



Sudan University of Science and Technology
College of Graduate Studies



The Corrosion Inhibition Efficiency of some Nitrogen Containing Compounds

Mild Steel, A QSAR Model

كفاءة مثبطات التآكل لبعض مركبات النيتروجين على الفولاذ الطري

نموذج علاقة النشاطية بالبناء التركيبي

**A Thesis Submitted in Partial Fulfillment for the Requirements of the Degree
of M.Sc. in Chemistry**

BY

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إِسْتِفْتَا ح

بِسْمِ اللَّهِ الرَّحْمَنِ الرَّحِيمِ

قال تعالى:

اللَّهُ لَا إِلَهَ إِلَّا هُوَ الْحَيُّ الْقَيُّومُ ۚ لَا تَأْخُذُهُ سِنَّةٌ وَلَا نَوْمٌ ۚ لَهُ مَا فِي السَّمَاوَاتِ وَمَا فِي الْأَرْضِ ۚ مَنْ ذَا الَّذِي يَشْفَعُ عِنْدَهُ إِلَّا بِإِذْنِهِ ۚ يَعْلَمُ مَا بَيْنَ أَيْدِيهِمْ وَمَا خَلْفَهُمْ ۚ وَلَا يُحِيطُونَ بِشَيْءٍ مِّنْ عِلْمِهِ إِلَّا بِمَا شَاءَ ۚ وَسِعَ كُرْسِيُّهُ السَّمَاوَاتِ وَالْأَرْضَ ۖ وَلَا يَئُودُهُ حِفْظُهُمَا ۚ وَهُوَ الْعَلِيُّ الْعَظِيمُ

صدق الله العظيم

سورة البقرة الآية (255)

Dedication

I dedicate this research to my parents, my husband, my children, my brothers and sisters.

Acknowledgement

Firstly thanks to Allah, Almighty, for giving me the strength to complete this research.

I would like to express my special thanks to my supervisor Dr. Mohammed Suleiman who gave me the golden opportunity to do this wonderful research, which help me to know about so many new things. I would also like to thank my family and friends who helped me a lot in finalizing this research.

Abstract

Computational methods have become more developed and increasingly used in the corrosion inhibition studies. Quantitative Structure-Activity Relationship modeling (QSAR) is one of the major computational tools employed in computational chemistry. It is becoming more desirable for predicting of corrosion inhibition efficiency. In this research a QSAR was used to predict the inhibition efficiency of 2,5-bis (4-diphenol)-1,3,4-thiadiazole [DPHT] on mild steel in 1M HCl solution compared to inhibition efficiency of some nitrogen containing compounds. ACD ChemSketch software was used to draw the chemical structures of these compounds. The obtained results showed that the ability of the molecule to adsorb on the steel surface is dependent on the group in para position in phenyl substituent. Replacement of hydrogen atom in para position in phenyl substituent by an electron-releasing group arises an enhancement in the inhibition efficiency and vice versa with electron withdrawing groups. We predicted that the 2,5-bis (4-diphenol)-1,3,4-thiadiazole must have a high inhibition efficiency, in the range of (90-98)%.

المستخلص

أصبحت الطرق الحاسوبية أكثر تطوراً وتستخدم بشكل متزايد في دراسة تثبيط التآكل. نموذج علاقة النشاطية بالبناء وهو أحد أهم الأدوات التي استخدمت في الكيمياء الحاسوبية، واصبحت مرغوبة أكثر في التنبؤ بكفاءة مثبطات التآكل. تم استخدامها للتنبؤ بكفاءة تثبيط المركب 1,3,4- 2,5-bis(4- diphenol)- thiadiazole[DPHT] على الفولاذ الطري في وجود محلول حمض الهيدروكلوريك (1مولاري) مقارنة بكفاءة تثبيط بعض مركبات النيتروجين. استخدمت برمجيات ACD chemsketch في رسم التركيب الكيميائي لهذه المركبات. لقد وجد أن قابلية الجزيء لكي يمتص على سطح الفولاذ يعتمد على المجموعة الوظيفية الموجودة في الموقع بارا في مستبدل حلقة الفينيل. استبدال ذرة الهيدروجين في الموقع بارا في الفينيل بمجموعة مانحة للإلكترونات يؤدي إلى زيادة كفاءة التثبيط، واستبدالها بمجموعة ساحبة للإلكترونات يؤدي إلى نقصان كفاءة التثبيط. توقعنا أن كفاءة تثبيط المثبط 1,3,4- 2,5-bis(4- diphenol)- thiadiazole[DPHT] يجب أن تكون عالية (90-98)%.

