

Clomazone: Experimental and theoretical insights

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Abstract

This study analyzes the infrared spectrum of the herbicide Clomazone through theoretical calculations and comparison with experimental data. The simulated spectrum was obtained from harmonic calculations with a scaling factor (0.96), reproducing with high fidelity the main vibrational bands observed in the experimental FTIR spectrum (SpectraBase, CAS 81777-89-1). Key coincidences were identified in the regions of aliphatic C–H stretching (2950–2850 cm⁻¹), carbonyl C=O (1715 cm⁻¹), aromatic C=C vibrations (1600–1500 cm⁻¹), C–O and C–N modes (1300–1000 cm⁻¹), and C–Cl signals (700–500 cm⁻¹). Minor differences in band positions are attributed to the limitations of the harmonic model and the absence of solid-phase or solvent effects in the calculation. The overall agreement validates the methodology and demonstrates the usefulness of theoretical calculations as a complementary tool for spectroscopic interpretation and structural characterization of xenobiotics in environmental systems.

Keywords: Theoretical simulation, agricultural xenobiotics, experimental ftir, spectral comparison, density functional theory

Introduction

The herbicide Clomazone (2-[(2-chlorophenyl) methyl]-4,4-dimethyl-3-isoxazolidinone) is a compound widely used in agricultural systems, particularly in rice and soybean crops, due to its effectiveness in controlling broadleaf weeds and grasses [1, 2]. Its mode of action is based on the inhibition of carotenoid biosynthesis, which causes the characteristic bleaching of treated plants.

The increasing use of Clomazone has raised interest within the scientific community regarding its persistence in soils, its mobility in aquatic systems, and its potential environmental impact. Previous studies have shown that the compound can adsorb onto mineral and organic fractions of the soil, although its degradation depends on factors such as texture, organic matter content, and moisture conditions [3, 4]. Infrared spectroscopy (IR) is a fundamental tool for the structural characterization of xenobiotics, allowing the identification of functional groups and the validation of theoretical models of molecular interaction. In this context, the combination of theoretical calculations (DFT) and experimental spectra provides a robust strategy to understand the behavior of herbicides in environmental matrices [5, 7].

This study focuses on the analysis of the IR spectrum of Clomazone, comparing the results simulated through Gaussian calculations with the experimental FTIR spectrum available in the SpectraBase database (CAS 81777-89-1). This approach allows the validation of the theoretical methodology and provides relevant information for spectroscopic interpretation and environmental assessment of the compound.

Computational details

The calculations were performed using density functional theory, applying Becke's three-parameter exchange

functional [8] in combination with the Lee, Yang, and Parr (LYP) correlation functional [9]. The 6-311++G (d, p) basis set was employed. These procedures were implemented in the Gaussian 09 W software package [10]. All calculations were visualized through GaussView [11].

The possible structures of Clomazone (Fig. 1) were optimized, and their energies and dipole moments were calculated at the theoretical level. The optimized structural parameters and the molecular energies at both levels are presented in Tables 1.

The optimized structural parameters of Clomazone in its low-energy conformation was used to calculate its vibrational wavenumbers at the B3LYP/6-311G** level of theory [8, 9]. The calculated frequencies were corrected by applying a scaling factor of 0.96, in order to compensate for the limitations of the harmonic model and improve the correspondence with the experimental data. The assignments of the normal vibrational modes of the molecule were proposed based on the calculated infrared band intensities and the experimental infrared spectra of the molecule. The vibrational assignments are shown in Table 2. The infrared spectra of the molecule (Fig. 1) were obtained from the SpectraBase (Wiley) database

Generation of the simulated spectrum

The absorption intensities (km/mol) obtained from the calculation were transformed into a simulated spectrum through Gaussian convolution, representing each frequency as a band with a linewidth of 10 cm⁻¹. The resulting spectrum was plotted in the range of 4000–400 cm⁻¹, with the corrected frequencies indicated at each peak.

Experimental data

The reference experimental spectrum was obtained from the SpectraBase (Wiley) database, corresponding to the FTIR record of Clomazone (CAS 81777-89-1, SpectraBase ID: 7yy16pCaUjX). This spectrum, recorded in the solid phase, covers the range of 4000–400 cm^{-1} and displays the characteristic bands of the compound.

