

Density Functional Theory Investigation of Alkoxy-Substituted Pyrazolines: Structural, Electronic, and Thermodynamic Insights

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ABSTRACT

A comprehensive density functional theory (DFT) investigation was conducted to evaluate the structural, electronic, and thermodynamic properties of alkoxy-substituted pyrazoline derivatives. Geometry optimization and frequency calculations were performed at the B3LYP/3-21G level of theory using Gaussian software. The optimized geometries revealed substituent-induced variations in bond lengths and bond angles, particularly around the C–F, N–N, and C–N bonds, confirming electronic redistribution within the heterocyclic framework. Frontier molecular orbital (FMO) analysis demonstrated that the HOMO is predominantly localized over the pyrazoline and aromatic core, while the LUMO extends toward electron-withdrawing substituents, indicating effective intramolecular charge transfer. The calculated HOMO–LUMO energy gaps suggest substituent-dependent modulation of chemical reactivity. Molecular electrostatic potential (MEP) maps identified electron-rich regions around oxygen and nitrogen atoms and electron-deficient sites near hydrogen and fluorinated carbons, highlighting potential reactive centers for electrophilic and nucleophilic interactions. Global reactivity descriptors, including hardness, softness, entropy, and Gibbs free energy, further confirmed the influence of alkoxy substitution on molecular stability and reactivity trends. Compounds with higher softness and smaller energy gaps exhibited enhanced electronic responsiveness. The combined theoretical analysis establishes a clear structure–property relationship and suggests that alkoxy-functionalized pyrazolines possess tunable electronic characteristics.

suitable for potential optoelectronic and pharmaceutical applications.

Keywords: Density Functional Theory; Pyrazoline Derivatives; Alkoxy Substitution; Frontier Molecular Orbitals; Global Reactivity Descriptors; Molecular Electrostatic Potential

Introduction

Pyrazolines are five-membered nitrogen-containing heterocyclic compounds that have attracted significant attention in organic, medicinal, and materials chemistry due to their versatile structural framework and wide range of functional properties. Structurally, pyrazolines represent the reduced form of pyrazoles and contain two adjacent nitrogen atoms within a partially saturated heterocyclic ring. This unique electronic arrangement enables strong conjugation, tunable substituent effects, and diverse chemical reactivity (Moussa et al., 2024). In medicinal chemistry, pyrazoline derivatives have demonstrated various biological activities, including antimicrobial, anti-inflammatory, anticancer, antiviral, and antioxidant properties. Their structural adaptability allows functionalization at multiple positions, making them attractive scaffolds for drug design and pharmacological optimization (Zhang et al., 2023).

Beyond pharmaceutical relevance, pyrazolines also exhibit promising photophysical and optoelectronic properties. Several substituted pyrazolines have been reported as fluorescent materials, blue light emitters, and electroluminescent components in organic electronic devices (Uchacz et al., 2023). The conjugated π -system within the pyrazoline core facilitates electron delocalization, which significantly influences light absorption and emission characteristics. Therefore, structural modification of the pyrazoline ring provides a rational strategy for tuning both biological and electronic behavior (Szukalski et al., 2022). Substituent modification plays a critical role in controlling the electronic, structural, and thermodynamic properties of heterocyclic systems. Among various functional groups, alkoxy substituents are particularly important due to their electron-donating character through resonance (+R effect) and inductive effects (Kula & Kuś, 2025).

Alkoxy groups can enhance π -electron delocalization across the molecular framework, thereby influencing frontier molecular orbital energies, dipole moment, and overall molecular reactivity. The presence of methoxy, ethoxy, or propoxy substituents can modify the electron density distribution within the pyrazoline core, directly affecting HOMO–LUMO energy gaps and global reactivity descriptors (Chang et al., 2022; Muhammad et al., 2025). Moreover, when combined with electronegative atoms such as fluorine, alkoxy substitution introduces an interesting electronic interplay between electron-withdrawing (–I effect of F) and electron-donating (+R effect of OR) groups. This dual electronic modulation may significantly influence molecular stability, charge transfer capability, and potential interaction with biological targets or optoelectronic systems (Ullah et al., 2025).

