Exploration of Dihydrothieno[2,3-c] Isoquinolines As Luminescent Materials and Corrosion Inhibitors

Islam S. Marae, Mahmoud H. Mahross, Badriah S. Al-Farhan, Mohamed Abdel-Hakim, Etify A. Bakhite,* and Marwa M. Sayed

ABSTRACT: The reaction of the starting compound, 7-acetyl-4-cyano-1,6-dimethyl-8-phenyl-7,8-dihydroisoquinoline-3(2H)-thione, with some N-aryl-2-chloroacetamides or chloroacetonitrile, in the presence of sodium acetate trihydrate, gave the corresponding substituted 3-methylsulfanyl-7-acetyl-4-cyano-1,6-dimethyl-8-phenyl-7,8-dihydroisoquinolines. Upon heating of the latter compounds with sodium methoxide in methanol, they underwent intramolecular Thorpe-Zeigler cyclization, affording the target isomers 1-amino-2-(substituted)-5,8-dimethyl-6-phenyl-6,7-dihydrothieno[2,3-c]isoquinolines (DHTIQs). The chemical structures of all produced substances were characterized by elemental and spectral analyses. The photophysical characteristics of the produced DHTIQs (He1-Ph-Cl, He2-Ph-CH3, He3-Ph, and He4-CN) have been investigated as luminous compounds. Potentiodynamic, surface morphology, and theoretical calculations were used to study the behavior of the synthesized DHTIQs as corrosion inhibitors on mild steel in a 1.0 M sulfuric acid solution.

1. INTRODUCTION

Luminescent compounds have received significant interest in material science due to their specific applications for fluorescent sensors, light sources, optical-recording systems, and information displays.1−7 Recently, we published a paper on luminescent compounds containing a thieno[2,3-b]pyridine moiety, which showed aggregation-induced emission (AIE) behavior with high absolute quantum yields.8 On the other hand, organic corrosion inhibitors that contain heteroatoms such as nitrogen, oxygen, sulfur, and phosphorus work well in a wide variety of acidic solutions.9,10 The efficiency of the inhibitor depends on its stability, and the inhibitor particles must contain molecules or atoms capable of electrostatic attraction with the metal surface through the transfer of electrons.11 Only a few studies have been published on the use of quinoline, isoquinoline, and some of its derivatives as corrosion inhibitors in various mediums.12−16 Most previous studies indicate that isoquinoline derivatives are effective inhibitors and their inhibition efficiencies increase as their concentrations increase.17−19 Moreover, the literature survey revealed only a few publications on the synthesis and applications of 7,8-dihydroisoquinoline derivatives. Therefore, the present study focuses on synthesizing and characterizing some 6,7-dihydrothieno[2,3-c]isoquinoline derivatives and studying their applications as fluorescent materials and corrosion inhibitors.

2. RESULTS AND DISCUSSION

2.1. Synthesis of Dihydrothienoisouquinoline (DHTIQ) Derivatives. The target dihydrothienoisouquinoline products were prepared by starting from a readily available compound, 7-acetyl-4-cyano-1,6-dimethyl-8-phenyl-7,8-dihydroisoquinoline-3(2H)-thione (1). Thus, the reaction of compound 1 with N-aryl-2-chloroacetamide 2a−2c or chloroacetonitrile (3) by refluxing in ethanol in the presence of sodium acetate trihydrate gave the corresponding 2-(substituted methylsulfanyl)-7,8-dihydroisoquinoline-4-carbonitriles 4a−4c or 5, respectively (Scheme 1). The subsequent compounds (4a−4c or 5) underwent intramolecular Thorpe-Zeigler cyclization after being treated with sodium methoxide in methanol, yielding the appropriate isomers. 1-Amino-2-(substituted)-6,7-dihydrothieno[2,3-c]isoquinolines 6a−6c or 7 (DHTIQs) were coded as 6a, He1-Ph-Cl; 6b, He2-Ph-CH3; 6c, He3-Ph; and 7, He4-CN (Scheme 1).

2.2. Characterization of Dihydrothienoisouquinoline (DHTIQ) Derivatives. Elemental and spectral analyses

Received: May 30, 2022
Accepted: October 7, 2022
Published: October 19, 2022
 Scheme 1. Synthesis of Dihydrothienoisooquinoline Derivatives (DHTIQs; 6a−6c and 7)

Figure 1. UV−visible spectra (left) and energy band gaps (right) of He1-Ph-Cl (6a), He2-Ph-CH₃ (6b), He3-Ph (6c), and He4-CN (7).
confirmed the chemical structures of all newly synthesized compounds (cf. Experimental Section and Figures S1–S9).

