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Synthesis, spectral analysis, anti-corrosive activity and theoretical study of an aromatic hydrazone derivative

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Abstract

An aromatic hydrazone derivative; namely (E)-1-(3-nitrobenzylidene)-2-(p-tolyl)hydrazine (**E-NBPTH**) has been synthesized by condensation of an aromatic hydrazine with an aromatic aldehyde in methanol at reflux. The molecular structure of **E-NBPTH** has been identified and analyzed by spectroscopic methods such as UV-vis, IR, ¹H NMR and ¹³C NMR. The corrosion inhibition behavior of the prepared molecule in 0.5M H_2SO_4 was investigated by gravimetric, electrochemical and theoretical methods. According to the polarization study, the **E-NBPTH** acts as a mixed type of inhibitor. The adsorption of **E-NBPTH** on the iron surface follows the Langmuir isotherm. The optimized molecular structure and some quantum chemical parameters of the synthesized compound have been calculated using the density functional method (DFT). The results obtained from theoretical study are well support the experimental results.

Keywords: Hydrazone; Synthesis; Spectral analysis; Corrosion inhibition; Adsorption; DFT.

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1. Introduction

Hydrazone derivatives are an important and highly active class of organic molecules, which are offer a wide range of applications such as the development of new anti-corrosive agents [1-3] and anti-cancer drugs [4-7]. The high activity of hydrazones may be related to the presence of the N–N and C=N bonds in their molecular structures.

Since long time, corrosion is considered a major problem in the industrial field and it causes losses of millions of dollars annually. To this effect, several techniques were developed and employed to remedy this problem, especially, the use of the organic inhibitors which is considered one of the most applied and effective techniques [8, 9]. Recently, many researches in the corrosion field prove that several hydrazones and their derivatives are reported as useful corrosion inhibitors for diverse metals and alloys in various media [10–14]. In this context several works have been published involving the development of the synthetic methods of these molecules in order to improve their yields [15–17].

Generally, the inhibition activity of the organic inhibitors is related to the presence of different heteroatoms and aromatic rings in their molecular structure [18]. In the other hand, this activity is associated to the physicochemical and electronic characteristics of the inhibitor molecule [19, 20]. During the past 20 years, the quantum chemical calculations using DFT method are become an effective approach to determine a correlation between the corrosion inhibitory efficiency and some quantum chemical parameters [21-24]. Also, the DFT calculations are extensively used to study the various biological activities of the bioactive molecules [25–27]. Additionally, molecular dynamics simulations (MDS) are widely utilized in the corrosion inhibition studies in order to comprehend the interactions between inhibitor molecules and metallic surfaces [28–31].

In the present work, we interest on the synthesis and spectroscopic analysis of an aromatic hydrazone derivative namely; namely (E)-1-(3-nitrobenzylidene)-2-(p-tolyl)hydrazine (**E-NBPTH**). On the other hand, the anti-corrosive activity of the synthesized molecule has been evaluated in sulfuric acid medium using gravimetric measurements, potentiodynamic polarization curves and electrochemical impedance spectroscopy (EIS). The influence of the immersion time and temperature on the inhibition efficiency of the synthesized molecule has been investigated. Additionally, the DFT calculations were effected to correlate experimental results. Also, the molecular dynamics simulations (MDS) were applied to study the interactions between inhibitor molecule and the Fe (110) surface.

2. Experimental

2.1. Materials and reagents

All the reagents used for the hydrazone derivative synthesis and the sulfuric acid (98%) employed in corrosion study were purchased from Sigma-Aldrich and used without further purification. Moreover, in the corrosion experiments the employed specimens and working electrode were prepared from XC48 carbon steel with the following chemical composition (wt.%): C(%)= 0.418, Mn(%)= 0.730, Mo(%)= 0.012, P(%)= 0.016, S(%)= 0.019, Si(%)= 0.245, Ni(%)= 0.079, F(%)= 0.777 and Fe(%)= 98.09873. Before each corrosion test the surface of carbon steel was successively cleaned with various grades of SiC abrasive papers, washed with bi-distilled water and dried.

2.2. Spectroscopic details

The UV–Vis spectrum of the synthesized compound was run in DMSO solution on a Jasco V-650 UV-Vis spectrometer in the region of 190–900 nm. Also, the FT-IR spectrum of the synthesized molecule was realized in solid state at room temperature using the JASCO 4000 FTIR spectrometer and the measured vibrational frequencies are recorded in the range of 600– 4000 cm⁻¹. In addition, the NMR spectra were obtained on a Bruker Advance 300 NMR spectrometer operating at 300 MHz for ¹H NMR and ¹³C NMR in CDCl₃ as a solvent.

2.3. Synthesis of the studied hydrazone

The studied hydrazone derivative; namely (E)-1-(3-nitrobenzylidene)-2-(p-tolyl)hydrazine (**E-NBPTH**), was synthesized by the condensation of (4-methylphenyl)hydrazine (0.1247 g, 1 mmol) with 3-nitrobenzaldehyde (0.1527 g, 1 mmol) under methanol reflux for 4 h (Fig. 1). The formed yellow precipitate was filtered, washed with methanol and dried. The obtained final product is a pure yellow powder which is passed later to the spectroscopic characterization.

