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MOLECULAR-LEVEL ASSESSMENT OF THE CORROSION INHIBITION PROPERTIES OF ONO-TYPE SCHIFF BASES USING DFT CALCULATIONS AND MOLECULAR DYNAMICS SIMULATIONS

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This study presents a molecular-level evaluation of two ONO-type Schiff bases using density functional theory (DFT) and molecular dynamics (MD) simulations to elucidate their anticorrosion performance. The Schiff bases, synthesized from *o*-aminophenol with *o*-hydroxyacetophenone (SB1) and 3,5-di-*tert*-butylsalicylaldehyde (SB2), were investigated in terms of their electronic structure, reactivity descriptors, and adsorption behavior on the Fe(110) surface. DFT calculations at the B3LYP/6-311+G(d,p) level in an aqueous phase revealed key differences in molecular properties such as frontier orbital energies, dipole moment, energy gap, and charge distribution. Mulliken population analysis and Fukui functions identified the primary reactive centers, emphasizing the role of heteroatoms in surface adsorption interactions. Global reactivity descriptors were also evaluated to compare the inhibitors' electron-donating and accepting capabilities. Complementary MD simulation provided insight into the effect of the geometry of molecules and substituents on the adsorption process. SB1 showed a more favorable space orientation and stronger surface interaction, while steric hindrance from bulky *tert*-butyl groups in SB2 limited its adsorption efficacy. This integrated computational approach offers a detailed understanding of structure–activity relationships in corrosion inhibitors and supports the rational design of next-generation materials for metal protection.

Keywords: density functional theory (DFT), quantum chemical calculations, molecular dynamics (MD) simulation, organic corrosion inhibitors, Schiff bases, quantum chemical descriptors, adsorption.

ТФТ-ЕСЕПТЕУЛЕРІ МЕН МОЛЕКУЛАЛЫҚ ДИНАМИКАЛЫҚ ҮЛГІЛЕУ АРҚЫЛЫ ONO-ТИПТІ ШИФФ НЕГІЗДЕРІНІҢ КОРРОЗИЯҒА ҚАРСЫ ҚАСИЕТТЕРІН МОЛЕКУЛАЛЫҚ ДЕҢГЕЙДЕ БАҒАЛАУ

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Осы зерттеуде коррозияға қарсы қасиеттерін анықтау мақсатында ONO-тиіпті екі Шифф негізіне тығыздық функционалы теориясы (ТФТ) және молекулалық динамика (МД) әдістері қолданылып, молекулалық деңгейде бағалау жүргізілді. *О*-аминфенол мен *о*-гидроксиацетофеноннан (SB1), сондай-ақ 3,5-ди-*трет*-бутилсалицил альдегидтен (SB2) синтезделген Шифф негіздерінің электрондық құрылымы, реактивтілік сипаттамалары және Fe(110) бетіне адсорбциялану тәртібі зерттелді. B3LYP/6-311+G(d,p) деңгейінде су фазасында жүргізілген DFT есептеулері молекулалық қасиеттерде - шекаралық орбитальдар энергиясы, дипольдік момент, энергетикалық аралық және заряд-тардың таралуы секілді - негізгі айырмашылықтарды көрсетті. Малликен бойынша зарядтарды тарату және Фукуи функцияларын талдау реакцияға бейім алғашқы орталықтарды анықтап, беткі адсорбциялық әрекеттесулердегі гетероатомдардың рөлін айқындады. Ингибиторлардың электрон беру және қабылдау қабілеттерін салыстыру үшін жаһандық реактивтілік дескрипторлары да бағаланды. Қосымша MD модельдеуі молекулалық геометрия мен орынбасар топтардың адсорбция процесіне әсерін нақтылауға мүмкіндік берді. SB1 молекуласы метал бетіне қолайлырақ орналасып, күштірек әрекеттесу көрсетсе, SB2 құрамындағы көлемді трет-бутил топтары стереоқиындық

тудырып, оның адсорбциялық тиімділігін шектеді. Мұндай кешенді есептік әдіс коррозия ингибиторларының құрылымы мен белсенділігі арасындағы өзара байланысты тереңірек түсінуге жол ашады және металдарды қорғауға арналған жаңа буындағы материалдарды ұтымды жобалауға ықпал етеді.

Түйін сөздер: тығыздық функционалы теориясы (ТФТ), кванттық-химиялық есептеулер, молекулалық-динамикалық (МД) модельдеу, органикалық коррозия ингибиторлары, Шифф негіздері, кванттық-химиялық дескрипторлар, адсорбция.

