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Thermochemical and Ab Initio Studies of Biodiesel Fuel Surrogates: 1,2,3-Propanetriol Triacetate, 1,2-Ethanediol Diacetate, and 1,2-Ethanediol Monoacetate[†]

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This work has been undertaken to obtain new thermochemical data for ethanediol and propanetriol acetates and to improve the group contribution methodology for the prediction of the thermodynamic properties of compounds relevant to biodiesel. Standard molar enthalpies of formation in the gaseous state of a series of 1,2-ethanediol monoacetate, 1,2-ethanediol diacetate, and 1,2,3-propanetriol triacetate have been obtained from combustion calorimetry and results from the temperature dependence of the vapor pressure measured by the transpiration method. To verify the experimental data, ab initio calculations of all compounds have been performed. Enthalpies of formation derived from the Gaussian 03 second-order Møller–Plesset (G3MP2) method are in good agreement with the experimental results. The strength of the hydrogen bond in 1,2-ethanediol monoacetate and in 1,2-ethanediol have been obtained using ab initio calculations and the group additivity method.

1. Introduction

Biodiesel is defined as a fuel made from natural, renewable sources, such as new and used vegetable oils or animal fats, for use in a diesel engine. Biodiesel has physical properties very similar to petroleum diesel fuel. Derived from renewable sources, biodiesel can be used without any modification in engine design. Biodiesel can be easily synthesized by transesterification of vegetable oils to their end state of the mix of monoalkyl esters of long-chain fatty acids. This has prompted interest in the thermochemical properties of aliphatic esters.^{1–3} This effort complements and extends earlier work on many aliphatic esters by our group.^{4–9} The aim of this work was an experimental and computational study to gain thermochemical properties of biodiesel components. Direct studies of typical biodiesels are currently difficult because the laboratory experiments would have to be performed on complex mixtures and also because the modeling and simulation is not sufficiently developed to be able to address such large molecules.¹⁰ Hence, we have chosen to work on model compounds—1,2-ethanediol monoacetate, 1,2-ethanediol diacetate, and 1,2,3-propanetriol triacetate—which are, with regard to shape, relevant to the main and side products of biodiesel synthesis and therefore are useful with regard to providing insight into the thermochemistry of the synthetic processes. It has also been determined recently that 1,2-ethanediol monoacetate is a very promising candidate as an oxygenating additive to diesel fuels.¹¹

Precise knowledge of the thermochemical properties of biodiesel and its precursors is not only desirable for modeling

the synthesis process but even more so for obtaining better insight into the combustion process within combustion engines. This, together with kinetic information, would allow optimization of the combustion process, with respect to efficiency and completeness of the reaction (i.e., reduction of environmentally relevant combustion products, including carbon dioxide). These data are necessary to bridge the next 20 years in which fossil diesel will be increasingly replaced by biodiesel until the so-called designer fuels are available. These designer fuels are produced by gasification and Fischer–Tropsch synthesis. The resulting fuels can be optimized for the intended purpose. Until then, car manufacturers must design their engines to cope with biodiesel. Whereas the adaptation of current diesel engines to fossil fuel has been performed mainly by trial and error over the past 100 years, the determination of thermochemical data for biodiesel and related compounds shall serve to accelerate this optimization process considerably. So far, only the heats of combustion and some other physical data of normal *saturated* fatty acids and their methyl esters have been determined in the 1960s.^{58,59}

In this work, we explore the thermochemistry of 1,2-ethanediol monoacetate, 1,2-ethanediol diacetate, and 1,2,3-propanetriol triacetate, including the vaporization enthalpies ($\Delta_f^{\circ}H_m$) and the standard enthalpies of formation in the liquid state ($\Delta_f^{\circ}H_m(l)$), using experimental methods (combustion calorimetry and vapor pressure measurements). For a validation of the experimental data on these compounds, high-level ab initio calculations of the $\Delta_f^{\circ}H_m(g)$ value of these molecules have been performed using the Gaussian 03 program package. Using the new experimental results, a group contribution methodology for predicting the thermodynamic properties of compounds relevant to biodiesel has been developed.