2.3. Photophysical Properties. Figure 1 shows the measured compounds' UV–visible and energy band gap spectra. The optical properties are measured in DMF solution at a concentration of $10^{-4}$ M. Each of these compounds exhibits two absorption bands, at $\lambda_{\text{max}}$ = 310 nm and $\lambda_{\text{max}}$ = 388 nm for He1-Ph-Cl (6a), at $\lambda_{\text{max}}$ = 302 nm and $\lambda_{\text{max}}$ = 386 nm for He2-Ph-CH$_3$ (6b), at $\lambda_{\text{max}}$ = 298 nm and $\lambda_{\text{max}}$ = 386 nm for He3-Ph (6c), and at $\lambda_{\text{max}}$ = 290 nm and $\lambda_{\text{max}}$ = 368 nm for He4-CN (7). These bands are attributed to $n-\pi^*$ and $\pi-\pi^*$ electronic transitions. The N-arylcarbamoyl group at position 2 of the DHTIQs increases conjugation, resulting in a higher $\lambda_{\text{max}}$ $\pi-\pi^*$ transition maximum and absorbance intensity. The replacement in the N-phenylcarbamoyl moiety also caused the red shift and change in absorbance intensity. The change is...
greater for the electron-withdrawing group (e.g., chlorine atom) than for the electron-donating one (e.g., a methyl group). It tends to lower the electrons’ density, leading to a decrease in HOMO level. On the other hand, the absence of a(n) (un)substituted \( N \)-phenylcarbamoyl group from the structure produces a blue shift, and the existence of an
electron-withdrawing cyano group lowers the conjugation $\lambda_{\text{max}}$ of $n-\pi^*$ and $\pi-\pi^*$ transitions by reducing the HOMO level and hence increasing excitation energy.\textsuperscript{21,25} The values of the energy band gap of DHTIQs (6a = 2.85 eV, 6b = 2.87 eV, 6c = 3.00 eV, and 7 = 2.88 eV) are inconsistent with their structures. With no substituent on the phenyl ring of the N-arylcarbamoyl group, the amount of energy required for excitation is reduced. In addition, the presence of electron-withdrawing groups in that ring facilitates the transition and requires little energy.

The emission spectra of these DHTIQs at different excitation wavelengths with a concentration of $10^{-4}$ in DMF are shown in Figures 2 and 3. Upon excitation of the samples with various wavelengths ($\lambda_{\text{ex}} = 315$ nm, $\lambda_{\text{ex}} = 360$ nm, $\lambda_{\text{ex}} = 395$ nm, $\lambda_{\text{ex}} = 450$ nm), the results indicate that (i) all DHTIQs exhibit nearly the same emission wavelength (at $\lambda_{\text{em}}$ = 514 nm for He1-Ph-Cl, at $\lambda_{\text{em}}$ = 521 nm for He2-Ph-CH$_3$, at $\lambda_{\text{em}}$ = 513 nm for He3-Ph, and at $\lambda_{\text{em}}$ = 509 nm for He4-CN) with different intensities and, (ii) for all of them, the highest emission intensity is found at $\lambda_{\text{ex}} = 360$ nm except for He3-Ph, which has its highest emission intensity at $\lambda_{\text{ex}} = 395$ nm. The emission behavior of the DHTIQs at $\lambda_{\text{ex}} = 360$ nm is displayed in Figure 4; among all compounds, the highest emission intensity is observed for He1-Ph-Cl. The emission intensities exhibited by DHTIQs can be arranged in the following order: He1-Ph-Cl > He3-Ph > He4-CN > He2-Ph-CH$_3$, this may be attributed to the structural effect on emission spectra via stabilization of the $\pi-\pi^*$ transition and destabilization of the $n-\pi^*$ one, i.e., the resonance effect caused by changing the substituent in the phenyl ring of the N-arylcarbamoyl group at position 2.\textsuperscript{23,24} The color of emission is quantized by the Commission Internationale de l’Eclairage (CIE) chromaticity diagram (Figures 2 and 3). The CIE coordinates are given in Table S1. All samples emit a green color with different intensities and, for all of them, the highest emission intensity is observed in DMF.

2.4. Electrochemical Studies. 2.4.1. Open Circuit Potential OCP. Figure S10 displays the curves between $E$ (mV) vs time (min) at a current of zero for MS immersed in the blank solution and three concentrations (100, 200, and 500 ppm) of the tested inhibitors (He1-Ph-Cl, He2-Ph-CH$_3$, He3-Ph, and He4-CN). $E_{\text{corr}}$ moves to the negative potential for blank solution curves relative to $E_{\text{corr}}$. This change is due to the breakdown of the oxide film on the MS surface until it reaches the corrosion cell’s $E_{\text{corr}}$. The addition of various concentrations of the testing inhibitors caused the $E_{\text{corr}}$ value to shift to greater positive potential than the blank solution. The latter effect is due to the formation of an adsorbed layer of inhibitor molecules on the active sites of the MS surface. Data extracted from OCP are illustrated in Table S2; it is clear that the increasing concentration of tested inhibitors from 100 to 500 ppm causes $E_{\text{corr}}$ to shift to a positive direction more than for the blank solution.