ОЦЕНКА АНТИКОРРОЗИОННЫХ СВОЙСТВ ОСНОВАНИЙ ШИФФА ONO-ТИПА НА МОЛЕКУЛЯРНОМ УРОВНЕ С ИСПОЛЬЗОВАНИЕМ DFT-РАСЧЕТОВ И МОЛЕКУЛЯРНО-ДИНАМИЧЕСКОГО МОДЕЛИРОВАНИЯ

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В настоящем исследовании на молекулярном уровне проведена оценка антикоррозионных свойств двух оснований Шиффа ONO-типа с использованием методов теории функционала плотности (ТФП) и молекулярной динамики (МД). Основания Шиффа, синтезированные из *о*-аминофенола, *о*-гидроксиацетофенона (SB1) и 3,5-ди-*трет*-бутилсалицилового альдегида (SB2), были исследованы с точки зрения их электронной структуры, характеристик реакционной способности и поведения при адсорбции на поверхности Fe(110). Расчеты методом DFT на уровне B3LYP/6-311+G(d,p) в водной фазе выявили ключевые различия в молекулярных свойствах, таких как энергии граничных орбиталей, дипольный момент, энергетическая щель и распределение заряда. Анализ распределения зарядов по Малликену и функций Фукуи выявили первичные реакционные центры, подчеркнув роль гетероатомов в поверхностных адсорбционных взаимодействиях. Для сравнения способности ингибиторов отдавать и принимать электроны также были оценены глобальные дескрипторы реакционной способности. Дополнительное МД-моделирование позволило получить представление о влиянии геометрии молекул и заместителей на процесс адсорбции. SB1 показал более благоприятную пространственную ориентацию и более сильное поверхностное взаимодействие, в то время как стерические препятствия из-за объёмных *трет*-бутильных групп в SB2 ограничивали эффективность его адсорбции. Такой комплексный вычислительный подход обеспечивает детальное понимание взаимосвязи структуры и активности ингибиторов коррозии и способствует рациональному проектированию материалов нового поколения для защиты металлов.

Ключевые слова: теория функционала плотности (ТФП), квантово-химические расчеты, молекулярно-динамическое (МД) моделирование, органические ингибиторы коррозии, основания Шиффа, квантово-химические дескрипторы, адсорбция.

Introduction. Corrosion is a pervasive issue that leads to significant material degradation and economic losses across various industries. Organic corrosion inhibitors have emerged as an effective and versatile solution to mitigate corrosion, particularly in aggressive environments such as acidic media. These inhibitors function by adsorbing onto the metal surface, forming a protective barrier that reduces the interaction between the metal and the corrosive environment. Organic inhibitors, often containing heteroatoms like nitrogen, oxygen, and sulfur, as well as π-electron systems, exhibit strong adsorption due to their ability to donate and accept electrons [1]. Their efficiency, environmental compatibility, and tunable molecular structures make them a focus of extensive research for sustainable corrosion protection. These inhibitors are widely used in acidic environments for applications such as descaling, acid pickling, and oil-well protection, demonstrating high inhibition efficiency [2].

Schiff bases offer several advantages over other organic corrosion inhibitors. Schiff bases contain imine (−C=N−) groups and heteroatoms (nitrogen, oxygen), which provide multiple active sites for adsorption onto metal surfaces, enhancing their inhibition efficiency [3]. Their molecular structure allows strong interactions with metal surfaces, forming stable protective films that effectively block corrosion processes [4]. In addition, Schiff bases can be easily synthesized and modified to optimize their properties for specific environments, making them adaptable to various industrial applications[5].

The mechanisms of organic inhibitors, including adsorption and electron transfer, are well-studied using computational and experimental approaches [6]. Quantum chemical calculations and molecular dynamics simulations, play a crucial role in the research and development of modern corrosion inhibitors. Quantum chemical methods, such as Density Functional Theory (DFT), are used to calculate molecular reactivity descriptors (e.g., HOMO-LUMO energies, dipole moments, Fukui functions) to predict the adsorption behavior and inhibition efficiency of inhibitors on metal surfaces [7]. MD simulations provide insights into the dynamic interactions between inhibitor molecules and metal surfaces, including adsorption configurations, binding energies, and surface coverage. This helps evaluate the stability and effectiveness of inhibitors under realistic conditions [8]. These methods enable the design and optimization of inhibitors by identifying key structural features. These methods also help to explain the experimental results.

In this work, the inhibitory properties of two ONO-type Schiff bases (Figure 1) synthesized by condensation of *o*-aminophenol and *o*-hydroxyacetophenone (SB1), as well as *o*-aminophenol and 3,5-di-*tert*-butylsalicylaldehyde (SB2), were investigated using DFT calculations and MD simulation.

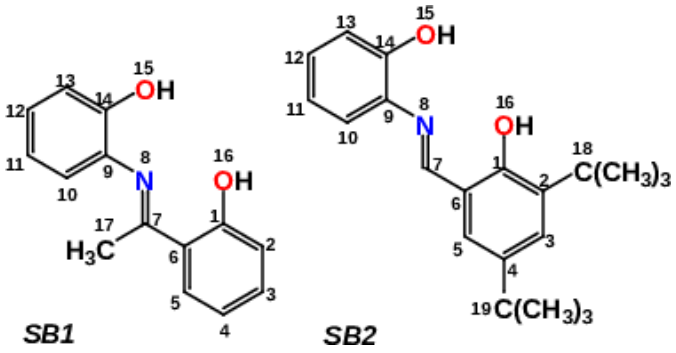


Fig.1 - Chemical structure with atomic enumeration of investigated ONO-type Schiff bases

Materials and methods. All quantum chemical calculations were performed on a desktop PC with Windows 11, a 12th-generation Intel(R) Core(TM) i7-12700H 2.30 GHz, 16 GB RAM, using GAMESS software [9]. Initially, full geometry optimization was achieved using the Molecular Mechanics (MM+) force field. The results from MM+ were then used as input and re-optimized using the semi-empirical PM3 method to obtain the equilibrium geometry. Final geometry optimization and quantum chemical parameters were obtained by density functional theory (DFT) calculations.