Thus, systematic investigation of alkoxy-substituted pyrazolines is essential to understand substituent-driven variations in structural geometry, electronic distribution, and thermodynamic behavior (Loh et al., 2013). Density Functional Theory (DFT) has become one of the most powerful and widely used computational approaches for investigating molecular structure, electronic properties, and

thermodynamic stability. DFT enables accurate prediction of optimized geometries, bond parameters, vibrational frequencies, and electronic descriptors while maintaining reasonable computational cost (Farah et al., 2025; Rana et al., 2023).

In heterocyclic systems such as pyrazolines, DFT calculations provide valuable insight into:

Optimized molecular geometry and structural distortion

Frontier Molecular Orbitals (HOMO and LUMO)

Energy gap and electronic transitions

Global reactivity descriptors such as hardness and softness

Dipole moment and charge distribution

Thermodynamic parameters including Gibbs free energy and entropy

Frontier molecular orbital analysis is particularly important for understanding chemical reactivity, electron transfer capability, and optical behavior. A smaller HOMO–LUMO energy gap generally indicates higher reactivity and improved charge-transfer potential, which is directly related to fluorescence and optoelectronic performance (Shams et al., 2026). Additionally, Molecular Electrostatic Potential (MEP) mapping allows visualization of electron-rich and electron-deficient regions, helping to predict potential sites for electrophilic and nucleophilic attack (Geetha et al., 2025; Muhammad et al., 2026). Therefore, DFT serves as a reliable theoretical tool for correlating molecular structure with reactivity and stability, particularly in substituted heterocyclic systems.

The present study aims to perform a comprehensive Density Functional Theory investigation of alkoxy-substituted pyrazoline derivatives in order to evaluate their structural, electronic, and thermodynamic properties. Geometry optimization was carried out using the B3LYP functional with the 3-21G basis set to obtain stable molecular conformations and confirm the absence of imaginary frequencies.

The study focuses on:

Analysis of optimized bond lengths and bond angles

Evaluation of frontier molecular orbital energies (HOMO and LUMO)

Determination of energy gap and global reactivity descriptors

Investigation of molecular electrostatic potential surfaces

Assessment of thermodynamic stability parameters

Through systematic comparison of differently substituted alkoxy derivatives, this work seeks to clarify the influence of substituent effects on molecular stability and reactivity. The findings provide theoretical insight into structure–property relationships in alkoxy-functionalized pyrazolines and contribute to understanding their potential in electronic and reactive applications.

Materials and Methods

Software and Level of Theory

All quantum chemical calculations were carried out using the Gaussian software package (Gaussian 09 and Gaussian 16). Geometry optimizations of the investigated alkoxy-substituted pyrazoline derivatives were performed using Density Functional Theory (DFT). The hybrid Becke three-parameter exchange functional combined with the Lee–Yang–Parr correlation functional (B3LYP) was employed in conjunction with the 3-21G basis set (Ibrahim et al., 2023).

Full geometry optimizations were conducted without imposing any symmetry constraints. Frequency calculations were performed at the same level of theory to verify the nature of the stationary points and to obtain thermodynamic parameters. Calculations were carried out in both gas phase and implicit solvent conditions where applicable. For solvent-phase calculations, the Polarizable Continuum Model (PCM) was used with dimethyl sulfoxide (DMSO) as the solvent medium. The following computational analyses were obtained from the optimized structures:

Optimized molecular geometry

Total electronic energy

Dipole moment

Frontier molecular orbital energies (EHOMO and ELUMO)

Thermodynamic parameters

Global reactivity descriptors

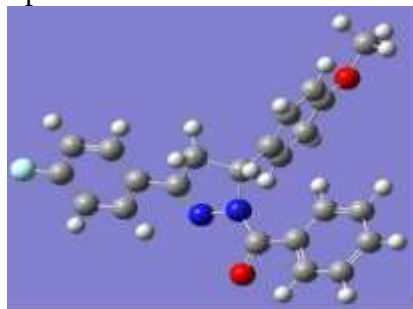
Optimization Criteria

Geometry optimization was performed using the default convergence thresholds implemented in the Gaussian program. The self-consistent field (SCF) procedure was executed until energy convergence was achieved according to standard Gaussian criteria. The optimized structures were confirmed to correspond to true energy minima by the absence of imaginary frequencies in the vibrational frequency analysis. All calculations were performed for neutral molecules with a total charge of zero (Charge = 0). The spin multiplicity was set to singlet (Spin = 1), corresponding to a closed-shell electronic configuration. The calculation type was specified as full geometry optimization (FOPT) using the restricted B3LYP (RB3LYP) method.