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[†] This paper is dedicated to Prof. Dr. Christoph Rüchardt (University of Freiburg, Germany) on the occasion of his 80th birthday.

2. Experimental Section

2.1. Materials. Samples of 1,2,3-propanetriol triacetate (or triacetin) [CAS No. 102-76-1] and 1,2-ethanediol diacetate [CAS No. 111-55-7] were of commercial origin (Fluka and Aldrich), having a mass-fraction purity of ~ 0.99 , and were purified by repeated distillation in vacuum. A sample of 1,2-ethanediol monoacetate [CAS No. 102-76-1] was prepared and purified according to the established procedure (see Supporting Information).^{12,13} Gas chromatography (GC) showed no traceable amounts of impurities in samples after they were purified. The samples were analyzed with a gas chromatograph (Model 5890 Series II, Hewlett–Packard) that was equipped with a flame ionization detector and a integrator (Model 3390A, Hewlett–Packard). The carrier gas (nitrogen) flow was $7.2 \text{ dm}^3 \text{ h}^{-1}$. A capillary column HP-5 (stationary phase cross-linked 5% PH ME silicone) was used, with a column length of 30 m, an inside diameter of 0.32 mm, and a film thickness of $0.25 \mu\text{m}$. The standard temperature program of the gas chromatograph was $T = 323 \text{ K}$ for 180 s, followed by a heating rate of 10 K/min to $T = 523 \text{ K}$.

2.2. Measurements of the Vapor Pressures Using the Transpiration Method. Vapor pressures were determined using the method of transpiration in a saturated nitrogen stream,^{14,15} and vaporization enthalpies of esters were obtained applying the Clausius–Clapeyron equation. About 0.5 g of the sample was mixed with glass beads and placed in a thermostatted U-shaped tube that had a length of 20 cm and a diameter of 0.5 cm. Glass beads with a diameter of 1 mm provided a surface that was sufficient for the vapor–liquid equilibration. At constant temperature ($\pm 0.1 \text{ K}$), a nitrogen stream was passed through the U-tube and the transported amount of gaseous material was collected in a cooling trap. The flow rate of the nitrogen stream was optimized to reach the saturation equilibrium of the transporting gas at each temperature under study. The mass of compound collected within a certain time interval was determined by dissolving it in a suitable solvent with a certain amount of an internal standard (hydrocarbon). This solution was analyzed using a gas chromatograph that was equipped with an autosampler. The uncertainty of the sample amount, which was determined by GC analysis, was assessed to be within 1%–3%. The saturation vapor pressure (p_i^{sat}) at each temperature T was calculated from the amount of product collected within a definite period of time. Assuming that Dalton's law of partial pressures applied to the nitrogen stream saturated with the substance i of interest is valid, values of p_i^{sat} were calculated:

$$p_i^{\text{sat}} = \frac{m_i R T_a}{V M_i} \quad (1)$$

where

$$V = V_{\text{N}_2} + V_i \quad (V_{\text{N}_2} \gg V_i)$$

where $R = 8.314472 \text{ J K}^{-1} \text{ mol}^{-1}$, m_i is the mass of the transported compound, M_i is the molar mass of the compound, and V_i its volume contribution to the gaseous phase. V_{N_2} is the volume of the transporting gas and T_a is the temperature of the soap bubble meter. The volume of the transporting gas V_{N_2} was determined from the flow rate and time measurements. Data of p_i^{sat} have been obtained as a function of temperature and were fitted using the following equation:¹⁴

$$R \ln \left(\frac{p_i^{\text{sat}}}{p_0} \right) = a + \frac{b}{T} + \Delta_i^{\text{g}} C_p \ln \left(\frac{T}{T_0} \right) \quad (2)$$

where a and b are adjustable parameters and $\Delta_i^{\text{g}} C_p$ is the difference between the molar heat capacities of the gaseous and the liquid phase. T_0 , which appears in eq 2, is an arbitrarily chosen reference temperature (which has been chosen to be 298.15 K). Consequently, from eq 2, the expression for the vaporization enthalpy at temperature T is derived:

$$\Delta_i^{\text{g}} H_m(T) = -b + \Delta_i^{\text{g}} C_p T \quad (3)$$

Values of $\Delta_i^{\text{g}} C_p$ have been calculated according to a group additivity procedure developed by Chickos.¹⁶ Experimental results and parameters a and b are listed in Table 1. We have checked the experimental and calculation procedures with measurements of vapor pressures of n -alcohols.¹⁴ It turned out that vapor pressures derived from the transpiration method were reliable within 1%–3%, and their accuracy was governed by the reproducibility of the GC analysis. To assess the uncertainty of the vaporization enthalpy, the experimental data were approximated with the linear equation $\ln(p_i^{\text{sat}}) = f(T^{-1})$, using the method of least squares. The uncertainty in the enthalpy of vaporization was assumed to be identical with the deviation of experimental $\ln(p_i^{\text{sat}})$ values from this linear correlation. Experimental results are presented in Table 1.

2.3. Combustion Calorimetry. An isoperibol bomb calorimeter was used to measure the energy of combustion of esters. From a practical point of view, careful encapsulation of a sample is important in the combustion calorimetry of liquids. In the present study, we used commercially available polyethene bulbs (NeoLab, Heidelberg) with a volume of 1 cm^3 as the sample container for liquids, to reduce the capillary effect and make the encapsulation easier. The liquid specimen was transferred to the polyethene bulbs with a syringe. The narrow neck of the container was compressed with special tweezers and was sealed by heating with hot air. The loaded container then was placed in the bomb and burned in oxygen at a pressure of 3.04 MPa. Results from combustion experiments are given in Table 2. The detailed procedure has been described previously.¹⁷ The combustion products were examined for carbon monoxide (Dräger tube) and unburned carbon, but none was detected. The energy equivalent of the calorimeter (ϵ_{calor}) was determined with a standard reference sample of benzoic acid (Standard Reference Material SRM 39i, National Institute for Standards and Technology (NIST)). The correction for nitric acid formation was based on the titration with $0.1 \text{ mol dm}^{-3} \text{ NaOH(aq)}$. The atomic weights used were those recommended by the International Union of Pure and Applied Chemistry (IUPAC) Commission.¹⁸ The sample masses were reduced in a vacuum, taking into consideration their density values (see Table S1 in the Supporting Information). To convert the energy of the actual bomb process to that of the isothermal process, and reduce it to standard states, the conventional procedure¹⁹ was applied. It was not possible to remove small amounts of water (~ 100 – 300 ppm) from the liquid samples prepared for thermochemical measurements. The exact amount of water in each sample was measured by using Karl Fisher titration, and the appropriate corrections to the mass of the sample have been performed.

2.4. Computations. Standard ab initio molecular orbital calculations were performed with the Gaussian 03 Rev. 04 series of programs.²⁰ Energies were obtained at the Gaussian 03 second-order Møller–Plesset (G3MP2) level of theory. G3 theory is a procedure that is used to calculate the energies of

Table 1. Vapor Pressures (p) and Enthalpies of Vaporization ($\Delta_f^s H_m$) Obtained by the Transpiration Method