List of contents

No	Title	Page no
	إستفتاح	I
	Dedication	II
	Acknowledgement	III
	Abstract	IV
	المستخلص	V
	List of contents	VI
<p style="text-align: center;">Chapter one:</p> <p style="text-align: center;">Introduction & Literature review</p>		
1-	Introduction	1
1-1	Computational chemistry	1
1-1-1	Definition of Computational chemistry	1
1-1-2	Uses of computational chemistry	2
1-1-3	Questions investigated in computational chemistry	2
1-1-4	The tools of computational chemistry	3
1-2	QSAR	5
1-2-1	Definition of QSAR	5
1-2-2	Modeling methods	6
1-2-2-1	Methods for regression problems	6

1-2-2-2	Methods for classification problems	7
1-2-3	Software for QSAR development	8
1-2-3-1	Structure drawing or file conversion	9
1-2-3-2	3D structure generation	10
1-2-3-3	Descriptor calculation	11
1-2-3-4	Modeling	12
1-3	Corrosion inhibitors	13
1-3-1	Mechanisms of actions of inhibitors	13
1-3-2	Types of corrosion inhibitors	14
1-3-3	Mild steel	16
1-4	Literatures review	16
	Objectives of the study	18
Chapter two:		
Experimental		
2-	Experimental	19
Chapter three:		
Results and discussion		
3-	Results and discussion	22
4-	Conclusion	26

	References	27
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List of figures

	Fig.1. Chemical structures of the investigated compounds	20
	Fig.2. 2,5-bis(4-diphenol)-1,3,4-thiadiazole [DPHT]	25

List of table

	Table 1: Inhibition efficiencies values	22
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Chapter one

Introduction and literature review

Chapter one

Introduction and Literature Review

1- Introduction

1-1 Computational chemistry:

1-1-1 Definition of computational chemistry:

Computational Chemistry is the modeling of chemical phenomenon using computers rather than chemicals [1]. It's generally used when a mathematical method is sufficiently well developed that it can be automated for implementation on a computer. Very few aspects of chemistry can be computed exactly, but almost every aspect of chemistry has been described in a qualitative or approximately quantitative computational scheme. The biggest mistake a computational chemist can make is to assume that any computed number is exact. However, just as not all spectra are perfectly resolved, often a qualitative or approximate computation can give useful insight into chemistry if the researcher understands what it does and does not predict [2]. Computational chemistry is fairly cheap, it is fast compared to experiment, and it is environmentally safe (although the profusion of computers in the last decade has raised concern about the consumption of energy and the disposal of obsolescent machines). It does not replace experiment, which remains the final arbiter of truth about nature. Furthermore, to make something – new drugs, new materials – one has to go into the lab. However, computation has become so reliable in some respects that, more and more, scientists in general are employing it before embarking on an experimental project, and the day may come when to obtain a grant for some kinds of experimental work you will have to show to what extent you have computationally explored the feasibility of the proposal [3].

1-1-2 Uses of computational chemistry:

Computational chemistry is used in a number of different ways: One particularly important way is to model a molecular system prior to synthesizing that molecule in the laboratory. Although computational models may not be perfect, they are often good enough to rule out 90% of possible compounds as being unsuitable for their intended use. This is very useful information because synthesizing a single compound could require months of labor and raw materials, and generate toxic waste [2]. A second use of computational chemistry is in understanding a problem more completely. There are some properties of a molecule that can be obtained computationally more easily than by experimental means. There are also insights into molecular bonding, which can be obtained from the results of computations that cannot be obtained from any experimental method. Thus, many experimental chemists are now using computational modeling to gain additional understanding of the compounds being examined in the laboratory [2]. As computational chemistry has become easier to use, professional computational chemists have shifted their attention to more difficult modeling problems. No matter how easy computational chemistry becomes, there will always be problems so difficult that only an expert in the field can tackle them [2].

1-1-3 Questions investigated in computational chemistry:

Computational chemistry or molecular modeling is a set of techniques for investigating chemical problems on a computer. Questions commonly investigated computationally are:

1-1-3-1 Molecular geometry: the shapes of molecules bond lengths, angles and dihedrals [3].

1-1-3-2 Energies of molecules and transition states: this tells us which isomer is favored at equilibrium, and (from transition state and reactant energies) how fast a reaction should go [3].

1-1-3-3 Chemical reactivity: for example, knowing where the electrons are concentrated (nucleophilic sites) and where they want to go (electrophilic sites) enables us to predict where various kinds of reagents will attack a molecule [3].

1-1-3-4 IR, UV and NMR spectra: these can be calculated, and if the molecule is unknown, someone trying to make it knows what to look for [3].

1-1-3-5 The interaction of a substrate with an enzyme: seeing how a molecule fits into the active site of an enzyme is one approach to designing better drugs [3].

1-1-3-6 The physical properties of substances: these depend on the properties of individual molecules and on how the molecules interact in the bulk material. For example, the strength and melting point of a polymer (e.g. a plastic) depend on how well the molecules fit together and on how strong the forces between them are. People who investigate things like this work in the field of materials science [3].

1-1-4 The tools of computational chemistry:

In studying these questions computational chemists have a selection of methods at their disposal. The main tools available belong to five broad classes:

1-1-4-1 Molecular mechanics: is based on a model of a molecule as a collection of balls (atoms) held together by springs (bonds). If we know the normal spring lengths and the angles between them, and how much energy it takes to stretch and bend the springs, we can calculate the energy of a given collection of balls and springs, i.e. of a given molecule; changing the geometry until the lowest energy is

found enables us to do a geometry optimization, i.e. to calculate a geometry for the molecule [3].