2.4.2. Tafel Polarization. Figure 5 shows potentiodynamic polarization curves of the corrosion of mild steel in 1.0 M H$_2$SO$_4$ solution before and after adding various concentrations of the tested inhibitors. It observed that the presence of DHTIQs in different concentrations causes shifting in Tafel slopes. This indicated that (i) the adsorption of inhibitor molecules on the surface of MS electrodes and (ii) the $E_{\text{corr}}$ of used inhibitors differs positively from that of the blank solution, and the difference does not reach 85 mV, which proved that these inhibitors are mixed ones\textsuperscript{25} where there are reductions in the anodic and cathodic Tafel slope. Table 1 records the parameters extracted from TF such as $I_{\text{corr}}$, $E_{\text{corr}}$, CR, IE%, and $\theta$ of MS with and without inhibitors. In the absence of studied inhibitors, it is clear that $I_{\text{corr}}$ increases to reach 2990 ($\mu$A/cm$^2$) and CR increases to reach 2757 mpy. In addition to different concentrations of inhibitors of the blank solution, decreases in each $I_{\text{corr}}$, CR, and IE% were observed. For example, $I_{\text{corr}}$, CR, and IE% for MS exposed to 500 ppm of the He1-Ph-Cl derivative is 150 $\mu$A/cm$^2$, 138 mpy, and 95%, respectively. For MS exposed to 500 ppm of the He1-Ph-Cl derivative, it is observed decreasing in $I_{\text{corr}}$, CR, and IE%.

2.4.3. Adsorption Isotherm. The adsorption isotherm is carried out by covering the inhibitor molecules on MS surfaces ($\theta = $ IE%/100) in corrosive media. The nature of the interaction between the MS surface and the inhibitor molecules solution is determined by the sort of adsorption that occurs (physiosorption or chemisorption). The Langmuir isotherm is shown by plotting $C_{\text{inh}}$ against $C_{\text{inh}}$/\theta as follows in eq 1, illustrated in Figure 6a; $K_{\text{ads}}$ obtained from this plotting is equal to the inverse of the intercept and slope near the unity value. By following the values of the slope and $K_{\text{ads}}$, it is clear that the type of this adsorption is a Langmuir adsorption isotherm.

$$\frac{C_{\text{inh}}}{\theta} = \frac{1}{K_{\text{ads}}} + C_{\text{inh}} \quad (1)$$

The equilibrium constant of adsorption ($K_{\text{ads}}$) is related to the Gibbs free energy of adsorption ($\Delta G_{\text{ads}}$) by the following modified eq 2:

$$\Delta G_{\text{ads}} = -2.303RT \log(55.5 \times K_{\text{ads}}) \quad (2)$$

Table S3 records the values of $\Delta G_{\text{ads}}$, slope, log $K_{\text{ads}}$, and correlation coefficient $R^2$ for MS exposed to free solution before and after adding different inhibitors. It is observed that the negative values of $\Delta G_{\text{ads}}$ are indicated spontaneously.\textsuperscript{26} In this work, the importance of $\Delta G_{\text{ads}}$ varied from $-20.6$ to $-19.6$ kJ/mol; these values emphasized that the adsorption process between the MS surface and inhibitor molecules obeyed physisorption.

2.4.4. SEM Examination. SEM gives information about the shape of the surface morphology alteration according to acid attack of the surface of MS electrodes before and after adding
Figure 6. (a) Langmuir adsorption isotherm plots for the corrosion of mild steel in 1 M H$_2$SO$_4$ solution after adding concentrations of He1-Ph-Cl, He2-Ph-CH$_3$, He4-CN, and He3-Ph, respectively. (b) SEM of bar mild steel electrode, (c) polished mild steel electrode in 1.0 M H$_2$SO$_4$, and (d) mild steel immersed in a blank solution with 500 ppm of He1-Ph-Cl.

Table 2. Some Descriptors of Quantum Studies of DHTIQs by Method and Base Set DFT/B3LYP/6-311G (d,p)

| comp.    | ΔE   | I     | u     | η    | σ     | S     | $−\Delta N$ |
|----------|------|-------|-------|------|-------|-------|-------------|
| He1-Ph-Cl| 0.05719 | 0.2730 | 0.2444 | 0.0286 | 34.9725 | 0.0143 | 8.5669 |
| He2-Ph-CH$_3$ | 0.05722 | 0.2733 | 0.2447 | 0.0286 | 34.9545 | 0.0143 | 8.5546 |
| He4-CN   | 0.05910 | 0.2744 | 0.2449 | 0.0296 | 33.8407 | 0.0148 | 8.2860 |
| He3-Ph   | 0.06028 | 0.2774 | 0.2472 | 0.0301 | 33.1802 | 0.0151 | 8.2036 |

Figure 7. Optimized structures of DHTIQs by method and base set DFT/B3LYP/6-311G (d,p).
the highest concentration of the best inhibitor, 500 ppm of He1-Ph-Cl, with high inhibition efficiency. Figure 6b illustrates SEM pictures of the MS surface after eliminating the corrosion product from the surface (after polishing). Figure 6c shows images of the MS surface after being immersed for 24 h in a blank solution; it is observed from these pictures that the surface of MS had a strong attack and deterioration because of the reaction of the ions of aggressive media sulfate anions. Figure 6d shows a picture of an MS surface immersed in 500 ppm of He1-ph-Cl for 24 h in the presence of a blank solution; it is obvious that the acid media attack on the MS surface was detected or delayed, resulting in the formation of a protective layer of inhibitor molecules on the surface of MS electrodes, which is the cause for MS corrosion protection.

