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## Article

# Thermodynamic Properties of Two Cinnamate Derivatives with Flavor and Fragrance Features

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**Abstract:** The standard molar enthalpies of formation in the liquid phase for ethyl (*E*)-cinnamate and ethyl hydrocinnamate, two cinnamate derivatives with notable flavor and fragrance characteristics, were determined experimentally using combustion calorimetry in an oxygen atmosphere. To derive the gas-phase enthalpies of formation for these derivatives, their enthalpies of vaporization were measured using a high-temperature Calvet microcalorimeter and the vacuum drop microcalorimetric technique. Additionally, a computational analysis employing the G3(MP2)//B3LYP composite method was conducted to calculate the gas-phase standard enthalpies of formation at  $T = 298.15$  K for both compounds. These findings enabled a detailed assessment and analysis of the structural and energetic effects of the vinyl and ethane moieties between the phenyl and carboxylic groups in the studied compounds. Considering the structural features of ethyl (*E*)-cinnamate and ethyl hydrocinnamate; a gas-phase enthalpy of hydrogenation analysis was conducted to explore their energetic profiles more thoroughly

**Keywords:** fragrance compounds; enthalpy of combustion; enthalpy of vaporization; enthalpy of formation; hydrogenation enthalpy; ethyl (2*E*)-3-phenylacrylate; ethyl 3-phenylpropanoate

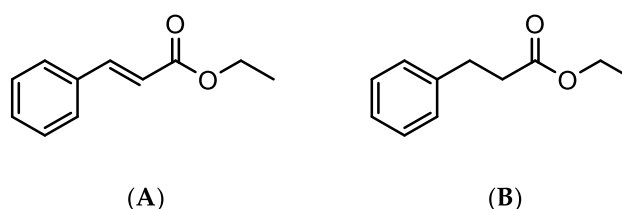
## 1. Introduction

Understanding the thermodynamic properties of ethyl (*E*)-cinnamate and ethyl hydrocinnamate, in the liquid phase at room temperature, namely their enthalpies of vaporization and formation, is crucial, since this knowledge facilitates the prediction of their behavior under various conditions, ensuring safety to handle and to process, optimizing industrial procedures, and offering valuable insights for forecasting of related compounds [1]. Moreover, in the fine chemicals industry, where most chemical reactions are exothermal and compounds often exist in a metastable state, proper management of thermal energy involved is very relevant. The release of energy during these reactions, if not controlled, can lead to severe consequences, highlighting the importance of reliable data for the thermodynamic properties of chemicals required in industrial processes.

This study integrates a broad research project whose main goal is to determine thermodynamic properties of essential fragrance classes, addressing current knowledge gaps and enhancing estimation methods for environmental risk assessment of similar compounds [2–4]. Herein, a comprehensive comparative analysis of the thermodynamic properties of ethyl (*E*)-cinnamate and ethyl hydrocinnamate is provided, depicted by structural formulas in Figure 1.

Regarding the liquid compounds ethyl (*E*)-cinnamate and ethyl hydrocinnamate, they are widely found across several industries, such as the flavor and fragrance, biomedical, pharmaceutical, agricultural and polymer sectors. Despite their similar basic structures, characterized by an ethyl ester linked to a phenyl group, the structural differences exhibited by these compounds lead to varied chemical properties and applications. Ethyl (*E*)-cinnamate (IUPAC name: ethyl (2*E*)-3-phenylacrylate) features a phenyl ring attached to an acrylic acid ester with a *trans* double bond, giving it unique chemical reactivity and sensory properties, such as a sweet and fruity odor [5]. This makes its use common in perfumes, cosmetics, food products, household cleaners, and detergents

[6–8]. In the biomedical research, ethyl (*E*)-cinnamate is used in a new tissue-clearing method (2Eci) for imaging large 3D structures while preserving fluorescence and being non-toxic [9]. Concerning the polymer industry, this compound serves as a "green plasticizer" for polylactide (PLA), enhancing its ductility and impact strength, improving processability, and offering a sustainable alternative to petroleum-derived plasticizers [10]. Its molecular structure enhances chain mobility, cohesion, and compatibility, leading to better performance in biodegradable materials. Moreover, it is an intermediate in pharmaceutical synthesis [11] and agricultural chemical production [12]. On the other hand, ethyl hydrocinnamate (IUPAC name: ethyl 3-phenylpropanoate) presents a phenyl ring connected to a saturated propanoic acid ester. The absence of a double bond in the side chain makes its structure more stable and less reactive compared to ethyl (*E*)-cinnamate. This stability, combined with its sweet, floral odor, makes this cinnamate derivative a desirable component in the flavor and fragrance industry [13,14].



**Figure 1.** Structural formulae of ethyl (*E*)-cinnamate (A) and ethyl hydrocinnamate (B).

This work involved the use of calorimetric techniques to study the thermodynamic properties of the two cinnamate derivatives. The investigation encompassed: (a) determination of the corresponding standard molar enthalpy of formation in the liquid phase,  $\Delta_f H_m^\circ(l)$ , by static-bomb combustion calorimetry experiments; and (b) determination of both enthalpies of vaporization,  $\Delta_v H_m^\circ$ , via high-temperature microcalorimetry. These two parameters enabled the derivation of standard molar enthalpies of formation for both molecules in the gaseous phase,  $\Delta_f H_m^\circ(g)$ , at  $T = 298.15$  K. Additionally, computational studies were conducted using the G3(MP2)//B3LYP composite method to estimate the  $\Delta_f H_m^\circ(g)$  of the two compounds.

The gas phase serves as a reference state in thermodynamics for establishing and discussing of the relationships related with the structure, energy, and reactivity of molecules. In gaseous phase, the molecules are widely spaced, being predominant intramolecular interactions, while intermolecular forces among molecules are often negligible. Focusing on the gaseous phase allows to "isolate" the contributions of intramolecular interactions, thereby simplifying the analysis of the relationship between molecular structure and thermodynamic properties. The standard molar enthalpy of formation in the gaseous state,  $\Delta_f H_m^\circ(g)$ , is a critical thermodynamic parameter used in this context.