1-1-4-2 Ab Initio calculations: are based on the Schrodinger equation. This is one of the fundamental equations of modern physics and describes, among other things, how the electrons in a molecule behave. Ab initio calculations are relatively slow: the geometry and IR spectra of propane can be calculated at a reasonably high level in minutes on a personal computer, but a fairly large molecule, like a steroid, could take perhaps days [3].

1-1-4-3 Semiempirical calculations: are, like ab initio, based on the Schrödinger equation. However, more approximations are made in solving it, and the very complicated integrals that must be calculated in the ab initio method are not actually evaluated in semiempirical calculations: instead, the program draws on a kind of library of integrals that was compiled by finding the best fit of some calculated entity like geometry or energy (heat of formation) to the experimental values. This plugging of experimental values into a mathematical procedure to get the best calculated values is called parameterization (or parametrization). It is the mixing of theory and experiment that makes the method “semiempirical”. Semiempirical calculations are slower than molecular mechanics but much faster than ab initio calculations. Semiempirical calculations take roughly 100 times as long as molecular mechanics calculations, and ab initio calculations take roughly 100–1,000 times as long as semiempirical. A semiempirical geometry optimization on a steroid might take seconds on a PC [3].

1-1-4-4 Density functional calculations:(DFT calculations, density functional theory) are, like ab initio and semiempirical calculations, based on the Schrodinger equation. However, unlike the other two methods, DFT does not calculate a

conventional wave function, but rather derives the electron distribution (electron density function) directly. A functional is a mathematical entity related to a function. Density functional calculations are usually faster than ab initio, but slower than semiempirical. DFT is relatively new (serious DFT computational chemistry goes back to the 1980s, while computational chemistry with the ab initio and semiempirical approaches was being done in the 1960s) [3].

1-1-4-5 Molecular dynamics calculations apply the laws of motion to molecules. Thus one can simulate the motion of an enzyme as it changes shape on binding to a substrate, or the motion of a swarm of water molecules around a molecule of solute; quantum mechanical molecular dynamics also allows actual chemical reactions to be simulated [3].

1-2 QSAR:

1-2-1 Definition of QSAR:

QSARs, or quantitative structure–activity relationships, are mathematical models that attempt to relate the structure-derived features of a compound to its biological or physicochemical activity [4]. It is a computational modeling method which has been applied in many disciplines of chemistry. QSAR works on the assumption that structurally similar compounds have similar activities. Therefore, these methods have predictive and diagnostic abilities. They can be used to predict the biological activity such as class (e.g., inhibitor versus noninhibitors) of compounds before the actual biological testing. They can also be used in the analysis of structural characteristics that can give rise to the properties of interest [4].

The advantage of using QSAR over other modeling techniques is that it takes into account the full complexity of the biological system without requiring information about the binding site. The disadvantage is that the method will not distinguish

between the contribution of binding and transport properties in determining drug activity [2].

1-2-2 Modeling Methods:

A good QSAR model should possess high prediction power and prediction reliability. In general, methods for constructing QSAR can be divided into two groups: methods for regression problems or classification problems. The methods are organized into the two groups in the following section:

1-2-2-1 Methods for regression problems:

1-2-2-1-1 Multiple Linear Regressions:

Multiple linear regression (MLR) is one of the most fundamental and common modeling method for regression QSAR.

1-2-2-1-2 Partial Least Squares:

Partial least squares (PLSs) assumes a linear relationship between feature vector, X , and target property, y^{\wedge} , but unlike MLR, PLS is more appropriate when the number of features greatly exceed the number of samples and when features are highly collinear [5].

1-2-2-1-3 Feedforward Backpropagation Neural Network: Artificial neural network (ANN) attempts to imitate a biological neural network and is inspired from the structure, processing, and learning method of a biological brain [5].

1-2-2-1-4 General Regression Neural Network:

One of the difficulty of building a neural network is the lack of automation in the selection of parameters and network topology. Coupled with many iterations that

may be needed by the backpropagation method to converge to an acceptable error, model building is usually a time-consuming process [5].

1-2-2-1-5 Gaussian Processes:

Gaussian process (GP) is a generalization of the Gaussian probability distribution to an infinitely large pool of possible functions and it is formally defined as a collection of random variables, any finite number of which has a joint Gaussian distribution. GP is one of the kernel methods for model development and have been applied in QSAR modeling of ADMET and aqueous solubility, and hERG inhibitors [5].

1-2-2-2 Methods for classification problems:

1-2-2-2-1 Logistic Regression:

Logistic regression (LR) is similar to linear regression in many ways. LR is used to model the probability of the occurrence of some event as a linear function of a set of predictors [5].

1-2-2-2-2 Linear Discriminant Analysis:

Linear discriminant analysis (LDA) is commonly used for classification problems and also for dimensionality reduction. It works on data that has categorical target properties and molecular descriptors that are continuous variables [5].

1-2-2-2-3 Decision Tree and Random Forest:

A decision tree (DT) is a structure with hierarchical arrangement of nodes and branches. A DT has three types of nodes: a root node, internal nodes, and leaf nodes. A root node does not have any incoming branches, while an internal node has one incoming branch and two or more outgoing branches [5].

