Synthesis of tolyl guanidine as copper corrosion inhibitor with a complementary study on electrochemical and in silico evaluation

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A rapid and new synthetic route for N,N'-di-o-tolyl guanidine (DTG) synthesis from cheap materials is reported. The performance of DTG as an excellent inhibitor for delaying copper (Cu) corrosion with an efficiency higher than 98% at 20 \times 10^{-6} \text{ M} in an acidic solution was investigated via electrochemical measurements. These measurements included PDP, EFM, and EIS spectroscopy. The experimental data indicated that DTG has an efficient inhibiting effect on the corrosion of Cu in acidic media. The DTG was adsorbed on the Cu surface via chemical adsorption and followed the Langmuir route. The PDP measurements revealed that DTG acted as a mixed inhibitor. Furthermore, EIS data showed that the DTG adsorbed through the metal/electrolyte interface. This resulted in forming a DTG protective layer on the Cu surface, thereby impeding the dissolution of Cu in the acidic solution. The corrosive solution containing the DTG inhibitor after immersion of the Cu specimen for 48 h, which promoted the formation of a complex between the Cu cation and DTG, was investigated via ultraviolet/visible spectroscopy. In addition, the formation of a DTG protective layer on the Cu surface was confirmed via scanning electron microscopy and atomic force microscopy analysis of the Cu surface morphology. Moreover, the active centers for interaction with the Cu surface in an acidic solution were investigated via in silico evaluation of DTG.

Copper (Cu) is considered a useful material due to its thermal stability, high electrical conductivity, and good mechanical properties. This material is used extensively for evaporators, conductors, condensers, pipelines, heat exchangers, and pipelines. Although resistant to most environments, Cu is corroded in aggressive acidic media, leading to economic losses. Organic corrosion inhibitors with nitrogen hetero atoms exhibit good inhibition efficiency. Their mode of operation involves the adsorption of ions or molecules on a metal surface (MS).

Current studies on Cu corrosion focus primarily on developing green corrosion inhibitors with good inhibitive performances without environmental pollution. Guanidines are used in medicinal chemistry and are efficient corrosion inhibitors in different corrosive media. These substances are highly functionalized compounds with three nitrogen atoms, two methyl donating groups, and \pi-electrons in the rings.

Based on the initial findings and our work on the synthesis and chemistry of nitrogen compounds, we have developed a synthetic route for the synthesis of N,N'-di-o-tolyl guanidine (DTG). In the present work, DTG, which was selected as a corrosion inhibitor for Cu in an acidic solution, was studied via electrochemical, surface morphological, spectroscopic, and theoretical methods.

Experimental procedure

Materials and instrumentation. Analytical grade chemicals were used in this work. The solution of the DTG was prepared at different concentrations (5 \times 10^{-6} – 20 \times 10^{-6} \text{ M}) in a solution of 0.5 M HCl. The working electrode was a cylindrical-shaped Cu rod (99.99% purity), welded with Cu-wire and embedded in resin with a 0.5 cm² surface area (cover one side) open to exposure. Electrochemical study data were plotted and fitted in the Echem Analyst, version 5.50 (Gamry Instruments, Warminster, PA, USA). After immersion in test solutions, the

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Surface morphology of the Cu samples was examined via SEM (JEOL JSM-53000) and AFM (N9498S Agilent Technologies) analysis.

