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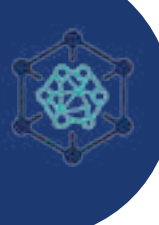
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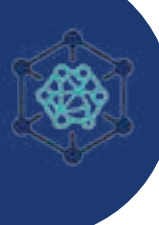
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Research Article

Synthesis of *E*-Chalcone Derivatives Bearing Different Substituent Groups and Evaluation of Substituent Effects on Their Spectroscopic Properties

Görkem Özcan¹Bleda Can Sadıkoğulları¹ Emre Can Uysal¹ Ayse Daut Özdemir^{1*} ¹Department of Chemistry, Faculty of Science and Letters, Istanbul Technical University, Istanbul, Türkiye**Abstract**

Chalcones are simple yet significant structures containing various examples of enolate chemistry. Nowadays, these compounds can be synthesized in various ways, such as through methods like Claisen-Schmidt condensation. This method is commonly used due to its ease of application, high efficiency, and method diversity in synthesis. Due to their unsaturated structures, chalcone derivatives can be used in different addition reactions. They can be modified with various functional groups to achieve desired properties using simple starting reactants. These advantages make chalcone derivatives suitable for a wide range of applications. Beyond their wide range of medicinal applications – driven by notable pharmacological properties such as anticancer, anti-HIV, and antibacterial activities – chalcone derivatives have also attracted considerable attention in materials chemistry as both optical sensors and heterocyclic intermediates for chemosensor applications. In this study, various chalcone derivatives bearing suitable functional groups were synthesized, and their structures were characterized while their optical properties were systematically investigated. The structural analyses performed following the syntheses not only confirmed the structures of the synthesized compounds but also examined and substantiated the effects of the functional groups present on the corresponding molecular scaffold in terms of NMR and optical properties.

Keywords: *E*-Chalcone, Claisen–Schmidt Condensation, Functional Group Effect.

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1. Introduction

The synthesis of novel compounds for industrial and scientific applications represents one of the continuously evolving areas of organic chemistry. In this context, the synthesis of novel chalcone derivatives has attracted considerable attention owing to their diverse physicochemical and biological properties. Chalcones are the molecules in which two aromatic rings bonded with α,β -unsaturated ketone structure [1]. They are polyphenolic compounds with colors ranging from yellow to orange, abundantly found in plants, and serving as the biogenetic precursors of flavonoids and isoflavonoids [2]. Stereochemically, they can exist as *E* and *Z* isomers. The *Z*- configuration is generally unstable because of strong steric hindrance between the carbonyl group and the aromatic ring, whereas the *E*- isomer is thermodynamically more stable (Figure 1a) [2]. Considering the *s*-cis and *s*-trans conformers of the molecule, the most stable chalcone isomer identified experimentally is the *trans*-(*s*-cis)-chalcone. This enhanced stability is attributed to the complete planar geometry of the molecule [3]. Chalcone derivatives are planted with secondary metabolites with diverse biological activities which play an important role in organic chemistry and specially in natural product chemistry. They have been used in different application areas such as the pharmaceutical industry due to their choleretic, anti-ulcer, antimicrobial, anti-HIV, anticancer, and central nervous system (CNS) activities [1-8]. Metochalcone (a choleretic drug) and sofalcone (an anti-ulcer and mucoprotective agent) are well-known examples of chalcone derivatives used in clinical applications [8-10] (Figure 1b). Besides these applications they can be served as chemical probes, fluorescent dyes, and sensors which chalcone derivatives functionalized with electron-withdrawing and/or electron-donating groups on their aromatic rings exhibit fluorescent properties [11-15] (Figure 1c).

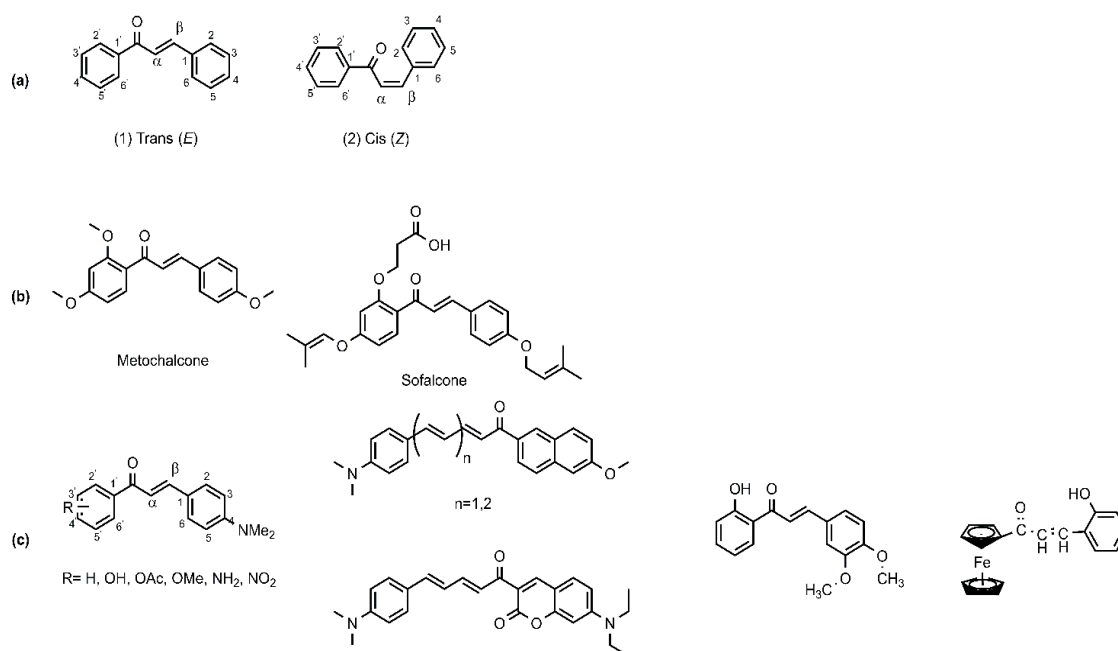


Figure 1. *E*- and *Z*- isomers of chalcones (a), Chemical structures of approved and clinically evaluated chalcones (b), Literature examples of chalcone derivatives (c) [11-15].

Additionally, chalcone derivatives used in chemical probes, fluorescence dyes, chemosensors [3,16,17] as well as intermediates in the production of sweeteners and as components of perfumes [18].

Because of their relatively simple synthesis and ease of structural modification, chalcones are widely used as versatile intermediates in the synthesis of more complex molecules [19]. For the synthesis of chalcone molecules, cross-aldol condensation which is known as Claisen-Schmidt condensation, is commonly used (Figure 2).



Also, Figure 3 presents examples of the Wittig reaction and coupling reactions, which are among the alternative methods currently employed for the synthesis of chalcones. Within the scope of this study, a series of *E*-chalcone derivatives were synthesized, and their structural characterization is presented in detail. The structural characterization of the synthesized compounds was discussed with particular emphasis on the effects of the substituent groups. Moreover, the optical properties of the synthesized dyes were investigated through absorption and emission studies. The chalcone derivatives synthesized in this study are listed in Table 1.

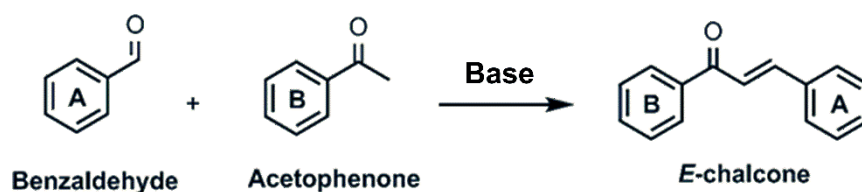


Figure 2. Synthesis of *E*-chalcone

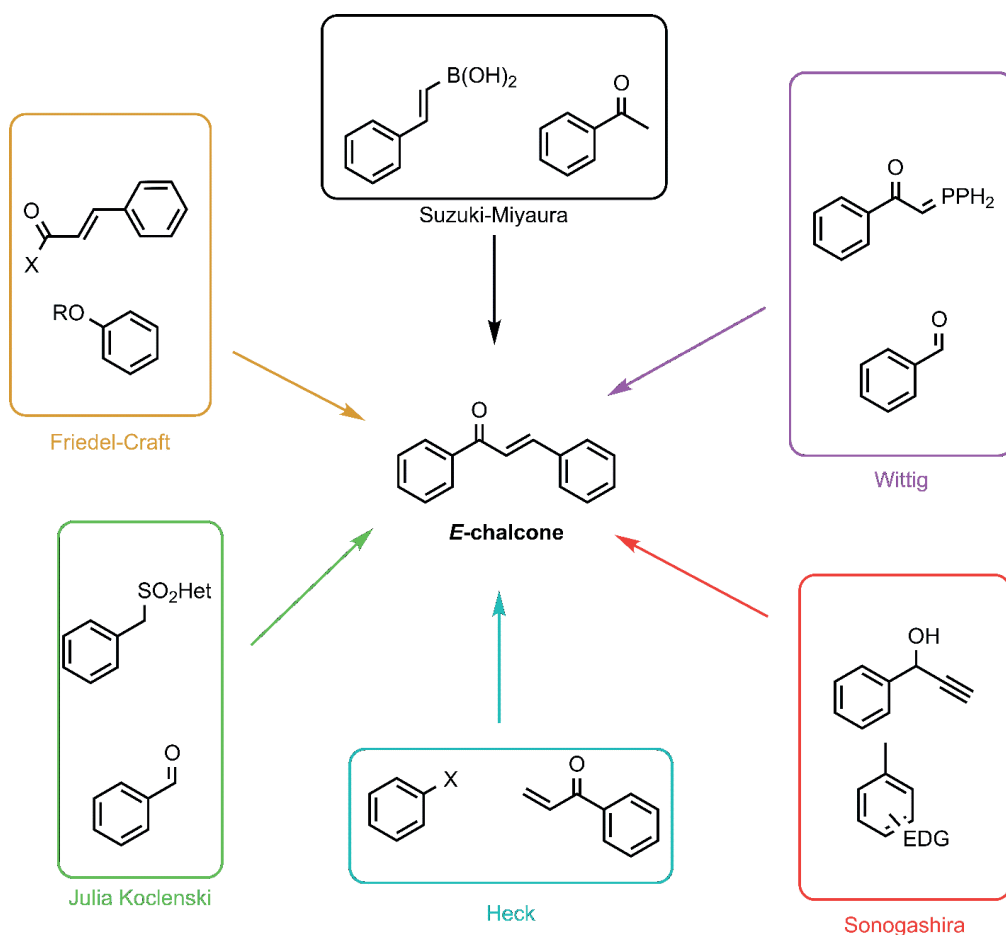


Figure 3. Various synthetic routes for the synthesis of *E*-chalcone [3]

2. Materials and Methods

All chemicals used for the syntheses (benzaldehyde, 2-hydroxybenzaldehyde, pyrene-1-carbaldehyde, acetophenone, 4-hydroxyacetophenone, sodium hydroxide, and hydrochloric acid) were purchased from Sigma-Merck and used without further purification. All solvents employed throughout this study (ethyl acetate, hexane, ethanol, dimethyl sulfoxide, and acetonitrile) were distilled when supplied in technical grade; otherwise, they were used as received.



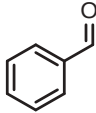
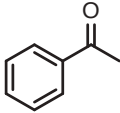
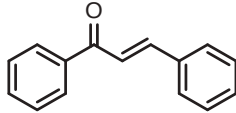
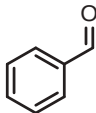
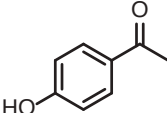
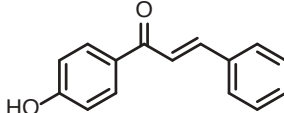
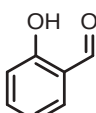
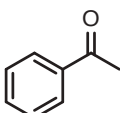
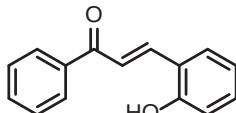
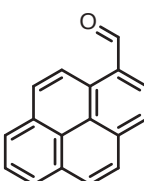
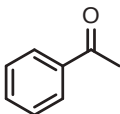
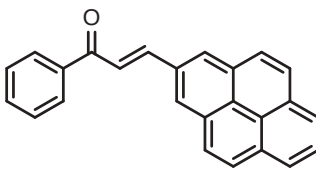
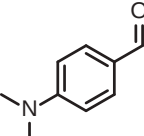
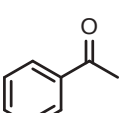
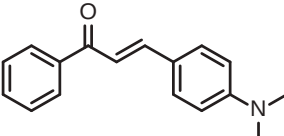
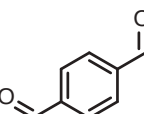
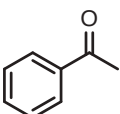
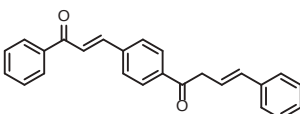


Structural characterization was performed using a Varian nuclear magnetic resonance (NMR) spectrometer, and all spectra were processed using MestReNova software. The chemical shifts of protons and carbons (500 MHz for ^1H NMR and 125 MHz for ^{13}C NMR) are reported in parts per million (ppm) relative to tetramethylsilane (TMS) as the internal standard. UV-Vis absorption spectra were recorded over the 190–1100 nm range using a T80+ UV-Vis spectrophotometer with 10 mm path-length quartz cuvettes. Fluorescence measurements were carried out at room temperature using an Agilent Cary Eclipse fluorescence spectrophotometer with a 10 mm path-length quartz cuvette.

2.1 Experimental Setup and Procedures

The α,β -unsaturated ketone compounds were synthesized via the Claisen–Schmidt condensation reaction. Equimolar amounts of a substituted acetophenone and an aromatic aldehyde derivative (1.25 mmol of the aromatic aldehyde derivative) were dissolved in ethanol and added dropwise at room temperature to a 10% aqueous sodium hydroxide solution (EtOH/H₂O, 4:5 v/v). The reaction mixture was stirred for 16 h, and the reaction progress was monitored by TLC. Upon completion, the mixture was neutralized with 4 N HCl in an ice bath. The reaction mixture was then stored in a refrigerator (+4 °C) overnight, allowing the product to precipitate. The precipitated solid was collected by filtration, washed with cold ethanol, and dried. When necessary, the crude products were further purified by recrystallization from ethanol [20-23].

Table 1. Synthesized *E*-chalcone derivatives

Aromatic Aldehyde Derivative	Substituted Acetophenone Compound	Synthesized Chalcone Derivative	Compound Name (Yield)
 Benzaldehyde	 Acetophenone	 <i>E</i> -chalcone	Chalcone-3 (90%)
 Benzaldehyde	 4-hydroxyacetophenone	 4'-hydroxy- <i>E</i> -chalcone	Chalcone-5 (95%)
 2-hydroxybenzaldehyde	 Acetophenone	 2-hydroxy- <i>E</i> -chalcone	Chalcone-6 (97%)
 Pyrene-1-carboxaldehyde	 Acetophenone	 (<i>E</i>)-1-phenyl-3-(pyren-2-yl)prop-2-en-1-one	Chalcone-7 (84%)
 4-dimethylaminobenzaldehyde	 Acetophenone	 4-dimethylamino- <i>E</i> -chalcone	Chalcone-9 (92%)
 terephthalaldehyde	 Acetophenone	 bis- <i>E</i> -chalcone	Chalcone-12 (86%)

Chalcone-3 (^1H NMR, 500 MHz, CDCl_3): 8.04 (d, 2H); δ = 7.83 (d, 1H); δ = 7.67 (d, 2H); δ = 7.60 (t, 1H); δ = 7.53 (m, 3H); δ = 7.44 (m, 3H). **Chalcone-3** (^{13}C NMR, 126 MHz, CDCl_3): 190.60, 144.87, 138.23, 134.90, 132.80, 130.56, 128.98, 128.64, 128.52, 128.46, 122.12.

Chalcone-5 (^1H NMR, 500 MHz, CDCl_3): 8.02 (d, 2H); δ = 7.83 (d, 1H); δ = 7.67 (d, 2H); δ = 7.60 (t, 1H); δ = 7.53 (m, 3H); δ = 7.44 (m, 3H). **Chalcone-5** (^{13}C NMR, 126 MHz, CDCl_3): 188.95, 160.10, 144.27, 135.02, 131.18, 131.17, 130.42, 128.95, 128.40, 121.84, 115.49.

Chalcone-6 (^1H NMR, 500 MHz, CDCl_3): 10.29 (s, 1H), 8.09 (d, 2H), 8.05 (d, 1H), 7.89 – 7.81 (m, 2H), 7.64 (t, 1H), 7.56 (t, 2H), 7.27 (t, 1H), 6.94 (d, 1H), 6.87 (t, 1H). **Chalcone-6** (^{13}C NMR, 126 MHz, CDCl_3): 189.98, 157.74, 140.03, 133.35, 132.53, 129.23, 129.11, 128.80, 121.83, 121.40, 119.87, 116.70.





Chalcone-7 (^1H NMR, 500 MHz, CDCl_3): 9.02 (d, 1H), 8.58 (d, 1H), 8.45 (d, 1H), 8.26 – 8.04 (m, 9H), 7.85 (d, 1H), 7.68 – 7.61 (m, 1H), 7.58 (d, 2H). **Chalcone-7** (^{13}C NMR, 126 MHz, CDCl_3): 190.23, 141.44, 138.42, 132.92, 132.86, 131.27, 130.68, 130.32, 128.72, 128.69, 128.65, 128.61, 127.31, 126.30, 126.06, 125.92, 125.01, 124.92, 124.55, 124.14, 123.83, 122.53.

Chalcone-9 (^1H NMR, 500 MHz, CDCl_3): 8.07 – 7.97 (m, 2H), 7.81 (d, 1H), 7.62 – 7.46 (m, 5H), 7.35 (d, 1H), 6.70 (d, 2H), 3.05 (s, 6H). **Chalcone-9** (^{13}C NMR, 126 MHz, CDCl_3): 190.71, 152.06, 145.89, 139.08, 132.16, 130.44, 128.47, 128.32, 116.89, 111.83, 40.14.

Chalcone-12 (^1H NMR, 500 MHz, CDCl_3): 8.08 – 8.00 (m, 4H), 7.82 (d, 2H), 7.70 (s, 4H), 7.64 – 7.51 (m, 8H). **Chalcone-12** (^{13}C NMR, 126 MHz, CDCl_3): 190.28, 143.58, 138.04, 136.88, 133.00, 128.99, 128.72, 128.55, 123.03

2.1.1. UV-Vis and Fluorescence Spectroscopic Analysis

The stock solutions of Chalcone-3 (1 mM), Chalcone-5 (1 mM), and Chalcone-7 (5 mM) were prepared in acetonitrile, whereas the stock solution of Chalcone-6 (1 mM) was prepared in dimethyl sulfoxide (DMSO). UV-Vis absorption measurements were performed over the concentration range of 0–80 μM , and the corresponding calibration curves were constructed. Also, owing to the presence of the pyrene moiety, the fluorescence emission spectrum of Chalcone-7 was recorded over the concentration range of 0–20 μM , and the corresponding fluorescence calibration curve was established.

3. Results

The functional groups present in a molecular structure, and their positions are among the key factors influencing the properties of the final product. In this study, we confirmed the structures of the synthesised *E*-chalcone derivatives through structural characterisation and investigated the effects of the functional groups on their properties.

The structural characterization of all synthesized compounds was carried out using ^1H NMR and ^{13}C NMR spectroscopy. Examination of the ^1H NMR spectra presented in Figure 4 revealed a coupling constant of approximately 15 Hz for the $\text{O}=\text{C}-\text{CH}=\text{CH}_2$ moiety. This large coupling constant clearly indicates the trans (*E*-) configuration of the double bond. Furthermore, the proton attached to the $\text{O}=\text{C}-\text{CH}$ fragment resonates at 7 ppm or higher, which can be attributed to the reduced shielding of this proton resulting from the extensive conjugation within the *E*-chalcone framework. Analysis of the chemical shifts corresponding to the $\text{O}=\text{C}(\text{R})-\text{CH}=\text{CH}_2-\text{R}$ moiety showed that, for each derivative, the proton attached to the β -carbon is less shielded than the proton attached to the α -carbon. This observation can be explained by the partial positive charge developed at the β -carbon due to the α,β -unsaturated carbonyl system. Based on the ^1H NMR analyses, the effects of different substituents can be evaluated by taking Chalcone-3 as the reference compound. Accordingly, Table 2 was prepared to summarize the chemical shifts of the α - and β -protons.

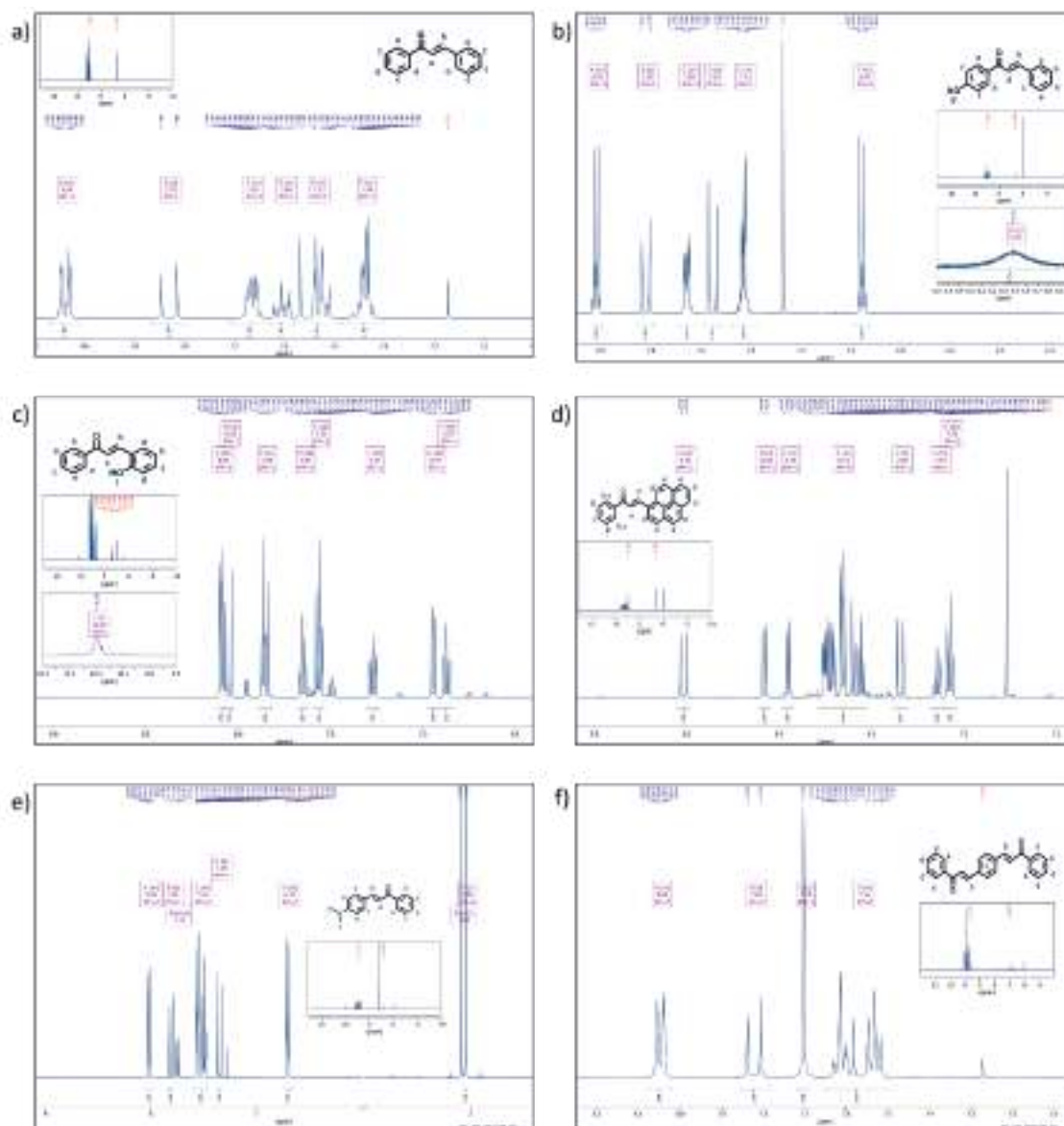


Figure 4. ¹H NMR spectra of Chalcone-3 (a), Chalcone-5 (b), Chalcone-6 (c), Chalcone-7 (d), Chalcone-9 (e) and Chalcone-12 (f)



**Table 2.** Chemical shifts of the α - and β -protons as a functional groups

Synthesized Derivative	Schematic representation and NMR chemical shifts (in ppm) of the α - and β -protons	Chemical Shift Analysis
Chalcone-3		Reference Compound
Chalcone-5		Although the hydroxyl function is an electron-donating group, no significant effect was observed due to the electron-withdrawing nature of the carbonyl group and its distance from the α , β -unsaturated bond.
Chalcone-6		While the hydroxyl function is an electron-donating group, the opposite effect was observed due to intramolecular hydrogen-bond formation involving the β -proton.
Chalcone-7		The extensive π -electron delocalization within the pyrene moiety increases <i>E</i> -chalcones' electron density, leading to reduced shielding of the β -position proton.
Chalcone-9		The electron-donating nature of the $N(CH_3)_2$ group leads to increased shielding, particularly at the α -position compared to the β -position, due to electron delocalization throughout the α , β -unsaturated system.
Chalcone-12		Chalcone-12 does not contain any additional functional groups.

Similarly, examination of the ^{13}C NMR spectra (Figure 5) revealed the absence of a signal at approximately 200 ppm, indicating that no aldehyde functionality remained in the final products. Furthermore, comparison with the starting ketones showed a noticeable shift in the resonance of the carbonyl carbon. This shift can be attributed to the fact that the synthesized *E*-chalcone derivatives are phenylstyryl ketone analogues, possessing greater electron density and a higher degree of π -electron delocalization than the corresponding starting ketones.

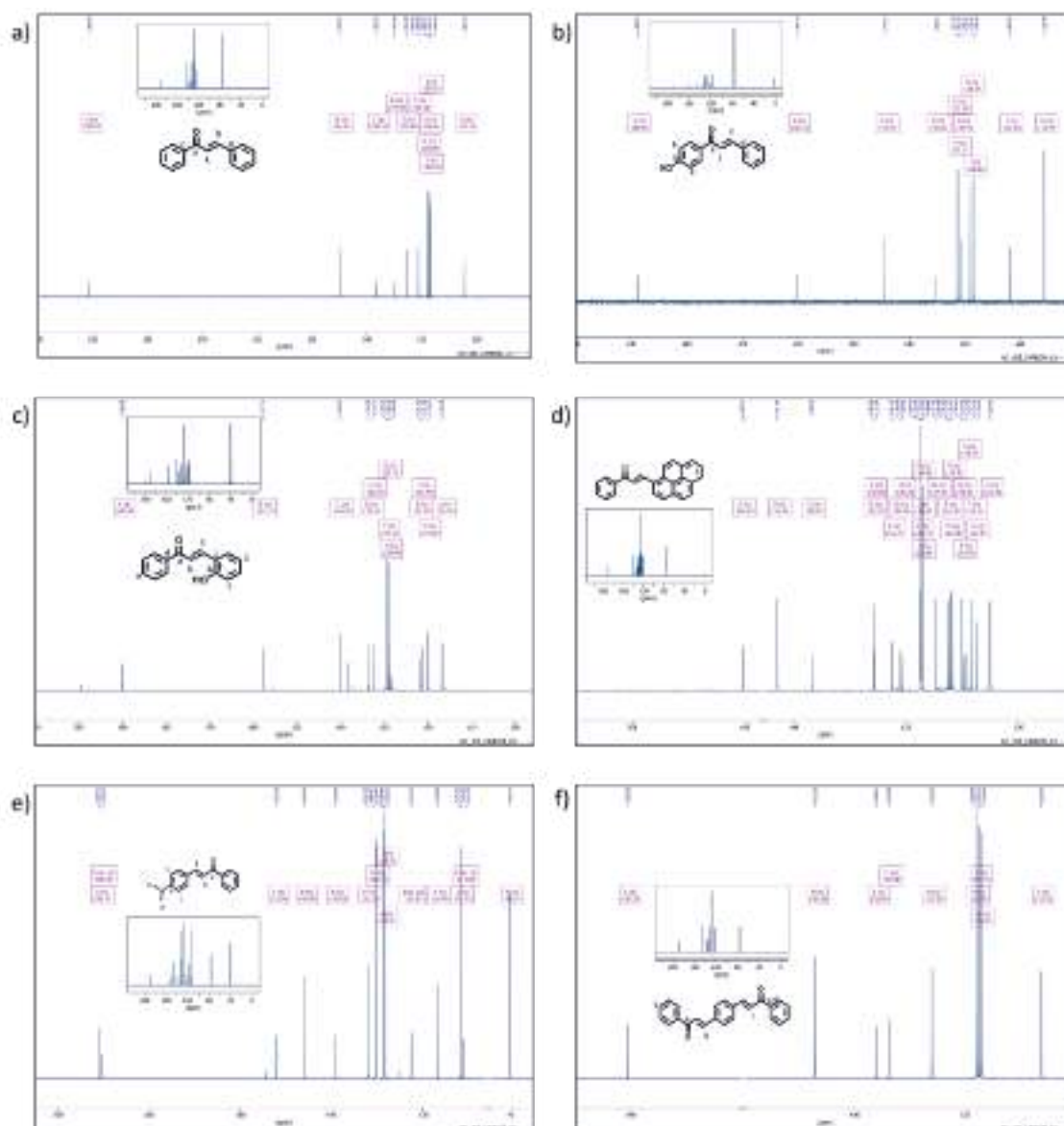


Figure 5. ^{13}C NMR spectra of Chalcone-3 (a), Chalcone-5 (b), Chalcone-6 (c), Chalcone-7 (d), Chalcone-9 (e) and Chalcone-12 (f)

The UV-Vis absorption spectra and the corresponding calibration curves of Chalcone-3, Chalcone-5, Chalcone-6, and Chalcone-7 are presented in Figure 7. Examination of the UV-Vis absorption spectra clearly demonstrate the electron-donating effect of the hydroxyl group through a red (bathochromic) shift in the maximum absorption wavelength. Furthermore, comparison of Chalcone-5 and Chalcone-6 shows that positioning the hydroxyl group on the aldehyde-derived aromatic ring increases the number of possible resonance structures within the conjugated system. As a result, a noticeable broadening of the absorption band is observed in the UV-Vis spectra. In addition, the UV-Vis absorption spectrum of Chalcone-6 exhibits a distinct double-peaked profile. Unlike the other derivatives, the absorption of Chalcone-7 is red-shifted to approximately 400 nm, which can be attributed to the presence of the pyrene moiety. Comparison with the absorption spectrum of pyrene itself clearly demonstrates the optical changes induced by the α,β -unsaturated conjugated system.

In addition to the UV-Vis absorption study, the fluorescence emission spectrum of Chalcone-7 was recorded because of its pyrene functionality, and the corresponding calibration curve is presented in Figure 6.