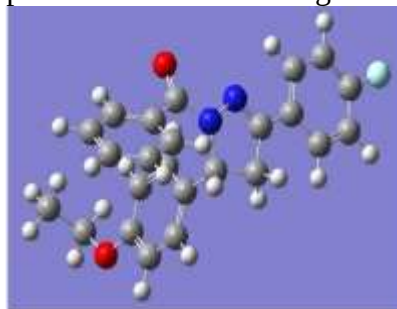
Results

Optimized Molecular Geometry

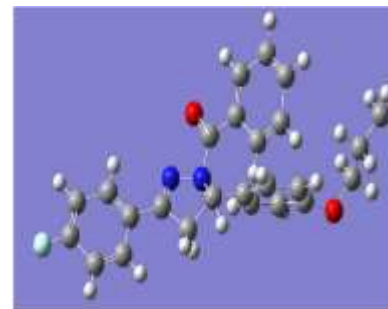
The optimized molecular geometries of alkoxy-substituted pyrazoline derivatives (1b–3b) were obtained at the B3LYP/3-21G level of theory. Full geometry optimization was performed without symmetry constraints. All optimized structures were confirmed as true minima by the absence of imaginary frequencies. The DFT-optimized structures of compounds 1b, 2b, and 3b are presented in Figure 1. The optimized molecular structure of compound 1b is shown in Figure 2.



Pyrazoline 1b



Pyrazoline 2b



Pyrazoline 3b

Figure 1 DFT Structures of Pyrazolines (1b,2b and 3b)

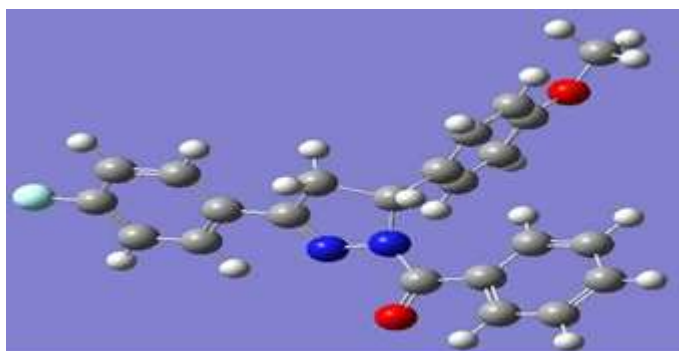


Figure 2 Optimized Molecular Structure for Pyrazoline (1b)

The optimized structures show that the pyrazoline ring retains its five-membered framework. The alkoxy substituents are positioned at the para position of the aromatic ring. The fluorine atom is bonded to the aromatic carbon, and oxygen atoms are present within the alkoxy and carbonyl functionalities. The calculated bond lengths and bond angles were obtained directly from the optimized geometry. Selected bond parameters are summarized in Table 1. The C–F bond, N–N bond, C–N bonds, and C–O bonds are clearly identified in the optimized structure. Minor variations in bond lengths are observed among compounds 1b–3b due to differences in alkoxy chain length. The optimized geometries obtained in the gas phase show slightly longer bond distances compared to typical experimental solid-state values.

Geometry Convergence and Stability

Geometry optimization was performed using the B3LYP/3-21G level of theory. The total electronic energy was monitored throughout the optimization process. The energy minimization was completed in 21 optimization steps. The total energy decreased progressively during the initial optimization cycles and gradually approached convergence. The final optimized energy obtained for compound 1b was -1240.819635 Hartree. Energy stabilization was observed after step 7, and convergence criteria were fully satisfied at step 21. The absence of imaginary frequencies in the frequency calculation confirms that the optimized structure corresponds to a stable minimum on the potential energy surface (Figure 7).