**Synthesis and characterization of inhibitor DTG.** To a magnetically stirred solution of o-toluidine 1 (1.07 g, 10 mmol) in EtOH (15 mL), a solution of cyanic bromide 2 (1.27 g, 12 mmol) in EtOH (5 mL) was added gradually at 0 °C until the exotherm subsided and was then refluxed for 1.5 h. The mixture was filtered and the filtrate was neutralized using 1 M NaOH. Subsequently, the precipitate was filtered off and recrystallized from aqueous EtOH, yielding DTG (2.16 g, 90%) as a white solid. Rₐ=0.38 (hexane/EtOAc, v/v, 1/4) and M.p 175–177 °C. FT–IR (KBr): 3452, 3386 (NH), 1631 (C=C), 1575 (C=N).¹H NMR (500 MHz, DMSO): δ 2.14 (s, 6H), 5.08 (br s, 2H), 6.77–6.80 (t, J = 6.79 Hz, 3H), 7.01–7.04 (t, J = 7.02 Hz, 3H), 7.07–7.09 (d, J = 7.08 Hz, 3H). ¹³C NMR (125 MHz, DMSO): δ 147.69, 130.03, 126.16, 121.79, 121.24, 18.12. HRMS (ESI/QTOF) m/z: [M]+ Calcd for C₁₅H₁₇N₃ 239.1422, found 239.1427.

**Electrochemical technique.** Electrochemical measurements (PDP, EFM, and EIS spectroscopy) were performed using three-electrode cell systems with the Cu sample as the working electrode (WE; surface area cover one side): 0.5 cm²). Platinum and saturated calomel electrode (SCE) served as the counter and reference electrodes. Before each measurement, the surface of the WE exposed to air was abraded with various grades (800, 1200, 1500, and 2000) of emery papers. Afterward, the electrode was rinsed with distilled water, degreased with acetone, rinsed with distilled water again, and dried with soft paper. The electrode was then dipped into the test solution for 45 min until a steady-state open circuit potential (Eocp) was achieved. All measurements were performed in a fresh test solution at a constant temperature of 30 °C ± 1 °C. PDP measurements were performed by polarizing the WE (scan rate: 0.5 mV s⁻¹) at OCP in the range of ± 250 mV. EIS measurements were conducted at 100 kHz and 10 alternating current (AC) amplitude of ± 10 mV at the OCP. In addition, EFM measurements were conducted at two frequencies (2.0 and 5.0 Hz). The base frequency was 0.1 Hz and a potential disturbance signal of 10 mV.

**UV–Visible spectra measurement.** UV–visible spectra measurements were performed on the DTG solution (20 × 10⁻⁶ M) before and after dipping Cu at 30 °C for 28 h. All spectra were recorded using a PG instruments T80 + spectrometer with a dual-beam operated at a bandwidth of 1.0 nm in 190–1100 nm.

**Cu surface analysis (SEM and AFM).** In preparation for the morphology study, the abraded Cu samples were immersed in test solutions at 30 °C for 48 h. The samples were then removed, rinsed with deionized water, and dried. Properties of the DTG protective layer on the Cu surface were evaluated via SEM and AFM analysis.

**Quantum chemical calculations (QCCs).** Density functional theory (DFT) calculations were performed using the Gaussian program package (version 9.0; Pittsburgh, PA, USA). Furthermore, the DTG geometry optimization was performed using the B3LYP functional DFT level with the 6–31G++ (d, p) basis set in the aqueous phase.

**Results and discussion**

**Synthesis of the DTG inhibitor.** The synthetic approach for DTG synthesis is depicted in Fig. 1. The reaction of o-toluidine 1 with cyanic bromide 2 in refluxing ethanol yielded the targeted DTG inhibitor (Fig. 1). The spectra of DTG concurred with the proposed structure (vide Figs. 2, 3, 4). Various spectroscopic methods were used to characterize the structure of DTG. Characteristic bands occurring at 1631 and 1575 cm⁻¹ in the infrared (IR) spectra are assigned to C=C and C=N bonds (Fig. 2). Similarly, the peaks at 3452 and 3386 cm⁻¹ are attributed to the –NH group. ¹H NMR spectra reveal two characteristic signals at 2.14 and 5.08 ppm, which are associated with Me and NH protons (Fig. 3). In the ¹³C NMR spectra, peaks associated with the C=N and C–NH resonate at 147.69 and 130.03 ppm (Fig. 4).

