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Synthesis and Theoretical Study of New Barbituric Acid Derivatives as Corrosion Inhibitors for Mild Steel

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Two barbiturates namely, 5-(4-nitrobenzylidene)pyrimidine-2,4,6-trione [**N1**] and 5-amino-2-[4-((2,4,6-trioxotetrahydropyrimidin-5-ylidene)methyl)phenoxy]benzoic acid [**N2**] were synthesized. The molecular structure, electronic construction and efficiency of inhibition studied using density functional theory (DFT) was achieved by B3LYP/6-31G. The quantum chemical characteristics such as EHOMO, ELUMO, E_{gap}, negative charge density, total energy, and differences of bond length and angles. Corrosion inhibition potentials was studied varying with different concentration, temperature and time. In order to determine the reactivity, the available sites attacked by nucleophile or electrophile was analyzed. The correlation and theoretical results agreed with the experimental data. The prepared compounds structure were confirmed by TLC, FTIR, UV-visible and ^{1}H, ^{13}C NMR techniques.

Keywords: Barbiturates, Quantum chemical properties, Corrosion inhibition, Density functional theory.

INTRODUCTION

The industrial fields suffered numerous losses due to corrosion and the protection process is the best technique against the corrosion. Inhibitor of corrosion among the various ways used to protect the metal surface from the degradation and destruction, it is considered the best protection methods in industry. These methods were used because it is cheap and considered as traditional method [1-4]. The theoretical and experimental experiments have been conducted to calculate the properties of inhibitory substance. Due to their anti-corrosive properties, inhibitors used in different industries, but some of them appeared affect in the environment. Therefore, researchers have focussed on preparing the friendly environmentally inhibitors, such as organic inhibitors [5-12].

Mild steel is an alloy made by combining two or more metallic elements and the iron is present in higher percentage, to give the greater resistance to corrosion in acidic or basic medium [13]. The chemical inhibitor methods stay the best effective and practical method among different methods used in treating corrosion problems. For this reason, evolution the types of inhibitors for corrosion based organic compounds includes sulphur, nitrogen, and oxygen atoms in their structure are attracted the interest of the scientist in the scope of corrosion and industrial chemistry [14]. Organic compounds are the most efficient inhibitors due to including some affected factors such as electronegativity, and conjugation. Physical and chemical properties of the molecule like size, donor-acceptor atoms, orbital *p* character,electronic structure, and types of functional group are affected on the adsorption on the surface of the metal [15]. Donor-acceptor organic compounds considered excellent corrosion inhibitors due to their important rule in moving the electrons to unoccupied *d* orbital of metal surface forming the coordinating covalent bonds. Also, they accepted electrons from surface ofmetal to form another bonds [16,17]. However, barbituric acid is considered to be the main substance that enters the formation of inhibitory substances. Barbituric acid is suitable for condensation reaction with cyclic amide and active methylene group and converted into acid in aqueous medium to produce barbiturates [18,19].

The geometry of molecule structure effected on adsorption on the metal surface where planar molecules are trending to absorb the metal surface better than those molecules having less planar. Quantum calculations are found suitable tool for the elucidate the mechanism of corrosion inhibition [20-22].

EXPERIMENTAL

Quantum chemical calculations: B3LYP level will be used to study the quantum physical calculations. This includes studying the relation between the structure of molecules and the efficiency of corrosion inhibition of molecules that create a correlation between structural and electronic characteristics of molecules and experimental data. Density functional theory (DFT) used to optimize the molecules geometry by Becke's three parameter interchange functional along with Lee-Yang-Parr correlation functional (B3LYP) [23].

