorbital (LUMO).

Globalhardness(η) measuresthe resistanceofanatomtoacharge transfer [15]anditis estimatedusingtheequation:

$\eta \cong -\frac{1}{2}(E_{HOMO}- E_{LUMO})$ (2)

Globalsoftness(σ)describesthecapacityofanatom orgroupofatomstoreceiveelectrons and itis estimated byusingthe equation:

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

whereηis theglobal hardness values

Globalelectrophilicityindex (ω)isestimated byusingtheelectronegativityandchemical hardness parameters through theequation:

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

Ahighvalueofelectrophilicity describesagoodelectrophilewhileasmallvalueof electrophilicitydescribesagood nucleophile.

Electron affinity(EA)isrelated to E_{LUMO}throughthe equation:

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

Ionization potential (IP) is related to theE_{HOMO}through theequation:

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

The changein thenumber of electrons transferredis estimated through theequation

$\Delta N = \chi_{Fe} - \chi_{inh} / 2(\eta_{Fe} - \eta_{inh})$ (7)

whereχ_{Fe} andχ_{inh}denotetheabsoluteelectronegativityofironandthein hibitormolecule respectively;η_{Fe}andη_{inh}denotetheabsolute hardnessofironandthe inhibitormoleculerespectively. The values of χ_{Fe} and η_{Fe} are taken as 7 $eVmol^{-1}$ and 0 $eVmol^{-1}$ respectively [16].

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. If both processes occur charge transfer to the molecule and back donation from the molecule, energy change is directly related to the hardness of the molecule.

$\Delta E_{Backdonation} = \eta/4.$ (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 increase.

Electronic chemical potential (μ) = $1/2(E_{LUMO} + E_{HOMO})$ (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. $\mu = (\mu x^2 + \mu y^2 + \mu z^2)^{1/2}$ (10)

$\alpha_0 = 1/3\ (\alpha_{XX} + \alpha_{YY} + \alpha_{ZZ})$ (11)

$\beta_0 = (\beta x^2 + \beta y^2 + \beta z^2)^{1/2}$ (12)

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

The results obtained from the calculations were tabulated and the values were compared with that of urea ($0.11x10^{-30}$esu)[13] , since it is one of the molecules used in the study of the NLO properties of the molecules. And the values obtained for urea was 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)].

RESULTS AND 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

Figure 1

OPTIMISED GEOMETRICAL PARAMETERS

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 compound under study are represented in figure

2.

