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Carbozone Compound Corrosion Inhibition Efficiency in Relation to Quantum Chemical Parameters: A QSAR Study for Predictive Models

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الملخص:

تتناول هذه المقالة استخدام مركبات الكاربوزونات كمثبطات للتآكل والارتباط بين معاملاتها الكيميائية الكمومية والمعاملات الديناميكية الجزيئية مع كفاءتها في تثبيط التآكل، حيث أظهرت النتائج أن استخدام مؤشر مركب من المعلمات الكمومية يمكن أن يصف بدقة الأداء المثبط للتآكل لجزيئات الكاربوزون، ويمكن تطوير نموذج QSAR التنبؤي باستخدام المنهجيات الإحصائية لدراسة التنبؤ بالسلوك المثبط للتآكل للمركبات العضوية وتوليد مثبطات جديدة للتآكل. ويساعد تضمين طاقة الامتزاز في المعادلة غير الخطية في تقليل عدد الواصفات المستخدمة في النموذج بشكل عام، ويجب على الباحثين التركيز بشكل أكبر على هذه المعايير في الأبحاث المستقبلية نظرًا لأن لديها القدرة على تعزيز النتائج.

الكلمات الدالة: مثبطات التآكل، نماذج QSAR، مركبات الكاربوزون، المعلمات الكيميائية الكمومية، الديناميكا الجزيئية

Abstract

This article discusses the use of carbozones compounds as corrosion inhibitors and the correlation between their quantum chemical parameters and molecular dynamic parameters with their corrosion inhibition efficiency. The results show that the use of a composite index of quantum parameters can accurately describe the corrosion inhibitory performance of carbozone molecules. A predictive QSAR model can be developed using the study's statistical methodologies to predict corrosion inhibitory behavior of organic compounds and generate new corrosion inhibitors. The inclusion of adsorption energy in the nonlinear equation assist decrease the number of descriptors utilized in the model. Overall, Researchers should focus more on these criteria in future research since they have the potential to enhance results.

Keywords: Corrosion inhibitors, QSAR models, Carbozone compounds, Quantum chemical parameters, Molecular dynamics.

1. Introduction:

Many sectors, including oil and gas, nuclear, and automotive, struggle with corrosion. Inhibitors of corrosion are frequently used to prevent corrosion on metal surfaces (Revie, 2008). For a variety of metals and alloys, carbozones compounds have demonstrated encouraging results as corrosion inhibitors(Roberge, 2019). For a range of metals and alloys, compounds of carbozones have been the subject of extensive investigation as corrosion inhibitors(Zaferani et al., 2013). Numerous computational methods, including quantum chemistry calculations, Monte Carlo simulations, and quantitative structure-activity relationship (QSAR), have been used to study their performance(Gece, 2008).

Quantum chemical and molecular simulations have been extensively used to examine the electronic properties (flow of electrons) of the inhibitor molecules and how they impact the efficacy of inhibition. The calculated efficiency of the inhibitor has been improved by using quantum calculations and molecular dynamics simulations to better understand how the inhibitor molecule interacts with the metal surface(Quadri et al., 2021). QSAR models, which have been used to create a measurable relationship between the inhibitor molecule's structure and its inhibitory activity, have been used to predict the inhibitory action of new inhibitor molecules(Khaled, 2011).

In previous research(Eddy & Ita, 2011) the IE has been correlated with quantum parameters and their R^2 was ranged from 0.79 to 0.83. To enhance R^2, we suggest correlating the molecular dynamics and quantum chemistry characteristics of carbozone compounds with the IE_{exp} at various inhibitor doses. Table (1) and Figure (1) display the chemical formulas, nomenclature, and structure of the some carbozones used in this work.