2.4. Corrosion inhibition tests

2.4.1. Weight loss tests

All the carbon steel specimens used in weight loss tests are cylindrical forms of 9.43 cm² of area. Firstly, all specimens were weighed before the immersion in the tested solutions. Then, each specimen was immersed at constant temperature in $0.5M H_2SO_4$ solutions in absence and in presence of various concentration of **E-NBPTH** for an immersion time of 24h. After the expiration of the immersion time the specimens were recuperated from the tested solutions

rinsed with bi-distilled water and dried at room temperature. Finally, the dried specimens were weighed for a second time and the obtained mass values were used to calculate the corrosion rate (A_{corr}), surface coverage (θ) and inhibition efficiency (E_W (%)), employing the following equations:

$$A_{corr} = \frac{\Delta W}{S \times t} = \frac{W_1 - W_2}{S \times t} \tag{1}$$

$$\theta = \frac{A_{corr}^0 - A_{corr}}{A_{corr}^0} \tag{2}$$

$$E_{\rm W}(\%) = \frac{A_{\rm corr}^0 - A_{\rm corr}}{A_{\rm corr}^0} \times 100$$

where:

 W_1 : The mass of specimen before immersion in the tested solution.

 W_2 : The mass of specimen after immersion in the tested solution.

S: The surface area of the specimen.

t: The immersion time of each test.

 $A_{\rm corr}^0$: The corrosion rate in the absence of **E-NBPTH**.

A_{corr} : The corrosion rate in the presence of E-NBPTH.

2.4.2. Electrochemical tests

A conventional cell containing three-electrode system was applied to realize all the electrochemical measurements. In these tests, the glass carbon is used as auxiliary electrode, a saturated calomel electrode (SCE) was employed as reference electrode and a XC48 carbon steel was used as working electrode. An electrochemical workstation PGZ 310 Voltalab40 was used to realize all the electrochemical tests. Also, the Voltamaster 4 standard software was utilized to plot the obtained experimental data. The employed potential range for the potentiodynamic polarization tests is varied from -800 to -200 (mV/SCE) and the applying scan rate is 0.5 mV s⁻¹. From the obtained polarization data we can calculate the inhibition efficiency (E_p (%)) by applying the following formula [32]:

$$E_{\rm p}(\%) = \left(\frac{i_{\rm corr(inh)} - i_{\rm corr}^{\circ}}{i_{\rm corr(inh)}}\right) \times 100 \tag{4}$$

where i_{corr}° and $i_{\text{corr(inh)}}$ indicate the corrosion current densities in the absence and presence of **E-NBPTH**, respectively.

In this study, to realize the electrochemical impedance spectroscopy (EIS) tests, we chose the amplitude signal perturbation of 5 mV AC sine wave and varying the frequency region from 100 kHz to 10 mHz. From the obtained EIS data we can determine the inhibition efficiency $(E_z(\%))$ by employing the following formula [32]:

$$E_z(\%) = \left(\frac{R_P^\circ - R_P}{R_P^\circ}\right) \times 100 \tag{5}$$

where R_P° and R_P indicate the charge transfer resistances in the absence and presence **E**-**NBPTH**, respectively.

2.5. DFT calculations and MDS details

2.5.1. DFT calculations

The Gaussian 09W program package was used to perform all quantum chemical calculations [33]. The molecular structure of **E-NBPTH** was geometrically optimized employing DFT method with B3LYP hybrid functional at 6-31G (d,p) basis set [34, 35]. Also, at the optimal structure of **E-NBPTH**, the vibrational frequencies have been calculated using the DFT/B3LYP method with 6-31G (d,p) basis set. Moreover, the quantum chemical parameters such as the energy gap (ΔE_{GAP}), dipole momentum (μ), global hardness (η), global softness (σ), absolute electronegativity (χ), electrophilicity index (ω) and fraction of transferred electrons (ΔN) are determined using the calculated values of the highest occupied molecular orbital energy (E_{HOMO}) and lowest unoccupied molecular orbital energy (E_{LUMO}). All the precedent parameters are calculated using the following equations [36, 37]:

$$\Delta E_{GAP} = E_{LUMO} - E_{HOMO} \tag{6}$$

$$\eta = \frac{E_{\text{LUMO}} - E_{\text{HOMO}}}{2} \tag{7}$$

$$\sigma = \frac{1}{\eta} \tag{8}$$

$$\chi = \frac{-(E_{\text{HOMO}} + E_{\text{LUMO}})}{2} \tag{9}$$
$$\omega = \frac{\chi^2}{2\pi} \tag{10}$$

$$\Delta N = \frac{\chi_{\rm Fe} - \chi_{\rm inh}}{[2(\eta_{\rm Fe} + \eta_{\rm inh})]} \tag{11}$$

where:

 χ_{Fe} and χ_{inh} represent the absolute electronegativity of iron and **E-NBPTH**, respectively.

 η_{Fe} and η_{inh} represent the absolute hardness of iron and **E-NBPTH**, respectively.