2.4.5. Quantum Calculation. Quantum calculations introduce information on some descriptors that describe the stability or activity of inhibitor derivatives that can correlate with experimental inhibition efficiency. $E_{\text{HOMO}}$ means the molecule’s ability to eject electrons that are equal in mean ionization potential by inverse charge of the value from these descriptors. In the first step, good corrosion inhibitors are those organic molecules that present electrons into the unoccupied orbital of the metal and accept free electrons from the metal. Likewise, lower values of $E_G$, which are calculated from $E_{\text{HOMO}} + E_{\text{LUMO}}$ orbitals, lead to good inhibition efficiency because the energy releasing the electron from the highest occupied orbital will be small. In this study, comparing the stable and active inhibitors, it is clear from Table 2 that the $E_G$ value of He1-Ph-Cl is lower than those of other inhibitors that have the highest value, which means that He1-Ph-Cl is more active than other derivatives (more stable). Because each electronegativity $\chi$ and chemical potential $\mu$ have
been linked to $E_{HOMO}$ and $E_{LUMO}$. He1-Ph-Cl has a high value for each and a lower value for EG. Also, because hardness $\eta$ is connected to EG, He1-Ph-Cl, which has a low EG, must have a lower hardness $\eta$ than other compounds with a high EG, causing the other compounds to have a higher hardness value.

Figure 7 shows the optimized compounds of the tested inhibitors under the obvious mentioned method and base set. Figure 8 depicts $E_{HOMO}$ and $E_{LUMO}$ for all tested inhibitors; it is clear from these images that $E_{HOMO}$ sites on the structure differ from $E_{LUMO}$. The sites of $E_{HOMO}$ and $E_{LUMO}$ for all tested compounds differ from one another, indicating the previously mentioned differences in activity or stability. Figure S11 shows the Mulliken charge population analysis (MCPA) for all tested centers of the inhibitors.

3.2. Instrumentations. All compounds’ melting points used herein are purchased from Sigma-Aldrich at analytical grade and are used as received without purification. Analytical TLC was used to assess the purity of the compounds. Visualization was accomplished with iodine and under a UV lamp.

3.3. Synthesis of the New Target Dihydrothienoisoquinoline Derivatives (DHTIQs).

3.3.1. Synthesis of 7-Acetyl-4-cyano-1,6-dimethyl-8-phenyl-7,8-dihydroisoquinoline-3(2H)-thione (I).

3.3.2. Synthesis of Substituted 3-Methylsulfanyl-7-acetyl-4-cyano-1,6-dimethyl-8-phenyl-7,8-dihydroisoquinolines (4a–4c) and 5: General Method. A mixture of compound 1 (2.92 g, 0.01 mol), appropriate N-aryl-2-chloroacetamide 2a–2c or chloroacetonitrile (3; 0.01 mol), and sodium acetate trihydrate (1.50 g, 0.011 mol) in ethanol (60 mL) was heated under reflux for 1 h and then left at room temperature overnight. The formed solid was collected and recrystallized from ethanol to give colorless crystals of 4a–4c or 5.
3.3.2.4. 4-Cyan-3-cyanomethylsulfanyl-1,6-dimethyl-8-phenyl-7,8-dihydroisoquinolines (5). 5 was synthesized by using chloroacetonitrile (3), m.p.: 125–127 °C. Yield: 4.6 g (85%). IR: 3054, 3281 (NH, NH); 2972, 2924 (−C=CH, αliph., aliph.); 1645 (−C=CH, aliph.); 1654 (−C=CH, aliph.); 2251 (C≡N, nonconjugated); 2212 (C≡C, conjugated). \(^1\)H NMR (CDCl\(_3\)): \(7.22–7.24\) (m, 3H, ArH); 7.98–7.80 (dd, \(J = 10, 2H, ArH\)); 6.61 (s, 1H, C=N); 4.20–4.22 (dd, \(J = 10, 2H, CH\)); 3.97–4.07 (dd, 2H, S, CH); 5.52, 3.50–3.54 (dd, 1H, C=H); 2.36 (3H, CH\(_3\)); 1.89 (3H, CH\(_3\)). \(^13\)C NMR (126 MHz, DMSO-\(_d_6\)): 158.67, 157.44, 149.63, 144.20, 142.93, 139.45, 136.90, 139.33, 128.93, 127.35, 126.97, 125.22, 122.00, 119.45, 118.27, 37.78, 37.05. Anal. calc. for C\(_{25}\)H\(_{25}\)N\(_2\)OS (459.12): C, 73.73; H, 5.45; N, 9.87%. Found: C, 74.16; H, 5.42; N, 9.91%.

