Efficient Synthesis of 6,7-Dihydro-5H-cyclopenta[b]pyridine-3-carbonitrile Compounds and Their Applicability As Inhibitor Films for Steel Alloy Corrosion: Collective Computational and Practical Approaches

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ABSTRACT: An effective method for designing new heterocyclic compounds of 6,7-dihydro-5H-cyclopenta[b]pyridine-3-carbonitrile derivatives (CAPDs) was presented through cyclocondensation reaction between 2,5-diarylidenecyclopentanone derivatives and propanedinitrile, and the cyclocondensation reaction succeeded using a sodium alkoxide solution (sodium ethoxide or sodium methoxide) as the reagent and the catalyst. The synthesized CAPD derivatives were employed as novel inhibitors for carbon steel (CS) corrosion in a molar H$_2$SO$_4$ medium. The corrosion protection proficiency was investigated by electrochemical measurements (open circuit potential vs time ($E_{OCP}$ vs $t$), potentiodynamic polarization plots (PDP), and electrochemical impedance spectroscopy (EIS)) and surface morphology (scanning electron microscopy (SEM)) examinations. The results show that the CAPD derivatives exhibit mixed type inhibitors and a superior inhibition efficiency of 97.7% in the presence of 1.0 mM CAPD-1. The adsorption of CAPD derivatives on the CS interface follows the Langmuir isotherm model, including physisorption and chemisorption. Scanning electron microscopy (SEM) exploration confirmed the adsorption of the CAPD derivatives on the CS substrate. Monte Carlo (MC) simulations and DFT calculations revealed that the efficacy of the CAPD molecules correlates well with their structures, and this protection was attributed to their adsorption on the CS surface.

1. INTRODUCTION

Carbon steel (CS) is a widespread engineering and structural material in manufacturing applications$^{1,2}$ because of its outstanding mechanical property and low cost. However, CS is vulnerable to corrosion through industrial operations, for example, industrial cleaning, acid pickling, acidizing, etc.$^{3-5}$ The industrial cleaning performed by H$_2$SO$_4$ is utilized more often than HCl and HNO$_3$. It could be ascribed to its cheap price; it does not cause pitting corrosion and its stability at higher temperature. Moreover, the addition of an inhibitor is a successful method utilized in the protection of metal from corrosion in acidic environments during industrial processes. At present, the most applicable corrosion inhibitors utilized in acidic environments relate to organic compounds, which include some species having a heteroatoms (nitrogen, sulfur, and oxygen) or conjugated-bonds.$^{6-9}$ Its corrosion protection efficiency lies with the adsorption and surface-covering capabilities, which are associated with the electron density, the molecular structure of various efficient groups, the charge of the metal surface, the medium temperature, etc.$^{10,11}$ The heteroatoms and conjugated bonds might offer the electron lone pair and form a coordinate bond with vacant d-orbital on the metal interface (i.e., chemisorption).$^{12-14}$ Furthermore, the protective layer is formed by electrostatic attraction between the charged metal surface and the protonated inhibitor compound via physical adsorption.$^{15,16}$ The adsorption films can successfully retard the attack of corrosive medium.

Heterocyclic components containing nitrogen are seemingly the essential component in the structure of numerous novel designs and the synthesis of organic components and they naturally exist as alkaloid compounds, which are vital for use as medicinal drug compounds.$^{17}$ The pyridine moiety is more attractive because of its widespread chemical applications.$^{18,19}$ For example, 3-cyanopyridine derivatives have many uses, such as IKKb inhibitors and A2A adenosine receptor antagonists.$^{20}$ Recently, several protocols have been reported to produce 3-cyanopyridine derivatives. Even so, most of these method-
ologies are subject to restrictions of the highest temperatures, the time of the reaction is very high, and the yield is very low.\textsuperscript{,21} Nowadays, to find an environmentally friendly catalyst that works in normal conditions is still a significant challenge for producing 3-cyanopyridine derivatives. The heterocyclic molecules used as corrosion inhibitors are revealed to have the most efficient corrosion inhibition. These molecules contain heteroatoms like nitrogen, sulfur, oxygen, benzene rings, π-bonds, and various functional groups that give noteworthy coverage of the metal surface and permit corrosion inhibition.\textsuperscript{,22} Concerning eco-friendly safety concerns, numerous heterocyclic compounds that are considered to be natural/green, such as pharmaceutical molecules, biomolecules, and natural extracts, have been established as inhibitors for metal corrosion.\textsuperscript{,23}

In this work, the CAPD derivatives including 2-ethoxy-4-(pyridin-2-yl)-7-(pyridin-2-ylmethylidene)-6,7-dihydro-5H-cyclopenta[b]pyridine-3-carbonitrile (CAPD-1), 2-methoxy-4-(pyridin-2-yl)-7-(pyridin-2-ylmethylidene)-6,7-dihydro-5H-cyclopenta[b]pyridine-3-carbonitrile (CAPD-2), 2,4,6-tris(2-pyridinylmethylene)cyclopentanone (CAPD-3), and 7-(2-methoxybenzylidene)-4-(2-methoxyphenyl)-2-ethoxy-6,7-dihydro-5H-cyclopenta[b]pyridine-3-carbonitrile (CAPD-4) were synthesized and employed as efficient corrosion inhibitors for CS in a molar H\textsubscript{2}SO\textsubscript{4} medium. The electrochemical investigations (\textit{E}_{OCP} vs \textit{t}, PDP, and EIS) were utilized to study the corrosion protection performance. SEM was executed to explore the microstructure and the steel surface. The electrochemical calculations and MC simulations demonstrated that the efficiency of the CAPD molecules relate to their structures, and this protection was ascribed to their adsorption on the CS surface.

2. EXPERIMENTAL DETAILS

2.1. Materials and Apparatus. All commercially obtainable reagents were obtained from Aldrich, Merck, and Fluka and were utilized without further refinement. All chemical reactions were observed by thin-layer chromatography (TLC) using precoated plates of G/UV-254 silica-gel (Merck 60F254) of 0.250 mm thickness with UV light (254.0 nm/365.0 nm) for visualization. Melting points were determined with a melting point device (Kofler). FTIR were measured with a Pt-ATR spectrometer (FT-IR-ALPHABROKER) by the attenuated total reflection (ATR) technique. \textsuperscript{1}H and \textsuperscript{13}C NMR spectra for all the prepared molecules were measured in \textit{d}_\textsubscript{6}-DMSO on a Bruker AG spectrometer Bio Spin at 400.0 and 100.0 MHz, respectively. Elemental investigations were attained on a CHN-analyzer (PerkinElmer).

2.2. General Process for Preparation of Compounds CAPD-1–CAPD-4. A mixture of 2,5-dibenzylidenedecyclopentanone derivatives (0.02 mol) (2,5-bis(2-pyridinylmethylene)cycclopentanone (0.02 mol, 5.24 g), 2,5-bis(2-pyridinylmethyl)cycclopentanone (0.02 mol, 5.24 g), 2,5-bis(2-methoxybenzylidene)cyclopentanone (0.02 mol, 6.40 g), sodium alkoxide (0.02 mol) (sodium ethoxide 1.36 g or sodium methoxide 1.08 g), and propanedinitrile (0.02 mol, 1.32 g) (in the case that uses sodium ethoxide, the solvent of the reaction is ethanol; in the case using sodium methoxide, the solvent of the reaction is methanol) were refluxed for 1 h at 80 °C. The reaction mixture was allowed to cool at room temperature and diluted with 150 mL of dist. H\textsubscript{2}O. The crude product was then filtered off and washed three times with dist. H\textsubscript{2}O, and the solvent of crystallization was ethanol to produce a high purity product of cyclopentapyridine derivatives.

2.3. Characterization Data of CAPD-1–CAPD-4. 2-Ethoxy-4-(pyridin-2-yl)-7-(pyridin-2-ylmethylidene)-6,7-dihydro-5H-cyclopenta[b]pyridine-3-carbonitrile (CAPD-1). Yield 77%; gray crystal; melting point: 149–151 °C. IR (ATR) \textit{\nu}_{\text{max}} 3067, 3032 (C=H arom.), 2977, 2935 (C–H aliph.), 2204 (C=O), 1599 (C=N) cm\textsuperscript{-1}. \textsuperscript{1}H NMR (400 MHz, DMSO-\textit{d}_6) \textit{\delta} 1.43 (t, \textit{J} = 7.0 Hz, 3H, \textit{CH}_3–\textit{CH}_2), 2.87 (t, \textit{J} = 5.8 Hz, 2H, \textit{CH}_2–\textit{CH}_2\textit{Cycld}), 3.09 (t, \textit{J} = 4.1 Hz, 2H, \textit{CH}_2–\textit{CH}_2\textit{Cycld}), 4.61 (q, \textit{J} = 7.0 Hz, 2H, \textit{CH}_2–\textit{CH}_2\textit{Cycld}), 7.31–7.59 (m, 9H, (8CH\textsubscript{arom.} + CH=)). \textsuperscript{13}C NMR (DMSO-\textit{d}_6 100 MHz) \textit{\delta} 14.8, 27.2, 28.9, 63.4, 93.7, 116.0, 125.8, 128.7, 129.2, 129.4, 129.6, 130.0, 131.0, 135.2, 136.9, 141.3, 153.0, 161.9, 164.9. Anal. Calc. for C\textsubscript{22}H\textsubscript{18}N\textsubscript{2}O (354.40): C, 74.56; H, 5.12; N, 15.81. Found: C, 74.42; H, 5.01; N, 15.67 (Figure S1).