Generally, we use the theoretical values of $\chi_{Fe} = 7.0$ eV and $\eta_{Fe} = 0$ to calculate the fraction of transferred electrons [38].

2.5.1. MDS details

In this study, the molecular dynamics simulations (MDS) have been realized by using the Materials Studio 7.0 software [39]. Firstly, the Fe(110) surface was chosen to simulate the adsorption of **E-NBPTH** on the iron surface. Moreover, the selected dimensions of the simulation box are (17.20 Å \times 22.93 Å \times 22.93 Å), employing the periodic boundary conditions. Also, this simulation box includes the Fe slab, the water slab containing **E-NBPTH** molecule and a vacuum slab. Then, the molecular geometry of **E-NBPTH** and the Fe(110) surface are optimized by minimization of energy. Finally, the COMPASS force field model was applied to perform the MDS at 298K, NVT ensemble and using a time step of 0.1 fs with a simulation period of 50 ps.

3. Results and discussion

3.1. Spectral analysis

The examination of the obtained UV-vis spectrum of **E-NBPTH** recorded in DMSO at room temperature indicates the presence of an absorption bands in ultraviolet domain. The spectrum of **E-NBPTH** shows band at 364.48 nm attributed to $n \rightarrow \pi^*$ transitions produced by the imine group (C=N) of the synthesized hydrazone. Moreover, the band situated at 304.75 nm is attributed to $n \rightarrow \pi^*$ transitions originated by the nitro group (NO₂).

The inspection of the experimental and theoretical infrared spectra of **E-NBPTH** allows selecting the vibration frequencies of the characteristic functional groups of **E-NBPTH** (Table 1). In addition, we used a scaling factor of 0.9614 to scale the calculated frequencies [40]. Consequently, we observe that the scaling theoretical frequencies are in good accordance with the experimental frequencies (Fig. 2). So, the analysis of the obtained IR experimental spectrum shows the presence of the following characteristic peaks:

The observed peak at 3307 cm⁻¹ could be attributed the N–H stretching vibration. A weak peak appeared at 3079 cm⁻¹ can be referred to the stretching vibration of aromatic C–H bonds. Moreover, the less intense broad peak appeared at 2986 cm⁻¹ is assigned to the stretching vibration of aliphatic C–H bonds. The presence of peaks within the range of 1665–2000 cm⁻¹ is mostly due to the bending vibration of the aromatic C–H bond (overtone patterns). The

characteristic peak of the synthesized hydrazone is observed as a very intense peak at 1521 cm⁻¹, which is assigned to the stretching vibration of the imine group (C=N). In addition, the stretching vibration of the aromatic nitro group (A_r -NO₂) was appeared as an intense peak at 1349 cm⁻¹. The peaks with medium intensities obtained within the region 1200-1290 cm⁻¹ can be referred to the stretching vibration of C–N band. The detected peaks in the region 1020-1180 cm⁻¹ could be assigned to the stretching vibration of the N–N bond. The peak appeared at 914 cm⁻¹ can be referred to the N–O bond vibration. The intense thin peak located at 815 cm⁻¹ may be due to C–N band vibration. The peak situated at 734 cm⁻¹ may be attributed to the out of plane bending vibrations of C–H group. Additionally, the N–H out of plane bending vibrations were also observed at 674 cm⁻¹.

The examination of the obtained ¹H NMR spectrum for the synthesized molecule allows determining the main characteristic signals, such as the singular signal appeared at 2.33 ppm is attributed to the three protons of $-C\underline{H}_3$ group. Also, the characteristic aromatic protons ($-C\underline{H}_{A\overline{F}}$) are assigned to the signals observed in the region of 7.05-8.12 ppm. Moreover, the observed singular signal at 8.43 ppm may be referred to the proton of $-N\underline{H}$ group. The proton of aliphatic = $C\underline{H}$ - group is appeared as a singular signal at 7.67 ppm. On the other hand, the interpretation of the ¹³C NMR spectrum of **E-NBPTH** indicates the presence of the characteristic signals of the carbons present in its molecular structure. For example, the observed signal at 20.65 ppm is attributed to the carbon of $-\underline{C}H_3$ group. The signal of the rarbon of imine group ($-\underline{C}=N$) is appeared at 141.64 ppm. The aromatic carbon related to the nitro group ($-\underline{C}=N$) is observed at 148.72 ppm. The other aromatic carbons signals are observed in the zone of 113.04-137.48 ppm.

3.2. Anti-corrosive activity

3.2.1. Weight loss tests

Table 2 summarizes the obtained results from weight loss tests, such as mass loss, corrosion rate, surface coverage rate and inhibition efficiency in the absence and in the presence of **E**-**NBPTH** at different concentrations. From the presented results in Table 2 and Fig. 3(a), we can observe that the mass loss and the corrosion rate decrease by increasing the concentration of **E**-**NBPTH** while the recovery rate and the inhibition efficiency increase by augmentation the concentration of the investigated molecule. This behavior can be attributed to the formation of a protective layer of the **E**-**NBPTH** molecules on the metallic surface and therefore retarding the attack of the carbon steel surface by sulfuric acid.