3.3.3.4. 1-Amino-2-cyano-5,8-dimethyl-6-phenyl-6,7-dihydrothieno[2,3-c]isoquinoline (7). 7 was obtained by cyclization of compound 5. Yield: 1.5 g (90%). m.p.: 240–241 °C. IR: 3395, 3328, 3232 (NH, NH); 2188 (C≡N); 1640 (C≡C). \(^1\)H NMR (DMSO-\(_d_6\)): 7.13–7.19 (m, 4H, C=H and ArH); 6.95–6.97 (2H, ArH); 6.60 (2H, NH); 4.34–4.36 (dd, \(J = 10, 1H, C=H\)); 2.87–2.92 (dd, 1H, C=H); 2.40–2.44 (dd, 1H, C=H); 2.25 (3H, CH\(_3\)); 1.81 (3H, CH\(_3\)). \(^13\)C NMR (126 MHz, DMSO-\(_d_6\)): 159.62, 158.31, 152.62, 145.13, 142.63, 139.69, 128.94, 127.71, 120.71, 125.64, 117.95, 117.38, 114.43, 74.24, 37.65, 37.05, 24.67, 22.74. MS: m/z 331, 315, 15%. Anal. calc. for C\(_{25}\)H\(_{25}\)N\(_2\)OS (331.11): C, 72.48; H, 5.17; N, 12.68%. Found: C, 72.26; H, 5.10; N, 12.82%.

3.4. Preparing Studied Surface and Tested Media. The mild steel (MS) specimen composition is (wt %) Fe 98%. For the electrochemical studies, the MS specimens were divided into 1 × 1 × 1 cm\(^3\). The surfaces of all studied specimens were polished with different grades of emery polishing papers such as 1200 and 1400, then degreased with acetone and finally dried. The corrosive solutions were prepared by analytical grade 97% H\(_2\)SO\(_4\) (Sigma-Aldrich Laborchemikalien, German) with dilution by bidistilled water.

3.5. Preparation of Corrosive and Inhibitor Solutions. The inhibitors (He1-Ph-Cl, He2-Ph-CH\(_2\), He3-Ph, and He4-CN) were prepared by weighing 0.05 g of the tested inhibitors and dissolving it into 100 cm\(^3\) of 1.0 M H\(_2\)SO\(_4\) to obtain 500 ppm of each inhibitor that was diluted to 100 and 200 ppm to execute the experimental task.

3.6. Electrochemical Techniques. The potentiodynamic method used in this study includes open circuit potential (OCP) for immersion MS electrode potential (\(E_{corr}\)) in the blank solution without and with inhibitor concentrations to obtain a steady-state potential (\(E_{ss}\)), which is near the corrosion potential (\(E_{corr} \approx E_{eq}\)). Potentiodynamic polarization (PP) records parameters such as corrosion potential (\(E_{corr} \), mV), corrosion current density (\(I_{corr} \), \(\mu A/cm^2\)), corrosion rate (CR, millimeter per year, mpy), inhibition efficiency percentage (IE%), and surface coverage (\(\theta = IE\%\)). OCP is performed using a reference electrode as SEC and working MS, but in PP experiments, a counter electrode (Pt wire) is added with the obvious OCP electrodes. OCP and PP curves were performed with an E&G potentiostat/galvanostat instrument, model 273A. TF was scanned at ±250 mV vs E\(_{corr}\) with a rate of scan of 0.3 mV/s. CR and IE% for the tested inhibitors were calculated from \(I_{corr}\) mathematically according to eqs 3 and 4, respectively.

\[
CR = 0.13 \times \frac{I_{corr} \times Eq.Wt}{\rho \times A}
\]  

where CR is the corrosion rate (mpy); \(I_{corr}\) is the corrosion current density (\(\mu A/cm^2\)), which records the current value at which the corrosion process takes place; Eq. Wt. is the equivalent weight of the metal (gm/eq) equal to 55.8 atomic mass; \(A\) is the area (cm\(^2\)) immersed in tested solutions; \(\rho\) is the density (gm/cm\(^3\)) equal to 7.874 g/cm\(^3\); and 0.13 is the metric and time conversion factor.
CR and CR1 are the corrosion rates without and with inhibitors, respectively.

3.7. Quantum Calculations. Quantum calculations introduce some parameters related to the reactivity and stability of tested inhibitors, such as the energy gap (EG), ionization potential (I), chemical potential (μ), global hardness (η), global softness (σ), softness (S), and the fraction of electrons transferred (ΔN). Eqs 5–11 summarize the studied quantum chemical descriptors shown as follows:

$$
\Delta E = EG = E_{\text{LUMO}} - E_{\text{HOMO}}
$$

(5)

$$
I = -E_{\text{HOMO}}
$$

(6)

$$
\mu = -\chi = \frac{E_{\text{LUMO}} + E_{\text{HOMO}}}{2}
$$

(7)

$$
\eta = \frac{(E_{\text{LUMO}} - E_{\text{HOMO}})}{2}
$$

(8)

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

(9)

$$
S = \frac{1}{2\eta}
$$

(10)

$$
\Delta N = \frac{(\chi_{\text{Fe}} - \chi_{\text{inh}})}{2(\eta_{\text{Fe}} + \eta_{\text{inh}})}
$$

(11)

