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Protection of Titanium from Corrosion in Acid Media (0.25N HCl) by Meloxicam Drug and Theoretical Study

Rasha Abd Jasim, Sura Khaleel Ibrahim, Muna Sarhan Sando and Ahlam Mohammed Farhan
Department of Chemistry, College of Science for Women, University of Baghdad, Baghdad, Iraq

Abstract: An inhibitor for protective titanium from corrosion was used in acid media at 298 K, the inhibitor was meloxicam drug, the best inhibitor for protection titanium from corrosion was meloxicam drug in acid media because the efficiency increases with the increase of concentration for meloxicam drug at 400 ppm and weight loss decreases with increasing concentration. Structural geometries of meloxicam drug was suggested in solid state and in gas phase by using theoretical treatments, using (Hyper Chem. 8) program for the molecular mechanics, semi-empirical and Ab-initio calculations. The heat of formation (ΔH°_f), binding Energy (ΔE_b) and Total Energy (ΔE_T) for Meloxicam (M) was calculated by the semi-empirical (PM3, ZINDO/1) and Ab-initio (6-31G*), methods at 273 K. Furthermore, the electrostatic potential of the meloxicam (M) was calculated to investigate the reactive sites of the molecule. The semi-empirical (PM3) and Ab-initio (6-31G*) were used to evaluate the vibration and electronic spectra for the organic molecule Meloxicam (M) and the data of theoretically calculated were compared with the experimented values. The theoretically obtained frequencies agreed well with those found, experimentally as well as the, calculations helped to assign unambiguously the most diagnostic bands.

Key words: Protection of titanium, corrosion, Meloxicam drug, theoretical study, geometries, semi-empirical

INTRODUCTION

The safety and economics for metals are affected by fundamental process for corrosion due corrosion. The best methods was used acid media for the protection from corrosion by inhibitors (Al-Bonayan, 2015; Trabanelli, 1991; Ali *et al*., 2014). The metal was interacted with aqueous acid, the result corrosion, for example, pickling process in alloy because alloy is brought in contact with highly concentrated acids because of the corrosion of alloys lead to economic losses if this process will not combated (Rubaye *et al*., 2015; El-Etre, 2008). In descaling, cleaning and pickling this processes use acids. The rate dissolution metal is reducing effectiveness by inhibitors (Shukla *et al*., 2012; Xu *et al*., 2014; Kosari *et al*., 2014; Bobina *et al*., 2013). In acid solution, the inhibitor adsorption on surface of metal is usually free of oxides (Kadhum *et al*., 2014). Survey of literature shows the compounds for derivatives of organic are containing sulfur, for example amines, amino acid and azoles (Fouda *et al*., 2016; Kumar *et al*., 2006), this compound is a very good protective from corrosion of titanium in different media because this compound was perceived that attendance of heteroatom, for example, S, N, P and O (Fouda *et al*., 2016). The functional group are -N = N, R-OH, -CHO in organic compounds when adsorption on surface metal is influenced by the steric factor, aromiticity, the electronic structure and functional group, molecular weight and molecular area (Morad, 2008; Quraishi *et al*., 2000; Abdallah, 2004; Schorr and Yahalom, 1972; Naqvi *et al*., 2011). The passivaton layer is thin film on surface of metal, this is protective from corrosion, the anodic inhibitor and cathodic inhibitor are reduced (Al-Sultani and Abdulsada, 2013; Rani and Basu, 2012; Kadhum *et al*., 2014).

MATERIALS AND METHODS

Solution preparation: The test solution was prepared by adding 21.17 mL from HCl conc. in 1000 mL of distilled water.

Sample preparation: The titanium specimen was used in test have dimension of 2.5 cm, the specimen was cleaned with distilled water and finally with ethanol. Therefore, the titanium specimens are kept in desiccators.

Chemical composition of titanium sample: The chemical composition of titanium were display in Table 1.

