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Research Article

Computational modelling of kinetics and thermodynamics of eco-friendly dimerization of cyclopentadiene

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ABSTRACT

This study explores the application of computational modeling in optimizing the kinetics and thermodynamics of the dimerization of cyclopentadiene, a fundamental organic reaction with relevance in polymer and pharmaceutical industries. Using Density Functional Theory (DFT) at B3LYP level with 6-311++G (2df, 2P) basis set in Spartan software. Geometric parameters such as bond length, bond angle and dihedral angle, atomic charge distribution for the reactant (GS), transition state (TS) and the product (PRD) were obtained and activation parameters were calculated at 373K. The study evaluates reaction pathways which show endo- and exo-pathways that minimize energy consumption and byproduct formation, aligning with the principles of green chemistry. A lower activation enthalpy (98.84KJ/mol) means the endo pathway has a lower energy barrier and kinetically favored compared with the activation enthalpy for exo-pathway (115.893 kJ/mol) which indicates that the exo-pathway requires more energy to proceed, making it slower than the endo pathway under the same conditions. In conclusion, this computational DFT study demonstrates that the endo pathway for cyclopentadiene dimerization is kinetically preferred due to its lower activation enthalpy (98.84" kJ/mol") compared to the exo pathway (115.893" kJ/mol"), offering valuable insights for optimizing reaction conditions at 373 K. These results highlight efficient, low-energy routes that reduce byproduct formation.

Keywords: Computational Chemistry; Dimerization; Cyclopentadiene; Density Functional Theory; Thermodynamics; Kinetics

Introduction

Computational modeling has emerged as a powerful tool in modern organic chemistry, providing valuable insights into reaction mechanisms, transition states, activation energies, and thermodynamic feasibility. Quantum chemical methods such as Density Functional Theory (DFT), ab initio calculations, and semi-empirical approaches enable accurate predictions of molecular geometries, reaction intermediates, and potential energy surfaces. Likewise, kinetic modelling helps quantify reaction rates and elucidate how factors such as temperature, substituent effects, and solvent environments influence reaction outcomes. These computational approaches not only complement experimental studies but also reduce trial-and-error experimentation, thereby supporting the design of cleaner and more efficient synthetic routes. The application of computational techniques as eco-friendly reaction method is particularly advantageous because green chemistry innovations often involve novel reaction conditions or unconventional activation modes, requiring precise molecular-level interpretation [1].

By modelling the kinetics and thermodynamics of these environmentally benign reactions, chemists can identify optimal pathways, evaluate competing mechanisms, and predict reaction efficiency with high accuracy. This research aims to investigate the kinetic and thermodynamic parameters of the dimerization of cyclopentadiene organic reactions using state-of-the-art computational tools. By analyzing transition state structures, activation barriers, enthalpic and entropic contributions, and overall reaction feasibility, the study provides a comprehensive theoretical foundation for advancing sustainable organic synthesis.

The global push toward sustainable development has placed increasing pressure on chemists to design reactions that minimize environmental harm. Although eco-friendly organic reactions such as solvent-free syntheses, biocatalytic processes, microwave-assisted reactions, and transformations using green solvents have shown promise, their mechanisms are often not fully understood. Experimental studies alone cannot adequately capture transient intermediate species, energy barriers, and subtle electronic effects that govern reaction efficiency. Without detailed insight into the kinetics and thermodynamics of these reactions, optimizing reaction conditions and predicting outcomes remain challenging. There is, therefore, a need for comprehensive computational modelling that can elucidate reaction pathways, activation energies, and thermodynamic profiles to guide the development of cleaner, more efficient organic transformations. This research thus aimed to computationally investigate the kinetics and thermodynamics of the dimerization of cyclopentadiene. To evaluate activation energies, reaction rate constants, and temperature dependence using kinetic modelling approaches. To compute thermodynamic parameters such as enthalpy (ΔH), Gibbs free energy (ΔG), and entropy (ΔS) for each reaction step and to propose optimized eco-friendly reaction pathways based on computational insights.

Kinetics determines how fast a reaction proceeds and under which conditions, while thermodynamics indicates whether a reaction is energetically favorable. Both are vital for designing efficient green reactions. Experimental techniques often fall short due to the instability of intermediates and the complexity of reaction coordinates. Thus, computational modelling provides a robust platform for predicting kinetic and thermodynamic behavior. Density Functional Theory (DFT) remains the most widely used computational method for modelling organic reactions due to its balance of accuracy and computational cost. It enables the determination of optimized structures, transition state geometries, activation energies, and molecular orbitals. In combination with transition state theory and kinetic modelling tools, DFT allows for evaluation of reaction rate constants and mechanistic pathways.

In chemistry, sustainability requires developing eco-friendly reactions that minimize waste, reduce energy consumption, and improve efficiency [2]. The dimerization of cyclopentadiene serves as a model system for understanding these principles and as a classic Diels–Alder reaction, it provides a platform to investigate how computational modeling of kinetics and thermodynamics can predict reaction. Such insights not only deepen scientific understanding but also guide the design of greener synthetic strategies. The principles of eco-friendly chemistry, and its very definition (design of chemical products and processes to reduce or eliminate the use and generation of hazardous substances) entail the design concept in a variety of regards, and the benign-by-design concept [3] has developed into a key criterion: substances and processes need to be designed in such a way that they are inherently benign (not harmful) to human health and to the environment [4].

Designing molecules with specific properties requires the possibility of predicting their properties before the actual synthesis. Computational chemistry has made molecular design rational by being able to predict the properties of not-yet-synthesized molecules [5]. The results of molecular calculations enable a preliminary selection, singling out the promising molecules among a high number of possibilities; only the promising ones are then synthesized and experimentally tested.

The dimerization of cyclopentadiene (CPD) to dicyclopentadiene (DCPD) is a well-studied organic reaction, primarily proceeding via a Diels-Alder cycloaddition mechanism. This reaction is characterized by its reversibility and the formation of two main isomers: endo-DCPD and exo-DCPD. The equilibrium between CPD monomer and its dimer is temperature-dependent, with the dimerization being favored at lower temperatures due to its exergonic nature. Specifically, equilibrium constant measurements indicate a ΔH° of −18 kcal/mol and a ΔS° of −40 eu for the dimerization, signifying a significant enthalpy-driven process. By including the retro Diels-Alder reaction of endo DCPD and the formation of CPD trimers, results obtained show that the kinetic model accurately predicts concentrations of CPD, endo-DCPD, exo-DCPD and co-dimers with respect to time [6].