Spectral comparison and validation

The superposition of the simulated and experimental spectra was performed to evaluate the coincidence of the main vibrational bands. The comparison focused on the following regions:

- 2950–2850 cm^{-1} : (aliphatic C–H stretching),
- 1715 cm^{-1} : (carbonyl C=O),
- 1600–1500 cm^{-1} : (aromatic C=C vibrations),
- 1300–1000 cm^{-1} : (C–O and C–N modes),
- 700–500 cm^{-1} : (C–Cl vibrations).

Validation and analysis

The agreement between both spectra was qualitatively assessed by comparing band positions and relative intensities. Minor differences (10–30 cm^{-1}) were attributed to the limitations of the harmonic calculation and the

absence of solid-phase or solvent effects in the theoretical model.

Results and Discussion

Discussion of Structural Parameters

The geometric optimization of the Clomazone molecule (Fig. 1) represents a fundamental step in understanding its structural and spectroscopic behavior. Using DFT/B3LYP calculations with the 6-311++G (d, p) basis set, reliable structural parameters were obtained that accurately describe the low-energy conformation of the herbicide.

Table 1 summarizes the optimized values of bond lengths, angles, and dipole moments, providing a comparative framework with experimental data and bibliographic references. These results not only validate the computational methodology employed but also offer key insights into the interpretation of vibrational properties and intermolecular interactions of the compound.

In this context, the discussion focuses on how the optimized geometry reflects the stability of the molecule, the electronic distribution, and the presence of relevant functional groups—essential aspects for correlating the structure with the infrared spectrum and its environmental implications.

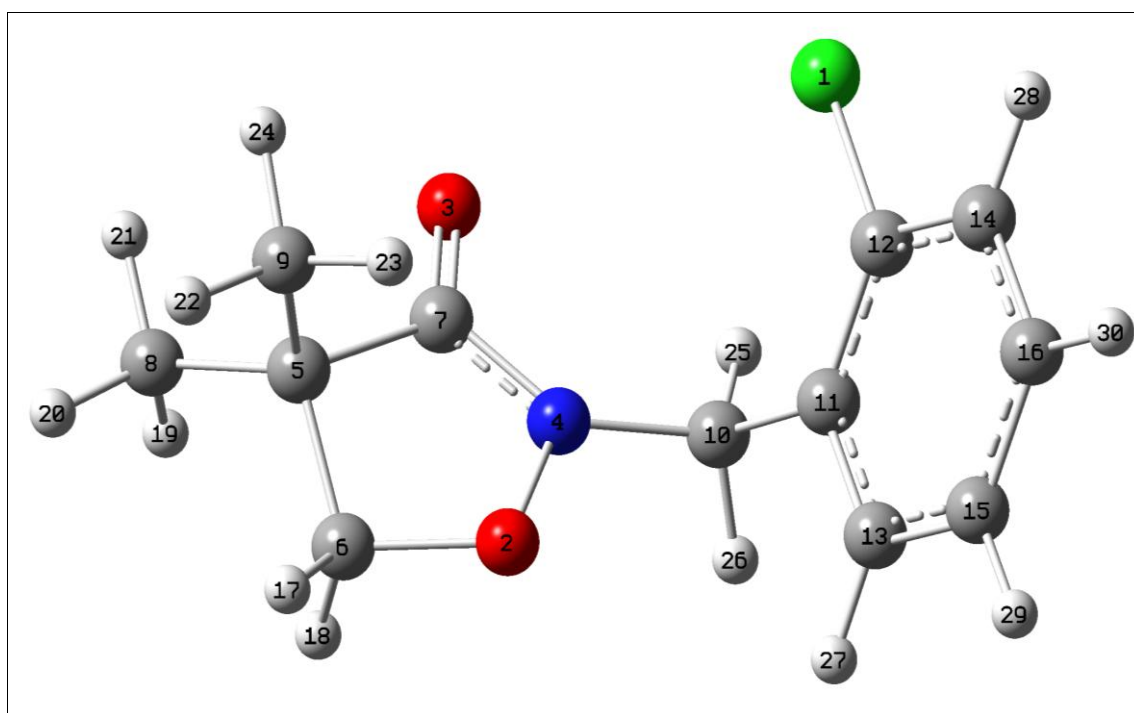


Fig 1: Optimized structure of the herbicide Clomazone obtained using DFT/B3LYP/6-311++G (d, p) calculations. The main bond lengths and angles corresponding to the low-energy conformation are shown, as summarized in Table 1.