To calculate optimized geometrical structure, atomic charges, and energies, the B3LYP functional with the 6-311+G(d,p) basis set was used. All DFT calculations were carried out in the aqueous phase because electrochemical corrosion occurs in aqueous media. The solvent (H_2O) was incorporated via the Conductor-like Screening Model (COSMO) [10].

The following quantum chemical indices describing global reactivity were considered: the energy of the highest occupied molecular orbital (E_{HOMO}), the energy of the lowest unoccupied

molecular orbital (E_{LUMO}), the energy gap (ΔE_{gap}), ionization potential (IP), electron affinity (EA), electronegativity (χ), global hardness (η), softness (σ), electrophilicity (ω), nucleophilicity (ε), back-donation energy (E_{b-d}), total negative charge (TNC, TNC/n, where n is the total number of atoms in the molecule), and the fraction of transferred electrons (ΔN), considered according to the following equations [11]:

$$\Delta E_{gap} = E_{LUMO} - E_{HOMO} \quad (1)$$

$$IP = -E_{HOMO} \quad (2)$$

$$EA = -E_{LUMO} \quad (3)$$

$$\chi = \frac{IP + EA}{2} \quad (4)$$

$$\eta = \frac{IP - EA}{2} \quad (5)$$

$$\sigma = \frac{1}{\eta} \quad (6)$$

$$\omega = \frac{\chi^2}{2\eta} \quad (7)$$

$$\varepsilon = \frac{1}{\omega} \quad (8)$$

$$\Delta E_{b-d} = -\frac{\eta}{4} \quad (9)$$

$$\Delta N = \frac{\chi_{Fe} - \chi_{inhibitor}}{2(\eta_{Fe} - \eta_{inhibitor})} \quad (10)$$

where χ_{Fe} and χ_{inh} are the absolute electronegativities of the iron atom and the inhibitor molecule, respectively; η_{Fe} and η_{inh} the absolute hardness of the iron atom and the inhibitor molecule, respectively. The electronegativity of iron is 7 eV, and the total hardness is 0 eV.

According to Koopman's theorem, the HOMO energy is related to IP while the LUMO energy is related to EA. Electronegativity (χ) and global hardness (η) were evaluated based on the finite difference approximation as linear combinations of the calculated IP and EA. The global softness (σ) is the reciprocal of the global hardness. The global electrophilicity index (ω) describes the stabilization of a molecule after the acquisition of an additional number of electrons. The nucleophilicity index (ε) is the reciprocal of the global electrophilicity index [12].

Molecular dynamics simulation. The intensity of the interactions between the examined inhibitor and metal surface was determined using molecular dynamics (MD) simulations. MD simulation is a modern computational technique crucial for theoretical studies of the interaction between inhibitors and metal surfaces.

The MD simulations were carried out by using the GROMACS 2020.4 software [13]. Adsorption energy was calculated by Equation (11):

$$E_{adsorption} = E_{total} - (E_{Fe(110)} + E_{inhibitor}) \quad (11)$$

where $E_{adsorption}$ is the adsorption energy (or interaction energy) corresponding to the amount of energy released or absorbed as 1 mole of adsorbate molecules is adsorbed on the adsorbent, E_{total} is the total energy of the whole system (surface $Fe(110)$ + inhibitor molecule), $E_{Fe(110)}$ is the energy of the metal, and $E_{inhibitor}$ is the energy of the inhibitor molecule. The binding energy is regarded as the reciprocal of the adsorption energy of the inhibitor molecule as follows (12):

$$E_{binding} = -E_{adsorption} \quad (12)$$

where $E_{binding}$ is the binding energy.

The $Fe(110)$ metal structure was chosen due to its lowest surface energy, thermodynamic stability and the largest area of the Fe crystal [14].

Results and discussion. The inhibitory properties of Schiff bases are investigated using quantum chemical methods, focusing on the electronic structure and reactivity descriptors. Density Functional Theory (DFT) calculations provided insights into molecular orbitals, charge

distribution, and adsorption behavior on metal surfaces to evaluate the mechanisms underlying their corrosion inhibition performance.

Frontier molecular orbitals (FMO) energies and molecular electrostatic potential (MEP). The electronic properties of Schiff bases, including their reactivity and adsorption behavior on metal surfaces, can be effectively analyzed using Frontier Molecular Orbitals (FMOs) and Molecular Electrostatic Potential (MEP). Optimized geometry, HOMO, LUMO energies and density distribution, energy gap ΔE_{gap}, and MEP for SB1 and SB2 molecules calculated using the DFT/B3LYP/6-311+G(d,p) method are presented in Figure 2. The positively charged lobe is indicated by the blue color, and the negatively charged lobe is indicated by the red color.