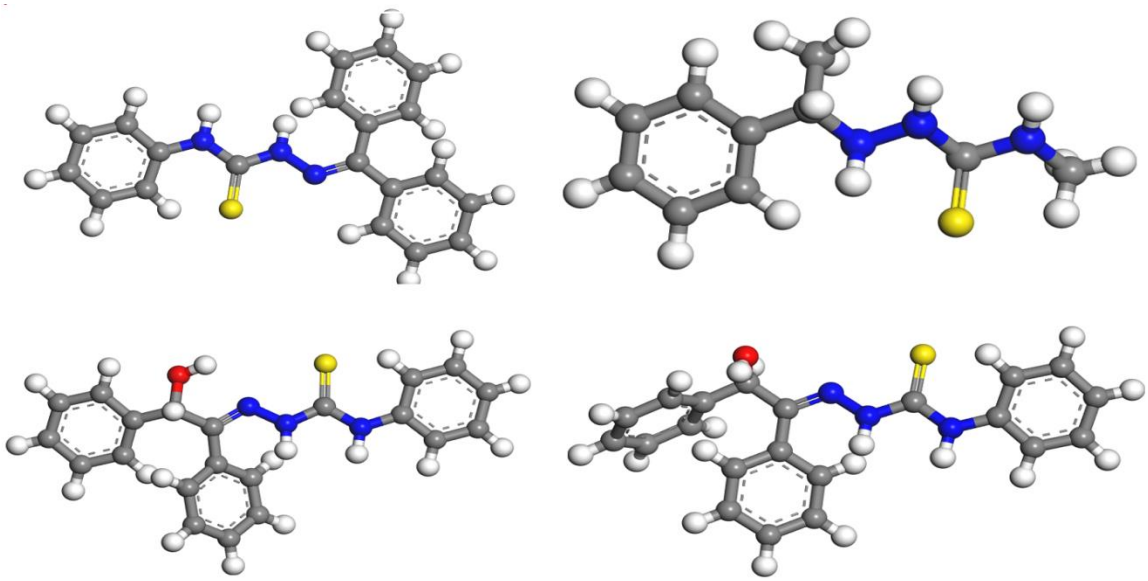

Figure 1 Structures of carbozones

Table (1): Full names, abbreviations and chemical formations of selected carbozones compounds

NO	Full name	abbreviations	chemical formations
1	(Diphenylmethylene)-N-phenylhydrazinecarbothioamide	DPHCARB	C20 H17 N3 S
2	(E)-N-methyl-2-(1-phenylethylidene)hydrazinecarbothioamide	PHCARB	C10 H15 N3 S
3	(E)-2-(2-oxo-1,2-diphenylethylidene)-N-phenylhydrazinecarbothioamide	ODPPHCARB	C21 H19 N3 O S
4	E)-2-(2-hydroxy-1,2-diphenylethylidene)-N-phenylhydrazinecarbothioamide	HDPPCARB	C21 H19 N3 O S

2. Materials and methods

2.1. Quantum Chemical Calculations:

The chosen compounds have already been tested as mild steel corrosion inhibitors in 0.1 M HCl at 303 K using Gravimetric method measurements. Values for experimental inhibition efficiency (IE_{exp}) were collected from data on Gravimetric method measurements(Eddy & Ita, 2011). It was looked at how the quantum chemical calculation parameters E_{HOMO}, E_{LUMO}, and related to inhibitory effectiveness.

Quantum chemical calculations require the Schrödinger equation to be resolved in order to achieve the electronic structure and molecular properties of molecules. The most important factors in the context of corrosion inhibitors are the inhibitor's electronic properties, such as its highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energies(Ouchenane et al., 2021). The well-known quantum mechanics computer software Material Studio version 5.5 was used to carry out the quantum chemistry computations in this investigation. Three semi-empirical equations, AM1, PM3, and PM6, were used in the computations, and they were all implemented using the VAMP module at the restricted Hartree-Fock (RHF) level. The molecular models of interest had to be sketched using the Materials Visualizer's sketch tools before the quantum chemical calculations could be carried out. After the molecules were drawn, they needed to be cleaned and hydrogenated before moving on to the geometry optimization process. Figure (1) displays the cleaned carbozones(Hermann et al., 2020). Utilizing the VAMP module, the geometry optimization stage was carried out. The setup dialog was entered and the Vamp module was launched to begin this process. The objective was changed to geometry optimization inside this dialog, and the Hamiltonian calculation techniques were modified to the AM1, PM3, and PM6 techniques, respectively. The Materials Studio software's AM1, PM3, and PM6 techniques were used to execute all of the study's quantum computations at the restricted Hartree-Fock (RHF) level with comprehensive geometry optimization. This process made it possible to determine the relevant molecules' quantum chemical properties with accuracy. Calculations based on quantum

chemistry provide a complete understanding of these factors and how they impact the efficacy of the inhibition(Dagdag, El Harfi, El Gouri, et al., 2019).