The hydrogenation enthalpy of ethyl (*E*)-cinnamate to ethyl hydrocinnamate in the gas phase,  $\Delta_{hyd} H_m^\circ(g)$ , will be calculated using the experimental enthalpy of formation values obtained in this study and compared with literature values, together with a detailed analysis of the hydrogenation enthalpy of isomers (*E/Z*), which offers a valuable foundation for future research in this area. Nowadays, hydrogenation reactions are a central focus of scientific research due to the quest for sustainable, efficient, and carbon-neutral energy storage solutions [15], since hydrogen, with its high energy output and environmentally friendly characteristics, is emerging as a promising candidate for future energy systems. However, storing and transporting hydrogen poses significant challenges due to its low volumetric energy density and the complexities of handling gaseous substances. Therefore, reactions that enable the chemical storage and release of hydrogen, particularly those involving Liquid Organic Hydrogen Carriers (LOHCs), are essential for efficient and secure hydrogen storage [16].

In relation to the current state of research, a study conducted by Kozlovskiy et al. [17] investigated a series of esters, including ethyl (*E*)-cinnamate, phenethyl acetate, phenethyl propionate, phenethyl butyrate, and phenethyl hexanoate. The vapor pressures of these compounds were determined within the range of 298.15 K up to their boiling temperatures, using gas chromatography. The purity of the compounds does not seem to pose an obstacle in this study, as

gas chromatography effectively separates impurities. This capability underscores a key advantage of the technique, enabling the evaluation of pure component properties within mixed substances. Previous thermodynamic investigations on three liquid pyridine acetyl derivatives, conducted using identical experimental methodologies [18], yielded good results.

## 2. Materials and Methods

### 2.1. Materials, Treatment and Purity Control

Ethyl (*E*)-cinnamate (CAS Registry number 4192-77-2) and ethyl hydrocinnamate (CAS Registry number 2021-28-5) were obtained as commercial products from TCI Europe. According to the certificates of analysis for each batch, the sample of ethyl (*E*)-cinnamate (lot number HRRDM) had a mass fraction of 0.999, while ethyl hydrocinnamate (lot number 2PWUE) had a purity of 0.998. Prior to the thermodynamic studies, the ethyl hydrocinnamate was further purified through fractional distillation under reduced pressure, achieving a purity greater than 0.999. In contrast, the ethyl (*E*)-cinnamate was used directly in its as-received form, as its purity was already deemed sufficient for calorimetric analysis. To assess the purity, liquid samples of ethyl (*E*)-cinnamate and ethyl hydrocinnamate were subjected to gas-liquid chromatography using a baseline subtraction or baseline correction technique. In this process, dimethylformamide (DMF) was initially injected as a solvent to establish a baseline and identify any background signals or residual compounds in the system before analyzing the sample. Following this, a mixture of the compound and DMF was injected. In the resulting chromatograms, peaks present in the DMF baseline were excluded, allowing for the isolation and integration of peaks corresponding to the compound and any potential impurities. This analysis determined the purity of ethyl (*E*)-cinnamate to be 0.9999 and that of ethyl hydrocinnamate to be 0.9990. Purity control analyses were conducted with gas-liquid chromatography on an Agilent 4890 apparatus equipped with an HP-5 column (15 m long and 0.530 mm diameter, with 5% diphenyl and 95% dimethylpolysiloxane in the composition) with a flame ionization detector (FID) powered by hydrogen. The gas used during the experiments was a mixture of nitrogen and compressed air.

The density values used for ethyl (*E*)-cinnamate and ethyl hydrocinnamate were, respectively:  $1.05 \text{ g}\cdot\text{cm}^{-3}$  [19] and  $1.02 \text{ g}\cdot\text{cm}^{-3}$  [20].

Other materials were used in this work to calibrate the calorimetric systems, including benzoic acid (CAS Registry number 65-85-0) with a purity of 0.999996, which served as the calorimetric standard for combustion calorimetry calibrations. This Standard Reference Material (SRM) 39j [21] was obtained from the National Institute of Standards & Technology (NIST). Additionally, undecane (CAS Registry number 1120-21-4), with a purity of  $\geq 0.990$ , was used as the recommended reference material for the calibration of the high temperature Calvet microcalorimeter, sourced from Sigma-Aldrich®.

The standard atomic weights of the elements used throughout this paper were those suggested by the IUPAC Commission in 2021 [22].

### 2.2. Combustion Calorimetry

The combustion energies of the liquid samples of ethyl (*E*)-cinnamate and ethyl hydrocinnamate were obtained using static-bomb combustion calorimetry in oxygen equipped with a twin-valve 1108 Parr Instrument Company bomb, with an internal volume of  $0.342 \text{ dm}^3$ . The equipment and experimental procedure used have been previously described in detail [23], with the most relevant aspects summarized below.

The energy equivalent of the static-bomb combustion calorimeter, with the empty bomb,  $\epsilon(\text{cal})$ , was determined using benzoic acid standard reference material (SRM) 39j from the NIST [Error! Bookmark not defined.]. This certified material has a massic energy of combustion of  $(-26434 \pm 3) \text{ J}\cdot\text{g}^{-1}$  when burned under standard bomb conditions. The energy equivalent of the calorimeter,  $\epsilon(\text{cal})$ , was found to be  $(16002.6 \pm 1.7) \text{ J}\cdot\text{K}^{-1}$ , based on an average water mass added to the calorimeter of

3119.6 g; the uncertainty reported represents the standard deviation of the mean from six experiments.

In the sample preparation process, to prevent vaporization and subsequent loss of mass, the liquid samples were placed inside polyester bags made of Melinex®, following the procedure described by Skinner and Snelson [24]. During bomb assembly, the Melinex bag containing the sample was placed into a platinum crucible with a cotton thread fuse attached to the platinum ignition wire (Goodfellows, diameter = 0.05 mm). Additionally, 1.00 cm<sup>3</sup> of deionized water was added to the bottom of the bomb to maintain a vapor phase saturated with water throughout the experiment. The bomb was sealed, purged twice to remove air, and then filled with oxygen ( $x_{O_2} \geq 0.99995$ ) at a pressure of 3.04 MPa. Subsequently, the bomb was placed inside the calorimeter along with 3119.6 g of distilled water, which served as the calorimetric liquid for this system.