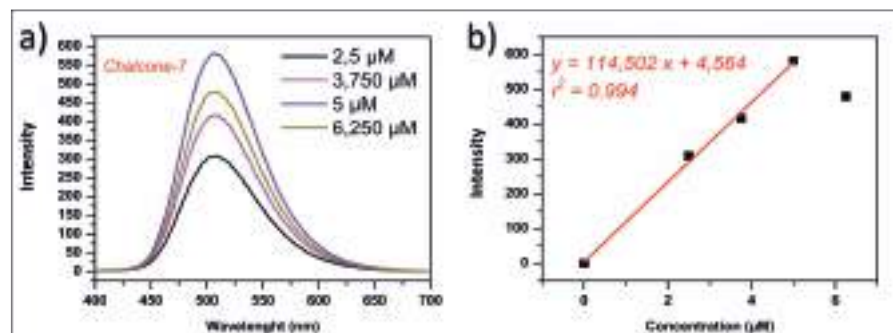


Figure 6. Fluorescence emission spectrum of Chalcone-7 (a), and the corresponding calibration curve (b)

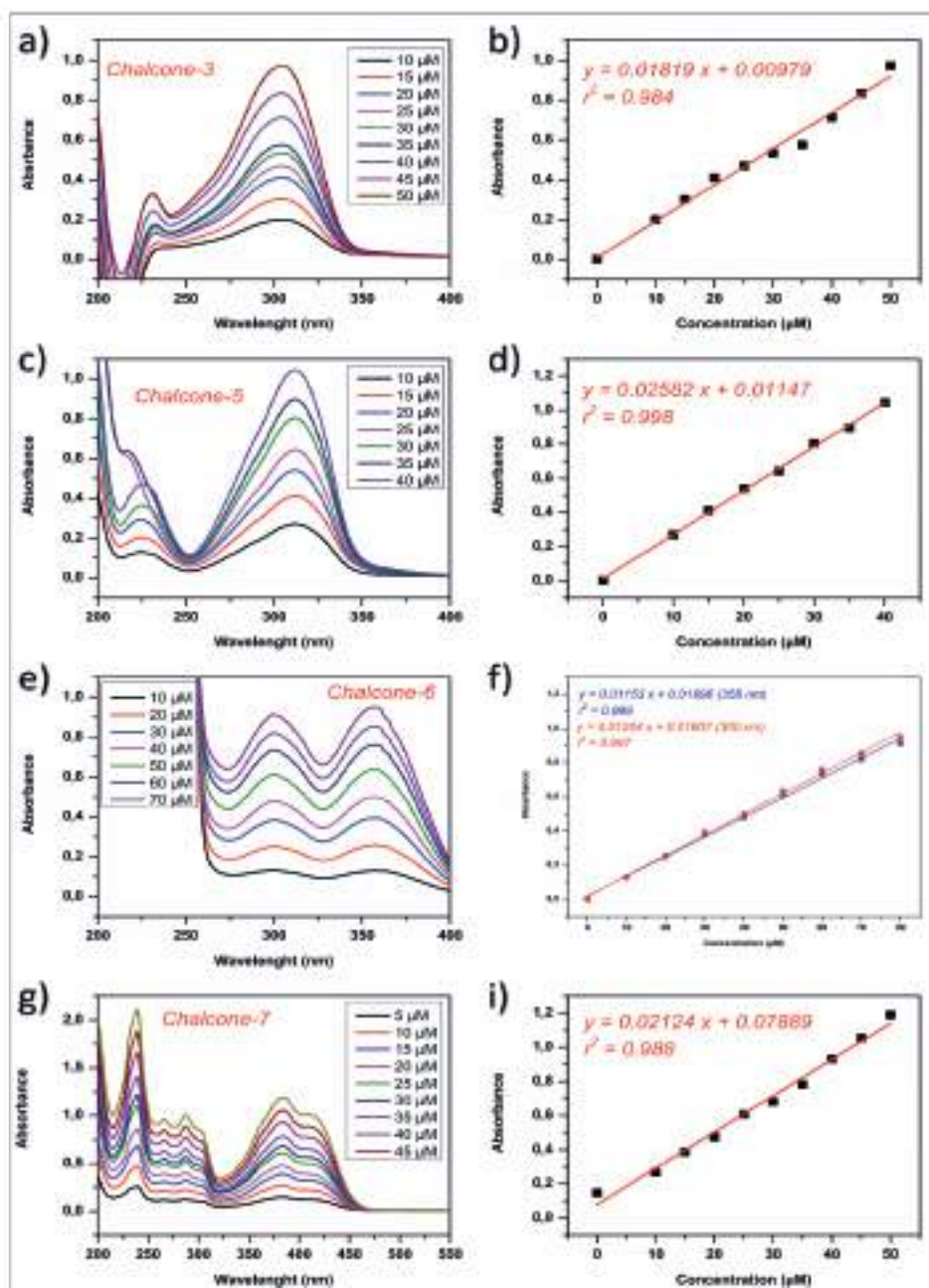


Figure 7. UV-Vis absorption spectrum of Chalcone-3 (a) and the corresponding calibration curve (b), UV-Vis absorption spectrum of Chalcone-5 (c), and the corresponding calibration curve (d), UV-Vis absorption spectrum of Chalcone-6 (e), and the corresponding calibration curve (f), UV-Vis absorption spectrum of Chalcone-7 (g), and the corresponding calibration curve (h).



4. Conclusions

Herein a series of substituted *E*-chalcone derivatives were successfully synthesized via Claisen-Schmidt condensation with high yields (up to 97%) under basic conditions in line with literature [20-23], and the resulting structures were confirmed by spectroscopic characterization. In this study, The Claisen-Schmidt reaction was performed in the synthesis of targeted chalcones, in which the reaction pathway proceeds through an aldol addition followed by dehydration step, whereby the base-catalyzed enolate of the methyl ketone attacks the carbonyl carbon of the benzaldehyde, and subsequent elimination of water furnishes the conjugated α,β -unsaturated ketone framework with the thermodynamically favored *E*- geometry [9]. Given that chalcones possess remarkable versatility as synthetic intermediates – specifically because of their α,β -unsaturated ketone core serving as an electrophilic Michael acceptor – that can be utilized in the construction of heterocyclic scaffolds, [24, 25] a comprehensive identification of substituent effects will provide valuable insights into their electronic tuning and chemical behavior. In the study, these effects were discussed over synthesized six different chalcones demonstrating that the optical and electronic properties of *E*-chalcones can be precisely fine-tuned by strategic functional group positioning and electronic modification. These structurally characterized derivatives provide a robust foundational library for the ongoing development of further heterocyclic scaffolds that can be utilized in various fields, such as fluorescent probes and chemosensors.

References

- [1] Patil CB, Mahajan SK, Katti SA. Chalcone: a versatile molecule. *J Pharm Sci Res* 2009;1(3):11-22.
- [2] Gomes M, Muratov E, Pereira M, Peixoto J, Rosseto L, Cravo P, et al. Chalcone Derivatives: Promising Starting Points for Drug Design. *Molecules* 2017;22:1210. doi: 10.3390/molecules22081210.
- [3] Rammohan A, Reddy JS, Sravya G, Rao CN, Zyryanov GV. Chalcone synthesis, properties and medicinal applications: a review. *Environ Chem Lett* 2020;18:433–58. doi: 10.1007/s10311-019-00959-w
- [4] Mahapatra DK, Bharti SK, Asati V. Chalcone scaffolds as anti-infective agents: Structural and molecular target perspectives. *Eur. J. Med. Chem.* 2015;101:496–524. doi: 10.1016/j.ejmech.2015.06.052.
- [5] Goyal K, Kaur R, Goyal A, Awasthi R. Chalcones: A review on synthesis and pharmacological activities. *J. Appl. Pharm. Sci.* 2021;11:001–14. doi: 10.7324/japs.2021.11s101
- [6] Królicka E, Kieć-Kononowicz K, Łazewska D. Chalcones as Potential Ligands for the Treatment of Parkinson's Disease. *Pharmaceuticals* 2022;15:847. doi: 10.3390/ph15070847.
- [7] Liu W, He M, Li Y, Peng Z, Wang G. A review on synthetic chalcone derivatives as tubulin polymerisation inhibitors. *J Enzyme Inhib Med Chem* 2021;37:9–38. doi: 10.1080/14756366.2021.1976772.
- [8] K. Sahu N, S. Balbhadra S, Choudhary J, V. Kohli D. Exploring Pharmacological Significance of Chalcone Scaffold: A Review. *CMC* 2012;19:209–25. doi: 10.2174/092986712803414132.
- [9] Zhuang C, Zhang W, Sheng C, Zhang W, Xing C, Miao Z. Chalcone: A Privileged Structure in Medicinal Chemistry. *Chem Rev* 2017;117:7762–810. doi: 10.1021/acs.chemrev.7b00020.
- [10] Higuchi K, Watanabe T, Tanigawa T, Tominaga K, Fujiwara Y, Arakawa T. Sofalcone, a gastroprotective drug, promotes gastric ulcer healing following eradication therapy for *Helicobacter pylori*: A randomized controlled comparative trial with cimetidine, an H₂-receptor antagonist. *J of Gastro and Hepatol* 2010;25. doi: 10.1111/j.1440-1746.2010.06232.x.





- [11] Mellado M, Sariego-Kluge R, Valdés-Navarro F, González C, Sánchez-González R, Pizarro N, et al. Synthesis of fluorescent chalcones, photophysical properties, quantitative structure-activity relationship and their biological application. *Spectrochim. Acta - A: Mol. Biomol. Spectrosc.* 2023;291:122332. doi: 10.1016/j.saa.2023.122332.
- [12] Ghorpade M, Rajput D, Mahalingam P, Kanvah S. Live cell imaging of lipid droplets: fluorescent chalcones as probes for lipophagy and lipid-mitochondria interactions. *J Mater Chem B* 2025;13:1338–49. doi: 10.1039/d4tb01871k.
- [13] Ratnawati D, Kartini I, Pranowo HD, Kurniawan YS, Wahyuningsih TD. Enhancement of the sensitivity of chalcone derived from vanillin as chemosensor agents for Hg(II) ions through cyclization reaction with arylhydrazine. *Chin. J. Anal. Chem.* 2024;52:100395. doi: 10.1016/j.cjac.2024.100395.
- [14] Liu Y, Zhang Z, Yin D, Huang Y, Liu Y, Li J, et al. A simple and highly selective chalcone fluorescent chemical sensor for the detection of tryptophane. *Polyhedron* 2025;265:117303. doi: 10.1016/j.poly.2024.117303.
- [15] Bhagya RS, Shetty P, Sunil D, Muthamma K, Kulkarni SD. Pyrene-based aggregation-induced emissive chalcone pigment in water-based flexographic ink for security printing. *Bull Mater Sci* 2025;48. doi: 10.1007/s12034-025-03441-2.
- [16] Rurack K, Bricks JL, Reck G, Radeaglia R, Resch-Genger U. Chalcone-Analogue Dyes Emitting in the Near-Infrared (NIR): Influence of Donor-Acceptor Substitution and Cation Complexation on Their Spectroscopic Properties and X-ray Structure. *J Phys Chem A* 2000;104:3087–109. doi: 10.1021/jp994269k.
- [17] Gupta A, Garg S, Singh H. Development of chalcone-based derivatives for sensing applications. *Anal Methods* 2020;12:5022–45. doi: 10.1039/d0ay01603a.
- [18] Manchanayakage R. *One-Pot Synthesis of Chalcone Epoxides via Claisen Schmidt Condensation and Epoxidation*. ACS Symposium Series 2016:111–22. doi: 10.1021/bk-2016-1233.ch007.
- [19] Farooq S, Ngaini Z. Synthesis, Molecular Docking and Antimicrobial Activity of α , β -Unsaturated Ketone Exchange Moiety for Chalcone and Pyrazoline Derivatives. *ChemistrySelect* 2020;5:9974–9. doi: 10.1002/slct.202002278.
- [20] Kagatkar S, Sunil D, Kekuda D, Satyanarayana MN, Kulkarni SD, Sudhakar YN, et al. Pyrene-based chalcones as functional materials for organic electronics application. *Mater. Chem. Phys.* 2023;293:126839. doi: 10.1016/j.matchemphys.2022.126839.
- [21] Pereira R, Silva AMS, Ribeiro D, Silva VLM, Fernandes E. Bis-chalcones: A review of synthetic methodologies and anti-inflammatory effects. *Eur J Med Chem* 2023;252:115280. doi: 10.1016/j.ejmech.2023.115280.
- [22] Silva WA, Andrade CKZ, Napolitano HB, Vencato I, Lariucci C, Castro MiriamRC de, et al. Biological and structure-activity evaluation of chalcone derivatives against bacteria and fungi. *J Braz Chem Soc* 2013;24:133–44. doi: 10.1590/s0103-50532013000100018.
- [23] Nurkenov OA, Ibraev MK, Schepetkin IA, Khlebnikov AI, Seilkhanov TM, Arinova AE, et al. Synthesis, Structure, and Anti-Inflammatory Activity of Functionally Substituted Chalcones and Their Derivatives. *Russ J Gen Chem* 2019;89:1360–7. doi: 10.1134/s1070363219070028.
- [24] Balan-Porcărașu M, Roman G. Novel chalcone analogs derived from 4-(benzyloxy)benzaldehyde. *Ovidius University Annals of Chemistry* 2023;34:112–20. doi: 10.2478/auoc-2023-0015.
- [25] Amin M, Shaykoon M, Marzouk A, Beshir E, Aburahama G. Recent Updates on Synthetic Strategies of Chalcone Scaffold and their Heterocyclic Derivatives. *J Adv. Biomed Pharm Sci* 2023;0:124–32. doi: 10.21608/jabps.2023.198509.1184.



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Research Article

Experimental Vibration Analysis of a Cantilever Beam Under Magnetic Levitation

Abdullah Turan^{1*} ¹ Department of Mechanical and Metal Technology, Sirnak Vocational School, Sirnak University, Sirnak, Türkiye**Abstract**

In this study, it is aimed to experimentally model a cantilever beam under the effect of electromagnetic force using a magnetic levitation (maglev) system and to investigate its vibration behavior. In the experimental setup, the free end of an aluminum beam fixed at one end is coated with a ferromagnetic material and exposed to the magnetic field generated by electromagnets. In this way, a contactless damping mechanism is achieved within the system.

In the established experimental setup, the dynamic responses of the beam were measured under excitations applied at different frequencies, and frequency response functions were obtained. Using these data, the natural frequency and damping characteristics of the system were determined, and subsequently, experimental modeling was carried out using a second-order transfer function through optimization methods.

Additionally, by varying the magnitude of the electromagnetic force, its effect on the damping ratio of the system was examined, and it was observed that increasing the magnetic force significantly reduces the vibration amplitude. Consistent with similar studies in the literature, it has been confirmed that the contactless electromagnetic damping method provides effective vibration suppression without altering the system dynamics compared to conventional mechanical dampers.

The obtained results demonstrate that maglev-based electromagnetic systems offer high accuracy and applicability in the experimental modeling of flexible structures and active vibration control. This study provides an experimental contribution to the literature on the modeling of beam systems using a contactless damping approach.

Keywords: Magnetic Levitation, Electromagnetic Damping, Beam Modeling, Experimental Analysis

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1. Introduction

In modern engineering applications, flexible beam-type structures (such as robotic arms, space structures, energy harvesting devices, and vibration sensors) exhibit sensitive dynamic behavior in response to external excitations. Accurate determination of the natural frequencies, mode shapes, and damping ratios of these structures plays a critical role in vibration control, structural health monitoring, and parameter identification. In particular, systems actuated by magnetic forces overcome the limitations of conventional mechanical excitation by enabling contactless actuation.

The dynamic behavior of flexible beam structures has long been studied in engineering systems for applications such as vibration control, structural health monitoring, and energy harvesting. Analytical models based on Euler–Bernoulli beam theory are commonly used as fundamental tools for predicting natural frequencies and mode shapes; however, experimental validation is essential due to material heterogeneity, boundary conditions, and additional components present in real systems [1].

Many studies have investigated the modal parameters of cantilever (fixed-free) beams with an attached tip mass. The additional mass significantly reduces the natural frequencies, alters the mode shapes, and affects the damping characteristics of the system. This effect is widely utilized in areas such as energy harvesting devices, parametric resonance, and structural parameter identification. Experimental and numerical studies have demonstrated the systematic influence of the added mass on frequency response functions (FRFs) [2].

In recent years, beam systems actuated by magnetic forces that provide contactless excitation have attracted increasing attention. Studies involving ferromagnetic tip coatings or magnetic actuators have enabled the acquisition of cleaner and more repeatable FRF data compared to traditional mechanical excitations. This approach has proven effective in applications such as active vibration control, electromagnetic damping, and magnetically coupled energy harvesting [3].

Guo, et al. [4] conducted a theoretical, simulation-based, and experimental study on the effects of added mass in weight-sensing structures, systematically revealing the different impacts of mass distribution, center of gravity, and stiffness distribution on natural frequencies. The results showed that added mass parameters significantly alter the frequencies, providing an important basis for the design of high-precision measurement systems.

Beam systems actuated by magnetic forces or incorporating magnetic coupling have become prominent due to their contactless excitation advantages. Feng, et al. [5] designed and experimentally investigated a broadband vibration energy harvester based on orthogonally magnetically coupled dual cantilever beams. By adjusting the magnetic angle and spacing, they optimized the coupling between two piezoelectric oscillators to widen the frequency bandwidth. Experimental results demonstrated that the proposed magnetic coupling configuration significantly improved energy harvesting efficiency and broadened the operating frequency range.

Electromagnetic actuation and damping techniques have also been effectively applied to ferromagnetic beams. Siddiqui, et al. [6] implemented electromagnetic damping on a flexible cantilever beam made of ferromagnetic material and experimentally compared vibration reduction under different electromagnetic force levels. Using a constant DC power supply, they proposed a new method and showed that increasing electromagnetic force significantly improves the damping ratio. Similarly, Gospodarič, et al. [7] developed an active electromagnetic damping system for a laterally vibrating ferromagnetic cantilever beam. Using a switching current amplifier and a pair of electromagnets, they aimed to actively control vibrations. Experimental results confirmed that the proposed system effectively reduces lateral vibrations.

Studies investigating the effect of added mass under different environmental conditions are also available in the literature. Sedlar, et al. [8] performed experimental modal analysis on a cantilever



beam partially submerged in water, comparing modal parameters in air and water environments and quantitatively determining the “added (virtual) mass” effect. Using modal added mass calculations along with model updating and reduction techniques, they showed that the frequency decrease in water is largely due to the added mass effect.

In the literature, processing experimentally obtained FRF data in MATLAB to develop parametric models is a common approach. However, studies systematically investigating variable added mass configurations combined with ferromagnetic tip coatings and performing FRF-based modeling under magnetic excitation are limited. The present study aims to fill this gap by coating the free end of a cantilever aluminum beam with ferromagnetic material to make it sensitive to magnetic forces, altering system dynamics with different added masses, and analyzing experimentally obtained FRFs for each configuration using MATLAB to develop a mathematical model. This approach provides a practical experimental framework for modal analysis and parameter identification of magnetically actuated flexible structures.

In this context, an aluminum beam fixed at one end and free at the other was designed, and its free end was coated with ferromagnetic material to make it responsive to magnetic forces. Different magnitudes of added masses were integrated into the system to gradually modify its dynamic characteristics, and experimental frequency response functions were obtained for each configuration. The acquired data were analyzed using MATLAB to develop the mathematical model of the system. This study aims to experimentally demonstrate the effect of the combination of magnetic actuation and variable mass on the modal analysis of flexible beams and to contribute a practical modeling approach to the literature.

2. Conceptual Framework

In this study, an aluminum beam fixed at one end and free at the other was first designed. The free end of the beam was coated with a ferromagnetic material to enable observation of the effect of magnetic forces on the beam motion. Then, different magnitudes of added masses were placed on the beam to alter the modal characteristics of the system. After each mass addition, the experimentally obtained frequency response functions were recorded in detail and analyzed in MATLAB, and the parametric modeling of the system was successfully completed.

3. Methods

The beam, made of Al 6063 material, was fixed at one end, while its free end was coated with ferromagnetic material and positioned inside the maglev device to be influenced by magnetic forces.

The dimensions of the aluminum beam used are $(360 \times 40 \times 0.7)$ mm. The chemical composition of the material is given in Table 1, and its mechanical properties are presented in Table 2.

Table 1. Chemical Composition of Al 6063 Material [9]

Fe	Si	Cu	Mn	Mg	Zn	Cr	Zi	Other
0.35	0.2-0.6	0.1	0.1	0.45-0.9	0.1	0.1	0.15	0.15

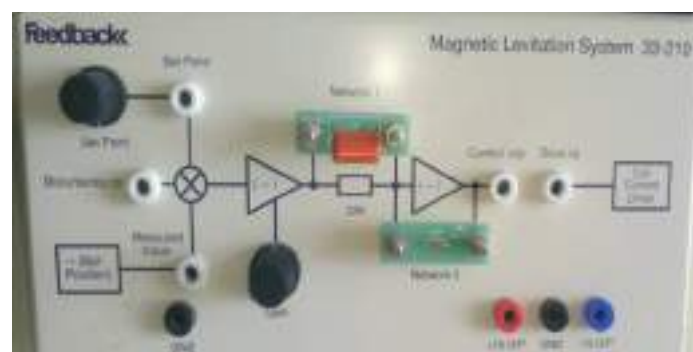


Table 2. Mechanical Properties of Al 6063 Material [9]

Temper	Yield (MPa) min-max	Strength min-max	Tensile Strength (MPa) min-max	Elongation (%50) min-max	Hardness (Brinell) min-max
0	50		100	26	25
T1	90		150	24	45
T4	90		160	21	50
T5	110-175		150-215	12	60
T6	170-210		205-245	12	75
T8	240		260	9	80

3.1. Magnetic Levitation System

In the experimental setup, a maglev device (Magnetic levitation system 33 – 210) was used to generate a magnetic field and determine the amplitude of vibrations in the cantilever beam (Figure 1). The maglev unit consists of a connection interface panel with a mechanical unit on which a coil is mounted. An infrared sensor is connected to the mechanical unit. Figure 2 shows the control panel of the maglev device.

**Figure 1.** Magnetic levitation system**Figure 2.** Control panel of the maglev device

The Maglev system measures 370 mm x 250 mm x 260 mm and weighs approximately 10 kg. The system has an internal power supply and can operate independently in analog mode without any computer control software.

3.2. Data Card

PCI 1711U data card was used in the experimental setup. The technical specifications of the 1711U DAQ card are given in Table 3. Here, the data card reads analog and digital inputs from all input lines.

Table 3. Specifications of the PCI-1711U DAQ Card

16-channel single-ended analog input
12-bit A/D converter with sampling rates up to 100 kHz.
Programmable gain
Automatic channel/gain display
FIFO panel memory (1,024 samples)
2 x 12-bit output channels
16-channel digital input and 16-channel digital output
Programmable calculator on the panel

To allow the free end of the fixed aluminum beam to be affected by the magnetic force coming from the coil, a low-carbon steel piece (35 x 40 x 1.7 mm) was glued to it with a special adhesive. The reason for gluing the low-carbon steel to the end of the aluminum beam is that the greatest vibration occurs in this region. The experimental system was set up by positioning the free end of the aluminum beam so that it was aligned with the coil and position sensors in the magnetic levitation device (Figure 3).

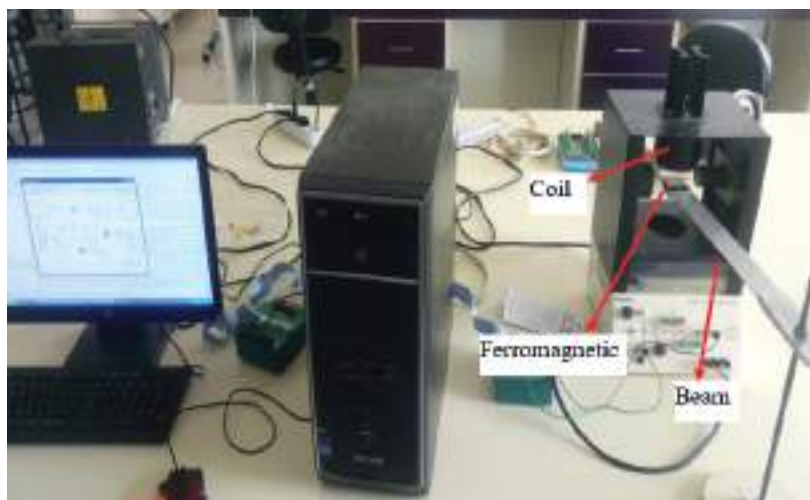


Figure 3. Experimental setup

The aim is to dampen the vibrations generated in the aluminum beam under magnetic forces. Subsequently, the system was modeled by integrating different mass values into the beam, and the experimentally determined frequency response functions were analyzed in the Matlab program.

4. Results and Discussion

In digital mode, the maglev system operates using MATLAB®/Simulink software. Feedback software for Simulink is provided for implementing control algorithms and the interface between the PC and the maglev system hardware. It runs in a MATLAB® environment that enables the determination of system parameters and modeling of the system. Figure 4 shows the MATLAB®/Simulink block diagram of the system. Real-time experiments were digitally configured and performed using this block diagram.

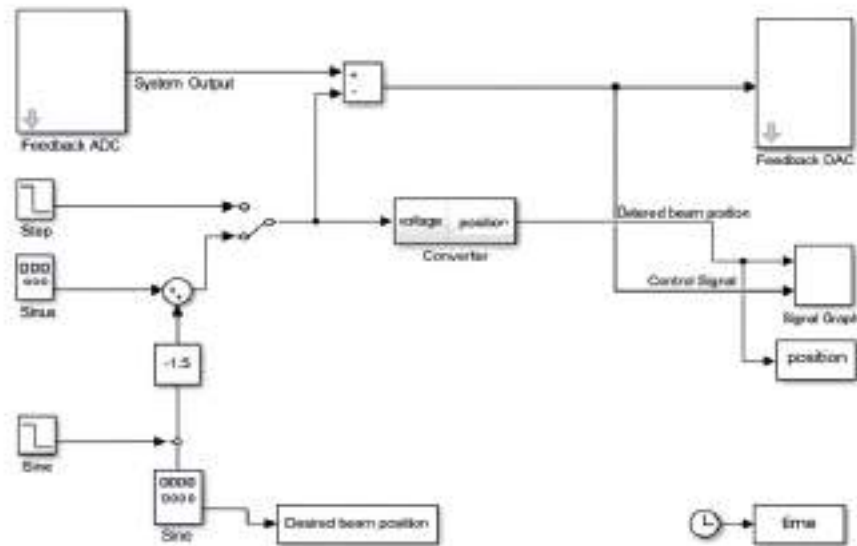


Figure 4. MATLAB® / Simulink model of the maglev system

In this study, the natural frequency of the beam was first determined by sending signals with a constant amplitude of 0.2 mm at different frequencies in the range of 2-10 Hz with a sinusoidal input to the system. The graphs below show the steady-state responses obtained in response to the sinusoidal inputs sent to the system (Figures 5-8). The response with the highest amplitude shows us that the resonance frequency of the system is the frequency given for the input. Therefore, knowing that the resonance frequency is also the natural frequency of the system, it is revealed that the natural frequency is 5.96 Hz (Figure 6(a)).

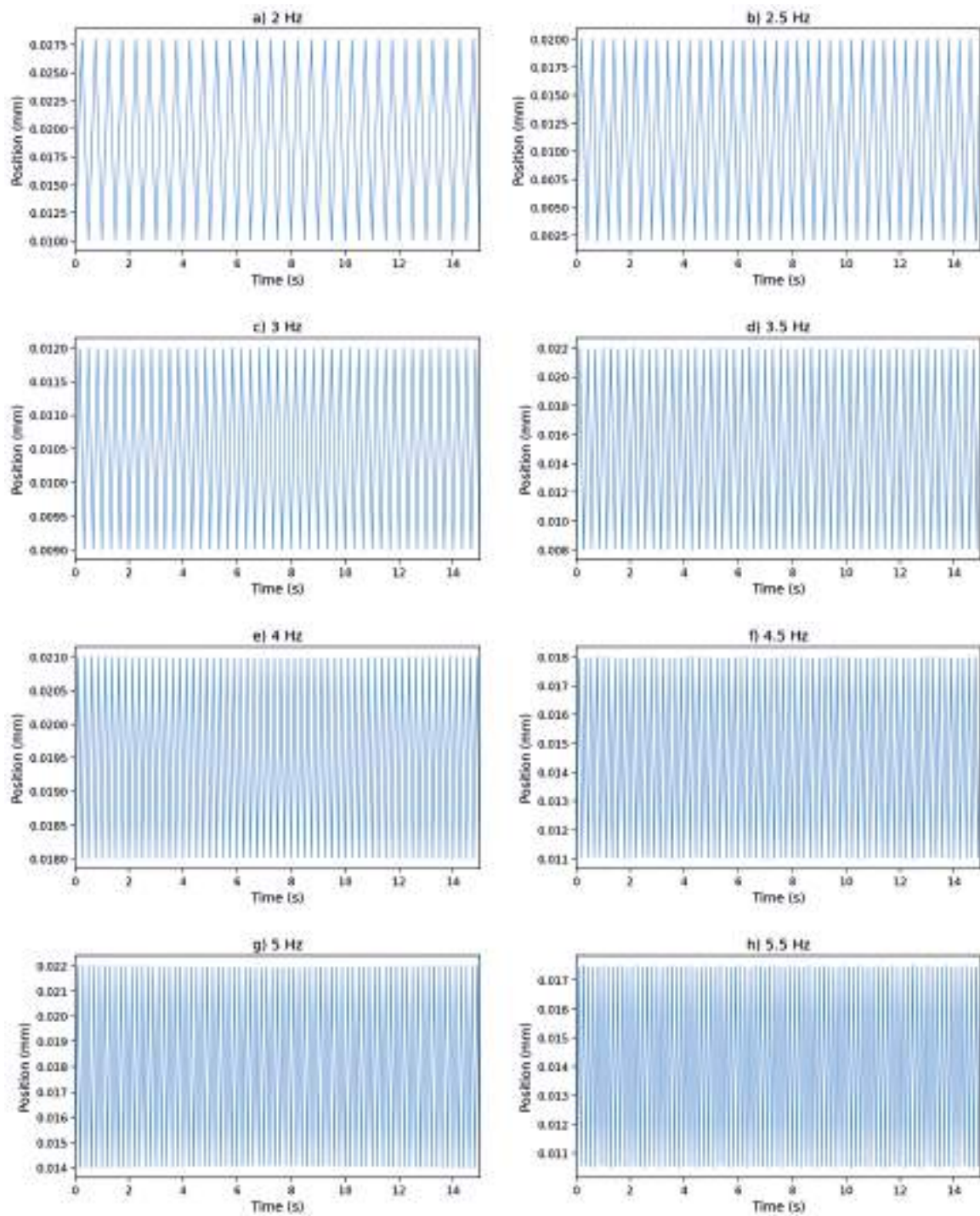


Figure 5. Responses obtained to sinusoidal inputs of different frequencies



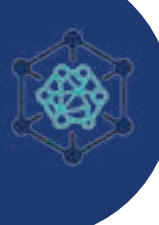
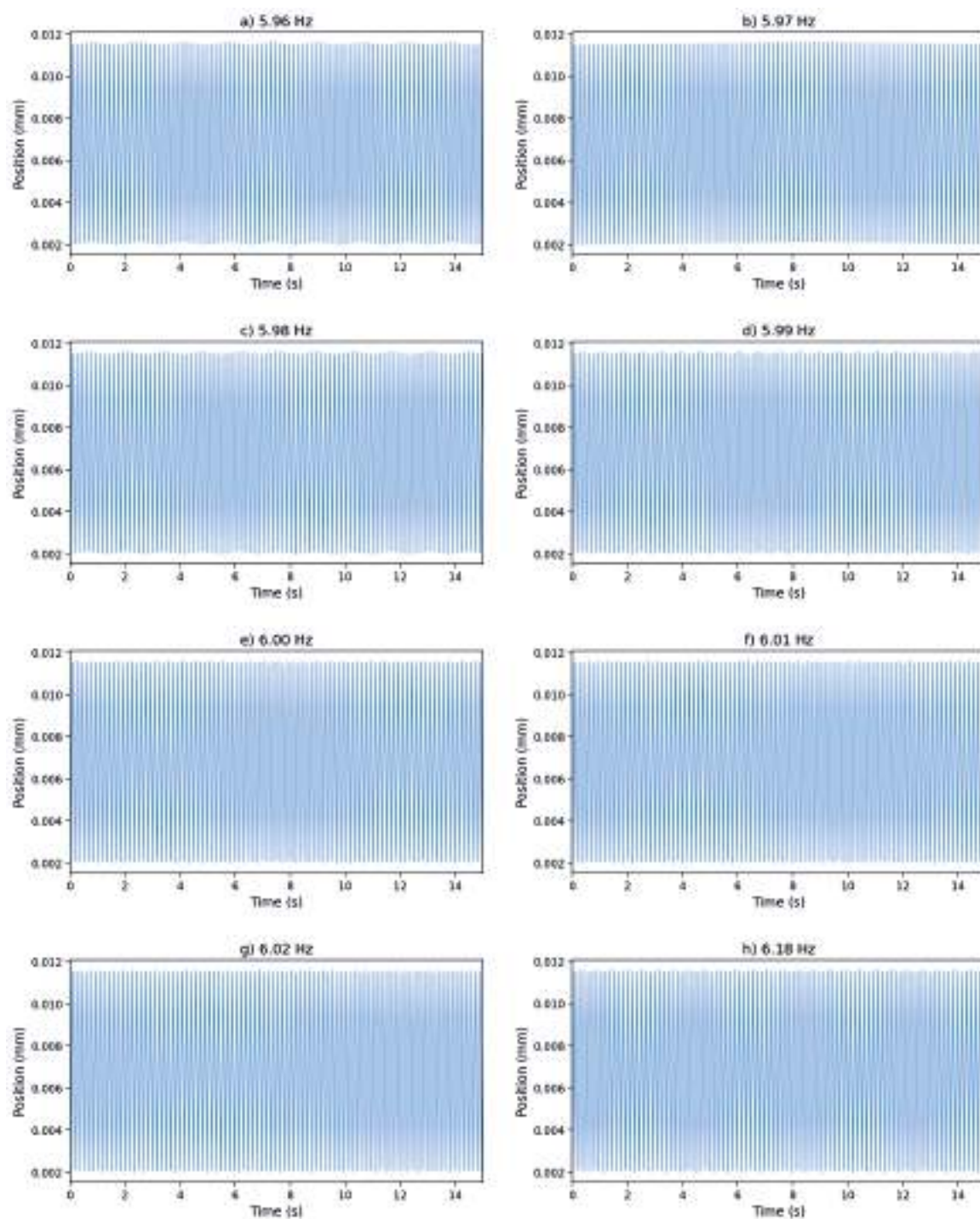