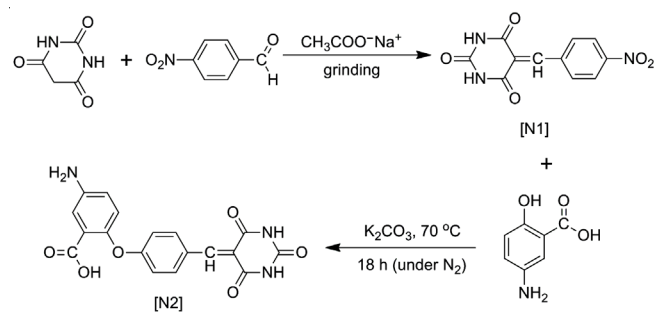
This study includes the calculation of theoretical physical and chemical parameters like energy of the lowest unoccupied molecular orbital (E_{LUMO}), highest occupied molecular orbital (E_{HOMO}), energy gap (ΔE), electron affinity (A), ionization potential (I), softness (S), global hardness (η), electronegativity (χ) and chemical potential (K) in eV [24,25].

Melting points were conducted in Stuart 30 apparatus and are uncorrected. The FTIR spectral analysis is conducted using Bruker spectrometer device. UV spectra recorded with double beam Spectrophotometer PG CECIL- CE7200 device. ^{1}H and ^{13}C NMR spectra recorded on a Bruker AC 400 NMR device in $CDCl_3$-*d* and DMSO-d_6 with TMS as a reference. Elemental analyses were done on CHN-Elemental analysis, Euro EA 1106. Starting chemical compounds were obtained from Fluka or Aldrich.

Mild steel composition (wt %): C: 0.370 %; Si: 0.230 %; Mn: 0.680 %, S: 0.016 %, Ni: 0.059 %, Co: 0.009 %, Cu: 0.160 % and Fe as balance. The mild steel surface was abraded and polished with 360 to 1600 grade of emery paper. The dimensions of the steel for this work in the form of a rectangle (10 cm × 2 cm × 0.5 cm) shape.

Synthesis of 5-(4-nitrobenzylidene)pyrimidine-2,4,6-trione [N1]: Barbituric acid (0.015 mol, 2 g), 4-nitrobenzaldehyde (0.015 mol, 2.26 g) and sodium acetate (0.015 mol, 1.23 g) were mixed in the mortar. The mixture were finely grounded at room temperature and then the mixture was dissolved in 10 mL of DMSO, and finally the solution was poured in cold water (**Scheme-I**). The product was washed with boiling water and ethanol which afforded solid yellow product in 73 % yield, m.p. decomp. > 300 ºC). The reaction was monitored by TLC (acetone:chloroform::3:2, R_f = 0.67). IR (KBr, ν_{max}, cm^{-1}): 3326 (N-H), 3117 (C-H arom.), 3120 (-C=C-H), 1692 (C=O amide), 1615 (C=C alkene), 1617 (C=C arom.), 1514, 1488 (NO_2), 1396 (C-NO_2), 1346 (C-NH), 850 (C=C alkene bend.), 775 (C=C arom. ring bend.). ^{1}H NMR (ppm): δ 8.84 (s, 2H, NH), 8.34-8.41 (d, 2H, Ar-H), 7.88 (d, H, Ar-H), 7.35 (d, H, Ar-H), 6.69 (s, 1H, HC=). ^{13}C NMR (ppm): δ 192.32 (C, C=O), 154.34 (C, C=O), 150.59 (C, C=C), 144.91 (C, C=O), 130.61 (C, C-NO_2), 127.82 (C, C-Ar), 124.24 (C, C-Ar), 122.78 (C, C-Ar), 90.42 (C, H-C=), 40.30-38.64 (C, DMSO solvent). Anal. calcd. (found) % for $C_{11}H_7N_3O_5$: C, 50.57 (50.73); H, 2.68 (2.65); N, 16.09 (16.22).