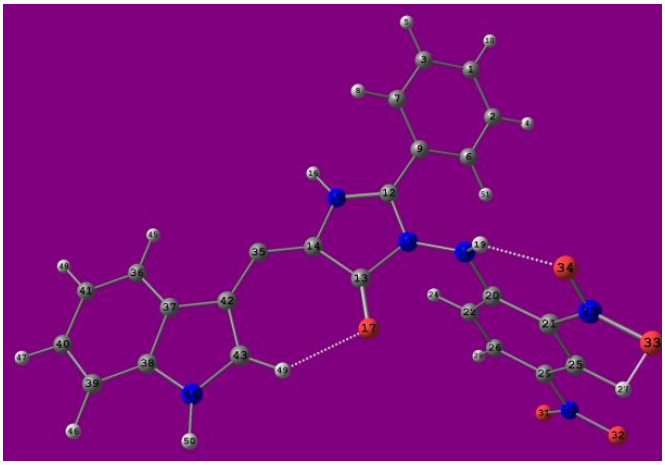


Figure 2Optimised Geometry Of The Molecule

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

Table 1. The calculated bond length

atoms	bond length	atoms	bond length	atoms	bond length	atoms	bond length	atoms	bond length
R(1-2)	1.396	R(9-12)	1.458	R(18-20)	1.376	R(26-29)	1.401	R(39-40)	1.393
R(1-3)	1.397	R(11-12)	1.375	R(20-21)	1.425	R(29-30)	1.463	R(39-46)	1.086
R(1-10)	1.085	R(11-13)	1.46	R(20-22)	1.415	R(30-31)	1.232	R(40-41)	1.408
R(2-4)	1.085	R(11-18)	1.379	R(21-23)	1.459	R(30-32)	1.231	R(40-47)	1.086
R(2-6)	1.392	R(12-15)	1.322	R(21-25)	1.395	R(35-42)	1.42	R(41-48)	1.086
R(3-5)	1.085	R(13-14)	1.45	R(22-24)	1.082	R(36-37)	1.399	R(42-43)	1.407
R(3-7)	1.391	R(13-17)	1.225	R(22-26)	1.379	R(36-41)	1.392	R(43-44)	1.358
R(6-9)	1.407	R(14-15)	1.421	R(23-33)	1.226	R(36-45)	1.085	R(43-49)	1.081
R(6-51)	1.083	R(14-35)	1.391	R(23-34)	1.245	R(37-38)	1.411	R(44-50)	1.009
R(7-8)	1.086	R(15-16)	1.013	R(25-27)	1.081	R(37-42)	1.463	R(17-49)	2.146
R(7-9)	1.408	R(18-19)	1.019	R(25-29)	1.382	R(38-39)	1.396	R(19-34)	1.842
				R(26-28)	1.083	R(38-44)	1.396	R(27-33)	2.318

Table 2. The calculated bond angle

In between	angle	In between	ngle	In between	angle	In between	angle	In between	angle	In between	angle
	119.8	A(8-7-9)	19.9	A(13-14-35)	119.4	A(21-23-34)	118.5	A(29-30-32)	117.8	A(38-39-40)	116.9
A(2-1-10)	120.1	A(7-9-12)	19.1	A(13-17-49)	107.4	A(21-25-27)	119.8	A(31-30-32)	124.9	A(38-39-46)	121.8
A(1-2-4)	120.1	A(9-12-11)	28.5	A(15-14-35)	116.6	A(21-25-29)	119.4	A(35-42-37)	123.1	A(38-44-43)	110.3
A(1-2-6)	120.5	A(9-12-15)	25.9	A(14-15-16)	118.1	A(24-22-26)	119.9	A(35-42-43)	132.2	A(38-44-50)	124.9
A(3-1-10)	120.1	A(12-11-13)	21.3	A(14-35-42)	122.6	A(22-26-29)	121.2	A(37-36-41)	118.8	A(40-39-46)	121.3
A(1-3-5)	120.2	A(12-11-18)	24.5	A(19-18-20)	114.7	A(22-26-29)	119.6	A(37-36-45)	119.2	A(39-40-41)	121.1
A(1-3-7)	120.2	A(11-12-15)	25.5	A(18-19-34)	129.5	A(33-23-34)	123.1	A(36-37-38)	119	A(39-40-47)	119.3
A(4-2-6)	119.4	A(13-11-18)	22.4	A(18-20-21)	122.2	A(23-33-27)	89.1	A(36-37-42)	132.8	A(41-40-47)	119.5
A(2-6-9)	120.1	A(11-13-14)	104	A(18-20-22)	120.5	A(23-34-19)	109.3	A(41-36-45)	122	A(40-41-48)	119.1
A(2-6-51)	119.8	A(11-13-17)	20.8	A(21-20-22)	117.2	A(27-25-29)	120.9	A(36-41-40)	121.2	A(42-43-44)	110.2
A(5-3-7)	119.6	A(11-18-19)	16.5	A(20-21-23)	122.5	A(25-27-33)	96.5	A(36-41-48)	119.7	A(42-43-49)	127.9
A(3-7-8)	119.7	A(11-18-20)	119	A(20-21-25)	121.2	A(25-29-26)	121.1	A(38-37-42)	108.1	A(44-43-49)	121.9
A(3-7-9)	120.4	A(12-15-14)	15.1	A(20-22-24)	118.5	A(25-29-30)	119.3	A(37-38-39)	122.9	A(43-44-50)	124.8
A(9-6-51)	120.1	A(12-15-16)	26.7	A(20-22-26)	121.6	A(26-26-29)	119.3	A(37-38-44)	106.7	A(43-49-17)	135.2
A(6-9-7)	119.1	A(14-13-17)	35.3	A(23-21-25)	116.3	A(26-29-30)	119.6	A(37-42-43)	104.7		
A(6-9-12)	121.8	A(13-14-15)	104	A(21-23-33)	118.4	A(29-30-31)	117.3	A(39-38-44)	130.4		

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 [19]. Mulliken charges arising from the Mulliken population analysis provides 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 [20,21]. Effective atomic charge calculations have an important role in the application of quantum chemical calculation to molecular system because of atomic charges effect dipole moment, molecular polarizability, electronic structure, acidity–basicity behavior and a lot of properties of molecular systems.