Experimental studies, using differential scanning calorimetry (DSC), have provided valuable data on reaction rates and activation energies [7]. For instance, at 120 °C, the rate constant for cyclopentadiene dimerization has been reported as $1.13\times10^{-3}M^{-1}S^{-1}$ [8]. The reaction exhibits regioselectivity and stereoselectivity, with the endo-isomer typically being the kinetically favored product at lower temperatures due to secondary orbital interactions, while the exo-isomer becomes more prevalent at higher temperatures or under thermodynamic control [9] [10] [11] used a microreactor to study the rate and kinetic parameters of the reaction system, and discovered that the kinetics of the decomposition and condensation of DCPD investigated systematically at 5MPa, 180-240°C showed that DCPD has two isomers, endo-dicyclopentadiene(endo-DCPD) and exo-dicyclopentadiene(exo-DCPD), and can be thermally decomposed into cyclopentadiene (CPD) the reaction is reversible.

In a review, Svatunek,[12] presented an overview including an exploration of both the primary computational analysis methods and their application in the main areas of biorthogonal chemistry as (3 + 2) and [4 + 2] cycloadditions addition reaction.

Computational modeling has proven instrumental in elucidating the two-stage mechanism of cyclopentadiene dimerization, with studies focusing on re-optimizing transition structures using various density functionals [12]. These computational approaches help overcome experimental limitations and provide a deeper understanding of the reaction at the molecular level. Sustainable chemistry, often synonymous with green chemistry, is a proactive approach to environmental protection through the design of chemical products and processes that minimize environmental impact and human health risks.

Recent research has explored novel methods such as conducting dimerization within organic acid capsules and has been shown to facilitate clean and swift reactions, demonstrating the potential of confinement as a tool for accelerated and greener chemical processes [14]. The full Integrated Computational Framework, which employs DFT-based methods to obtain transition states to compute thermodynamic parameters such as ΔG, ΔH, ΔS for endo/exo isomers and kinetic parameters and, using computational approach which also reduces reliance on costly experimental processes, long exposure to hazardous chemicals expresses the novelty in this research.

Computational Methodology

Conformational search was done using molecular mechanics force field (MMFF) on the structure of the reactants to obtain the structure that has the lowest energy that is the most stable structure [15]. Reaction path calculation was done to ascertain the mechanism of the reaction using $C_2 - C_9$ and $C_5 - C_{10}$ for exo-pathway, $C_2 - C_8$ and $C_3 - C_7$ for endo-pathway as the reaction coordinate. The calculation was done in 20 iterations by gradually changing the bond distance between the carbon-carbon bonds in the reactant form to ascertain the correct reaction mechanism. Geometry optimization was carried out on the structures of the reactants, transition state and product using Density Functional Theory (DFT) at B3LYP level with 6-311++G (2df, 2P) basis set in Spartan software to obtain the heat of formation, bond length, bond angle dihedral angle and atomic charges. The transition state value was obtained by building the mechanism which follows Diel-Alder-1-3 Cyclopentadiene cycloaddition of endo and exo -ts confirmed by a single negative eigen value in the Hessian matrix intrinsic reaction coordinate and characterized by only one imaginary IR value. The values obtained were used to calculate the kinetic and thermodynamic parameters at 373K. Vibrational and Electronic spectroscopy characterization was carried out on the reactants, transition state and products to provide insight into the vibrational and electronic vibration of the compounds [16].

Thermodynamic and Kinetic Calculation of Endo and Exo Pathways in a Diels–Alder Cycloaddition

The dimerization reaction of cyclopentadiene is a bimolecular reaction. Thermodynamic calculations were obtained through calculations on the ground state (GS), transition state (TS) and products. Statistical mechanically calculated enthalpy and entropy were used, knowing that the large portion of the energy in a molecule is contained in its bonds and physical conformation which is not the true representation of the total energy in the molecule hence the sum of the ground state energy (GSE) of the molecule and the statistical mechanically calculated enthalpy are used to arrive at a closer approximation of the true energy of the molecule.

The following are the equations used:

$$H_1 = GSE_1 + H_1^{sm} \quad (1)$$

'sm' means statictical mechanically calculated energy

$$\text{So, } \Delta H_{rxn} = (GSE_{product} + H_{pro}^{sm}) - (GSE_{reactant} + H_{reactant}^{sm}) \text{ calculated at 373K} \quad (2)$$

Activation energy was calculated using: $E_a = \Delta H + RT$ (3)

Entropy of Reaction:

$$\Delta H_{rxn} = S_{product} - S_{reactant} \quad (4)$$

Gibbs free Energy was calculated using the modifed version considering that G = H – TS so

$$\Delta G^* = \Delta H^* - T\Delta S \quad (5)$$

Using Transition State Theory

$$k(T) = \frac{K_B' T}{h} \exp\left[\frac{-\Delta G^*}{RT}\right] \text{ and } k(T) = \frac{K_B' T}{h} \exp\left[\frac{-Ea}{RT}\right] \quad (6)$$

$$k = A \exp\left[\frac{-Ea}{RT}\right]$$

Results

Reaction Mechanisms

The dimerization of cyclopentadiene is a classic [4+2] cycloaddition (Diels–Alder reaction): This reaction is characterized by its reversibility and the formation of two main isomers: endo-DCP and exo-DCP with two cyclopentadiene molecules (one acting as the diene, the other as the dienophile). The Transition state is a 6-membered cyclic transition state which proceeds through the breaking of three (3) π -bonds- C2 – C3, C4 – C5, C9 – C10 and formation of one (1) new π -bond - C3 – C4 and two (2) σ -bonds- C3 – C9 and C5 – C10 for exo-pathway and C2 – C3, C4 – C5, C7 – C8 formation of one (1) new π -bond - C3 – C4 and two (2) σ -bonds- C3 – C8 and C5 – C7 for endo-pathway as shown in Figure 1