1-2-2-2-4 k-Nearest Neighbor:

k-nearest neighbor (kNN) is a type of lazy learner whereby it delays the learning of the training data until it is needed to classify an unknown sample. It is useful for QSAR studies because QSAR works on the assumption of compounds with similar structure should have similar activities [5].

1-2-2-2-5 Probabilistic Neural Network:

Probabilistic neural network (PNN) is similar to the general regression neural network, but it is used in classification problems. PNN is effective in nonlinear mapping, pattern recognition, estimation of target property and likelihood ratios[5].

1-2-2-2-6 Support Vector Machine:

Support vector machine (SVM) is based on the structural risk minimization principle from statistical learning theory, and it is probably one of the most well-known kernel methods for model development [5].

1-2-3 Software for QSAR development:

There are many commercial or free software available for QSAR development. These include specialized software for drawing chemical structures, interconverting chemical file formats, generating 3D structures, calculating chemical descriptors, developing QSAR models, and general-purpose software that have all the necessary components for QSAR development.

1-2-3-1 Structure drawing or file conversion:

1-2-3-1-1 ChemDraw:

Isa commercial software for chemical structure drawing and editing. It may be packaged with other programs such as ChemDraw ActiveX/ Plugin Viewer,

Chem3D, ChemBioFinder, and ChemNMR which enhance the functionality of the program. Besides drawing and editing of chemical structures, the program offers integration of the drawn structure into Microsoft Office documents, conversion of structure from name (or name from structure), ^{13}C and ^1H NMR prediction, query of online databases, and many other features [5].

1-2-3-1-2 ACD/ChemSketch:

ACD/ChemSketch is a software for drawing of chemical structures that comes with other functionalities such as calculation of molecular properties, 2D and 3D structure cleaning, structure naming, and prediction of logP. The software is available in two versions: the commercial and freeware version. The freeware version does not include ACD/Dictionary, technical support, ACD/Lab extension for ChemDraw, and the function to search files by structure [5].

1-2-3-1-3 Open Babel:

Conversion of files at different stages of QSAR development may be necessary to satisfy the input requirements of various software. The file conversion can be easily done by using software like Open Babel. Open Babel is an open-source program that enables users to search, convert files, analyze or store data from molecular modeling projects. Open Babel can convert over 90 chemical file formats, and it also has compounds preprocessing functionality like adding hydrogen bond, convert dative bonds, and generate 3D coordinates[5].

1-2-3-2 3D structure generation:

1-2-3-2-1 CORINA:

CORINA is one of the commercial software offered by Molecular Networks. It is used for generating three-dimensional structure of small- and medium sized

compounds, necessary as a preprocessing step prior to calculation of 3D molecular descriptors or structure-based docking studies [5].

1-2-3-2-2 Concord:

Concord is available as one of SYBYL applications. It is a commercial software that converts 2D inputs into 3D structures rapidly. The main benefits of Concord includes the variety of built-in geometry optimization options and its capability of handling inputs and outputs of common industry-standard formats [5].

1-2-3-2-3 Frog:

Frog is an online tool for 3D conformation generation from 1D or 2D information using Merck molecular force field [5].

1-2-3-2-4 smi23d:

smi23d is an open-source program that can be downloaded and compiled for use in Windows or Linux. The program generates 3D structures from SMILES string [5].

1-2-3-3 Descriptor calculation:

1-2-3-3-1 ADRIANA.Code:

ADRIANA.Code is one of the commercial software offered by Molecular Networks for computing molecular descriptors [5].

1-2-3-3-2 Dragon:

Dragon is a commercial software for the computation of molecular descriptors [5].

1-2-3-3-3 Molconn-Z:

Molconn-Z is a commercial software for molecular descriptor calculation that works on multiple platforms, for example, Windows, Mac OS X, and Linux. It calculates molecular connectivity chi indices, kappa shape indices, electrotopological state indices, topological indices, counts of subgraphs, and vertex eccentricities [5].

1-2-3-3-4 PaDEL-Descriptor:

We released the first version of PaDEL-Descriptor in 2008 and have recently updated it to version 2.0. PaDEL-Descriptor is an open-source Java-based software developed using the Chemistry Development Kit for the calculation of molecular descriptors and fingerprints. Currently, it can calculate 797 descriptors and 10 types of fingerprints which includes 1D, 2D, and 3D descriptors, for example, atom-type electrotopological state descriptors, McGowan volume, molecular linear free energy relation descriptors, ring counts, WHIM, Petitjean shape index, count of chemical substructures identified by Laggner, and binary fingerprints and count of chemical substructures identified by Klekota and Roth [5].

1-2-3-4 Modeling:

1-2-3-4-1 KNIME:

Konstanz Information Miner (KNIME) is an open-source platform with pipelining ability for data integration, processing, analysis, and exploration [5].

1-2-3-4-2 RapidMiner:

RapidMiner is an open-source system with a large collection of algorithms for data analysis and model development. There are more than 500 operators for data

processing, model development, evaluation, and visualization, and it also integrates another modeling library, WEKA [5].