**Electrochemical measurements.** PDP measurements. PDP measurements depend on the DTG nature (anodic, cathodic, or mixed-type inhibitor), mode of adsorption on the MS (physical, chemical, or mixture of both), and the mechanism of the DTG reaction with metal in the corrosive medium. Figure 5 shows the PDP curves obtained for Cu in test solutions with/without different concentrations of DTG at 30 °C. The kinetic corrosion parameters such as the corrosion potential (Ecorr), Icorr, the anodic Tafel slope (βa), and the cathodic Tafel slope (βc) are calculated from the analysis of the PDP plots (Table 1). The corrosion inhibition efficiency (% IEcorr) and the degree of surface coverage (θ) can be calculated from the Icorr values obtained via Tafel extrapolation of PDP curves and are given as follows²⁷:

![Figure 1. Synthesis of the DTG.](https://doi.org/10.1038/s41598-022-18755-y)
Icorr and \( I_i \) are the corrosion current density of Cu electrodes in the test solutions.

\[
IE_{PDP} = \left[ \frac{I_{corr} - I_i}{I_{corr}} \right] \times 100 = \theta \times 100.
\]

(1)

\( I_{corr} \) and \( I_i \) are the corrosion current density of Cu electrodes in the test solutions.

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**Figure 2.** FT–IR spectrum of the DTG inhibitor.

**Figure 3.** \(^1\)HNMR spectrum of the DTG inhibitor in DMSO-\(d_6\).
Figure 4. $^{13}$C NMR spectrum of the DTG inhibitor in DMSO-$d_6$.

Figure 5. PDP curves for Cu in test solutions with/without of DTG.

Table 1. PDP kinetic parameters for (DTG).

| Conc. (µM) | $I_{corr}$ (µA cm$^{-2}$) | $-E_{corr}$ (mV vs. SCE) | $\beta_a$ (mV dec$^{-1}$) | $\beta_c$ (mV dec$^{-1}$) | $\theta$ | %IEPDP |
|------------|--------------------------|--------------------------|--------------------------|--------------------------|---------|--------|
| Blank      | 428                      | 548                      | 105                      | 185                      | -       | -      |
| 5 $\times$ 10$^{-6}$ | 84.74                     | 489                      | 91.2                     | 120.3                    | 0.502   | 80.2   |
| 10 $\times$ 10$^{-6}$ | 50.93                     | 4491                     | 92.2                     | 131.2                    | 0.881   | 88.1   |
| 15 $\times$ 10$^{-6}$ | 25.68                     | 485                      | 74.8                     | 128.5                    | 0.938   | 93.8   |
| 20 $\times$ 10$^{-6}$ | 8.56                      | 484                      | 88.5                     | 119.8                    | 0.983   | 98.3   |
Both anodic (Cu dissolution) and cathodic (H₂ evolution reduction) have been inhibited after DTG was added to the corrosive medium (Fig. 3 and Table 1). This is suggests that DTG molecule acts as a mixed-type inhibitor. The %IE₉₀₀ increases with increasing DTG concentration.

The Ecorr values may also be used to classify inhibitors as cathodic, anodic, or mixed. When the difference in Ecorr values without and with inhibitors is greater than 85 mV 85 mV, the inhibitor molecules are classified as cathodic or anodic. Table 1, demonstrates that the displacement of the Ecorr values of the produced inhibitor molecules assembled on the surfaces of mild steel is less than 85 mV in the current study. As a result, the investigated DTG inhibitor acts as a mixed-type inhibitor.

However, the negative shifting of the Ecorr values, and the β values are significantly higher than the β values in the presence of DTG. This suggests that the effect of DTG on cathodic H₂ evolution is more prominent than that on anodic (Cu dissolution) in an acidic medium. In addition to, the %IE₉₀₀ values increase, and the magnitude of Icorr decreases with increasing DTG doses (Table 1). This reduction indicates that the rate of electrochemical reaction decreased due to the formation of a protective DTG layer on the MS.