2-Methoxy-4-(pyridin-2-yl)-7-(pyridin-2-ylmethylidene)-6,7-dihydro-5H-cyclopenta[b]pyridine-3-carbonitrile (CAPD-2). Yield 75%; white crystal; m.p.: 171–173 °C. IR (ATR) \textit{\nu}_{\text{max}} 3058, 3021 (C=H arom.), 2994, 2951 (C–H aliph.), 2219 (C=O), 1602 (C=N) cm\textsuperscript{-1}. \textsuperscript{1}H NMR (400 MHz, DMSO-\textit{d}_6) \textit{\delta} 2.89 (t, \textit{J} = 6.0 Hz, 2H, \textit{CH}_2–\textit{CH}_2\textit{Cycld}), 3.10 (t, \textit{J} = 6.0 Hz, 2H, \textit{CH}_2–\textit{CH}_2\textit{Cycld}), 4.13 (s, 3H, OMe), 7.43–7.60 (m, 9H, (8CH\textsubscript{arom.} + CH=)). \textsuperscript{13}C NMR (DMSO-\textit{d}_6 100 MHz) \textit{\delta} 27.3, 28.9, 54.8, 93.7, 116.0, 125.9, 128.3, 128.7, 129.2, 129.6, 130.0, 131.0, 135.2, 136.9, 141.3, 153.0, 161.9, 165.3. Anal. Calc. for C\textsubscript{23}H\textsubscript{20}N\textsubscript{2}O (340.40): C, 74.10; H, 4.74; N, 16.46. Found: C, 73.97; H, 4.61; N, 16.39 (Figure S2).

2-Methoxy-4-(pyridin-4-yl)-7-(pyridin-4-ylmethylidene)-6,7-dihydro-5H-cyclopenta[b]pyridine-3-carbonitrile (CAPD-3). Yield 82%; white crystal; m.p.: 180 °C. IR (ATR) \textit{\nu}_{\text{max}} 3067, 3032 (C=H arom.), 2977, 2935 (C–H aliph.), 2111 (C=O), 1620 (C=N) cm\textsuperscript{-1}. \textsuperscript{1}H NMR (400 MHz, DMSO-\textit{d}_6) \textit{\delta} 2.92 (m, 4H, \textit{CH}_2–\textit{CH}_2\textit{Cycld}), 3.09 (t, \textit{J} = 4.1 Hz, 2H, \textit{CH}_2–\textit{CH}_2\textit{Cycld}), 3.71–3.86 (m, 4H, \textit{CH}_2–\textit{CH}_2\textit{Cycld}), 4.02 (s, 3H, OMe), 7.43–7.59 (m, 9H, (8CH\textsubscript{arom.} + CH=)). \textsuperscript{13}C NMR (DMSO-\textit{d}_6 100 MHz) \textit{\delta} 14.8, 27.1, 28.9, 54.9, 93.8, 115.9, 116.0, 124.6, 128.2, 129.2, 129.4, 130.8, 131.3, 132.8, 133.8, 135.0, 135.7, 142.0, 142.1,
7-(2-Methoxybenzylidene)-4-(2-methoxyphenyl)-2-ethoxy-6,7-dihydro-5H-cyclopenta[b]pyridine-3-carbonitrile (CAPD-4). Yield 75%; yellow crystal; m.p.: 160–161 °C. IR (ATR) νmax 3058, 3021 (C−H arom.), 2981, 2966 (C−H aliph.), 2214 (C≡N), 1605 (C=O) cm−1. 1H NMR (400 MHz, DMSO-d6) δ 1.43 (t, J = 6.9 Hz, 3H, CH3-CH2-O), 2.89 (t, J = 5.9 Hz, 2H, CH2-CH2-cyc.), 3.07 (t, J = 4.7 Hz, 2H, CH2-CH2-cyc.), 3.81, 3.85 (s, 6H, 2OMe), 4.59 (q, J = 6.8 Hz, 2H, O-CH2-CH3), 7.00−7.02 (d, 2H, 2CHarom), 7.02−7.12 (d, 2H, 2CHarom), 7.43 (s, 1H, CH=), 7.49−7.51 (d, 2H, 2CHarom), 7.53−7.55 (d, 2H, 2CHarom). 13C NMR (100 MHz, DMSO-d6) δ 14.8, 27.3, 28.8, 55.7, 55.8, 63.2, 93.0, 114.7, 114.8, 116.4, 125.5, 127.3, 129.7, 130.5, 130.6, 131.2, 138.9, 152.5, 159.5, 160.7, 162.2, 165.1. Anal. Calcd for C26H22N2O2 (412.48): C, 75.71; H, 5.86; N, 6.79. Found: C, 75.77; H, 5.79; N, 6.70 (Figure S4).

2.5. Corrosion Protection Experiments. The corrosion experiments were accomplished by a Gamry galvanostat/ potentiostat/ZRA electrochemical-workstation (Reference 600+) at a temperature range of 25–55 °C in 1.0 M H2SO4 as an aggressive solution. A Pt-sheet and silver/silver chloride electrodes, respectively. The working electrode is a CS alloy immersed in the acidic solution, within the potential series. The EIS plots were fitted by Gamry Framework software EIS300 with an appropriate equivalent circuit. Each corrosion experiment was reiterated three times to validate the results’ reproducibility.

2.6. Corrosion Protection Capacity (PC) Calculation. PC (%) was computed from the potentodynamic polarization method by the following equation:

$$PC = 100 \left(1 - \frac{j_{corr}^1}{j_{corr}^2}\right)$$

where $j_{corr}^1$ and $j_{corr}^2$ are corrosion current densities ($j_{corr}$) in the blank and occurrence of different inhibitor concentrations, respectively. $PC_E$ was also calculated from the impedance experiments by the following equation:

$$PC_E = 100 \left(1 - \frac{R_p^0}{R_p^1}\right)$$

where $R_p^0$ and $R_p^1$ are the polarization resistances ($R_p$) in the absence and existence of diverse additive concentrations, respectively. The part of surface covered (θ) is correlated to the PC as:

$$\theta = \frac{PC}{100}$$

2.7. Surface Analysis before and after Corrosion Inspection. The surface morphology of the uninhibited and inhibited systems after 48 h immersed in molar sulfuric acid medium at 298 K was inspected by a SEM apparatus (JSM-LV model) at 20 kV as the accelerating voltage.

2.8. Computational Details. The energy minimization of the protonated form of the investigated cycloalkanapyridine derivative (CAPD) molecules in aqueous media was researched employing DFT calculations with the B3LYP-functional and DNP 4.4 basis set executed in Materials Studio V. 7.0 program in the Dmol3 module. The results obtained from DFT calculation including the highest occupied molecular orbital ($E_{HOMO}$), the lowest unoccupied molecular orbital ($E_{LUMO}$), the hardness ($\eta$), the energy gap ($\Delta E$), the electronegativity ($\chi$), the global softness ($\sigma$), the vertical ionization potential (IP), the electron affinity (EA), the number of electrons transferred ($\Delta N$), the protonated form of the investigated cycloalkanapyridine molecules on the iron (110) surface were revealed by operating the locator module. First, the

PC$_{cor}$ = 100 $\left(1 - \frac{j_{corr}^1}{j_{corr}^2}\right)$

where $j_{corr}^1$ and $j_{corr}^2$ are corrosion current densities ($j_{corr}$) in the blank and occurrence of different inhibitor concentrations, respectively. $PC_E$ was also calculated from the impedance experiments by the following equation:

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$IP = -E_{HOMO}$

$EA = -E_{LUMO}$

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

$\eta = \frac{1}{\sigma} = \frac{E_{LUMO} - E_{HOMO}}{2}$

$\omega = \frac{\chi^2}{2\eta}$

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

$\Delta E_{back-donation} = \frac{-\eta}{4}$

where, $\phi$ denotes Fe (110) function work, $\chi_{inh}$ signifies the inhibitor electronegativity, $\eta_{inh}$ and $\eta_{Fe}$ are the chemical hardness of inhibitor and Fe (0 eV), respectively.