Figure 6. Responses obtained to sinusoidal inputs of different frequencies



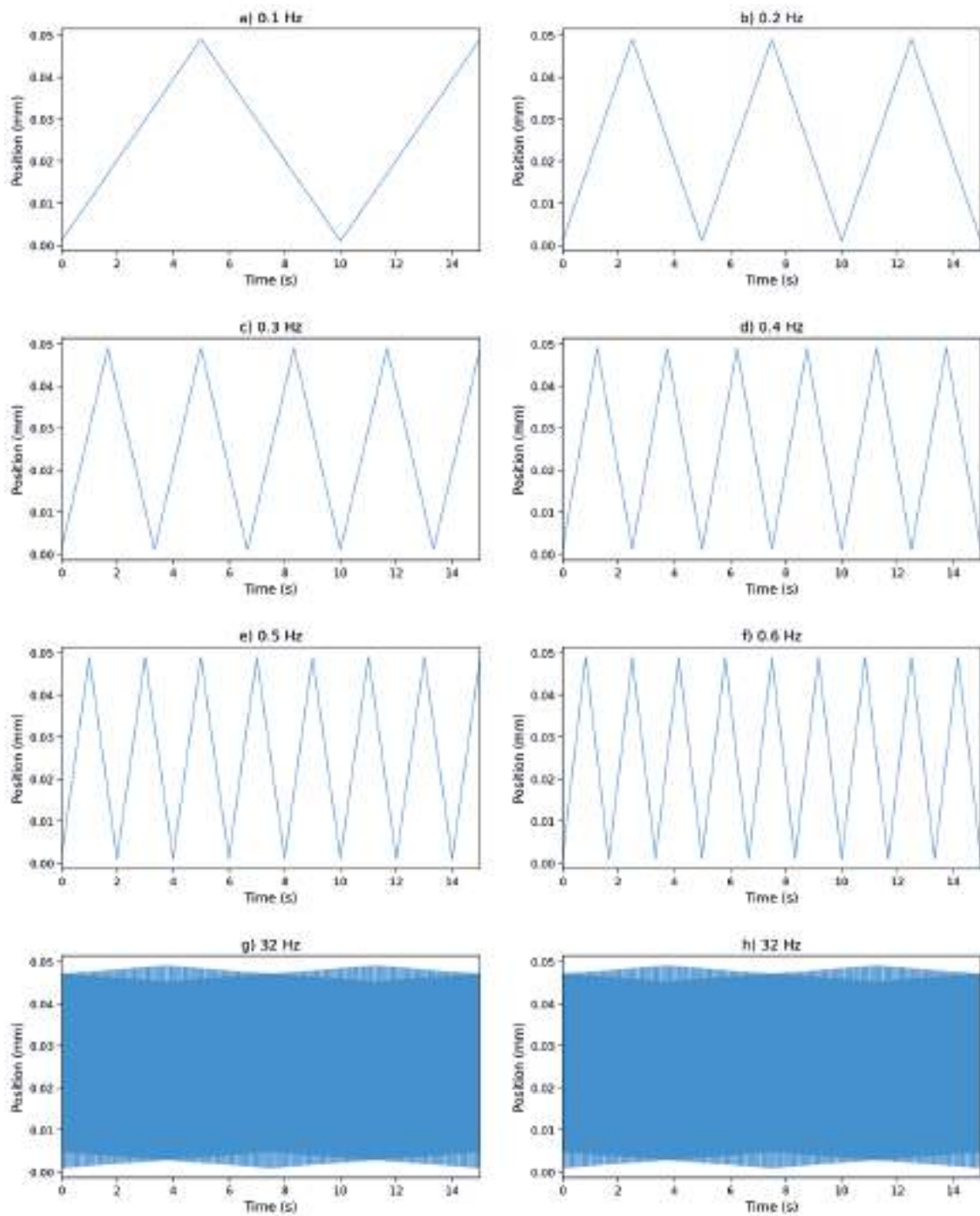


Figure 7. Responses obtained to sinusoidal inputs of different frequencies



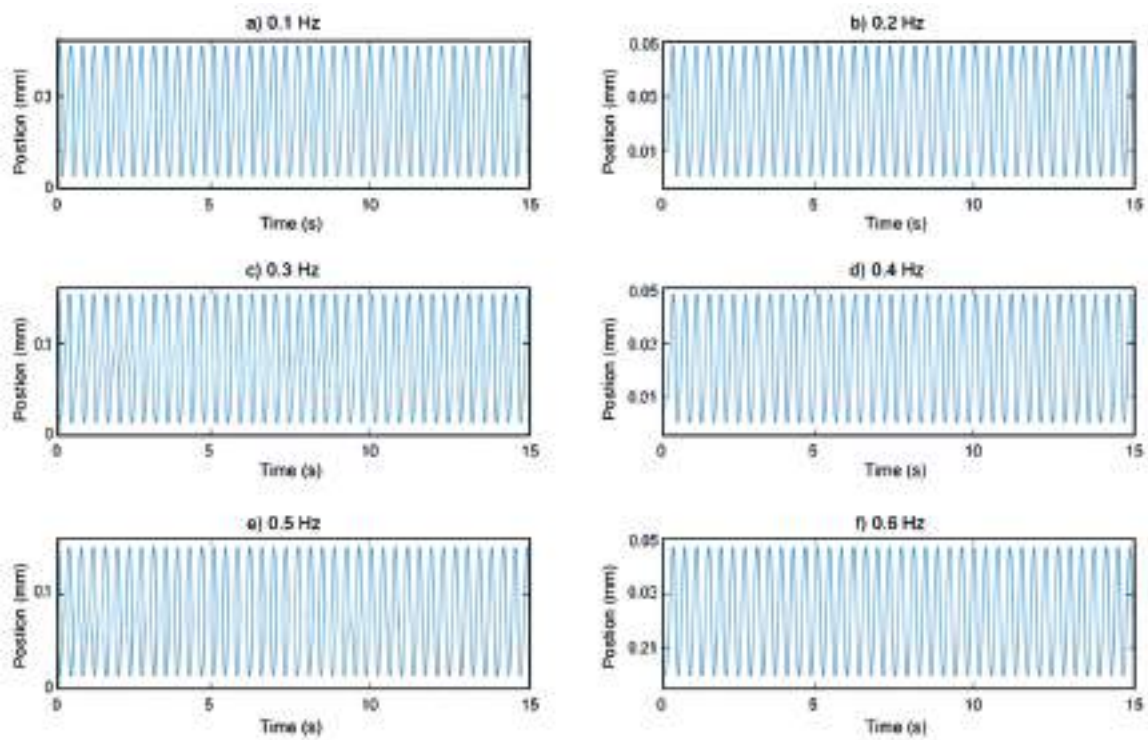


Figure 8. Responses obtained to sinusoidal inputs of different frequencies

Amplitude values were calculated in dB based on the steady-state responses obtained for different frequency (Hz) inputs, and Figure 3.9 was obtained corresponding to the input frequencies. Here, the frequency values were also converted to rad/s. The peak point in the graph is the natural frequency of the system and was calculated as 37.45 rad/s.

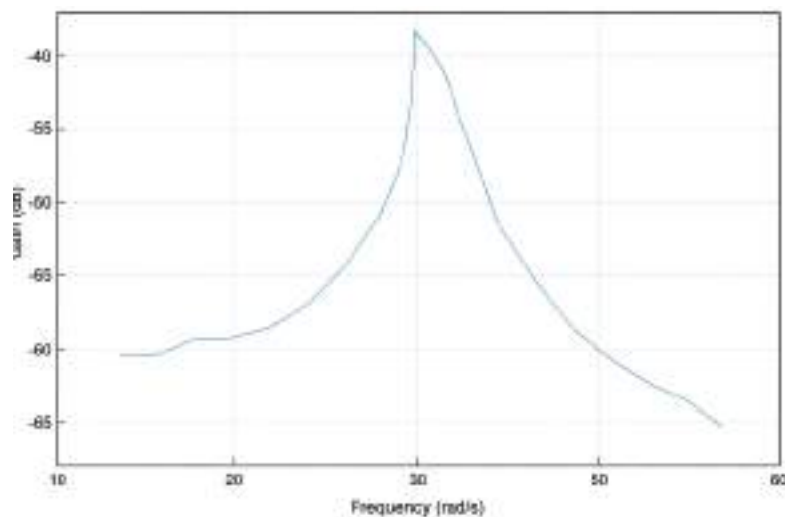


Figure 9. Amplitude-frequency graph obtained from experimental data

The characteristic equation was then used to obtain the system's transfer function (Equation 1).



$$G(s) = \frac{k}{s^2 + 2\xi\omega_n s + \omega_n^2} \quad (1)$$

Here, the natural frequency was experimentally determined as $\omega_n = 37.44$ rad/s. k and ξ represent the gain and damping ratios, respectively. The data obtained in the Matlab program were plotted on the Bode diagram (Figure 10), and the specified gain and damping ratio values were optimized using the `fmincon` command to obtain the closest gain and damping ratio values, thus obtaining the system's transfer function. The optimization results showed an error rate of 4.741% and a correlation coefficient of $R^2 = 0.9562$. Therefore, it can be said that the system's transfer function was successfully obtained through optimization (Figure 11).

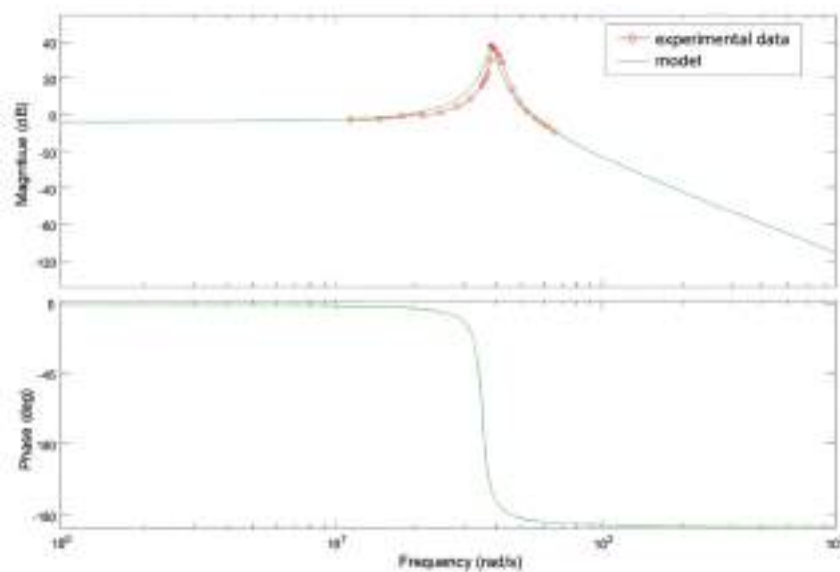


Figure 10. Experimental data and the plotting of the bode graph

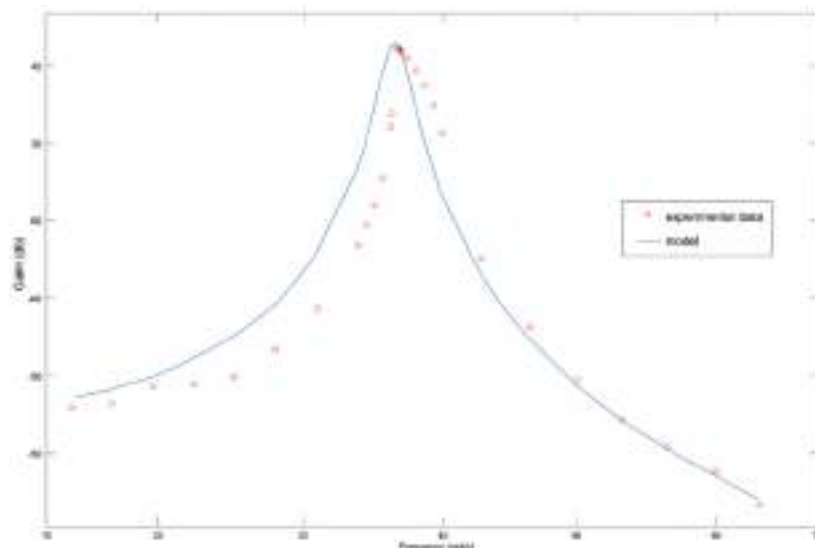


Figure 11. The graph obtained as a result of optimization

Figure 11 was obtained to provide a more detailed view of Figure 10. Through the optimization performed, $k=1.0913$ and $\xi=0.0304$ were found. Therefore, the transfer function of the system was obtained as follows (Equation 2).



$$G(s) = \frac{1.0913}{s^2 + 2.276s + 1402.34} \quad (2)$$

Finally, the phase angles of the obtained continuous response curves were calculated and plotted on the Bode diagram, resulting in Figure 12.

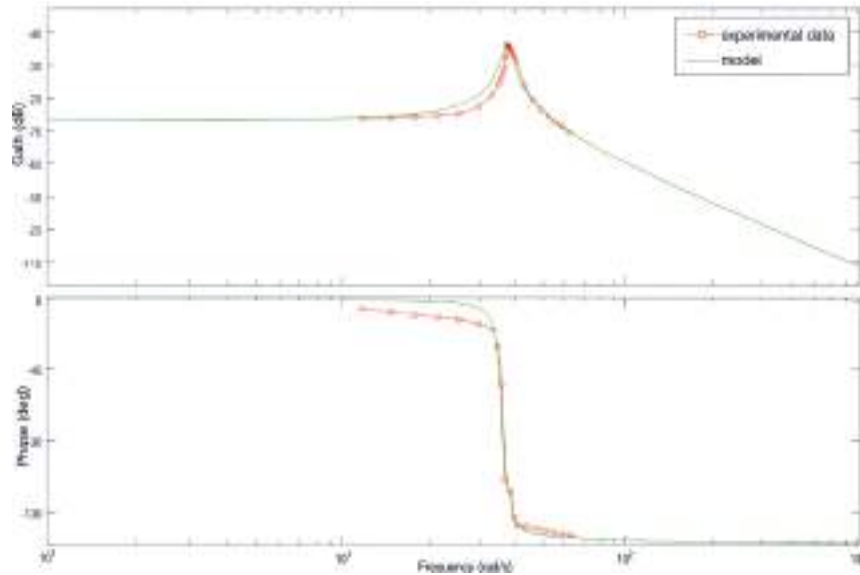


Figure 12. Experimental data and bode plot plot (Phase angle)

4. Conclusions

In this study, the dynamic behavior of a fixed-free aluminum beam under the influence of electromagnetic force was experimentally investigated using a magnetic levitation-based system, and the mathematical model of the system was successfully obtained. By coating the free end of the beam with ferromagnetic material, a contactless excitation and damping mechanism was created, thereby minimizing classical mechanical contact-related errors. As a result of the experimental analyses, the natural frequency of the system was consistently determined using both time-domain and frequency-domain data. Findings obtained from the frequency response functions showed that the system has a natural frequency of approximately 5.96 Hz (37.45 rad/s). This value is consistent with experimental observations and clearly reveals the resonant behavior of the system. The second-order transfer function of the system was obtained with high accuracy through optimization studies performed in MATLAB. The agreement of the obtained model with the experimental data was confirmed with an error rate of 4.741% and a correlation coefficient of $R^2 = 0.9562$. These results show that the proposed modeling approach reliably represents the system dynamics. Furthermore, when the effect of electromagnetic force on the system was examined, it was observed that as the magnetic effect increased, the vibration amplitude decreased and effective damping was achieved in the system. This shows that the electromagnetic damping method offers high efficiency along with the advantage of contactless control.

In conclusion, it has been shown that magnetic levitation-assisted electromagnetic systems are an effective, precise, and applicable method for experimental modeling of flexible structures and vibration control. This study provides an experimental contribution to the frequency response function-based modeling approach, especially in magnetically driven systems, and creates an important infrastructure for future studies in fields such as active vibration control, smart structures, and energy harvesting systems.



References

- [1] Abbas, Q., Nawaz, R., Yaqoob, H., Ali, H.M., and Jamil, M.M Nonlinear vibration analysis of cantilever beams: Analytical, numerical and experimental perspectives. *Partial Differential Equations in Applied Mathematics*. 2025;13. Doi.10.1016/j.padiff.2025.101115
- [2] Meesala, V. C. Modeling and analysis of a cantilever beam tip mass system. Master's thesis, Virginia Tech].2018. VTechWorks.
- [3] Jiang, J., Liu, S., Feng, L., and Zhao, D. A Review of Piezoelectric Vibration Energy Harvesting with Magnetic Coupling Based on Different Structural Characteristics. *Micromachines*, 2021;12(4), 436. <https://doi.org/10.3390/mi12040436>
- [4] Guo, G., Zhong, S., Zhang, Q., Zhong, J., and Liu, D. Effect of Additional Mass on Natural Frequencies of Weight-Sensing Structures. *Sensors*, 2023;23(17), <https://doi.org/10.3390/s23177585>
- [5] Feng, Y., Wang, J., Chen, X., and Liu, P. Experimental study of a broadband vibration energy harvester based on orthogonal magnetically coupled double cantilever beam. *Micromachines*, 2025;16(6), 722. <https://doi.org/10.3390/mi16060722>
- [6] Siddiqui, M. R., Ahmad, I., Khan, M., and Ahmad, S. M. Experimental analysis of electromagnetic vibration damping of a cantilever beam. In 2015 15th International Conference on Control, Automation and Systems (ICCAS) (pp. 736-4611). IEEE.
- [7] Gospodarič, B., Vončina, D., and Bučar, B. Active electromagnetic damping of laterally vibrating ferromagnetic cantilever beam. *Mechatronics*, 2007;17(6), 291-298. 10.1016/J.MECHATRONICS.2007.04.002
- [8] Sedlar, D., Lozina, Ž., and Vučina, D. Experimental investigation of the added mass of the cantilever beam partially submerged in water. *Tehnički vjesnik*, 2011;18(4), 589-594.
- [9] The Aluminum Association. *Aluminum standards and data 2024*. The Aluminum Association.





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Research Article

DFT and HF Study of Structural, Spectroscopic, Thermochemical, and Electronic Properties of 2-Ethoxy-5-fluoro-1H-pyrimidin-4-one

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Abstract

A comprehensive quantum-chemical investigation of 2-ethoxy-5-fluoro-1H-pyrimidin-4-one ($C_6H_7FN_2O_2$) was carried out using density functional theory (DFT) and Hartree-Fock (HF) methods at the B3LYP/6-31+G(d,p) and HF/6-31+G(d) levels to elucidate its structural, spectroscopic, thermochemical, charge distribution, and electronic properties. The optimized geometry reveals a stable heterocyclic structure in which the pyrimidinone ring, fluorine substituent, carbonyl group, and ethoxy moiety collectively govern the molecular electronic structure. The calculated geometrical parameters indicate good agreement between the theoretical approaches, confirming the reliability of the optimized molecular model. Theoretical ^1H and ^{13}C NMR chemical shifts were evaluated using the GIAO method and compared with available experimental data recorded in $CDCl_3$. The DFT calculations reproduce the experimental chemical shifts more accurately than the HF method, highlighting the importance of electron-correlation effects in predicting magnetic shielding constants. Significant deshielding is observed for carbon atoms bonded to electronegative nitrogen, oxygen, and fluorine atoms, whereas the ethoxy-group carbons and hydrogen atoms exhibit comparatively lower chemical shifts. Atomic charge distributions were also analyzed using both Mulliken population and atomic polar tensor (APT) schemes. The results reveal pronounced electronic polarization within the molecule, with carbonyl oxygen, fluorine atom, and pyrimidine nitrogen atoms carrying substantial negative charge densities,

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while several carbon and hydrogen atoms exhibit positive charge accumulation. The calculated charge distribution confirms the existence of efficient intramolecular charge redistribution regulated by the combined electron-withdrawing effects of fluorine and carbonyl functionalities. Additionally, thermochemical calculations indicate that the molecule possesses favorable energetic stability, while the calculated dipole moment displays its polar molecular nature. Frontier molecular orbital (FMO) analysis displays that the HOMO is mainly localized over the pyrimidinone ring and heteroatom-rich regions, whereas the LUMO is concentrated around the carbonyl- and fluorine-containing portions of the heterocyclic structure. This spatial separation facilitates intramolecular charge-transfer processes. The HOMO-LUMO energy gap together with the derived global reactivity descriptors, including electronegativity, chemical hardness, softness, chemical potential, and electrophilicity index, indicate a balanced combination of electronic stability and chemical reactivity. UV-Vis spectral analysis reveals that the electronic absorption behavior is dominated by $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions involving the conjugated heterocyclic system and heteroatom lone-pair electrons. Furthermore, electrostatic potential (ESP) and molecular electrostatic potential (MEP) analyses identify the carbonyl oxygen atom, fluorine atom, and ring nitrogen atoms as the most electron-rich regions, while the N-H and ethoxy hydrogen atoms constitute the principal positive potential zones. All in all, the theoretical results obtained show that 2-ethoxy-5-fluoro-1H-pyrimidin-4-one possesses a highly polarized electronic structure, well-defined reactive centers, and favorable charge-transfer characteristics. The findings provide a detailed understanding of its structural stability, spectroscopic behavior, and reactivity patterns, suggesting potential relevance in pharmaceutical, agrochemical, and functional-material applications [1,2,3].

Keywords: 2-Ethoxy-5-fluoro-1H-pyrimidin-4-one; Atomic charge distribution; UV-Vis spectroscopy; FMO analysis; Thermochemical properties.

1. Introduction

Heterocyclic compounds containing pyrimidine rings constitute one of the most important classes of organic molecules owing to their central role in medicinal chemistry, biochemistry, and materials science. Pyrimidine derivatives form the structural backbone of several naturally occurring nucleobases and exhibit a broad spectrum of biological activities, including antiviral, antibacterial, antifungal, antitumor, and anti-inflammatory properties. Consequently, understanding the structural and electronic characteristics of pyrimidine-based molecules has attracted considerable interest from both experimental and theoretical researchers [1–3].

Among fluorinated heterocycles, fluoropyrimidine derivatives have received particular attention because the introduction of fluorine significantly modifies molecular polarity, electronic distribution, metabolic stability, intermolecular interactions, and biological activity. Owing to its high electronegativity and small atomic radius, fluorine can alter charge density distribution and molecular reactivity without substantially perturbing the molecular structure. The characteristics mentioned have made fluorinated pyrimidines important building blocks in pharmaceutical synthesis and medicinal chemistry, especially in the development of antimetabolites, antiviral agents, and anticancer drugs [4–6].

The compound investigated in the present work, 2-ethoxy-5-fluoro-4-pyrimidinone (also known as 2-ethoxy-5-fluoro-1H-pyrimidin-4-one, 2-ethoxy-5-fluoropyrimidin-4(¹H)-one, 4(¹H)-pyrimidin one, 2-ethoxy-5-fluoro-, and 5-fluoro-2-ethoxy-4-pyrimidinone), belongs to the fluorinated pyrimidinone family and possesses the molecular formula C₆H₇FN₂O₆. The molecule contains a conjugated pyrimidinone ring incorporating two nitrogen atoms, a fluorine substituent, and an ethoxy functional group, providing a chemically versatile framework with potentially interesting electronic and spectroscopic properties [7–9]. Furthermore, this compound has been reported as an intermediate and





impurity related to fluoropyrimidine-based pharmaceutical compounds and fluorouracil derivatives, further increasing its chemical significance.

From a molecular physics perspective, the coexistence of electron-withdrawing fluorine, heteroatomic nitrogen centers, and oxygen-containing functional groups generates a complex electronic environment regulated by intramolecular charge transfer, orbital delocalization, hydrogen-bonding tendencies, and tautomeric effects. The features discussed can strongly influence molecular stability, frontier molecular orbitals, dipole moment, nonlinear optical behavior, and spectroscopic signatures [10–13]. Despite the potential importance of the fluorinated pyrimidinone derivative, detailed investigations concerning its electronic structure, quantum-chemical descriptors, charge-transfer characteristics, and spectroscopic properties remain relatively limited.

Recent advances in quantum computational theories such as Hartree-Fock (HF) and especially density functional theory (DFT) have provided powerful tools for investigating molecular systems at the atomic level. Particularly, DFT calculations enable accurate prediction of optimized molecular geometries, vibrational frequencies, electronic transitions, molecular electrostatic potential distributions, frontier molecular orbital energies, global reactivity descriptors, and intermolecular interaction sites. The integration of experimental spectroscopy with quantum-chemical calculations therefore provides a comprehensive understanding of the structure-property relationships governing molecular behavior [14–17]. Accordingly, the primary objective of the present study is to perform a comprehensive atomic and molecular-level investigation of 2-ethoxy-5-fluoro-4-pyrimidinone using advanced quantum-chemical approaches. Detailed analyses of molecular geometry, electronic structure, frontier molecular orbitals, charge distribution, molecular electrostatic potential, global reactivity descriptors, and spectroscopic characteristics are conducted to elucidate the fundamental physicochemical properties of this fluorinated pyrimidinone derivative. The obtained results are expected to contribute to a deeper understanding of fluorinated heterocyclic compounds and to provide valuable theoretical insight for future pharmaceutical, chemical, and materials-related applications.

The presence of a fluorine substituent, an ethoxy functional group, and a heteroaromatic pyrimidinone ring makes 2-ethoxy-5-fluoro-4-pyrimidinone ($C_6H_7FN_2O_2$) an attractive molecular system for both experimental and theoretical investigations. The coexistence of electron-withdrawing fluorine atoms and electron-donating alkoxy groups within the same conjugated heterocyclic framework generates a complex electronic environment characterized by charge redistribution, orbital delocalization, and intramolecular polarization effects. Furthermore, pyrimidinone derivatives constitute an important class of heterocyclic compounds widely employed as intermediates in pharmaceutical synthesis, medicinal chemistry, and biologically active molecular architectures. Consequently, understanding the relationship between molecular structure, electronic configuration, and chemical reactivity is essential for elucidating the physicochemical behavior of such fluorinated heterocyclic systems [18, 19].

In recent decades, computational quantum chemistry has emerged as an indispensable tool for investigating molecular systems at the atomic and electronic levels. The rapid development of computational methodologies and high-performance computing resources has enabled accurate prediction of structural, spectroscopic, thermodynamic, and electronic properties that are often difficult or impossible to determine exclusively through experimental techniques [20, 21]. Among the available theoretical approaches, HF and DFT calculation methods remain the most widely utilized methods for studying organic and heterocyclic molecules owing to their favorable balance between computational efficiency and predictive accuracy [22].

The HF method represents one of the earliest and most fundamental *ab initio* quantum-mechanical approaches for solving the many-electron Schrödinger equation. Within the self-consistent field (SCF) framework, each electron is assumed to move in the average electrostatic field generated by all other electrons. The molecular wavefunction is expressed as a single Slater determinant, ensuring compliance with the Pauli exclusion principle and antisymmetric requirements. Although HF accurately accounts



for exchange interactions, it neglects dynamic electron-correlation effects arising from instantaneous electron–electron interactions. As a consequence, HF calculations often overestimate total energy, HOMO-LUMO energy gaps, and molecular stability while underestimating electron delocalization phenomena [23]. Nevertheless, HF calculations provide valuable baseline information regarding molecular geometries, orbital distributions, atomic charge populations, and electronic structure trends, making them useful reference points for more sophisticated theoretical methods.

To overcome the limitations associated with the neglect of electron correlation, DFT calculations have become the dominant computational framework in modern molecular physics and computational chemistry. Unlike wavefunction-based approaches, DFT describes the electronic system through the electron density as the fundamental variable, substantially reducing computational complexity while maintaining high accuracy. The theoretical foundations established by Hohenberg, Kohn, and Sham demonstrated that the ground-state properties of many-electron systems can be uniquely determined from the electron density distribution [24, 25]. In particular, hybrid exchange-correlation functions such as B3LYP, which combine exact HF exchange with gradient-corrected correlation functions, have proven highly successful for predicting molecular structures, vibrational frequencies, dipole moments, charge-transfer characteristics, and electronic properties of organic molecules [26]. On this basis, compared with HF calculations, DFT level of theory provides a more realistic description of electron correlation effects, accordingly, improving the prediction of bond lengths, bond angles, total energies, ionization potentials, electron affinities, and frontier molecular orbital energies. Furthermore, DFT enables detailed analyses of molecular electrostatic potential (MEP) surfaces, natural bond orbital (NBO) interactions, charge-transfer pathways, chemical hardness, electrophilicity, nucleophilicity, and other global reactivity descriptors. These parameters play a critical role in understanding intermolecular interactions, biological activity, spectroscopic behavior, and the fundamental chemical reactivity of heterocyclic compounds [27].