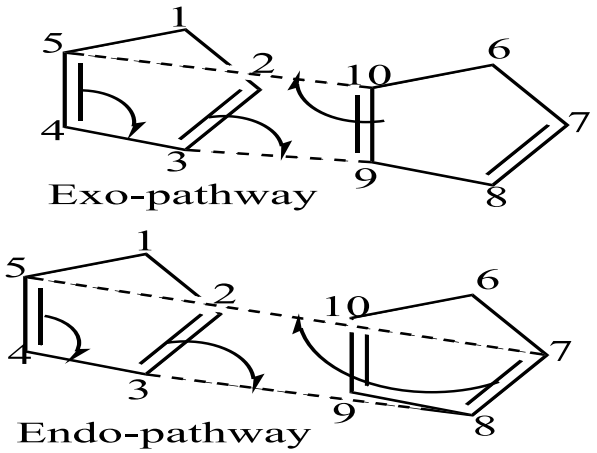

Figure 1. Reaction Mechanism

Geometry optimization

Geometry optimization serves as a foundational step in computational modeling, ensuring that molecular structures achieve their lowest-energy configurations on the potential energy surface. In this study on the kinetics and thermodynamics of cyclopentadiene dimerization, we employed density functional theory (DFT) with the B3LYP level with 6-

311++G (2df, 2P) basis set to optimize the geometries of the monomeric cyclopentadiene, the endo- and exo-dimer transition states, and the resulting Diels-Alder adduct. The results reveal a preference for the endo pathway. Result obtained for the bond length Table 1 showed that the reaction was initiated from $C_4 - C_5$ (1.347Å) with the release of an electron to the $C_3 - C_4$ (1.469Å) in the ground state as observed in the initial bond length which is the normal bond length for a single carbon-carbon bond and $C_4 - C_5$ (1.421Å), $C_3 - C_4$ (1.401Å) for endo and $C_4 - C_5$ (1.413Å), $C_3 - C_4$ (1.401Å) for exo in the transition state, showing elongation of the bond length indicating bond stretching and $C_4 - C_5$ (1.522Å), $C_3 - C_4$ (1.336Å) in endo and $C_4 - C_5$ (1.515Å), $C_3 - C_4$ (1.343Å) indication of fully formed products (Figures 2, 3 and 4)

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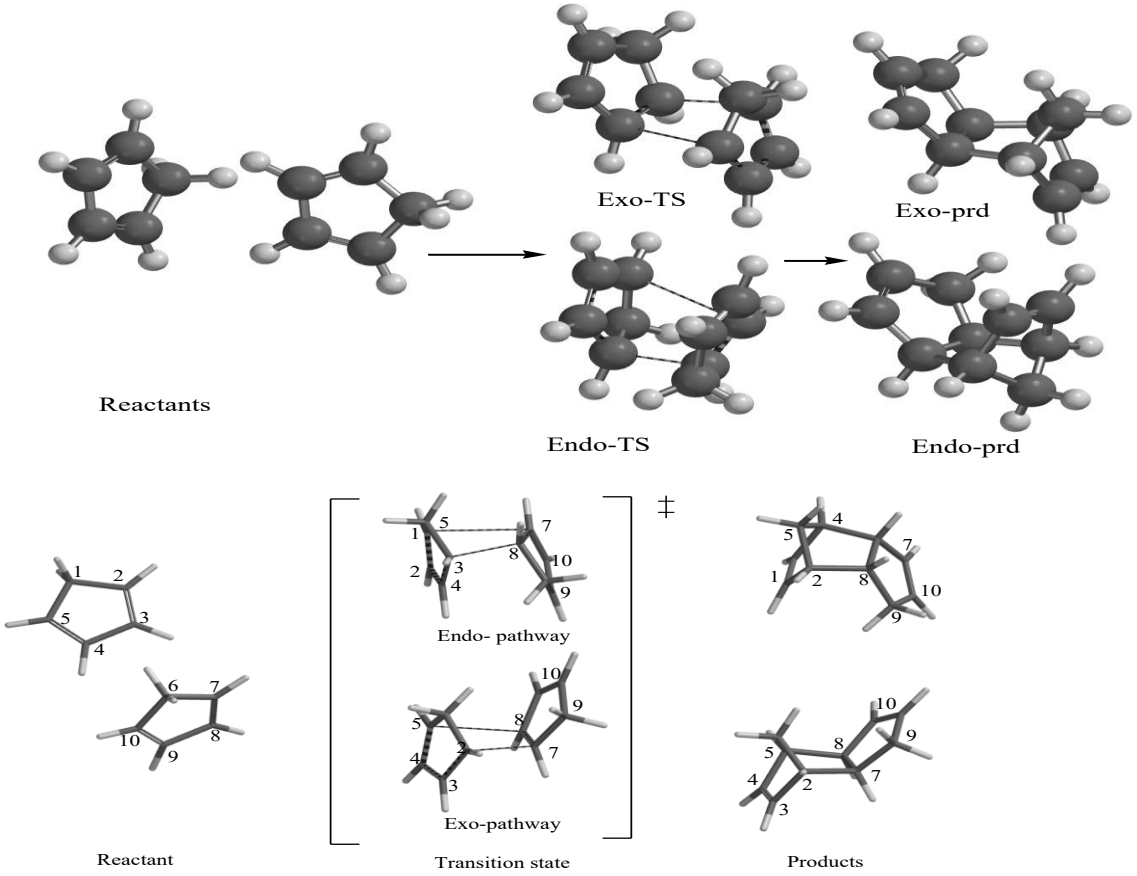

Figure 2. Structures of the reactants, transition state and product in two different presentations