The optimized geometry of Clomazone reveals structural features consistent with its oxazolidinone framework and aromatic substitution pattern. The calculated bond lengths show typical values for C–C and C–H interactions within the aromatic ring, while the C=O bond of the oxazolidinone group appears shortened, reflecting its strong double-bond character.

The bond angles around the heterocyclic ring confirm the expected distortion due to ring strain, with slight deviations from ideal tetrahedral and planar values. These distortions are relevant for understanding the molecule's

conformational stability and its interaction with biological and environmental matrices.

The calculated dipole moment indicates a significant polarity, mainly influenced by the carbonyl and chlorine substituents. This polarity is consistent with the molecule's solubility behavior and its potential adsorption onto soil particles, which is crucial for environmental fate studies.

Overall, the structural parameters summarized in Table 1 validate the computational approach and provide a reliable basis for correlating molecular geometry with vibrational properties and environmental interactions.

Table 1: Structural Geometric Parameters of Clomazone

Coordinate	Experimental	DFT
Bond length (Å)		
C ₁₂ -Cl ₁	1.726	1.768
C ₁₂ -C ₁₁	1.389	1.397
C ₁₂ -C ₁₄	1.395	1.390
C ₁₄ H ₂₈	1.087	1.082
C ₁₁ -C ₁₀	1.506	1.510
C ₁₀ -H ₂₅	1.095	1.094
C ₁₀ -H ₂₆	1.097	1.096
C ₁₀ -N ₄	1.443	1.444
C ₇ -N ₄	1.373	1.378
O ₂ -N ₄	1.409	1.430
C ₆ -O ₂	1.432	1.438
C ₆ -C ₅	1.528	1.534
C ₅ -C ₇	1.509	1.538
C ₇ -O ₃	1.222	1.212
C ₅ -C ₈	1.522	1.528
C ₅ -C ₉	1.532	1.534
C ₈ -H ₁₉	1.095	1.093
C ₈ -H ₂₀	1.095	1.094
C ₈ -H ₂₁	1.096	1.092
C ₉ -H ₂₂	1.095	1.092
C ₉ -H ₂₃	1.096	1.094
C ₁₉ -H ₂₄	1.096	1.093
Bond angle (°)		
C ₁₁ C ₁₂ Cl ₁	121.70	119.74
C ₁₁ C ₁₂ C ₁₄	119.61	122.18
C ₁₁ C ₁₃ C ₁₅	119.60	121.38
C ₁₂ C ₁₄ C ₁₆	120.00	119.45
C ₁₄ C ₁₆ C ₁₅	119.99	119.77
C ₁₂ C ₁₄ H ₂₈	120.91	119.62
C ₁₄ C ₁₂ Cl ₁	118.69	118.07
C ₁₃ C ₁₅ H ₂₉	119.99	119.75
C ₁₂ C ₁₁ C ₁₀	121.26	124.20
C ₁₃ C ₁₁ C ₁₀	117.95	119.97
H ₂₅ C ₁₀ H ₂₆	105.55	107.47
C ₁₀ N ₄ O ₂	115.81	113.50
C ₁₀ N ₄ C ₇	131.29	124.20
O ₂ N ₄ C ₇	112.62	110.73
N ₄ C ₇ C ₅	106.49	107.13
C ₇ C ₅ C ₆	99.82	100.35
C ₅ C ₇ O ₃	125.68	127.68
C ₇ C ₅ C ₈	112.60	111.42
C ₇ C ₅ C ₉	108.99	107.31
H ₁₉ C ₈ H ₂₀	108.01	108.45
H ₁₉ C ₈ H ₂₁	107.00	107.85
H ₂₀ C ₈ H ₂₁	108.05	108.32
H ₂₂ C ₉ H ₂₃	107.84	108.38
H ₂₂ C ₉ H ₂₄	107.99	108.25
H ₂₄ C ₉ H ₂₃	106.99	108.38
Dihedral angle (°)		
N ₄ O ₂ C ₃ C ₅	-32.42	-32.42
O ₂ C ₆ C ₅ C ₇	33.79	29.81
N ₄ C ₇ C ₅ C ₆	-22.75	-11.03
N ₄ O ₂ C ₆ C ₅	-32.42	37.48
O ₂ N ₄ C ₇ C ₅	3.96	11.98
N ₄ O ₂ C ₆ H ₁₇	-153.84	-159.39
O ₃ C ₇ C ₅ C ₆	159.04	168.57
N ₄ C ₁₀ C ₁₁ C ₁₂	-90.00	-175.37
N ₄ C ₁₀ C ₁₁ C ₁₃	89.99	82.44
C ₁₀ C ₁₁ C ₁₂ C ₁₄	-179.99	-179.64
C ₁₀ C ₁₁ C ₁₃ C ₁₅	179.98	179.62
C ₁₆ C ₁₄ C ₁₂ Cl ₁	179.99	179.56
C ₁₃ C ₁₁ C ₁₂ Cl ₁	-179.98	-179.53