The temperature of the calorimetric liquid was monitored using a Hewlett–Packard 2804A quartz crystal thermometer, which has an uncertainty of  $\pm(1 \cdot 10^{-4})$  K, and was interfaced with a computer running the LABTERMO program to acquire the temperature and calculate the adiabatic temperature [25]. The sample was ignited at  $T = (298.1500 \pm 0.0001)$  K by discharging a 1400  $\mu$ F capacitor through the platinum ignition wire. Prior to ignition, 100 temperature readings were recorded, followed by 200 readings after ignition. The surrounding thermostatic bath was maintained at approximately 301.15 K using a temperature controller. During the combustion experiments, gravimetric analysis was used to collect carbon dioxide, and acid–base titration was employed to quantify the nitric acid. The mass of carbon dioxide produced directly corresponded to the amount of compound burned in each experiment. The formation of nitric acid was attributed to possible contamination from nitrogen residues inside the bomb, potentially originating from oxygen used to fill the bomb and incomplete ventilation.

The compounds and combustion aids were weighed using a Mettler AE240 balance with a precision of  $\pm (2 \cdot 10^{-5})$  g. The mass of water added to the calorimetric vessel was measured using a Mettler PC 8000 balance with a sensitivity of  $\pm (1 \cdot 10^{-1})$  g. Additionally, a Mettler Toledo AT201 balance with a precision of  $\pm (3 \cdot 10^{-5})$  g (for the range of 100 to 200 g) was used in the gravimetric determination of carbon dioxide.

### 2.3. High-Temperature Calvet Microcalorimetry

The standard molar enthalpy of vaporization of the two compounds were determined using a high-temperature Calvet microcalorimeter (Setaram HT1000D, Lyon, France), by the vacuum drop microcalorimetric technique, which has been described by Skinner et al. [26] for the study of solids and adapted and tested for liquid vaporizations by Ribeiro da Silva et al. [27]. The equipment characteristics together with procedure have been described in detail in the literature [28].

The temperature,  $T$ , of the hot reaction vessel of the calorimeter was set to 345 K for the vaporization measurements of ethyl (*E*)-cinnamate and 376 K for ethyl hydrocinnamate. The mass of sample used in each run was 4 to 6 mg. The thermal corrections for the glass capillary tubes were determined from separate experiments and were minimized by dropping tubes of nearly equal mass, to within  $\pm (1 \cdot 10^{-4})$  g, into each of the twin calorimetric cells. The Calvet microcalorimeter was calibrated in situ, for the predefined temperatures, by determining the enthalpy of vaporization of undecane as a reference substance [29]. The procedure used in the calibration experiments was the same used as for the compound experiments. The values used for the standard molar enthalpy of vaporization, at  $T = 298.15$  K, for undecane was  $(56.6 \pm 0.6)$  kJ·mol<sup>-1</sup> [Error! Bookmark not defined.]. The derived calibration constants for the different temperatures using undecane were  $k_{cal}$  ( $T \approx 345$  K) =  $(1.0321 \pm 0.0081)$  and  $k_{cal}$  ( $T \approx 376$  K) =  $(1.0234 \pm 0.0027)$ ; these values were obtained as the average of six independent experiments, where the uncertainty corresponds to the standard deviation of the mean.

### 2.4. Computational Methodology

Theoretical calculations of the molecular structures were performed using the Gaussian-09 software [30]. These calculations were based on a variation of the Gaussian-3 (G3) theory [31],

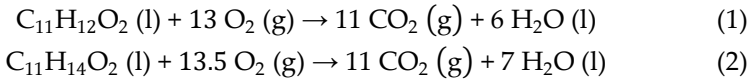
specifically the composite method G3(MP2)//B3LYP [32]. A conformational analysis was conducted to identify and quantify the various conformations for each cinnamate derivative. The conformer compositions, calculated according to the Boltzmann distribution, were subsequently used in the calculation of the final value of the gas-phase enthalpy of formation. Hypothetical gas-phase group substitution reactions were used to estimate the gas-phase enthalpy of formation of ethyl (*E*)-cinnamate and ethyl hydrocinnamate. The good agreement found between the experimental and the estimated values for the gas-phase enthalpy of formation of compounds studied in previous works [2–34], give us confidence for the use of the G3(MP2)//B3LYP approach and the same type of reactions.

3. Results and Discussion

3.1. Experimental Studies

3.1.1. Enthalpies of Combustion and Formation in the Liquid Phase

The general combustion reactions for ethyl (*E*)-cinnamate and ethyl hydrocinnamate are illustrated in Equations (1) and (2), respectively:



The internal energy change associated with the isothermal bomb process,  $\Delta U(\text{IBP})$ , was calculated using Equation (3), where  $\Delta T_{\text{ad}}$  refers to the temperature change in the calorimeter, which has been adjusted for heat exchange and stirring work,  $\Delta m(\text{H}_2\text{O})$  is the difference between the mass of water added to the calorimeter and the baseline mass of 3119.6 g assigned to  $\varepsilon(\text{cal})$ ,  $\varepsilon_f$  is the energy equivalent of the bomb contents in the final state,  $\Delta U(\text{ign})$  is the electric energy necessary for ignition, and  $c_p(\text{H}_2\text{O, l})$  is the specific heat capacity of liquid water at constant pressure.

$$\Delta U(\text{IBP}) = -\{\varepsilon(\text{cal}) + \Delta m(\text{H}_2\text{O}) \cdot c_p(\text{H}_2\text{O, l}) + \varepsilon_f\} \Delta T_{\text{ad}} \tag{3}$$