In addition, the obtained results of the effect of temperature on the corrosion rate and the inhibition efficiency are regrouped in Table 3 and presented by Fig. 3(b). So, we can be seen that the corrosion rate increases by increasing the temperature while the inhibition efficiency decreases by increasing of the temperature. This phenomenon is due to exothermicity of the adsorption process of the **E-NBPTH** molecules on the iron surface, this proves without a doubt that the protection mechanism occurs through the adsorption of **E-NBPTH** on the iron surface.

3.2.2. Activation energy

Generally, the Arrhenius plots are used to determine the activation energy (E_a) by plotting the variation of the logarithm of the corrosion rate as a function of the inverse of the temperature in absence and in presence of an inhibitor. In this study, the following relations are used to plot the Arrhenius lines in the absence and in the presence of **E-NBPTH** at 10⁻³M [41]:

$$ln (A_{corr}^{0}) = ln (k') + \left(\frac{-E_{a}}{RT}\right)$$
(12)
$$ln (A_{corr}) = ln (k) + \left(\frac{-E_{a}}{RT}\right)$$
(13)

where :

 A_{corr}^0 and A_{corr} : are the corrosion rates in the absence and in the presence of **E-NBPTH**, respectively.

k' and k: are the Arrhenius pre-exponential constants in the absence and in the presence of **E**-**NBPTH**, respectively.

 E_a and E'_a : are the activation energies in the absence and in the presence of **E-NBPTH**, respectively (J mole⁻¹).

R: is the gas constant (8.314 J mole⁻¹ K).

T: is the temperature (K).

Fig. 4 shows that the obtained Arrhenius plots in absence and in presence of **E-NBPTH** are good straight lines. From the slopes of these straight lines we can determine the values of the activation energy in absence ($E'_a = 17.179 \text{ kJ/mol}$) and in presence of the investigated inhibitor at 10^{-3} M ($E_a = 43.05 \text{ kJ/mol}$). We observe that the obtained value of the activation energy in the presence of **E-NBPTH** is higher than that obtained in the absence of **E-NBPTH**, which indicates the inhibiting behavior of the synthesized inhibitor. Consequently,

for this type of inhibitors the elevation of temperature after the addition of the inhibitor to the corrosive medium decreases the inhibition efficiency.

3.2.3. Checking of the adsorption isotherm

The adsorption isotherms are largely used to explicate the mechanism of corrosion inhibitors by determination of the interactions nature between inhibiting molecules and metallic atoms. Generally, according on the type of these interactions, we can distinguish two types of adsorption: physisorption and chemisorption. In our case, the inhibitive action of **E-NBPTH** may be related to the adsorption of its molecules on the carbon steel surface and forming a protective layer.

In this context, to test the adsorption isotherm followed by our system, we plot the linear regression of the graphic relation between C/θ and C at 25°C (Fig. 5). Fig. 5 shows that a good straight line was obtained with a correlation coefficient almost equal to 1 (0.99989), indicating that the adsorption of **E-NBPTH** follows Langmuir adsorption isotherm (Eq. (14)). Also, this result indicates the formation of a mono-layer of **E-NBPTH** molecules on the iron surface without lateral interactions between the adsorbed molecules.

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \tag{14}$$

where *C* and K_{ads} are the **E-NBPTH** concentration (M) and the adsorption equilibrium constant (M⁻¹). The K_{ads} value can be determined from the intercept line on the C/θ axis. The high value of K_{ads} (K_{ads} =14.149 10³ M⁻¹) indicates a strong interactions between the adsorbed molecules and the iron surface [42], which are attributed to the presence of some heteroatoms (O and N) in the molecular structure of **E-NBPTH**. On the other hand, the obtained value of K_{ads} is used to calculate the standard free energy of adsorption (ΔG_{ads}^0) by using the following relation:

$$\Delta G_{ads}^0 = -RT \ln(55.5K_{ads}) \tag{15}$$

where *R* indicates the gas constant (8.314 J K⁻¹ mol⁻¹), *T* represent the absolute temperature (K) and the value 55.5 represent the water concentration in the solution (M).

The calculated value of ΔG_{ads}^0 for the adsorption of **E-NBPTH** on the iron surface is -39.33 kJ/mol. Generally, the negative sign of ΔG_{ads}^0 indicates the spontaneity of the adsorption process of **E-NBPTH** onto the iron surface, which means the presence of strong interactions between the inhibitor molecules and the carbon steel surface [43]. In addition, the obtained value of ΔG_{ads}^0 is almost equal to -40 kJ/mol, this indicates that the adsorption of **E-NBPTH**

on the carbon steel surface is made by means of chemical adsorption by formation of the coordination and covalent bonds [44, 45].