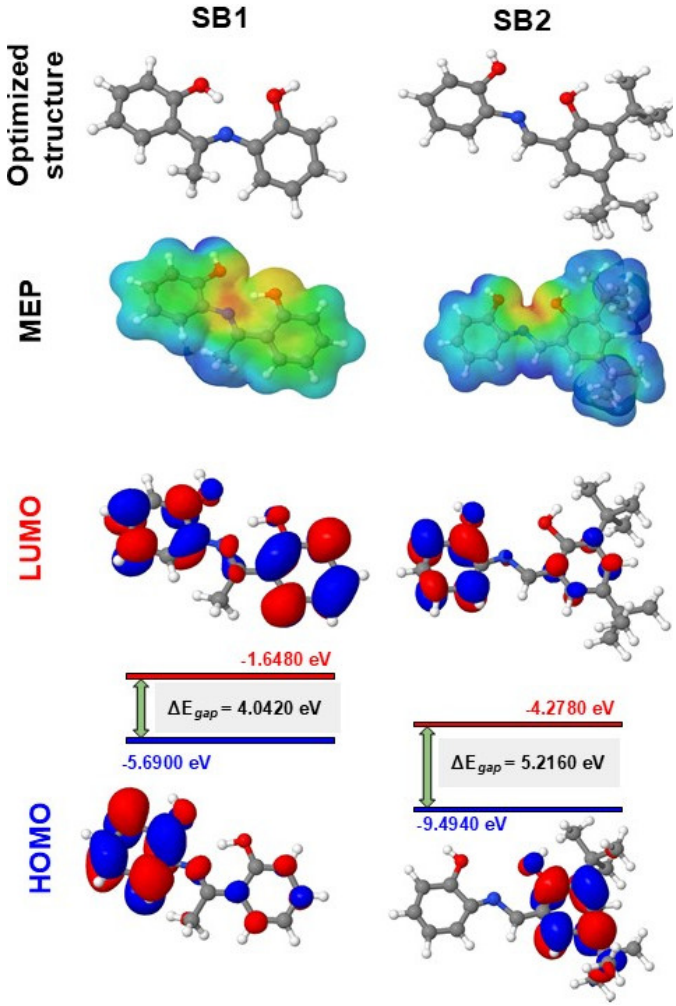


Fig.2 - HOMO, LUMO energies and density distribution, energy gap (ΔE_{gap}), and MEP for SB1 (A) and SB2 (B) molecules calculated using DFT/B3LYP/6-311+G(d,p) method

As evident from the optimized structures, both Schiff bases belong to the C_1 point group and exhibit non-planar geometries. This conformational behavior can be attributed to the free rotation around C*C σ-bonds and the steric repulsion between similarly charged functional groups, such as -OH.

The MEP maps reveal electron-rich regions (depicted in red) and electron-deficient regions (in blue). Both SB1 and SB2 exhibit areas of negative electrostatic potential localized around oxygen and nitrogen atoms, suggesting these sites as potential adsorption centers on the metal surface. Notably,

SB1 displays more intense and spatially confined electron-rich zones, indicating stronger and more specific interaction sites for bonding with metal. The high electron density around the donor atoms (O and N) enhances the likelihood of chemisorption, which is one of the key factors for the mechanism in the inhibition of metal corrosion.

In the SB1 molecule, the HOMO is primarily localized on the phenolic ring and the azomethine (-CH=N) group, particularly around the oxygen and nitrogen atoms. This indicates that these regions are electron-rich and capable of donating electrons to the vacant *d*-orbitals of metal atoms during adsorption. The LUMO is also distributed over the azomethine group and partially over the adjacent aromatic ring, suggesting that these sites are favorable for accepting back-donated electrons from the metal surface, thereby enhancing adsorption stability. In contrast, in the SB2 molecule, the HOMO is delocalized over the aromatic ring but exhibits lower electron density on the heteroatoms compared to SB1, implying a reduced ability to donate electrons to the metal. The LUMO is primarily located on the azomethine moiety and parts of the aromatic system. Its delocalized nature suggests a reduced capacity for back-donation, potentially lowering the efficiency of adsorption. Therefore, the co-localization of the HOMO and LUMO near the donor atoms (N and O) in SB1 indicates a strong potential for bidirectional interactions with the metal surface, involving both electron donation and back-donation. In contrast, the FMOs in SB2 are more dispersed and less concentrated near key donor sites, suggesting weaker and less specific interactions with the metal surface.

The HOMO energy reflects a molecule's ability to donate electrons to the metal surface. SB1 exhibits a higher HOMO energy compared to SB2, indicating a stronger electron-donating capability, which promotes adsorption onto the metal surface and facilitates the formation of a protective film. The LUMO energy is associated with the molecule's capacity to accept electrons. SB2 possesses a lower LUMO energy, suggesting a greater ability to accept electrons, which may enhance back-donation interactions from the metal. Furthermore, SB1 displays a smaller energy gap (ΔE_{gap}) than SB2, indicating higher chemical reactivity and a stronger potential for interaction with the metal surface.

The obtained results indicate that SB1 is more chemically reactive and has stronger inhibition potential than SB2, owing to its higher HOMO energy (enhanced electron-donating ability), lower ΔE_{gap} (greater chemical reactivity), and more favorable MEP distribution (stronger adsorption affinity toward the metal surface).