For MC simulations, the proper adsorption arrangements of the protonated form of the CAPD molecules on the iron (110) interface were revealed by operating the locator module adsorption in the Materials Studio V. 7.0 program. First, the
adsorbate species had been optimized running the COMPASS force field.\(^\text{31}\) Afterward, in a simulation box \((37.24 \text{ Å} \times 37.24 \text{ Å} \times 59.81 \text{ Å})\), adsorption of the examined inhibitors, \(\text{SO}_4^{2-}\) ions, \(\text{H}_2\text{O}\) molecules, and hydronium ions with the \(\text{Fe(110)}\) surface was achieved.\(^\text{32}\)

3. RESULTS AND DISCUSSION

3.1. Synthesis. In this work, we are introducing a novel method for synthesizing some new components of highly functionalized 2-alkoxy-4-(aryl)-7-(aryl-2-ylmethylidene)-6,7-dihydro-5H-cyclopenta[b]pyridine-3-carbonitrile derivatives (CAPD-1–CAPD-4) through the facile method via cyclocondensation reaction between 2,5-diarylidenecyclopentanone and propanedinitrile. The cyclocondensation reaction successfully employed sodium alkoxide solution as the reagent and the catalyst (Scheme 1).

![Scheme 1. Design of 2-Alk oxy-4-(aryl)-7-(aryl-2-ylmethylidene)-6,7-dihydro-5H-cyclopenta[b]pyridine-3-carbonitriles (CAPD-1–CAPD-4)](https://example.com/scheme1.png)

This methodology compromises a flexible method in tuning the molecular complexity and diversity. The reflux time to proceed to completion was \(-2\) h and highly pure compounds were acquired in outstanding yields, without employing any chromatographic technique, just simply filtration and recrystallization. The proposed mechanism for the preparation of 2-alkoxy-4-(aryl)-7-(aryl-2-ylmethylidene)-6,7-dihydro-5H-cyclopenta[b]pyridine-3-carbonitriles (CAPD-1–CAPD-4) were undertaken preparation of diarylidene cycloaldenone derivatives 3 by Knoevenagel condensation between cyclopentanone 2 and aromatic aldehydes 1 (2 mol) (Scheme 2). The reaction progressed via Michael addition of propanedinitrile to form \(\alpha, \beta\)-unsaturated cycloketones to produce adduct A, which undergoes a nucleophilic attack through alkoxide anion \(\text{RO}^-\), giving intermediate B. In this moment, intermediate B easily undergoes cyclization and dehydration to produce the wanted compounds, which was postulated previously.\(^\text{37}\)

The structures of the designed compounds CAPD-1–CAPD-4 were approved on the basis of their IR spectrum, NMR spectrum, and elemental analysis. For example, the IR spectrum of 2-ethoxy-4-(pyridin-2-yl)-7-(pyridin-2-ylmethylidene)-6,7-dihydro-5H-cyclopenta[b]pyridine-3-carbonitrile (CAPD-1) exhibited an absorption band at 2204 cm\(^{-1}\) due to the \(\text{C}==\text{N}\) group. Its \(^1\text{H}\) NMR spectrum exhibited the occurrence of triplet signals at 1.43 ppm, which represents the methyl of OEt and two triplet signals at \(d\) 2.87 and 3.09 ppm discriminatory of cyclic \(\text{CH}_2\text{−CH}_2\). It also displayed a quartet signal at 4.61 ppm for OEt group and multiplet signals at 7.31–7.59 ppm, indicating aromatic protons and a \(\text{CH}==\text{N}\) vinyl group. The \(^13\text{C}\) NMR spectrum of 2-ethoxy-4-(pyridin-2-yl)-7-(pyridin-2-ylmethylidene)-6,7-dihydro-5H-cyclopenta[b]pyridine-3-carbonitrile (CAPD-1) displayed 15 signals at 116.00, 125.77, 128.31, 128.74, 129.19, 129.43, 129.64, 129.97, 131.04, 135.18, 136.87, 141.41, 152.97, 161.91, and 164.93, which are characteristic the carbons of aromatic and \(\text{CH}==\text{N}\) vinylic groups; 93.73, which indicates a \(\text{C}==\text{N}\) group; 63.38, which belongs to the methylene (\(\text{CH}_2\)) group of the ethoxy group; and two \(\text{CH}_2\) cyclic groups are shown at 27.22 and 28.90 ppm, with the final the methyl of the ethoxy group appearing at 14.79 ppm.

3.2. Corrosion Mitigation Performance by the Cycloalkanapyridine Derivatives. 3.2.1. E\(_{\text{ocp}}\) vs Time Examinations. The variation in \(E_{\text{ocp}}\) vs time plots for CS alloy in molar sulfuric medium without and with diverse concentrations of CAPD-1 (A) and with \(1 \times 10^{-3}\) M of different cycloalkanapyridine derivatives at 25 °C is presented in Figure 1. As previously stated, this was completed to confirm that the investigated corrosion inhibitor systems reach quasi-equilibrium prior EIS experiments.\(^\text{33}\) From the data in Figure 1, it is observable that the 2000 s to 35 min of \(E_{\text{ocp}}\) was definite and adequate quasi-equilibrium was attained for entire corrosion systems. Moreover, the data expose that the \(E_{\text{ocp}}\) in the presence of cycloalkanapyridine inhibitors was honorable at the beginning of the experiments compared to that of the blank medium, whereas for the blank \(\text{H}_2\text{SO}_4\) medium, the \(E_{\text{ocp}}\) increased over time up to 2000 s, and then the \(E_{\text{ocp}}\) for the solution containing inhibitors was still constant from 2000 to 3000 s. This is reveals of the impact of cycloalkanapyridine derivative adsorption on the steel alloy deterioration route.\(^\text{34}\) Furthermore, Figure 1 shows that the modification in the \(E_{\text{ocp}}\) values of the acid solution containing additives compared to the blank medium (free inhibitor) is smaller than 0.085 V vs OCP, indicating that the studied cycloalkanapyridine derivatives classifying as inhibitors of anodic/cathodic-type (mixed-type inhibitors).\(^\text{35}\) For example, at 3000 s, the value of \(E_{\text{ocp}}\) for the uninhibited system is \(-0.432\) V, and in the presence of 1.0 mM of CAPD-1, CAPD-2, CAPD-3, and CAPD-4, the values are \(-0.427, -0.425, 0.426, \) and \(-0.431\) V, respectively; the largest change is 0.007 V. According to these findings, cycloalkanapyridine derivatives are categorized as mixed-kind inhibitors and impede steel alloy deterioration in \(\text{H}_2\text{SO}_4\) by reducing both the cathodic and anodic reactions.\(^\text{36}\)

3.2.2. PDP Studies. PDP measurements were attained for the CS alloy in 1.0 M sulfuric acid without and with diverse concentrations of CAPD-1 (A) and with different cycloalkanapyridine derivatives at 25 °C and \(1 \times 10^{-3}\) M are depicted in Figure 2A, B. Comparable plots were acquired for...
the other additive compounds (CAPD-2, CAPD-3, and CAPD-4). For entirely the four cycloalkanapyridine derivatives experienced as corrosion protection additives, the cathodic and anodic branches shifted to smaller current density area in the occurrence of the inhibitors related to the uninhibited system. This indicates that the tested inhibitors diminish the $j_{\text{cor}}$ and consequently decrease the rate of corrosion. The Tafel diagrams correspondingly display some changes in the corrosion potential ($E_{\text{cor}}$) to more cathodic or anodic areas relative to the uninhibited solution. The shift direction is not unvarying, as it differs with additive dose. This proposes that the cycloalkanapyridine derivatives mutually influenced the cathodic and anodic deterioration reactions.

The corrosion restrictions for the corrosion process in the blank and inhibited medium containing various inhibitor doses were attained from the PDP diagrams via Tafel extrapolations to the $E_{\text{cor}}$. The acquired findings are recorded in Table 1. The detected modification in $E_{\text{cor}}$ of the inhibited solution compared to the free-inhibitor containing system is usually less than 0.085 V for the four tested cycloalkanapyridine derivatives. This indicates that the tested cycloalkanapyridine derivatives may be categorized as mixed-kind inhibitors.37 Moreover, the modification in the $E_{\text{cor}}$ appears to be insignificant, with a maximum change of approximately ±0.023 V (Table 1). This phenomenon proposes that the insertion of the inspected compounds to the corrosive solution only weakly disturbs (or does not disturb) the CS alloy interface.38 Such a minor modification in the $E_{\text{cor}}$ has also been ascribed to the geometric hindering of the efficient locations on the metal interface by the additive species.39

The Tafel slope values (anodic $\beta_a$ and cathodic $\beta_c$) differ marginally with the additive dose, but are deprived of a modest certain design. Nevertheless, the anodic $\beta_a$ and cathodic $\beta_c$ values in the case of inhibitor containing solutions are usually greater than those of the uninhibited system. The difference in the anodic $\beta_a$ and cathodic $\beta_c$ values with alteration in the inhibitor dose likewise appears to be more obvious for anodic $\beta_a$ than cathodic $\beta_c$. These interpretations indicate the construction of CAPD−iron complexes in the higher and lower oxidation states on the CS alloy interface.40 This is indicative of more protective performances of the cycloalkanapyridine derivatives on the anodic site than the cathodic one.