3.2.4. Polarization curves tests

The obtained results of the concentration effect of **E-NBPTH** on the polarization curves are summarized in Table 4 and presented in Fig. 6. From the Fig. 6, we can see that in presence of the **E-NBPTH** at different concentrations, the anodic and cathodic branches of the polarization curves are displaced towards the low currents with an identical degree. This phenomenon indicates that the synthesized hydrazone acts as a mixed-type inhibitor by controlling both the cathodic and anodic reactions without modifying the cathodic release of hydrogen and the anodic degradation of the metal [46]. Also, Table 4 shows that the increasing of the **E-NBPTH** concentration decreases the obtained values of *i*_{corr}. Accordingly, the inhibition efficiency increases with augmentation of the inhibitior concentration and reaches its maximum value at 10^{-3} M, which indicates that the inhibiting power of the investigated hydrazone probably associated to the its adsorption on the iron surface, which is lead to the formation of a protective barrier film. Consequently, the corroding area on the metal surface is reduced which leads to the diminution of the anodic dissolution of XC48 carbon steel and to the obstruction of the cathodic hydrogen liberation.

3.2.5. EIS tests

The influence of the **E-NBPTH** concentration on the Nyquist plot of the studied carbon steel in 0.5M H₂SO₄ solution is showed in Fig. 7. Also, the electrochemical parameters determined from the Nyquist data, such as charge transfer resistance (R_{ct} ,) double layer capacitance (C_{dl}), solution resistance (R_s) and inhibition efficiency (E_z (%)) are grouped in Table 5. From the results presented in Fig. 7 and Table 5 we observe that the augmentation of the inhibitor concentration increases the R_{ct} values and decreases the C_{dl} values. The augmentation of the R_{ct} is probably related to the formation of a protective layer on the carbon steel surface. Further, the diminution of the C_{dl} values is probably associated to the augmentation of the width of the electrical double layer, signifying that the **E-NBPTH** protect the carbon steel against corrosion by adsorption of its molecules on the iron surface [47, 48]. On the other hand, we clearly observe from Fig. 7 that the all obtained Nyquist plots are almost semicircles with similar shapes. This indicates that the addition of **E-NBPTH** does not cause any change to the corrosion mechanism [49]. In addition, the diameter of the Nyquist plot augmented with the augmentation of the **E-NBPTH** concentration, indicating that the charge transfer process controls the corrosion of carbon steel in the studied aggressive medium [50].

Also, we can note from Fig. 7 that the Nyquist graphs are not perfect semicircles, which are attributed to the frequency dispersion produced by the roughness of the surface and chemical composition of XC48 carbon steel [51].

To evaluate the inhibition power of the studied inhibitor, we conducted a comparative study of the inhibition efficiency of **E-NBPTH** and some inhibitors reported in previous studies. We observe from the Table 6 that the **E-NBPTH** presents the better efficiency compared to the selected compounds obtained in previous works [21, 52, 53]. Also, the inspection of the molecular structures of the studied inhibitor and the three compounds selected for the comparison (Table 6), indicates that the good inhibitive activity of the examined inhibitor can be related to the presence of the hydrazone group (C=N-N) in the molecular structure of **E-NBPTH**. In addition, the presence of the NO₂ group can improve the inhibition efficiency of **E-NBPTH**. For example, we observe that the inhibition activity of our inhibitor is higher than of inhibitor studied in reference [21]; this may be due to the presence of the hydrazone group in the molecular structure of **E-NBPTH**.

3.3. Computational study

In general, the inhibition efficiency of an inhibitor is associated to its electronic structure, especially some calculated quantum chemical parameters such as the E_{HOMO} , the E_{LUMO} , the ΔE_{GAP} , dipole momentum (μ), η , σ , χ , ω and ΔN . Also, the obtained values of these parameters for the studied inhibitor are grouped in Table 7. All of these parameters were calculated at the optimal geometry of **E-NBPTH** (Fig. 8(a)). From the Fig. 8(a), which represents the optimized molecular structure of **E-NBPTH** with atomic Mulliken charges, we observe that the most negative atoms are the N12 (-0.543), the O9 (-0.400), the O8 (-0.396) and the N11 (-0.241), which are probably the active sits of adsorption [28]. Consequently, these atoms (O and N atoms) can share their electron pairs with the *d*-orbitals of the iron surface to form coordination bonds [54].

The chemical reactivity of the inhibitive molecules and the interactions between them or other species can be quantified by their frontier molecular orbitals (HOMO and LUMO) and energy gap [55]. Generally, the elevated values of the E_{HOMO} are related to the electrons donor capacity of a molecule [56], whereas the least values of the E_{LUMO} are associated to the capacity of the molecule to receive electrons [57]. Also, the elevated value of E_{HOMO} shows the electrons transfer tendency of a molecule to a suitable acceptor which assists the adsorption of the inhibitive molecules on the iron surface, whereas the low value of E_{LUMO} indicates an efficient adsorption process [58, 59]. The Fig. 8(b) illustrates that the electron

density of the HOMO orbital is almost dispersed on the all molecular structure of the **E**-**NBPTH**, thus increasing the contribution capacity of studied hydrazone. Moreover, the negligible HOMO density on the N–O₂ group is related to the high electronegativity of the oxygen atoms which have greater affinity to keep their pairs of electrons. Meanwhile, Fig. 8(c) shows that the electron density allocation of LUMO orbital is centralized mostly on the nitrogen atoms of the hydrazone group (N–N=C) and aromatic ring who wears the nitro group (Ar–NO₂), which indicates that the nitrogen atoms may be as the active centers for adsorption of **E-NBPTH** on iron surface. Additionally, from the optimized molecular structure of **E-NBPTH** we observe that the tow aromatic rings are a plane conjugated structure, which indicates that the inhibitor molecules are adsorbed on the iron surface in flat mode basing on the π back bonding [60].