Mulliken atomic charge distribution (MACD) and Fukui functions analysis. Mulliken charge distribution analysis provides essential information on the electronic structure of corrosion inhibitor molecules by estimating the partial atomic charges [15]. Atoms with higher negative charges, typically heteroatoms such as nitrogen, oxygen, or sulfur, are identified as potential adsorption centers capable of donating electrons to the vacant orbitals of metal atoms. Additionally, the charge distribution influences total molecular polarity and orientation during adsorption on metal surfaces, and consequently is a valuable tool for understanding and predicting the corrosion inhibition performance of organic molecules.

In turn, Fukui functions are mathematical descriptors derived from Density Functional Theory (DFT) that quantify the reactivity of specific atomic sites in a molecule [16]. They indicate how the electron density of a molecule changes upon gaining or losing electrons, making them useful for identifying the most reactive sites in a molecule potentially suitable for nucleophilic, electrophilic or radical attack. Therefore, Fukui functions are integral to understanding the electronic properties and reactivity of corrosion inhibitors at the molecular level.

The condensed Fukui functions are calculated using the finite-difference approximation as follows:

$f_k^+ = P_k(N+1) - P_k(N)$ (For nucleophilic attack)

$f_k^- = P_k(N) - P_k(N-1)$ (For electrophilic

attack)

$f_k^0 = \frac{P_k(N+1)-P_k(N-1)}{2}$ (For radical attack)

The results of the calculation of Mulliken atomic charges and the values of the Fukui functions for ONO-type Schiff bases are presented in Table 1. For simplicity, the charges and Fukui functions of the hydrogen (H) atoms were removed.

Table 1 - Mulliken atomic charges and Fukui functions calculated using DFT/B3LYP/6-311+G(d,p) for ONO-type Schiff bases

Atoms*	P*k*(N)	P*k*(N+1)	P*k*(N-1)			
SB1						
C(1)	0.2454	0.3213	-0.3244	0.0759	-0.0790	-0.0015
C(2)	0.0902	-0.1359	-0.1046	-0.0457	0.0144	-0.0156
C(3)	-0.0669	-0.0746	0.0116	-0.0077	-0.0785	-0.0431
C(4)	-0.1032	-0.0974	-0.0842	0.0058	-0.0190	-0.0066
C(5)	-0.0688	-0.1289	-0.0572	-0.0601	-0.0116	-0.0358
C(6)	-0.1900	-0.0480	-0.2005	**0.1420**	0.0105	0.0762
C(7)	0.2863	0.1802	0.3241	-0.1061	-0.0378	-0.0719
N(8)	-0.5385	-0.5096	-0.5697	0.0289	**0.0312**	0.0300
C(9)	0.1197	0.1951	0.2121	0.0754	-0.0924	-0.0085
C(10)	-0.0682	-0.1382	-0.0699	-0.0700	0.0017	-0.0341
C(11)	-0.0977	-0.0827	-0.0602	0.0150	-0.0375	-0.0112
C(12)	-0.0844	-0.1067	-0.0689	-0.0223	-0.0155	-0.0189
C(13)	-0.1040	-0.1654	-0.0334	-0.0614	-0.0706	-0.0660
C(14)	0.1784	0.2870	0.1939	0.1086	-0.0155	**0.0465**
O(15)	-0.3654	-0.4101	-0.3417	-0.0447	-0.0237	-0.0342
O(16)	-0.3734	-0.4759	-0.2864	-0.1025	-0.0870	-0.0947
C(17)	-0.3276	-0.2665	-0.3067	0.0611	-0.0209	0.0201
SB2						
C(1)	0.1309	0.3687	0.2464	**0.2378**	-0.1155	**0.1766**
C(2)	0.0683	-0.0389	-0.0519	-0.1072	0.1202	-0.1137
C(3)	0.0701	0.0521	-0.0446	-0.0180	0.1147	-0.0663
C(4)	0.0437	-0.0314	-0.0373	-0.0751	0.0810	-0.0780
C(5)	-0.0425	0.0249	-0.0694	0.0674	0.0269	0.0202
C(6)	-0.0881	-0.1802	-0.1207	-0.0921	0.0326	-0.0623
C(7)	0.1598	0.2850	0.1061	0.1252	0.0537	0.0357
N(8)	-0.3201	-0.5249	-0.5653	-0.2048	**0.2462**	-0.2255
C(9)	0.0426	0.1361	0.1816	0.0935	-0.1390	0.1162

C(10)	-0.0075	-0.0350	-0.1255	-0.0275	0.1180	-0.0727
C(11)	-0.1335	-0.1027	-0.0999	0.0308	-0.0336	0.0322
C(12)	-0.0566	-0.0446	-0.1326	0.0120	0.0760	-0.0320
C(13)	-0.1342	-0.0829	-0.1334	0.0513	-0.0008	0.0260
C(14)	0.2204	0.2120	0.1496	-0.0084	0.0708	-0.0396
O(15)	-0.3689	-0.3665	-0.3835	0.0024	0.0146	-0.0061
O(16)	-0.4093	-0.2961	-0.4622	0.1132	0.0529	0.0301
C(18)	-0.2399	-0.2536	-0.1980	-0.0137	-0.0419	0.0141
C(19)	-0.2875	-0.2919	-0.2502	-0.0044	-0.0373	0.0164

* - *atomic enumeration is in accordance with Fig.1.*

The Mulliken atomic charge distribution analysis shows that regions of high electron density are located on the heteroatoms (nitrogen and oxygen) of both molecules. Therefore, these atoms serve as potential adsorption centres and contribute to the formation of a protective film on the metal surface. In both molecules, the nitrogen atom of the imine group (N8) has the highest electron density and is identified as the primary electrophilic centre, as confirmed by the corresponding Fukui function values.