Corresponding Author: Rasha Abd Jasim, Department of Chemistry, College of Science for Women, University of Baghdad, Baghdad, Iraq

Table 1: The chemical composition of titanium

Si (%)	Fe (%)	Cu (%)	Mn (%)	Mg (%)	Cr (%)	Zn (%)	V (%)	Others
<0.25	<0.40	<0.05	<0.05	<0.05	<0.05	<0.05	<0.03	<0.02

Electrochemical techniques

Open Circuit Potential measurements (OCP): The equilibrium potential is calculated from OCP when calculate E_{corr} (corrosion potential) with no current. The corrosion cell has titanium work electrode and standard saturated calomel electrode, SCE, placed in same compartment, all electrodes are immersed in (0.25 N) HCl solution with the presence of different concentration from meloxicam dugs and absence.

Potentiodynamic polarization: The variation of electrode potential with electrical current was calculated from electrical current. The change scan rate was 5 mV from a low potential of -200+OCP-200+OCP mV (SCE) with electrode potential are calculated potentiodynamic current-potential curves. All potententils were measured against SCE. The test used corrosion program (Voltamaster 4) combined with Potentiostat PGZ 301 Voltalab 40.

Theoretical treatment: HyperChem is a sophisticated molecular modeler, editor and powerful computational package, that is known for its quality, flexibility and ease of use (Cook, 1998). It can plot orbital wave functions resulting from semi-empirical (PM3, ZINDO/1) and Ab-initio (6-31G*) quantum mechanical calculations as well as the electrostatic potential. The total charge density or the total spin density can also be determined during semi-empirical calculation, this information is useful in determining reactivity and correlating calculation results with experimental data. The possible types of prediction of molecules are: Geometry optimization calculations which employs energy minimization algorithms to locate stable structures, bond distances, molecular dynamics which provide the thermodynamic calculations and dynamic behavior of molecules, plot the electrostatic potential field (HOMO and LUMO), vibrational and electronic spectr (Choinacki and Pruchnik, 2001; Atkins and Friedman, 2005).

RESULTS AND DISCUSSION

Weight loss measurements: The Inhibition Efficiency (% IE) was calculated by using the equation:

$$\% IE = \theta \times 100 = [1-(o_{corr}(inh)/i_{corr}(free)] \times 10$$

where, i_{corr} (free) (corrosion current densities in without inhibitor) and i_{corr} (inh) (corrosion current densities in with inhibitor) (Fouda *et al.*, 2013). The inhibition efficiency for titanium in 0.25 MHCl in the absence and presence of various concentrations of the (drug) increased with increasing the concentration of the inhibitor and the weight loss decrease with increasing in the concentration (Abdel Hameed, 2011). Table 2 and Fig. 1 and 2 shows the Inhibition Efficiency (% IE) and the best weight loss in acid media at 293 K.

Table 2: The inhibition efficiency (% IE) and the weight loss in 0.25 M HCl at 293 K various concentrations of the (drug)

Con. of drug	WL (mg/L)	IE (%)
0	76.8	0.00
10	73.2	25.90
100	46.1	32.40
200	42.5	63.60
300	39.1	65.30
400	11.1	97.76

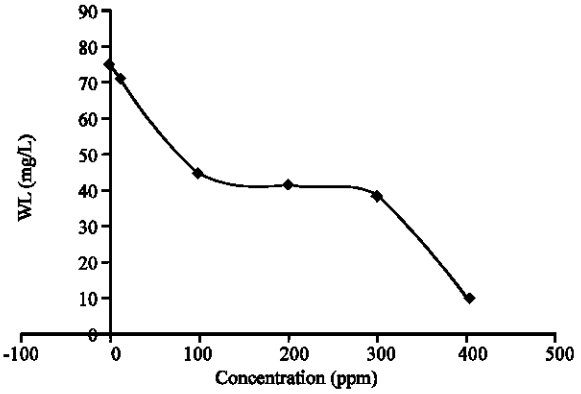

Fig. 1: The best weight loss in higher concentration for titanium in 0.25N HCl at 293 K

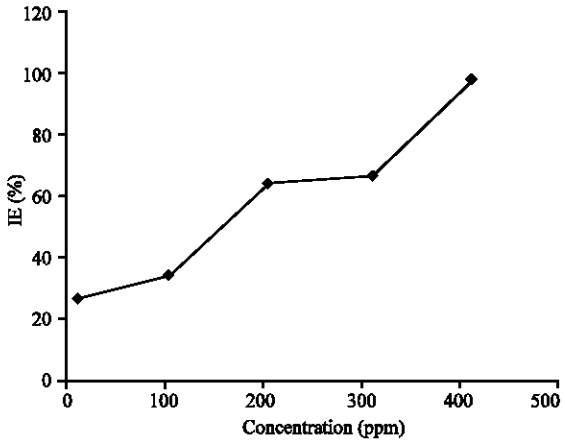

Fig. 2: The best inhibition efficiency in higher concentration for titanium in 0.25N HCl at 293 K