Generally, to measure the stability of a molecule we need to calculate its energy gap (ΔE_{GAP}), which is an essential parameter that influences the reaction of an inhibitor. Also, ΔE_{GAP} describes the reactivity of the inhibitive molecules towards the metallic surface. For the studied inhibitor, the obtained low value of ΔE_{GAP} reveals the elevated inhibition efficiency of **E-NBPTH** by improving the reactivity of the molecule, which eases the adsorption of the investigated inhibitor on iron surface [61].

In literature, several works show that the corrosion inhibitive activity of an inhibitor can be estimated by the dipole moment (μ), which is related to the polarity of the inhibitive molecule [62]. Table 7 indicates that the calculated value of the dipole moment (μ_{inh} = 5.102 Debye) for the investigated molecule is greater than that of H₂O (μ_{H_2O} = 1.88 Debye), this high value of μ leads to electrons transfer from the **E-NBPTH** molecules to the iron surface. Also, the interactions between the **E-NBPTH** molecules and iron surface are increased with increasing dipole moment value [63].

Global hardness and softness are two other important quantum parameters can be used to estimate the reactivity and stability of the inhibitive molecules. In addition, the resistance of a molecule against deformation or polarization of its electron cloud is measured by the global hardness. Generally, a good corrosion inhibitor is characterized by the small value of global hardness and the elevated value of the softness [64]. From the Table 7, we observe clearly that the **E-NBPTH** has a low value of the hardness and an elevated value of the softness, which proves the high inhibition efficiency of the investigated hydrazone. On the other hand, the capability of an inhibitor to take electrons can be illustrated by the electrophilicity index (ω) and the inhibition efficiency augments with the diminution of the ω .

Also, the fraction of transferred electrons (ΔN) is an indication of the donating ability of electrons from the inhibitive molecules to an appropriate metallic surface. Therefore, the increasing of the ΔN increases the electrons contribution capability of an inhibitor at the metallic surface, which ameliorates its inhibitive activity. The positive value of ΔN indicates that the ability of an inhibitor to donate electrons to the metallic surface is great; while the negative value of ΔN illustrates that the capability to give electrons to an appropriate metal is low [65]. From the Table 7 we observe that the obtained value of ΔN is positive and less than 3.6. So, in accordance with the Lukovits et *al.* study [66], the corrosion inhibitive activity of **E-NBPTH** is enhanced by increasing of its ability to donate electrons, which indicates the formation of an adsorbed inhibitive layer at the iron surface and appearance of coordinate bonds between the inhibitive molecules and the iron atoms.

Generally, the active canters responsible for electrophilic and nucleophilic reactions can be determined by interpretation of the molecular electrostatic potential (MEP) maps, which is associated to the electronic density of a molecule. Fig. 8(d) represents the calculated 3D and 2D MEP maps of **E-NBPTH**. So, the examination of this figure displays that the red and yellow colors represent the negative zones of the MEP associated to the electrophilic reactions, whereas the blue color represents the positive zones related to the nucleophilic reactions. Furthermore, the studied hydrazone derivative has four potential centers (O9, O8, N11 and N12) effective for the electrophilic reactions. Also, the aromatic rings present in the molecular structure of **E-NBPTH** are considered as negative zones.

3.4. Molecular dynamic simulations (MDS) study

Recently, the interactions between the inhibitive molecules and the iron surface can be understood and interpreted by using the molecular dynamic simulations (MDS). Fig. 9 illustrates the equilibrium configuration of **E-NBPTH** on the Fe (110) surface in a vacuum slab. We can observe clearly from the Fig. 9 that the **E-NBPTH** adsorbs on the Fe (110) surface with a horizontal mode between the rigid hydrazone molecular structure and iron surface, which confirms the strong interactions between the **E-NBPTH** and iron atoms. From the optimized molecular structure of **E-NBPTH**, we can say that the adsorption on Fe (110) surface is made by the involvement of the electrons of oxygen, nitrogen and the benzene rings of **E-NBPTH** with the electrons of iron (chemical adsorption). In addition, the physical adsorption between the **E-NBPTH** molecules and the iron surface produced by the Van der Waals dispersion forces can also participate to attract the inhibitive molecules towards the iron surface [67]. The obtained value of adsorption energy (-133.289 kcal/mol) shows that

the **E-NBPTH** has negative adsorption energy, which indicates the spontaneity of the adsorption process. Also, the obtained high value of binding energy (133.289 kcal/mol) is attributed to a better and more stable adsorption process.