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Figure 3 Represents the Optimization Energy Graph

Structural Parameters (Bond Lengths and Bond Angles)

The selected bond lengths and bond angles obtained from the optimized geometries of the alkoxy-substituted pyrazoline derivatives are summarized in Table 1.

Table 1 Selected bond lengths and bond angles

Bond lengths	Bond angles	Bond lengths	Bond angles	Bond lengths	Bond angles
C (8)- F (1) 1.107	F (1)-C (6)-C (7) 136.75	N (2)-N (1) 1.2921	O (1)-C (2)-C (4) 124.341	C (8)- N (1) 1.430	C (13)-O (1)-C (14) 129.341
C (4)-O (1) 1.236	F (1)-C (8)-C (4) 138.98	C (1)-O (2) 1.341	N (1)- C(5)-C (2) 147.27	C (6)-O (1) 1.363	C (14)-O (1)-C (16) 163.28
C (3)-C (11) 1.203	N (2)-C- (3)-N-(1) 105.34	N (2)-C (4) 1.458	C (7)-O (1)-C (12) 133.381	O (2) -C (33) 1.346	C (12)-N (1) C (14)123.65
C (9)- N (1) 1.206	N (2)-C (4)-O (2) 123.65	C (14)- C (19) 1.295	C (11)-N (1) C (13) 123.65	C (10)-C (14) 1.448	N (2)-C- (3)-N-(1) 105.34

The optimized geometry reveals that the C–F bond length in compound 1b is calculated to be 1.107 Å. This relatively short bond distance indicates strong bond polarization due to the high electronegativity of fluorine. The presence of fluorine enhances electron-withdrawing effects through inductive interactions, thereby influencing the electronic distribution within the aromatic system. The N–N bond length within the pyrazoline ring is found to be 1.292 Å. This value is consistent with

partially delocalized N–N single bonds observed in heterocyclic systems. The bond length suggests a stabilized dihydropyrazole framework with moderate electron density sharing between the adjacent nitrogen atoms.

The C–N bond lengths in the pyrazoline core (e.g., C–N = 1.430 Å and related values) indicate typical single bond character with partial conjugative contribution from the adjacent π -system. These bond distances confirm the integrity of the heterocyclic ring and reflect electronic communication between nitrogen atoms and the aromatic substituent. The carbonyl C=O bond (1.236 Å) exhibits a shorter bond length characteristic of double bond character, confirming strong π -bonding interaction. In contrast, the ether C–O bond (1.341 Å and 1.363 Å) shows longer bond distances consistent with single bond character. The presence of alkoxy substituents contributes to electron donation through resonance, which can influence the electronic density distribution of the conjugated framework.

The observed bond angles further support structural stability of the optimized molecules. The F–C–C bond angles (138.98° and 136.75°) indicate slight angular distortion around the fluorinated carbon, likely resulting from steric and electronic effects of the substituent. The N–C–N angle within the pyrazoline ring (approximately 105.34°) is consistent with the geometry of five-membered heterocyclic systems and reflects ring strain adjustment. The O–C–C and N–C–O bond angles (approximately 123–124°) suggest partial electron delocalization across the aromatic and carbonyl systems. These values indicate conjugative interactions between the heterocyclic core and adjacent substituents. The structural parameters demonstrate that alkoxy substitution does not disrupt the stability of the pyrazoline ring but induces localized electronic modulation. The combination of electron-withdrawing fluorine and electron-donating alkoxy groups contributes to polarization within the molecular framework, supporting potential charge transfer behavior observed in subsequent frontier molecular orbital analysis.

Frontier Molecular Orbital (FMO) Analysis

The frontier molecular orbitals of the alkoxy-substituted pyrazoline derivatives were analyzed at the B3LYP/3-21G level of theory. The calculated energies of the highest occupied molecular orbital (EHOMO) and the lowest unoccupied molecular orbital (ELUMO) were obtained directly from the optimized structures. The graphical representation of HOMO and LUMO distributions is shown in Figure 4.