$$+ \Delta U(\text{ign})$$

The method outlined by Hubbard et al. [34] was employed to determine the standard massic energy of combustion,  $\Delta_c u^\circ$ , for combustions taking place in a bomb calorimeter at constant volume. Additionally, several factors must be considered to accurately account for the energy associated with side reactions. These factors include the standard formation energy of nitric acid solution, the energy from the combustion of the cotton fuse, the energy from the combustion of carbon resulting from incomplete combustion, the combustion energy of Melinex (used as a combustion aid), and the ignition energy. Detailed combustion results for the two cinnamate derivatives can be found in Tables S1 and S2, which are included in Supplementary Materials as supplementary data. The average  $\Delta_c u^\circ$ , for ethyl (*E*)-cinnamate and ethyl hydrocinnamate in the liquid phase obtained from six combustion experiments are  $(-32496.1 \pm 4.3)\text{ J}\cdot\text{g}^{-1}$  and  $(-33110.5 \pm 5.9)\text{ J}\cdot\text{g}^{-1}$ , respectively; the stated uncertainty represents the standard deviation of the mean. From these values, the standard molar internal energy,  $\Delta_c U_m^\circ(\text{l})$ , and enthalpy,  $\Delta_c H_m^\circ(\text{l})$ , for the combustion reactions in Equations (1) and (2) were derived, as presented in Table 1. The standard molar enthalpies of formation in the liquid phase,  $\Delta_f H_m^\circ(\text{l})$ , for each cinnamate derivative, at  $T = 298.15\text{ K}$ , were calculated from the  $\Delta_c H_m^\circ(\text{l})$  values and the following  $\Delta_f H_m^\circ$  values for the species involved in the combustion reaction, at reference temperature:  $(-285.830 \pm 0.042)\text{ kJ}\cdot\text{mol}^{-1}$  [35] for  $\text{H}_2\text{O (l)}$  and  $(-393.51 \pm 0.13)\text{ kJ}\cdot\text{mol}^{-1}$  [Error! Bookmark not defined.] for  $\text{CO}_2\text{ (g)}$ .

**Table 1.** Standard ( $p^\circ = 0.1\text{ MPa}$ ) molar values for ethyl (*E*)-cinnamate (EEC) and ethyl hydrocinnamate (EHC) at  $T = 298.15\text{ K}$  in the liquid phase obtained from combustion calorimetry experiments.

| Compound | $\Delta_c U_m^\circ(\text{l}) / \text{kJ}\cdot\text{mol}^{-1}$ | $\Delta_c H_m^\circ(\text{l}) / \text{kJ}\cdot\text{mol}^{-1}$ | $\Delta_f H_m^\circ(\text{l}) / \text{kJ}\cdot\text{mol}^{-1}$ |
|----------|----------------------------------------------------------------|----------------------------------------------------------------|----------------------------------------------------------------|
| EEC      | $-5726.2 \pm 2.4^1$                                            | $-5731.2 \pm 2.4^1$                                            | $-312.4 \pm 2.8^2$                                             |
| EHC      | $-5901.2 \pm 2.8^1$                                            | $-5907.4 \pm 2.8^1$                                            | $-422.0 \pm 3.2^2$                                             |

<sup>1</sup> The stated uncertainty was determined by accounting for the combined standard uncertainty, which includes the contributions from the calibration with benzoic acid and Melinex®, along with the coverage factor  $k = 2$ , corresponding to a 0.95 confidence level [36]; <sup>2</sup> The stated uncertainty was calculated by considering the combined standard uncertainty, which factors the contribution of the species involved in the respective combustion reactions (Equations (1) and (2)), and the coverage factor  $k = 2$ , corresponding to a 0.95 confidence level [Error! Bookmark not defined.].

3.1.2. Enthalpy of Vaporization

The main vaporization results for the two cinnamate derivatives are summarized in Table 2, with detailed results available in Tables S3 and S4 included in Supplementary Materials as supplementary data. The observed enthalpy of vaporization at the experimental temperature  $T$  for each compound, represented by  $\Delta_{l,298.15K}^{g,T}H_m^\circ$ , is the average of six experiments. These values were adjusted to  $T = 298.15$  K using Equations (4) and (5) and the molar heat capacities in the gaseous phase for each compound. These capacities, within the temperature range of 200 K to 600 K (Table S5 of Supplementary Materials), were calculated through statistical thermodynamics using vibrational frequencies from B3LYP calculations with the 6-31G(d) basis set, scaled by a factor of  $0.960 \pm 0.022$  [37].

**Table 2.** Standard ( $p^\circ = 0.1$  MPa) molar enthalpies of vaporization for ethyl (*E*)-cinnamate (EEC) and ethyl hydrocinnamate (EHC) obtained from high-temperature microcalorimetry experiments.

| Compound | $T/K$ | $\Delta_{l,298.15K}^{g,T}H_m^\circ/\text{kJ}\cdot\text{mol}^{-1}$ | $\Delta_{298.15K}^T H_m^\circ(\text{g})/\text{kJ}\cdot\text{mol}^{-1}$ | $\Delta_l^g H_m^\circ / \text{kJ}\cdot\text{mol}^{-1}$ |
|----------|-------|-------------------------------------------------------------------|------------------------------------------------------------------------|--------------------------------------------------------|
| EEC (l)  | 345.6 | $82.8 \pm 0.8^1$                                                  | $10.4 \pm 0.2^2$                                                       | $72.4 \pm 2.5^3$                                       |
| EHC (l)  | 376.1 | $86.4 \pm 0.3^1$                                                  | $18.6 \pm 0.4^2$                                                       | $67.9 \pm 1.7^4$                                       |

<sup>1</sup>The quoted uncertainty corresponds to the estimated standard deviation of the mean for six experiments; <sup>2</sup>The quoted uncertainty includes the root-mean-square deviation of the third-degree polynomial used and the uncertainty of the vibrational frequency scaling factor for the B3LYP/6-31G(d) method [Error! Bookmark not defined.]; <sup>3</sup>The combined standard uncertainty (which includes the uncertainty associated to calibration experiments with undecane) and the coverage factor  $k = 2.10$  (for 0.95 level of confidence with 18 effective degrees of freedom, calculated by the Welch-Satterthwaite formula) were used to determine the quoted uncertainty [Error! Bookmark not defined.]. <sup>4</sup>The combined standard uncertainty (which includes the uncertainty associated to calibration experiments with undecane) and the coverage factor  $k = 2.18$  (for 0.95 level of confidence with 12 effective degrees of freedom, calculated by the Welch-Satterthwaite formula) were used to determine the quoted uncertainty [Error! Bookmark not defined.].

$$\Delta_{298.15K}^T H_m^\circ(\text{g}) = \int_{298.15K}^T C_p^\circ(\text{g})dT \tag{4}$$

$$\Delta_l^g H_m^\circ = \Delta_{l,298.15K}^{g,T} H_m^\circ - \Delta_{298.15K}^T H_m^\circ(\text{g}) \tag{5}$$