Potentiodynamic polarization: Polarization curves of titanium metal in hydrochloric acid solution containing different concentration of Meloxicam drug are shown in Fig. 3. Corrosion current (i_{corr}), corrosion potential

Table 3: The parameters of potentiodynamic polarization method for the corrosion of titanium in 0.25M HCl at 293 temperature

Cons. of inh.	I_{corr} (mA/cm^2)	-E_{corr} (mV)	bc (mV/Dec)	-ba (mV/Dec)	WL (mg/L)
0	173.34	267.4	268.7	241.0	76.8
10	128.51	236. 9	172.9	198.2	73.2
100	117.24	259.2	187.5	189.4	46.1
200	63.14	251.3	131.7	132.8	42.5
300	60.21	246.1	122.5	146.4	39.1
400	3.90	107.4	217.4	84.2	11.1

Table 4: The degree of surface coverage titanium metal in 0.25 M HCl at 293 K various concentrations of the (drug)

Con .of inhibitor (ppm)	Q	IE (%)
0	0.000	0.00
10	0.259	25.90
100	0.324	32.40
200	0.636	63.60
300	0.653	65.30
400	0.9776	97.76

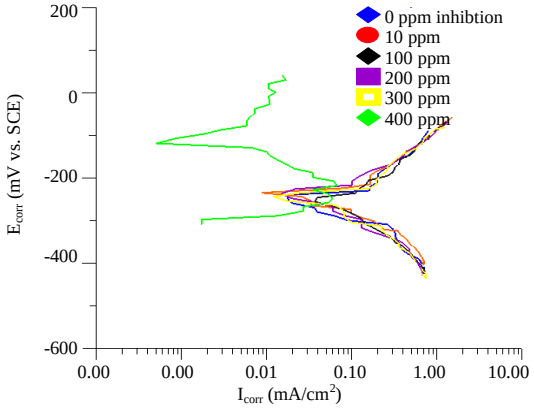

Fig. 3: The polarization curves of titanium metal in 0.25 M HCl solution with and without different concentration of Meloxicam drug at room temperature

(E_{corr}), anodic Tafel slope (ba) and cathodic Tafel slope (bc) were measured from Tafel plots. Table 3 shows the resulting data of the corrosion potential E_{corr} (mV)/corrosion current density (i_{corr}) (mA/cm^2), cathodic and anodic tatel slopes bc and ba (mV/Dec) and weight loss (mg/L). The data show that the corrosion current density (i_{corr}) decreased with increasing the concentration of Meloxicam drug becase the meloxicam drug which adsorption on metal surface (Mahdi, 2014).

Effect of surface coverage (θ) on corrosion: The degree of surface coverage can be calculated from the Eq. 2.

$$IE\% = \theta \times 100\,[1\text{-}i^{\circ}_{corr}/i_{corr}] \times 100 \qquad (2)$$

where, i°_{corr} the current densities of drug and icorr the current densities of blank (Fouda *et al*., 2014). The result was the best degree of surface coverage (θ) in higher concentration of drug, this is shown in Fig. 4 and Table 4.

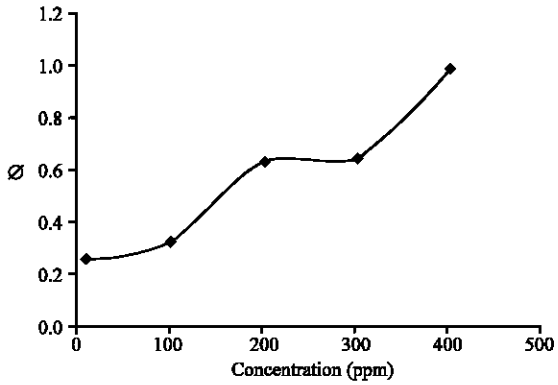

Fig. 4: The degree of surface coverage of titanium metal in 0.25M HCl solution with and without different concentration of Meloxicam drug at room temperature