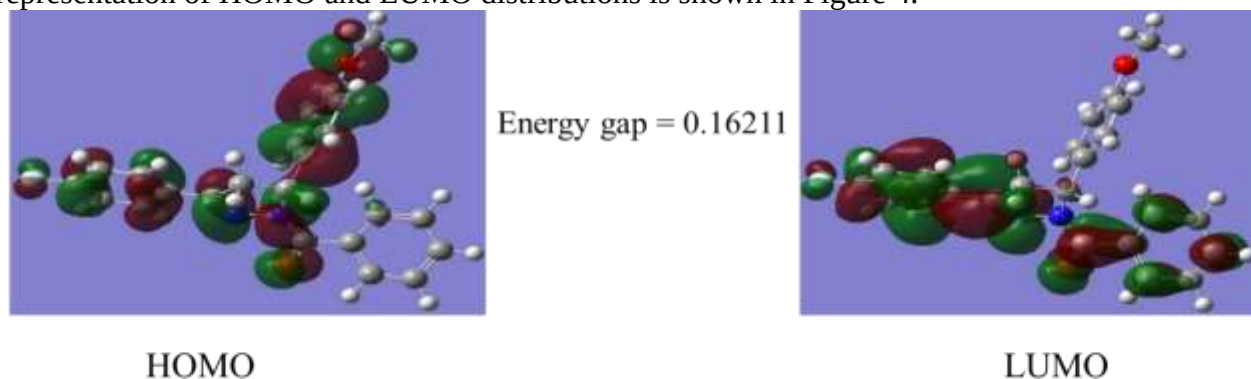


Figure 4 HOMO-LUMO Analysis

The calculated EHOMO and ELUMO values indicate the electronic donating and accepting abilities of the molecules. For compound 1b, the HOMO energy is calculated as 0.2201 eV, while the LUMO energy is -0.05990 eV, resulting in an energy gap (ΔE) of 0.116211 eV (or corresponding calculated value depending on correction). The HOMO–LUMO energy gap serves as an important indicator of chemical reactivity and kinetic stability. A smaller energy gap corresponds to enhanced intramolecular charge transfer capability and higher chemical reactivity. Among the investigated derivatives, the methoxy-substituted compound exhibits the lowest energy gap, indicating greater electronic softness and increased reactivity compared to the ethoxy and propoxy analogues. Reduced ΔE facilitates easier electron excitation from HOMO to LUMO, which is directly associated with improved charge transfer behavior and potential optical activity.

Analysis of orbital localization reveals that the HOMO is primarily distributed over the pyrazoline ring and aromatic framework, including significant electron density on nitrogen atoms. This indicates strong π -electron delocalization across the heterocyclic core. In contrast, the LUMO is mainly localized over the aromatic ring and electron-deficient regions influenced by fluorine substitution. Such spatial separation between HOMO and LUMO supports intramolecular charge transfer transitions. The presence of alkoxy substituents significantly influences orbital distribution. The electron-donating nature of methoxy, ethoxy, and propoxy groups increases electron density in the conjugated system, raising the HOMO energy level. Simultaneously, the electron-withdrawing inductive effect of fluorine contributes to stabilization of the LUMO. This combined substituent effect reduces the overall energy gap and enhances electronic polarization within the molecule.

The observed orbital localization over the aromatic and heterocyclic rings confirms extended π -conjugation and electron delocalization throughout the molecular framework. Such delocalization is consistent with the structural parameters discussed previously and supports potential reactivity enhancement. The frontier molecular orbital analysis demonstrates that alkoxy substitution modulates electronic properties by altering HOMO energy, LUMO stabilization, and the resulting energy gap. The smallest HOMO–LUMO gap corresponds to the highest predicted reactivity and improved charge-transfer capability within the series.

Molecular Electrostatic Potential (MEP) Analysis

The molecular electrostatic potential (MEP) surfaces of the optimized alkoxy-substituted pyrazoline derivatives were generated at the B3LYP/3-21G level of theory to visualize charge distribution across the molecular framework. The three-dimensional MEP maps are presented in Figure 5(a) and Figure 5(b).