4. CONCLUSIONS

Four dihydrothienoisoquinoline (DHTIIQ) derivatives were successfully synthesized in this article, and their structures were studied using elemental and spectral studies. The physical properties of the synthesized DHTIIQs were investigated, and they have good luminescence properties. In a 1.0 M sulfuric acid solution, DHTIIQ derivatives were tested as anticorrosion agents for mild steel. The findings demonstrate that all examined compounds have a high inhibition ratio, reaching 95% for compound He1-Ph-Cl, following the pattern He1-Ph-Cl > He2-Ph-CH3 > He3-CN > He4-Ph as concentration increases. The Tafel polarization plots show that these compounds are mixed-type inhibitors, and the adsorption isotherm follows the Langmuir isotherm. The free energy recorded between −20.6 and −19.6 kJ/mol indicates the presence of a physisorption isotherm, and quantum calculation using the Gaussian 09 program yielded results that were consistent with the experimental results. In addition, SEM images of mild steel with and without inhibitors were studied. Tissue engineering, bioimaging, sensors/microporous polymers for achieving the robust visible-light-driven hydrogen evolution from water. Appl. Catal., B 2021, 285, 119802−119841.

(1) Grimsdale, A. C.; Leak Chan, K.; Martin, R. E.; Jokiss, P. G.; Holmes, A. B. Synthesis of lightemitting conjugated polymers for applications in electroluminescent devices. Chem. Rev. 2009, 109, 897–1091.

(2) Anthony, J. E. Functionalized acenes and heteroacenes for organic electronics. Chem. Rev. 2006, 106, 5028–5048.

(3) Farinola, G. M.; Ragni, R. Electroluminescent materials for white organic light emitting diodes. Chem. Soc. Rev. 2011, 40, 3467–3482.

(4) Feng, H.-T.; Zheng, X.; Gu, X.; Chen, M.; Lam, J. W. Y.; Huang, X.; Tang, B. Z. White-light-emission formation from two complementary colored luminescence dyes. Mater. Chem. Front. 2018, 30, 1285–1290.

(5) Yang, T.; Wang, T.; Yin, P.; Yin, W.; Zhang, S.; Lei, Z.; Yang, M.; Ma, Y.; Duan, W.; Ma, H. A general concept for the white light emission formation from two complementary colored luminescence dyes. Mater. Chem. Front. 2019, 3, 505–512.

(6) Elewa, A. M.; Elsayed, M. H.; El-Mahdy, A. F.M.; Chang, C.-L.; Ting, L.-Y.; Lin, W.-C.; Lu, C.-Y.; Chou, H.-H. Triptycene-Based Discontinuously-Conjugated Covalent Organic Polymer Photocatalysts for Visible-Light-Driven Hydrogen Evolution from Water. Appl. Catal., B 2021, 285, 119802–119841.

(7) Elewa, A. M.; El-Mahdy, A. F. M.; Elsayed, M. H.; Mohamed, M. G.; Koo, S.-W.; Chou, H.-H. Sulfur-doped triazine-conjugated microporous polymers for achieving the robust visible-light-driven hydrogen evolution. Chem. Eng. J. 2021, 421, 129825−12937.

(8) EL-Mahdy, A. F. M.; Bakhtee, E. A.; Abdel-Hafez, Sh. H.; Ibrahim, O. F.; Abd-Allah, H. H. M.; Marae, I. S. J. Heterocycl. Chem. 2022, 59, 359–370.

(9) Popova, A.; Christov, M.; Zvetanova, A. Effect of the molecular structure on the inhibitor properties of azoles on mild steel corrosion in 1 M hydrochloric acid. Corros. Sci. 2007, 49, 2131–2143.

(10) Bentiss, F.; Lebrini, M.; Lagrene, M. Thermodynamic characterization of metal dissolution and inhibitor adsorption processes in mild steel/2,5-bis(n-thienyl)-1,3,4-thiadiazoles/hydrochloric acid system. Corros. Sci. 2005, 47, 2915–2931.

(11) Fouda, A. S.; Al-Sarawy, A. A.; El-Katori, E. E. Pyrazolone derivatives as corrosion inhibitors for C-steel HCl solution. Desalination 2006, 201, 1–13.

■ AUTHOR INFORMATION

Corresponding Author
Etify A. Bakhite — Chemistry Department, Assiut University, Assiut 71516, Egypt; orcid.org/0000-0003-3994-5629; Phone: +201006670292; Email: etify@au.edu.eg

Authors
Islam S. Marae — Chemistry Department, Faculty of Science, Assiut University, Assiut 71516, Egypt

Mahmoud H. Mahross — Chemistry Department, Faculty of Science, Al-Azhar University, Assiut 71524, Egypt

Badriah S. Al-Farhan — Chemistry Department, Faculty of Girls for Science, King Khalid University, Abha 62529, Saudi Arabia

Mohamed Abdel-Hakim — Chemistry Department, Faculty of Science, Al-Azhar University, Assiut 71524, Egypt

Marwa M. Sayed — Chemistry Department, Faculty of Science, New Valley University, El-Kharja 72511, Egypt; orcid.org/0000-0002-9043-0092

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.2c03361

Notes
The authors declare no competing financial interest.