Geometry Optimization

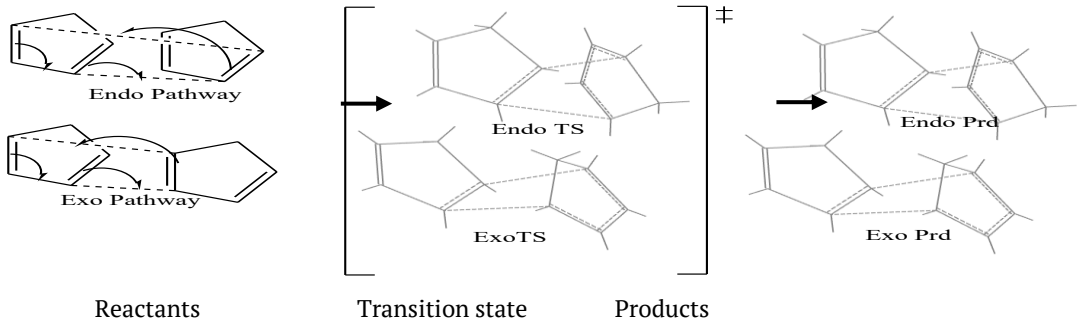

Figure 3: Structure of the optimized reactants, transition state and products

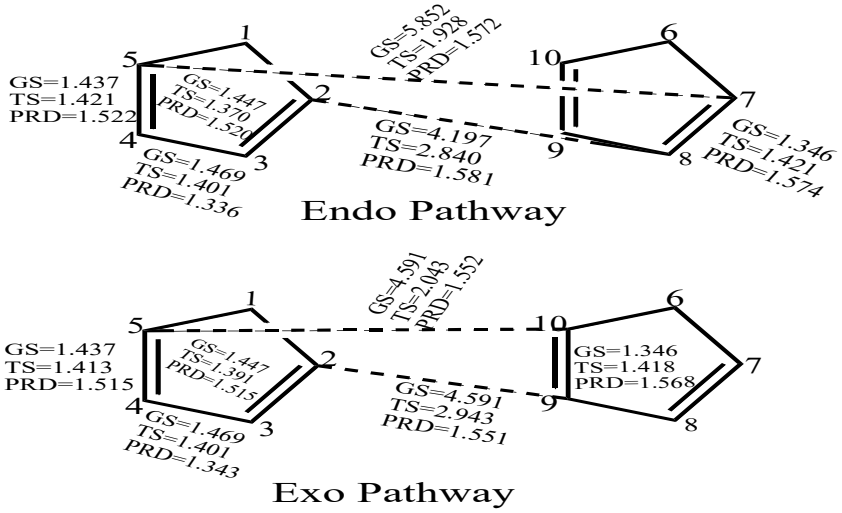

Figure 4. Structure of the transition state for Exo and Endo-pathways showing the variation of bond length in the ground, transition and product state.

Table 1. Bond Length

Bond Length	GS	TS		Product	
		Endo	Exo	(Endo)	(Exo)
$C_1 - C_2$	1.505	1.526	1.498	1.548	1.535
$C_1 - C_5$	1.505	1.503	1.515	1.549	1.533
$C_2 - C_3$	1.347	1.370	1.391	1.520	1.515
$C_3 - C_4$	1.469	1.401	1.401	1.336	1.343
$C_4 - C_5$	1.347	1.421	1.413	1.522	1.515
$C_6 - C_7$	1.505	1.507	1.422	1.552	1.494
$C_7 - C_8$	1.346	1.421	1.350	1.574	1.336
$C_8 - C_9$	1.469	1.422	1.452	1.422	1.496
$C_9 - C_{10}$	1.346	1.366	1.418	1.366	1.568
$C_6 - C_{10}$	1.505	1.350	1.421	1.510	1.535
C_2 - C_9 (exo)	4.591	-	2.493	-	1.551
$C_5 - C_{10}$ (exo)	4.591	-	2.043	-	1.552
$C_2 - C_8$ (endo)	4.197	2.840	-	1.581	-
$C_5 - C_7$ (endo)	5.852	1.928	-	1.572	-

Bond Angle and Dihedral Angle Variations in the Dimerization of Cyclopentadiene

In the ground state of cyclopentadiene, the conjugated diene framework generally maintains near-planar geometry, with C=C–C bond angles close to 120° and dihedral angles that preserve conjugation along the π-system. As the molecules approach each other during the [4+2] cycloaddition, significant geometric distortion occurs to achieve the orbital overlap in the transition state (TS). The variation in bond angles (Table 2) and dihedral angles (Table 3) due to distortion is as shown in Table 2.

In the TS, the reacting carbons bend out of their equilibrium positions: bond angles at the terminal carbons of the diene contract from ~120° toward ~109–112°, while the forming σ-bonds distort the dihedral angles from near-planar alignment to values that bring the dienophile and diene lobes into proximity. This enforced geometry introduces angle strain and torsional strain, which together contribute to the activation energy barrier.

Upon product formation, the bicyclic dicyclopentadiene relieves some of the TS strain. Bond angles at the bridgehead carbons adjust to ~108–110°, consistent with sp^3 hybridization, while the dihedral angles lock into the rigid bicyclic framework. Thus, the variation in bond and dihedral angles (Table 3) progressing from planar in the ground state, to distorted in the TS, (Figure 4) and then to strained but stabilized values in the product illustrates the structural reorganization characteristic of pericyclic reactions.

Table 2. Bond Angle

Bond Angle	GS	TS		Product	
		Endo	Exo	Endo	Exo
C_1-C_2-C_5	109.11	108.61	107.66	100.04	98.22
C_3-C_4-C_5	109.29	108.55	108.50	107.67	107.22
C_4-C_5-C_1	109.11	105.84	106.04	99.87	98.22
C_6-C_7-C_8	109.14	106.02	109.54	106.24	112.83
C_8-C_9-C_{10}	109.29	110.10	108.89	112.65	103.69
C_9-C_{10}-C_6	109.14	108.90	106.74	112.96	106.55

Table 3. Dihedral Angle

Dihedral Angle	GS	TS		Product	
		Endo	Exo	Endo	Exo
C_1 -C_2 -C_3 -C_4	0.12	-9.69	8.16	0.37	33.69
C_6 - C_7 - C_8 - C_9	0.04	21.45	20.61		5.95

The Diels–Alder cycloaddition of the dimerization of cyclopentadiene exhibits nearly identical thermodynamic parameters (Table 4) for both endo and exo product formation. The enthalpy change of reaction (ΔH°) is −27.23 kJ mol^{-1} for both pathways, indicating that formation of the endo and exo adducts is equally exothermic. This observation suggests that the σ-bond framework and overall bonding interactions in the final cycloadducts are energetically equivalent, consistent with classical descriptions of Diels–Alder reactions in which product

stability is governed largely by the same set of newly formed σ bonds. The entropy change of reaction (ΔS°) is similarly comparable for both pathways (endo= −36.02 J mol^{-1} K^{-1}, exo = −35.90 J mol^{-1} K^{-1}). The negative entropy values (Table 4) reflect the intrinsic nature of the Diels–Alder reaction as a bimolecular, concerted cycloaddition, in which two reactant molecules combine to form a single, more ordered cyclic product. The similarity in ΔS° values implies that both endo and exo approaches experience comparable losses in translational and rotational entropy.