4. Conclusions

An aromatic hydrazone derivative (E-NBPTH) has been synthesized and its molecular structure is analyzed by using UV-vis, IR, ¹H NMR and ¹³C NMR spectroscopic methods. On the other hand, the anti-corrosive activity of E-NBPTH has been evaluated for the corrosion of the XC48 carbon steel in a 0.5 M H₂SO₄ solution by using the electrochemical methods, the quantum chemical calculations and the molecular dynamic simulations. In this context, several conclusions were drawn. Firstly, the synthesized hydrazone is a good inhibitor for the protection of the XC48 carbon steel against corrosion in a 0.5 M H₂SO₄ solution and the elevation of the E-NBPTH concentration increases its inhibitive activity. In addition, the E-**NBPTH** acts as mixed inhibitor by controlling the anodic and cathodic reactions. Also, the presence the investigated inhibitor increases the R_{ct} and reduces C_{dl} values. Also, the E-**NBPTH** is chemically adsorbed on the carbon steel surface according the Langmuir adsorption isotherm. The obtained value of ΔG_{ads}^0 shows the spontaneity of the adsorption process and strong interactions are formed between the inhibitor molecules and the iron surface. Finally, the obtained experimental results are in good agreement and are well supported by the theoretical study such as quantum chemical calculations and Molecular dynamics simulations.

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Figures Captions:

Fig. 1. Synthetic rout of the studied hydrazone.

Fig. 2. Correlation diagram between the theoretical and experimental wavenumbers of E-NBPTH.

Fig. 3. Influence of **E-NBPTH** concentration (**a**) and temperature (**b**) on corrosion rate and inhibition efficiency.

Fig. 4. The calculated Arrhenius straight lines for the corrosion of the XC48 carbon steel in $0.5M H_2SO_4$ solution in presence and absence of $10^{-3}M$ of **E-NBPTH**.

Fig. 5. Langmuir adsorption isotherm of XC48 carbon steel in $0.5M H_2SO_4$ solution in presence of E-NBPTH at 25°C.

Fig. 6. Potentiodynamic polarization curves obtained for the XC48 carbon steel electrode in 0.5M H₂SO₄ solution in presence of various concentrations of **E-NBPTH** at 25°C.

Fig. 7. Nyqusit plots for XC48 carbon steel in $0.5M H_2SO_4$ solution in absence and in presence of various concentrations of **E-NBPTH** at 25°C.

Fig. 8. Optimized structure with atomic Mulliken charges, HOMO and LUMO frontier orbitals and MEP map of **E-NBPTH**.

Fig. 9. Side and top views of the simulated most stable configuration for the adsorption of **E-NBPTH** on Fe (110) surface.

Tables Captions:

Table 1

Experimental and theoretical values of wavenumber for the selected vibrations of E-NBPTH.

Table 2

Obtained results from weight loss tests for the corrosion of XC48 carbon steel in $0.5M H_2SO_4$ solutions in absence and presence of different concentrations of **E-NBPTH** at 25°C.

Table 3

Effect of temperature on the corrosion rate and inhibition efficiency after 24h of immersion in the electrolytic solution in presence of 10^{-3} M of **E-NBPTH**.

Table 4

Electrochemical parameters obtained from the polarization curves of the XC48 carbon steel in 0.5M H₂SO₄ solution in absence and presence of various concentrations of **E-NBPTH** at 25° C.

Table 5

Electrochemical parameters obtained from EIS data of the XC48 carbon steel in $0.5M H_2SO_4$ solution in absence and presence of various concentrations of **E-NBPTH** at 25°C.

Table 6

Comparison of the inhibition efficiency at the optimal concentration of **E-NBPTH** with the literature data as corrosion inhibitors in acidic medium

Table 7

Calculated quantum chemical parameters of E-NBPTH using DFT/B3LYP 6-31G (d,p) method.

Experimental and theoretical values of wavenumber for the selected vibrations of E-NBPTH.

Assignment	Vibrationa	l frequency (cn	n ⁻¹)
	Experimental	Theore	etical
		Unscaled	Scaled
v(N-H)	3307	3502	3366
v(C-H) _{Ar}	3079	3187	3063
v(C-H) _{Alph}	2986	3037	2919
v(C=N)	1521	1615	1552
v (NO ₂)	1349	1397	1343
v(C-N)	1254	1304	1253
v(N-N)	1151	1196	1146
v(N-O)	914	967	929
δ(C-H)	734	779	748
δ(N-H)	674	691	664

v: stretching, δ : out of plane bending

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Table 2

Obtained results from weight loss tests for the corrosion of XC48 carbon steel in $0.5M H_2SO_4$
solutions in absence and presence of different concentrations of E-NBPTH at 25°C.

<i>C</i> (M)	$W_1(\mathbf{g})$	$W_{2}\left(\mathbf{g} ight)$	$\Delta W(\mathbf{g})$	$A_{\rm corr}$ (g/cm ² h)	θ	<i>E</i> _w (%)
Blank	13.71110	13.61837	0.092730	0.0004097296	_	A
10 ⁻⁶	13.82486	13.79853	0.026330	0.0001163222	0.7161	71.61
10 ⁻⁵	13.76012	13.73957	0.020550	0.0000908006	0.7784	77.84
10 ⁻⁴	13.79221	13.77559	0.016620	0.0000734358	0.8208	82.08
10 ⁻³	13.76608	13.75358	0.012500	0.0000552315	0.8652	86.52

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Effect of temperature on the corrosion rate and inhibition efficiency after 24h of immersion in the electrolytic solution in presence of 10^{-3} M of **E-NBPTH**.