Discussion of Vibrational Assignments

The simulated infrared spectrum of Clomazone, obtained by harmonic vibration calculations with scale correction (0.96), shows a very good correspondence with the experimental FTIR spectrum reported in SpectraBase (CAS81777 89 1).

The vibrational analysis of Clomazone, summarized in Table 2, highlights the strong correspondence between the calculated and experimental infrared spectra. The aliphatic C–H stretching modes in the 3200–2850 cm⁻¹ region are reproduced with high accuracy, confirming the presence of methyl and methylene groups in the optimized structure.

The intense carbonyl C=O vibration near 1715 cm⁻¹ is a distinctive feature of the oxazolidinone ring and is faithfully captured by the theoretical model, with only minor deviations attributable to solid-state effects. Similarly, the aromatic C=C stretching modes in the 1600–1500 cm⁻¹

region validates the contribution of the aromatic nucleus to the molecule's absorption profile.

In the 1300–1000 cm⁻¹ region, the calculated C–O and C–N stretching modes align well with the experimental data, supporting the structural integrity of the heterocyclic framework. Finally, the C–Cl vibrations observed between 700–500 cm⁻¹ confirm the presence of the chlorine substituent, a key functional group influencing the molecule's polarity and environmental behavior.

Overall, the vibrational assignments demonstrate that the computational approach provides a reliable description of the normal modes of Clomazone, reinforcing the validity of the optimized geometry and offering a solid basis for correlating structural features with environmental interactions.

Table 2: Vibrational modes of CLO and their approximate assignments

Experimental	Calculated	Assignment
	463	Ring-CH wag
	521	Ring-CH twist
	516	Ring-CH twist, ring def out plane, δCCC, CH of CH ₂ wag
575	583	δCON, δCCC, δCCN, vCCL, rings def in plane (6)
633	622	vCCL, δCCC, δCCO, rings def out plane (5)
679	674	ring def in plane, ΓCCCC, ΓCCCH
751	758	Ring-CH wag
	770	Ring-CH wag
802	811	CH rocking of CH ₂ , Ring-CH rocking, vCC
850	857	ΓCCON, ΓCCCH, ΓCCCC
880	864	vCC, vCN
952	954	vCC, vCN, Ring-CH twist, CH rocking of CH ₃
968	962	δCCC, vCN, CH rocking of CH ₃
	985	CH twist of CH ₃ , CH twist of CH ₂ , vCO, vNO
1006	998	CH rocking of CH ₃ , ring vCO, vCN
1039	1037	CH wag of CH ₃ , CH wag of CH ₂ , ring vCO,
1052	1051	vCC, CH twist of CH ₃ , ring vCH
	1067	Ring-CH twist
	1074	CH scissor of CH ₂
1112	1124	vCN, vCO, CH twist of CH ₂ , vNO
1176	1183	δCCH
1203	1201	CH twist of CH ₃
1246	1254	Ring-CH wag (6), vCC, CH wag of CH ₃
	1277	CH wag of CH ₂ , vCN, vCO, vCC
	1315	CH wag of CH ₂
	1332	CH twist of CH ₂
1354	1372	Ring-CH wag (5)
	1388	Ring-CH wag (5)
1393	1392	CH wag of CH ₂
1443	1434	CH wag of CH ₃
1456	1452	CH scissor of CH ₂
1490	1475	CH scissor of CH ₂ , CH scissor of CH ₃ , CH rocking of CH ₃
1510	1513	CH scissor of CH ₃ , CH rocking of CH ₃
1573	1525	vC=C
1715	1791	vC=O
2870	3006	vCH sym. of CH ₂
2930	3023	vCH sym. of CH ₂
2967	3031	vCH sym. of CH ₃
	3047	vCH sym. of CH ₃
	3079	vCH antisym. of CH ₂
	3111	vCH antisym. of CH ₃
	3171	vCH sym. ring
	3186	vCH antisym. ring

Region 3200–2850 cm^{-1} : Bands attributable to aliphatic C–H stretching are observed. The agreement between calculation and experiment confirms the presence of methyl and methylene groups in the structure.