Synthesis of 5-amino-2-(4-((2,4,6-trioxotetrahydropyrimidin-5(2*H*)-ylidene)methyl)phenoxy)benzoic acid (N2): A mixture compound **N1** (0.015 mol, 3.91 g), 5-amino salicylic acid (0.015 mol, 2.29 g) and K_2CO_3 (0.015 mol, 2.07 g) in DMF (10 mL) was heated at 70 ºC and stirred for 9 h under nitrogen atmosphere, then K_2CO_3 (0.015 mol, 2.07 g) added and continued to stir for another 9 h. The reaction mixture was cooled to room temperature and washed by 1 N HCl followed by distilled water (**Scheme-I**). The solid brown colour product (**N2**) in 81% yield and m.p. > 250 ºC was obtained. The reaction was monitored by TLC (acetone:chloroform 3:2, R_f = 0.54). IR (KBr, ν_{max}, cm^{-1}): 3400 (-NH_2), 3300 (-NH), 3300-2700 (-COOH), 3040 (C-H arom.), 3118 (C=C-H), 1709 (C=O carboxyl), 1680 (C=O amide), 1581 (C=C alkene), 1507,1462 (C=C arom.), 1396 (C-NH_2), 1346 (C-NH), 1019 (Ar-O-Ar), 850 (C=C arom. ring bend.). ^{1}H NMR (ppm): δ 10.17 (s, H, COOH), 10.14 (s, 2H, NH), 8.44 (s, 2H, NH_2), 8.18-8.44 (d, 4H, Ar-H), 7.29-7.26 (d, 3H, Ar-H), 6.04 (s, 1H, HC=). ^{13}C NMR (ppm): δ 170.61 (C, COOH), 164.12 (2C, C=O), 152.69 (C, Ar-O), 151.53 (C, C=C), 148.07 (C, C=O), 142.58 (C, Ar-O), 138.30 (C, Ar-N), 128.83 (C, C-Ar), 126.17 (2C, C-Ar), 123.92 (2C, C-Ar), 122.49 (2C, C-Ar), 120.55 (C, H-C=), 116.64 (2C, C-Ar). Anal. calcd. (found) % for $C_{18}H_{13}N_3O_6$: C, 58.85 (58.92); H, 3.54 (3.62); N, 11.44 (11.38).



Scheme-I: Synthesis of barbituric acid derivatives

RESULTS AND DISCUSSION

The geometry of a molecule determines many of its physical and chemical properties. It is necessary to find the relaxation of molecule, in which the optimized structure of molecule is the structure in minimum energy which were obtained with DFT method by three-parameter hybrid-functional of Becke's (B3LYP), these forms are shown in Fig. 1 by using B3LYP/6-31G level, which is selected because it has a lower total energy as shown in Table-1. The results of the parameters of geometrical optimization of [**N1**] and [**N2**] compared with experimental results and proved that FT-IR, ^{1}H NMR and ^{13}C NMR data are identical.

TABLE-1
E_{HOMO} AND E_{LUMO} OF BARBITURIC ACID (**N**), **N1** AND **N2** BY BASIS SET 6-31G AT B3LYP

Molecular	E_{HOMO} (eV)	E_{LUMO} (eV)
Barbituric acid (**N**)	-6.89309	-1.06096
N1	-7.70153	-3.28818
N2	-5.97227	-2.60273

It seems that the electron transfer of reacting species happened because the interaction between LUMO and HOMO. The tendency of electron donation from molecule indicated by measures the energy of HOMO (E_{HOMO}) which promoting the adsorption of inhibitor molecules on the surface of mild steel with good inhibition efficiency. While the ability of