As a result, the Gibbs free energy change of reaction (ΔG°) is identical for both products (−13.80 kJ mol^{-1}), confirming that both cycloaddition pathways are thermodynamically favorable. Using ΔG^{o}=RTlnKThe calculated equilibrium constants (Keq) for both endo and exo (8.6 x 10^{1}) products are virtually indistinguishable, indicating that thermodynamic control would yield an approximately equimolar mixture of endo and exo adducts. This behavior aligns with well-established observations that many Diels–Alder reactions display minimal thermodynamic differentiation between endo and exo products [7][17]. Despite the thermodynamic equivalence of the two products, the kinetic parameters reveal a strong preference for the endo pathway, consistent with the endo rule originally articulated by Alder and Stein.

The activation energy (E_a) for endo cycloaddition (101.305 kJ mol^{-1}) is substantially lower than that for the exo pathway (115.412 kJ mol^{-1}). This significant energy difference (~14 kJ mol^{-1}) indicates that the endo transition state is more easily accessible. The enthalpy of activation (ΔH*) further supports this conclusion, with values of 98.854 kJ mol^{-1} for the endo pathway compared to 115.894 kJ mol^{-1} for the exo pathway. In the context of a Diels–Alder reaction, this lower activation enthalpy for the endo approach is typically attributed to secondary orbital interactions between the π orbitals of electron-withdrawing substituents on the dienophile and the developing π system of the diene in the transition state [18].

These interactions stabilize the endo transition state without significantly affecting the final product energy, thereby enhancing the reaction rate. The Gibbs free energy of activation (ΔG*) is markedly lower for the endo pathway (92.896 kJ mol^{-1}) than for the exo pathway (107.462 kJ mol^{-1}). According to transition-state theory, reaction rates are exponentially dependent on ΔG*, making this difference decisive in determining product distribution, so a 1 kcal mol^{-1} error in Gibbs activation energy can lead to a 5-fold error in the TST rate constant at 298 K, with a 2 kcal mol^{-1} can cause 29-fold error [19]. This energetic preference is directly reflected in the rate constants, where the endo reaction exhibits a rate constant of 1.3 x 10^{27} M^{-1} s^{-1}, compared to 8.2 x10^{28} M^{-1} s^{-1} for the exo reaction. The difference of one-order-of-magnitude difference confirms that the reaction proceeds through the endo transition state under kinetic control, even though both products are thermodynamically equivalent.

The entropy of activation (ΔS*) is negative for both pathways (endo= −15.273 J mol^{-1} K^{-1}, exo= −14.673 J mol^{-1} K^{-1}), reflecting the highly ordered nature of the concerted transition state in a Diels–Alder reaction. The slightly more negative ΔS* for the endo pathway suggests a more constrained transition state geometry, consistent with the closer approach and alignment required to maximize secondary orbital interactions. The Arrhenius pre-exponential factors (log A) are very similar (endo= 12.09, exo= 12.13), indicating comparable collision frequencies and molecular orientations for productive encounters. Therefore, differences in reaction rate arise primarily from activation energy differences rather than entropic or steric factors, reinforcing the role of transition-state stabilization in endo selectivity.

In summary, these results provide a clear mechanistic idea of the Diels–Alder cycloaddition. While the endo and exo cycloadducts are thermodynamically indistinguishable, the endo pathway is strongly kinetically favored due to a significantly lower activation barrier and a more stabilized transition state. This behavior is fully consistent with the endo rule and supports the interpretation that secondary orbital interactions dominate the transition-state energetics, rather than influencing the final product stability. Thus, under typical reaction conditions especially at lower temperatures and shorter reaction times the Diels–Alder reaction is expected to yield predominantly the endo product, even though equilibrium considerations alone would predict similar amounts of both products.

Table 4. Kinetics and thermodynamic parameters of the dimerization of cyclopentadiene

Parameters	Endo pathway	Exo pathway
$\Delta H_{reaction}$ (kJ/mol)	-27.23	-27.23
$\Delta S_{reaction}$ (J/mol.K)	-36.02	-35.90
$\Delta G_{reaction}$ (kJ/mol)	-13.80	-13.80
K_{eq}	8.6 x 10^{1}	8.6 x 10^{1}
Log A	12.88	12.91
ΔH^{*} (kJ/mol)	98.845	113.413
Rate, k ($M^{-1}s^{-1}$)	1.3x10^{27}	8.2x10^{28}
ΔG^{*} (kJ/mol)	92.895	107.462
ΔS^{*} (kJ/mol.K)	-15. 273	-14.673
Ea (kJ/mol)	101.305	115.412

Vibrational and Electronic Spectroscopy

The dimerization of cyclopentadiene proceeds through a Diels–Alder reaction, yielding two stereoisomers: the endo and exo adducts of dicyclopentadiene. Infrared (IR) spectroscopy provides important evidence for distinguishing these products, as the differences in stereochemistry subtly influence the vibrational modes of functional groups in the molecules. The IR value both experimental and calculated as shown for endo and exo dimers are bicyclic hydrocarbons, and their IR spectra (Table 5) share common features: C–H stretching: Strong absorptions around 3000–2850 cm^{-1} for aliphatic C–H bonds. C=C stretching weak to medium bands near 1640–1680 cm^{-1}. C–H bending (deformation) bands between 1450–1375 cm^{-1}. Fingerprint region (1000–700 cm^{-1}) which is rich in bands due to skeletal vibrations of the bicyclic framework.

For the Endo Adduct, there is a slight shift in C–H bending bands due to steric crowding. Stronger absorption band in the out-of-plane C–H bending region (≈ 750–700 cm^{-1}), reflects the constrained geometry. A more pronounced ring strain effects, leading to subtle shifts in skeletal vibrations is shown in the 1000–900 cm^{-1} region. In the Exo adduct, a C–H stretching frequencies appear cleaner, with less overlap compared to the endo isomer and the out-of-plane C–H bending bands are weaker than in the endo, due to reduced steric crowding. A slightly different absorption intensity in the 1450–1375 cm^{-1} region (Figures 5a &5b), reflects the changes in bond vibrations caused by the exo geometry. As shown in Figure 5, both isomers show overall similar spectral profiles because they share the same functional groups, but relative band intensities and subtle shifts are diagnostic.