**EFM measurements.** The EFM technique is a rapid and non-destructive technique that determines the Icorr value without previous knowledge of the Tafel constants. The causality factors (CF-2) and (CF-3) indicate the validity of the EFM measurements. The EFM inter modulation spectra (frequency vs. frequency) of the Cu in 0.5 M HCl solution with or without various concentrations of the DTG are shown in Fig. 6. The EFM parameters (e.g., Icorr, βa, βc, CF-2, and CF-3) were determined from the large spectra. The θ values were calculated as follows:

\[
IE_{EFM} = \left( \frac{I_{corr} - I_{E}}{I_{corr}} \right) \times 100 = \theta \times 100. \tag{2}
\]

Icorr and I represent the aforementioned corrosion current densities. The Icorr values decrease with increasing DTG concentration, owing to the protective thin film formed on the Cu surface. The CF-2 and CF-3 are close to their theoretical values (2 and 3, respectively), indicating the validity of the experimental EFM data (Table 2). Moreover, the EFM results are consistent with the PDP measurement results.

**EIS measurements.** EIS measurements were used to investigate the kinetic parameters for electron transfer reactions at the Cu electrode/electrolyte interface. Nyquist plots were obtained for the Cu electrode in 0.5 M HCl solution at an open-circuit potential after 45 min in immersion test solutions (Fig. 7a). A depressed semicircle corresponding to a single charge transfer process during the dissolution of Cu in the corrosive medium, which is unaffected by the existence of the DTG, occurs in the Nyquist plot.

Although a defined frequency was utilized to obtain the impedance at each data point, a Nyquist plot does not display any frequency value. To solve this deficiency, a Bode plot was created to show which frequency was utilized to generate a data point. The Bode plots (Fig. 7b) reveal a single maximum at intermediate frequencies, with this maximum broadening in the presence of DTG due to the creation of a protective layer on Cu surface. Higher values of phase angle and impedance for inhibited solution compared to uncontrolled solution reflect the inhibition effect of (EATPB). Furthermore, these values rise on the rise in the concentration of studied DTG. EIS plots were modeled and fitted using a suitable equivalent circuit (Fig. 7c).

The charge transfer resistance (Rcorr) and double-layer capacitance (Cdl) values are deduced from the Nyquist plot analysis (Table 3). The (%IE₉₀₀) and (θ) are calculated from the (Rcorr) (vide Eq. 3):

\[
IE_{EIS} = \left( \frac{R_{corr} - R^{b}_{corr}}{R_{corr}} \right) \times 100 = \theta \times 100. \tag{3}
\]

Rcorr and Rcorr are the charge transfer resistance values with or without DTG, respectively.

The constant phase element (CPE) is applied to the state of capacitance (C) to represent a frequency-independent phase shift between an applied alternating potential and its current response. The CPE may be mathematically defined as follows:

\[
Z_{CPE} = \frac{1}{Y_{0}(j\omega)^{n}}. \tag{4}
\]

Z_{CPE}, the impedance of CPE; Y₀, a proportional factor; W, angular frequency; j, (−1)½; and n, is related to (among others) the electrode surface roughness, distribution of reaction rates, and non-uniform current distribution. Nyquist plots associated with a model containing (CPE) rather than (C) and the (Rcorr) correspond closely to the experimental results. The values of (n) corresponding to the 0.5 M HCl solution with DTG are lower than those of the solution without DTG, indicating the reduction of surface heterogeneity due to DTG adsorption onto the MS (Table 3). The Rcorr values increase with increasing DTG concentration, while CPE values decrease, leading to a maximum %IE₉₀₀ (95.2%) at high concentration. This result indicates that DTG adsorption occurred at the metal/electrolyte interface, resulting in an adsorbed film on the Cu surface, which impedes the dissolution of the surface in the corrosive acidic medium.