The $j_{\text{cor}}$ declines with an increase in [inhibitor dose], resulting in an increase in protection capability ($PC_T$). The $PC_T$ of CAPD-1, CAPD-2, CAPD-3, and CAPD-4 increases from 46.9, 43.6, 42.5, and 40.4% at 0.04 mM up to 97.7, 94.4, 91.9, and 90.5% at 1.0 mM, respectively. The $PC_T$ of CAPD compounds increases incessantly as the inhibitor dose increases from 0.04 to 1.0 mM. The protection capacities $PC_T$ follow the order CAPD-1 > CAPD-2 > CAPD-3 > CAPD-4. The increase in $PC_T$ with amassed inhibitor dose

![Figure 1. $E_{\text{cor}}$ vs time plots for CS alloy in molar sulfuric acid solution (A) without and with diverse concentrations of CAPD-1 and (B) with $1 \times 10^{-3}$ M of different cycloalkanapyridine derivatives at 25 °C.](https://doi.org/10.1021/acsomega.2c02639)

![Figure 2. PDP plots for CS alloy in molar sulfuric solution (A) without and with diverse concentrations of CAPD-1 and (B) with $1 \times 10^{-3}$ M of different cycloalkanapyridine derivatives at 25 °C.](https://doi.org/10.1021/acsomega.2c02639)
Table 1. Polarization Parameters for CS Alloy in Molar Sulfuric Acid Solution without and with Diverse Concentrations of Cycloalkanapyridine Derivatives at 25 °C

| inhibitor code | Cₜ (mol L⁻¹) | ʃₑ (μA cm⁻²) | −Eₑ/N (Ag/AgCl) | ʃₛ (mV dec⁻¹) | ʃₚ (mV dec⁻¹) | 0 | PCₜ (%) |
|---------------|--------------|--------------|-----------------|----------------|----------------|---|---------|
| blank         | 0.0          | 367.8        | 0.447           | 93.9           | 226.7          |   |         |
| CAPD-1        | 4.0 × 10⁻³   | 195.3        | 0.429           | 103.1          | 232.4          | 0.469 | 46.9 |
|               | 8.0 × 10⁻³   | 141.2        | 0.426           | 103.5          | 233.4          | 0.616 | 61.6 |
|               | 2.0 × 10⁻⁴   | 79.8         | 0.438           | 105.8          | 230.8          | 0.783 | 78.3 |
|               | 6.0 × 10⁻⁴   | 26.5         | 0.439           | 99.8           | 229.6          | 0.928 | 92.8 |
|               | 1.0 × 10⁻³   | 8.4          | 0.442           | 96.8           | 230.1          | 0.977 | 97.7 |
| CAPD-2        | 4.0 × 10⁻³   | 207.4        | 0.430           | 105.7          | 236.6          | 0.436 | 43.6 |
|               | 8.0 × 10⁻³   | 148.6        | 0.435           | 101.2          | 237.7          | 0.596 | 59.6 |
|               | 2.0 × 10⁻⁴   | 86.4         | 0.415           | 105.6          | 232.5          | 0.765 | 76.5 |
|               | 6.0 × 10⁻⁴   | 39.3         | 0.425           | 109.9          | 242.8          | 0.893 | 89.3 |
|               | 1.0 × 10⁻³   | 20.6         | 0.418           | 109.5          | 234.3          | 0.944 | 94.4 |
| CAPD-3        | 4.0 × 10⁻³   | 211.5        | 0.451           | 108.8          | 229.6          | 0.425 | 42.5 |
|               | 8.0 × 10⁻³   | 155.5        | 0.446           | 102.6          | 234.9          | 0.577 | 57.7 |
|               | 2.0 × 10⁻⁴   | 89.1         | 0.428           | 99.4           | 234.3          | 0.758 | 75.8 |
|               | 6.0 × 10⁻⁴   | 45.6         | 0.437           | 106.8          | 229.6          | 0.876 | 87.6 |
|               | 1.0 × 10⁻³   | 29.8         | 0.442           | 115.8          | 228.9          | 0.919 | 91.9 |
| CAPD-4        | 4.0 × 10⁻³   | 219.2        | 0.433           | 103.7          | 229.8          | 0.404 | 40.4 |
|               | 8.0 × 10⁻³   | 158.5        | 0.421           | 104.1          | 232.5          | 0.569 | 56.9 |
|               | 2.0 × 10⁻⁴   | 95.9         | 0.429           | 106.6          | 234.9          | 0.739 | 73.9 |
|               | 6.0 × 10⁻⁴   | 57.3         | 0.449           | 98.2           | 230.7          | 0.844 | 84.4 |
|               | 1.0 × 10⁻³   | 34.9         | 0.438           | 113.1          | 233.4          | 0.905 | 90.5 |

might be ascribed to the increase in the adsorbed species number of the additive on the metal substrate. The molecule numbers that adsorb on the efficient places on the CS alloy rise with cumulative [inhibitor dose], resulting in an improvement in the part of the covered surface coverage, and accordingly, an increase in PCₜ.

3.2.3. EIS Studies. Intensely, the impedance method has been confirmed to be an efficient approach for evaluating the inhibitor performance. This is due to the additive layer on a steel interface changing the EIS responses of the metal. To determine the influence of cycloalkanapyridine derivatives on the deterioration performance of the CS alloy in molar H₂SO₄ solution at 298 K, we completed EIS experimentalism. Nyquist and Bode and Bode phase modules for the CS alloy in molar H₂SO₄ solution with and without diverse concentrations of CAPD-1 and with a 1.0 × 10⁻³ M (optimum dose) concentration of different cycloalkanapyridine derivatives at 25 °C are presented in Figures 3 and 4. Overall, to small at middle frequencies, only a capacitive loop is detected for every dose, indicative of a charge-organized deterioration process. Nevertheless, by comparing the Nyquist graphs at 1 × 10⁻³ M and 6.0 × 10⁻⁴ M (higher doses) inhibited systems to others (Figure 3A), it is observed that the Nyquist diagrams did not dismiss at the Zₘ axis and designates a “degradation” process of EIS because of a slowdown in the process of charge transfer produced by the developing of the protecting layer on the steel interface. Solomon et al. stated a comparable observation for a 5.0 g of chitosan + 5.0 mM potassium iodide mixture that was used as inhibitor for St37-steel in a 15% H₂SO₄ solution. Zheng et al. described a comparable behavior for steel in a H₂SO₄ medium comprising 1-butyl-3-methyl-I H-benzenimidazolium iodide inhibitor.

To comprehend the physical procedures happening at the CS alloy/solution interface, the impedance findings of the uninhibited and inhibited systems were demonstrated by the equivalent circuit (EEC) presented in Figure 5C, whose collection was acquainted by the impedance singleness (Figure 5A, B). Correspondingly, the EEC in Figure 5D was utilized to model the impedance results attained for the inhibited system and its assortment was well-versed by the deterioration phenomenon in Figure 5B. The fittingness of the designated EECs is exemplified in the illustrative fitted diagrams given in Figure 5C, D. The lesser values of x² (Table 2) show that the designated EECs were appropriate. The EECs consist of electrolyte resistance (Rₑ), polarization resistance (Rₛ), and a CPE (constant phase element). In addition, the EEC in Figure 5d comprises the element film resistance (Rₚ) in the circumstance of an inhibited system; CPE is utilized rather than a perfect capacitor attributable to the steel surface inhomogeneity as revealed by the semicircle insufficiency in Figure 5A. The frequency reliant on the EIS response of the whole EECs in Figure 5C, D could be designated by simple circuit exploration assumed in eqs 1 and 2, respectively. This permits the popularization of the Rₛ by eq 3 as follows:

$$
\left| Z \right| = \left( \frac{1}{Z_{φ}} - \frac{1}{Z_{α}} \right)^{-1} + Z_{Rₛ}
$$

(11)

$$
\left| Z \right| = \left( \frac{1}{Z_{φ}} + \frac{1}{Z_{θ}} + \frac{1}{Z_{CPE}} \right)^{-1} + Z_{Rₛ}
$$

(12)

$$
\left( \frac{1}{Rₚ} \right) = \left( \frac{1}{R_{f}} \right) + \left( \frac{1}{R_{c}} \right)
$$

(13)