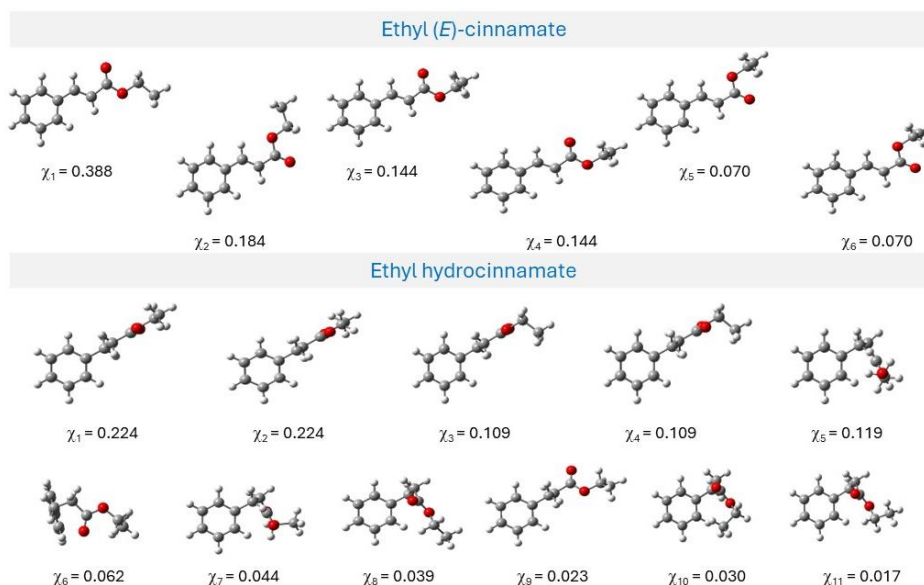
The standard molar enthalpies of vaporization at  $T = 298.15$  K were found to be  $(72.4 \pm 2.5)$   $\text{kJ}\cdot\text{mol}^{-1}$  for ethyl (*E*)-cinnamate and  $(67.9 \pm 1.7)$   $\text{kJ}\cdot\text{mol}^{-1}$  for ethyl hydrocinnamate.

As mentioned in the literature review presented in the introduction, Kozlovskiy et al. [Error! Bookmark not defined.] studied the vapor pressures of ethyl (*E*)-cinnamate over a temperature range from 298.15 K to its boiling point using gas chromatography. They reported a value of  $(70.4 \pm 1.4)$   $\text{kJ}\cdot\text{mol}^{-1}$ , which is consistent with the value obtained through our calorimetric technique, considering the associated uncertainties.

3.2. Computational Studies

The computational study of ethyl (*E*)-cinnamate and ethyl hydrocinnamate, using the G3(MP2)//B3LYP approach, revealed several minima on the potential energy surface, as anticipated,

due to the various possible rearrangements of each substituent in the gaseous phase. Figure 2 reports the conformational composition,  $\chi_i$  for the most stable predominant molecular geometries, calculated assuming a Boltzmann distribution of the possible equilibrium structures. Conformations with residual probability and negative frequencies were excluded from the final conformational composition. Detailed results of the conformational analysis are provided in Tables S6 and S7 of Supplementary Materials.



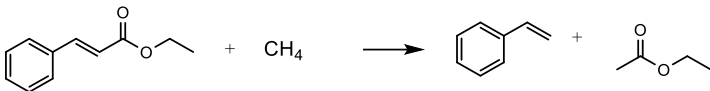
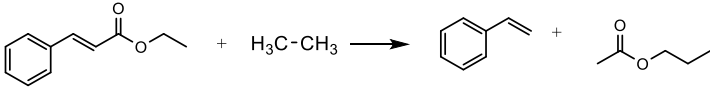
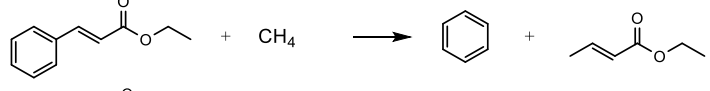
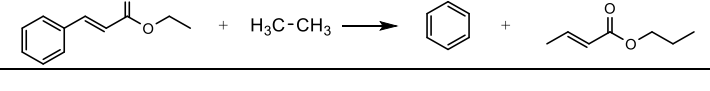
**Figure 2.** Conformational composition,  $\chi_i$ , for the most stable predominant molecular geometries, corresponding to minima on the potential energy surface, obtained using the G3(MP2)//B3LYP composite method for cinnamate derivatives. Atom color code: grey, C; red, O; white, H.

The only structural differences between the compounds are that ethyl (*E*)-cinnamate features a vinyl group ( $-\text{CH}=\text{CH}-$ ) with a *trans* double bond relative to the ester group, whereas ethyl hydrocinnamate has an ethyl group ( $\text{CH}_2-\text{CH}_2-$ ) instead, making it the ethyl ester of hydrocinnamic acid. In ethyl (*E*)-cinnamate, the vinyl group is conjugated with the benzene ring, creating a significant energy barrier to rotation around the single bond connecting them. This conjugation restricts rotation, keeping the vinyl group coplanar with the ring and limiting the number of conformers in six. In contrast, ethyl hydrocinnamate lacks this conjugation, as the benzene ring connects to the side chain via an ethyl group, allowing more flexible rotation and resulting in eleven conformers.

The estimation of the gas-phase enthalpy of formation for both compounds under investigation, using hypothetical substitution reactions (isodesmic or homodesmotic) relies on the similarity of bonding environments between reactants and products, which helps to cancel out systematic errors. However, a limitation of these reactions is that they require experimental gas-phase enthalpies of formation for all auxiliary molecules involved. To reduce the risk of depending on potentially inaccurate experimental data for any given species, multiple working reactions are used, replicating a procedure that has proven to be quite effective in previous studies [2–34].