■ REFERENCES

(1) Grimsdale, A. C.; Leak Chan, K.; Martin, R. E.; Jokiss, P. G.; Holmes, A. B. Synthesis of lightemitting conjugated polymers for applications in electroluminescent devices. Chem. Rev. 2009, 109, 897–1091.

(2) Anthony, J. E. Functionalized acenes and heteroacenes for organic electronics. Chem. Rev. 2006, 106, 5028–5048.

(3) Farinola, G. M.; Ragni, R. Electroluminescent materials for white organic light emitting diodes. Chem. Soc. Rev. 2011, 40, 3467–3482.

(4) Feng, H.-T.; Zheng, X.; Gu, X.; Chen, M.; Lam, J. W. Y.; Huang, X.; Tang, B. Z. White-light-emission formation from two complementary colored luminescence dyes. Mater. Chem. Front. 2018, 30, 1285–1290.

(5) Yang, T.; Wang, T.; Yin, P.; Yin, W.; Zhang, S.; Lei, Z.; Yang, M.; Ma, Y.; Duan, W.; Ma, H. A general concept for the white light emission formation from two complementary colored luminescence dyes. Mater. Chem. Front. 2019, 3, 505–512.

(6) Elewa, A. M.; Elsayed, M. H.; El-Mahdy, A. F.M.; Chang, C.-L.; Ting, L.-Y.; Lin, W.-C.; Lu, C.-Y.; Chou, H.-H. Triptycene-Based Discontinuously-Conjugated Covalent Organic Polymer Photocatalysts for Visible-Light-Driven Hydrogen Evolution from Water. Appl. Catal., B 2021, 285, 119802–119841.

(7) Elewa, A. M.; El-Mahdy, A. F. M.; Elsayed, M. H.; Mohamed, M. G.; Koo, S.-W.; Chou, H.-H. Sulfur-doped triazine-conjugated microporous polymers for achieving the robust visible-light-driven hydrogen evolution. Chem. Eng. J. 2021, 421, 129825−12937.

(8) EL-Mahdy, A. F. M.; Bakhtee, E. A.; Abdel-Hafez, Sh. H.; Ibrahim, O. F.; Abd-Allah, H. H. M.; Marae, I. S. J. Heterocycl. Chem. 2022, 59, 359–370.

(9) Popova, A.; Christov, M.; Zvetanova, A. Effect of the molecular structure on the inhibitor properties of azoles on mild steel corrosion in 1 M hydrochloric acid. Corros. Sci. 2007, 49, 2131–2143.

(10) Bentiss, F.; Lebrini, M.; Lagrene, M. Thermodynamic characterization of metal dissolution and inhibitor adsorption processes in mild steel/2,5-bis(n-thienyl)-1,3,4-thiadiazoles/hydrochloric acid system. Corros. Sci. 2005, 47, 2915–2931.

(11) Fouda, A. S.; Al-Sarawy, A. A.; El-Katori, E. E. Pyrazolone derivatives as corrosion inhibitors for C-steel HCl solution. Desalination 2006, 201, 1–13.
(12) Eddy, N. O. Ethanol extract of phyllanthus amarus as a green inhibitor for the corrosion of mild steel in H2SO4. *Port. Electrochim. Acta* 2009, 27, 579–589.

(13) Abdel-Aal, M. S.; Morad, M. S. Inhibiting effects of some quinolines and organic phosphonium compounds on corrosion of mild steel in 3 M HCl solution and their adsorption characteristics. *Br. Corros. J.* 2001, 36, 253–260.

(14) Shylesha, B. S.; Venkatesha, T. V.; Praveen, B. M.; Srinath, K. V. Corrosion Inhibition Effect of Substituted Quinoline and Its Condensation Products on Mild Steel in Acidic Media. *Anal. Bioanal. Electrochem.* 2011, 3, 249–260.

(15) Abdel-All, M. S.; Ahmed, Z. A.; Hassan, M. S. Inhibiting and accelerating effects of some quinolones on the corrosion of zinc and some binary zinc alloys in HCl solution. *J. Appl. Electrochem.* 1992, 22, 1104–1109.

(16) Singh, M.; Bhattamishra, A. K.; Das, N. N. J. Metall. Mater. Sci. 2009, 51, 45–54.

(17) Ebenso, E. E.; Obot, I. B.; Murulana, L. C. Quinoline and its derivatives as effective corrosion inhibitors for mild steel in acidic medium. *J. Electrochem. Sci.* 2010, 5, 1574–1586.

(18) Al-Uqaily, R. A. H. Inhibition by 1-methylisoquinoline for mild steel corrosion in 1 M HCl media. *Am. Sci. Res. J. Eng., Technol. Sci.* 2015, 14, 55–63.

(19) Al-Uqaily, R. A. H.; Albayaty, S. A. Study a corrosion inhibitor of 1-isoquinolinyl phenyl ketone for mild steel in acidic medium as HCl acid. *J. Phys. (Paris)* 2019, 052014.

(20) Shi, M.-M.; Lin, J.-J.; Shi, Y.-W.; Ouyang, M.; Wang, M.; Chen, H.-Z. Achieving blue luminescence of Alq3 through the pull-push effect of the electron-withdrawing and electron-donating substituents. *Chen. Mater. Chem. Phys.* 2009, 115, 841–845.