The CPE impedance defined by the formula in eq 4

$$
Z_{CPE} = \frac{1}{Y₀} \left( ω₀ \right)^{n}
$$

(14)

where \( j \), Y₀, and \( ω₀ \) are an imaginary number, the CPE constant, and the angular frequency, respectively. \( n \) denotes the CPE exponent most frequently utilized as a heterogeneity indicator. The \( n \) values are recorded in Table 2.
It was observed in Figures 3 and 4 that the impedance diameter and the Bode and phase angle modules increase in the occurrence of cycloalkanapyridine derivatives. An additional increase is also detected with cumulative inhibitor dose. This confirms the corrosion mitigation by the prepared cycloalkanapyridine derivatives inhibitors. The results in Table 2 reveals that the detected augmentation in Figure 3 in the occurrence of cycloalkanapyridine derivatives and with incremental inhibitor doses is due to an improvement of the polarization resistance of the metal, probably attributable to the additive adsorption on the electrode substrate. For example, in the blank H$_2$SO$_4$ solution, the $R_p$ of the CS alloy is 27.21 Ω cm$^2$ but improved to 50.32, 45.74, 42.96, and 39.76 Ω cm$^2$ in the occurrence of $4.0 \times 10^{-5}$ mol L$^{-1}$ and this confirmed the inhibition efficiency of the CS alloy surface by 45.9, 40.5, 36.6, and 31.5% in the presence of CAPD-1, CAPD-2, CAPD-3, and CAPD-4. The $R_p$ and $\eta I$ augmented progressively with a rise in inhibitor dose and reached a maximum of 671.61, 950.3, 525.31, and 411.84 Ω cm$^2$ and 95.9, 95.3, 94.8, and 93.3%, respectively, at $1.0 \times 10^{-3}$ mol L$^{-1}$ CAPD-1, CAPD-2, CAPD-3, and CAPD-4. It is reasonable to state that the assets and the film thickness of the adsorbed inhibitor enhanced with increased concentrations of CAPD-1, CAPD-2, CAPD-3, and CAPD-4 compounds. To validate the assertion of an enhanced adsorbed layer with increasing inhibitor dose, we inspected the values of the $Y_f$ and $Y_0$. Commonly, the restrictions $Y_f$ and $Y_0$ describe the features of a surface film of the CS alloy and the smaller the value, the superior the surface layer. As can be observed in Table 2, the value of $Y_0$ for the uninhibited medium is 75.6 μΩ$^{-1}$ s$^{-1}$ cm$^{-2}$, whereas that of the $4.0 \times 10^{-5}$ mol L$^{-1}$ inhibited medium is 12.56, 16.65, 26.99, and 31.61 μΩ$^{-1}$ s$^{-1}$ cm$^{-2}$ in the presence of CAPD-1, CAPD-2, CAPD-3, and CAPD-4, respectively. These demonstrations that the layer designed on the CS alloy interface in H$_2$SO$_4$ solution containing $4.0 \times 10^{-5}$ mol L$^{-1}$ CAPD-1, CAPD-2, CAPD-3, and CAPD-4 displayed superior characteristics compared to the alloy surface film designed in the blank corrosive medium. Moreover, the value $Y_0$ reduced in the presence $1.0 \times 10^{-3}$ mol L$^{-1}$ inhibitor to 1.45, 3.21, 4.26, and 5.12 μΩ$^{-1}$ s$^{-1}$ cm$^{-2}$, respectively, for CAPD-1, CAPD-2, CAPD-3, and CAPD-4 inhibited mediums settling the assertion of superior surface layer features in the existence of greater dose of CAPD-1, CAPD-2, CAPD-3, and CAPD-4 compounds.

Figure 3. Nyquist plots for CS alloy in molar sulfuric acid solution (A) without and with different concentrations of CAPD-1 and (B) with $1 \times 10^{-3}$ M of different cycloalkanapyridine derivatives at 25 °C.

Figure 4. (A) Bode and (B) Bode phase modules for CS alloy in molar sulfuric acid solution without and with different concentrations of CAPD-1 at 25 °C.
Figure 5. Descriptive fitted diagrams of CS alloy for (A) blank medium and (B) inhibited system and equivalent circuit used in modeling findings for (C) blank and (D) inhibited system.

Table 2. Impedance Parameters for CS Alloy in 1.0 M H$_2$SO$_4$ Solution without and with Diverse Concentrations of Cycloalkanapyridine Derivatives at 25 °C

| Inhibitor Code | $C_i$ (mol L$^{-1}$) | $R_i$ (Ω cm$^2$) | $R_P$ (Ω cm$^2$) | $C_d$ (μF cm$^{-2}$) | Y$_0$ (μΩ$^{-1}$ s$^{-1}$ cm$^{-2}$) | Y$_f$ (μΩ$^{-1}$ s$^{-1}$ cm$^{-2}$) | $n$ | $\chi^2$ (× 10$^{-5}$) | $\theta$ | PC$_E$ (%) |
|----------------|---------------------|------------------|------------------|---------------------|-----------------------------------|-----------------------------------|-----|---------------------|-------|---------|
| blank          | 0.0                 | 0.33             | 27.21            | 957.5               | 75.6                              | 0.733                             | 4.68 |                     |       |         |
| CAPD-1         | 4.0 × 10$^{-3}$     | 0.65             | 50.32            | 159.2               | 12.56                             | 0.821                             | 10.27| 0.666               | 5.25  | 0.459   | 45.9   |
|                | 8.0 × 10$^{-3}$     | 0.80             | 68.60            | 108.5               | 8.57                              | 0.832                             | 7.01 | 0.746               | 5.28  | 0.603   | 60.3   |
|                | 2.0 × 10$^{-4}$     | 0.78             | 130.56           | 88.5                | 6.71                              | 0.914                             | 5.49 | 0.762               | 5.33  | 0.791   | 79.1   |
|                | 6.0 × 10$^{-4}$     | 1.59             | 264.35           | 47.6                | 3.82                              | 0.850                             | 3.12 | 0.830               | 5.40  | 0.897   | 89.7   |
|                | 1.0 × 10$^{-3}$     | 2.28             | 671.61           | 25.7                | 1.45                              | 0.903                             | 1.18 | 0.757               | 5.81  | 0.695   | 95.9   |
| CAPD-2         | 4.0 × 10$^{-3}$     | 0.57             | 45.74            | 213.5               | 16.65                             | 0.833                             | 13.62| 0.810               | 5.28  | 0.405   | 40.5   |
|                | 8.0 × 10$^{-3}$     | 0.65             | 62.36            | 146.1               | 10.95                             | 0.830                             | 8.95 | 0.772               | 5.31  | 0.763   | 65.3   |
|                | 2.0 × 10$^{-4}$     | 0.64             | 118.69           | 119.2               | 9.54                              | 0.841                             | 7.80 | 0.745               | 5.33  | 0.771   | 71.7   |
|                | 6.0 × 10$^{-4}$     | 1.27             | 246.31           | 63.6                | 4.47                              | 0.857                             | 3.65 | 0.745               | 5.52  | 0.889   | 88.9   |
|                | 1.0 × 10$^{-3}$     | 1.19             | 590.53           | 33.9                | 3.21                              | 0.905                             | 2.626| 0.799               | 5.56  | 0.953   | 95.3   |
| CAPD-3         | 4.0 × 10$^{-3}$     | 0.49             | 42.96            | 341.7               | 26.99                             | 0.855                             | 22.08| 0.873               | 5.96  | 0.366   | 36.6   |
|                | 8.0 × 10$^{-3}$     | 0.52             | 59.21            | 233.6               | 18.43                             | 0.835                             | 15.06| 0.727               | 5.81  | 0.540   | 54.0   |
|                | 2.0 × 10$^{-4}$     | 0.73             | 107.89           | 190.7               | 15.52                             | 0.855                             | 12.69| 0.790               | 5.56  | 0.747   | 74.7   |
|                | 6.0 × 10$^{-4}$     | 1.19             | 222.97           | 102.3               | 8.72                              | 0.861                             | 7.135| 0.771               | 4.96  | 0.878   | 87.8   |
|                | 1.0 × 10$^{-3}$     | 1.47             | 525.31           | 53.8                | 4.26                              | 0.894                             | 3.48 | 0.783               | 5.16  | 0.948   | 94.8   |
| CAPD-4         | 4.0 × 10$^{-3}$     | 0.47             | 39.76            | 399.8               | 31.61                             | 0.855                             | 25.86| 0.813               | 5.97  | 0.315   | 31.5   |
|                | 8.0 × 10$^{-3}$     | 0.55             | 56.34            | 273.3               | 21.63                             | 0.905                             | 17.69| 0.727               | 5.91  | 0.517   | 51.7   |
|                | 2.0 × 10$^{-4}$     | 0.65             | 100.98           | 223.2               | 17.76                             | 0.901                             | 14.53| 0.822               | 5.65  | 0.731   | 73.1   |
|                | 6.0 × 10$^{-4}$     | 1.12             | 204.56           | 119.7               | 8.97                              | 0.909                             | 7.33 | 0.819               | 5.07  | 0.866   | 86.6   |
|                | 1.0 × 10$^{-3}$     | 1.38             | 411.84           | 63.3                | 5.12                              | 0.896                             | 4.185| 0.824               | 5.74  | 0.933   | 93.3   |
The assertion of an increase in the adsorbed layer thickness with increasing concentration could be acceptable by allowing for variance in the double layer capacitance ($C_{dl}$) with inhibitor dose. Consequently, the Helmholtz model given in eq 5 is accepted to elucidate the relationship between thickness and $C_{dl}$. It is inferred from this model that a decline in the dielectric constant or an increase in the film thickness leads to a diminution in $C_{dl}$. The values of $C_{dl}$ recorded in Table 2 were computed, which was suitable for the investigated systems. Meanwhile, diffusion routes were not disclosed or calculated. From Table 2, it is observed that the $C_{dl}$ value gradually declined with cumulative inhibitor dose and reached a smallest value of 25.7, 33.9, 53.8, and 63.3 μF cm$^{-2}$ at 1.0 mmol L$^{-1}$ CAPD-1, CAPD-2, CAPD-3, and CAPD-4, respectively. Similarly, the $R_p$ and $\eta_I$ show that it reasonable that the inhibitive action of the inhibitor with cumulative dose is due to an increase in the adsorbed layer thickness. Lastly, the close steadiness of the $n$ value (i.e., 0.733–0.909) discloses a capacitive interface:

$$C_{dl} = \frac{\varepsilon \varepsilon_0 A}{d} = Y_0 \left( \frac{1}{R_{ct}} + \frac{1}{R_i} \right)^{1-1/n}$$

where $\varepsilon$ signifies the local dielectric constant, $\varepsilon_0$ represents the air permittivity, $A$ symbolizes the electrode surface area, and $d$ represents the adsorbed film thickness.

### 3.3. Adsorption Considerations, Effect of Temperature, and Corrosion Mitigation Mechanism Analysis

Analysis of adsorption isotherm models allows for the clarification of the inspected cycloalkanapyridine derivative mitigation mechanism via its adsorptive behavior and strength. Numerous models of adsorption isotherms, for example, the Flory–Huggins, Frumkin, Temkin, Langmuir, and Freundlich models, were utilized to appropriate the PDP findings to comprehend how the molecules of the inhibitor are absorbed on the CS alloy interface. Remarkably, the monolayer adsorption of the Langmuir model was found to be the best-fit pattern ($R^2 > 0.999$) for the prepared compounds, signifying that the investigated layers are monofilms, where the $[\text{CAPD}] / \theta$ is plotted vs the $[\text{CAPD}]$ (cf. Figure 6) as per the following equation:

$$\frac{[\text{CAPD}]}{\theta} = \frac{1}{K_{ads}} + [\text{CAPD}]$$

where $[\text{CAPD}]$, $K_{ads}$ and $\theta$ are the CAPD concentration in mol/L, the adsorption constant, and the part of the covered surface, respectively.

The calculated parameters are recorded in Table 3. The line regression slope is observed to be $\sim 1$, which shows that the adsorption of CAPD compounds onto the CS alloy interface

| Inhibitor | $r^2$ | $s$ (slope) ± | $K_{ads}$ (L mol$^{-1}$) | $\Delta G_{ads}^0$ (kJ mol$^{-1}$) |
|-----------|------|--------------|----------------|-----------------|
| CAPD-1    | 0.99982 | 0.975 0.0079 | $1.88 \times 10^4$ | $-37.22$ |
| CAPD-2    | 0.99987 | 1.090 0.0078 | $1.78 \times 10^4$ | $-37.07$ |
| CAPD-3    | 0.99894 | 1.030 0.0051 | $1.69 \times 10^4$ | $-36.93$ |
| CAPD-4    | 0.99971 | 1.050 0.0121 | $1.64 \times 10^4$ | $-36.84$ |
follows the Langmuir model. The order of the \( K_{ads} \) values are CAPD-1 (1.88 \( \times 10^4 \) L mol\(^{-1}\)) > CAPD-2 (1.78 \( \times 10^4 \) L mol\(^{-1}\)) > CAPD-3 (1.69 \( \times 10^4 \) L mol\(^{-1}\)) > CAPD-4 (1.64 \( \times 10^4 \) L mol\(^{-1}\)), which agrees with the corrosion inhibition capacity of the CAPD compounds. Generally, the greater the \( K_{ads} \) value, the superior the protection performance. The \( K_{ads} \) value computed from the intercept of y-axes was utilized to determine the adsorption free energy (\( \Delta G_{ads}^0 \)) by the next equation:\(^{58} \)

\[
\Delta G_{ads}^0 = -RT\ln(K_{ads}C_{water}); \quad C_{water} = 55.50 \text{ mol/L}
\] (17)

Where the negative signal of the \( \Delta G_{ads}^0 \) approves that the adsorption route is certainly spontaneous. Furthermore, the value of \( \Delta G_{ads}^0 \) provides a strong symptom about the adsorption process nature. In this regard, it is usually decided in the previous works that \( \Delta G_{ads}^0 \) values or \( >-40 \) kJ/mol designate its chemical adsorption route.\(^{59} \) The value of \( \Delta G_{ads}^0 \) (\( \Delta G_{ads}^0 = -37.22, -37.07, -36.93, \) and \(-36.84 \) kJ mol\(^{-1}\)) for CAPD-1, CAPD-2, CAPD-3, and CAPD-4, respectively) attained in the present study shows that a relatively complex mixed adsorption (chemisorption and physisorption nature) is complicated and that is a predominantly chemisorption.\(^{60} \) This infers a main electrostatic attraction (physical adsorption) among the CAPD molecule and the CS alloy in addition to electron sharing or transfer (chemical adsorption) among CAPD molecules and the steel interface that possibly affects both cathodic and anodic locations.\(^{44} \)

The prepared cycloalkanapyridine derivatives demonstrated respectable protection capacities that follow the order CAPD-1 > CAPD-2 > CAPD-3 > CAPD-4 (Table 1). Their corrosion mitigation capabilities may be due to the particular molecular construction characteristics and the occurrence of heteroatoms (nitrogen atom in pyridine ring), which function as robust adsorption positions and augment its inhibition efficacy. The carbon steel alloy interface accumulates a negative charge when dipped into H\(_2\)SO\(_4\) solution because sulfate ions adsorb on the steel interface \([Fe + SO_4^{2-} \rightarrow (FeSO_4^{2-})_{ads}]\). In an acidic medium, cycloalkanapyridine compounds might be simply protonated, \([CAPD] + H^+ \rightarrow [CAPDH]^+\), because of their great electron density, producing a positively charged CAPD molecule. The physisorption can take place through electrostatic attraction between the metal negatively charged and protonated \([CAPDH]^+\) species.\(^{61} \) Furthermore, chemisorption can take place through attraction of the unshared electrons on hetero atoms and/or aromatic ring \(\pi\)-electrons of CAPD molecules with unoccupied d-orbitals of iron atoms on a carbon steel alloy, leading to construction of coordinate bond.\(^{62} \) As exemplified in Figure 7, the inhibition mechanism has been planned to clarify the adsorption mode of CAPD molecules on the metal substrate. CAPD-1 was the most effective one because it comprises 3C=N and an O atom, so it shares more electrons with the molecule. The CAPD-4 compound is the smallest, most efficient one because it has a solitary C=N and an O atom.

To study the effect of temperature influence on the protection efficiency, we measured the PDP measurements of CS in 1.0 M H\(_2\)SO\(_4\) in the absence and presence of 1.0 mM CAPD-1, CAPD-2, CAPD-3, and CAPD-4 at 298–328 K. The calculated \( j_{corr} \) (\( \mu A \text{ cm}^{-2} \)) and inhibition capacity (\( PC_T \)) are presented in Figure S5. The \( j_{corr} \) values for the prepared compounds were smaller than those of the uninhibited system in the investigated temperature range. In addition, from Figure SSB, the prepared CAPD compounds were found to be accurately efficient in hindering the CS corrosion mainly at 50 °C. On the basis of the findings in Figure SSB, the protection capacity values were increased as a solution temperature increased. According to the relationship between \( T \) and \( PC_T \), the predominance adsorption mechanism is might be chemisorption.\(^{61} \)

3.4. Surface Morphology by SEM Micrographs. The SEM micrographs of CS alloy substrates immersed in molar sulfuric acid medium for 48 h before and after dipping in blank and inhibited systems are shown in Figure 8. Before dipping, the morphology of the CS alloys surface was freshly refined and does not contain any contaminants, as realized in Figure 8A. After immersion in molar H\(_2\)SO\(_4\), as a corrosive medium, the morphology of the CS alloy surface becomes rough and porous and contains some cracks, as displayed in Figure 8B, and the CS alloy was harshly rusted (corroded). Figure 8C, D shows the morphological characteristics of the protected systems containing 1.0 \( \times 10^{-3} \) mol/L CAPD-4 and CAPD-1, respectively.