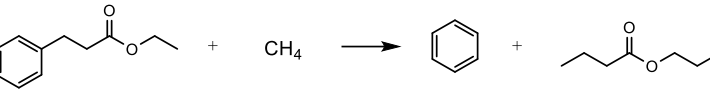
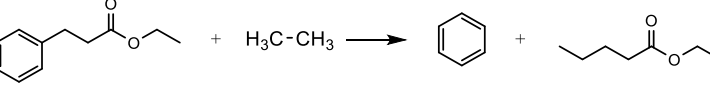
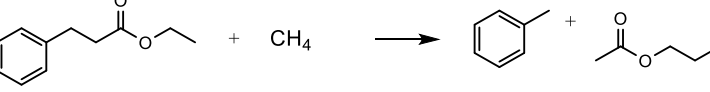
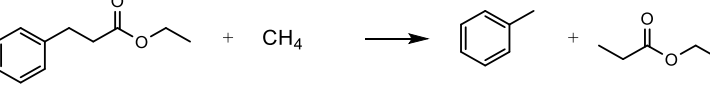
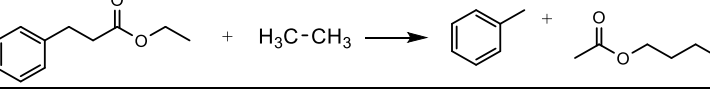
In this approach, the reaction enthalpy,  $\Delta_r H_m^\circ(\text{g})$ , is calculated as outlined in Equation (6), for each of the hypothetical gas-phase reactions, using the absolute standard enthalpies,  $H_{298.15\text{K}}^\circ$ , of the molecules involved. Subsequently, Equation (7), along with the experimentally determined standard molar enthalpies of formation for all the chemical species in the hypothetical reactions, was used to estimate  $\Delta_f H_m^\circ(\text{g})$  for the species of interest, specifically the two molecules under study: ethyl (*E*)-cinnamate (see Table 3) and ethyl hydrocinnamate (see Table 4). The relevant data for these chemical species are provided in the supplementary material in Table S8 of Supplementary Materials.

**Table 3.** Hypothetical gas-phase reactions proposed for calculating the gas-phase enthalpy of formation,  $\Delta_f H_m^\circ(g)$ , for ethyl (*E*)-cinnamate, along with the corresponding calculated values for the enthalpies of reaction  $\Delta_r H_m^\circ(g)$ , at  $T = 298.15$  K. All values account for the conformer distribution of the six minimum conformers.

| Hypothetical Gas-Phase Reactions                                                   | Eq. | $\Delta_r H_m^\circ(g)$<br>/ $\text{kJ}\cdot\text{mol}^{-1}$ | $\Delta_f H_m^\circ(g)$<br>/ $\text{kJ}\cdot\text{mol}^{-1}$ |
|------------------------------------------------------------------------------------|-----|--------------------------------------------------------------|--------------------------------------------------------------|
|  | I   | 24.46                                                        | -245.66                                                      |
|  | II  | 13.55                                                        | -246.54                                                      |
|  | III | 29.83                                                        | -249.33                                                      |
|  | IV  | 18.95                                                        | -247.75                                                      |
| Mean value                                                                         |     | -247.3 ± 2.5 <sup>1</sup>                                    |                                                              |

<sup>1</sup>The quoted uncertainty defines an interval having a 0.95 level of confidence (coverage factor used  $k = 3.18$  for 3 degrees of freedom).

**Table 4.** Hypothetical gas-phase reactions proposed for calculating the gas-phase enthalpy of formation,  $\Delta_f H_m^\circ(g)$ , for ethyl hydrocinnamate, along with the corresponding calculated values for the enthalpies of reaction  $\Delta_r H_m^\circ(g)$ , at  $T = 298.15$  K. All values account for the conformer distribution of the eleven minimum conformers.

| Hypothetical Gas-Phase Reactions                                                     | Eq. | $\Delta_r H_m^\circ(g)$<br>/ $\text{kJ}\cdot\text{mol}^{-1}$ | $\Delta_f H_m^\circ(g)$<br>/ $\text{kJ}\cdot\text{mol}^{-1}$ |
|--------------------------------------------------------------------------------------|-----|--------------------------------------------------------------|--------------------------------------------------------------|
|  | I   | 25.27                                                        | -353.27                                                      |
|  | II  | 13.34                                                        | -352.84                                                      |
|  | III | 15.42                                                        | -355.31                                                      |
|  | IV  | 13.67                                                        | -355.31                                                      |
|  | V   | 3.86                                                         | -354.86                                                      |
| Mean value                                                                           |     | -353.7 ± 1.7 <sup>1</sup>                                    |                                                              |

<sup>1</sup>The quoted uncertainty defines an interval having a 0.95 level of confidence (coverage factor used  $k = 2.78$  for 4 degrees of freedom).

$$\Delta_r H_m^\circ(g) = \Sigma H_{298.15K}^\circ(g, \text{ products}) - \Sigma H_{298.15K}^\circ(g, \text{ reagents}) \tag{6}$$

$$\Delta_f H_m^\circ(g) = \Sigma \Delta_f H_m^\circ(g, \text{ products}) - \Sigma \Delta_f H_m^\circ(g, \text{ reagents}) \tag{7}$$

The estimated values of the gas-phase standard molar enthalpy of formation,  $\Delta_f H_m^\circ(g)$ , obtained for ethyl (*E*)-cinnamate is  $(-247.3 \pm 2.5) \text{ kJ}\cdot\text{mol}^{-1}$  based on four reactions, while for ethyl hydrocinnamate it is  $(-353.7 \pm 1.7) \text{ kJ}\cdot\text{mol}^{-1}$  from five reactions.

#### 4. Discussion

Experimental determination of the standard molar gas-phase enthalpy of formation,  $\Delta_f H_m^\circ(g)$ , often involves starting with the enthalpy of formation in the condensed state, where both intermolecular and intramolecular interactions are considered. By combining this with the enthalpy of phase transition, the intermolecular interactions can be effectively canceled out, isolating the contributions of intramolecular interactions for analysis. This approach fulfills the initial objective of the work by allowing for a clearer understanding of the effects of molecular structure on thermodynamic properties and chemical behavior.