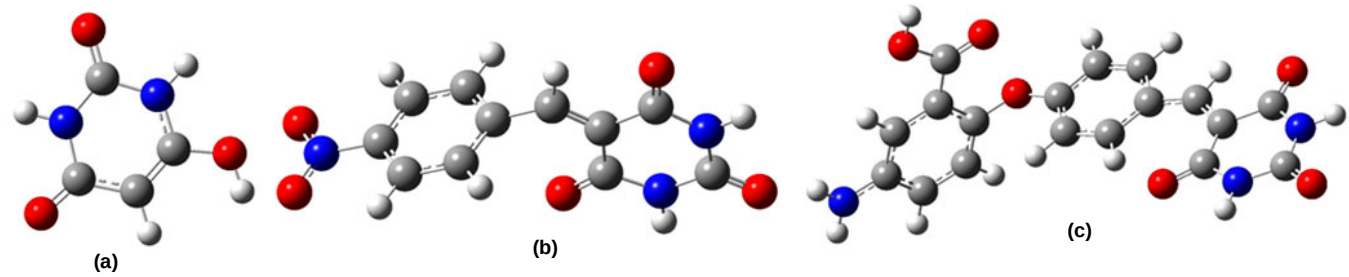


Fig. 1. (a) Optimized geometry for barbituric acid at the B3LYP/ 6-31G basis set, (b) Optimized geometry for **N1** at the B3LYP/ 6-31G basis set, (c) Optimized geometry for **N2** at the B3LYP/ 6-31G basis set

molecule to acceptance of electrons indicates by E_{LUMO}. The ability of inhibitor to bind on the metal surface increased with increasing of HOMO energy and decreased of LUMO energy. The physical and chemical reactivity of molecules proved by the frontier molecular orbital theory (FMO) [26,27].

The ΔE gap is a function of inhibitor reactivity on behalf of the adsorption on metal surface. The % IE (inhibition efficiency) value of molecule depends on ΔE value, where ΔE decreases resulting to increase the % IE value. In addition, good inhibition efficiency depends on lower values of energy differences, due to that energy which need to remove the electron from the orbital are low [28]. Therefore, the rigid molecules have high ΔE gap [29], so soft basis inhibitors are the most effective for metals than hard molecules (Tables 2 and 3) [30].

TABLE-2
ENERGY OF THE BARBITURIC ACID (**N**), **N1** AND **N2** MOLECULES BY BASIS SET 6-31G AT B3LYP

Molecules	Total energy of molecules (a.u)	Total energy of each atom (a.u)	Energy gap (eV)
Barbituric acid (**N**)	-489.880	-486.916	5.832134
N1	-963.382	-957.223	4.413352
N2	-1309.012	-1299.599	3.369538

The UV-visible spectra of compounds barbituric acid (**N**), **N1** and **N2** in DMSO displayed broad CT bands at end absorptions reaching into 417 nm (Fig. 2). Compound **N** has an absorption peak at 263 nm, compound **N1** has additional absorption

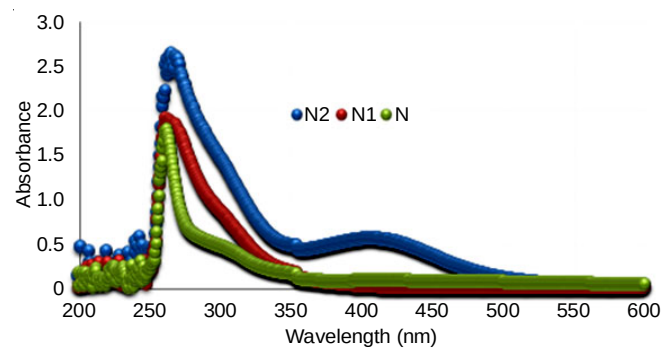


Fig. 2. UV-visible spectra of compounds **N2** (blue line), **N1** (red line) and **N** (green line) recorded in DMSO (1×10^{-4} M)

peaks correspond to nitrobenzaldehyde entity observed at λ_{max} = 306 nm while compound **N2** displayed a absorption peak maxima λ_{max} = 417 nm reflecting the effective of conjugation to nitrobenzaldehyde and 5-amino salicylic acid units. It is interesting to note that the onset wavelength of these compounds **N**, **N1** and **N2**, corresponds to an optically determined band gap energy E_{gap} = 2.75, 3.90 and 4.60 eV, respectively, which is close to the theoretical value (Table-2).