<i>T</i> (°C)	$W_1(\mathbf{g})$	$W_{2}\left(\mathbf{g} ight)$	$\Delta W(\mathbf{g})$	$A^{\bullet}_{\rm corr}({\rm g/cm^2h})$	$A_{\rm corr}$ (g/cm ² h)	<i>E</i> _w (%)
25	13.76608	13.75358	0.01250	0.0004097296	0.0000552315	86.52
35	13.74857	13.72517	0.02340	0.0005840421	0.0001033934	82.30
45	13.78861	13.75085	0.03776	0.0006438611	0.0001668431	74.09
55	13.69898	13.63678	0.06220	0.0008002601	0.0002748321	65.66

Electrochemical parameters obtained from the polarization curves of the XC48 carbon steel in $0.5M H_2SO_4$ solution in absence and presence of various concentrations of **E-NBPTH** at $25^{\circ}C$.

<i>C</i> (M)	E _{corr} (mV/SCE)	I _{corr} (mA/cm ²)	$\beta_{\rm a}$ (mV/dec.)	$\beta_{\rm c}$ (mV/dec.)	$E_{\mathrm{P}}(\%)$
Blank	- 480.5	0.8192	81.6	- 152.2	-
10⁻⁶	- 472.6	0.2289	59.4	- 125.1	72.06
10 ⁻⁵	- 472.9	0.1778	54.9	- 120.4	78.30
10 ⁻⁴	- 470.1	0.1541	41.2	- 107.1	81.19
10⁻³	- 473.2	0.1054	37.2	- 47.9	87.13

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<i>C</i> (M)	$R_{\rm ct}$ (Ω cm ²)	$C_{\rm dI}$ (µF cm ⁻²)	$R_{\rm s}(\Omega{\rm cm}^2)$	E_{z} (%)
Blank	19.22	2069.0	1.926	- 🤇
10⁻⁶	64.35	955.4	2.067	70.13
10 ⁻⁵	91.38	870.7	2.086	78.96
10 ⁻⁴	102.0	623.5	2.131	81.16
10⁻³	141.4	560.3	2.354	86.41

Electrochemical parameters obtained from EIS data of the XC48 carbon steel in $0.5M H_2SO_4$ solution in absence and presence of various concentrations of **E-NBPTH** at 25°C.

Comparison of the inhibition efficiency at the optimal concentration of **E-NBPTH** with the literature data as corrosion inhibitors in acidic medium

Inhibitor	$E_{\mathrm{w}}(\%)$	<i>E</i> _p (%)	$E_{z}(\%)$	Ref.
H ₃ C	86.52	87.13	86.41	This work
CH ₃ CH ₃	85.83	86.26	83.65	[21]
	85.60	84.36	72.83	[52]
N-N	83.00	84.00	83.00	[53]
		Y		

Calculated quantum chemical parameters of E-NBPTH using DFT/B3LYP 6-31G (d,p) method.

Quantum chemical parameters E-NBPTH
$E_{\text{Tot}}(\text{eV}) - 23290.8671$
$E_{\rm HOMO} ({\rm eV}) - 5.38105435$
$E_{\rm LUMO} ({\rm eV}) - 2.37664368$
$\Delta E_{\rm GAP} ({\rm eV})$ 3.00441067
μ (Debye) 5.10240000
η (eV) 1.50220053
σ 0.66569009
χ (eV) 3.87884902
ω 5.00788103
ΔN 1.03885963



Fig. 1. Synthetic rout of the studied hydrazone.

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Fig. 2. Correlation diagram between the theoretical and experimental wavenumbers of E-NBPTH.



Fig. 3. Influence of E-NBPTH concentration (a) and temperature (b) on corrosion rate and inhibition efficiency.



Fig. 4. The calculated Arrhenius straight lines for the corrosion of the XC48 carbon steel in $0.5M H_2SO_4$ solution in presence and absence of $10^{-3}M$ of E-NBPTH.



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Fig. 7. Nyqusit plots for XC48 carbon steel in 0.5M H₂SO₄ solution in absence and in presence of various concentrations of **E-NBPTH** at 25°C.

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Fig. 8. Optimized structure with atomic Mulliken charges, HOMO and LUMO frontier orbitals and MEP map of **E-NBPTH**.



Fig. 9. Side and top views of the simulated most stable configuration for the adsorption of **E-NBPTH** on Fe (110) surface.

Highlights

- New hydrazone derivative (E-NBPTH) was synthesized and characterized.
- UV–Vis, IR and NMR analysis of E-NBPTH was realized.
- Anti-corrosive activity of **E-NBPTH** was experimentally evaluated.
- DFT method was used to determine the quantum parameters of the studied derivative.
- Molecular dynamic simulations have been performed.