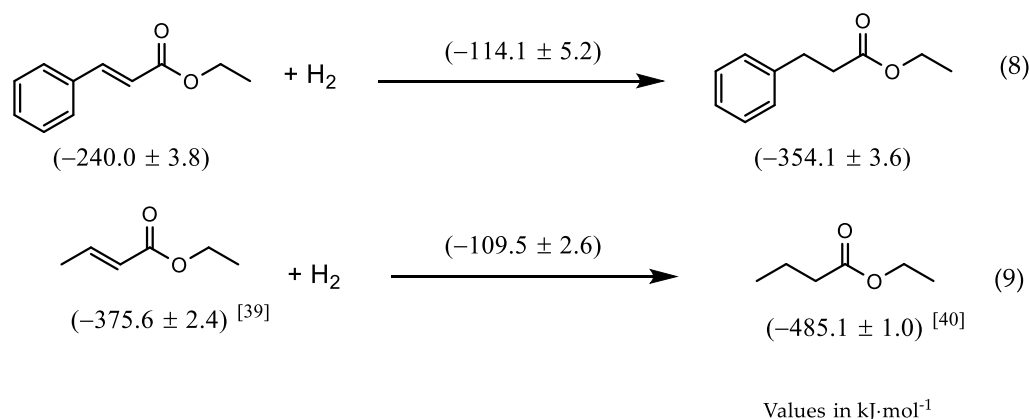
In Table 5, the standard ( $p^\circ = 0.1$  MPa) molar enthalpies of formation (liquid and gas) and vaporization for ethyl (*E*)-cinnamate and ethyl hydrocinnamate obtained in this study are compiled. Comparing the experimental values with the computational values obtained for the  $\Delta_f H_m^\circ(g)$ , the difference for ethyl (*E*)-cinnamate is  $7.3 \text{ kJ}\cdot\text{mol}^{-1}$ , while for ethyl hydrocinnamate it is  $0.4 \text{ kJ}\cdot\text{mol}^{-1}$ . The difference for ethyl (*E*)-cinnamate falls within the acceptable range established for experimental and computational values [38].

**Table 5.** Compilation of the standard ( $p^\circ = 0.1$  MPa) molar enthalpies of formation (liquid and gaseous) and vaporization for ethyl (*E*)-cinnamate (EEC) and ethyl hydrocinnamate (EHC).

|     | $\Delta_f H_m^\circ / \text{kJ}\cdot\text{mol}^{-1}$ | $\Delta_f H_m^\circ(l) / \text{kJ}\cdot\text{mol}^{-1}$ | $\Delta_f H_m^\circ(g) / \text{kJ}\cdot\text{mol}^{-1}$ |                    |
|-----|------------------------------------------------------|---------------------------------------------------------|---------------------------------------------------------|--------------------|
|     |                                                      |                                                         | experimental                                            | computational      |
| EEC | $72.4 \pm 2.5^1$                                     | $-312.4 \pm 2.8^1$                                      | $-240.0 \pm 3.8^2$                                      | $-247.3 \pm 2.5^1$ |
| EHC | $67.9 \pm 1.7^1$                                     | $-422.0 \pm 3.2^1$                                      | $-354.1 \pm 3.6^2$                                      | $-353.7 \pm 1.7^1$ |

<sup>1</sup> Standard uncertainties with 0.95 confidence level. <sup>2</sup> Standard uncertainties calculated through the RSS method.

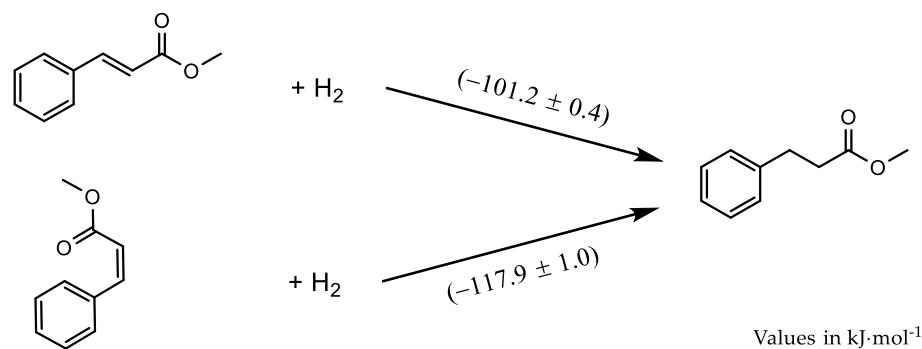
Considering the structural differences between the compounds studied, understanding the enthalpic difference associated with the hydrogenation of ethyl (*E*)-cinnamate to ethyl hydrocinnamate requires knowledge of the experimental  $\Delta_f H_m^\circ(g)$  values. This information is relevant for a comprehensive understanding of the hydrogenation process. Figure 2 illustrates the hydrogenation reaction of ethyl (*E*)-cinnamate to ethyl hydrocinnamate (eq. 8), with the gas-phase hydrogenation enthalpy at 298.15 K being  $\Delta_{\text{hyd}} H_m^\circ(g) = -114.1 \pm 5.2 \text{ kJ}\cdot\text{mol}^{-1}$ , calculated using Hess Law. The hydrogenation enthalpy for the reaction of ethyl (2*E*)-butenoate to ethyl butyrate (Equation (9)) was also calculated, which involves only the substituents without the benzene ring, yielding a value of  $-109.5 \pm 2.6 \text{ kJ}\cdot\text{mol}^{-1}$ ; this result is consistent with the previous value when accounting for the associated uncertainty.



**Figure 2.** Hydrogenation reactions with corresponding enthalpy of hydrogenation values for the conversion of ethyl (*E*)-cinnamate to ethyl hydrocinnamate and ethyl (2*E*)-2-butenate to ethyl butyrate. Refs [39,40].

Williams [41] pioneered the design of the first hydrogen calorimeter specifically for measuring enthalpy of hydrogenation in solution. The setup used a conventional reaction calorimeter with a

Dewar flask, but required hydrogen-tight conditions. The sample was in a glass ampoule, broken by an externally controlled mechanical device to start the reaction. Williams investigated the hydrogenation of methyl (*Z*)-cinnamate and methyl (*E*)-cinnamate to methyl hydrocinnamate at 302 K (Figure 3), using glacial acetic acid as the solvent for both reactions. This enthalpy value at this temperature is close to 298 K, given the minimal difference in heat capacities (at constant pressure) between the methyl cinnamate derivatives and hydrogen, making any corrections unnecessary. The enthalpy of hydrogenation was  $-117.9 \pm 1.0 \text{ kJ}\cdot\text{mol}^{-1}$  for methyl (*Z*)-cinnamate and  $-101.2 \pm 1.0 \text{ kJ}\cdot\text{mol}^{-1}$  for methyl (*E*)-cinnamate. It is important to note that for methyl (*Z*)-cinnamate, the fusion enthalpy value was used to calculate the gas-phase hydrogenation enthalpy due to the compound being solid, which may explain the observed lower enthalpy value.