The Mulliken charges of each atom for optimized Geometry of molecule under investigation were calculated and gathered in Table 3.

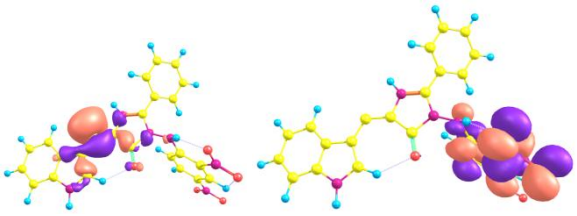
Table 3.The calculated Mulliken charge values

atom	charge	atom	charge	atom	charge	atom	charge	atom	charge	atom	charge
C1	-0.07323	H10	0.105235	H19	0.324179	H28	0.151887	C37	0.084969	H46	0.07673
C2	-0.09464	N11	-0.47386	C20	0.366471	C29	0.235043	C38	0.265297	H47	0.078336
C3	-0.08957	C12	0.53742	C21	0.216171	N30	0.385912	C39	-0.09784	H48	0.076299
H4	0.106605	C13	0.358854	C22	-0.11681	O31	-0.39766	C40	-0.10581	H49	0.161672
H5	0.106561	C14	0.15689	N23	0.385386	O32	-0.3954	C41	-0.0958	H50	0.266015
C6	-0.08873	N15	-0.5586	H24	0.127223	O33	-0.38062	C42	-0.05249	H51	0.102994
C7	-0.11532	H16	0.27654	C25	-0.10581	O34	-0.43421	C43	0.095956		
H8	0.103734	O17	-0.54365	C26	-0.07906	C35	-0.2221	N44	-0.60548		
C9	0.101567	N18	-0.44779	H27	0.18429	C36	-0.13331	H45	0.092553		

As seen from Table 2 that C1, C2, C3, C6, C7, C22, C25, C26, C39, C40, C41, and C45 atoms exhibit a negative charge which is donor atoms. All the other carbon atoms exhibit a positive charge, which is an acceptor atom of both methods. All the H atoms have positive charges. N23 and O30 atoms also exhibit a positive charge, which are acceptor atoms. All the other nitrogen and all the oxygen atoms in the molecule possess negative charge were donor atoms. These atoms may also play an important role in the biological activity of the compound.

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[22]. In molecular interaction, the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) play the key role. HOMO is the orbital which has ability to donate electrons and its energy corresponds to ionization potential (I. P.), while LUMO has electrons accepting ability, and its energy corresponds to electron affinity (E. A.). HOMO-LUMO surfaces of molecules shown in **Figure 3**



HOMOLUMO

Figure 3

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

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
Ionisation potential (IP)	4.5672
Electron affinity(EA)	2.9990
Global hardness(η)	0.7841
Chemical softness(□)	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

THERMODYANAMIC PARAMETERS

The dipolemoment is (μ in Debye) is another important electronic parameter which provides the information on the polarity and the reactivity indicator of the molecule. The calculated dipole moment of the compound is5.9254.The high value of dipole moment results stronger intermolecular interactions and high reactivity.

ANTI CORROSIVE ANALYSIS

Values of Δ*N* -2.0513 show that the inhibition efficiency resulting from electron donation agrees with Lukovit's study[23]. If Δ*N* < 3.6, the inhibition efficiency increases by increasing 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.

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 molecule the value of urea molecule which is prototypical molecule is used as threshold value for the purpose of comparison. The Mean polarizabilityα_0 *is*29.7855X10^{-24}esuand 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 0.3728×10 $^{-30}$cm5/esu] and from the resultant values we identified that 5-((1*H*-indol-3-yl)methyl)-3-((2,4-dinitrophenyl)amino)-2-phenylimidazolidin-4-one possess comparatively good NLO property indicating that this might a good OLED material.

CONCLUSION

The optimized geometry parameters such as bond angle, bond length, of the previously synthesised5-((1*H*-indol-3-yl)methyl)-3-((2,4-dinitrophenyl)amino)-2-phenylimidazolidin-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 in order to elucidate the adsorption and corrosion inhibition behavior of the molecules. The anticorrosive ability of the molecule was established. The Non linear optical character of the same was determined from dipolemoment and hyperpolarisability values.

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