Compared with the corroded CS alloy surface, the specimens dipped in molar sulfuric acid medium with 1.0 \( \times 10^{-3} \) mol/L CAPD-4 was slicker; there were rare moderate scratches (Figure 8C). Furthermore, the specimen interface treated with CAPD-1 was nearly as smooth as the pristine CS alloy surface (Figure 8D). These findings show that cycloalkanapyridine derivatives might adsorb on the CS alloy substrate and form a protecting layer, resulting in a decline of contact between the corrosive medium and CS alloy.

3.5. Computational Calculations (DFT). Figure 9 involves the optimized structures, HOMO, and LUMO distribution for the protonated form of the CAPD molecules, and the correlated theoretical parameters are arranged in Table 4. Pursuant to the FMO theory, the capacity of the acceptor or donor at the inhibitor/steel interface is designated by \( E_{LUMO} \) and \( E_{HOMO} \).\(^{51} \) Therefore, the corrosion inhibition capacity is boosted for an inhibitor compound that has large \( E_{HOMO} \) and small \( E_{LUMO} \) values. As designated in Table 4, the CAPD-1 compound has a maximum \( E_{HOMO} \) value of –5.52 eV in comparison CAPD-2, CAPD-3, and CAPD-4 molecules (–5.61, –5.96, –6.26 eV). As revealed in Figure 9, for the compound molecules, it manifests that the \( E_{HOMO} \) level was placed on the pyridinium, cyano, methoxy and ethoxy moieties.

![Figure 7. Proposed mechanisms for inhibitor molecule adsorption on the CS alloy substrate in H\(_2\)SO\(_4\) solution.](https://pubs.acs.org/acsom/figure/acso/2d2022_acsomer_2022_article/2d5d9f22_2d2022_acsomer_2022_article_2439.png)
signifying that these places are favored for electrophilic attacks on the steel surface. These depictions approve the capability of inhibitor molecule for adsorption on the metal interface and therefore, improvement in the protection proficiency which was in great agreement with the experimental findings. Conversely, the $E_{\text{LUMO}}$ value is $-4.75$ eV for the CAPD-1 molecule (Table 4) lower than CAPD-2, CAPD-3, and CAPD-4 molecules ($-4.51$, $-4.40$, $-3.41$ eV). The lower $E_{\text{LUMO}}$ value for the CAPD-1 molecule shows the great protection capacity of the CAPD-1 molecule, which concurs well with the earlier outcomes.

Similarly, the $\Delta E$ (energy gap) is a critical parameter to improve the corrosion protection capacity of the additive compound, which augments as the value of $\Delta E$ is diminished. As reported in Table 4, the CAPD-1 molecule has a slighter $\Delta E$ value ($0.77$ eV) than CAPD-2, CAPD-3, and CAPD-4 molecules ($1.10$, $1.56$, $2.85$ eV), which indicates a greater propensity of the CAPD-1 compound to be adsorbed on the steel surface. The moderately low $A$ and high $I$ for CAPD molecules indicate that CAPD molecules have the ability to exchange electrons with the metal surface and are adsorbed on its surface, forming a protective layer.

Generally, most inhibitors have moderately small electronegativity values ($\chi$), demonstrating the inhibitor electron provision propensity to the steel interface. On the other hand, the high electronegativity values ($\chi$) also exhibit a great electron accepting capability of the inhibitor species to receive the electron from steel surface atoms and create a sturdier bond with the steel surface. As exhibited in Table 4, it seems that the electronegativity for CAPD molecules is slightly high, indicating that the examined molecules have back-donation ability and construct a harder bond with the steel surface.

Moreover, the stability and reactivity of the inhibitor molecule can be assessed from the softness ($\sigma$) and hardness ($\eta$), i.e., soft compounds possess an inhibition capability greater than those of hard compounds because of the smooth electron transfer to the metal surface via the adsorption, so they act as efficient inhibitors for steel corrosion. As illustrated in Table 4, CAPD-1 molecules have larger $\sigma$ values and smaller $\eta$ values than CAPD-2, CAPD-3, and CAPD-4 molecules, providing smooth provision of electrons to the metal substrate and excellent protection abilities.

Furthermore, the $\Delta E_{\text{back-donation}}$ and the electron transfer fraction are pivotal strictures for the inhibitor's ability for electron accepting or donating. Therefore, if the $\Delta N$ values are greater than zero, electron transfer from the inhibitor molecule to metal surface atoms is feasible, whereas if the $\Delta N$ values are less than zero, electron transfer from steel surface atoms to the
inhibitor compound is feasible (i.e., back-contribution). According to the data recorded in Table 4, the values of $\Delta N$ for the examined molecules are greater than zero, demonstrating that CAPD molecules are able to contribute electrons to the steel surface. Furthermore, the $\Delta E_{\text{back-donation}}$ will be $<0$ when $\eta > 0$, with the electron relocating from the metal to a molecule, pursued by a back-contribution from the inhibitor molecule to the metal, and this is animatedly favored. In Table 4, the values of $\Delta E_{\text{back-donation}}$ values for CAPD molecules are negative, which shows that back-contribution is desired for the CAPD molecules and forms a forceful bond.

Furthermore, the dipole-moment is a decisive stricture that favoritisms in predictive mechanism of corrosion protection. The augmentation in dipole moment affords boosts the distortion energy and increases the inhibitor adsorption on the metal substrate. Consequently, the increase in dipole moment indicates a progress in corrosion inhibition ability. As divulged in Table 4, the CAPD-1 molecule has superior dipole moment value (8.89 debye) than CAPD-2, CAPD-3, and CAPD-4 molecules (7.87, 6.93, and 5.67 debye), which supports the greater affinity for the CAPD-1 compound to be adsorbed on the metal interface and enrich the protection.

| CAPD-1 | HOMO | LUMO |
|--------|------|------|
| ![Image](optimized_structure1.png) | ![Image](HOMO1.png) | ![Image](LUMO1.png) |
| CAPD-2 | ![Image](optimized_structure2.png) | ![Image](HOMO2.png) | ![Image](LUMO2.png) |
| CAPD-3 | ![Image](optimized_structure3.png) | ![Image](HOMO3.png) | ![Image](LUMO3.png) |
| CAPD-4 | ![Image](optimized_structure4.png) | ![Image](HOMO4.png) | ![Image](LUMO4.png) |

**Figure 9.** Optimized configuration and LUMO and HOMO orbital occupation for the studied CAPDs molecules using DFT method.
The local reactivity of the CAPD compounds can be evaluated by reckoning the Fukui directories ($f_k^+$ and $f_k^-$), the local electrophilicity ($\omega_k^\pm$), the local softness descriptor ($\sigma_k^\pm$), and the dual descriptors ($\Delta f_k$, $\Delta \sigma_k$, and $\Delta \omega_k$) from the following equations:\(^{21}\)

\[
\sigma_k^\pm = f_k^\pm 
\]

\[
\omega_k^\pm = \sigma_k^\pm 
\]

\[
\Delta f_k = f_k^+ - f_k^- 
\]

\[
\Delta \sigma_k = \sigma_k^+ - \sigma_k^- 
\]

\[
\Delta \omega_k = \omega_k^+ - \omega_k^- 
\]

For clarification, the most meaningful results are revealed in Table S1. The evaluated Fukui directories (Table S1) detected

| params                          | CAPD-1  | CAPD-2  | CAPD-3  | CAPD-4  |
|---------------------------------|---------|---------|---------|---------|
| $E_{\text{HOMO}}$ (eV)          | $-5.52$ | $-5.61$ | $-5.96$ | $-6.26$ |
| $E_{\text{LUMO}}$ (eV)          | $-4.75$ | $-4.51$ | $-4.40$ | $-3.41$ |
| $\Delta E = E_{\text{LUMO}} - E_{\text{HOMO}}$ (eV) | 0.77    | 1.10    | 1.56    | 2.85    |
| vertical ionization potential (IP) | 5.52    | 5.61    | 5.96    | 6.26    |
| electron affinity (EA)          | 4.75    | 4.51    | 4.40    | 3.41    |
| electronegativity ($\chi$)      | 5.13    | 5.06    | 5.18    | 4.83    |
| global hardness ($\eta$)        | 0.39    | 0.55    | 0.78    | 1.42    |
| global softness ($\sigma$)      | 2.59    | 1.81    | 1.28    | 0.70    |
| global electrophilicity index ($\omega$) | 34.15   | 23.20   | 17.15   | 8.21    |
| no. of electrons transferred ($\Delta N$) | 2.42    | 1.76    | 1.16    | 0.76    |
| $\Delta E_{\text{back-donation}}$ | $-0.10$ | $-0.14$ | $-0.20$ | $-0.36$ |
| dipole moments ($\mu$) Debye    | 8.89    | 7.87    | 6.93    | 5.67    |

For clarification, the most meaningful results are revealed in Table S1. The evaluated Fukui directories (Table S1) detected