(Theoretical studies)

Electrostatic potentials: Electron distribution governs the electrostatic potential of the Meloxicam drug (M). The Electrostatic Potential EP describes the interaction of energy of the molecular system with a positive point charge. (EP) is useful for finding sites of reaction in a molecule; positively charged species tend to attack a molecule where the electro static potential is strongly negative (electrophonic attack) (Ramachandran *et al*., 2008; Cummins and Gready, 1994; Al-Shafey *et al*., 2014). The EP of the Molecule (M) was calculated and plotted as 2D and 3D contour to investigate the reactive sites of the molecule as display in Fig. 5. Also, one can interpret the stereochemistry and rates of many reactions involving "soft" electrophiles and nucleophiles in terms of the properties of frontier orbital (HOMO, Highest Occupied Molecular Orbital) and (LUMO, Lowest Unoccupied Molecules) can be shown in Fig. 6 via. adopting HyperChem. -8.07 program.

(II) Optimized geometries and energies: The program HyperChem-8.07 is used for the semi-empirical (PM_3,ZINDO/1) and Ab-initio(6-31G*) calculation at optimized geometries energies (Foresman and Frisch,1996; Lakshmi *et al*., 2008). In gas phase for heat of formation (ΔH_f), binding Energy (ΔE_b) and Total Energy (ΔE_T) for the Meloxicam drug (M) was calculated and tabulated in Table 5.

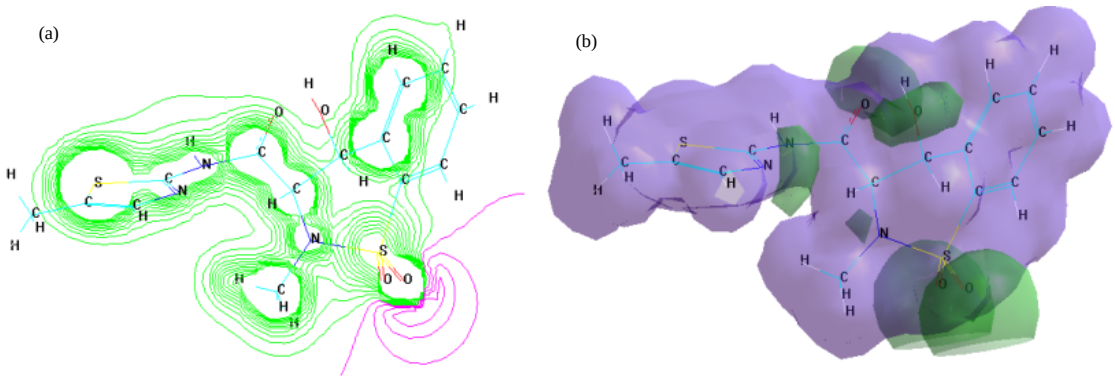

Fig. 5: Electrostatic Potential as 2D&3D Counters for Meloxicam drug (M); a) EP of M in 2D and b) EP of M in 3D

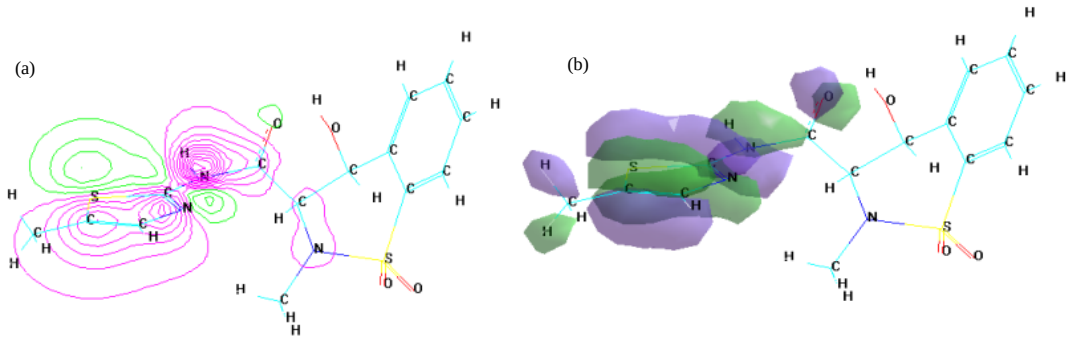

Fig. 6: HOMO and LUMO Sites for the Meloxicam drug(M); a) HOMO and LUMO in 2D for M and b) HOMO and LUMO in 3D for M