The combined application of HF and DFT methodologies display a comprehensive theoretical framework for investigating the electronic behavior of 2-ethoxy-5-fluoro-4-pyrimidinone. Comparative analyses between the two methods allow assessment of the role of electron correlation in determining molecular stability, geometric parameters, and electronic distributions. Moreover, detailed examination of frontier molecular orbitals (HOMO and LUMO), energy-gap characteristics, molecular electrostatic potential maps, and global reactivity descriptors provide valuable insight into charge-transfer mechanisms, reactive sites, intermolecular interactions, and potential physicochemical applications of the molecule.

Accordingly, the primary objective of the present study is to perform a comprehensive quantum-chemical investigation of 2-ethoxy-5-fluoro-4-pyrimidinone using HF and DFT approaches. Optimized molecular geometries, total energies, electronic structures, charge distributions, spectroscopic findings, frontier molecular orbitals, molecular electrostatic potential distributions, and reactivity parameters are systematically analyzed to establish fundamental structure–property relationships. The results obtained are expected to contribute to a deeper understanding of fluorinated pyrimidinone derivatives and provide theoretical guidance for future studies involving heterocyclic pharmaceuticals, molecular electronics, and functional organic materials.

2. Computational details for 2-ethoxy-5-fluoro-4-pyrimidinone

A comprehensive quantum-chemical investigation was performed to elucidate the structural, electronic, thermodynamic, atomic charge distributions (Mulliken population analysis and the Atomic Polar Tensor), nuclear magnetic resonance (^1H and ^{13}C) chemical shifts, and fundamental optical properties of 2-ethoxy-5-fluoro-4-pyrimidinone with the formula of $\text{C}_6\text{H}_7\text{FN}_2\text{O}_2$. The title molecule belongs to the fluorinated pyrimidinone family, featuring a central heteroaromatic pyrimidine ring. It is characterized by a fluorine atom attached to the fifth carbon (C_5) and an ethoxy group at the second carbon (C_2). The chemical impact of these specific substitutions depends heavily on the molecular





structure of title molecules. The simultaneous presence of electron-withdrawing fluorine and electron-donating ethoxy functionalities within the same conjugated heterocyclic framework generates a complex electronic environment characterized by charge redistribution, orbital hybridization, and intramolecular polarization effects. Furthermore, the carbonyl oxygen and ring nitrogen atoms introduce additional possibilities for electron delocalization, resonance stabilization, and intermolecular interactions. The structural features mentioned make 2-ethoxy-5-fluoro-4-pyrimidinone an attractive molecular system for detailed theoretical investigation.

Full geometry optimization calculations were initially carried out to determine the equilibrium structure corresponding to the global minimum on the potential energy surface so as to obtain a fundamental understanding of the physicochemical behavior of the title compound. Subsequently, a series of quantum-chemical analyses, including thermodynamic parameter calculations, frontier molecular orbital (HOMO-LUMO) analysis, molecular electrostatic potential (MEP) mapping, electrostatic potential (ESP) surface visualization, total electron-density distribution, and simulated UV-Vis absorption spectra, were performed for 2-ethoxy-5-fluoro-4-pyrimidinone for the first time. These calculations provide detailed information about molecular stability, charge-transfer behavior, electron delocalization pathways, and the influence of fluorine and ethoxy substituents on the electronic structure of the pyrimidinone framework. Moreover, the MEP and ESP surfaces facilitate the identification of electrophilic and nucleophilic regions, allowing prediction of potential reactive sites and intermolecular interaction centers within the molecule. The scientific results obtained enable us to better understand the molecular reactivity, electronic structure, intramolecular charge transfer (ICT), and aromatic electron delocalization, with particular emphasis on the influence of the electron-withdrawing substituents.

All quantum-chemical calculations were carried out within the framework of Density Functional Theory (DFT) using the widely employed B3LYP hybrid exchange–correlation functional [22–24]. The B3LYP functional combines Becke's three-parameter exchange functional with the Lee-Yang-Parr correlation functional and has demonstrated excellent reliability in predicting the structural, energetic, and electronic properties of heterocyclic organic molecules. The 6-31G(d,p) basis set [25], which includes polarization functions on all atoms, was employed to achieve an accurate description of molecular geometry, charge redistribution, and orbital interactions. The inclusion of polarization functions is particularly important for properly describing the lone-pair electrons associated with the nitrogen and oxygen atoms as well as the strong electronegativity effects introduced by fluorine substitution.

To further evaluate the electronic behavior and chemical reactivity of the title compound, several global quantum-chemical descriptors were calculated from the frontier molecular orbital energies according to Koopmans' approximation. These descriptors include the ionization potential (I), electron affinity (A), chemical softness (S), chemical hardness (η), electronegativity (χ), chemical potential (μ), electrophilicity index (ω), maximum electronic charge-transfer capability (ΔN_{max}), and also HOMO–LUMO energy gap (ΔE) parameters. Such parameters provide quantitative information regarding molecular stability, kinetic reactivity, electron-donating and electron-accepting tendencies, and the charge-transfer characteristics of 2-ethoxy-5-fluoro-4-pyrimidinone.

In addition, time-dependent density functional theory (TD-DFT) calculations and ZINDO computation methods were performed in the gas phase to simulate the electronic absorption spectrum and investigate the nature of electronic transitions responsible for the optical response of the molecule. The calculated excited-state properties were used to identify the dominant orbital contributions involved in the absorption process and to evaluate possible ICT transitions between the heteroaromatic pyrimidine ring and the substituent groups.

All quantum-chemical computations were performed using the Gaussian 09 software package [26]. Molecular visualization, frontier molecular orbital plotting, electron-density analysis, electrostatic potential mapping, and graphical representations were generated using GaussView and related molecular visualization tools [27]. The obtained theoretical results provide a detailed atomic-scale description of



the structural, electronic, optical, and reactive properties of 2-ethoxy-5-fluoro-4-pyrimidinone and establish a foundation for understanding its physicochemical behavior and potential applications in heterocyclic and pharmaceutical chemistry.

3. Results and Discussion

3.1. Optimized Molecular Geometry of 2-Ethoxy-5-fluoro-1H-pyrimidin-4-one

A detailed understanding of the molecular geometry of 2-ethoxy-5-fluoro-1H-pyrimidin-4-one is essential for elucidating its electronic structure, intermolecular interactions, and physicochemical behavior. The molecule consists of a fluorinated pyrimidinone ring bearing an ethoxy substituent, where the combined effects of heteroatoms, conjugation, and substituent-induced electronic polarization significantly influence the structural characteristics of the system [8, 9]. To obtain reliable geometrical parameters, full geometry optimizations were performed using both DFT/B3LYP/6-31+G(d,p) and HF/6-31+G(d,p) computational approaches. The optimized structure corresponding to the minimum-energy configuration was identified as the most stable conformer and subsequently employed for all theoretical investigations. The optimized molecular geometry together with the atom-numbering scheme is presented in Figure 1.

Selected bond lengths and bond angles calculated at the DFT/B3LYP/6-31+G(d,p) and HF/6-31+G(d,p) levels are summarized in Tables 1 and 2 in detail. To assess the consistency of the computational approaches, correlation analyses were carried out for the calculated geometrical parameters. The corresponding correlation plots are shown in Figs. 2 and 3. Excellent agreement between the two theoretical methods was obtained for bond length sizes, indicating that both approaches provide a reliable description of the molecular framework. The correlation coefficients are determined to be about 0.99678 for bond length distances and 0.90725 for bond angle parameters. Minor differences (especially for bond angles) observed between the HF and DFT results mainly originate from the treatment of electron-correlation effects.

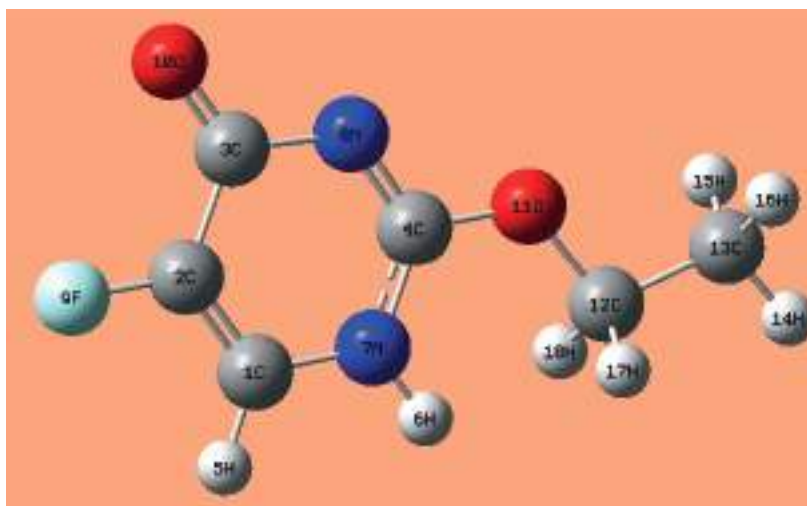


Figure 1. Optimized molecular structure pertaining to 2-ethoxy-5-fluoro-1H-pyrimidin-4-one



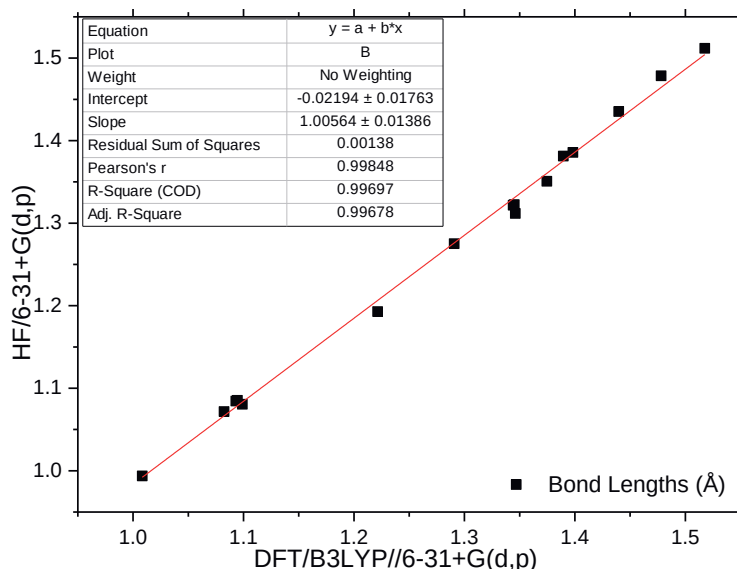


Figure 2. Bond length size correlations between HF and B3LYP calculation levels for 2-ethoxy-5-fluoro-¹H-pyrimidin-4-one compound

The maximum difference between bond length sizes is noted as 0.0344 Å for the C4-O11 atoms, as provided in Table 1. Similarly, the largest variation is detected as 6.1584° for the N7-C4-O11 atoms, as provided in Table 2. It is apparent that the environment plays a serious role on the molecular geometry of 2-Ethoxy-5-fluoro-1H-pyrimidin-4-one compound. As expected, the HF method generally predicts slightly shorter bond distances and somewhat larger bond angles because electron correlation is not explicitly included in the HF calculation formalism. In contrast, the B3LYP functional accounts for electron correlation through the exchange-correlation potential, providing a more realistic representation of electron-density distribution within the molecule [28–35]. Consequently, DFT calculation results better describe the effects of π -electron delocalization, lone-pair interactions, resonance stabilization, and intramolecular charge transfer occurring within the pyrimidinone ring.

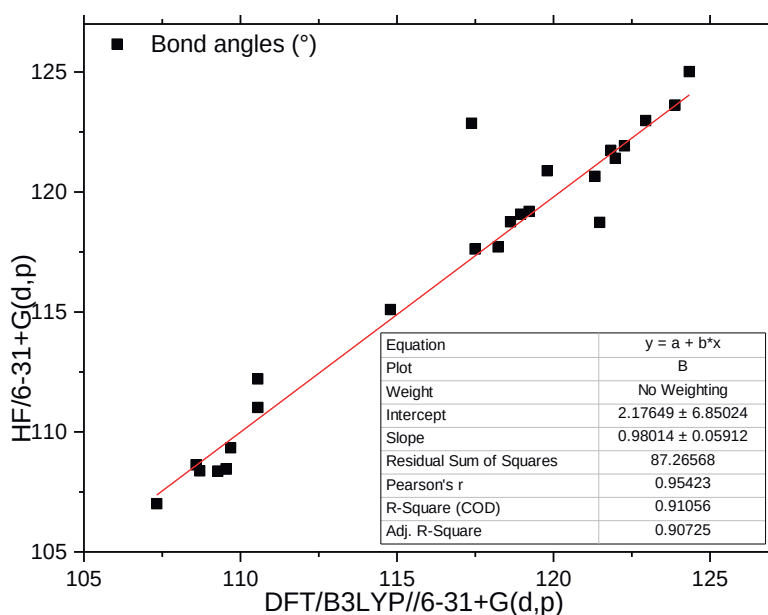


Figure 3. Bond angle correlations between HF and B3LYP calculation levels for 2-ethoxy-5-fluoro-¹H-pyrimidin-4-one compound



In more detail, the optimized structure reveals that the pyrimidinone ring maintains an essentially planar geometry, which facilitates efficient electron delocalization throughout the heterocyclic framework. Hence, the C-O and C-C bonds associated with the ethoxy substituent exhibit values characteristic of alkoxy-functionalized heterocyclic systems. The ethoxy group adopts a conformation that minimizes steric repulsion while preserving favorable electronic communication with the pyrimidinone ring. Numerically, the C3=O10 bond (1.2214 Å at DFT and 1.1929 Å at HF) of the pyrimidinone moiety exhibits the characteristic features of a carbonyl double bond, whereas the bond length distances of C₄-O₁₁ and C₁₂-O₁₁ bonds are calculated to be about 1.3461 Å and 1.4397 at B3LYP and 1.3117 Å and 1.4352 at HF calculation methods, respectively. As expected, the single bond length is longer than the double bond between the oxygen and carbon atoms. Moreover, the adjacent C-N and C-C bonds show intermediate bond lengths arising from resonance effects within the conjugated system. In this respect, the bond distances between C₁-N₇ and C₄-N₇ atoms are computed as 1.3896 Å and 1.3747 Å at DFT/B3LYP//6-31+G(d,p) and 1.3813 Å and 1.3507 Å at HF/6-31+G(d,p) calculation levels, respectively. Besides, the length between H6 and N7 atoms is found to be about 1.0083 Å and 0.9937 Å using DFT and HF calculation levels of theory, respectively. The difference stems from the conjugated atom effect and delocalization. As for the bond length sizes between carbon and carbon atoms, the highest calculation is obtained as 1.5176 Å and 1.5118 Å for C12-C13 length, whereas the minimum lengths of 1.3452 Å and 1.3225 Å ascribes to bond length for C1-C2 atoms at DFT/B3LYP//6-31+G(d,p) and HF/6-31+G(d,p) levels of theory, respectively.

Table 1. Theoretical bond length sizes for optimized geometric parameters of 2-ethoxy-5-fluoro-1H-pyrimidin-4-one molecule

Atoms	Bond lengths (Å)	
	DFT/B3LYP/6-31G(d,p)	HF/6-31G(d,p)
C ₁ -C ₂	1.3452	1.3225
C ₁ -H ₅	1.0824	1.0717
C ₁ -N ₇	1.3896	1.3813
C ₂ -C ₃	1.4781	1.4786
C ₂ -F ₉	1.3441	1.3217
C ₃ -N ₈	1.3982	1.3857
C ₃ -O ₁₀	1.2214	1.1929
C ₄ -N ₇	1.3747	1.3507
C ₄ -N ₈	1.2908	1.2751
C ₄ -O ₁₁	1.3461	1.3117
H ₆ -N ₇	1.0083	0.9937
O ₁₁ -C ₁₂	1.4397	1.4352
C ₁₂ -C ₁₃	1.5176	1.5118
C ₁₂ -H ₁₇	1.099	1.0806
C ₁₂ -H ₁₈	1.099	1.0806
C ₁₃ -H ₁₄	1.0945	1.0853
C ₁₃ -H ₁₅	1.0931	1.0844
C ₁₃ -H ₁₆	1.0931	1.0844

At the same time, the presence of electronegative nitrogen and fluorine atoms induces noticeable polarization of neighboring bonds, leading to slight deviations from idealized bond parameters. In this context, the bond lengths between carbon and nitrogenous atoms are determined to be about





1.3982 Å and 1.2908 Å at DFT method and 1.3857 Å and 1.2751 Å at HF calculation level of theory, respectively. The C-F bond length falls within the typical range reported for fluorinated heteroaromatic compounds, revealing the strong electronegativity and electron-withdrawing nature of fluorine. On this basis, the length of C₂-F₉ atoms is computed as about 1.3441 (DFT) and 1.3217 (HF). Additionally, the bond lengths between carbon and hydrogen atoms are determined between 1.0990 Å (C₁₂-H₁₇ and C₁₂-H₁₈) and 1.0824 Å (C₁-H₅) at DFT/B3LYP//6-31+G(d,p) and 1.0853 Å (C₁₃-H₁₄) and 1.0717 Å (C₁-H₅) at HF/6-31+G(d,p) levels of theory, respectively.

Table 2. Theoretical bond angles for optimized geometric parameters of 2-ethoxy-5-fluoro-1H-pyrimidin-4-one molecule

Atoms	Bond angles (°)	
	DFT	HF
C ₂ -C ₁ -H ₅	123.8802	123.6194
C ₂ -C ₁ -N ₇	118.6273	118.7556
H ₆ -C ₁ -N ₇	117.4925	117.625
C ₁ -C ₂ -C ₃	121.9714	121.4048
C ₁ -C ₂ -F ₉	119.798	120.886
C ₃ -C ₂ -F ₉	118.2306	117.7092
C ₂ -C ₃ -N ₈	114.79	115.1003
C ₂ -C ₃ -O ₁₀	122.2662	121.923
N ₈ -C ₃ -O ₁₀	122.9438	122.9767
N ₇ -C ₄ -N ₈	124.3378	125.0154
N ₇ -C ₄ -O ₁₁	118.2785	112.1201
N ₈ -C ₄ -O ₁₁	117.3836	122.8646
C ₁ -N ₇ -C ₄	118.9495	119.0734
C ₁ -N ₇ -H ₄	119.221	119.1921
C ₄ -N ₇ -H ₆	121.8295	121.7344
C ₃ -N ₈ -C ₄	121.324	120.6505
C ₄ -O ₁₁ -C ₁₂	121.4767	118.7302
O ₁₁ -C ₁₂ -C ₁₃	107.3287	107.0097
O ₁₁ -C ₁₂ -H ₁₇	109.5467	108.4578
O ₁₁ -C ₁₂ -H ₁₈	109.5473	108.4578
C ₁₃ -C ₁₂ -H ₁₇	110.5559	112.2091
C ₁₃ -C ₁₂ -H ₁₈	110.5559	112.209
H ₁₇ -C ₁₂ -H ₁₈	109.2778	108.3687
C ₁₂ -C ₁₃ -H ₁₄	109.6885	109.3423
C ₁₂ -C ₁₃ -H ₁₅	110.5603	111.0192
C ₁₂ -C ₁₃ -H ₁₆	110.5587	111.0192
H ₁₄ -C ₁₃ -H ₁₅	108.7014	108.3768
H ₁₄ -C ₁₃ -H ₁₆	108.7015	108.3768
H ₁₅ -C ₁₃ -H ₁₆	108.5811	108.6291

The calculated bond angles within the heterocyclic ring are generally close to the values expected for an sp²-hybridized conjugated system. Small deviations from ideal trigonal-planar geometry arise from the presence of heteroatoms, the carbonyl functionality, and substituent-induced electronic effects. The nearly planar arrangement of the ring atoms promotes conjugation and contributes to the stability of the 2-ethoxy-5-fluoro-1H-pyrimidin-4-one molecular structure.



All in all, the optimized geometry demonstrates that 2-ethoxy-5-fluoro-1H-pyrimidin-4-one possesses a rigid and highly conjugated heterocyclic framework with significant electron delocalization. The structural parameters obtained from both HF and DFT quantum calculations exhibit good agreement and confirm the suitability of the selected computational methodology for describing the molecular architecture of the title compound. The geometrical results obtained provide a reliable basis for subsequent analyses of electronic properties, charge distribution, spectroscopic behavior, and intermolecular interactions.

3.2. Thermochemical Properties of 2-ethoxy-5-fluoro-1H-pyrimidin-4-one molecular structure

The thermochemical properties of 2-ethoxy-5-fluoro-1H-pyrimidin-4-one were investigated using the DFT/B3LYP and HF methods with the 6-31+G(d,p) basis set to evaluate its energetic stability, thermal behavior, and molecular polarity. Thermodynamic parameters obtained from the optimized molecular geometry, including total electronic energy, zero-point vibrational energy (ZPVE), thermal energy, entropy, heat capacity, rotational constants, and dipole moment components, are summarized in Table 3. The zero-point vibrational energies were corrected using appropriate scaling factors of 0.977 for B3LYP and 0.909 for HF method to compensate for the systematic overestimation of harmonic vibrational frequencies. The absence of imaginary frequencies in the optimized structure confirms that the molecule resides at a true minimum on the potential energy surface, indicating the stability of the optimized configuration. The calculated total electronic energies display the stabilization arising from conjugation within the pyrimidinone ring and the electronic effects of the fluorine, carbonyl, nitrogen, and ethoxy substituents. According to table, total electronic energy values for 2-ethoxy-5-fluoro-1H-pyrimidin-4-one molecule are found to be about -592.65749664 and -589.37101891 a.u. at B3LYP/6-31+G(d,p) and HF/6-31G+(d,p) levels of theory. The ZPVE values provide valuable information regarding the intrinsic vibrational stability of the molecule. The vibrational contributions arise primarily from C=O stretching, C-F vibrations, N-H motions, C-N and C-O bond vibrations, as well as skeletal deformations of the heterocyclic ring. The presence of multiple heteroatoms significantly influences the vibrational energy distribution and contributes to the overall thermodynamic stability of the system [36, 37]. Accordingly, the scaled ZPVE parameters are determined as about 81.88557456 and 82.58282271 kcal.mol⁻¹ at DFT/B3LYP//6-31G(d,p) and HF/6-31G(d,p) calculation levels, respectively. The models point out the zero-point correction values of about 0.133565 and 0.144779 kcal.mol⁻¹, respectively. Furthermore, these values verify the energetic stability of the molecular framework and indicate an extended network of partial π -electron delocalization encompassing the aromatic, carbonyl, and alkoxy-functionalized heterocyclic systems.





Table 3. Fundamental thermodynamic quantities: heat capacities ($\text{cal mol}^{-1} \text{K}^{-1}$), entropies ($\text{cal mol}^{-1} \text{K}^{-1}$), thermal energies ($\text{cal mol}^{-1} \text{K}^{-1}$), zero-point energies (kcal mol^{-1}), zero-point corrections (Hartree/Particle), dipole moment (Debye), and rotational constants (GHz) for 2-ethoxy-5-fluoro- ^1H -pyrimidin-4-one molecule

Parameters	DFT/B3LYP//6-31+(d,p)	HF/6-31+(d,p)
Total energy	-592.65749664	-589.37101891
Zero-point vibrational energy	81.88557456	82.58282271
Zero-point correction	0.133565	0.144779
Thermal correction to Energy	0.143923	0.154339
Thermal correction to Enthalpy	0.144867	0.155283
Thermal correction to Gibbs Free Energy	0.096842	0.109105
Sum of electronic and zero-point Energies	-592.523932	-589.226240
Sum of electronic and thermal Energies	-592.513574	-589.216680
Sum of electronic and thermal Enthalpies	-592.512630	-589.215736
Sum of electronic and thermal Free Energies	-592.560655	-589.261914
Rotational constant	3.00642	2.87807
	0.58011	0.61900
	0.48930	0.51265
Entropy		
Total	101.078	97.190
Translational	41.082	41.082
Rotational	30.311	30.244
Vibrational	29.684	25.863
Heat capacity		
Total	37.321	34.481
Translational	2.981	2.981
Rotational	2.981	2.981
Vibrational	31.360	28.520
Thermal Energy		
Total	90.313	96.849
Translational	0.889	0.889
Rotational	0.889	0.889
Vibrational	88.535	95.072
μ_x	7.1762	-4.8287
μ_y	-7.5607	-6.3334
μ_z	0.0004	0
μ	10.4241	7.9642

The entropy values are derived from translational, rotational, and vibrational contributions, with the vibrational component representing a substantial fraction of the total entropy due to the large number of accessible vibrational modes associated with the heterocyclic framework and the ethoxy substituent. On this basis, the total entropy is calculated to be 101.078 and 97.190 $\text{cal mol}^{-1} \text{K}^{-1}$, comprising translation (41.082 and 41.082), rotational (30.311 and 30.244), and vibrational (29.684 and 25.863) contributions.



Likewise, the calculated heat capacities indicate the ability of the molecule to absorb and store thermal energy through vibrational excitation processes. The relatively large vibrational contribution demonstrates that internal molecular motions play a dominant role in determining the thermal behavior of the compound. Hence, the molar heat capacity at constant volume (C_v) displays the thermal energy stored primarily via the vibrational excitations of the functional groups and the aromatic ring. As detailed in Table 3, the DFT/B3LYP model calculation yields a total C_v of 37.321 cal mol⁻¹ K⁻¹ (comprising 2.981 translational, 2.981 rotational, and 31.360 vibrational contributions). In comparison, the HF computational method results in a total C_v of 34.481 cal mol⁻¹ K⁻¹ (with 2.981 translational, 2.981 rotational, and 28.520 vibrational parts). Similarly, the total thermal energies are determined as about 90.313 cal mol⁻¹ K⁻¹ (with 0.889 translational, 0.889 rotational, and 88.535 vibrational parts) and 96.849 cal mol⁻¹ K⁻¹ (with 0.889 translational, 0.889 rotational, and 95.072 vibrational parts) at DFT and HF calculation techniques, respectively. The calculated rotational constants (A, B, and C) confirm that 2-ethoxy-5-fluoro-1H-pyrimidin-4-one behaves as an asymmetric-top molecule. This behavior originates from the non-uniform mass distribution generated by the fluorine atom, carbonyl group, ring nitrogen atoms, and ethoxy side chain. Although the pyrimidinone ring remains essentially planar, the ethoxy substituent introduces a degree of conformational flexibility that contributes to the asymmetric rotational characteristics. Calculated at the DFT/B3LYP//6-31G(d,p) and HF/6-31+G(d,p) levels of theory, respectively, the rotational constants are 3.00642 (2.87807) GHz, 0.58011 (0.61900) GHz, and 0.48930 (0.51265) GHz, indicating an asymmetric top molecular configuration. The dipole moment constitutes an important descriptor of molecular behavior. For the title compound, the total dipole moments are calculated to be 10.4241 D (B3LYP) and 7.9642 D (HF). The corresponding Cartesian components (μ_x , μ_y , and μ_z) are 7.1762, -7.5607, and 0.0004 D for the B3LYP model, compared to -4.8287, -6.3334, and 0 D for the HF model. The calculated dipole moment components indicate a significant degree of molecular polarity arising from the combined electron-withdrawing effects of the fluorine atom and carbonyl group together with the electron-donating character of the ethoxy substituent. Furthermore, the presence of ring nitrogen atoms enhances charge separation within the molecular framework. Such electronic polarization facilitates intermolecular interactions, including dipole-dipole attractions, hydrogen bonding, and charge-transfer processes, which may be important for the biological and physicochemical properties of the compound [38–413].

To sum up, the thermochemical results demonstrate that 2-ethoxy-5-fluoro-1H-pyrimidin-4-one is an energetically stable and polar heterocyclic system. Its thermodynamic behavior is governed by the synergistic effects of heteroatom substitution, π -electron delocalization, and intramolecular charge redistribution, providing a solid foundation for understanding its electronic structure and spectroscopic properties.

3.3. UV–Vis Spectral Analysis

The electronic absorption properties of 2-ethoxy-5-fluoro-1H-pyrimidin-4-one were investigated to gain insight into its excited-state behavior and optical characteristics. The UV–Vis spectrum was simulated using time-dependent density functional theory (TD-DFT), time-dependent Hartree-Fock, and ZINDO calculation methods, and the major electronic transitions were analyzed in terms of excitation energies, oscillator strengths, and frontier orbital contributions. Since the results were close to each other, the calculated transitions determined by ZINDO calculation model [44] are summarized in Table 4.

The absorption behavior of the molecule is primarily governed by the conjugated pyrimidinone ring, the carbonyl group, the fluorine substituent, and the ethoxy functionality. Owing to the presence of heteroatoms with non-bonding electron pairs and an extended π -electron framework, the observed electronic transitions mainly involve $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ excitations. These transitions are characteristic of heterocyclic carbonyl-containing systems and significantly influence the optical response of the molecule [45].





The most intense absorption bands originate predominantly from $\pi \rightarrow \pi^*$ transitions involving the frontier molecular orbitals. The HOMO is mainly localized over the pyrimidinone ring, oxygen atoms, and nitrogen-containing regions, whereas the LUMO is distributed over the conjugated heterocyclic framework and carbonyl-containing portions of the molecule. This orbital arrangement facilitates intramolecular charge redistribution upon excitation and contributes to the electronic polarization of the system.

In addition to the dominant $\pi \rightarrow \pi^*$ transitions, weaker $n \rightarrow \pi^*$ transitions are observed due to excitation of lone-pair electrons located on the oxygen and nitrogen atoms. The mentioned transitions generally exhibit lower oscillator strengths because they are partially symmetry-forbidden; however, they remain important for understanding the photophysical behavior of the molecule.

The calculated absorption wavelengths and oscillator strengths indicate that the electronic transitions are strongly influenced by the electron-withdrawing fluorine atom and carbonyl group. The fluorine substituent modifies the electron density distribution within the pyrimidine ring, while the carbonyl group introduces low-lying antibonding orbitals that participate in electronic excitation processes. The ethoxy substituent further contributes to electron delocalization and affects the intensity of the absorption bands through inductive and resonance interactions.

Table 4. Theoretical absorption spectra (ZINDO) for 2-ethoxy-5-fluoro-1H-pyrimidin-4-one molecule

CI-expansion coefficient					
Excitations	Energy (eV)	Singlet-A	Wavelength (nm)	Oscillator strength (f)	Translations
Excited State 1					
41→43	2.8272	0.63886	438.54	0.00051	HOMO→LUMO+1
41→44		-0.11908			HOMO→LUMO+2
41→46		-0.27711			HOMO→LUMO+4
Excited State 2					
42→43	3.9973	0.30663	310.17	0.0446	LUMO→ LUMO+1
42→44		0.62133			LUMO→ LUMO+2
Excited State 3					
39→43	4.0348	0.27549	307.28	0.0030	HOMO-2→ LUMO+1
37→38					HOMO→LUMO
41→42		0.44289			

The simulated spectrum displays that electronic excitation is accompanied by efficient charge redistribution within the heterocyclic framework. Such behavior is indicative of moderate intramolecular charge-transfer character, which is commonly observed in fluorinated heterocyclic compounds containing electron-rich and electron-deficient regions within the same molecular skeleton.