Table 5. Vibrational Spectroscopy (Cm^{-1})

IR	Experimental (Cm^{-1})	Calculated (Cm^{-1})
$C\text{-}H_{(stretching)}$ Aliphatic	3000-2850	3000 -2850
$C\text{-}C_{(stretching)}$	1630 Aromatic 1600-1475 2150-2100 C-C Alkyne	1640 -1680
$C\text{-}H_{(bending)\ deformation}$	1450 and 1375, 1465	1450 -1375
C-H fingerprint region	1000 -500	1000 -700

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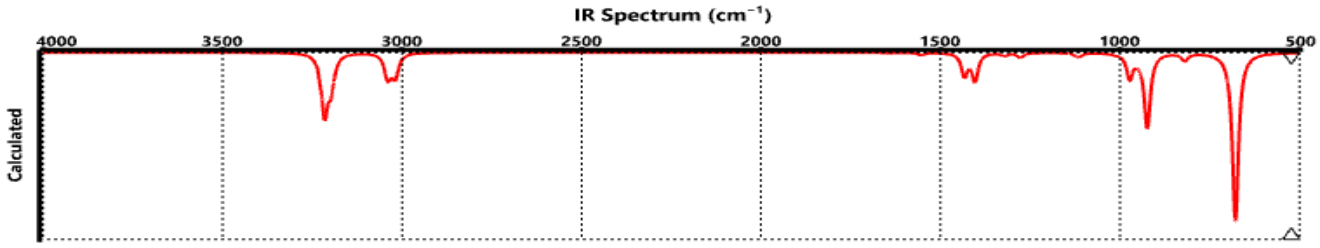
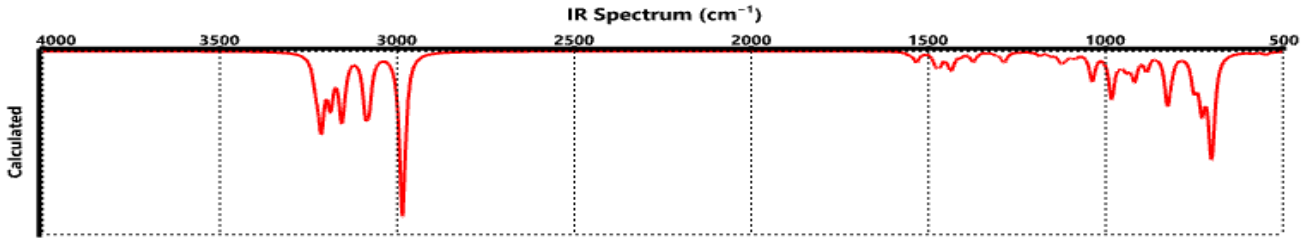
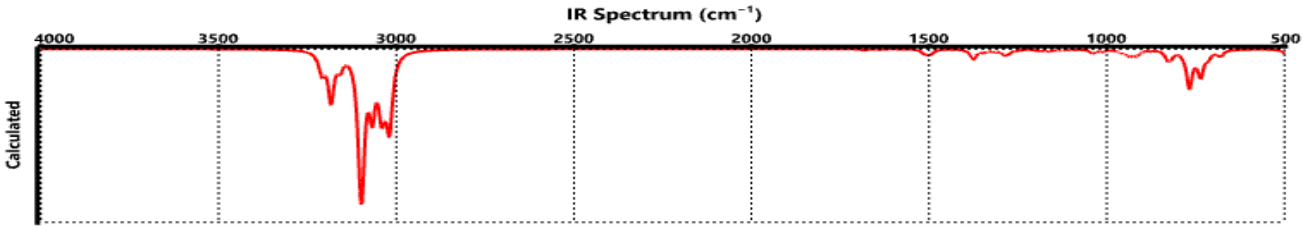


Ground State

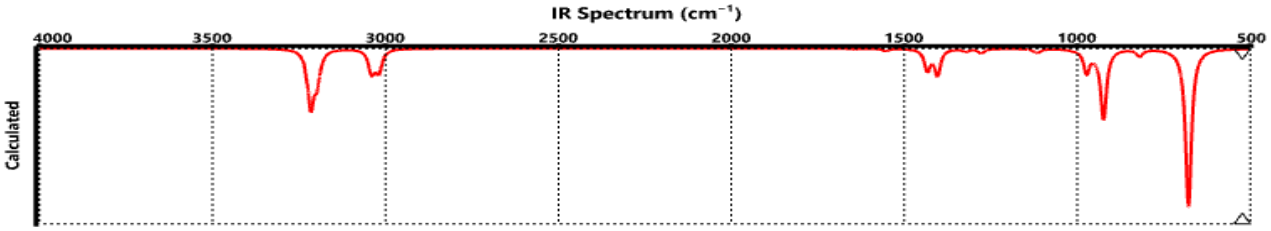


TS(Endo)

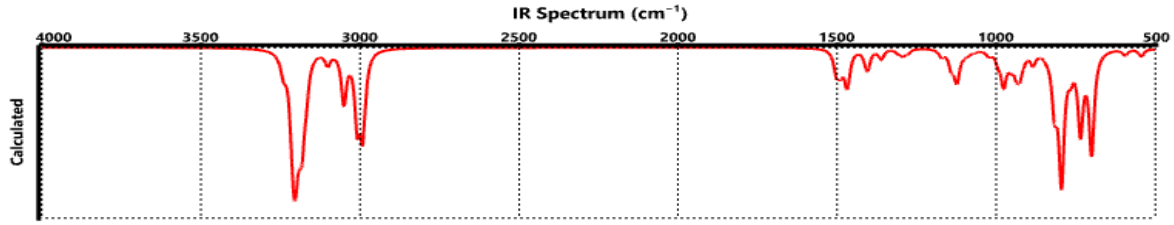


Prd Endo)

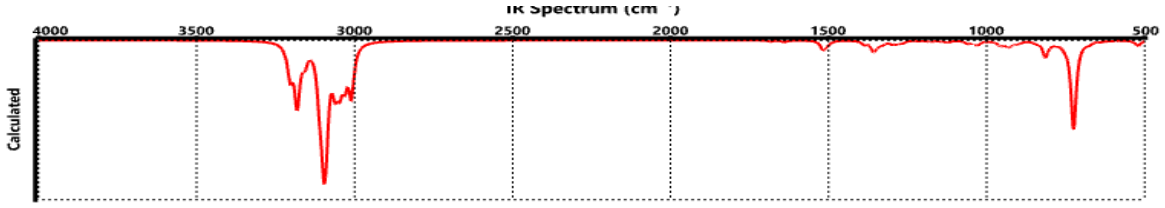
Figure 5a. Infra-Red spectra at the ground, transition and product state for the Endo- pathways



Prd (Exo)



Ground state



TS (Exo)

Figure 5b. Showing the Infra-Red spectra at the ground, transition and product state for the Exo pathway

In conclusion, the IR spectra of the endo and exo dicyclopentadiene products confirm their structural differences, even though both share the same functional groups. The endo isomer is characterized by stronger out-of-plane C–H bending vibrations and more crowded skeletal absorptions, while the exo isomer shows comparatively simpler patterns with reduced band intensities which aids in distinguishing the stereoisomers and supports the mechanistic understanding of cyclopentadiene dimerization.