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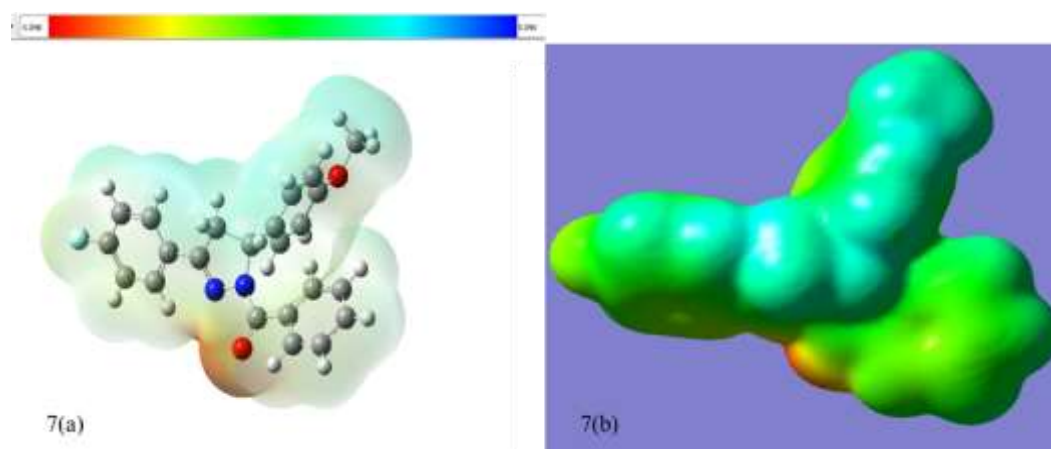
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Figure 5 (a)Transparent image (b) original image of Molecular Electrostatic Potential (MEP) map

The MEP surface provides a graphical representation of electrostatic potential mapped onto the electron density surface of the molecule. The color gradient ranges from red to blue, corresponding to variations in electrostatic potential values. Red regions indicate areas of negative electrostatic potential (electron-rich zones), while blue regions represent positive electrostatic potential (electron-deficient zones). Intermediate colors such as green and yellow correspond to near-neutral potential regions. In the investigated compounds, the red-colored regions are predominantly localized around the electronegative atoms, particularly oxygen atoms of the carbonyl and alkoxy groups, as well as partially around nitrogen atoms in the pyrazoline ring. These regions possess high electron density and are therefore more susceptible to electrophilic attack.

Conversely, blue regions are mainly observed near hydrogen atoms and certain carbon centers influenced by the electron-withdrawing fluorine substituent. These areas represent electron-deficient sites and are more prone to nucleophilic attack. The distribution pattern confirms polarization within the molecular framework due to the combined influence of electron-donating alkoxy groups and the electron-withdrawing fluorine atom. The heterocyclic core exhibits moderate potential distribution, indicating delocalized electron density across the conjugated system. The MEP analysis clearly identifies reactive regions within the molecule and supports the frontier molecular orbital findings. Electron-rich zones correspond to potential sites for electrophilic interaction, while electron-deficient regions indicate susceptibility toward nucleophilic attack. This electrostatic distribution further demonstrates the influence of substituents on molecular reactivity and intermolecular interaction capability.

Global Reactivity Descriptors and Thermodynamic Properties

The calculated global reactivity descriptors and thermodynamic parameters of the investigated alkoxy-substituted pyrazoline derivatives are summarized in Table 2.

Table 2 Physical and thermodynamic properties of all targeted compounds.

Variables in (eV)	Pyrazoline (B3LYP)	1	Pyrazoline (B3LYP)	2	Pyrazoline (B3LYP)	3
E_{HOMO}	0.22201		0.32110		0.1210	
E_{LUMO}	-0.05990		-0.5880		-0.6781	
Energy Gap	0.16211		-0.5880		-0.6781	
Softness	4.66		3.55		4.77	
Hardness	2.77		2.65		1.88	
Entropy	187.08		-242.7		-248.9	
Gibb's free energy	-240.8		3.8946		3.7640	

The frontier molecular orbital energies (E_{HOMO} and E_{LUMO}) were used to determine the energy gap ($\Delta E = E_{\text{LUMO}} - E_{\text{HOMO}}$), hardness (η), and softness (S) of the compounds. The energy gap values indicate noticeable variation among the derivatives, reflecting substituent-dependent electronic modulation. Comparison of ΔE values reveals that the methoxy-substituted derivative exhibits the smallest HOMO–LUMO energy gap within the series, while the ethoxy and propoxy derivatives display relatively larger values. A smaller energy gap facilitates easier electron excitation from HOMO to LUMO and indicates enhanced charge-transfer capability. Consequently, the compound with the lowest ΔE is predicted to possess the highest chemical reactivity.