The weight loss of mild steel in 1, 3 and 5 N of H_2SO_4 in absence and existence of inhibitor at 25, 35 and 45 ºC, respectively and time are shown in Table-4. The weight loss of mild steel in H_2SO_4 solutions increased with increasing the time and temperature. Also, the results explained that the rate of corrosion for mild steel in H_2SO_4 solutions increasing with increase

TABLE-3
QUANTUM PARAMETERS FOR BARBITURIC ACID (**N**), **N1** AND **N2** MOLECULES BY BASIS SET 6-31G AT B3LYP

Molecular	η (eV)	S (eV)	K (eV)	IP (eV)	EA(eV)
Barbituric acid (**N**)	6.362612	0.078584	-5.832134	6.89309	1.06096
N1	6.057441	0.082543	-4.413352	7.70153	3.28818
N2	4.670904	0.107046	-3.369538	5.97227	2.60273

TABLE-4
RATE OF CORROSION FOR MILD STEEL WITH AND WITHOUT INHIBITOR

Conc. of H_2SO_4	Corrosion rate (g/h cm^2)	Without inhibitor			With inhibitor (**N2**)		
		25 °C	35 °C	45 °C	25 °C	35 °C	45 °C
1 N	1 h	5.59441×10^{-6}	3.20848×10^{-5}	3.5524×10^{-5}	1.53039×10^{-5}	4.49486×10^{-6}	1.0274×10^{-5}
3 N		2.92161×10^{-5}	2.76755×10^{-5}	2.41304×10^{-5}	7.32682×10^{-6}	2.7087×10^{-6}	7.1714×10^{-6}
5 N		1.14619×10^{-5}	3.31957×10^{-5}	0.000249375	1.42045×10^{-6}	1.18007×10^{-6}	1.0708×10^{-6}
1 N	3 h	4.28322×10^{-6}	1.47546×10^{-5}	7.1122×10^{-6}	5.76484×10^{-6}	5.70678×10^{-5}	6.90053×10^{-5}
3 N		9.16667×10^{-6}	3.13213×10^{-5}	4.7442×10^{-5}	4.74393×10^{-6}	1.52041×10^{-5}	4.02469×10^{-5}
5 N		1.08333×10^{-5}	7.14493×10^{-5}	0.000116979	1.58810×10^{-6}	7.43735×10^{-6}	1.23834×10^{-6}
1 N	5 h	3.94231×10^{-6}	7.64555×10^{-6}	3.91785×10^{-5}	9.99144×10^{-6}	5.76865×10^{-5}	9.54885×10^{-5}
3 N		8.08051×10^{-6}	6.07877×10^{-6}	7.49174×10^{-5}	5.60391×10^{-6}	7.3514×10^{-6}	4.97432×10^{-5}
5 N		1.00508×10^{-5}	6.54435×10^{-5}	0.00021017	1.88374×10^{-6}	6.03596×10^{-6}	9.58042×10^{-6}

the temperature and time of contact. Besides that the rate of corrosion decrease with increase of concentration of the inhibitor. Mild steel weight loss in the blank solution is more than that in existence of inhibitor. Therefore, it can be concluded that compound **N2** is a good inhibitor for corrosion on mild steel surface in different concentrations of H_2SO_4.

Conclusion

Two new barbiturates (**N1** and **N2**) were synthesized and investigated as corrosion inhibitors for mild steel. The mild steel corrosion inhibition achieved by lose weight method in 1,3 and 5 M H_2SO_4 solutions at different temperatures ans times The negative charge density of the atoms increased due to double bonds which shorter than single bonds. Total energy of each atom larger than the total energy of molecules due to the binding energy. The presence of new barbiturates as inhibitor causes the decrease of corrosion with increasing temperature, acid concentration and time. The relation between electronic and molecular structures and efficiency of inhibition were investigated using density functional theory (DFT) study which performed on the B3LYP/6-31G. Compound **N2** displayed good inhibition efficiency. The results show that the acidic corrosion was reduced with the addition of a suitable concentration of compound **N2**. The efficiency of inhibition increased with inhibitor concentration, but decreased with temperature. These results confirmed that compound **N2** tendency to give a good inhibition. The best results recorded for compound **N2** showed that it behaved as a good inhibitor with 99 % efficiency inhibition at a concentration of 20 ppm of compound **N2** and 1N H_2SO_4 at 25 ºC.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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