1-2-3-4-3 WEKA:

WEKA has a rich compilation of modeling methods and tools for data preprocessing, classification, regression, clustering, and visualization, which are organized into different sections in the WEKA Explorer [5].

1-2-3-4-4 Orange:

Orange is a free program that offers tools for some simple data preparation, evaluation, visualization, classification, regression, and clustering [5].

1-2-3-4-5 TANAGRA:

TANAGRA is an open-source software containing tools for data analysis, statistics, modeling, and database exploration [5].

1-2-3-4-6 MATLAB:

MATLAB is a commercial software that provides an interactive system for algorithm development, data visualization, data analysis, and numeric computation with wide application in image processing, financial analysis, computational biology, and so on. Data can be analyzed easily with ready-to-use functions, but users are also allowed to customize some of these tools or add their own algorithms for use. It also has functions to integrate MATLAB-based algorithms with external applications and languages such as Microsoft Excel, Java, and C++. This enables developed QSAR models to be easily distributed as stand-alone programs or software modules.

1-2-3-4-7 R:

R is a free software environment for graphical and statistical analysis that can run on Windows, Linux, and Mac OS X. It has a variety of statistical tools like linear or nonlinear modeling, classical statistical tests, time-series analysis, classification, and clustering [5].

1-3 Corrosion inhibitors:

Corrosion is destructive attack of a metal by its reaction with the environment. It's responsible for numerous losses mainly in the industrial scope. It is clear that the best way to combat it is prevention. Among the various methods to avoid or prevent destruction or degradation of metal surface, the corrosion inhibitor is one of the best known methods of corrosion protection and one of the most useful on the industry. This method is following stand up due to low cost and practice method. [6] [7] [8].

1-3-1 Mechanisms of actions of inhibitors:

Inhibitors are substances or mixtures that in low concentration and in aggressive environment inhibit, prevent or minimize the corrosion [7].

Generally the mechanism of the inhibitor is one or more of three that are cited below:

- the inhibitor is chemically adsorbed (chemisorption) on the surface of the metal and forms a protective thin film with inhibitor effect or by combination between inhibitor ions and metallic surface;
- the inhibitor leads a formation of a film by oxide protection of the base metal;

- the inhibitor reacts with a potential corrosive component present in aqueous media and the product is a complex [9].

1-3-2 Types of corrosion inhibitors:

1-3-2-1 Anodic inhibitors:

Anodic inhibitors usually act by forming a protective oxide film on the surface of the metal causing a large anodic shift of the corrosion potential. This shift forces the metallic surface into the passivation region. They are also sometimes referred to as passivators. Chromates, nitrates, tungstate, molybdates are some examples of anodic inhibitors [10].

1-3-2-2 Cathodic inhibitors:

Cathodic inhibitors act by either slowing the cathodic reaction itself or selectively precipitating on cathodic areas to limit the diffusion of reducing species to the surface. The rates of the cathodic reactions can be reduced by the use of cathodic poisons. However, cathodic poisons can also increase the susceptibility of a metal to hydrogen induced cracking since hydrogen can also be absorbed by the metal during aqueous corrosion or cathodic charging. The corrosion rates can also be reduced by the use of oxygen scavengers that react with dissolved oxygen. Sulfite and bisulfite ions are examples of oxygen scavengers that can combine with oxygen to form sulfate [10].

1-3-2-3 Mixed Inhibitors:

Mixed inhibitors work by reducing both the cathodic and anodic reactions. They are typically film forming compounds that cause the formation of precipitates on the surface blocking both anodic and cathodic sites indirectly. Hard water that is high in calcium and magnesium is less corrosive than soft water because of the

tendency of the salts in the hard water to precipitate on the surface of the metal forming a protective film. The most common inhibitors of this category are the silicates and the phosphates. Sodium silicate, for example, is used in many domestic water softeners to prevent the occurrence of rust water. In aerated hot water systems, sodium silicate protects steel, copper and brass. However, protection is not always reliable and depends heavily on pH. Phosphates also require oxygen for effective inhibition. Silicates and phosphates do not afford the degree of protection provided by chromates and nitrites, however, they are very useful in situations where non-toxic additives are required [10].

1-3-2-4 Volatile Corrosion Inhibitors:

Volatile Corrosion Inhibitors (VCI), also called Vapor Phase Inhibitors (VPI), are compounds transported in a closed environment to the site of corrosion by volatilization from a source. In boilers, volatile basic compounds, such as morpholine or hydrazine, are transported with steam to prevent corrosion in the condenser tubes by neutralizing acidic carbon dioxide or by shifting surface pH towards less acidic and corrosive values. In closed vapor spaces, such as shipping containers, volatile solids such as salts of dicyclo-hexylamine, cyclohexylamine and hexamethylenamine are used. When these inhibitors come in contact with the metal surface, the vapor of these salts condenses and is hydrolyzed by any moisture to liberate protective ions. It is desirable, for an efficient VCI, to provide inhibition rapidly while lasting for long periods. Both qualities depend on the volatility of these compounds; fast action wanting high volatility while enduring protection requires low volatility [10].