Table 5: Conformation Energetic in (KJ.mol^{-1}) for the Meloxicam drug (M)

	PM3			ZINDO/1			Ab-initio (6-31G*)
Compound	ΔH°_f	ΔE_b	ΔE_T	ΔH°_f	ΔE_b	ΔE_T	ΔE_T
M	-301.61	-16563.25	-378674.28	-30978.59	-47240.21	-582725.35	-4764824.65

Optimized vibrational spectra for the Meloxicam drug (M): Theoretically calculated wave numbers for the Meloxicam drug (M) show some deviations from the experimental values (Lipkowitz *et al*., 2003; Quack and Merkt, 2011). These deviations are generally acceptable in theoretical calculation (Hassan *et al*., 2016; Seeger *et al*., 1991) and are described in Table 6.

Theoretical electronic spectra for the Meloxicam drug (M): The electronic spectra of the molecule has been calculated and the wave number for these Meloxicam drug (M) showed some deviations from the experimental values as shown in Table 7. These deviations in theoretical calculation are generally acceptable due to couplings between the electronic spectra modes and the approximation that each normal mode of the electronic spectra interacts independently electronic spectra beam (Abbott *et al*., 2004; Hehre, 1986). The most diagnostic calculated electronic spectra were chosen for the assignment of the Meloxicam drug (M). All the theoretical electronic spectra of all compound was calculated by using the semi-empirical (PM3) and Ab-intio ((3-21G)).

Optimized geometries and energy of Meloxicam drug (M): Theoretically probable structures of Meloxicam drug (M) have been calculated to find the most possible model building stable structure for Meloxicam drug (M) was showed in Fig. 7 the calculation optima geometries for the Meloxicam drug. The outcomes of the semi-empirical (PM3, ZINDO/1) and Ab-initio (6-31G*) methods of calculation in gas phase for ΔH_f and ΔE_b are tabulated in Table 6.