Furthermore, the presence of *tert*-butyl substituents increases the susceptibility of nitrogen atoms to electrophilic attack, which is attributed to the electron donor properties of *tert*-butyl groups, increasing the total electron density in the molecule. This effect also makes the C(1) atom a potential center of radical attack.

Carbon atoms C(6) in SB1 and C(1) in SB2 were identified as potential centers for nucleophilic attack in both molecules. The shift in the nucleophilic reaction center is likewise attributed to the presence of *tert*-butyl groups. Acting as first-kind orientants, they increase the electron density in the aromatic system, particularly at the *ortho*- and *para*-positions. In the presence of a hydroxyl group, this results in a significant enhancement of electron density at the C(1) atom.

The combination of high electron density and favorable Fukui function values at key heteroatoms strongly supports the effective adsorption of the investigated inhibitor molecules onto the steel surface. This charge distribution further underpins the ability of the Schiff bases to interact with the steel surface through both electron donation and acceptance mechanisms, thereby enhancing their corrosion inhibition efficiency.

Molecular reactivity descriptors. Molecular reactivity descriptors are quantitative parameters that characterize the electronic structure and chemical reactivity of molecules. In the study of corrosion inhibitors, these descriptors are used to predict and understand the interaction between inhibitor molecules and metal surfaces. These descriptors are essential for designing and optimizing corrosion inhibitor structures for high efficiency and stability. Quantum chemical descriptors calculated for the investigated Schiff bases molecules in aqueous phase are listed in Table 2.

Table 2 - Molecular reactivity descriptors calculated for ONO-type Schiff bases calculated using DFT/B3LYP/6-311+G(d,p) in aqueous phase

Descriptor	**SB1**	**SB2**
Total energy (E*tot*), a.u.	-746.25	-1021.14

Dipole moment (μ), D	2.8142	1.7517
Ionization energy (IP), eV	5.6900	9.4940
Electron affinity (EA), eV	1.6480	4.2780
Electronegativity ( ), eV	3.6690	6.8860
Chemical hardness (η), eV	2.0210	2.6080
Chemical softness (σ), eV	0.4948	0.3834
Electrophilicity index (ω), eV	6.7308	23.7085
Nucleophilicity index (ε), eV	0.1486	0.0422
Back-donation energy (E*b-d*, eV)	-0.5053	-0.6520
Fraction of transferred electrons (ΔN)	-0.8241	-0.0219
TNC	-2.4783	-3.5265
TNC/*n*	-0.0826	-0.0691
Inhibition efficiency (in 0.5 mol·dm^{-3} H2SO4) [17], %	86,55	56,05

The calculated total energy values (E_{tot}) indicate greater stability of SB2 molecule. The dipole moment (μ) reflects the polarity of the inhibitor molecule and provides insights into its adsorption behavior. A higher dipole moment generally indicates stronger molecular polarity, which can enhance the interaction between the inhibitor and the metal surface through electrostatic forces. Molecules with significant dipole moments tend to learn more effectively on the metal surface, promoting the formation of a compact and stable protective film. The calculation results indicate that SB1 has a higher dipole moment and, accordingly, has more intense inhibitory properties, which is consistent with experimental data.

Ionization energy (IE) and electron affinity (EA) are key descriptors of the electronic properties of corrosion inhibitors. Ionization energy reflects the ability of a molecule to donate electrons; a lower IE indicates that the molecule can more easily donate electrons to the vacant *d*-orbitals of metal atoms, enhancing adsorption. Electron affinity measures the tendency of a molecule to accept electrons. Therefore, a higher EA suggests a stronger ability to accept electrons from the metal surface. Together, these parameters describe the molecule's ability to engage in donor - acceptor interactions with the metal, stabilizing the adsorbed layer and improving corrosion inhibition efficiency. The calculated values of the ionization energy indicate that SB1 is a more effective inhibitor, which is also consistent with the experimental results. The values of electron affinity indicate that the most effective inhibitor should be SB2. Most likely, this result is due to the presence of *tert*-butyl groups, which make charges on potential electrophilic centers more positive, thereby increasing acceptor properties of the whole molecule.

Electronegativity (χ) also plays a critical role in describing the properties of corrosion inhibitors. Molecules with high electronegativity tend to attract electrons, enabling them to form stable interactions with the partially positive metal atoms. A higher electronegativity value for SB2 molecule implies it' s more effective interaction with the metal surface and therefore has higher inhibitory properties. However, the lower inhibition efficiency is likely because the large *tert*-butyl groups create significant sterical hindrance.