1-3-3 Mild steel:

Mild Steel is one of the major construction materials used in the industries, which is extensively used in chemical and allied industries for the handling of acid, alkali and salt solutions. Hydrochloric acid is the most difficult of the common acids to handle from the standpoints of corrosion and materials of constructions. Extreme care is required in the selection of materials to handle the acid by itself, even in relatively dilute concentrations or in process solutions containing appreciable amount of hydrochloric acid. This acid is very corrosive to most of the common metals and alloys [11].

Mild steel is the most versatile, least expensive and widely used engineering material which has found extensive application in various industries. It is used in large tonnages in marine applications, nuclear power and fossil fuel power plant, transportation, chemical processing, petroleum production and refining, pipelines, mining, construction as well as metal processing equipment. However, the corrosion resistance of mild steel is relatively limited. This causes many corrosion problems to be arising in the related industries[12].

1-4 Literatures review:

QSAR methods are now being used for predicting the inhibition efficiencies for corrosion inhibitors in dry laboratories. Success depends upon having data on a large number of compounds available. The computational method has proved satisfactory for the inhibition efficiency estimations. High correlation was obtained with the multivariate correlation, i.e. all the indices combined together, where the prediction power was very high for genetic function approximation (GFA). Although GFA proved to be efficient in predicting ability, more work is still required toward understanding structure-property correlation on inhibition

corrosion studies, particularly concerning the analysis of different structural chemical descriptors. Understanding adsorption phenomena is of key importance in corrosion problems. Computational studies help to find the most stable adsorption sites for a broad range of materials. This information can help to gain further insight about corrosion system, such as the most likely point of attack for corrosion on a surface, the most stable site for inhibitor adsorption and the binding energy of the adsorbed layer [13].

Adsorption of organic compounds on metal surfaces may inhibit the anodic and/or cathodic processes. The presence of conjugated adsorption processes may change the corrosion potentials and the nature of cathodic depolarization processes and lead to the metal dissolution in the passivity region. It is clear that these complex processes cannot fully be accounted for by using (more or less heuristic) QSAR approaches. In spite of these limitations, QSAR is still an effective method that can be used together with experimental techniques to optimize corrosion inhibition efficiencies of prospective molecules. Investigation using substituent constants and quantum-chemical indices indicate that an optimal value in the parameters should exist [14].

Objectives of the study:

The objectives of this study are:

- Create a new corrosion inhibitor on mild steel in hydrochloric acid.
- Predict the inhibition efficiency of this new inhibitor using QSAR modeling.

Chapter two

Experimental

Chapter two

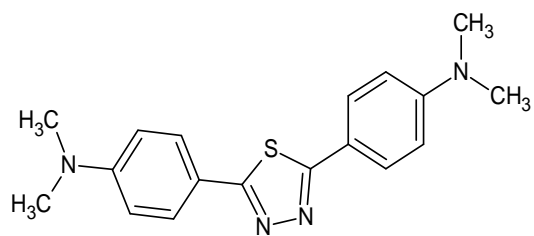
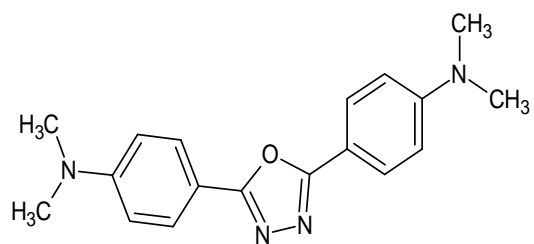
Experimental

2- Experimental:

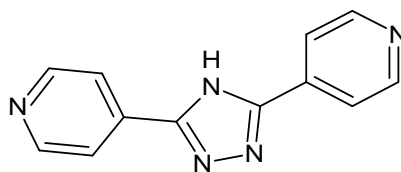
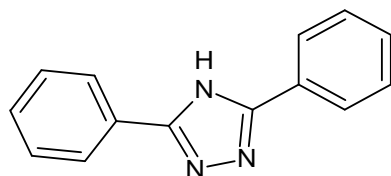
All corrosion inhibition data were obtained from the literature [15]. The experimental details are outlined briefly here as indicated in reference [15].

Materials—Results concerning 2,5-bis(4-dimethyl aminophenyl)–1,3,4-oxadiazole (DAPO), 2,5-bis(4-dimethylamino phenyl)–1,3,4-thiadiazole (DAPT), 2,5-bis(4-nitrophenyl)–1,3,4-oxadiazole (PNOX), 2,5-bis(4-aminophenyl)–1,3,4-oxadiazole (PAOX), 3,5-diphenyl-4H-1,2,4-triazole (DHT), 3,5-di(4-chloro phenyl)-4H-1,2,4-triazole (CHT), 3,5-di(4-pyridyl)-4H-1,2,4-triazole (PHT), and 3,5-di(4-methylthio phenyl)-4H-1,2,4-triazole (4-MTHT) were publish earlier [15]. Inhibitor efficiency of 2,5-bis (4-diphenol)-1,3,4-thiadiazole [DPHT] was measured in this study.