Ultraviolet (UV) spectroscopy (nm)

This UV data (Table 6) represents UV absorbance or transmittance measurements at specific wavelengths (in nanometers, nm). Wavelengths (nm) are points in the UV spectrum where measurements were taken. It ranges from190–400 nm, and shorter wavelengths (like 195 nm) are in the deep UV range. Absorbance values are unitless numbers (based on Beer–Lambert law), showing how much light is absorbed at each wavelength. So as shown in the Table 6, very low absorbance at 195.31 nm (8.74×10^{-7}) shows essentially no absorption and sharp increase to 0.188 at 224.17 nm which is likely to be the λmax (peak absorbance), suggests a strong π→π* or n→π* transition in the compound, and an indication of the presence of a conjugated system. It was observed that absorbance then drops again at higher wavelengths 246.87 and 259.71 nm) which is typical behavior after a peak.

Table 6. Ultraviolet Visible Absorbance (nm)

Wavelength (nm)/(Intensities)				
GS	TS		PRD	
	Endo	Exo	Endo	Exo
195.31(8.74×10^{-7})	210.16(0.104)	201.45(0.0031)	170.28(0.263)	169.37(0.246)
196.84(0.0021)	214.95(0.026)	215.48(0.116)	181.56(0.047)	174.97(0.021)
224.17(0.188)	240.08(0.025)	229.28(0.017)	183.20(0.013)	178.34(0.046)
225.61(0.058)	257.29(0.001)	232.69(0.009)	184.67(0.017)	184.86(0.009)
246.87(0.001)	261.42(0.002)	278.13(0.395)	200.28(0.0051)	199.38(0.004)
259.71(0.00034)	280.97(0.618)	281.29(0.133)	209.20(0.0021)	203.90(0.032)

The dimerization of cyclopentadiene is a classical Diels–Alder reaction that produces two stereoisomers of dicyclopentadiene: the endo and exo adducts. It contains a conjugated diene system (–C=C–C=C–), which gives rise to characteristic π–π* transitions. Ultraviolet (UV) spectroscopy (Figure 6) provides important insights into this transformation from reactant through transition state to product, since the process directly alters the conjugation and π–π* electronic transitions of the system.

The spectrum is dominated by a strong deep-UV band at 170.3 nm for endo and 169.4 nm for exo, with minor shoulders around 181–185 nm for endo-product and 175 – 185 nm for exo-product with negligible absorption >200 nm. This pattern points to high-energy electronic transitions (σ→σ* or short-range π→π*) and little to no extended conjugation in the compound. Upon dimerization, the conjugated diene system in cyclopentadiene as shown in Figures 6a & 6b is consumed to form a new bicyclic structure with isolated double bonds. The loss of conjugation shifts the absorption bands to shorter wavelengths (hypsochromic shift) and generally reduces their intensity. Dicyclopentadiene therefore shows weaker π–π* absorption in the UV region, typically in the 200–215 nm range, with diminished intensity compared to the monomer. A strong absorption band typically appears in the ~220–230 nm region, corresponding to electronic excitation of the conjugated π system and a weaker shoulder or band at around ~260–270 nm,

due to extended conjugation and possible n–π* transitions. The endo isomer has greater steric crowding and orbital overlap, which can cause slight red shifts in its UV spectrum compared to the exo isomer. The exo isomer is less sterically hindered, often leading to slightly sharper absorption peaks with less perturbation. These differences, though subtle, distinguish the stereoisomers in conjunction with other spectroscopic methods (IR, NMR).

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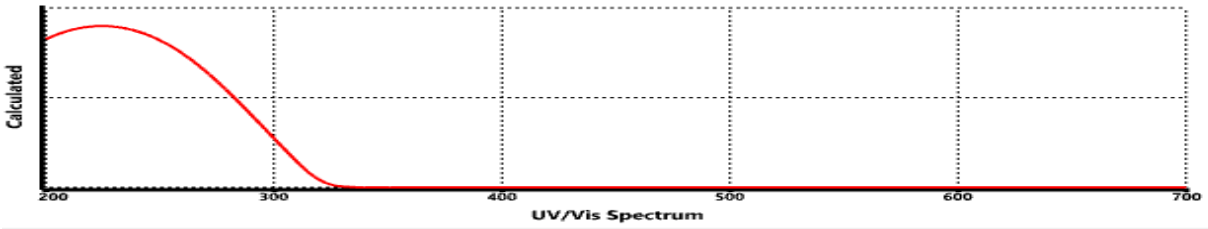
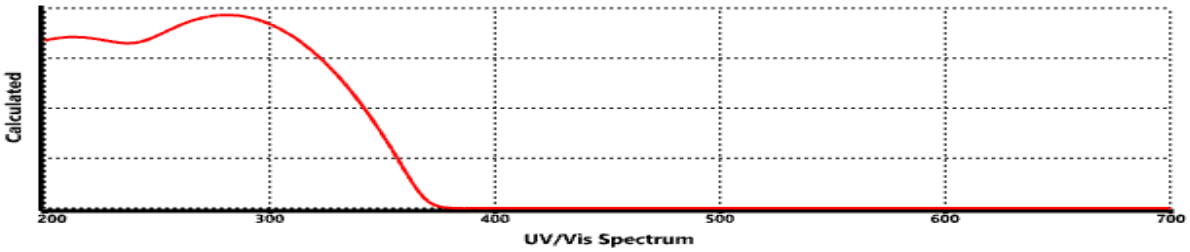
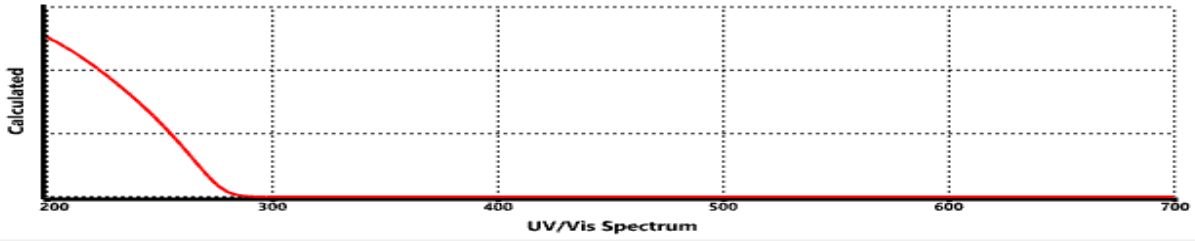