Chemical hardness (η) and softness (σ) are also important descriptors for understanding the reactivity of corrosion inhibitors. In corrosion inhibition, soft molecules are often more effective because their higher polarizability and greater reactivity enhance their ability to adsorb onto the metal, form stable complexes, and protect

the surface. Thus, chemical softness is typically associated with higher inhibition efficiency. A higher chemical softness value and a lower chemical hardness value for SB1 clearly indicate its more effective inhibitory properties.

Electrophilicity (ω) and nucleophilicity (*ε*) indexes provide insight into the chemical reactivity of corrosion inhibitors. High nucleophilicity and low electrophilicity show enhanced adsorption of inhibitor molecules on metal surfaces, and therefore they are critical for predicting and describing the efficiency of corrosion inhibitors. As can be seen, the values of both parameters also confirm the high effectiveness of SB1 as a corrosion inhibitor.

Back-donation energy ($E_{b\text{-}d}$) describes the ability of inhibitor molecules to accept electron density from the metal surface into their LUMO. A negative back-donation energy indicates that, in addition to donating electrons to the metal, the inhibitor can also accept electrons from the metal' s surface. This two-way electron transfer strengthens the adsorption interaction, leading to the formation of a more stable protective film. The results of the calculations indicate that both molecules, especially SB2, tend to accept electrons from the metal. However, the sterical hindrance caused by tert-butyl groups does not allow the orbitals to be at the distance necessary for back-donation and thereby reduces its inhibitory effectiveness.

The fraction of transferred electrons (ΔN) quantifies the extent of electron transfer from a corrosion inhibitor molecule to the metal surface. Generally, a higher ΔN value corresponds to a greater ability of the molecule to stabilize on the metal surface through donor–acceptor interactions, enhancing its corrosion inhibition efficiency. A negative ΔN suggests that both inhibitor molecules can accept electrons from the metal, which leads to the reduction of the adsorption intensity. A more negative ΔN value calculated for SB1 clearly indicates its lower propensity to accept electrons from the metal surface and, therefore, its higher inhibition efficiency.

The total negative charge (TNC) represents the sum of all negative atomic charges within a molecule, providing an overall measure of its electron-donating ability. A more negative TNC value indicates a greater capacity for electron donation to the metal surface, promoting stronger sorption and enhancing corrosion protection. The ratio TNC/*n*, where *n* is the number of atoms in the molecule, normalizes the total negative charge relative to molecular size, allowing for more accurate comparisons between inhibitors of different molecular weights. Higher TNC/*n* values suggest a more efficient distribution of electron density, which correlates with improved adsorption strength and inhibition efficiency. The values of these parameters for the studied molecules indicate a more efficient distribution of electron density in molecule SB1 and, consequently, its higher inhibition efficiency.

Thus, most of the calculated parameters clearly confirm the high inhibition efficacy of SB1 compared to SB2. The insignificant differences between the calculation results and the experimental data are explained by the peculiarity of the structure of SB2 molecule, in particular, the presence of two bulky *tert*-butyl groups and their steric effects.

Molecular dynamic simulation. Molecular dynamics (MD) simulation is used to study the dynamic behavior of molecules and their interactions. MD simulations provide insights into inhibitor molecules interaction with metal surfaces, including adsorption configurations, binding energies, and the formation of protective films. MD simulations help quantify the effectiveness of inhibitors by analyzing parameters like surface coverage, interaction energy, and molecular orientation. By simulating different molecular structures, MD makes it possible to identify characteristics that increase adsorption and corrosion resistance and thus help design more effective inhibitors. This approach significantly complements experimental results and quantum chemical methods, providing a dynamic perspective on inhibitor performance.

The top and side views of the optimal configurations of both studied Schiff bases on the Fe(110) surface are shown in Figure 3.

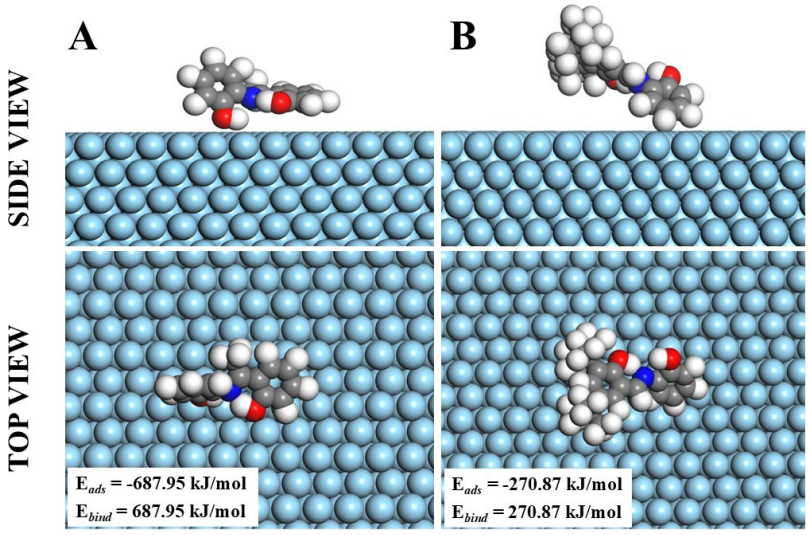


Fig. 3 - Side and top views of the most appropriate configuration for adsorption of SB1 (A) and SB2 (B) molecules on the Fe (110) surface obtained by MD simulations

As can be seen, the SB1 molecule lying flat on the Fe(110) surface. The corresponding values of the adsorption energy indicate a more effective interaction between the SB1 molecules and the Fe(110) surface. The presence of two bulky *tert*-butyl substituents in SB2 structure prevents effective adsorption of the inhibitor due to sterical hindrance. As a result, the inhibitor molecule is positioned at an angle, which also prevents effective interaction with the metal surface of all potential sorption centres, leading to the decrease of inhibition efficiency.