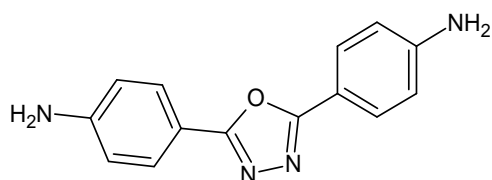
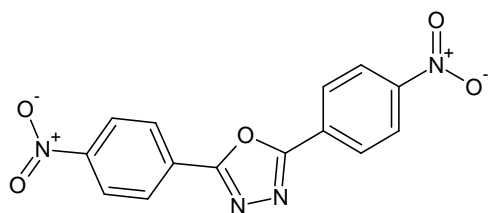
The organic compounds CHT, PHT, DHT, 4-MTHT, DAPO, PNOX, PAOX and DAPT were tested as corrosion inhibitors, and were prepared in the laboratory. The molecular formulas of these inhibitors were drawn using ACD chemsketch are shown in Figure 1. Mild steel strips composed of (wt%): 0.09% P, 0.38% Si, 0.01% Al, 0.05% Mn, 0.21% C, 0.05% S, and balance Fe were pre-treated prior to the experiments by grinding with emery paper SiC (grades 600 and 1200), then cleaned in ultrasonic bath with ethanol, rinsed with doubly distilled water and finally dried at room temperature. The aggressive solutions (1 M HCl) were prepared by dilution of an analytical reagent grade 37% HCl with doubly distilled water. The concentration of organic compounds employed was 1×10^{-4} M.



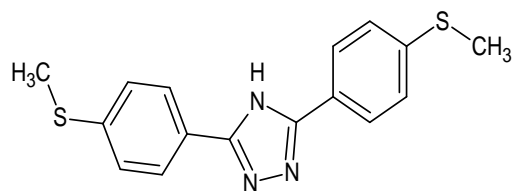
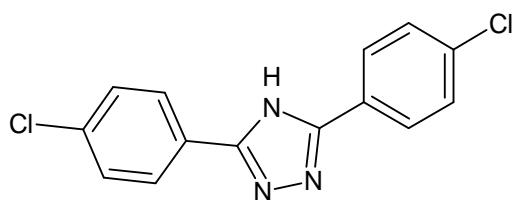
DAPTDPO



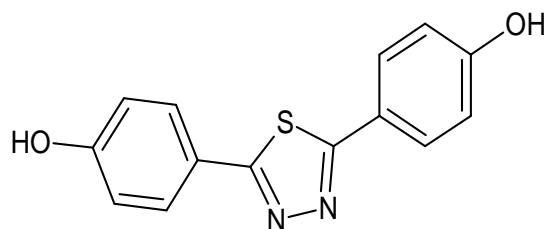
PHT DHT



PAOX PONX



4-MTHTCHT



DPHT

Fig. 1. Chemical structures of the investigated compounds.

The corrosion behavior of mild steel in 1 M HCl solution in the absence and presence of heterocyclic derivatives was investigated by the electrochemical impedance spectroscopy (EIS) at 30 °C after 24 h of immersion. The inhibition efficiency $I.E$ (%) is calculated by R_{ct} using Eq. 1, where R_{ct}^0 and R_{ct} are the charge transfer resistance values without and with inhibitor, respectively [15]:

$$I.E.(%) = \frac{R_{ct} - R_{ct}^0}{R_{ct}} \times 100$$

Chapter three

Results and Discussion

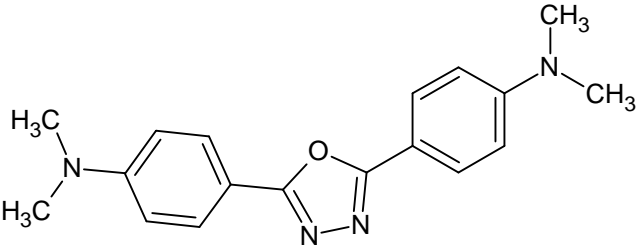
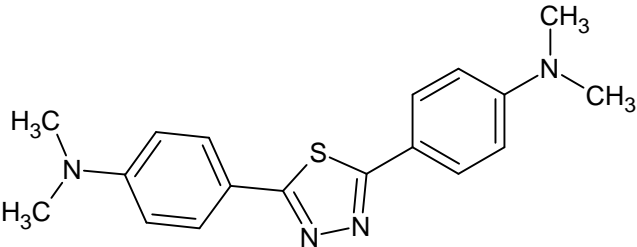
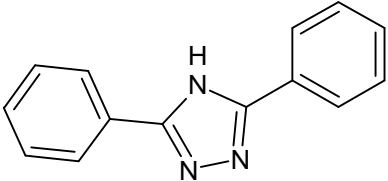
Chapter three

Results and Discussion

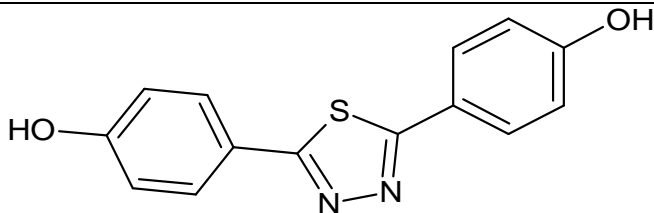
3- Results and Discussion:

The variation in inhibitive efficiency mainly depends on the type and nature of the substituents present in the inhibitor molecule and the electronic and structural properties of the inhibitor molecule such as functional groups, steric factors, aromaticity, electron density on donor atoms and p orbital character of donating electrons.