As shown in the table, the first excited state ($\lambda_{\text{max}}=438.54$ nm, meaning bang gap energy of 2.8272 eV) is mainly attributed to an $n \rightarrow \pi^*$ transition. This weakly allowed transition ($f=0.00051$) originates from the interaction of lone-pair electrons on the heteroatoms with the aromatic π^* orbitals. The second absorption band at 310.17 nm (3.9973 eV) corresponds to overlapping $\pi \rightarrow \pi^*$ transitions enhanced by conjugation and electron delocalization within the aromatic framework, despite exhibiting an oscillator strength of 0.0446. In contrast, the intense band observed at 307.28 nm ($f=0.0030$) is assigned



to a strongly allowed $\pi \rightarrow \pi^*$ transition involving aromatic bonds and interactions with substituent groups. Ultimately, the simulated absorption spectrum dispaly the combined influence of aromatic conjugation, substituent-induced electron withdrawal, and molecular asymmetry. Furthermore, the calculated excitation energies align with the HOMO-LUMO energy gap obtained from our DFT calculations, confirming the internal consistency of the theoretical results

In summary, the UV-Vis analysis reveals that the optical properties of 2-ethoxy-5-fluoro-¹H-pyrimidin-4-one are governed by a combination of $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ electronic transitions involving the pyrimidinone ring, carbonyl group, fluorine atom, and ethoxy substituent. The observed charge-transfer characteristics and electronic delocalization reveal potential relevance of this molecule in pharmaceutical chemistry, molecular recognition studies, and functional organic materials exhibiting photoresponsive behavior.

3.4. Atomic Charge Distribution Analysis

Atomic charge distribution analysis is an effective approach for elucidating the electronic structure, polarization behavior, and potential reactive centers of molecular systems. In the present work, the charge distribution of 2-ethoxy-5-fluoro-¹H-pyrimidin-4-one was investigated using both Mulliken population analysis and the APT quantum calculation method at the B3LYP/6-31+G(d,p) and HF/6-31+G(d,p) levels of theory. The calculated atomic charges are summarized in Table 5.

The Mulliken scheme provides information about electron partitioning among atoms based on molecular orbital populations, whereas the APT method evaluates atomic charges from the response of the molecular dipole moment to atomic displacements, thereby offering a more physically meaningful description of molecular polarization and vibrational charge transfer. Although the two approaches yield different absolute charge magnitudes, they display similar trends regarding electron-rich and electron-deficient regions within the molecule [46].

For the carbon atoms, significant variations in charge distribution are observed depending on the local chemical environment. At the B3LYP/6-31+G(d,p) level, the APT charges range from +0.043928 (C₁₃) to +1.335555 (C₄), while the HF calculations produce values between +0.103341 (C₁₃) and +1.534791 (C₄). The largest positive charges are associated with the pyrimidinone ring carbons directly influenced by neighboring electronegative heteroatoms, indicating substantial electron withdrawal from these centers. Mulliken charges exhibit a wider distribution, varying from -0.608786 (C₁₃) to +0.585759 (C₄) at the DFT level and from -0.513265 (C₁₃) to +0.660533 (C₄) at the HF level. These results reveal pronounced electronic polarization within the heterocyclic ring and demonstrate the strong influence of adjacent nitrogen, oxygen, and fluorine atoms on the carbon charge distribution.

The heteroatoms exhibit the most distinctive charge characteristics. The two ring nitrogen atoms carry substantial negative charges in all computational models. At the DFT level, the Mulliken charges of N₇ and N₈ atoms are calculated to be about -0.396664 and -0.524394, respectively, while the corresponding APT charges are -0.660181 and -0.911363. Similar trends are obtained from HF calculations, where the Mulliken charges are -0.601210 (N₇) and -0.563892 (N₈) and the APT charges reach -0.844255 (N₇) and -1.058551 (N₈). These pronounced negative values indicate significant electron accumulation around the nitrogen centers due to their high electronegativity and lone-pair electrons.

Likewise, the oxygen atoms associated with the carbonyl and ethoxy functionalities possess strongly negative charges. Within the DFT/APT calculations, O₁₀ and O₁₁ exhibit charges of -0.835030 and -0.977192, respectively, whereas the HF/APT computational method yields even more negative values of -0.995593 and -1.124224. Mulliken charges for these oxygen atoms vary between -0.274202 and -0.446017 at the DFT/6-31+G(d,p) level and between -0.521789 and -0.538003 at the HF/6-31+G(d,p) level of theory. The substantial negative charge concentration around oxygen atoms reflects strong localization of lone-pair electrons and highlights their importance as potential sites for electrophilic interactions and hydrogen-bond acceptance.



**Table 5.** Point Atomic Charge Distributions of 2-ethoxy-5-fluoro-¹H-pyrimidin-4-one molecule

Label	Atomic Charges (DFT/B3LYP/6-31+(d,p))		Atomic Charges (HF/6-31+(d,p))	
	APT	Mulliken	Mulliken	APT
C ₁	0.247416	-0.017684	0.192525	0.358597
C ₂	0.334330	0.349300	0.257602	0.255512
C ₃	1.141174	0.306533	0.535923	1.414255
C ₄	1.335555	0.585759	0.660533	1.534791
H ₅	0.083770	0.162581	0.207033	0.094600
H ₆	0.240749	0.303069	0.371543	0.292243
N ₇	-0.660181	-0.396664	-0.601210	-0.844255
N ₈	-0.911363	-0.524394	-0.563892	-1.058551
F ₉	-0.526765	-0.355736	-0.438026	-0.557283
O ₁₀	-0.835030	-0.446017	-0.538003	-0.995593
O ₁₁	-0.977192	-0.274202	-0.521789	-1.124224
C ₁₂	0.597981	0.130683	0.223949	0.652312
C ₁₃	0.043928	-0.608786	-0.513265	0.103341
H ₁₄	-0.004989	0.151770	0.147757	-0.021008
H ₁₅	0.011312	0.175607	0.140515	-0.019916
H ₁₆	0.011312	0.175609	0.140516	-0.019915
H ₁₇	-0.065997	0.141289	0.149145	-0.032450
H ₁₈	-0.066010	0.141284	0.149143	-0.032454

The fluorine atom (F₉) also exhibits a marked negative charge due to its exceptionally high electronegativity. The calculated APT charge amounts to -0.526765 at the B3LYP level and -0.557283 at the HF level, while the Mulliken charges are determined as -0.355736 and -0.438026, respectively. The results calculated indicate considerable electron density localization around the fluorine atom, contributing to the overall molecular polarity and influencing intermolecular interactions.

Hydrogen atoms should carry positive charges, consistent with electron withdrawal by neighboring electronegative atoms. At the DFT/Mulliken level, hydrogen charges vary from +0.141289 (H₁₈) to +0.303069 (H₆), while the HF calculations predict values between +0.140515 and +0.371543. However, APT model sometimes calculates negatively the hydrogen atoms. In this context, the APT charges exhibit a broader distribution, ranging from -0.066010 (H₁₈) to +0.597981 (C₁₂-associated environment), indicating the sensitivity of the APT method to local polarization effects and vibrational charge redistribution.



In conclusion, both Mulliken and APT analyses reveal a highly polarized electronic structure for 2-ethoxy-5-fluoro-¹H-pyrimidin-4-one. Significant negative charge accumulation is concentrated around the nitrogen, oxygen, and fluorine atoms, whereas positive charge density is primarily localized on selected carbon and hydrogen atoms. This non-uniform charge distribution originates from the combined effects of heteroatom electronegativity, lone-pair electron localization, π -electron delocalization within the pyrimidine ring, and electron-donating contributions from the ethoxy substituent, to be confirmed by simulation analyses. The observed charge anisotropy indicates the presence of efficient intramolecular charge-transfer pathways and provides valuable insight into the molecule's reactivity, intermolecular interactions, hydrogen-bonding capability, and potential electrophilic and nucleophilic attack sites.

3.5. NMR Spectral Analyses of 2-ethoxy-5-fluoro-¹H-pyrimidin-4-one Molecule

Nuclear magnetic resonance (NMR) spectroscopy is among the most informative analytical techniques for elucidating molecular structures and probing the electronic environments surrounding carbon and hydrogen nuclei. The chemical shifts observed in both ¹³C and ¹H NMR spectra are highly sensitive to electron density distribution, heteroatom substitution, resonance effects, hydrogen bonding interactions, and intramolecular charge transfer phenomena. Consequently, theoretical NMR calculations provide valuable insights into the electronic structure of heterocyclic compounds and serve as an important complement to experimental spectroscopic investigations [47].

In the present study, the ¹³C and ¹H NMR chemical shifts of 2-ethoxy-5-fluoro-¹H-pyrimidin-4-one were calculated using the Gauge-Independent Atomic Orbital (GIAO) approach at the HF/6-31G(d) and B3LYP/6-311+G(2d,p) levels of theory. The calculated isotropic shielding constants were referenced to tetramethylsilane (TMS), and the resulting chemical shift values were compared with available experimental data recorded in CDCl₃. The calculated and experimental NMR parameters are summarized in Table 6. The ¹³C NMR spectrum exhibits significant variations among the carbon atoms owing to the combined effects of the fluorine substituent, carbonyl functionality, ring nitrogen atoms, and ethoxy group. At the B3LYP/6-311+G(2d,p) level, the calculated chemical shifts span from 2.0137 ppm (C₁₃) to 179.845 ppm (C₃), while the HF calculations predict a range between 19.5334 ppm (C₁₃) and 197.365 ppm (C₃). The experimental values lie between 13.98 ppm (C₁₃) and 156.84 ppm (C₃). The most deshielded carbon resonance corresponds to C₃, which is directly influenced by the neighboring electronegative nitrogen atoms and carbonyl functionality within the pyrimidinone ring. Similarly, C₄ and C₂ exhibit large chemical shifts due to their participation in the conjugated heterocyclic framework and their proximity to electron-withdrawing heteroatoms. In contrast, the ethoxy carbon atom C₁₃ displays the lowest chemical shift value because of its aliphatic nature and relatively high local electron density. The carbon atom C₁₂, belonging to the ethoxy substituent, appears in the intermediate region, with calculated values of 53.2954 ppm (B3LYP) and 70.8150 ppm (HF), compared with the experimental value of 63.94 ppm.

A comparison of the computational approaches indicates that the B3LYP/6-311+G(2d,p) method reproduces the experimental ¹³C NMR trends more accurately than the HF method. The inclusion of electron-correlation effects within the DFT framework leads to a more realistic description of magnetic shielding and electronic delocalization in the heterocyclic ring system. Although some deviations remain for highly deshielded carbon centers, the overall agreement confirms the reliability of the DFT-based calculations.



**Table 6.** NMR chemical shifts of 2-ethoxy-5-fluoro-¹H-pyrimidin-4-one molecule

Atoms	TMS HF/6-31G(d)	TMS B3LYP/6-311+G(2d,p)	CH ₄ -HF/6-31G(d)	Exp. in CDCl ₃
C ₃	197.365	179.845	196.479	156.84
C ₄	163.133	145.613	162.248	153.66
C ₂	159.298	141.778	158.413	145.06
C1	120.514	102.994	119.629	135.16
C ₁₂	70.8150	53.2954	62.9298	63.94
C ₁₃	19.5334	2.0137	18.6481	13.98
	TMS HF/6-31G(d)	TMS B3LYP/6-311+G(2d,p)		Exp. in CDCl ₃
H ₆	8.4346	11.5776		12.77
H ₅	7.4795	7.9980		7.828
H ₁₇	4.0261	4.6235		4.324
H ₁₈	3.9617	4.0116		
H ₁₆	1.9969	2.2009		
H ₁₅	1.8589	2.0116		
H ₁₄	1.3332	1.4458		1.298

The calculated ¹H NMR chemical shifts also show satisfactory agreement with the experimental spectrum. At the B3LYP/6-311+G(2d,p) level, the proton chemical shifts vary between 1.4458 ppm (H₁₄) and 11.5776 ppm (H₆), whereas the HF calculations predict a range from 1.3332 ppm (H₁₄) to 8.4346 ppm (H₆). Experimentally observed proton resonances appear at 1.298 ppm (H₁₄), 4.324 ppm (H₁₇), 7.828 ppm (H₅), and 12.77 ppm (H₆). The highest chemical shift is associated with H₆, which is attached to the pyrimidinone ring and experiences strong deshielding due to the neighboring nitrogen and carbonyl groups, as well as possible intermolecular hydrogen-bonding interactions. The aromatic proton H₅ also resonates downfield owing to the electron-withdrawing influence of the fluorine substituent and the heterocyclic ring system. Conversely, the protons belonging to the ethoxy group (H₁₄-H₁₈) appear at lower chemical shifts, showing their relatively electron-rich aliphatic environment.

The overall agreement between the calculated and experimental ¹H NMR data confirms that the electronic structure of 2-ethoxy-5-fluoro-¹H-pyrimidin-4-one is well described by the applied quantum-chemical models. In particular, the DFT-based GIAO calculations reproduce the experimental trends more successfully than the HF approach, highlighting the importance of electron-correlation effects in accurately predicting magnetic shielding constants.

In summary, the theoretical NMR investigation supports the proposed molecular structure of 2-ethoxy-5-fluoro-¹H-pyrimidin-4-one and provides detailed information regarding the influence of fluorine substitution, heteroatom incorporation, and π -electron delocalization on the local magnetic environments of carbon and hydrogen nuclei. The close agreement between the experimental and calculated chemical shifts further confirms the validity of the optimized molecular geometry and the reliability of the computational methodology employed throughout this study.

3.6 Frontier Molecular Orbital Analysis of 2-ethoxy-5-fluoro-1H-pyrimidin-4-one

Frontier molecular orbital (FMO) analysis is an effective approach for understanding the electronic structure, charge-transfer characteristics, and chemical reactivity of molecular systems. In the present study, the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of 2-ethoxy-5-fluoro-¹H-pyrimidin-4-one were investigated to elucidate the electronic behavior of the molecule. The HOMO is associated with the electron-donating capability of the system, whereas



the LUMO represents its electron-accepting tendency (Fig. 4). Consequently, the HOMO–LUMO energy gap (ΔE) serves as an important descriptor of molecular stability, charge-transfer efficiency, electronic excitation, and chemical reactivity. In general, molecules with smaller energy gaps exhibit higher polarizability and reactivity, while larger gaps are indicative of greater kinetic stability.

The calculated frontier orbital energies at the DFT/B3LYP/6-31+G(d,p) and HF/6-31+G(d,p) levels provide valuable information regarding the electronic nature of the title compound. The obtained HOMO–LUMO gap indicates that 2-ethoxy-5-fluoro-1H-pyrimidin-4-one possesses a favorable balance between structural stability and electronic responsiveness [48, 49]. Such a characteristic is particularly important for heterocyclic compounds containing multiple electronegative atoms, where charge redistribution and orbital interactions play significant roles in determining physicochemical properties.

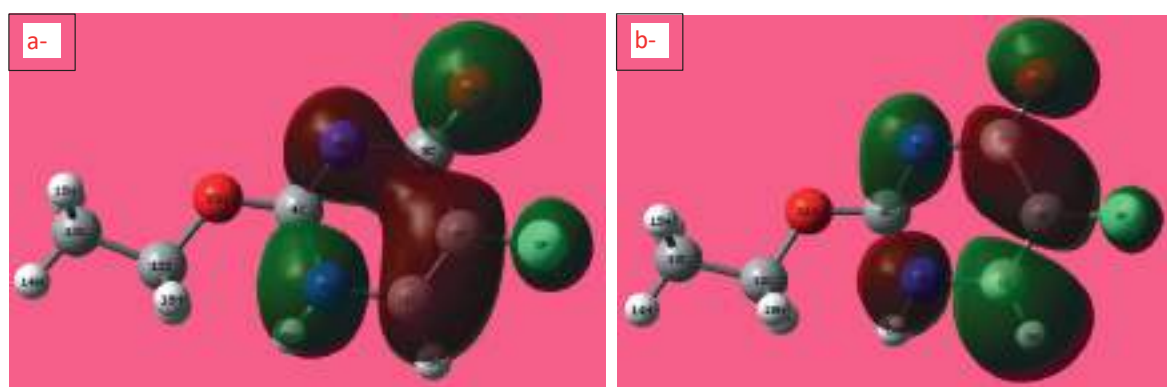


Figure 4. 3D spatial distributions of a-HOMO and b-LUMO orbitals of 2-ethoxy-5-fluoro-1H-pyrimidin-4-one

The three-dimensional (3D) orbital distributions reveal that the HOMO is predominantly localized over the pyrimidinone ring, especially around the nitrogen atoms, carbonyl oxygen atom, and the conjugated π -electron framework. The presence of lone-pair electrons on the heteroatoms contributes significantly to the HOMO density, indicating that these regions may act as electron-donating centers during intermolecular interactions. In contrast, the LUMO is mainly distributed over the pyrimidinone skeleton and carbonyl-containing region, extending partially toward the fluorine-substituted carbon atom. This distribution shows that electron acceptance preferentially occurs within the heterocyclic ring system, where the electron-withdrawing effects of the fluorine and carbonyl groups stabilize the incoming electron density.

The observed separation between the HOMO and LUMO regions indicates the possibility of ICT within the molecule. Upon electronic excitation, electron density is expected to migrate from the electron-rich heterocyclic and ethoxy-containing regions toward the more electron-deficient carbonyl- and fluorine-influenced portions of the pyrimidine ring. This charge-transfer process contributes to the optical and electronic properties of the molecule and is consistent with the electronic transitions observed in the UV-Vis absorption spectra.

In addition to the frontier orbital energies, several global reactivity descriptors can be derived from the HOMO and LUMO values, including IP, EA, η , S , χ , μ , and ω parameters, which provide quantitative information regarding the molecule's tendency to donate or accept electrons and its overall chemical reactivity. The calculated descriptors indicate that the title compound possesses moderate chemical hardness and appreciable softness, reflecting a balanced electronic structure capable of participating in both electrophilic and nucleophilic processes. Furthermore, the relatively high electronegativity arising from the fluorine, nitrogen, and oxygen atoms enhances the electron-withdrawing character of the molecule and contributes to its electronic stabilization.



**Table 7.** Calculated energies of 2-ethoxy-5-fluoro-¹H-pyrimidin-4-one molecule in ground state with singlet symmetry at B3LYP/6-31+G(d,p) basis set

Quantities	Values
Lowest MO Eigen value (a.u.)	-24.73744
Highest MO Eigen value (a.u.)	6.354210
HOMO (a.u.)	-0.25500
LUMO (a.u.)	-0.04667
HOMO–LUMO gap (a.u.), $ \Delta E $	0.208400
χ (Electronegativity) (a.u.), $[IP + EA]/2$	0.150835
μ , Chemical potential, $-[IP + EA]/2$	-0.150835
η (Chemical hardness) (a.u.) $[IP - EA]/2$	0.104200
ζ (Softness) (a.u.) ⁻¹ , $1/2\eta$	4.798464
ψ (Electrophilicity index) (a.u.), $\mu^2/2\eta$	0.109171
Maximum charge transfer index ($\Delta N_{\max} = -\mu/\eta$)	1.447553

To further quantify the electronic behavior, global reactivity descriptors were derived from the FMO energies (Table 7). The calculated values for electronegativity (0.150835 a.u.), chemical hardness (0.104200 a.u.), chemical softness (0.104200 a.u.), chemical potential (-0.150835 a.u.), maximum charge transfer index (1.447553), and the electrophilicity index (0.109171 a.u.) reveal moderate hardness and appreciable softness. This structural balance displays that the molecule is capable of engaging in both nucleophilic and electrophilic interactions.

To conclude, the FMO analysis demonstrates that 2-ethoxy-5-fluoro-1H-pyrimidin-4-one exhibits a highly polarized electronic structure governed by the combined effects of the pyrimidinone ring, fluorine substituent, carbonyl group, and ethoxy functionality. The distribution of the frontier orbitals highlights the important role of heteroatoms in controlling electron density and charge-transfer pathways. The mentioned findings provide a deeper understanding of the molecule's reactivity, stability, spectroscopic behavior, and potential utility in pharmaceutical, agrochemical, and functional-material applications.

3.7 Electrostatic Potential and Molecular Electrostatic Potential Analysis of 2-Ethoxy-5-fluoro-1H-pyrimidin-4-one

To gain deeper information about the electronic distribution and reactive sites of 2-ethoxy-5-fluoro-1H-pyrimidin-4-one compound, electrostatic potential (ESP) and molecular electrostatic potential (MEP) surfaces were generated at the B3LYP/6-31+G(d,p) level of theory. These surface maps provide a visual representation of the electron-density distribution throughout the molecule and facilitate the identification of regions susceptible to electrophilic and nucleophilic interactions. In addition, ESP and MEP analyses are valuable tools for predicting intermolecular interactions, hydrogen-bonding behavior, molecular recognition processes, and the preferred sites of chemical reactivity.

The simulated ESP map image given in Fig. 5 reveals a highly non-uniform charge distribution arising from the presence of electronegative fluorine, oxygen, and nitrogen atoms within the molecular structure. The most negative electrostatic potential regions are predominantly concentrated around the carbonyl oxygen atom and the ring nitrogen atoms of the pyrimidinone moiety. The electron-rich centers exhibit a strong tendency toward electrophilic attack and may serve as favorable hydrogen-bond acceptor sites. The fluorine atom also contributes to the negative electrostatic potential due to its high electronegativity, although its contribution is generally less pronounced than that of the carbonyl oxygen atom.

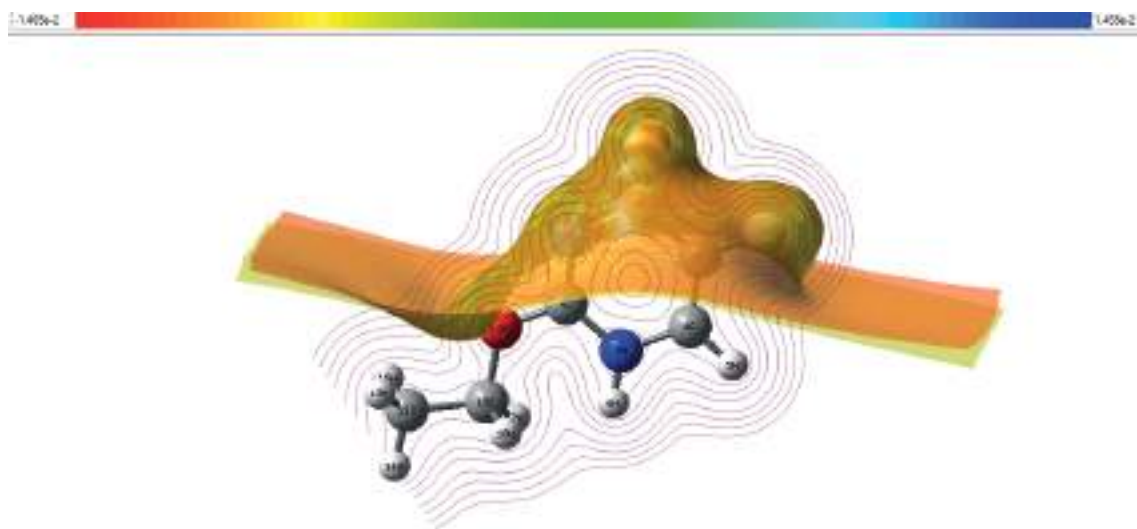


Figure 5. 3D plot for ESP map for 2-ethoxy-5-fluoro-¹H-pyrimidin-4-one molecule

The 3D MEP surface shown in Fig. 6 further highlights the distribution of positive and negative electrostatic potential over the molecular structure of 2-ethoxy-5-fluoro-1H-pyrimidin-4-one molecule. The regions represented by red and yellow colors correspond to areas of high electron density and negative potential, which are mainly localized around the carbonyl oxygen atom, fluorine substituent, and ring nitrogen atoms. The reported regions are expected to participate actively in intermolecular interactions involving electrophilic species. In contrast, the positive electrostatic potential regions, typically represented by blue colors, are primarily located around the hydrogen atoms of the N-H group and the ethoxy substituent. These electron-deficient regions may act as hydrogen-bond donors and are favorable sites for nucleophilic interactions.

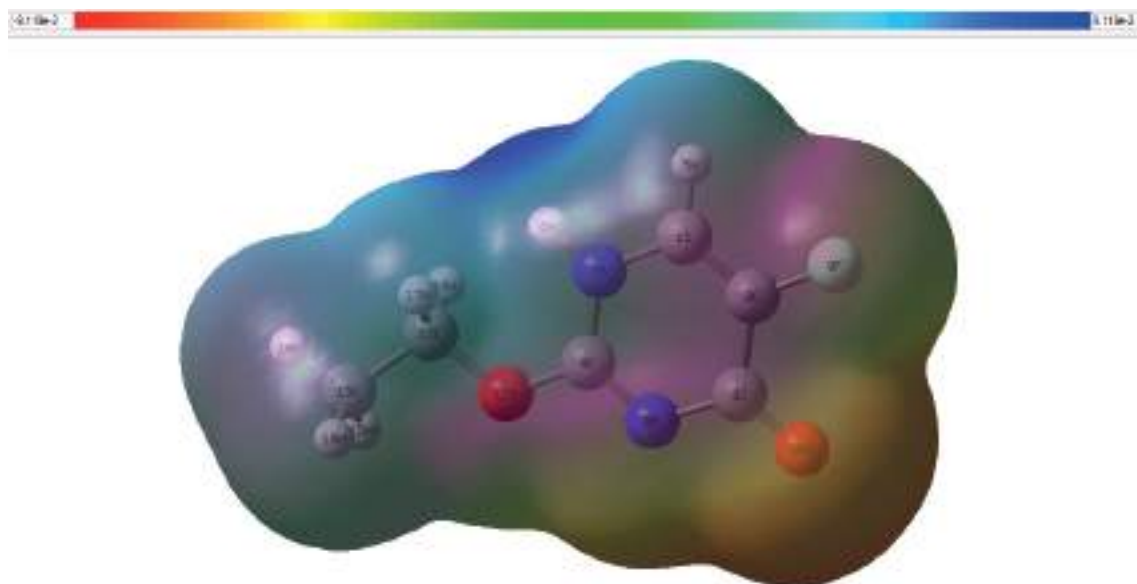


Figure 6. 3D plots of MEP image of 2-ethoxy-5-fluoro-1H-pyrimidin-4-one molecule

The intermediate potential regions distributed throughout the pyrimidinone ring indicate significant electron delocalization within the heterocyclic structure. The conjugative interaction among the carbonyl group, nitrogen atoms, fluorine substituent, and the π -electron system contributes to a





balanced redistribution of electron density across the molecule. Such delocalization plays a crucial role in stabilizing the molecular structure and influences both its spectroscopic and reactive properties.

The coexistence of well-defined electron-rich and electron-deficient regions demonstrates the polarized nature of 2-ethoxy-5-fluoro-¹H-pyrimidin-4-one compound. This polarization originates from the combined electron-withdrawing effects of the fluorine atom and carbonyl group, together with the electron-donating contribution of the ethoxy substituent. As a result, the molecule studied in the present work possesses multiple active sites capable of participating in various non-covalent interactions, including hydrogen bonding, dipole-dipole interactions, electrostatic attractions, and charge-transfer processes [50].

When considered alongside the frontier molecular orbital and UV-Vis analyses, the ESP and MEP results provide strong evidence for intramolecular charge redistribution within the molecule. The pronounced electronic polarization and favorable charge-transfer characteristics suggest that 2-ethoxy-5-fluoro-¹H-pyrimidin-4-one possesses desirable electronic properties that may be relevant to its chemical reactivity, biological activity, molecular recognition capability, and potential applications in pharmaceutical and functional-material research.

4. Conclusion

In the present study, a detailed quantum-chemical investigation of 2-ethoxy-5-fluoro-1H-pyrimidin-4-one was performed using DFT/B3LYP and HF computational approaches in order to examine its molecular structure, NMR characteristics, atomic charge distribution, thermochemical behavior, electronic properties, and reactivity descriptors. Geometry optimization confirmed the stability of the heterocyclic pyrimidinone structure and displayed that the fluorine substituent, carbonyl functionality, and ethoxy group collectively influence the molecular electronic environment. The optimized structural parameters obtained from both theoretical methods exhibited good consistency, supporting the reliability of the computational methodology.

Moreover, theoretical ¹H and ¹³C NMR analyses performed using the GIAO formalism successfully reproduced the experimental spectral trends. The B3LYP calculations provided closer agreement with the experimental chemical shifts than the HF quantum computational method, emphasizing the critical role of electron-correlation effects in accurately describing magnetic shielding environments. The observed chemical-shift distribution confirmed the strong deshielding influence of the fluorine atom, carbonyl group, and ring nitrogen atoms on adjacent nuclei.

Mulliken and APT atomic charge analyses also revealed significant electronic polarization within the molecule. The carbonyl oxygen atom, fluorine substituent, and pyrimidine nitrogen atoms were identified as the principal electron-rich centers, whereas several carbon and hydrogen atoms carried positive charges. Although the absolute charge magnitudes differed between the Mulliken and APT approaches, both methods consistently described the same qualitative charge-distribution pattern, confirming substantial intramolecular charge redistribution throughout the molecular structure.

Further, the thermochemical calculations indicated that the molecule possesses favorable energetic stability and a relatively polar character. Frontier molecular orbital analysis showed that the HOMO is primarily associated with the heteroatom-rich pyrimidinone ring, while the LUMO is concentrated in the carbonyl- and fluorine-influenced regions of the molecule. The resulting HOMO-LUMO separation facilitates intramolecular charge transfer and contributes significantly to the electronic and optical behavior of the compound. Global reactivity descriptors further indicated moderate chemical hardness together with appreciable softness, revealing that the molecule can participate in both electrophilic and nucleophilic interactions.

The simulated UV-Vis absorption spectrum revealed that the principal electronic transitions originate from $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ excitations involving the conjugated heterocyclic system and heteroatom lone



pairs. In addition, ESP and MEP surface analyses identified the carbonyl oxygen atom, fluorine atom, and pyrimidine nitrogen atoms as the most favorable sites for electrophilic interactions, whereas the N-H and ethoxy hydrogen atoms constitute the principal positive-potential regions capable of participating in hydrogen-bonding and nucleophilic interactions.

In summary, the combined structural, spectroscopic, thermochemical, and electronic analyses establish that 2-ethoxy-5-fluoro-¹H-pyrimidin-4-one possesses a stable and highly polarized donor-acceptor electronic structure characterized by efficient charge redistribution, well-defined reactive regions, and favorable electronic-response characteristics. The findings obtained from the present study provide a reliable theoretical foundation for future experimental investigations and indicate that this fluorinated pyrimidinone derivative may be a promising candidate for pharmaceutical, agrochemical, and advanced functional-material applications.