Thus, the results obtained from EIS corroborate the data obtained from PDP & EFM and indicate that adsorption films are formed. Owing to this adsorbed film, the number of active surface centers exposed to the corrosive acidic solution decreases and Cu dissolution and hydrogen evolution is delayed.
Figure 6. EFM spectra of Cu in test solutions with/ without of DTG.

| Conc., (µM) | icorr, (µA cm$^{-2}$) | βc, (mV dec$^{-1}$) | βa, (mV dec$^{-1}$) | CF-3 | CF-2 | θ | %IEEFM |
|------------|------------------------|---------------------|---------------------|-----|-----|---|--------|
| Blank      | 436                    | 143                 | 91                  | 2.85| 1.90|   |        |
| 5 × 10$^{-6}$| 98.1                   | 114                 | 96                  | 3.15| 1.81| 0.775| 77.5  |
| 10 × 10$^{-6}$ | 60.6                   | 110                 | 93                  | 2.88| 2.13| 0.861| 86.1  |
| 15 × 10$^{-6}$ | 33.1                   | 119                 | 98                  | 2.70| 1.86| 0.924| 92.4  |
| 20 × 10$^{-6}$ | 13.9                   | 99                  | 96                  | 3.16| 1.78| 0.968| 96.8  |

Table 2. EFM kinetic parameters of DTG.
Adsorption isotherm (AI) and thermodynamic parameters. AIs describe the interaction between both Cu surface and DTG. The efficiency of DTG depends mainly on their ability to adsorb onto the MS. The adsorption process includes the replacement of H₂O molecules at a metal/electrolyte solution interface and is described as follows:

\[
\text{Inh}_{(\text{sol})} + n\text{H}_2\text{O}_{(\text{ads})} \rightarrow \text{Inh}_{(\text{ads})} + n\text{H}_2\text{O}_{(\text{sol})}. \tag{5}
\]

\text{Inh}_{(\text{sol})} \text{ and } \text{Inh}_{(\text{ads})} \text{ are the DTG in the solution and adsorbed on the MS, correspondingly, and } n \text{ is the number of H}_2\text{O molecules replaced by DTG. Various types of AI can be considered to elucidate the nature of the interaction between the DTG and the Cu surface[47].}

The experimental data obtained from PDP measurements are applied to fitting various AIs in our work. The Langmuir AI yields the best fitting of the PDP results. From this model of AI, the degree of surface coverage (θ) is related to the DTG concentration (C) as follows[40]:

![Figure 7. Nyquist plots (a), and Bode plots (b) for copper in 0.5 M HCl solution with/without of different concentrations of DTG with using a suitable equivalent circuit model (c).](image)

| Conc (µM) | Rs (Ω cm²) | n  | Rs (Ω cm²) | CPE_{dl} (µF cm⁻²) | θ   | %IEEIS |
|----------|------------|----|------------|---------------------|-----|--------|
| Blank    | 2.09       | 0.578 | 410        | 243                 |     |        |
| 5 × 10⁻⁶ | 3.88       | 0.586 | 2015       | 45.0                | 0.815 | 81.5   |
| 10 × 10⁻⁶| 4.11       | 0.598 | 2390       | 41.6                | 0.872 | 82.8   |
| 15 × 10⁻⁶| 4.15       | 0.601 | 2950       | 33.7                | 0.932 | 86.1   |
| 20 × 10⁻⁶| 4.18       | 0.621 | 8710       | 11.6                | 0.973 | 95.2   |

Table 3. EIS kinetic parameters for DTG.
Linear plots of $C/\theta$ versus $C$ with strong correlation coefficients ($R^2$) of 0.997, and a slope that is very close to unity for the DTG (Fig. 8) are obtained. The high value of $K_{ads}$ ($93 \times 10^4$) from the plot’s intercept indicates strong adsorption of the DTG onto the Cu surface. The equilibrium constant ($K_{ads}$) of the adsorption process is associated with the standard free energy of adsorption ($\Delta G_{ads}$), which is given as follows:

$$\Delta G_{ads} \text{ values less than or equal to } -20 \text{ kJ mol}^{-1} \text{ (more positive) are consistent with electrostatic interaction between the charged DTG and charged Cu surface, which occurs through physisorption. While, } \Delta G_{ads} \text{ values of approximately } -40 \text{ kJ mol}^{-1} \text{ (more negative) or higher are related to charge or sharing electron transfer from the DTG to the metal surface via coordinate bond formation, which occurs through chemisorption.}$$

The calculated value of $\Delta G_{ads}$ in the present study is $-44.2 \text{ kJ mol}^{-1}$. This indicates that DTG is adsorbed physically on Cu surface in an acidic solution.