Table 1: inhibition efficiencies values (related to 10^{-4} M concentration).

Inhibitors	Inhibition efficiencies
 DAPO	89.8
 DAPT	93.9
	92.5

<p>DHT</p>	
<div data-bbox="289 283 690 472" data-label="Chemical-Block"> <p>The structure shows a 1,2,4-triazole ring connected at the 5-position to a pyridine ring and at the 3-position to another pyridine ring.</p> </div> <p>PHT</p>	<p>95.2</p>
<div data-bbox="198 583 787 829" data-label="Chemical-Block"> <p>The structure shows a 1,2,4-triazole ring connected at the 5-position to a 4-nitrophenyl group and at the 3-position to another 4-nitrophenyl group. The nitro groups are represented as O^- and N^+.</p> </div> <p>PNOX</p>	<p>7.4</p>
<div data-bbox="207 955 771 1144" data-label="Chemical-Block"> <p>The structure shows a 1,2,4-triazole ring connected at the 5-position to a 4-aminophenyl group and at the 3-position to another 4-aminophenyl group. The amino groups are represented as H_2N.</p> </div> <p>PAOX</p>	<p>97.9</p>
<div data-bbox="235 1260 738 1449" data-label="Chemical-Block"> <p>The structure shows a 1,2,4-triazole ring connected at the 5-position to a 4-chlorophenyl group and at the 3-position to another 4-chlorophenyl group. The chlorine atoms are represented as Cl.</p> </div> <p>CHT</p>	<p>10.6</p>
<div data-bbox="170 1564 803 1753" data-label="Chemical-Block"> <p>The structure shows a 1,2,4-triazole ring connected at the 5-position to a 4-methylthiophenyl group and at the 3-position to another 4-methylthiophenyl group. The methylthio groups are represented as H_3C and S.</p> </div> <p>4-MTHT</p>	<p>99.1</p>

 <p style="text-align: center;">DPHT</p>	90-98
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In a case of 2,5-disubstituted-1,3,4-oxadiazole, 3,5-disubstituted-4H-1,2,4-triazole and 2,5-disubstituted-1,3,4-thiadiazole, the ability of the molecule to adsorb on the steel surface is dependent on the group in para position in phenyl substituent. Replacement of hydrogen atom in para position in phenyl substituent by an electron-releasing group arises an enhancement in the inhibition efficiency and vice versa with electron withdrawing groups as shown in table 1. For example, in the organic compound oxadiazoles (DAPO, PNOX, PAOX) the inhibition efficiency is not similar due to the different substituents (methylamine, nitro, amine) respectively. Methylamine and amine are donating groups so the inhibition efficiency of DAPO and PAOX is high (comparing DAPO and PAOX, the inhibition efficiency of PAOX is higher than DAPO because amine has two pairs of electrons while methylamine has lone pair). Nitro group is withdrawing group so the inhibition efficiency of PNOX is very low. Depending on this property, we can predict that 2,5-bis(4-diphenol)-1,3,4-thiadiazole [DPHT] will have a high inhibition efficiency, in the range of (90-98)%.

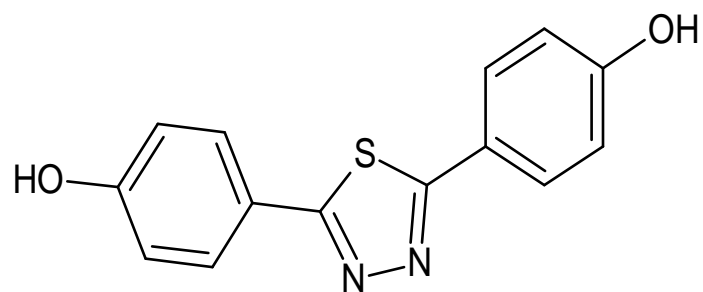


Fig. 2.2,5-bis(4-diphenol)-1,3,4-thiadiazole [DPHT]

4- Conclusion:

- At the present work QSAR was used to predict the inhibition efficiency of 2,5-bis (4-diphenol)-1,3,4-thiadiazole [DPHT] on mild steel in 1M HCl compared to inhibition efficiency of some nitrogen containing compounds.
- ACD ChemSketch software was used to draw the chemical structures of these compounds.
- The results showed that the ability of the molecule to adsorb on the steel surface is dependent on the group in Para position in phenyl substituent.
- Replacement of hydrogen atom in para position in phenyl substituent by an electron-releasing group arises an enhancement in the inhibition efficiency and vice versa with electron withdrawing groups.
- We predicted that the 2,5-bis (4-diphenol)-1,3,4-thiadiazole must have a high inhibition efficiency, in the range of (90-98)%.

References

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