GS

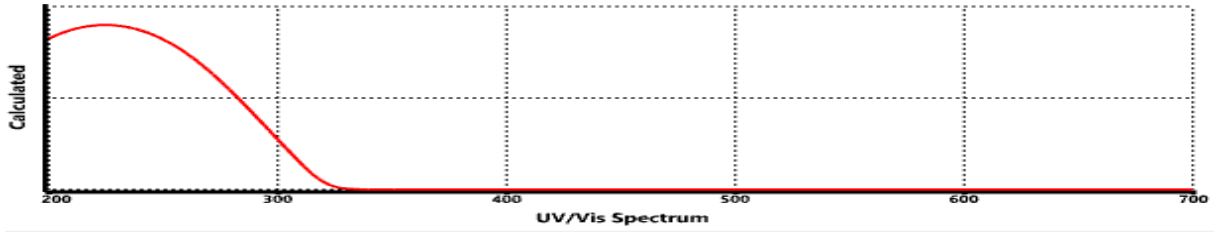


TS(Endo)

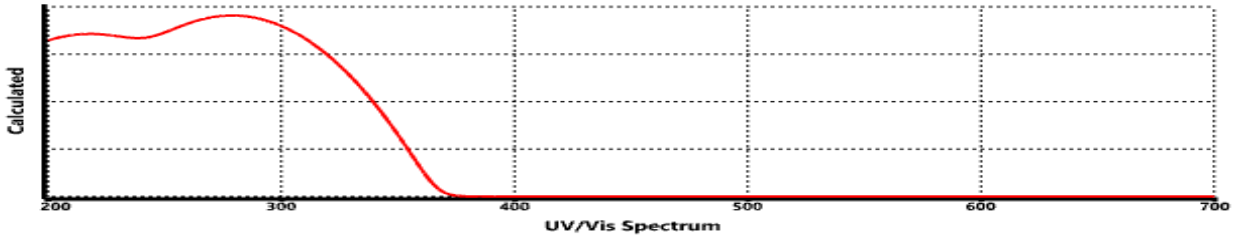


Prd (Endo)

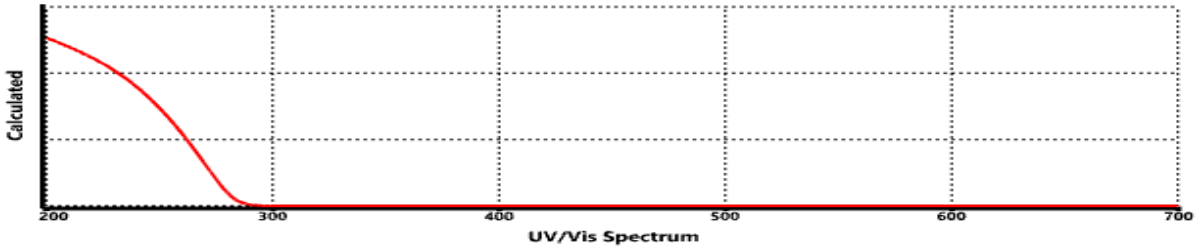
Figure 6a. UV-Visible spectra at the ground, transition and product state for the Endo- pathway



GS



Prd (Exo)



TS (Exo)

Figure 6. Showing the UV-Visible spectra at the ground, transition and product state for the Exo pathways

The UV spectroscopy serves as a straightforward tool to monitor the dimerization of cyclopentadiene, the disappearance of strong conjugated diene absorption bands and the appearance of weaker, higher-energy bands characteristic of isolated alkenes confirm the transformation. While endo and exo products exhibit only subtle UV differences, the overall shift in absorption patterns provides conclusive support for the loss of conjugation during dimerization. spectral change upon dimerization is the reduction of conjugation and the hypochromic shift of the absorption maxima. The monomer spectrum demonstrates the characteristic diene absorption, while the dimer spectrum resembles that of a simple alkene system. These UV changes provide strong spectroscopic evidence for the occurrence of the Diels–Alder dimerization reaction.

Conclusion

This study demonstrates the effectiveness of Density Functional Theory (DFT) at the B3LYP/6-311++G (2df, 2P) level in elucidating the kinetic and thermodynamic characteristics of the dimerization of cyclopentadiene. Detailed analysis of geometric parameters, atomic charge distributions, and activation parameters for the reactant, transition state, and product provided comprehensive insight into the reaction mechanism at 373 K. The computational results clearly distinguish between the endo and exo pathways, revealing that the endo pathway possesses a lower activation enthalpy (98.84 kJ/mol) compared to the exo pathway (115.893 kJ/mol). This confirms that the endo pathway is kinetically favored, proceeding with a lower energy barrier and thus a faster reaction rate under identical conditions. The higher activation enthalpy associated with the exo pathway indicates a less favorable and slower process.

Overall, the findings highlight the capability of computational modeling to predict reaction selectivity, optimize reaction conditions, and reduce energy consumption. By identifying energetically favorable pathways, this work supports the application of theoretical chemistry in promoting efficient and environmentally sustainable organic reactions.

Author Contributions

OOA: Conceptualization; Methodology; Review; Software Validation; Formal analysis; Investigation; Data curation; Writing original draft; Writing review. & editing. OOA then critically reviewed the following versions, read and approved the final version of the paper and its submission and have given consent for publication.

Declaration of Generative AI and AI-Assisted Technologies in Scientific Writing

Nothing to disclose.

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Data Availability Statement

All relevant data are available within the manuscript

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None

Conflict of Interest

The authors declare that they have no conflicts of interest.

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