**Analysis of test solution (UV–visible spectrometry).** The possibility of complexation between the DTG and the Cu electrode in the corrosive test solution was investigated through UV–visible spectroscopic measurements. A DTG concentration of $20 \times 10^{-6}$ M was employed (Fig. 9). Measurements were performed on
Cu samples before and after 48 h of immersion at 30 °C in a 0.5 M HCl solution containing the DTG. An absorption band for the electrolyte (0.5 M HCl solution) is observed, while the band occurs at 233 nm in the absorption spectrum obtained for the DTG inhibitor may be associated with π–π* and n–π* transitions. An absorption band at 242 nm and a new band at 295 nm occur in the spectrum obtained for DTG in 0.5 M HCl solution. This suggests that the DTG structure is modified from uncharged to protonated form in the solution. However, a band at 801 nm is observed in the absorption spectrum of the solution resulting from Cu immersion in the 0.5 M HCl DTG containing solution. This result confirms that ligand complex is formed between DTG and Cu ions released during the corrosion reaction in the acidic solution. Moreover, the ΔGads value is − 44.2 kJ mol⁻¹. This confirms the chemical interaction of Cu ion dissolution with DTG in an acidic solution.

Cu surface analysis (SEM and AFM). Figure 10 shows SEM and AFM images obtained for abraded Cu samples and after immersion in test solutions for 48 h at 30 °C. The SEM shows that the Cu surface is smooth (Fig. 10a) before immersion in the test solution. In the absence of DTG, the surface is corroded in the solution (Fig. 10b) and becomes rough and porous. However, the addition of DTG (Fig. 10c) reduces the damage generated on the surface, confirming the inhibitory action. The AFM images reveal an average roughness value (Ra) of 32.379 nm (measurement surface: 2.5 × 2.5 µm²) for the free Cu sample (Fig. 10d). However, the Ra of the measurement surface increases to 80.231 nm after the sample is immersed in 0.5 M HCl solution (Fig. 10e). This is attributed to the attack on the MS by the acidic solution. In the presence of DTG, the Ra of the surface decreases to 41.780 nm (Fig. 10f). This indicates that the DTG could form a protective layer on the Cu surface, thereby delaying the attack of the corrosive medium on the MS.

QCCs. To investigate the role of the DTG molecular structure and electronic properties in the interaction between DTG and MS, QCCs were performed using the DFT method. The presence of heteroatoms in DTG suggests a high tendency toward protonation in an acidic medium. Therefore, the influence of the molecular structure and electronic properties of the H⁺ form on the inhibition efficiency was investigated via the calculations. The optimized geometrical designs involving molecular orbitals (MO), highest occupied MO (HOMO), and lowest unoccupied MO (LUMO) energies are shown in Fig. 11 and the QCC results are shown in Table 4. Figure 11 shows that the HOMO location is distributed on the nitrogen atom (N3), and the LUMO location occurs on the benzene ring on the left side of the structure. This suggests that electrons are transferred and accepted from DTG. According to the frontier MO theory, the high energy value of E_HOMO (more negative) indicates the tendency of the molecule to donate e⁻ to acceptor molecules with an empty and low-energy orbital. Hence, the low energy value of E_LUMO (less negative) reveals the electron-acceptance tendency of the molecule (Table 4).