2.2. Monte Carlo simulations:

Monte Carlo simulations (MCS) may be used to study how the inhibitor molecule interacts with the metal surface at the molecular level. The mobility and behaviour of particular atoms and molecules over time are computed in MCS(Verma et al., 2020). In this context of corrosion inhibitors, MCS was used to look at the adsorption of the inhibitor molecules on the metal or oxidised metal surface.

In order to determine the adsorption energies (E_{ads}) of carbozones on the cleaved surface of Fe, MCS were used. The COMPASS was used throughout the MCS in this work(Musa, Jalgham, et al., 2012). The adsorption locator module, COMPASS as force field, and the summation Ewald technique were used to precisely compute the E_{ads} of chosen carbozones in MCS in a simulated cell (24.8×24.8×52.2) with periodic boundary conditions. The settings for structure optimization using energy minimization parameters must match the settings used in the MCS simulation. (Dagdag, El Harfi, Cherkaoui, et al., 2019).

2.3. Quantitative Structure-Activity Relationship (QSAR)

QSAR is a statistical technique for relating a molecule's structural and electrical characteristics to its biological or chemical activity(Verma et al., 2010). A quantifiable link between the structure of the inhibitor molecule (atoms arrangement in a molecule) and its inhibitory action may be established for corrosion inhibitors using QSAR. New inhibitor compounds' inhibitory action may be predicted using QSAR models, and their performance can be improved by changing their structural composition. The most crucial structural and electrical factors that govern the inhibitory action of the inhibitor compounds may also be found using QSAR models. High prediction power (R^2) and dependability are qualities that a successful QSAR model should have(Jalgham, 2021).

3. Results and discussion

3.1. Quantum Calculations Results.

Figure (2) displays the carbozones' HOMO and LUMO distributions as well as their PM3-based optimized structures. The carbozone compounds' inhibitory effects are determined by the density of electrons on the site the adsorption center; the higher the electron concentration at the adsorption position, the more potent the inhibitor. (El-Halabi et al.). The frontier orbital theory can be employed to guess the inhibitor molecule's adsorption sites.(Musa, Mohamad, et al., 2012). The majority of the HOMO and LUMO locations in the molecules of carbozone derivatives are found around the heteroatoms (S, and N), indicating that these are the preferred sites for adsorption. The site of an electrophilic attack typically occurs in the highest density region according to the frontier orbital approximation. Therefore, rather than carbon atoms, the bond with the chelate from S and N will be easily formed.(Ba-Abbad et al., 2012).