Figure 10. Graphical depiction of the dual descriptors ($\Delta f$, $\Delta \sigma$, and $\Delta \omega$) for the maximum active centers of the studied CAPDs molecules using the DFT method.
for the inhibitor species are ascribed to the sites at which the CAPD molecules will be adsorbed onto the Fe interface. Furthermore, the local dual descriptors are more accurate and comprise more tools than the Fukui directories ($f^+_k$ and $f^-_k$), the electrophilicity ($\omega^+_k$), and the local softness ($\sigma^-_k$); the graphical demonstration of the dual local descriptors of the greatest illustrative active centers are displayed in Figure 10. The attained outcomes show that the sites with $\Delta f^+_k$, $\Delta \sigma^-_k$, and $\Delta \omega^-_k < 0$ have the propensity to relocate electron to the steel surface. On the other hand, those sites with $\Delta f^-_k$, $\Delta \sigma^+_k$, and $\Delta \omega^+_k > 0$ have the ability to accept an electron from the steel. As could be seen in Figure 10, the highest active centers for electron donation are at C1, C4−C8, N9, C10, C12, N13, C14, N18, O24, N25 for CAPD-1; C1, C3−C6, C8, N9, C10, C12, N13, C14, N18, O24, N25 for CAPD-2; C1, C2, C4, C7, C10, C11, N12, N13, C14, C15, C17, C20, N21, C23, O24, N25, C26 for CAPD-3; and C1, C4, C7, C8, C10, N11, C13, C17, C18, C19, C20−C22, O24−O26, N27, C28 for CAPD-4. The active accepting centers are at C2, C15, C17, C19−C22 for CAPD-1; C2, C11, C15−C17, C19−C23 for CAPD-2; C3, C5, C6, C8, C9, C16, C18, C19, C22 for CAPD-3; and C2, C6, C12, C14−C16, C23, C30, C31 for CAPD-4.

Finally, molecular electrostatic mapping potential (MEP) could divulge the efficient sides of the CAPDs molecules and is evaluated through the Dmol³ module. The MEP maps is a 3D image descriptor aimed at discriminating the net electrostatic influence originated on a compound by the complete charge sharing. In MEP mapping revealed in Figure 11, the red area depicts the great electron density extent; where the MEP is exceedingly negative (nucleophilic interaction). In contrast, the blue area designate the maximum positive zone (electrophilic attraction). A visual investigation of Figure 11 supports that the extreme negative portions are mainly above nitrogen and oxygen atoms; however, there is a lower electron density over the aromatic system (benzene rings). These centers with greater electron density (i.e., red zone) in additive molecules may be the best for adsorption on the steel surface, creating durable adsorbed protecting films.

Conclusively, from DFT calculations, we can deduce that the CAPD compounds are effective inhibitors for CS alloy for many reasons such as high $E_{\text{HOMO}}$, low $\Delta E$, low $\eta$, high $\sigma$, and high $\Delta N$, which indicate the donation abilities of CAPD molecules and the strong adsorption on CS alloys via adsorption centers. These centers are disclosed via the local
dual descriptors and MEP, which are N and O atoms and benzene rings. Finally, the DFT calculations revealed that the order of inhibition efficiency was CAPD-1 > CAPD-2 > CAPD-3 > CAPD-4, which agrees with experimental findings.

### 3.6. MC Simulations

MC simulations were performed to distinguish the adsorption of the additive molecules with the steel interface in addition to suggesting an apparent idea for the adsorption process mechanism. Consequently, Figure 12 reveals the highest appropriate adsorption formations for the protonated form of the CAPD molecules on the metal interface in an acidic solution accomplished by the module of the adsorption locator, which is represented in a nearly flat arrangement, advising an enhancement in the adsorption and supreme surface covered part. Additionally, the reckoned results for the adsorption energies from the MC imitations are divulged in Table 5. It appears that the CAPD-1 molecule (−6241.48 kcal mol$^{-1}$) has a superior negative value of adsorption energy compared to the CAPD-2, CAPD-3, and CAPD-4 molecules (−6216.32, −6161.43, −6060.88 kcal mol$^{-1}$), which supposes the energetic adsorption of the

|       | Final Equilibrium Configurations | Side View | Top View |
|-------|----------------------------------|-----------|----------|
| CAPD-1| ![CAPD-1](image1)                | ![Side View CAPD-1](image2) | ![Top View CAPD-1](image3) |
| CAPD-2| ![CAPD-2](image4)                | ![Side View CAPD-2](image5) | ![Top View CAPD-2](image6) |
| CAPD-3| ![CAPD-3](image7)                | ![Side View CAPD-3](image8) | ![Top View CAPD-3](image9) |
| CAPD-4| ![CAPD-4](image10)               | ![Side View CAPD-4](image11) | ![Top View CAPD-4](image12) |

Figure 12. Highest proper adsorption arrangement for the CAPD molecules on the iron (110) surface accomplished by an adsorption locator module.
Table 5. Data and Descriptors Computed by the MC Simulations for the Adsorption of the CAPD Molecules on Fe (110)

| corrosion systems | adsorption energy/kcal mol⁻¹ | rigid adsorption energy (kcal mol⁻¹) | deformation energy/kcal mol⁻¹ | dE_{ads}/dN_i (kcal mol⁻¹) |
|-------------------|-----------------------------|-------------------------------------|------------------------------|---------------------------|
| Fe (110)          | -6241.48                    | -5760.45                            | -481.02                      | -471.73                   |
| CAPD-1 water      | -6216.32                    | -5738.96                            | -477.37                      | -454.99                   |
| SO₂⁻ ions         | -6161.43                    | -5718.02                            | -443.42                      | -429.90                   |
| Fe (110)          | -6060.88                    | -5643.42                            | -417.46                      | -403.34                   |
| CAPD-2 water      | -481.02                     | -471.73                             | -454.99                      | -437.46                   |
| SO₂⁻ ions         | -477.37                     | -454.99                             | -443.42                      | -429.90                   |
| Fe (110)          | -443.42                     | -429.90                             | -417.46                      | -403.34                   |
| CAPD-3 water      | -429.90                     | -417.46                             | -405.34                      | -391.45                   |
| SO₂⁻ ions         | -417.46                     | -405.34                             | -391.45                      | -377.54                   |
| Fe (110)          | -403.34                     | -391.45                             | -377.54                      | -363.63                   |
| CAPD-4 water      | -391.45                     | -377.54                             | -363.63                      | -349.73                   |
| SO₂⁻ ions         | -377.54                     | -363.63                             | -349.73                      | -335.82                   |

4. CONCLUSIONS

In the current exploration, the designing of a new heterocyclic compounds of 6,7-dihydro-SH-cycloenta[b]pyridine-3-carbonitrile derivatives (CAPDs) and their protection effect was inspected via diverse morphological (SEM) and electrochemical (OCP, PDP, EIS) inspections and combined theoretical studies (MC simulations and DFT calculations). The different empirical approaches were in good covenant, displaying that CAPD derivatives are efficient inhibitors, and the protection capacities augmented with the increase in inhibitor concentration, reaching to the maximum values 97.7% for CAPD-1 at 1.0 × 10⁻⁵. Furthermore, the PDP plots exhibited that the synthesized CAPD derivatives could control the process of corrosion by a mixed-kind mechanism. Surface morphology investigations revealed that by augmenting the surfactant dose the steel heterogeneity declined considerably. Furthermore, the adsorption of surfactants on CS substrate follows the Langmuir model involving physisorption and chemisorption. Together with experimental examinations, the DFT calculations showed that the effective electron-rich parts of CAPD molecules are the prime sites in their adsorption. MC simulations indicate that the occurrence of the oxygen and nitrogen atoms in CAPD derivatives structures play a significant role in the adsorption method. In covenant with the experiential results, the theoretical findings demonstrated that the order of inhibition efficiency was CAPD-1 > CAPD-2 > CAPD-3 > CAPD-4. Finally, this report affords a facile synthesis of 2-alkoxy-4-(aryl)-7-(aryl-2-ylmethylidene)-6,7-di-hydro-SH-cycloenta[b]pyridine-3-carbonitrile derivatives (pyridine and ortho methoxy phenyl). In future work, the study of electron-withdrawing groups will be our interest.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.2c02639.
Additional experimental descriptions of synthesis of compounds 4a–k; characterization data of CAPD-1–CAPD-4 compounds; 1H and 13C NMR spectra of CAPD-1–CAPD-4; change in corrosion current density, \( i_{\text{corr}} \) (\( \mu \text{Acm}^{-2} \)) and protection capacity, \( \text{PC}_{90} \), of CS alloy in 1.0 M \( \text{H}_2\text{SO}_4 \) solution containing 1.0 mM of CAPD-1, CAPD-2, CAPD-3, and CAPD-4 at different temperatures; and the evaluated Fukui directories (PDF)

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**Notes**

The authors declare no competing financial interest.

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