Figure 10. SEM (top row) and AFM images (bottom row) of the (a), (d) free Cu surface; surface in (b), (e) 0.5 M HCl and (c), (f) 0.5 M HCl with DTG.
The energy gap (ΔE_{LUMO−HOMO}) is an essential parameter associated with the DTG reactivity toward the MS. In the present study, the low value of (ΔE_{LUMO−HOMO}) reflects the high inhibition efficiency of DTG, which improves molecule reactivity, thereby facilitating the adsorption of DTG on the MS\textsuperscript{51}. The E_{HOMO} and E_{LUMO} of the DTG are associated with the ionization potential (I_pot) and electron affinity (E_{aff}), respectively\textsuperscript{52}:

\[ I_{pot.} = -E_{HOMO}, \]
\[ E_{aff.} = -E_{LUMO}. \]

The absolute electronegativity (\chi_{inh}) and global hardness (\eta_{inh}) of the DTG are obtained from I_p and E_a as follows:

![HOMO distribution](image1)

![LUMO distribution](image2)

**Figure 11.** The optimized geometrical structure, HOMO and LUMO distributions of DTG.

| E_{HOMO}/eV | E_{LUMO}/eV | ΔE/eV | I_{pot}/eV | E_{aff}/eV | \chi_{inh}/eV | \eta_{inh}/eV | ΔN |
|-------------|-------------|-------|-----------|-----------|---------------|---------------|----|
| -7.545      | -3.126      | 4.419 | 7.545     | 3.126     | 5.335         | 2.209         | -0.155 |

**Table 4.** QCC parameters for DTG.
The interaction between DTG and MSs occurs when electrons flow from the DTG with lower $\chi_{inh}$ to the metal with higher $\chi_{inh}$ until the chemical potential becomes equal. The fraction of electrons transferred ($\Delta N$) from the DTG to the MS is given as follows:

$$\Delta N = \frac{(\varphi_{Cu} - \chi_{inh})}{2(\eta_{Cu} + \eta_{inh})},$$  

where $\varphi$ is the work function of the Cu surface (4.65 eV)$^{52}$, while the absolute hardness of Cu ($\eta_{Cu}$) was estimated as zero when $I_{pot} = E_{aff}$ for bulk metallic atoms.

The $\Delta N$ will occur from the DTG to the MS if $\Delta N > 0$ and vice versa$^{52}$. Table 4 shows that the value of $\Delta N$ is negative, indicating that DTG accepts the electrons from the Cu surface. This result supports the experimentally determined protection efficiency.

The Mulliken atomic charges of the DTG in the $H^+$ form are listed in Table 5. As indicated in the table, the (1N, 3N, 4N, 5C, 8C, 9C, 10C, 12C, 14C, 15C, 16C, and 18C) heteroatoms have negative charges. This indicated that the DTG could be adsorbed onto the Cu surface by donating electrons from these atoms to the unoccupied d-orbitals of the Cu metal. The other atoms (2C, 6C, 7C, 11C, and 17C) have positive charges and can accept electrons from the 3d orbital of the Cu atoms. Therefore, an interaction occurs between DTG and MSs, thereby reducing the corrosion rate.

The adsorption of the DTG on the MS occurs via the donor–acceptor (DA) interaction. The Fukui Index (FI) analyses help to identify the active sites of the molecule responsible for electrophilic (Eu) or nucleophilic (Nu) agents. The presence of the Nu or Eu center facilitates the DTG–MTS interaction. FIs for Nu and Eu attacks, which are determined through natural population analysis (NPA), are given as follows$^{53}$:

$$\int_{k}^{+} = q_k(N + 1) - q_k(N) \text{For Nu attack,}$$  

$$\int_{k}^{-} = q_k(N) - q_k(N - 1) \text{For Eu attack,}$$

where, $q_k(N)$, $q_k(N - 1)$, and $q_k(N + 1)$ are the charge values of atom k in the neutral, cation, and anion states, respectively.