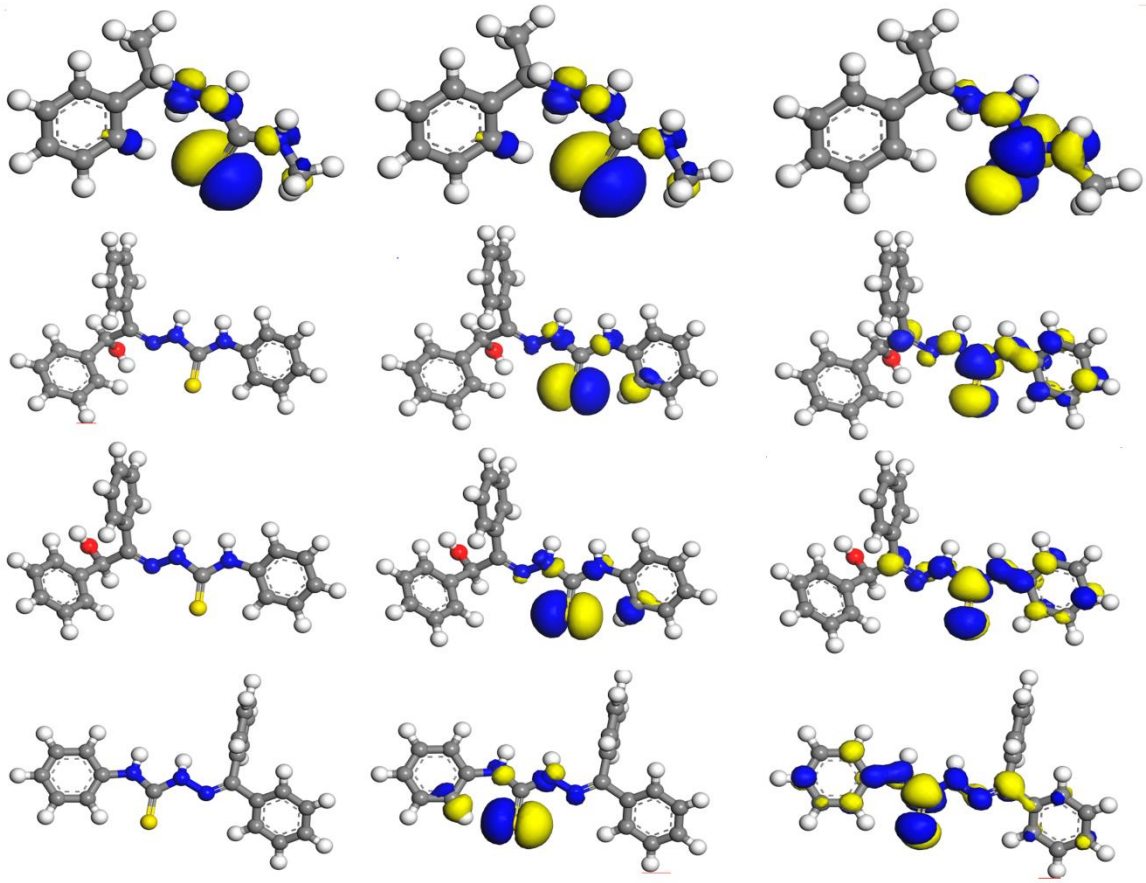

Figure (2): Optimized structures, HOMO and LUMO iso-surface distributions of carbozones using PM3.

Table (2): The calculated Quantum with the AM1,PM3 and PM6 methods

Structures		E_{HOMO} (eV)	E_{LUMO}(eV)	μ(Debye)
PHCARB	AM1	−8.619	−0.138	4.155
DPHCARB		−8.286	−0.567	5.509
HDPPCARB		−8.409	−0.553	5.742
ODPPHCARB		−8.388	−0.514	5.642
PHCARB	PM3	−8.860	−0.869	4.906
DPHCARB		−8.574	−1.002	4.746
HDPPCARB		−8.634	−1.060	3.406
ODPPHCARB		−8.646	−1.071	3.221
PHCARB	PM6	−8.659	0.108	5.594
DPHCARB		−8.418	−0.612	5.936
HDPPCARB		−8.545	−0.637	5.978
ODPPHCARB		−8.570	−0.594	7.999

3.2. MCS Results

On a system with a Fe surface, MCS were run. The maximum negative adsorption energy is PHCARB in Table (3). Table (3) showed that all of the investigated inhibitors had negative values for their adsorption energies, which implies that the interactions between carbozones and Fe surfaces frequently result in mechanisms of spontaneous adsorption and that the adsorbed inhibitors are persistent on the metal surface(Ouchenane et al., 2023).

Table (3): The output of MCS: adsorption energy E_{ads}.

Compound	PHCARB	DPHCARB	HDPPCARB	ODPPHCARB
E_{ads} (kJ/mol)	−111.778	−170.474	−178.158	−176.134

3.3. QSAR Results

Some carbozones underwent AM1, PM3, and PM6 methods to optimize their structures. IE_{exp} values of the inhibitors were obtained from published research(Eddy & Ita, 2011). Quantum parameters and IE need to be closely connected in order to provide reliable productivity assumptions. However, none of these traits are clearly correlated with IE_{exp}. The Lukovits model is a non-linear model (NLM), which was therefore used in this study(Jalgham et al., 2023). It evolved from Langmuir's adsorption isotherm, leading to the connection seen below. (1):

$$IE_{calc} = \frac{(Ax_j + B)C_i}{1 + (Ax_j + B)C_i} \quad (1)$$

$$IE_{calc}\%(AM1) = \frac{(3923.244E_{HOMO} - 42051.302E_{LUMO} - 6553.494\mu + 220.585E_{ads} + 88248.493)C_i}{1 + (3923.244E_{HOMO} - 42051.302E_{LUMO} - 6553.494\mu + 220.585E_{ads} + 88248.493)C_i} \quad (2)$$