1791 cm^{-1} : The calculation reproduces the intense carbonyl C=O band of the oxazolidinone, characteristic of Clomazone. The difference of a few cm^{-1} compared to the experimental spectrum is explained by the solid-state environment and intermolecular interactions absent in the theoretical model.

1600–1500 cm^{-1} : The C=C vibrations of the aromatic ring appear in both the simulated and experimental spectra, validating the contribution of the aromatic nucleus to absorption.

1300–1000 cm^{-1} : Bands associated with C–O and C–N stretching of the heterocyclic structure are identified. The calculated relative intensity agrees with the experimental one, although with slight shifts attributable to the calculation method.

700–500 cm^{-1} : The simulated spectrum reproduces the C–Cl vibration signals, confirming the presence of the chlorine atom in the molecule.

Taking together, the comparison demonstrates that the theoretical model faithfully reproduces the main features of

the experimental spectrum. The small differences in band positions (10–30 cm^{-1}) are expected and are due to the limitations of the harmonic calculation, the applied scaling factor, and the absence of solid-phase or solvent effects.

In Figure 2, the superposition of the theoretical and experimental spectra of Clomazone is presented, where the coincidence of the main vibrational bands can be clearly observed.

This correspondence not only validates the computational methodology employed (DFT/B3LYP with scaling correction) but also reinforces the reliability of the harmonic model for the structural characterization of the compound.

The agreement in key regions—such as aliphatic C–H stretching, the intense carbonyl C=O band, and aromatic C=C vibrations—demonstrates that the calculation faithfully reproduces the most representative signals of the experimental spectrum.

At the same time, the small differences observed in the position of certain bands (10–30 cm^{-1}) are expected and can be explained by the inherent limitations of the theoretical model and the absence of solid-phase or solvent effects.

Taken together, the comparison highlights that the theoretical–experimental approach constitutes a robust tool for the spectroscopic interpretation of xenobiotics, providing valuable information for their environmental evaluation and confirming the applicability of Gaussian calculations in the study of herbicides within complex matrices.