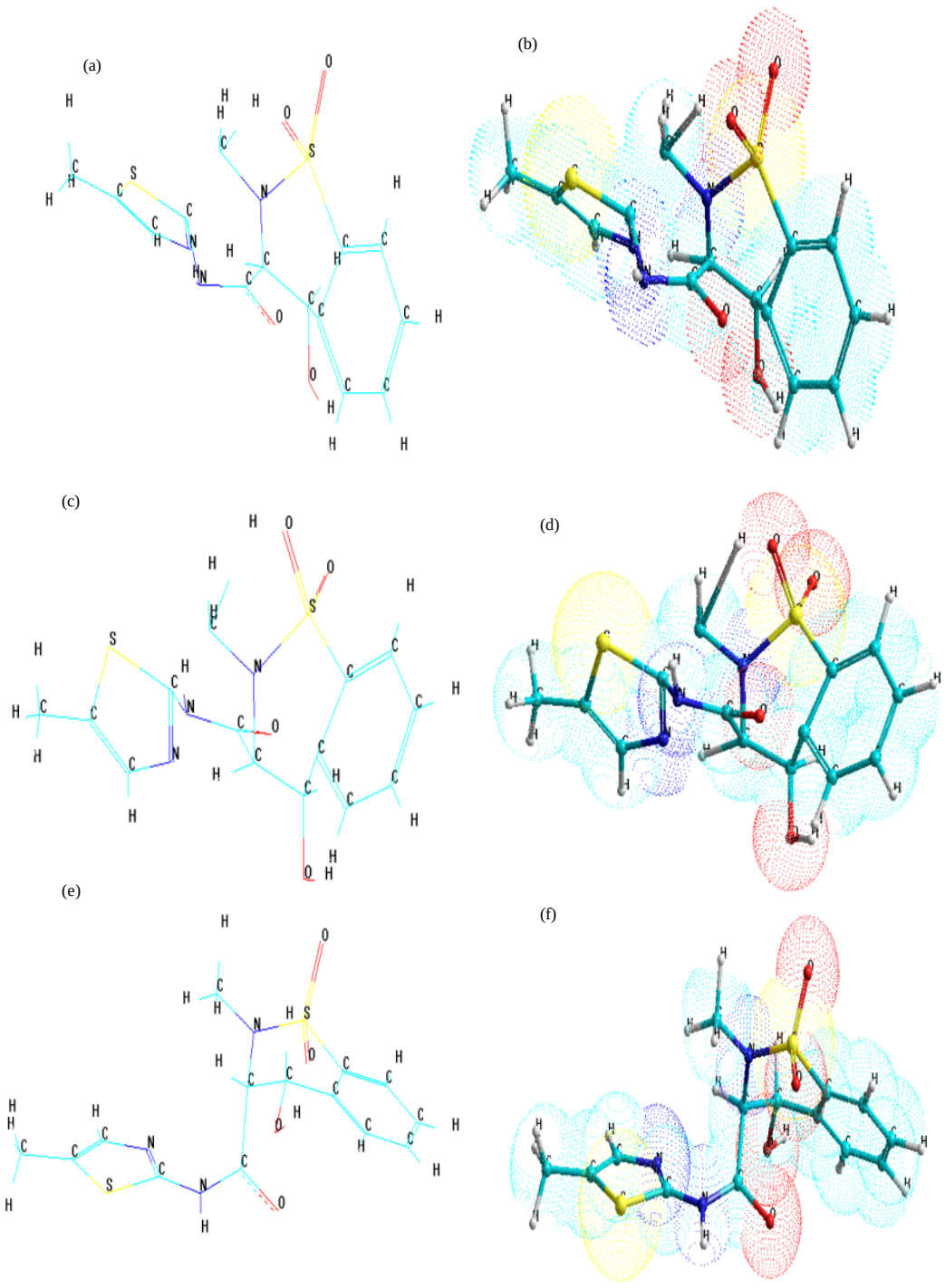

Fig. 7: Conformation structure of Meloxicam drug using HyperChem 8.07; a, b) PM3 for Meloxicam drug; c, d) Ab-initio for Meloxicam drug and e, f) ZINDO/1 for Meloxicam drug

Table 6: A comparison between experimental and theoretical vibrational frequencies for the Meloxicam drug (M) (cm^{-1})

Frequencies	Experimental	Theoretical using semi-empirical (PM3)	Error	Theoretical using Ab-Initio(6-31G*)	Error
νOH	3350	3863	13.279	3029	-10.597
νNH	3290	3342	1.555	3177	-3.556
νC = N	1652	1609	-2.672	1638	-0.854
νC = C	1597	1429	-11.756	1567	-1.914

Table 6: Continue

Frequencies	Experimental	Theoretical using semi-empirical (PM3)	Error	Theoretical using Ab-Initio(6-31G*)	Error
νS-O	1346	1245	-8.112	1333	-0.975
νC-S	762	760	-0.263	776	1.804
νC-H aromatic	3055	3073	0.585	2852	-7.117
νC-H alphatic	2997	3043	1.511	2816	-6.427
δS-O	825	821	-0.487	938	12.046
δC-H	844	846	0.236	881	4.199
νC-N	1300	1322	1.664	1309	0.687
Amide(I)	1770	1650	-7.272	1638	-8.058
Amide(II)	1454	1430	-7.069	1484	2.021

Table 7: A comparison between experimental and theoretical data of some bands electronic spectra for Meloxicam drug (M) (cm^{-1}) and their assignments

Compound	Maximum absorption (cm^{-1}) experimental	Theoretical using semi-empirical (PM3)	Error	Theoretical using Ab-initio(6-31G*)	Error	Assignments
M	25380	23069.8	-10.013	25416.6	0.144	n→π*
	32467	31334.6	-3.613	29983	-8.284	n→π*

CONCLUSION

Theoretical study in the gas phase by using semi-empirical and Ab-initio methods in order to show the most stable conformation and to the results were compared with the experimental data. The study aims to calculate the heat of formation and binding energy for all the probable geometries and to find the most active sites of the Meloxicam (M) by using the electrostatic potential calculations.

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