$$IE_{calc}\%(PM3) = \frac{(-8575.616E_{HOMO} + 15436.591E_{LUMO} + 4119.704\mu + 24.367E_{ads} - 98527.163)C_i}{1 + (-8575.616E_{HOMO} + 15436.591E_{LUMO} + 4119.704\mu + 24.367E_{ads} - 98527.163)C_i} \quad (3)$$

$$IE_{calc}\%(PM6) = \frac{(-6960.426E_{HOMO} - 72624.866E_{LUMO} + 329.781\mu + 906.921E_{ads} + 55447.802)C_i}{1 + (-6960.426E_{HOMO} - 72624.866E_{LUMO} + 329.781\mu + 906.921E_{ads} + 55447.802)C_i} \quad (4)$$

Since each semi-empirical equation was used independently to determine inhibition efficiency, three IE_{calc} values were produced. To prevent the repetition of irrelevant statistics, the average values of IE_{calc} ($IE_{calc(avg)}$) were determined. Using the values from Table (4) $IE_{calc(avg)}$ and IE_{exp} were plotted. as a starting line point, Figure 3 displayed the correlation coefficient R^2 between $IE_{calc(avg)}$ and IE_{exp}. The perfect correlation coefficient R^2 was discovered. Table (4) contains the IE_{calc} and R^2 values for each model(**Jalgham, 2023**).

Table (4): IE_{exp} and IE_{calc} obtained by suggest models.

				IE_{calc} %			
	R^2			1	1	1	1
	Compound	Ci	IE_{exp} (%)	Eq.(2)	Eq.(3)	Eq.(4)	$IE_{calc(avg)\%}$
1	PHCARB	5×10^{-4}	80.68	80.68	80.68	80.68	80.68
2	DPHCARB	5×10^{-4}	74.59	74.59	74.59	74.59	74.59
3	HDPPCARB	5×10^{-4}	44.02	44.02	44.02	44.02	44.02
4	ODPPHCARB	5×10^{-4}	36.01	36.01	36.01	36.01	36.01

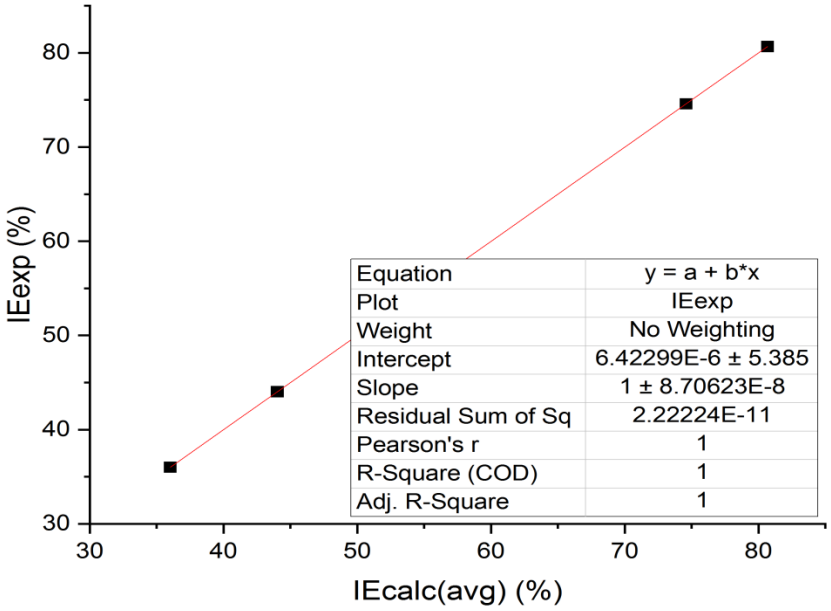

Figure (3): linear correlation between IE_{calc} and IE_{exp}

Conclusion:

The corrosion inhibitory performance (IE) of the carbozone molecules has been described in this paper using a composite index that incorporates a number of descriptor quantum parameters. As a result, we suggested that researchers concentrate more on these variables in their research. The equation's results, where R2 rose from 0 to 1, have been improved by Eads. Three QSAR technique were used to produce the relationships between IEexp and IEcalc of triazoles compounds in HCl acid and some quantum descriptors. When adsorption energy is incorporated into the nonlinear equation, regression analysis uses fewer quantum parameters. Eads might be able to reduce the number of descriptors to produce models that are shorter and simpler. **Acknowledgments**

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