FIs for the charged species $q_k(N)$, $q_k(N - 1)$, and $q_k(N + 1)$ DTG are listed in Table 5. The high values of $\int_{k}^{+}$ and $\int_{k}^{-}$ indices are related to Nu and Eu attacks, respectively. As indicated in Table 5, NC and C atoms of the DTG are the most susceptible active sites for electron acceptance or donation. Most atoms are available, and

| Atom | Mulliken atomic charges | FIs |
|------|------------------------|-----|
| 1N   | -4.4546                | 0.098 0.021 |
| 2C   | 3.5658                 | 0.094 0.087 |
| 3N   | -6.1454                | 0.097 0.011 |
| 4N   | -4.4125                | 0.097 0.044 |
| 5C   | -3.7244                | 0.074 0.016 |
| 6C   | 4.3232                 | 0.098 0.084 |
| 7C   | 0.3075                 | 0.096 0.084 |
| 8C   | -3.1541                | 0.076 0.025 |
| 9C   | -3.2323                | 0.074 0.021 |
| 10C  | -3.2116                | 0.074 0.023 |
| 11C  | 1.4456                 | 0.010 0.086 |
| 12C  | -3.2215                | 0.072 0.035 |
| 13C  | -0.6341                | 0.011 0.009 |
| 14C  | -3.5974                | 0.072 0.012 |
| 15C  | -3.1424                | 0.074 0.011 |
| 16C  | -3.5472                | 0.070 0.036 |
| 17C  | 3.6822                 | 0.094 0.011 |
| 18C  | -3.3589                | 0.071 0.036 |

Table 5. Calculated Mulliken atomic charges and FIs of DTG.
susceptible centers for electron acceptance from the Cu surface (Nu attack) are associated with the high values of $P_{\text{Nu}}$, occurring for 2C, 6C, 7C, 11C, and 17C atoms. These atoms are available and favorable centers for electron acceptance from the MS (Nu attack). The high values of $P_{\text{Nu}}$ are associated with the 1N, 3N, 4N, 5C, 9C, 10C, 12C, 14C, 15C, 16C, and 18C atoms. These atoms are available centers for electron donation to the MS for chemical bond formation (Eu attack). Therefore, the DTG acts as an electron DA, thereby facilitating its adsorption on the Cu surface. The data obtained from QCCs matches the experimental data.

**Corrosion inhibition mechanism.** The experimental and theoretical data showed that the adsorption mechanism is associated with the donor–acceptor interaction between the DTG and Cu surface. In generally the adsorption of organic compounds may be classified into two types of interactions: physical adsorption and chemical adsorption. The physical adsorption involves the existence of both the electrically charged surface of the metal and charged species in the corrosive medium. The metal's surface charge is created by the electric field that exists at the metal/solution interface. In contrast, a chemisorption process includes charge sharing or charge transfer from the inhibitor molecules to the metal surface to establish a coordinate type of bond. This is feasible if the surface has both a positive and a negative charge. The presence of a transition metal with unoccupied, low-energy electron orbitals (Cu$^+$ and Cu$^{2+}$ in our study) and an DTG inhibitor with molecules with relatively loosely bound electrons or heteroatoms with a lone pair of electrons is required for the inhibition effect$^{54}$. The DTG has N with a lone pair, and $n$-electrons enable chemical adsorption on the Cu atom with unoccupied sites. $\Pi$-antibonding orbitals of rings can accept the electrons from 4s or 3d of Cu atoms (retro-donation). On the other hand, Physical adsorption begins with Cl$^-$ ions interaction, followed by electrostatic interaction between the positively charged N atoms in protonated form of DTG and the negative charge on the Cl$^-$ ions adsorbed to the positively charged Cu surface in acid solution. This interaction leads to formation of a thin protective film that inhibits the Cu surface from interacting with corrosive species$^{55}$.

**Conclusions**

In this study, DTG is prepared and then characterized via different analytical and spectroscopic measurements. The main results of the study are summarized as follows:

1. DTG exhibited good inhibition efficiency for Cu and was used as a mixed inhibitor based on potentiodynamic polarization results.
2. DTG adsorptive interaction with the Cu surface retards dissolution of the surface in the corrosive solution.
3. The DFT calculations of DTG indicate a good correlation between theoretical and experimental approaches.

**Data availability**

All data generated or analysed during this study are included in this published article.

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M.M.A. did the preparation and characterization of the inhibitor. M.N.E.-H. did the electrochemical experiments, and theoretical calculations. All authors provided the concept, wrote and reviewed the manuscript.

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**Additional information**

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