References

- [1] Brown, D. J., Ellman, J. A., & Taylor, E. C. (2000). *The Pyridazines, Volume 57, Supplement 1*. John Wiley & Sons.
- [2] Joule, J. A., & Mills, K. (2012). *Heterocyclic chemistry at a glance*. John Wiley & Sons.
- [3] Katritzky, A. R., Ramsden, C. A., Joule, J. A., & Zhdankin, V. V. (2010). *Handbook of heterocyclic chemistry*. Elsevier.
- [4] Purser, S., Moore, P. R., Swallow, S., & Gouverneur, V. (2008). Fluorine in medicinal chemistry. *Chemical Society Reviews*, 37(2), 320-330. <https://doi.org/10.1039/B610213C>
- [5] Hughes, R. P., & O'Hagan, D. (2010). Graphical Abstracts/J. Fluorine Chem. 131 (2010) 1049–1056. *Journal of Fluorine Chemistry*, 131, 1049-1056. <https://doi.org/10.1016/j.jfluchem.2010.09.001>
- [6] Meanwell, N. A. (2018). Fluorine and fluorinated motifs in the design and application of bioisosteres for drug design. *Journal of medicinal chemistry*, 61(14), 5822-5880. <https://doi.org/10.1021/acs.jmedchem.7b01788>
- [7] Noser, A. A., Khalifa, M. M., Salman, I. N., & Salem, M. M. (2026). Advanced pyrimidinone chemistry: a comprehensive review of synthetic pathways and biological potency. *Chemical Papers*, 1-23. <https://doi.org/10.1007/s11696-026-04512-x>
- [8] Kawamura, S., & Sanemitsu, Y. (1993). A novel ring transformation of oxazinones and azetidinones into pyrimidinones. *The Journal of Organic Chemistry*, 58(2), 414-418. <https://doi.org/10.1021/jo00054a027>
- [9] Sharma, A. K., Jayakumar, S., Hundal, M. S., & Mahajan, M. P. (2002). Tandem sigmatropic shifts in [4+ 2] cycloaddition reactions of 1, 3-diazabuta-1, 3-dienes with butadienyketene: synthesis of pyrimidinone derivatives. *Journal of the Chemical Society, Perkin Transactions 1*, (6), 774-784. <https://doi.org/10.1039/B109675P>
- [10] Bayrakdar, A., Nivetha, G. F., Demircali, A., Kizak, H., Tasli, P. T., Yıldırım, F., ... & Smerat, A. (2026). Synthesis of New Pyrazolo Pyrimidine Disazo Dyes, Theoretical and Experimental Comparison of their Characteristic Properties and in silico Prediction of their Possible Antibacterial Activity. *Journal of Computational Biophysics and Chemistry*, 1-27. <https://doi.org/10.1142/S273741652650012X>
- [11] Sivaraman, B., Maji, L., Chagaleti, B. K., & Muthukumaradoss, K. (2026). Exploration of a Novel Imidazo [4, 5-b] pyridine-dihydropyrimidinone hybrids as aurora kinase a inhibitors: integrated pharmacophore modelling, docking and simulation approaches. *Molecular Diversity*, 1-22. <https://doi.org/10.1007/s11035-026-0123-4>





doi.org/10.1007/s11030-026-10823-1

- [12] Nangia, A. (2006). Supramolecular Synthesis of 1D Chains and 2D Layers in Hydrogen Bond Networks of Ureas and 2-Pyrimidinones. *Topics in Stereochemistry*, 25, 135-176. <https://doi.org/10.1002/0470008401.ch4>
- [13] Muthuraman, M., Le Fur, Y., Bagieu-Boucher, M., Masse, R., Nicoud, J. F., George, S., ... & Desiraju, G. R. (2000). C-H... O and C-H... N Hydrogen Bond Networks in the Crystal Structures of Some 1, 2-Dihydro-N-aryl-4, 6-dimethylpyrimidin-2-ones. *Journal of Solid State Chemistry*, 152(1), 221-228. <https://doi.org/10.1006/jssc.2000.8687>
- [14] Parr, R. G. (1989). Density functional theory of atoms and molecules. In *Horizons of Quantum Chemistry: Proceedings of the Third International Congress of Quantum Chemistry Held at Kyoto, Japan, October 29-November 3, 1979* (pp. 5-15). Dordrecht: Springer Netherlands.
- [15] Becke, A. D. (1993). Density-functional thermochemistry. III. The role of exact exchange. *The Journal of Chemical Physics*, 98(7), 5648-5652. <https://doi.org/10.1063/1.464913>
- [16] Lee, C., Yang, W., & Parr, R. G. (1988). Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. *Physical review B*, 37(2), 785. <https://doi.org/10.1103/PhysRevB.37.785>
- [17] Koopmans, T. (1934). Über die Zuordnung von Wellenfunktionen und Eigenwerten zu den einzelnen Elektronen eines Atoms. *physica*, 1(1-6), 104-113. [https://doi.org/10.1016/S0031-8914\(34\)90011-2](https://doi.org/10.1016/S0031-8914(34)90011-2)
- [18] Buyukuslu, H., Akdogan, M., Yildirim, G., & Parlak, C. (2010). Ab initio Hartree-Fock and density functional theory study on characterization of 3-(5-methylthiazol-2-yl-diazenyl)-2-phenyl-1H-indole. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 75(4), 1362-1369. <https://doi.org/10.1016/j.saa.2010.01.002>
- [19] Parlak, C., Akdogan, M., Yildirim, G., Karagoz, N., Budak, E., & Terzioglu, C. (2011). Density functional theory study on the identification of 3-[(2-morpholinoethylimino) methyl] benzene-1, 2-diol. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 79(1), 263-271. <https://doi.org/10.1016/j.saa.2011.02.043>
- [20] Gökce, H., & Bahçeli, S. (2025). Biological evaluation, spectroscopic characterization and DFT computations of an oxalamide derivative (BFMO). *Journal of Molecular Structure*, 143654. <https://doi.org/10.1016/j.molstruc.2024.143654>
- [21] Gökce, H., Bahçeli, S., & Alpaslan, G. (2024). Structural, vibrational, electronic, NLO and molecular docking analyses of two novel Cu (II) and Pd (II) complexes with pyridine and oxadiazole coordination. *Inorganic Chemistry Communications*, 168, 112852. <https://doi.org/10.1016/j.inoche.2024.112852>
- [22] D.C. Young, *Computational Chemistry: A Practical Guide for Applying Techniques to Real World Problems* (Electronic), JohnWiley & Sons Inc., New York, 2001.
- [23] A.D. Becke, *J. Chem. Phys.* 98 (1993) 5648. <https://doi.org/10.1063/1.464913>
- [24] P. J. Stephens, F. J. Devlin, C. F. Chabalowski, M. J. Frisch, *J. Phys. Chem.* 98 (1994) 11623. <https://doi.org/10.1021/j100096a001>
- [25] M.M. Francl, W.J. Pietro, W.J. Hehre, J.S. Binkley, M.S. Gordon, D.J. DeFrees, J.A. Pople, *J. Chem. Phys.* 77 (1982) 3654. <https://doi.org/10.1063/1.444267>
- [26] M.J. Frisch, et al., Gaussian 09, Revision A.02, Gaussian, Inc., Wallingford, CT (2009)
- [27] R. Dennington II, T. Keith, J. Millam, GaussView, Version 4.1.2, Semichem, Inc., Shawnee Mission, KS (2007)



- [28] Cyrański, M. K. (2005). Energetic aspects of cyclic π -electron delocalization: evaluation of the methods of estimating aromatic stabilization energies. *Chemical reviews*, 105(10), 3773-3811. <https://doi.org/10.1021/cr0300841>
- [29] Steinmann, S. N., Mo, Y., & Corminboeuf, C. (2011). How do electron localization functions describe π -electron delocalization?. *Physical chemistry chemical physics*, 13(46), 20584-20592. <https://doi.org/10.1039/C1CP21820E>
- [30] Palusiak, M., & Krygowski, T. M. (2007). Application of AIM Parameters at Ring Critical Points for Estimation of π -Electron Delocalization in Six-Membered Aromatic and Quasi-Aromatic Rings. *Chemistry—A European Journal*, 13(28), 7996-8006. <https://doi.org/10.1002/chem.200700232>
- [31] Sobczyk, L., Grabowski, S. J., & Krygowski, T. M. (2005). Interrelation between H-bond and π -electron delocalization. *Chemical reviews*, 105(10), 3513-3560. <https://doi.org/10.1021/cr0300839>
- [32] Snyder, J. P., & Carlsen, L. (1977). Lone pair-lone pair interactions in unsymmetrical systems: RSSR vs. RSOR. *Journal of the American Chemical Society*, 99(9), 2931-2942. <https://doi.org/10.1021/ja00451a014>
- [33] Xu, Y., Hao, J., Ju, H., He, S., Wang, J., Jia, C., & Guo, X. (2024). Identifying π - π and π -lone pair interactions in a single-molecule junction. *ACS Materials Letters*, 6(5), 1961-1967. <https://doi.org/10.1021/acsmaterialslett.4c00421>
- [34] Zhou, W., & Umezawa, N. (2015). Band gap engineering of bulk and nanosheet SnO: an insight into the interlayer Sn-Sn lone pair interactions. *Physical Chemistry Chemical Physics*, 17(27), 17816-17820. <https://doi.org/10.1039/C5CP02383B>
- [35] Fanchini, G., Tagliaferro, A., Conway, N. M. J., & Godet, C. (2002). Role of lone-pair interactions and local disorder in determining the interdependency of optical constants of a-C N: H thin films. *Physical Review B*, 66(19), 195415. <https://doi.org/10.1103/PhysRevB.66.195415>
- [36] Laury, M. L., Carlson, M. J., & Wilson, A. K. (2012). Vibrational frequency scale factors for density functional theory and the polarization consistent basis sets. *Journal of computational chemistry*, 33(30), 2380-2387. <https://doi.org/10.1002/jcc.23073>
- [37] Boo, B. H., Cho, H., & Kang, D. E. (2007). Ab initio and DFT investigation of structures and energies of low-lying isomers of Zn_xSex ($x=1-4$) clusters. *Journal of Molecular Structure: THEOCHEM*, 806(1-3), 77-83. <https://doi.org/10.1016/j.theochem.2006.11.006>
- [38] Antony, J., & Grimme, S. (2006). Density functional theory including dispersion corrections for intermolecular interactions in a large benchmark set of biologically relevant molecules. *Physical Chemistry Chemical Physics*, 8(45), 5287-5293. <https://doi.org/10.1039/B612585A>
- [39] Tsuzuki, S., & Uchimaru, T. (2020). Accuracy of intermolecular interaction energies, particularly those of hetero-atom containing molecules obtained by DFT calculations with Grimme's D2, D3 and D3BJ dispersion corrections. *Physical Chemistry Chemical Physics*, 22(39), 22508-22519. <https://doi.org/10.1039/D0CP03853J>
- [40] Jumabaev, A., Koyambo-Konzapa, S. J., Hushvaktov, H., Absanov, A., Khudaykulov, B., Holikulov, U., ... & Nsangou, M. (2024). Intermolecular interactions in water and ethanol solution of ethyl acetate: Raman, DFT, MEP, FMO, AIM, NCI-RDG, ELF, and LOL analyses. *Journal of Molecular Modeling*, 30(10), 349. <https://doi.org/10.1007/s00894-024-06132-7>
- [41] Mohammadi, M. D., Abdullah, H. Y., Qadir, K. W., & Suvitha, A. (2023). Theoretical investigation of intermolecular interactions between CNT, SiCNT and SiCGeNT nanomaterials with vinyl chloride molecule: a DFT, NBO, NCI, and QTAIM study. *Diamond and Related Materials*, 131, 109602. <https://doi.org/10.1016/j.diamond.2022.109602>





- [42] Xiao, J., Zhao, Y. P., Fan, X., Cao, J. P., Kang, G. J., Zhao, W., & Wei, X. Y. (2017). Hydrogen bonding interactions between the organic oxygen/nitrogen monomers of lignite and water molecules: A DFT and AIM study. *Fuel Processing Technology*, 168, 58-64. <https://doi.org/10.1016/j.fuproc.2017.08.030>
- [43] Furer, V. L., Potapova, L. I., & Kovalenko, V. I. (2017). DFT study of hydrogen bonding and IR spectra of calix [6] arene. *Journal of Molecular Structure*, 1128, 439-447. <https://doi.org/10.1016/j.molstruc.2016.09.009>
- [44] Tortorella, S., Talamo, M. M., Cardone, A., Pastore, M., & De Angelis, F. (2016). Benchmarking DFT and semi-empirical methods for a reliable and cost-efficient computational screening of benzofulvene derivatives as donor materials for small-molecule organic solar cells. *Journal of Physics: Condensed Matter*, 28(7), 074005. <https://doi.org/10.1088/0953-8984/28/7/074005>
- [45] Puchkovska, G. O., & Kostyukevych, S. (Eds.). (2002). *Spectroscopy of Molecules and Crystals*. SPIE.
- [46] Jeanmairet, G., Levy, N., Levesque, M., & Borgis, D. (2016). Molecular density functional theory of water including density-polarization coupling. *Journal of Physics: Condensed Matter*, 28(24), 244005. <https://doi.org/10.1088/0953-8984/28/24/244005>
- [47] Wolff, S. K., & Ziegler, T. (1998). Calculation of DFT-GIAO NMR shifts with the inclusion of spin-orbit coupling. *The Journal of Chemical Physics*, 109(3), 895-905. <https://doi.org/10.1063/1.476630>
- [48] Hsu, C. Y., Abdulazez, A. A., Priya, G. P., Ray, S., Pal, A., Yusupov, Y., ... & Alkhathami, A. G. (2026). Pt decorated BN nanocage as an effective sensor material for the detection of 5-Fluorouracil anticancer drug. *Materials Chemistry and Physics*, 132204. <https://doi.org/10.1016/j.matchemphys.2025.132204>
- [49] Ibrahim, A., El Aal, M. A., El-Zahed, H., & Mabied, A. F. (2026). DFT study on tunable electronic and adsorption properties of poly (vinyl alcohol)/copper oxide/graphene oxide hybrid nanostructures. *Scientific Reports*, 16(1), 16191. <https://doi.org/10.1038/s41598-026-89123-x>
- [50] Zhang, Y., Luo, Y., Zhang, Y., Yu, Y. J., Kuang, Y. M., Zhang, L., ... & Hou, J. G. (2016). Visualizing coherent intermolecular dipole-dipole coupling in real space. *Nature*, 531(7596), 623-627. <https://doi.org/10.1038/nature17428>



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Research Article

Network Intrusion Detection Using Machine Learning Algorithms on the NSL-KDD Dataset: A Comparative Experimental Study

Rasim Çekik¹ ¹Department of Computer Engineering, Faculty of Engineering, Sırnak University, Sırnak, Türkiye**Abstract**

The automatic detection of malicious activity in network traffic is one of the most critical components of today's cybersecurity infrastructure. This study presents a reproducible experimental comparison that evaluates the binary classification performance—specifically, the ability to distinguish between normal and attack traffic—of three different machine learning classifiers (Logistic Regression, Decision Tree, and Random Forest) on the NSL-KDD dataset, which is widely used in the intrusion detection literature. To this end, a common Python evaluation pipeline was established, consisting of steps such as converting categorical features (e.g., protocol type, service, flags) to numerical form, standardizing the features, performing stratified training/test splits, and evaluating the models using accuracy, precision, recall, F1-score, and the area under the receiver operating characteristic curve (ROC-AUC). The experimental results showed that the Random Forest model achieved the highest performance with 99.90% accuracy, a 99.89% F1-score, and an AUC of 1.00; this superiority was found to be statistically significant at $p < 0.001$ and was confirmed to be robust via 5-fold cross-validation. The results obtained quantitatively demonstrate the extent to which tree-based ensemble methods offer an advantage over linear models on NSL-KDD and show that the common evaluation protocol used can be easily extended to different datasets and classifiers.

Keywords: Intrusion Detection System, NSL-KDD, Machine Learning, Network Security, Random Forest, Comparative Evaluation

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1. Introduction

As the scale and complexity of computer networks have increased, the timely detection of malicious network activity—such as unauthorized access, denial-of-service attacks, and reconnaissance scanning—has become one of the fundamental requirements of enterprise security operations. The inadequacy of signature-based intrusion detection systems in detecting unknown attack types has led to a growing interest in machine learning-based approaches over the past two decades [1, 2]. A significant portion of the experimental work in this field is based on the KDD Cup 99 dataset, published in 1999, which was widely used in the attack detection literature for a long time [1]. However, a critical review by Tavallaee et al. [1] revealed that this dataset contained a high proportion of duplicate records in both the training and test sets, causing classifiers to become biased toward duplicate examples and, consequently, resulting in unreasonably high reported performance metrics. Developed to address these methodological issues, the NSL-KDD dataset has established itself in the literature as an improved version of KDD Cup 99 through the removal of duplicate records and the balancing of class distributions [1].

To date, a wide range of classical classifiers have been tested on NSL-KDD, ranging from linear models such as Logistic Regression [3] to individual tree-based methods such as Decision Trees [4] and ensemble approaches such as Random Forests [5, 6]. It has generally been reported that ensemble-based methods provide higher accuracy [7, 8]. However, in the majority of these studies, preprocessing steps—such as feature encoding, scaling, and training/test split—are applied in different ways, making it difficult to directly compare performance metrics reported in one study with those in another. Therefore, re-examining the same three classical classifiers under the same data preprocessing and evaluation steps still offers a valuable contribution toward bringing together these scattered findings in the literature on a consistent basis.

In this study, Logistic Regression, Decision Tree, and Random Forest classifiers were compared on the NSL-KDD dataset using a reproducible Python experimental workflow that applied the same preprocessing and evaluation steps. The findings were further analyzed using confusion matrices, ROC-AUC, and feature importance analyses to determine which network traffic features are discriminative in attack detection. The contributions of this study, which takes the form of a comparative evaluation, can be summarized as follows: (a) Preprocessing steps—including label binning, encoding of categorical features, standardization, and stratified training/testing splits—on the NSL-KDD dataset were combined into a single reproducible workflow; (b) Three existing classifiers were compared under the same conditions using five different metrics: accuracy, precision, sensitivity, F1-score, and AUC; (c) A feature importance analysis based on the Random Forest model is presented.

The remainder of the paper is organized as follows. Section 2 reviews the relevant literature. Section 3 introduces the NSL-KDD dataset. Section 4 explains the methods used in the comparison. Section 5 presents the experimental setup. Section 6 reports the experimental findings accompanied by tables and figures. Section 7 discusses the findings and concludes the study.

2. Related Works

A review of the literature on network intrusion detection indicates that the use of features extracted from raw network traffic in conjunction with classification algorithms achieves better performance in anomaly detection than traditional signature-based methods [9]. In line with this, the KDD Cup 99 dataset, which was developed and long regarded as the de facto standard of the field, has been extensively used in the literature. However, detailed analyses conducted on the dataset have shown that the excessive duplication rate, approximately 78% in the training set and around 75% in the test set, causes classifiers to become biased toward frequently observed records [1]. The NSL-KDD dataset removes these redundant records and performs subsampling according to difficulty levels, thus providing a more reliable and objective comparison ground for algorithm performance.



Revathi and Malathi [7] compared various algorithms such as SVM, Random Forest, k-NN, and decision trees on NSL-KDD and reported that ensemble-based methods generally provide higher accuracy compared to single classifiers. Furthermore, Dhanabal and Shantharajah [8] conducted a detailed analysis of the feature structure of NSL-KDD in terms of classification algorithms. Their study emphasized that proper encoding of categorical features such as protocol type, service, and flag is decisive on model performance. In addition, the Random Forest algorithm proposed by Breiman [5] is based on the principle of training numerous decision trees on bootstrap samples and combining them via majority voting, and it generally produces more robust results compared to linear models against overfitting in high-dimensional, noisy data. This characteristic of the algorithm makes it stand out in datasets such as NSL-KDD, which has 41 features and harbors complex interactions among classes.

In recent years, alongside classical machine learning algorithms, deep learning and large language model (LLM)-based approaches have been increasingly investigated on NSL-KDD and similar intrusion detection datasets. Kasula et al. [10] proposed a hybrid model combining Random Forest with LSTM networks to perform real-time anomaly detection in cloud environments, achieving a precision value of 94.78% on NSL-KDD and cloud log data. This study demonstrates that Random Forest continues to be used as a fundamental component even in complex hybrid architectures. Ali et al. [11], in their system called HuntGPT, combined a Random Forest classifier trained on the KDD99 dataset with explainable AI (XAI) techniques such as SHAP and LIME, along with a large language model-based chat interface, enabling security analysts to interpret detection results more easily. Ziems et al. [12], on the other hand, aimed to enhance the interpretability of decision tree-based models in network attack detection by converting the decision paths of decision tree models into natural language and generating explanations through large language models. These studies show that classical classifiers such as Logistic Regression, Decision Tree, and Random Forest still play a central role in the literature, both as standalone models and as components of more complex hybrid and LLM-supported architectures. This study aims to compare these three classical classifiers under a common and transparent evaluation protocol. To this end, the study presents a standardized preprocessing pipeline, an evaluation framework consisting of five different performance metrics, and a feature importance analysis, thereby providing a reproducible application infrastructure with a priority on interpretability and computational efficiency.

3. Dataset

In this study, the 'KDDTrain+' subset, which constitutes the training portion of the NSL-KDD dataset [13], was used for training network intrusion detection models. This dataset contains a total of 125,973 records, each consisting of 41 features, a class label, and a difficulty level score. The features in the dataset are grouped into four main categories based on their structural characteristics. The first of these, basic connection features, includes fundamental network parameters such as duration, protocol_type, service, flag, src_bytes, and dst_bytes. The second group, content features, encompasses attributes related to connection content and security, such as num_failed_logins, root_shell, and num_compromised. The third group, time-based traffic features, presents statistical data such as the number of connections within a specific time window (count), the number of connections to the same service (srv_count), and the SYN error rate (serror_rate), while the final group, host-based traffic features, describes host-oriented traffic patterns such as dst_host_count and dst_host_same_srv_rate.

Upon examining the data structure, it is observed that features such as protocol_type ('tcp', 'udp', 'icmp'), service, and flag take categorical values. To enable numerical-based classification algorithms to process these data effectively, these textual features need to be converted into appropriate numerical forms during the preprocessing stage. In the original dataset, the target variable consists of approximately 22 different classes representing various types of cyberattacks (e.g., neptune, smurf, satan, normal). However, in this study, in order to address the problem within a binary classification framework, the relevant labels were reduced to two fundamental classes: 0 for 'normal' records and 1 for 'attack'





records, created by consolidating all anomaly and attack types. The resulting class distribution, with 67,343 normal (53.5%) and 58,630 attack (46.5%) records, is shown in Figure 1.

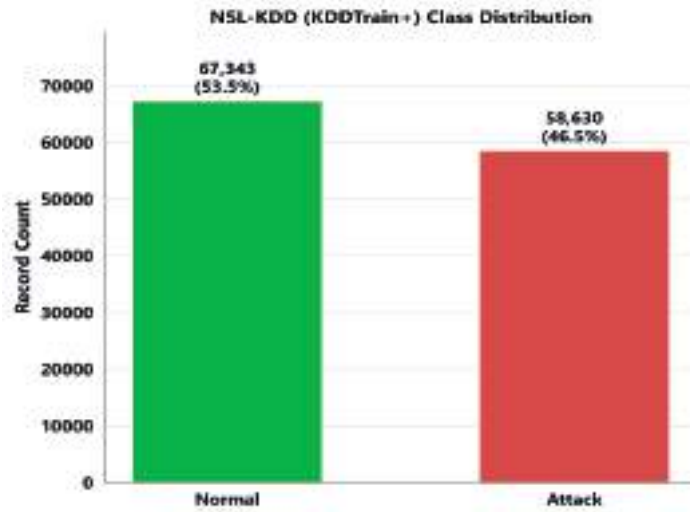


Figure 1. NSL-KDD (KDDTrain+) dataset class distribution

4. Materials and Methods

In this section, Logistic Regression, Decision Tree, and Random Forest algorithms are comparatively addressed on the NSL-KDD dataset under the same data preprocessing and evaluation steps. The preprocessing steps applied sequentially, the classification models included in the comparison, and the evaluation metrics used are described.

4.1. Preprocessing

The following preprocessing steps were applied sequentially on the raw dataset: (1) The label column representing the target variable was reduced in accordance with the binary classification architecture. (2) The categorical features in the dataset, namely protocol_type, service, and flag, were subjected to integer encoding to be converted into numerical format. (3) The transformed dataset was split into 70% training and 30% test sets using a stratified method to preserve the overall distribution ratio of the original classes. (4) All features were standardized using StandardScaler with the mean and standard deviation computed from the training set. The scaler was computed solely on the training data, and only the transformation was applied to the test data; this approach was preferred to prevent information leakage from the test set into the training process.

In the standardization step, a z-score transformation was applied for each feature value x , as shown in Equation (1):

$$z = \frac{x - \mu}{\sigma} \quad (1)$$

where μ and σ are the mean and standard deviation of the respective feature, computed solely on the training set [14].

4.2. Classification Models

In the classification phase, three different classifier families were compared: (i) Logistic Regression, based on linear decision boundaries and considered as the baseline model due to its high interpretability. (ii) Decision Tree, a single tree model that can learn non-linear decision boundaries by recursively partitioning the feature space. (iii) Random Forest, which has an ensemble learning-based architecture



where numerous decision trees are trained on bootstrap samples and combined via majority voting. The parameters used for running the methods are given in Table 1. All three models were trained and evaluated on the same training/test split and the same scaled feature set.

Table 1. Models used for comparison and the parameters employed in their implementation

Classifier	Parameter	Value	Description
Logistic Regression	max_iter	1000	Maximum number of iterations allowed for the optimization solver to converge
Decision Tree	criterion	gini (default)	Impurity measure used to assess split quality
Decision Tree	random_state	42	Fixing internal randomness sources of the tree (split selection)
Random Forest	n_estimators	100	Number of decision trees used in the ensemble
Random Forest	random_state	42	Fixing bootstrap sampling and feature subset selection
General (all models)	train/test split random_state	42	Fixed to ensure reproducibility of the data split

In the Logistic Regression model, given the weight vector w and the bias term b , the probability that a sample belongs to the attack class ($y = 1$) is calculated using the sigmoid function, as given in Equation (2):

$$P(y = 1 | x) = \frac{1}{1 + e^{-(w \cdot x + b)}} \quad (2)$$

The model parameters were optimized on the training set by minimizing the binary cross-entropy (log-loss) cost function, defined in Equation (3) [15]:

$$J(w, b) = -\frac{1}{N} \sum_{i=1}^N [y_i \log(\hat{p}_i) + (1 - y_i) \log(1 - \hat{p}_i)] \quad (3)$$

Here, N denotes the number of training samples, y_i represents the true label, and $\hat{p}_i$ denotes the predicted probability produced by the model for sample i .

In the Decision Tree model, each split is determined by selecting the feature and threshold value that maximize the reduction in class impurity at a node. For a node t , the Gini impurity is defined as in Equation (4):

$$\text{Gini}(t) = 1 - \sum_{k=1}^K p_k^2 \quad (4)$$

Here, K denotes the number of classes ($K = 2$ in this study), and p_k represents the proportion of samples belonging to class k at node t . The tree is constructed recursively by selecting splits that maximize the information gain, defined as the weighted impurity reduction between a parent node and its child nodes [6].

The Random Forest model consists of an ensemble of B decision trees ($B = 100$ in this study), each trained independently on a bootstrap sample generated through random sampling with replacement from the training data. The final class prediction is determined by majority voting among the individual trees, as given in Equation (5):





$$\hat{y} = \text{mode}\{h_1(x), h_2(x), \dots, h_B(x)\} \quad (5)$$

where $h_b(x)$ denotes the prediction of the b -th decision tree for sample x . By aggregating the predictions of multiple trees, Random Forest reduces variance and improves generalization performance compared with a single decision tree [5].

4.3. Evaluation Metrics

The performance of the trained models was assessed using five complementary metrics: accuracy, precision, recall, F1-score, and the area under the receiver operating characteristic curve (AUC-ROC). To prevent potentially misleading conclusions arising from the class imbalance commonly encountered in cybersecurity datasets, the evaluation was not based solely on overall accuracy. Instead, precision, recall, and F1-score values were also analyzed on a class-specific basis.

Furthermore, the confusion matrix of each model was examined to provide a detailed assessment of the rates of false positives (normal traffic incorrectly classified as attacks) and false negatives (attack traffic incorrectly classified as normal), the latter of which may lead to critical security vulnerabilities. Based on the values of true positives (TP), true negatives (TN), false positives (FP), and false negatives (FN) obtained from the confusion matrix, the evaluation metrics were mathematically defined as in Equations (6)–(9):

$$\text{Accuracy} = \frac{TP + TN}{TP + TN + FP + FN} \quad (6)$$

$$\text{Precision} = \frac{TP}{TP + FP} \quad (7)$$

$$\text{Recall} = \frac{TP}{TP + FN} \quad (8)$$

$$F_1\text{-Score} = \frac{2 \times \text{Precision} \times \text{Recall}}{\text{Precision} + \text{Recall}} \quad (9)$$

The Receiver Operating Characteristic (ROC) curve, which reflects the discriminative capability of a classification model, graphically illustrates the trade-off between the true positive rate (TPR) and the false positive rate (FPR) across different decision thresholds. The Area Under the Curve (AUC) metric, representing the area beneath the ROC curve, provides a threshold-independent measure of classification performance by quantifying the probability that a randomly selected attack instance is assigned a higher attack score than a randomly selected normal traffic instance [16].

5. Experimental Setup

The experiments were conducted in a Python 3.13 environment using the scikit-learn, pandas, NumPy, Matplotlib, and Seaborn libraries [14]. As the benchmark dataset, the training portion of the NSL-KDD dataset proposed by Tavallaee et al. [1] was utilized. The dataset file was obtained from the publicly accessible defcom17/NSL_KDD GitHub repository hosting the NSL-KDD dataset [13].

To ensure reproducibility, a fixed random seed was employed in all procedures involving randomness, including the training–test split and the internal randomization processes of the Decision Tree and Random Forest models. The random seed was fixed at 42 throughout all experiments. The hyperparameters of the models were intentionally restricted to commonly used default and baseline values reported in the



literature, without performing extensive optimization. The parameter settings used in the experiments are summarized in Table 1. This choice was motivated by the primary objective of the study, which is to reveal the relative differences among model families under a common preprocessing framework. Advanced hyperparameter optimization is considered as a direction for future research.

6. Experimental Results and Findings

This section presents the comparative performance results of the three classifiers evaluated on the NSL-KDD test set. The reported results include a performance table containing accuracy, precision, recall, F1-score, and AUC values, class-wise classification reports, a comparative model performance chart, confusion matrices, ROC curves, and a feature importance analysis based on the Random Forest model.

6.1. Overall Performance Comparison

Table 2 summarizes the accuracy, precision, recall, F1-score, AUC, and Average Precision (AP) values achieved by the three classifiers on the test set. Figure 2 provides a visual comparison of the models according to these key performance metrics.

According to the obtained results, the Random Forest model achieved the best overall performance among the three classifiers, with 99.90% accuracy, 99.89% F1-score, 1.00 AUC, and 1.00 AP. The Decision Tree model exhibited a performance level that was nearly indistinguishable from that of Random Forest, achieving 99.81% accuracy and 99.80% F1-score. In contrast, the Logistic Regression model, which relies on a linear decision boundary, lagged behind the two tree-based approaches, with 95.35% accuracy and 94.95% F1-score. Furthermore, the recall value of the Logistic Regression model (93.96%) was the lowest among the three models. This finding indicates that Logistic Regression was more prone to misclassifying a portion of attack instances as normal traffic compared with the Decision Tree and Random Forest models. Consequently, the tree-based methods demonstrated a superior capability for capturing the nonlinear relationships and complex patterns inherent in network intrusion detection data.

Table 2. Performance comparison of the models on the test set

Model	Accuracy (%)	Precision (%)	Recall (%)	F1-Score (%)	AUC	AP
Logistic Regression	95.3500	95.9700	93.9600	94.9500	0.9919	0.9904
Decision Tree	99.8100	99.8200	99.7700	99.8000	0.9981	0.9970
Random Forest	99.9000	99.9500	99.8400	99.8900	1.0000	1.0000

The superior performance of the two tree-based models, Decision Tree and Random Forest, compared with the linear model suggests that the relationships among the features in the NSL-KDD dataset are largely nonlinear in nature. By recursively partitioning the feature space and learning complex decision boundaries, tree-based methods are able to capture such interactions more effectively than the linear decision boundary employed by Logistic Regression. The fact that Random Forest achieved marginally better results than the single Decision Tree across all evaluation metrics further indicates that training multiple trees on bootstrap samples and aggregating their predictions through majority voting reduces the tendency of an individual tree to overfit, thereby decreasing model variance and improving generalization performance.

The observation that all models achieved AUC and AP values above 0.99 indicates that the binary classification problem (normal vs. attack traffic) is highly separable on the NSL-KDD test set, regardless of the selected decision threshold. However, this finding should be interpreted in conjunction with the dataset limitations discussed in Section 3.