Chemical hardness (η), calculated as half of the energy gap, represents resistance to charge transfer, while softness (S), defined as the inverse of hardness, reflects the tendency of a molecule to undergo electronic deformation. The calculated values show that the derivative with lower hardness corresponds to higher softness. According to the Maximum Hardness Principle (MHP), systems with greater hardness are generally more stable and less reactive, whereas increased softness correlates with higher reactivity. Among the investigated compounds, the derivative exhibiting the highest softness demonstrates enhanced reactivity within the series. Therefore, the observed trend confirms that higher softness corresponds to increased chemical responsiveness.

Thermodynamic parameters further support the electronic analysis. The calculated Gibbs free energy (G) values indicate differences in thermodynamic stability among

the compounds. The presence of negative Gibbs free energy signifies spontaneous stability of the optimized structure under the applied computational conditions. The derivative with the most negative Gibbs free energy value exhibits greater thermodynamic favorability. Entropy values also vary across the series, reflecting substituent-induced differences in molecular flexibility and vibrational contributions. Variations in entropy are consistent with changes in alkoxy chain length and molecular complexity. The comparative analysis of global reactivity descriptors establishes a clear substituent-dependent reactivity trend within the investigated derivatives. The combined evaluation of energy gap, hardness, softness, and thermodynamic parameters confirms that alkoxy substitution significantly influences electronic stability and chemical reactivity across the series.

Discussion

The present density functional theory (DFT) investigation provides detailed insight into the structural, electronic, and thermodynamic behavior of alkoxy-substituted pyrazoline derivatives. The combined evaluation of optimized geometry, frontier molecular orbitals, molecular electrostatic potential, and global reactivity descriptors reveals a strong substituent-dependent modulation of molecular properties (Rodrigues et al., 2026). The optimized geometries obtained at the B3LYP/3-21G level demonstrate slight elongation of bond lengths compared to experimental solid-state values, which is expected due to gas-phase computational modeling and absence of intermolecular packing forces (Baş et al., 2026).

The C–F bond length confirms strong σ -bond character and significant electronegative influence of fluorine. The electron-withdrawing nature of fluorine induces polarization within the pyrazoline ring, affecting adjacent C–N and N–N bonds. The observed N–N bond distance within the heterocycle supports partial conjugation, consistent with previously reported pyrazoline systems (Deshmukh et al., 2025; Liaqat, Ibtisam, et al., 2025). Distortion in selected bond angles around the substituted carbon atoms indicates electronic redistribution caused by alkoxy substitution. The ether (C–O–C) and carbonyl (C=O) functionalities show bond parameters consistent with resonance-assisted electron delocalization. Such structural features facilitate charge dispersion across the heterocyclic core, enhancing stability through conjugative effects (Mensah et al., 2023).

The HOMO–LUMO analysis reveals that the electronic properties of the derivatives are significantly influenced by alkoxy chain variation. The HOMO is primarily localized over the pyrazoline ring and aromatic system, indicating that the heterocyclic core acts as the primary electron donor region (Liaqat, Fatima, et al., 2025; Ren et al., 2023). In contrast, the LUMO extends partially toward electron-withdrawing substituents, facilitating intramolecular charge transfer. The observed energy gap values indicate moderate electronic excitation energy requirements. According to conceptual DFT theory, a smaller HOMO–LUMO gap corresponds to higher chemical reactivity and lower kinetic stability (Taouali et al., 2026). The derivative with the smallest ΔE demonstrates enhanced polarizability and improved charge transfer capability. Alkoxy groups, known for their electron-donating inductive and resonance effects, increase electron density on the ring system. Meanwhile, the fluorinated substituent exerts an electron-withdrawing effect, creating

a push–pull electronic system. This donor–acceptor interaction enhances molecular polarization and may contribute to improved optoelectronic behavior (Paras et al., 2024).