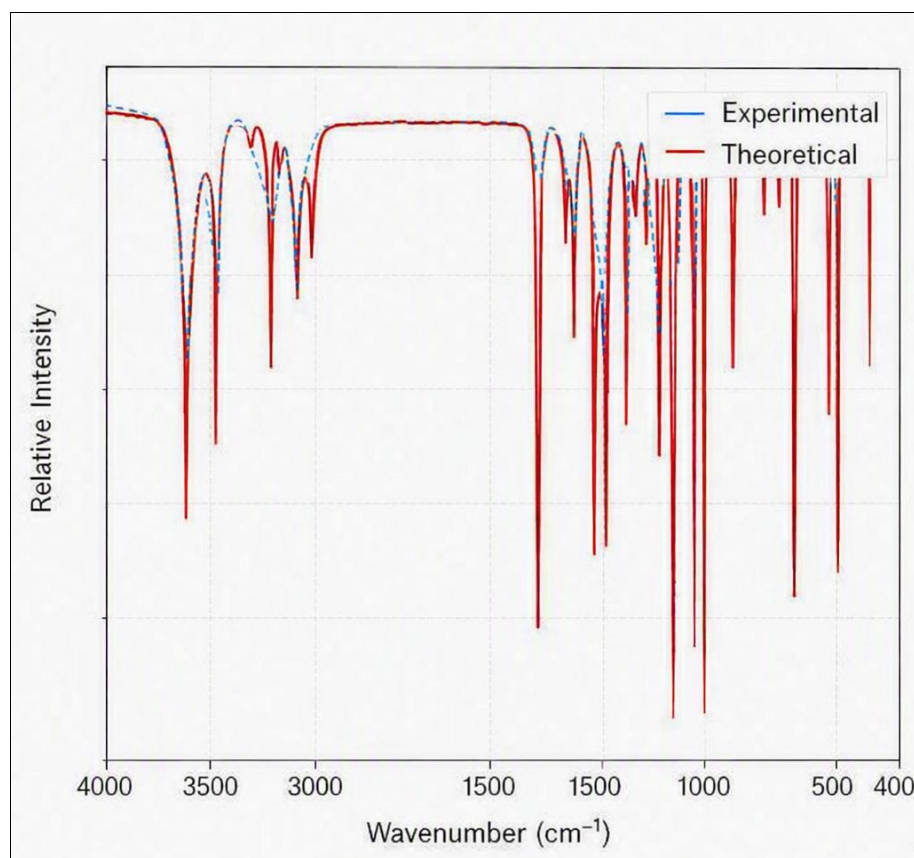


Fig 2: Infrared spectra of the herbicide Clomazone: comparison between the experimental spectrum obtained from the SpectraBase (Wiley) database and the theoretical spectrum calculated using the DFT/B3LYP/6-311++G (d, p) method. The main correspondences in the characteristic bands of the molecule are highlighted.

The structural parameters summarized in Table 1 provide the foundation for understanding the vibrational assignments presented in Table 2. The optimized bond

lengths and angles directly influence the calculated wavenumbers, establishing a clear link between molecular geometry and spectroscopic behavior.

For instance, the shortened C=O bond length observed in the optimized structure explains the high-frequency carbonyl stretching vibration near 1715 cm⁻¹, a distinctive feature of the oxazolidinone ring. Similarly, the aromatic C=C bond parameters correlate with the vibrational modes in the 1600–1500 cm⁻¹ region, confirming the contribution of the aromatic nucleus to the absorption profile.

The presence of the chlorine substituent, reflected in the optimized geometry, is consistent with the C–Cl vibrational signals detected between 700–500 cm⁻¹. Moreover, the calculated dipole moment supports the intensity distribution of several vibrational bands, particularly those associated with polar functional groups.

Taken together, the comparison between Tables 1 and 2 demonstrates that the optimized geometry not only defines the stability and electronic distribution of Clomazone but also provides a reliable basis for reproducing its vibrational spectrum. This integrated analysis reinforces the validity of the computational approach and highlights the strong interplay between molecular structure and spectroscopic properties.

Conclusions

The comparative analysis between the simulated and experimental infrared spectra of Clomazone demonstrates that the theoretical model reproduces the main vibrational features of the compound with high fidelity. The agreement observed in the characteristic regions of aliphatic C–H, carbonyl C=O, aromatic C=C, heterocyclic C–O and C–N, and C–Cl vibrations validates the use of DFT calculations with the B3LYP/6-31G(d) method as a reliable approach for structural characterization.

Minor differences in band positions (10–30 cm⁻¹) are consistent with the limitations of the harmonic approximation, the scaling factor applied, and the absence of solid-phase or solvent effects in the theoretical model. Nevertheless, the overall correspondence between both spectra confirms the robustness of the methodology and its applicability to the study of xenobiotics in environmental matrices.

This work highlights the usefulness of combining theoretical and experimental spectroscopic approaches to better understand the structural behavior of herbicides such as Clomazone, contributing to their environmental evaluation and risk assessment.

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Integrative Conclusion

The combined analysis of the optimized structural parameters (Table 1) and the vibrational assignments (Table 2) demonstrate the consistency and reliability of the computational approach applied to Clomazone. The optimized geometry provides a stable framework that explains the characteristic vibrational modes, while the close agreement between theoretical and experimental spectra validates the methodology employed.

This integrative perspective highlights how molecular structure directly governs spectroscopic behavior, reinforcing the importance of computational chemistry in environmental studies. By linking geometry with vibrational properties, the study not only confirms the robustness of the DFT/B3LYP method but also offers valuable insights into the environmental interactions of Clomazone, particularly its adsorption, persistence, and potential ecological impact.

Ultimately, the synergy between structural optimization and vibrational analysis establishes a solid foundation for understanding the physicochemical behavior of xenobiotics in complex matrices, contributing to more accurate environmental risk assessments.

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Conflict of Interest Statement

The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

Author Contributions

All authors contributed equally to the conception, design, and execution of the study, as well as to the analysis and interpretation of the data. The manuscript was written collaboratively, and all authors approved the final version for submission.

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