(21) Duvenhage, M. M.; Visser, H. G.; Ntwaeaborwa, O. M.; Swart, H. C. The effect of electron donating and withdrawing groups on the morphology and optical properties of Alq3. *Phys. B: Condens. Matter.* 2014, 439, 46–49.

(22) Ravi Kishore, V. V. N.; Aziz, A.; Narasimhan, K. L.; Periasamy, N.; Meenakshi, P. S.; Wategaonkar, S. On the assignment of the absorption bands in the optical spectrum of Alq3. *Synth. Met.* 2002, 126, 199–205.

(23) Balewski, L.; Sączewski, F.; Gdaniec, M.; Kornicka, A.; Cicha, K.; Jalińska, A. Synthesis and fluororescent properties of novel isoquinoline derivatives. *Molecules* 2019, 24, 4070.

(24) Motoyoshiya, J.; Fengqiang, Z.; Nishii, Y.; Aoyama, H. Fluorescence quenching of versatile fluorescent probes based on strongly electron-donating distyrylbenzenes responsive to aromatic chlorinated and nitro compounds, boronic acid and Ca2+. *Spectrochim. Acta A: Mol. Biomol. Spectrosc. Spectrochim Acta A* 2008, 69, 167–173.

(25) Li, W.-h.; He, Q.; Zhang, S.-t.; Pei, C.-l.; Hou, B.-r. Some new triazole derivatives as inhibitors for mild steel corrosion in acidic medium. *J. Appl. Electrochem.* 2008, 38, 289–295.

(26) Flis, J.; Zakroczymski, T. Impedance study of reinforcing steel in simulated pore solution with tannin. *J. Electrochem. Soc.* 1996, 143, 2458–2464.

(27) Ouakki, M.; Galai, M.; Rbba, M.; Aboussale, A. S.; Lakhriess, B.; Rifi, E. H.; et al. Quantum chemical and experimental evaluation of the inhibitory action of two imidazole derivatives on mild steel corrosion in sulphuric acid medium. *Heliyon* 2019, 5, No. e02759.

(28) Lukovits, I.; Kalmán, E.; Zucchi, F. Corrosion inhibitors—correlation between electronic structure and efficiency. *Corros. 2001, 57, 3–8.

(29) Rodriguez-Valdez, L. M.; Martínez-Villafañe, A.; Glossman-Mitnik, D. Computational simulation of the molecular structure and properties of heterocyclic organic compounds with possible corrosion inhibition properties. *J. Mol. Struct.: THEOCHEM 2005, 713, 65–70.*

(30) Fang, J.; Li, J. Theoretical study of corrosion inhibition of amides and thiosemicarbazones. *J. Mol. Struct.: THEOCHEM 2002, 593, 179–185.

(31) Zhou, W.; Zhang, J.; Liu, Y.; Li, X.; Niu, X.; Song, Z.; Min, G.; Wan, Y. Z.; Shi, L.; Feng, S. Characterization of anti-adhesive self-assembled monolayer for nanoimprint lithography. *Appl. Surf. Sci.* 2008, 255, 2885–2889.

(32) Obot, I. B.; Obi-Egbedi, N. O. Indene-1-one[2,3-b]quinoloxaline as an effective inhibitor for the corrosion of mild steel in 0.5M H2SO4 solution. *Mater. Chem. Phys.* 2010, 122, 325–328.

(33) Obot, I. B.; Obi-Egbedi, N. O.; Umoren, S. A. The synergistic inhibitive effect and some quantum chemical parameters of 2,3-diaminonaphthalene and iodide ions on the hydrochloric acid corrosion of aluminium. *Corros. Sci.* 2009, 51, 276–282.

(34) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A.; et al. *Gaussian 09;* Gaussian, Inc.: Wallingford, CT, 2009.

(35) Stephens, P.; Devlin, F.; Chabalowski, C.; Frisch, M. J. Ab initio calculation of vibrational absorption and circular dichroism spectra using density functional force fields. *J. Phys. Chem. 1994, 98, 11623–11627.*

(36) Marae, I. S.; Ibrahim, O. F.; Abdel-Hafez, Sh. H.; Mohamed, S. K.; Mague, J. T.; Bakhte, E. A.-G. Synthesis, characterization and crystal structure of some novel partially hydrogenated isoquinolines and their fused heterocyclic systems. *J. Heterocycl. Chem.* 2021, 59, 1230.

(37) Shams El Din, A. M.; Paul, N. J. Oxide film thickening on some molybdenum-containing stainless steels used in desalination plants. *Desalination* 1988, 69, 251–260.

(38) Pearson, R. G. Absolute electronegativity and hardness: applications to organic chemistry. *J. Org. Chem.* 1989, 54, 1423–1430.

(39) Padmanabhan, J.; Parthasarathi, R.; Subramanian, V.; Chattaraj, P. K. Electrophilicity-based charge transfer descriptor. *J. Phys. Chem. A* 2007, 111, 1358–1361.