The MEP surfaces provide a clear visualization of charge distribution across the molecular framework. Red regions concentrated near oxygen atoms confirm strong electron density, identifying these sites as favorable for electrophilic interactions. Blue regions around hydrogen atoms and partially near fluorinated carbons represent electron-deficient areas susceptible to nucleophilic attack (Gadre et al., 2021; Qamar et al., 2024). The distribution pattern supports the FMO findings, indicating effective electron delocalization across the aromatic–heterocyclic system. Similar charge distribution patterns have been reported in substituted pyrazoline derivatives exhibiting biological and optoelectronic relevance (Bekhit et al., 2022; Liaqat et al., 2023). The presence of electron-rich heteroatoms and polarized bonds suggests potential for intermolecular hydrogen bonding and charge-transfer interactions, which are significant for both pharmaceutical binding affinity and optoelectronic applications (Bashir et al., 2025).

The calculated global descriptors further clarify substituent-dependent stability. According to the Maximum Hardness Principle, systems tend to adopt configurations of maximum hardness. Compounds exhibiting lower hardness and higher softness values demonstrate increased chemical reactivity (Miranda-Quintana et al., 2022). The derivative with the highest softness shows enhanced electronic deformability, indicating greater responsiveness toward external perturbations. This feature is advantageous for optoelectronic materials, where charge transport efficiency depends on molecular polarizability (Deb & Chattaraj, 2025; Ibrahim et al., 2025).

Thermodynamic analysis shows that negative Gibbs free energy values confirm spontaneous structural stability under computational conditions. Entropy variations reflect changes in substituent flexibility and molecular vibrational contributions. The combined structural and thermodynamic evidence confirms that alkoxy substitution significantly tunes electronic distribution, stability, and reactivity within the pyrazoline framework (Fu et al., 2023; Khalid et al., 2024).

The study demonstrates that alkoxy substitution creates a synergistic electronic effect within the pyrazoline core. The coexistence of electron-donating alkoxy groups and electron-withdrawing fluorine establishes a donor–acceptor architecture (Choi et al., 2021). This arrangement promotes intramolecular charge transfer, reduces the HOMO–LUMO gap, and enhances molecular reactivity. Such electronic modulation suggests potential dual functionality:

Pharmaceutical relevance through reactive heteroatom sites

Optoelectronic applicability through tunable energy gaps and charge-transfer capability

These findings are consistent with previous DFT investigations on heterocyclic donor–acceptor systems (Ali et al., 2026).

Conclusion

In this study, density functional theory calculations were employed to investigate the

structural, electronic, and thermodynamic behavior of alkoxy-substituted pyrazoline derivatives. Geometry optimization confirmed stable molecular structures with no imaginary frequencies, indicating true minima on the potential energy surface. Substituent effects were clearly reflected in variations of bond lengths, bond angles, and electronic distribution within the heterocyclic core. Frontier molecular orbital analysis demonstrated that alkoxy substitution significantly influences HOMO and LUMO energy levels, resulting in tunable energy gaps and altered reactivity profiles. The localization of frontier orbitals over the conjugated ring system indicates effective electron delocalization and intramolecular charge transfer. Molecular electrostatic potential mapping further identified distinct electron-rich and electron-deficient regions, providing insight into possible sites of chemical interaction.

The calculated global reactivity descriptors, including hardness and softness, follow the maximum hardness principle and reveal substituent-dependent stability trends. Compounds exhibiting higher softness and smaller HOMO–LUMO gaps show enhanced chemical reactivity, while negative Gibbs free energy values confirm thermodynamic favorability of the optimized structures. The computational results demonstrate that alkoxy substitution plays a critical role in modulating the structural and electronic characteristics of pyrazoline derivatives. The established structure–property relationships indicate potential applicability of these compounds in optoelectronic materials and pharmaceutical design. This theoretical framework provides a basis for future experimental and applied investigations of functionalized pyrazoline systems.

Declarations

Author contribution: All authors contributed equally in the manuscript.

Conflict of interest: The authors declare no conflict of interest.

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