**Figure 3.** Hydrogenation reactions with corresponding experimental enthalpy of hydrogenation values for the conversion of methyl (*E*)-cinnamate and methyl (*Z*)-cinnamate to methyl hydrocinnamate at the temperature of 302 K.

Table 6 presents hydrogenation enthalpies values at 298.15 K compiled by Rogers [42] (NIST–JANAF Thermochemical Tables) for some linear alkenes, specifically for the *E* and *Z* isomers. A brief analysis of these values shows that the hydrogenation enthalpy for the *Z* (cis) isomers tends to be more negative compared to the *E* (trans) isomers. This can be explained by the fact that the *Z* isomer is generally less stable than the *E* isomer, which causes the *Z* isomer to release more energy upon hydrogenation due to the greater stability difference between the isomer and the resulting saturated product (alkane). Therefore, the hydrogenation enthalpy of the *Z* isomer tends to be more negative than that of the *E* isomer.

**Table 6.** Compilation of experimental values for the gas-phase hydrogenation enthalpy of some unbranched (*E/Z*) isomeric alkenes at the  $T = 298.15 \text{ K}$  [Error! Bookmark not defined.].

| Reactions                                     | $\Delta_{\text{hyd}}H_m^\circ(\text{g}) / \text{kJ}\cdot\text{mol}^{-1}$ |                  |
|-----------------------------------------------|--------------------------------------------------------------------------|------------------|
|                                               | Isomer E                                                                 | Isomer Z         |
| But-2-ene + $\text{H}_2 \rightarrow$ Butane   | $-114.5 \pm 0.4$                                                         | $-118.5 \pm 0.4$ |
| Pent-2-ene + $\text{H}_2 \rightarrow$ Pentane | $-114.6 \pm 0.4$                                                         | $-118.5 \pm 0.4$ |
| Hex-2-ene + $\text{H}_2 \rightarrow$ Hexane   | $-113.8 \pm 1.3$                                                         | $-115.8 \pm 0.8$ |
| Hex-3-ene + $\text{H}_2 \rightarrow$ Hexane   | $-112.3 \pm 1.7$                                                         | $-122.6 \pm 1.3$ |
| Hept-2-ene + $\text{H}_2 \rightarrow$ Heptane | $-114.1 \pm 0.5$                                                         | $-117.9 \pm 0.4$ |
| Hept-3-ene + $\text{H}_2 \rightarrow$ Heptane | $-114.7 \pm 0.3$                                                         | $-120.0 \pm 2.9$ |
| Oct-2-ene + $\text{H}_2 \rightarrow$ Octane   | $-115.5 \pm 0.7$                                                         | $-119.4 \pm 1.1$ |
| Oct-3-ene + $\text{H}_2 \rightarrow$ Octane   | $-115.8 \pm 0.4$                                                         | $-117.8 \pm 0.4$ |
| Oct-4-ene + $\text{H}_2 \rightarrow$ Octane   | $-115.0 \pm 0.7$                                                         | $-114.6 \pm 0.4$ |

5. Conclusions

With the present experimental and computational work on ethyl (*E*)-cinnamate and ethyl hydrocinnamate, two cinnamate derivatives with flavor and fragrance features, the main conclusions

that can be taken out are: a) from a structural perspective in the gas phase, the vinyl group in ethyl (*E*)-cinnamate restricts conformational flexibility due to conjugation with the benzene ring, whereas the ethyl group in ethyl hydrocinnamate allows greater flexibility and more conformers; b) minor discrepancies between experimental and computational values for the gas-phase enthalpy of formation were observed for both compounds, validating the computational method used; c) The enthalpy of hydrogenation in the gas-phase from ethyl (*E*)-cinnamate to ethyl hydrocinnamate is  $-114.1 \pm 5.2 \text{ kJ}\cdot\text{mol}^{-1}$ , consistent with values for similar reactions involving ethyl (*2E*)-butenoate.

**Supplementary Materials:** The following supporting information can be downloaded at the website of this paper posted on Preprints.org. **Supplementary contains** (ethyl (*E*)-cinnamate is abbreviated as EEC and ethyl hydrocinnamate as EHC): **Tables S1-S2.** Combustion results and standard ( $p^\circ = 0.1 \text{ MPa}$ ) massic energy of combustion, at  $T = 298.15 \text{ K}$ , for EEC and EHC, respectively. **Tables S3-S4.** Calvet microcalorimetry results for the processes of vaporization of EEC and EHC, respectively. **Table S5.** Standard ( $p^\circ = 0.1 \text{ MPa}$ ) molar heat capacities in the gaseous phase for EEC and EHC, obtained from statistical thermodynamics using the vibrational frequencies calculated at the B3LYP/6-31G(d) level of theory (scaled by a factor of  $0.960 \pm 0.022$ ). **Tables S6-S7.** Absolute standard enthalpies,  $H_{298.15 \text{ K}}^\circ$ , and entropies,  $S_{298.15 \text{ K}}^\circ$ , obtained by G3(MP2)//B3LYP composite method and the corresponding derived gas-phase standard molar enthalpies,  $\Delta_f H_m^\circ(\text{g})$ , entropies,  $\Delta_f S_m^\circ(\text{g})$ , and Gibbs energy of formation,  $\Delta_f G_m^\circ(\text{g})$ , at  $T = 298.15 \text{ K}$ , as well as the conformational composition,  $\chi_i$ , obtained for, respectively, EEC and EHC **Table S8.** G3(MP2)//B3LYP enthalpies with corresponding gas-phase standard ( $p^\circ = 0.1 \text{ MPa}$ ) molar enthalpies of formation, at  $T = 298.15 \text{ K}$ , for the molecular species.

**Author Contributions:** Experimental and computational investigation, Carlos A. O. Silva and Vera L. S. Freitas; Supervision, Vera L. S. Freitas and Maria D. M. C. Ribeiro da Silva; Writing – review & editing, Vera L. S. Freitas and Maria D. M. C. Ribeiro da Silva.

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**Data Availability Statement:** The data supporting the results reported in this study are not publicly available due to privacy and ethical restrictions. No new datasets were created beyond those already available in the literature and the data provided in this paper. For further information about the study, please contact the corresponding author.

**Conflicts of Interest:** The authors declare no conflicts of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript; or in the decision to publish the results.

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