Proposed adsorption mechanism. Based on the results obtained, a mechanism of sorption of the studied ONO-type Schiff bases on the Fe(110) surface was proposed and shown in Figure 4.

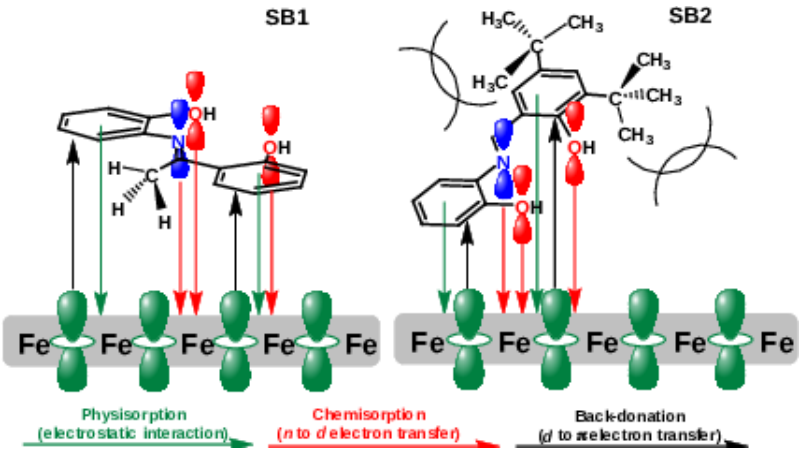


Fig.4 - Proposed adsorption mechanism for SB1 and SB2 on the Fe (110) surface in accordance with calculated descriptors

As can be seen, the SB1 molecule has a flatter orientation relative to the metal surface than the SB2. This is due to the presence of bulky *tert*-butyl substituents, which create steric hindrance to more effective adsorption. More positive changes in heteroatoms in SB2 molecule also reduce the adsorption efficiency due to weaker interactions with the metal surface.

SB1 exhibits higher inhibition efficiency (86.55%) due to its favorable electronic properties, including a higher dipole moment (2.8142 D), lower ionization energy (5.6900 eV), and greater chemical softness (0.4948 eV). These parameters enhance its ability to donate electrons to the metal surface, forming stable donor-acceptor interactions. Additionally, SB1' s flatter orientation relative to the metal surface facilitates effective adsorption through its heteroatoms, as supported by its higher total negative charge (TNC = -2.4783) and fraction of transferred electrons (ΔN=−0.8241). In contrast, SB2 shows lower inhibition efficiency (56.05%) due to steric hindrance caused by bulky *tert*-butyl groups, which limit its adsorption capacity. Despite its higher electronegativity (6.8860 eV) and electron affinity (4.2780 eV), these properties result in weaker donor-acceptor interactions and reduced adsorption intensity. The steric effects also prevent optimal alignment of adsorption centers, further decreasing its effectiveness. The back-donation of electrons from the *d*-orbitals of the metal enhances the interaction of SB1 with the Fe(110) surface. Despite the fact that the LUMO energy values for SB2 indicate its better ability to accept electrons from the metal surface, more efficient back-donation is observed for SB1 due to the localization of LUMO on both aromatic systems and the absence of steric hindrance.

Conclusion. This study employed density functional theory (DFT) and molecular dynamics (MD) simulations to evaluate the corrosion inhibition performance of two ONO-type Schiff bases. The quantum chemical calculations revealed that SB1 possesses more favorable electronic properties for corrosion inhibition, including a higher HOMO energy, lower energy gap (ΔE_{gap}), greater dipole moment, and enhanced chemical softness, all of which contribute to its excellent electron-donating ability and reactivity. The molecular electrostatic potential (MEP) maps and frontier molecular orbital (FMO) distributions indicated that SB1 provides more effective adsorption centers localized on heteroatoms, promoting stronger interactions with the metal surface. Mulliken charge analysis and Fukui function evaluations further supported the predominance of nitrogen and oxygen atoms as active sites for adsorption, particularly in SB1. The calculated global reactivity descriptors consistently pointed to SB1' s higher inhibitory efficiency. Moreover, MD simulations confirmed that SB1 adopts a favorable flat orientation on the Fe(110) surface, maximizing its surface coverage and interaction energy, while steric hindrance from bulky *tert*-butyl substituents in SB2 decreases its adsorption efficiency. In summary, SB1 demonstrated excellent corrosion inhibition performance compared to SB2, both theoretically and experimentally. These findings highlight the value of integrated approaches for the rational design of effective corrosion inhibitors.

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