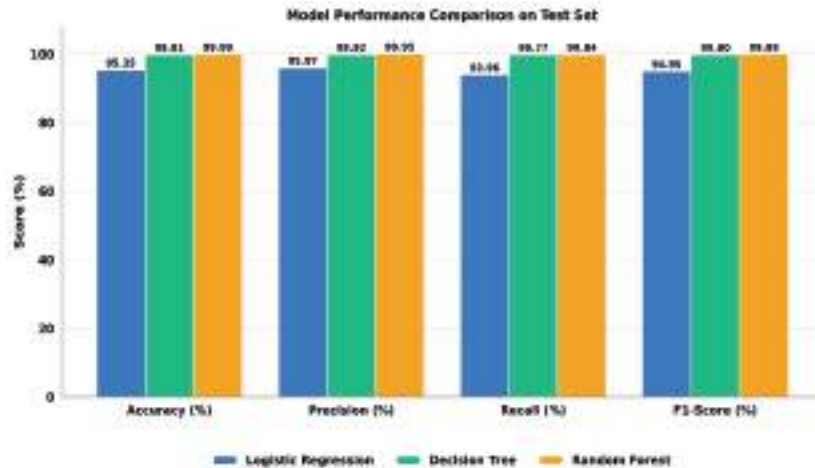


Figure 2. Comparison of the models based on accuracy, precision, recall, and F1-score

6.2. Class-Wise Performance

Table 3 presents the precision, recall, and F1-score values separately for the normal and attack classes for each classifier. Such a class-wise analysis is particularly important in intrusion detection applications because the recall value of the attack class has significant operational implications. A low recall value indicates that a portion of actual attack instances is incorrectly classified as normal traffic, resulting in false negatives. These errors are generally considered more critical than false positives because undetected attacks may lead to severe security breaches.

From this perspective, the Logistic Regression model achieved an attack-class recall of 93.96%, which is noticeably lower than the values obtained by the other two models. This finding suggests that the linear decision boundary employed by Logistic Regression fails to adequately separate some attack instances from normal traffic. In contrast, the Decision Tree and Random Forest models achieved attack-class recall values of 99.77% and 99.84%, respectively, thereby minimizing the number of missed attacks.

Table 3. Class-wise precision, recall, and F1-score results

Model	Class	Precision (%)	Recall (%)	F1-Score (%)	Support
Logistic Regression	Normal	94.83	96.56	95.69	20,203
Logistic Regression	Attack	95.97	93.96	94.95	17,589
Decision Tree	Normal	99.80	99.84	99.82	20,203
Decision Tree	Attack	99.82	99.77	99.80	17,589
Random Forest	Normal	99.86	99.96	99.91	20,203
Random Forest	Attack	99.95	99.84	99.89	17,589

The confusion matrices presented in Figure 3 enable a comparison of the three models in terms of their false positive and false negative rates. Regarding false negatives, out of the 17,589 attack records, Logistic Regression incorrectly classified 1,063 instances as normal traffic, while Decision Tree and Random Forest misclassified only 40 and 28 attack instances, respectively. In terms of false positives, among the 20,203 normal records, Logistic Regression incorrectly labeled 694 instances as attacks, whereas Decision Tree and Random Forest produced only 32 and 9 false alarms, respectively.

These findings demonstrate that the tree-based models maintain substantially lower false-negative rates



than the linear model, which is particularly important from an operational cybersecurity perspective. Since false negatives correspond to undetected attacks, minimizing such errors is crucial for maintaining the effectiveness of an intrusion detection system. Among the evaluated classifiers, Random Forest outperformed not only Logistic Regression but also the single Decision Tree model by achieving the lowest numbers of both false negatives and false positives. Consequently, Random Forest emerged as the most reliable model, simultaneously minimizing missed attacks and false alarms while providing the highest overall classification performance.

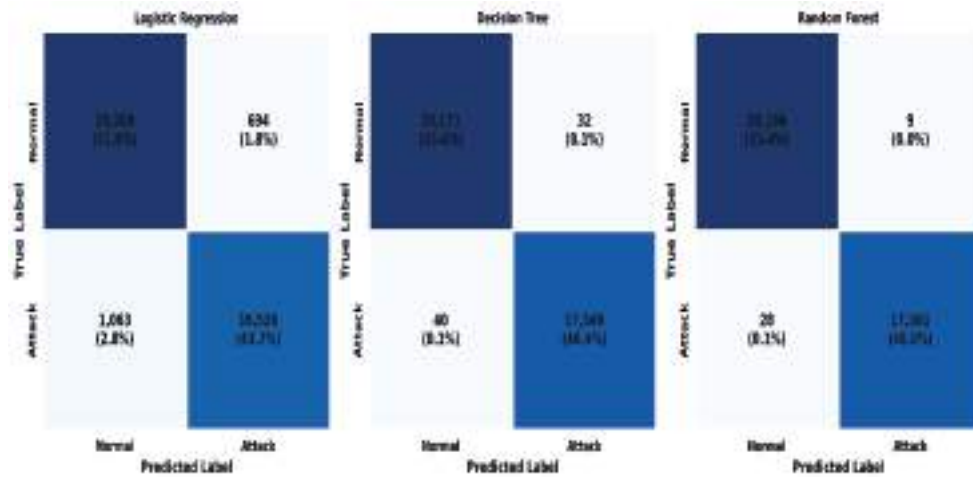


Figure 3. Confusion matrices of the evaluated models

Figure 4 presents the ROC curves and corresponding AUC values for the three classification models. The closer the ROC curve is to the upper-left corner of the plot and the closer its AUC value is to 1, the greater the model's ability to discriminate between classes. The ROC curves of the Decision Tree and Random Forest models rise almost vertically along the y-axis and nearly overlap throughout the graph, achieving AUC values of 0.9981 and 1.0000, respectively. These results indicate that both models possess an excellent capability to distinguish between normal and attack traffic.

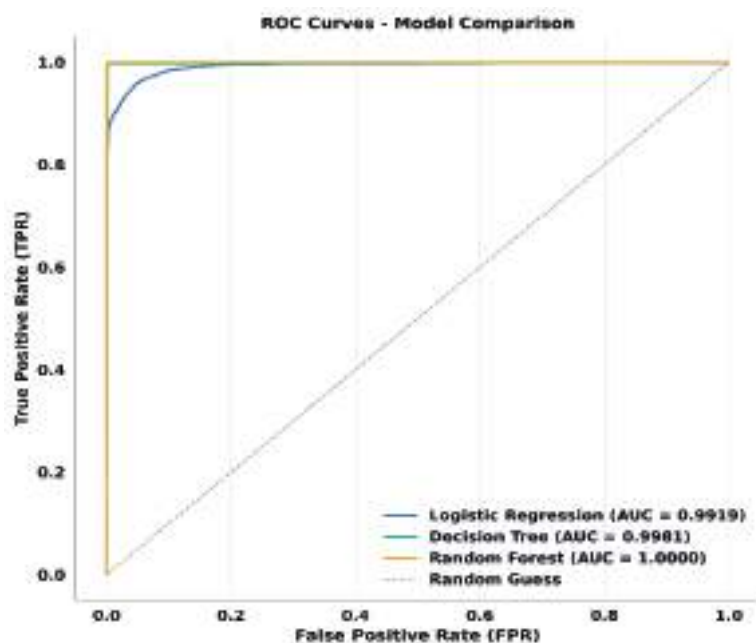


Figure 4. ROC curves and AUC comparison





In contrast, the ROC curve of the Logistic Regression model, with an AUC value of 0.9919, exhibits a noticeably flatter trajectory, particularly at low false-positive rates. This behavior suggests that the linear model produces more classification errors than the tree-based models when the decision threshold is set to a lower value. Although Logistic Regression still demonstrates strong discriminative performance overall, its lower AUC value reflects a reduced ability to capture the complex nonlinear relationships present in the NSL-KDD dataset compared with Decision Tree and Random Forest approaches.

Figure 5 illustrates the precision–recall (PR) curves and the corresponding Average Precision (AP) values for the three classification models. Since the class distribution in the dataset is moderately imbalanced, PR curves provide a complementary perspective to ROC curves by emphasizing the trade-off between precision and recall, particularly for the positive (attack) class.

The Random Forest model, with an AP value of 1.0000, and the Decision Tree model, with an AP value of 0.9970, maintain consistently high precision across nearly the entire recall range. This behavior indicates that both models are capable of identifying attack instances with very few false positives, even as recall approaches its maximum value.

In contrast, the Logistic Regression model achieved an AP value of 0.9904. Its precision–recall curve begins to decline noticeably once recall exceeds approximately 0.85, indicating a rapid decrease in precision at higher recall levels. Consequently, when the decision threshold is relaxed to capture a greater proportion of attack instances, the false-positive rate of Logistic Regression increases more rapidly than that of the tree-based models. This finding further highlights the superior ability of Decision Tree and Random Forest models to preserve a favorable balance between precision and recall across a wide range of operating conditions.

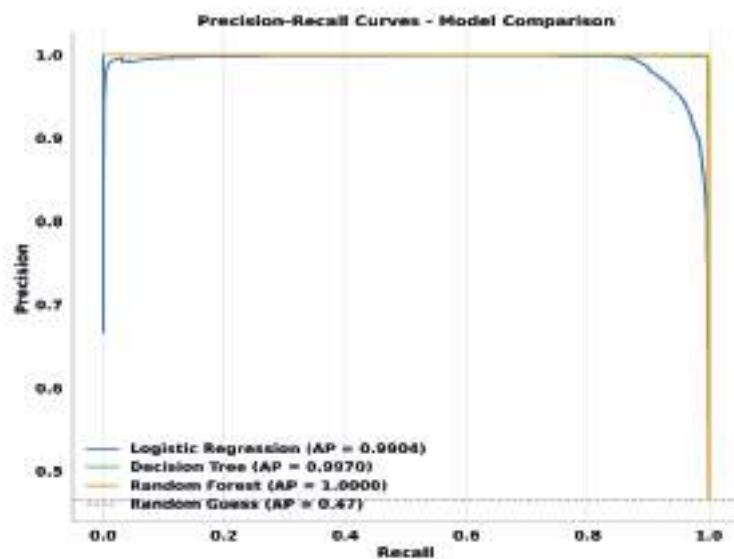


Figure 5. Precision–recall curves of the evaluated models

To assess the extent to which the results obtained from a single train–test split were affected by random variation, 5-fold cross-validation was performed. According to the results summarized in Table 4 and visualized through box plots in Figure 6, the Random Forest model demonstrated the highest average performance and the lowest variance, achieving a mean accuracy of 99.86% with a standard deviation of 0.01%, thereby confirming the model’s stability and robustness. In contrast, the Logistic Regression model exhibited both lower average performance and relatively higher variability, with a mean accuracy of 95.46% and a standard deviation of 0.14%.



These findings support the conclusion that the performance differences reported in Table 2 are not merely the result of random sampling effects associated with a particular train–test split, but rather reflect systematic differences in predictive capability among the evaluated models. The consistently high mean scores and low standard deviations observed for the tree-based methods indicate that their superior performance remains stable across different data partitions.

Table 4. Results of 5-fold cross-validation

Model	Mean Accuracy (%)	Accuracy Std. (%)	Mean F1-Score (%)	F1-Score Std. (%)	Mean AUC	AUC Std.
Logistic Regression	95.4600	0.1400	95.0700	0.1500	0.9917	0.0002
Decision Tree	99.7500	0.0500	99.7400	0.0600	0.9976	0.0005
Random Forest	99.8600	0.0100	99.8500	0.0100	1.0000	0.0000

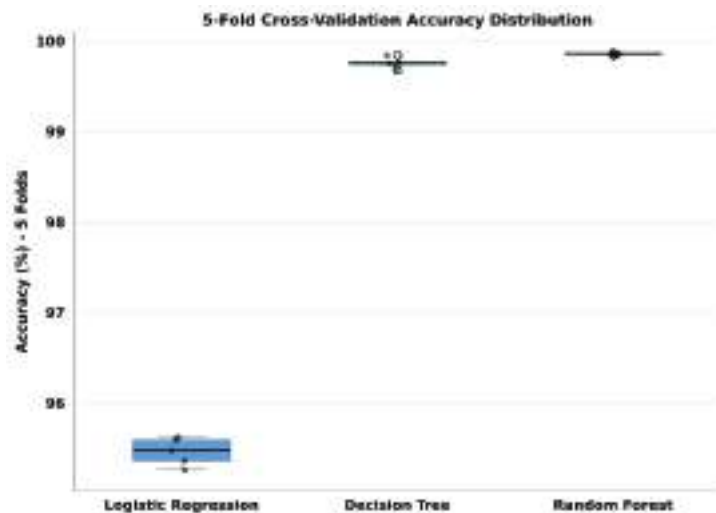


Figure 6. Cross-validation accuracy distributions

6.3. Statistical Significance Analysis

To determine whether the observed performance differences among the evaluated models were statistically significant, the McNemar test, a widely used method for pairwise comparison of binary classifiers, was applied. The results are presented in Table 5. The calculated p -values for all model pairs were found to be well below the significance threshold of 0.05, specifically at the $p < 0.001$ level, indicating that the observed differences in classification performance are not attributable to random chance but are statistically significant.

In particular, the differences between Logistic Regression and the tree-based models (Decision Tree and Random Forest) exhibited extremely strong statistical significance, with χ^2 values exceeding 1600 and corresponding $p < 0.001$. Furthermore, the performance difference between Decision Tree and Random Forest was also found to be statistically significant, yielding $\chi^2 = 18.35$ and $p = 1.8 \times 10^{-5}$. This result confirms that the performance gain achieved through the ensemble approach of Random Forest is genuine and cannot be attributed merely to measurement error or random variation.





Table 5. McNemar test results

Model A	Model B	Correct Only by A	Correct Only by B	Chi-Square (χ^2)	<i>p</i> -value	Significant ($p < 0.05$)
Logistic Regression	Decision Tree	39	1,724	1608.54	< 0.001	Yes
Logistic Regression	Random Forest	11	1,731	1696.30	< 0.001	Yes
Decision Tree	Random Forest	14	49	18.35	1.8×10^{-5}	Yes

6.4. Feature Importance Analysis

Figure 7 presents the fifteen most important features according to the Random Forest model. This analysis identifies the network traffic attributes that contribute most strongly to distinguishing between attack and normal traffic. Consequently, it not only enhances model interpretability but also provides valuable guidance for future feature selection studies.

The features with the highest importance scores are `src_bytes` and `dst_bytes`, followed by `dst_host_srv_count`, `same_srv_rate`, `dst_host_same_srv_rate`, and `flag`. These findings suggest that attack traffic is primarily differentiated from normal traffic through characteristics related to the volume of data transferred per connection and patterns of service access directed toward target hosts.

This observation is consistent with the nature of many cyberattacks. In particular, probing (probe) and denial-of-service (DoS) attacks typically generate either unusually high or unusually low byte-transfer volumes, as well as abnormally frequent and repetitive service requests directed at the same target host. As a result, traffic-volume-related features such as `src_bytes` and `dst_bytes`, together with service-similarity indicators such as `same_srv_rate` and `dst_host_same_srv_rate`, emerge as highly discriminative attributes for intrusion detection. The prominence of these features demonstrates that traffic behavior characteristics play a crucial role in distinguishing malicious activities from legitimate network operations.

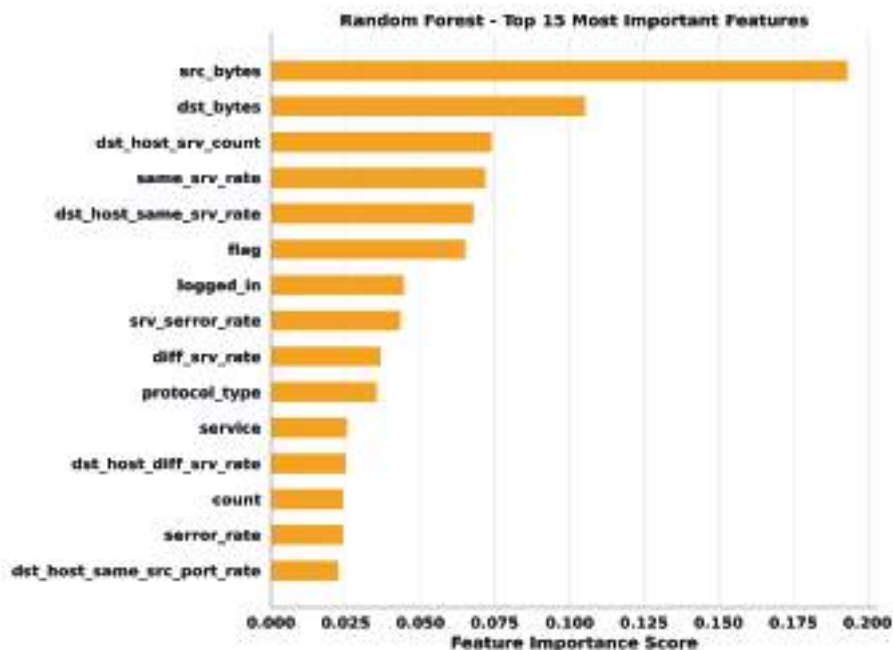


Figure 7. Random Forest feature importance ranking



7. Discussion and Conclusions

When the findings are considered collectively, the superiority of tree-based models over the linear model does not appear to be coincidental. This advantage is consistently observed across summary metrics such as accuracy and F1-score. The error distribution reflected in the confusion matrices also supports the same conclusion. The McNemar test confirms that this difference is statistically significant, while cross-validation demonstrates that it is not attributable to sampling randomness. This consistency indicates that the attack/normal classification problem in the NSL-KDD dataset contains nonlinear interactions among features that cannot be captured by the linear decision boundary of Logistic Regression but can be readily learned by tree-based models through recursive partitioning.

The nature of the differences among the models is as important as their magnitude. Even when two models achieve high accuracy, the distribution of error types may lead to different operational outcomes. In an intrusion detection system, a missed attack generally carries a higher cost than a false alarm. The false-negative rate of Logistic Regression is considerably higher than those of the tree-based models. This suggests that, despite its high overall accuracy, the model may not be considered sufficient as a standalone solution for operational deployment. Random Forest, on the other hand, maintains both false-negative and false-positive rates at low levels. In this regard, it emerges as a more balanced candidate from a security perspective, as it keeps both types of errors under control.

It is noteworthy that features related to the volume of data transferred per connection emerged as the most important variables in the feature importance analysis. This finding indicates that the model learned the distinction based not on random or superficial patterns, but on signals that can be associated with attack behavior. Therefore, the high performance achieved can be considered to be largely driven by meaningful learning.

On the other hand, the fact that all models achieved AUC and AP values above 0.99 should also be interpreted as a cautionary signal. Such high and closely clustered values may suggest that the NSL-KDD dataset is relatively separable compared with real-world network traffic. Consequently, whether the performance ranking observed in this study would be preserved to the same extent on noisier and more imbalanced real-world datasets remains an open question. In this context, it is recommended that: (i) additional validation be performed on the separate KDDTest+ dataset to provide a more robust assessment of model generalization capability; (ii) systematic hyperparameter optimization and the comparison of deep learning-based architectures be conducted under the same experimental protocol; (iii) classification be extended beyond the binary setting to perform a multiclass analysis of DoS, Probe, R2L, and U2R attack categories; and (iv) model complexity be reduced through feature selection based on the obtained feature importance rankings.

References

- [1] Tavallaee M, Bagheri E, Lu W, Ghorbani AA. A detailed analysis of the KDD CUP 99 data set. In: Proceedings of the 2009 IEEE Symposium on Computational Intelligence for Security and Defense Applications; 2009 Jul 8-10; Ottawa, Canada. p. 1-6. doi:10.1109/CISDA.2009.5356528
- [2] Lee W, Stolfo SJ. Data mining approaches for intrusion detection. In: Proceedings of the 7th USENIX Security Symposium; 1998 Jan 26-29; San Antonio, TX, USA.
- [3] Cox DR. The regression analysis of binary sequences. *J R Stat Soc Series B Stat Methodol.* 1958;20(2):215-232. doi:10.1111/j.2517-6161.1958.tb00292.x
- [4] Quinlan JR. Induction of decision trees. *Mach Learn.* 1986;1(1):81-106. doi:10.1007/BF00116251
- [5] Breiman L. Random forests. *Mach Learn.* 2001;45(1):5-32. doi:10.1023/A:1010933404324





- [6] Breiman L, Friedman J, Olshen RA, Stone CJ. Classification and Regression Trees. Boca Raton: Chapman and Hall/CRC; 2017. doi:10.1201/9781315139470
- [7] Revathi S, Malathi A. A detailed analysis on NSL-KDD dataset using various machine learning techniques for intrusion detection. *Int J Eng Res Technol*. 2013;2(12):1848-1853.
- [8] Dhanabal L, Shantharajah SP. A study on NSL-KDD dataset for intrusion detection system based on classification algorithms. *Int J Adv Res Comput Commun Eng*. 2015;4(6):446-452.
- [9] Lee W, Stolfo SJ. A framework for constructing features and models for intrusion detection systems. *ACM Trans Inf Syst Secur*. 2000;3(4):227-261. doi:10.1145/382912.382914
- [10] Kasula VK, Yadulla AR, Konda B, Yenugula M. Fortifying cloud environments against data breaches: a novel AI-driven security framework. *World J Adv Res Rev*. 2024;24:1613-1626.
- [11] Ali T, Kostakos P, Sheikhi S. HuntGPT: integrating machine learning-based anomaly detection and explainable AI with large language models (LLMs). *Telecom*. 2026;7(3):73.
- [12] Ziems N, Liu G, Flanagan J, Jiang M. Explaining tree model decisions in natural language for network intrusion detection. arXiv [Preprint]. 2023. arXiv:2310.19658. doi:10.48550/arXiv.2310.19658
- [13] Canadian Institute for Cybersecurity. NSL-KDD dataset [Internet]. Fredericton: University of New Brunswick; 2009. Available from: <https://www.unb.ca/cic/datasets/nsl.html>
- [14] Pedregosa F, Varoquaux G, Gramfort A, Michel V, Thirion B, Grisel O, et al. Scikit-learn: machine learning in Python. *J Mach Learn Res*. 2011;12:2825-2830.
- [15] Hastie T, Tibshirani R, Friedman J. The Elements of Statistical Learning: Data Mining, Inference, and Prediction. 2nd ed. New York: Springer; 2009. doi:10.1007/978-0-387-84858-7
- [16] Fawcett T. An introduction to ROC analysis. *Pattern Recognit Lett*. 2006;27(8):861-874. doi:10.1016/j.patrec.2005.10.010



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Research Article

Fragrance Microencapsulation by Oil-in-Water in-Situ Polymerization: Cationic Surface Functionalization for Long-Term Dispersion Stability

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Abstract

Today, many commercially available fabric softeners contain encapsulated fragrances to provide consumers with prolonged release of the fragrance even after extended storage periods. Among various techniques, in situ polymerization is one of the most common methods, as it offers a cost-effective and easily scalable method for fragrance encapsulation. In that regard, the primary performance requirements are generally fragrance protection and prolonged release. On the other hand, the dispersion stability of the microcapsules prior to addition to a fabric softener formulation is as important as the primary requirements since in many commercial applications, capsule systems are supplied as ready-to-use capsule dispersions. In this context, this study investigates the preparation of fragrance-loaded microcapsules using methanol-modified melamine-formaldehyde resin (MMF) and their post-curing modification with glycidyl trimethylammonium chloride to improve long-term dispersion stability. Optical microscopy and SEM analyses revealed predominantly spherical microcapsules with sizes in the 20-30 µm range, and TGA was conducted to support the presence of the thermally resistant MMF shell. It was found that modification with glycidyl trimethylammonium chloride did not alter the performance but provided long-term dispersion stability and suggested improved deposition and retention on the fabric after laundering.

Keywords: Cationic Functionalization, Colloidal Stability, Fragrance Microencapsulation.

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1. Introduction

The Fragrance materials are widely used in consumer products, such as detergents, fabric softeners, household cleaners, shampoos, shower gels, etc., to provide a pleasant and long-lasting dour [1]. However, their practical performance is often limited by their volatile and chemically sensitive nature, as many fragrance components can readily oxidize or degrade, such as essential oils and unsaturated compounds [1]. Additionally, in commercial household and personal care applications, maintaining a consistent fragrance character across different products is of utmost importance. For all these reasons, encapsulation of fragrance materials is done not only to protect the fragrance components from external factors such as air, light, heat, etc., but also to improve compatibility with different formulations. Among several applications, fabric softeners represent an important application area, as not only protection of fragrance material and improved compatibility in softener formulations needed, but also retention on fabric and prolonged release should be provided as the performance generally associated with longevity [1–3].

For that purpose, two distinct methodologies are often used: (i) encapsulation of the fragrances with polymeric material, which depends on the triggered release of fragrance upon mechanical stress, or (ii) use of pro-fragrances, which relies on the controlled degradation of fragrance under mild conditions like everyday sunlight exposure. In this context, fragrance encapsulation is more widely applied in consumer products, as it can be directly used with complex commercial fragrance blends, whereas pro-fragrance systems generally require specific molecular design, which limits their practical [2, 4–6].

Both in the literature and in many industrial applications, prepolymers are widely used for fragrance microencapsulation, including urea-formaldehyde (UF), melamine-formaldehyde (MF), polyurethane, and polyurea-based systems [1, 7–10]. Although conventional polymeric microcapsules are generally designed to protect fragrance components for shelf life and prolonged release, many of them do not provide additional advantages for capsule deposition and retention on the fabric surfaces, which is directly related to the performance of the consumer product, as quality and performance are often associated with the longevity of the fragrance.

In this study, to improve deposition on fabric surfaces, cationic functionality was introduced onto the capsule shell after oil-in-water (O/W) fragrance encapsulation, which was carried out by in situ polymerization of MMF resin as the shell-forming material.

2. Conceptual Framework

Microencapsulation of target materials can be done with several methods but can be classified to three main categories, (i) chemical methods, which includes in situ polymerization, interfacial polymerization, and photopolymerization, physicochemical methods which basically stands for coacervation techniques and lastly (iii) physical methods that consist of spray drying and solvent evaporation, that rely on the removal of a carrier phase to obtain encapsulated materials [1, 11–13].

In this context, fragrance microcapsules for fabric-softener applications are commonly produced by in situ or interfacial polymerization, as these methods provide rapid, cost-effective, scalable, and reproducible production routes suitable for commercial use [6]. Moreover, the capsule shell must retain its structural integrity not only during product formulation, storage, and transportation, but also after deposition onto the textile, including during drying, folding, wardrobe storage, and routine handling, thereby requiring a dense and sufficiently crosslinked polymeric shell to minimize diffusion and leakage and maximize the retention of encapsulated fragrance deposition on the fabric following laundering, ironing and subsequent storage [6].

Within this context, the present study is based on the chemical microencapsulation of two different fragrance mixtures through the in-situ polymerization of methanol-modified melamine-formaldehyde



resin in an oil-in-water emulsion system. To this end, all fragrance systems were prepared using the same encapsulation procedure, and the resulting microcapsule shells were subsequently subjected to cationic functionalization to enhance their affinity toward textile surfaces as well as improve the colloidal stability of the final formulation. Selected fragrance mixture was utilized for the individual analytical evaluations, including encapsulation yield by gravimetric analysis, encapsulation efficiency with UV-Vis spectroscopy, morphology with optical microscopy and scanning electron microscopy (SEM), and thermal characteristics with thermogravimetric analysis (TGA), while performances are evaluated with olfactory scoring.

3. Material and Methods

Two different fragrance mixtures were encapsulated through in situ polymerization of a methanol-modified melamine-formaldehyde prepolymer in an oil-in-water emulsion system using a modified procedure based on previously reported methods [7–9, 14]. The encapsulation performance of the formulations was evaluated by determining the encapsulation yield and efficiency, whereas the morphology and thermal characteristics of the microcapsules were examined using scanning electron microscopy and thermogravimetric analysis, respectively. The performance of the developed systems on textile substrates was further assessed through post-laundering olfactory evaluations. Each fragrance mixture was selected for specific analytical evaluations.

3.1. Materials and Instrumentation

Materials: The chemicals used in the encapsulation procedure were styrene-maleic anhydride copolymer (SMA, ScriptSet 520), methanol-modified melamine-formaldehyde resin (ALMUN 70, supplied by Gentaş Chemicals), sodium hydroxide ($\geq 97.0\%$, ACS reagent), hydrochloric acid (37 wt.%, ACS reagent), and glycidyl trimethylammonium chloride ($\geq 90\%$, technical grade), supplied by Sigma-Aldrich, dye colourant used in the study was supplied by Sensient. The commercial fragrance mixtures PINK Capsule ENC Last, and GREEN CAPSULE ENC Last were supplied by Parkim Fragrance House. Deionized water was used throughout the experiments, and all materials were used as received without further purification.

Instrumentation: Microcapsule synthesis was performed in a jacketed glass reactor equipped with an overhead mechanical stirrer and connected to a temperature-controlled circulating bath. The pH of the reaction mixtures was monitored using a calibrated pH meter. Optical microscopy images were recorded with marka model tip optical microscope. For SEM imaging a JEOL JSM-5600 scanning electron microscope is used after drying and coating with a thin gold-palladium layer under high vacuum. Thermogravimetric analysis was conducted using a Mettler Toledo TGA/SDTA851e instrument from room temperature to 700 °C at a heating rate of 10 °C/min under a nitrogen atmosphere. UV-vis measurements were taken in a T80 + UV/vis spectrophotometer with quartz cuvettes in the 190-1100 nm range (light path: 10 mm) after phase separation via centrifugation.

3.2. Preparation of Fragrance-Loaded Encapsulate

Fragrance encapsulation was carried out by in situ polymerization in an oil-in-water (O/W) emulsion using an overall water-to-fragrance mass ratio of 3:1, with the procedure initiated by adding SMA (5.0 g, 5% w/w relative to the fragrance) and NaOH (1.5 g, 30% w/w relative to SMA) to 200 g of deionized water in a jacketed glass reactor and stirring the mixture at 200 rpm and 80 °C until a clear solution was obtained and cooled down to room temperature after which selected fragrance mixture (100 g) directly added and the system was stirred at 500 rpm until homogeneous oil-in-water emulsion was formed followed by addition of methanol-modified melamine-formaldehyde prepolymer (20 g, 15% w/w relative to fragrance) in water (95 g) and firstly stirred at room temperature for 1 h to allow the prepolymer to distribute within the continuous phase and accumulate at the fragrance-water interface. The initial pH was measured and recorded, and the pH of the mixture was then adjusted to approximately 5.5 using 1 M HCl. The reactor was set to 90 °C, and the mixture was heated under



continuous stirring for an additional 2 hours. After the curing of the pre-polymer was completed, the reactor was set to room temperature, and glycidyl trimethyl ammonium chloride (5 mL, 5% v/w relative to the fragrance) was added to the reaction mixture and stirred continuously until the reaction mixture was cooled down to the set temperature. The pH of the resulting microcapsule was checked and adjusted to 7 with dilute NaOH to end curing and minimize the presence of unreacted formaldehyde, and finally diluted with selected fragrance (10 g, 10% w/w) to complete the resulting mixture that is ready to use in commercial fabric softener essence.

3. Results and Discussion

In the context of the present study, the performance of synthesized fragrance encapsulates was evaluated by their physicochemical characteristics and their olfactory behaviour on textiles. As the primary purpose of glycidyl trimethylammonium chloride functionalization was to improve the colloidal stability of the microcapsules within the ready-to-use fabric-softener formulation, prepared samples were collected and visually monitored immediately after preparation and after 1 day, 1 week, 1 month, and 6 months of storage (Figure 1).

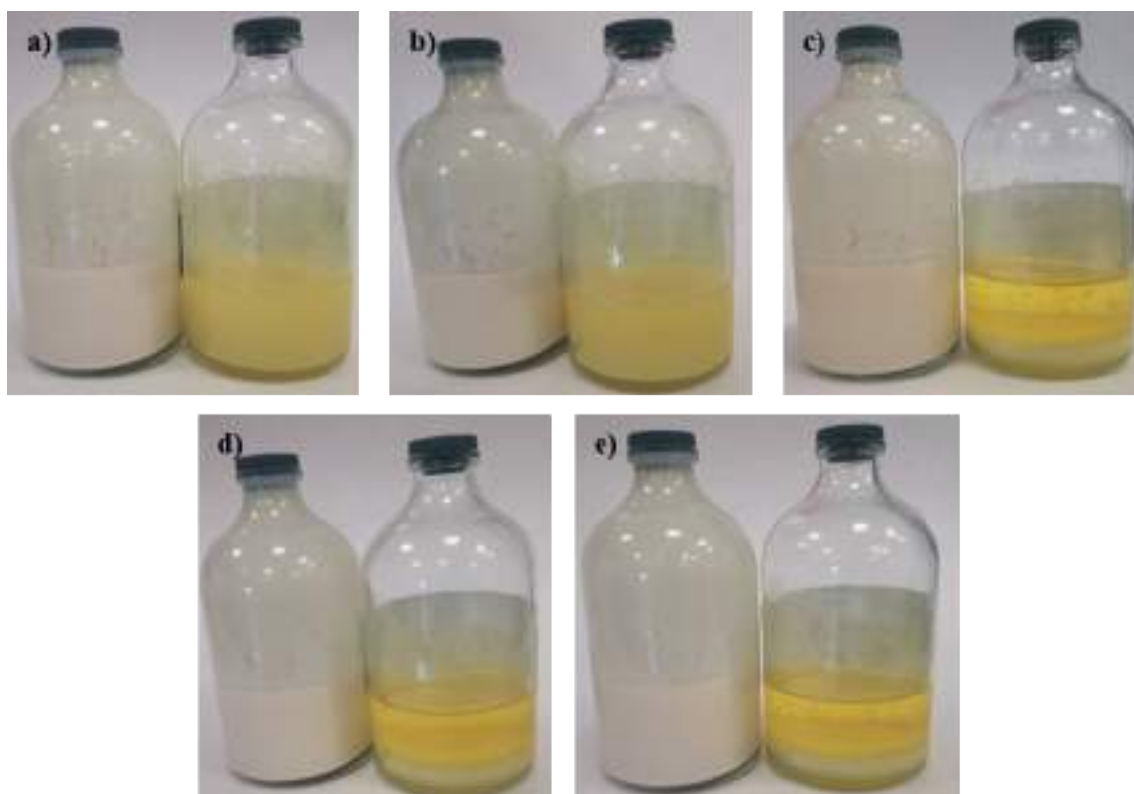
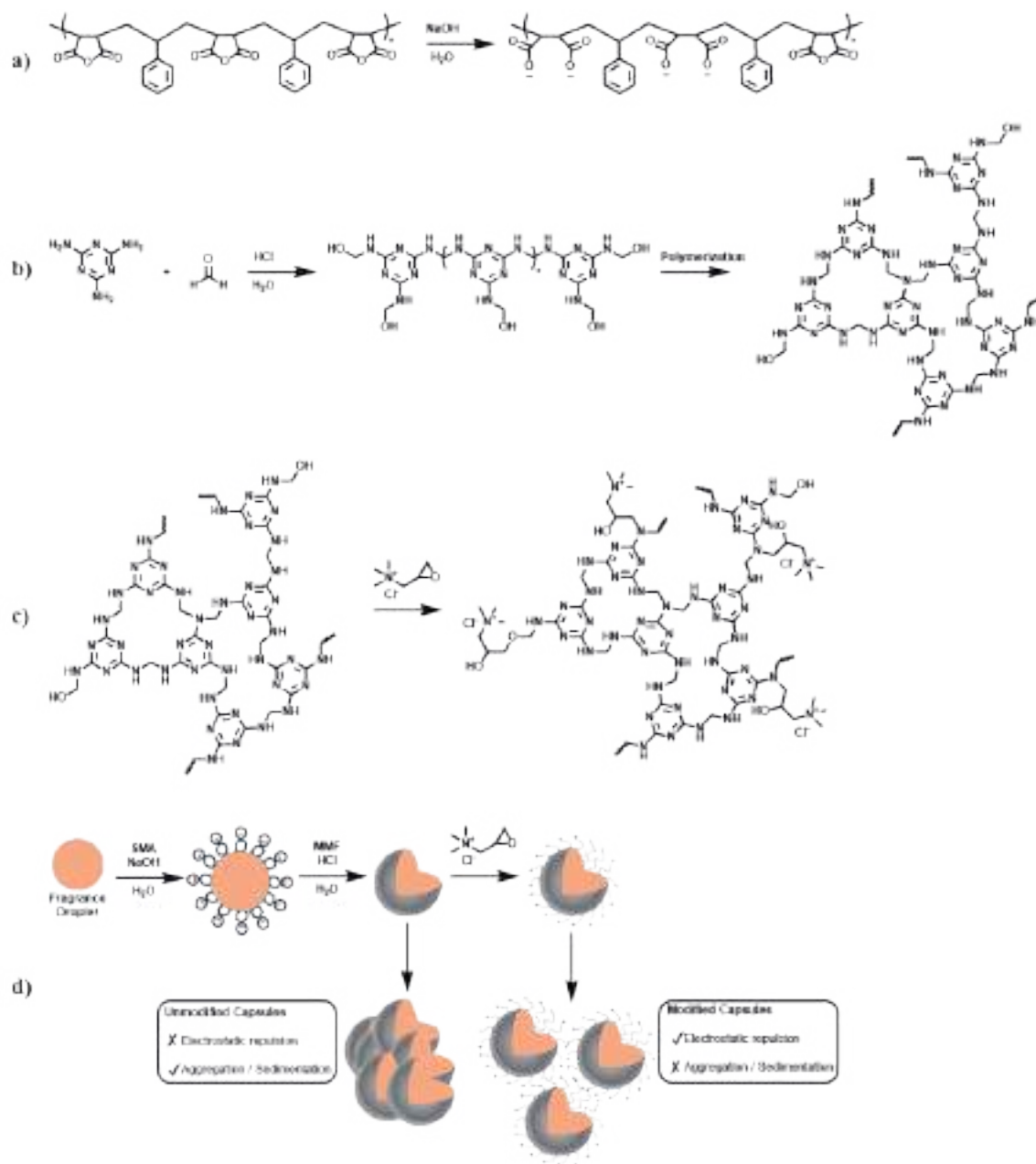


Figure 1. Ready-to-use formulations for Pink Capsule ENC Last (a) immediately after preparation, (b) 1 hour after preparation, (c) 1 week after preparation, (d) 1 month after preparation, (e) six months after preparation (left with glycidyl trimethyl ammonium chloride, right with no additive)

During this storage period, functionalized microcapsules remained uniformly dispersed, whereas unmodified capsules settled a few hours after preparation. This enhanced stability is attributed to the positive surface charge introduced by the quaternary ammonium groups, which increased electrostatic repulsion between neighboring microcapsules and thereby reduced their tendency to settle, and eliminated the dependence on additional suspension-stabilizing additives. The proposed mechanism for the encapsulation reaction and underlying this difference in dispersion behaviour is schematically illustrated in Scheme 1.



Scheme 1. Schematic overview of the structural representation of styrene-maleic anhydride copolymer before and after hydrolysis (a), *in situ* polymerization of MMF (b), post-curing cationic surface functionalization of the microcapsules with glycidyl trimethylammonium chloride (c), proposed influence of surface functionalization on dispersion behaviour (d)

In the context of the study to ensure capsulation, optical microscopy images were recorded at several stages of the reaction during the encapsulation process and are shown in Figure 2. According to the presented images, spherical and morphologically stable microcapsules were obtained after 2 hours of reaction with no apparent coalescence. Nevertheless, limited premixing conditions resulting from the absence of a high-shear emulsification device led to a relatively broad particle-size distribution, nevertheless, microcapsules with an average diameter of 20-40 μm were obtained, which fall within

the range accepted for commercial fabric-softener applications [6]. Also, the addition of glycidyl trimethylammonium chloride as a cationic agent after curing does not change the particle size.

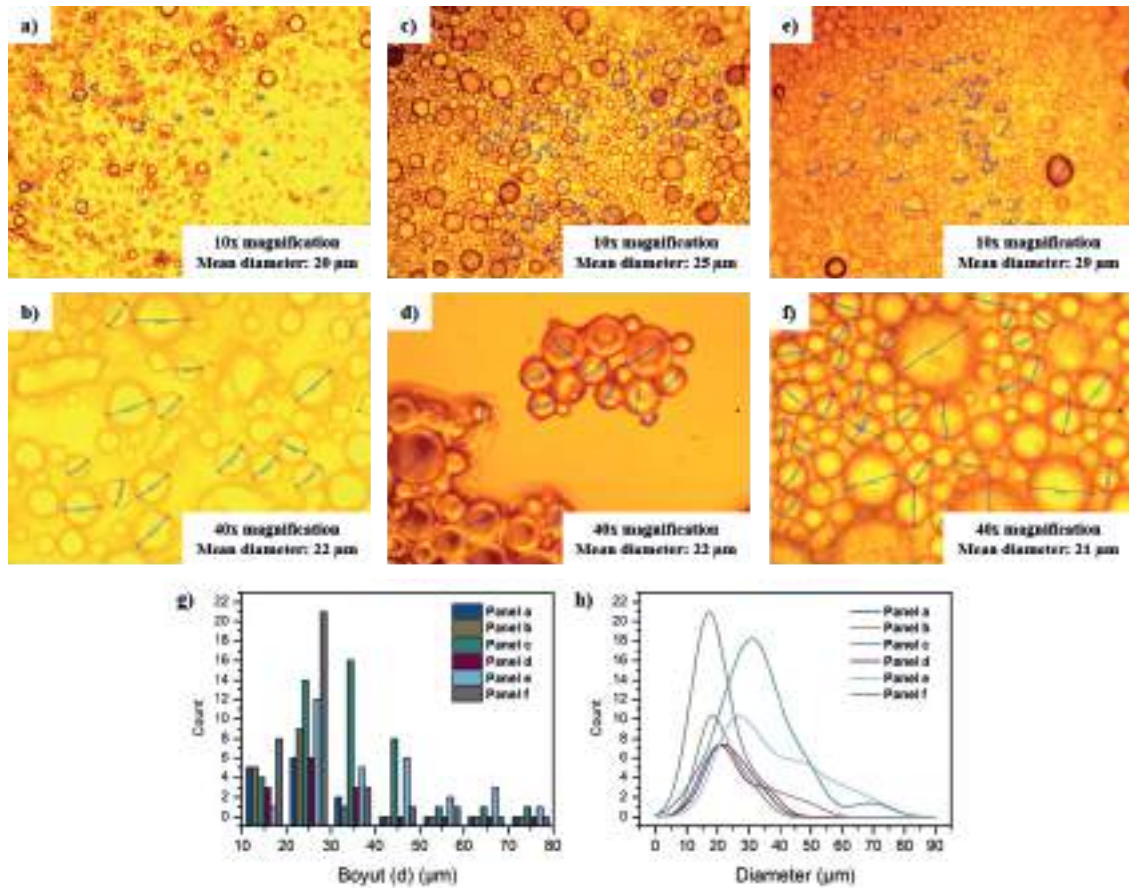


Figure 2. Optical microscopy images of fragrance-loaded microcapsules (Pink Capsule ENC Last) recorded after 30 min of reaction (a), (b), after 2 h of curing and before the addition of glycidyl trimethylammonium chloride (c), (d), after glycidyl trimethylammonium chloride addition and cooling to room temperature (e),(f), and particle-size histograms and distribution curve (g), (h). (Mean diameters were calculated from the particles measured in the corresponding images, smoothed curve was obtained with the Gaussian Kernel Method and derived from the same datasets)

To investigate the capsule structure and morphology, SEM images are also provided (Figure 3). In the light of images, predominantly spherical microcapsules are observed, which support the successful deposition and curing of the melamine-formaldehyde prepolymer around the fragrance droplets. Parallel to the optical microscopy images, a relatively broad particle-size distribution is also seen in the SEM images, as well as continuous film-like residue, which may be attributed to the limited premixing conditions that cause free MMF polymer in the continuous



phase of the encapsulation process. Importantly, treatment with glycidyl trimethylammonium chloride does not cause any morphological changes in the obtained fragrance-loaded capsules.

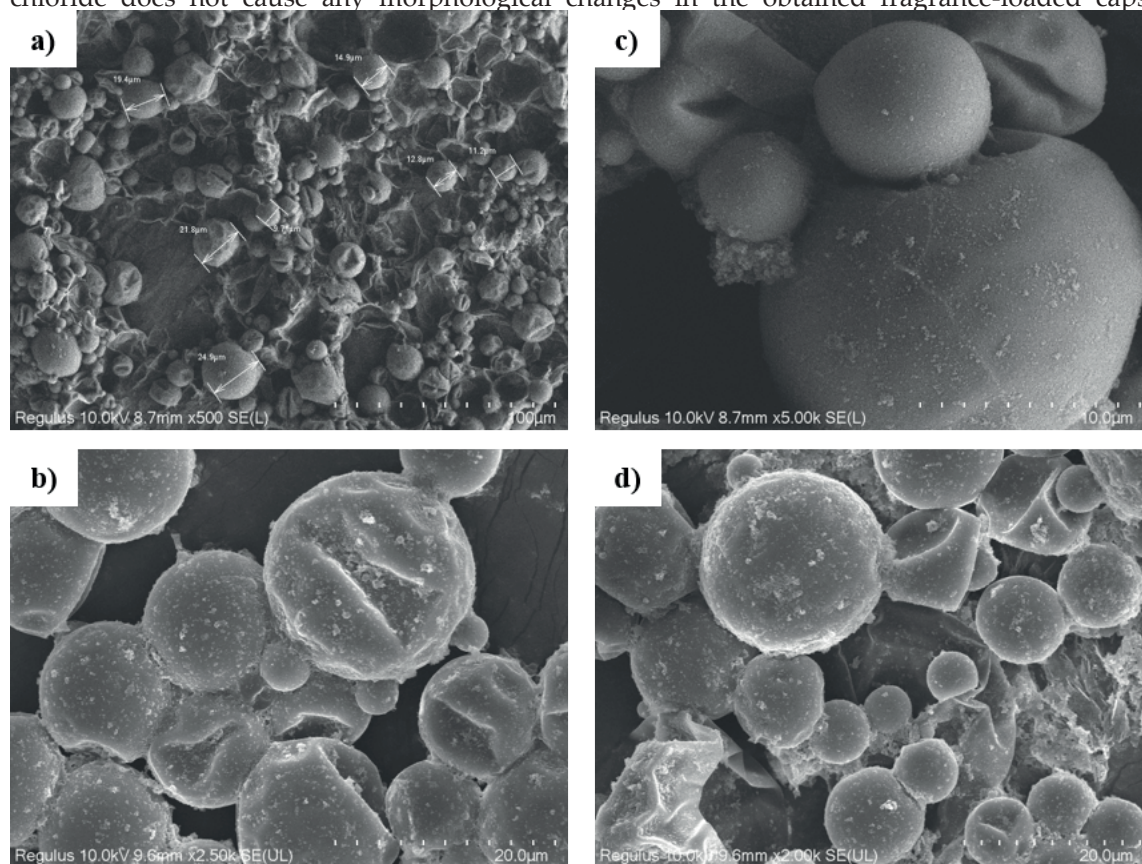


Figure 3. SEM images of fragrance-loaded (Pink Capsule ENC Last) microcapsules obtained at 500× magnification (a), 2500×magnification (b), 5000× magnification (c), 2000× magnification before treatment (d)

Overall, the SEM observations were consistent with the optical microscopy results, and both confirmed successful capsule formation. To further support the successful formation of the microcapsules and evaluate the thermal behaviour of the encapsulated fragrance systems, thermogravimetric analysis (TGA) was performed, and the resulting thermograms are presented in Figure 4.

According to the obtained thermograms, the fragrance mixture (Pink Capsule ENC Last), used as the core material, exhibited a rapid weight loss starting at approximately 60 °C, and continued until 200 °C resulting in a 90% weight loss and almost complete volatilization occurring at approximately 213 °C. The MMF resin, used as the shell material in the procedure, showed three weight loss stages including an initial loss below approximately 120 °C, a gradual degradation stage between approximately 120 and 300 °C, and a more pronounced mass-loss step at around 400 °C, followed by a residual mass of approximately 10-12% at 700 °C. As the encapsulated samples were analyzed directly as aqueous dispersions, a major weight-loss was observed at around 100 °C in both capsule dispersions and was primarily attributed to water evaporation. Although according to the gravimetrically determined solid content, the initial weight-loss was expected to be approximately 68%, the thermogram showed nearly 80% weight loss, which may be attributed to the added free fragrance, fragrance present on the capsule surface [15, 16], and volatile fragrance components gradually diffusing through the polymeric shell. The unmodified capsules showed a plateau between 110 °C and 300 °C, followed by a second mass-loss stage at approximately 300-350 °C, supporting the presence of a thermally resistant MMF-based shell. Unlike the unmodified capsules, the modified capsules did not exhibit a plateau but instead showed a gradual mass decrease between approximately 95 and 210 °C, followed by a second broad





weight-loss extending to approximately 320 °C. This change in thermal behaviour may be attributed to the use of glycidyl trimethylammonium chloride, which introduces hydrophilic quaternary ammonium groups

onto the capsule surfaces, causing a gradual weight-loss due to the presence and subsequent loss of bound water on the outer surface of the capsule shell. However, this change in thermal behaviour does not necessarily indicate reduced capsule performance.

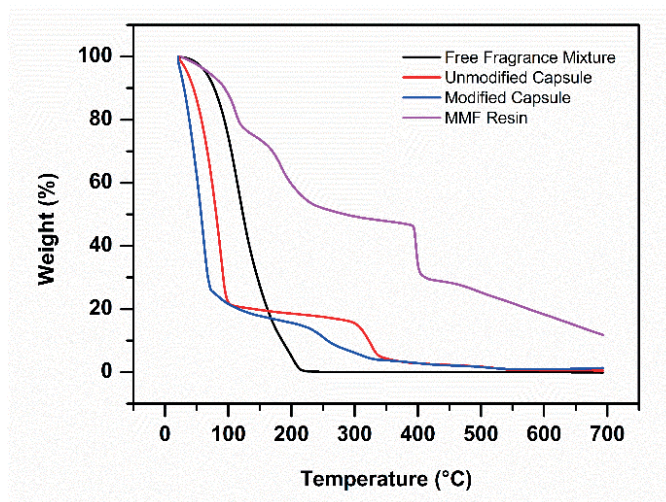


Figure 4. TGA diagrams

After the formation of the microcapsules had been supported by optical microscopy, SEM, and TGA analyses, the encapsulation process was further evaluated in terms of solid yield and encapsulation efficiency using gravimetric and UV-Vis spectrophotometric methods, respectively. To determine the solid yield, a 10.0 g aliquot was collected from the final microcapsule dispersion of Green Capsule ENC Last before the addition of free fragrance and air-dried at room temperature in the dark until a constant mass was obtained. The remaining dry residue was weighed directly, and the solid yield was calculated relative to the initial mass of the aliquot. According to the measured masses, the calculated solid contents range from 24.4% to 34.2% by weight. To determine the encapsulation efficiency, the same procedure was followed, with the only modification being the composition of the fragrance phase, which consisted of 99.0 g of the Green Capsule ENC Last fragrance mixture and 1.0 g of an oil-soluble dye employed as a tracer. To this end, the dye was completely dissolved in the corresponding fragrance mixture, and a calibration curve was constructed at the dye's maximum absorption wavelength (Figure 5). Aliquots were collected in three separate stages (i) initial fragrance and dye mixture to determine initial concentration (the collected sample was measured directly) (ii) after addition of prepolymer resin to estimate the amount transferred into the aqueous phase, and (iii) after completion of the curing process to quantify the dye remaining in the non-encapsulated oil phase. At each sampling stage except the first one, the aliquot was centrifuged to separate the oil phases, which were collected and analysed by UV-Vis spectrophotometry at the predetermined wavelength, and in each step, samples were taken as duplicates. The theoretical initial dye concentration was 10.10 mg/g, and according to the measurements, it was determined to be 10.8 ± 2.1 mg/g, which demonstrates sufficient agreement. Following the determination of the initial concentration, the reaction was carried out to the end of the emulsion step, which corresponds to 1 hour of mixing after the addition of the MMF resin. After centrifuging the samples, the separated oil phases were analysed by UV-Vis spectrophotometry, and a decrease in dye concentration was observed, which is accepted as the amount transferred to the aqueous phase during emulsification. According to the obtained spectra, the dye concentration remaining in the oil phases was determined as $7.09 \text{ mg/g} \pm 0.64 \text{ mg/g}$, indicating $33.6\% \pm 7.2\%$ of the dye transferred into

the aqueous phase during emulsification. Lastly, after completion of the curing process, unfortunately, not only did centrifugation fail to produce a visually distinguishable free-oil layer, but the collected supernatant also exhibited an absorbance response close to the baseline, thus no quantitative evaluation can be done; nevertheless, both observations indicated that residual non-encapsulated fragrance tracer remained after curing was negligibly low, thus qualitatively showing high encapsulation efficiency.

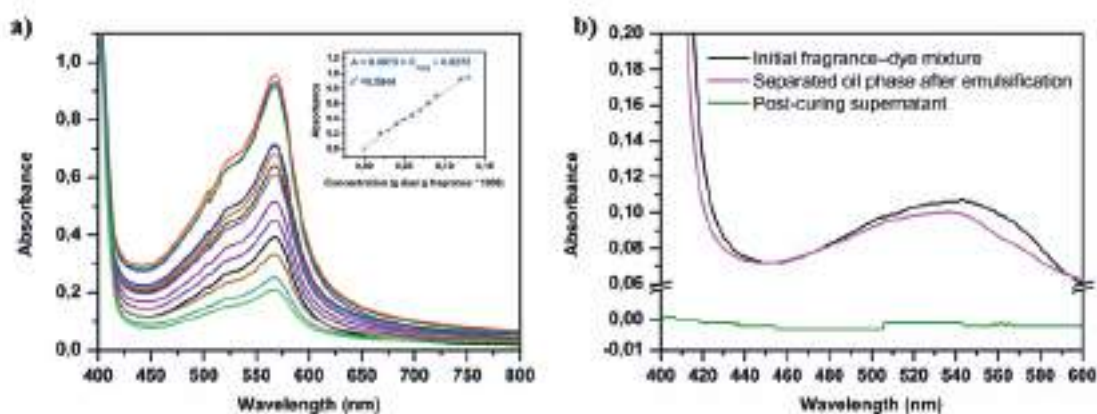


Figure 5. UV-Vis spectrophotometric analysis of the oil-soluble dye used as a tracer in the Green Capsule ENC Last encapsulation study, (a) absorption spectra of the calibration standards (inset as calibration curve), (b) representative absorption spectra of the several stages of the encapsulation reactionn

Finally, the olfactory performance of the fragrance-loaded microcapsules (Pink Capsule ENC Last) was evaluated on fabric samples following laundering. For this purpose, 1.0 g of each formulation was diluted with 99.0 g of the fabric-softener base, and laundering was performed at 30 °C for 17 min. For each encapsulated fragrance formulation, five separate laundering treatments were conducted using two towels per treatment, (i) a control treatment containing the corresponding free fragrance (FF), (ii) a treatment containing the microcapsule dispersion collected before the addition of glycidyl trimethylammonium chloride, without free-fragrance addition (UMC), (iii) functionalized microcapsules with glycidyl trimethylammonium chloride, without free-fragrance addition (CMC), (iv) blend of UMC with free-fragrance(UMC-FB), (v) blend of CMC with free fragrance (CMC-FB). All laundering treatments were performed under identical conditions. The fragrance intensity of the treated towels was evaluated immediately after laundering while the fabrics were still wet, and again after drying and storage for four days with and without rubbing to mimic and evaluate the effect of mechanical stress. All evaluation results were displayed in Table 1.

According to the results, the FF showed the highest olfactory intensity after laundering, as expected, with a radical decrease after storage, and without any significant increase after rubbing because no microcapsules were present in the system. In contrast, both microcapsule-only treatments (UMC and CMC) exhibited low olfactory intensity immediately after laundering and before rubbing, which was attributed to the absence of free fragrance on the fabric. On the contrary, after rubbing, olfactory scores were increased dramatically, indicating that microcapsules had been retained on the textile surface and mechanically ruptured, thereby releasing the encapsulated fragrance. Lastly, both blends (UMC-FB and CMC-FB) provide a satisfactory olfactory intensity both after laundering and storage, with a notable increase after rubbing. When four microcapsule-containing treatments (UMC, CMC, UMC-



FB, and CMC-FB) in both cases show that the use of glycidyl trimethylammonium chloride produced slightly higher olfactory scores, suggesting improved capsule deposition or retention on the fabric surface.

Table 1. Olfactory evaluation score of the tested fabrics

Treatment	After laundering	After 4 days of drying and storage	After rubbing
Free Fragrance (FF)	5	2	2
Unmodified Microcapsules (UMC)	1	1	3
Functionalized Microcapsules (CMC)	1	1	3.5
Unmodified Microcapsules Blend (UMC-FB)	3.5	3	4.5
Functionalized Microcapsules (CMC- FB)	3.5	3	5

4. Conclusions

In this work, synthesized fragrance-loaded microcapsules with MMF resin as shell material with in situ polymerization was accomplished, and post-curing functionalization of the capsule shells with glycidyl trimethylammonium chloride was done. Imaging analyses revealed predominantly spherical microcapsules with clearly distinguishable particle boundaries, while TGA results indicated sufficient thermal characteristics. According to the thermogram, post modification caused the plateau observed for the unmodified capsules to shift toward a more gradual, multistage mass-loss profile. Moreover, UV-Vis analysis showed that applied procedure provides a effective encapsulation with a negligible oil residue after curing in the continues phase. Post-curing modification of capsules with glycidyl trimethylammonium chloride not only provided the long-term dispersion stability to the ready-to-use fabric-softener formulation as expected without significant drawbacks but also resulted in slightly improved olfactory evaluation scores, which is attributed to the ionic interaction between cationic capsule with anionic fabric surfaces.

References

- [1] Podgornik, B. B., Sandiric, S., & Kert, M. (2021). Microencapsulation for Functional Textile Coatings with Emphasis on Biodegradability - A Systematic Review. *Coatings*, 11(11), 1371. <https://doi.org/10.3390/coatings11111371>
- [2] Lambole, S., Vuichoud, B., Saint Laumer, J. Y., & Herrmann, A. (2023). Release of Volatile Cyclopentanone Derivatives from Imidazolidin-4-One Profragrances in a Fabric Softener Application. *Molecules*, 28(1), 382. <https://doi.org/10.3390/molecules28010382>
- [3] Pithanthanakul, U., Vatanyoopaisarn, S., Thumthanaruk, B., Puttanlek, C., Uttapap, D., Kietthanakorn, B., & Rungsardthong, V. (2021). Encapsulation of fragrances in zein nanoparticles and use as fabric softener for textile application. *Flavour and Fragrance Journal*, 36(3), 319–432. <https://doi.org/10.1002/ffj.3648>
- [4] Zaitoon, A., Luo, X., & Lim, L. T. (2021). Triggered and controlled release of active gaseous/volatile compounds for active packaging applications of agri-food products: A review. *Comprehensive Reviews in Food Science and Food Safety*, 21(1), 541–579. <https://doi.org/10.1111/1541-4337.12874>



- [5] Herrmann, A. (2007). Controlled release of volatiles under mild reaction conditions: from nature to everyday products. *Angewandte Chemie (International Edition in English)*, 46(31), 5836–5863. <https://doi.org/10.1002/anie.200700264>
- [6] Murph, D. S. (2015). Fabric Softener Technology: A Review. *Journal of Surfactants and Detergents*, 18(2), 199–371. <https://doi.org/10.1007/s11743-014-1658-2>
- [7] Su, J. F., Wang, L. X., & Ren, L. (2004). Preparation and Characterization of Double-MF Shell MicroPCMs Used in Building Materials. *Journal of Applied Polymer Science*, 97(5), 1755–2174. <https://doi.org/10.1002/app.21205>
- [8] Su, J. F., Wang, W. Y., & Dong, H. (2012). Influence of temperature on the deformation behaviors of melamine-formaldehyde microcapsules containing phase change material. *Materials Letters*, 84, 158–161. <https://doi.org/10.1016/j.matlet.2012.06.074>
- [9] Fei, X., Zhao, H., Zhang, B., Cao, L., Yu, M., Zhou, J., & Yu, L. (2015). Microencapsulation mechanism and size control of fragrance microcapsules with melamine resin shell. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 469, 300–306. <https://doi.org/10.1016/j.colsurfa.2015.01.033>
- [10] Topbas, O., Sariisik, A. M., Erkan, G., & Ek, O. (2020). Photochromic Microcapsules by Coacervation and In Situ Polymerization Methods for Product-Marking Applications. *Iranian Polymer Journal*, 29, 117–132. <https://doi.org/10.1007/s13726-019-00781-9>
- [11] Jamekhorshid, A., Sadrameli, S. M., & Farid, M. (2014). A review of microencapsulation methods of phase change materials (PCMs) as a thermal energy storage (TES) medium. *Renewable and Sustainable Energy Reviews*, 31, 531–542. <https://doi.org/10.1016/j.rser.2013.12.033>
- [12] Massella, D., Giraud, S., Guan, J., Ferri, A., & Salaün, F. (2019). Textiles for health: a review of textile fabrics treated with chitosan microcapsules. *Environmental Chemistry Letters*, 17, 1787–1800. <https://doi.org/10.1007/s10311-019-00913-w>
- [13] Yu, C., Hu, J., Chen, Y., Yang, Q., Zhang, Y., Wang, C., & Chen, K. (2021). Rapid synthesis of strawberry microcapsules via Pickering emulsion photopolymerization for use in multifunctional fabric coatings. *Progress in Organic Coatings*, 152, 106110. <https://doi.org/10.1016/j.porgcoat.2020.106110> (Original metinde “Xu et al., 2021” olarak yazılmış olan atıf)
- [14] Sumiga, B., Knez, E., Vrtacnik, M., Ferik Savec, V., Staresinic, M., & Boh, B. (2011). Production of Melamine-Formaldehyde PCM Microcapsules with Ammonia Scavenger used for Residual Formaldehyde Reduction. *Acta Chimica Slovenica*, 58(1), 14–25. PMID: 24061938.
- [15] Yun, P., Devahastin, S., & Chiewchan, N. (2021). Microstructures of encapsulates and their relations with encapsulation efficiency and controlled release of bioactive constituents: A review. *Comprehensive Reviews in Food Science and Food Safety*, 20(2), 1119–2262. <https://doi.org/10.1111/1541-4337.12701>
- [16] Jafari, S. M., Assadpoor, E., He, Y., & Bhandari, B. (2008). Encapsulation Efficiency of Food Flavours and Oils during Spray Drying. *Drying Technology*, 26(7), 816–835. <https://doi.org/10.1080/07373930802135972>



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