T (K) ^a	m (mg) ^b	$V(N_2)$ (dm ³) ^c	flow (dm ³ h ⁻¹)	p (Pa) ^d	$p_{\text{exp}} - p_{\text{calc}}$ (Pa)	$\Delta_f^s H_m$ (kJ/mol)
1,2-ethanediol monoacetate; $\Delta_f^s H_m(298.15 \text{ K}) = 63.89 \pm 0.32 \text{ kJ/mol}$						
$\ln(p/\text{Pa}) = 304.87 - \frac{82789.41}{T(\text{K})} - 63.4 \ln\left(\frac{T(\text{K})}{298.15 \text{ K}}\right)$						
301.3	6.13	4.22	2.22	34.44	0.13	63.69
305.4	5.46	2.67	3.90	48.40	0.17	63.43
308.3	5.20	2.07	2.22	59.14	-1.86	63.25
311.9	4.99	1.47	3.68	79.96	-1.10	63.02
315.4	5.11	1.15	2.22	106.3	0.2	62.80
319.1	5.57	0.921	3.68	142.8	2.8	62.56
322.2	4.46	0.610	2.22	175.9	0.3	62.37
324.2	4.68	0.537	2.15	206.8	4.0	62.24
325.9	4.54	0.462	1.85	233.2	4.5	62.13
329.6	6.03	0.490	1.90	296.2	0.6	61.90
332.7	7.11	0.462	1.85	366.1	1.3	61.70
336.7	9.37	0.474	1.90	475.9	0.7	61.45
340.3	12.53	0.493	1.85	601.5	2.2	61.22
343.6	11.01	0.366	1.13	721.6	-15.8	61.01
346.3	13.09	0.360	1.20	864.0	-6.8	60.84
1,2-ethanediol diacetate; $\Delta_f^s H_m(298.15 \text{ K}) = 61.40 \pm 0.15 \text{ kJ/mol}$						
$\ln(p/\text{Pa}) = 317.21 - \frac{85434.25}{T(\text{K})} - 80.6 \ln\left(\frac{T(\text{K})}{298.15 \text{ K}}\right)$						
291.2	5.62	4.29	2.74	22.04	0.07	61.97
293.4	5.95	3.74	2.74	27.04	0.43	61.79
295.5	8.16	4.19	2.74	32.77	0.92	61.62
298.2	6.52	2.77	2.13	39.84	-0.12	61.40
300.4	5.08	1.82	2.74	47.38	-0.52	61.23
305.6	5.46	1.31	2.12	70.63	-1.97	60.81
306.2	5.91	1.32	2.74	75.92	-0.16	60.76
310.7	4.26	0.687	2.75	105.4	-2.0	60.40
312.2	5.35	0.777	2.12	118.1	-2.5	60.27
315.8	6.40	0.687	2.75	157.8	1.3	59.98
318.2	6.42	0.585	2.06	185.8	-0.1	59.79
319.2	7.39	0.635	2.12	199.1	-0.4	59.71
320.6	6.55	0.495	1.98	222.2	2.2	59.60
323.3	7.02	0.447	2.06	265.9	0.7	59.38
325.5	6.05	0.331	1.32	308.0	0.1	59.20
326.2	5.64	0.298	1.19	322.5	-0.1	59.15
328.4	8.00	0.363	1.45	373.1	-0.2	58.97
330.8	8.50	0.331	1.32	433.4	-3.1	58.78
333.3	8.91	0.290	1.34	520.7	8.4	58.57
334.2	9.52	0.298	1.19	547.1	4.8	58.50
1,2,3-propanetriol triacetate; ^e $\Delta_f^s H_m(298.15 \text{ K}) = 81.88 \pm 0.33 \text{ kJ/mol}$						
$\ln(p/\text{Pa}) = 374.98 - \frac{115182.27}{T(\text{K})} - 111.7 \ln\left(\frac{T(\text{K})}{298.15 \text{ K}}\right)$						
320.1	23.2	114.7	5.90	2.40	0.03	79.43
322.1	25.4	104.5	5.90	2.87	0.01	79.21
323.9	23.5	79.76	6.14	3.31	-0.05	79.01
325.9	12.5	35.45	5.89	3.89	-0.13	78.78
328.0	11.5	27.01	6.41	4.89	0.04	78.55
330.0	10.8	22.31	6.41	5.56	-0.21	78.33
333.0	9.3	13.66	5.94	7.59	0.13	77.99
335.9	12.8	15.15	5.90	9.57	0.07	77.67
338.0	7.4	7.13	5.94	11.52	0.23	77.43
340.0	13.7	11.80	5.90	13.14	-0.14	77.21
341.9	11.1	8.07	5.90	15.56	0.10	77.00
342.9	33.8	22.00	5.89	16.97	0.25	76.89
345.9	18.6	9.77	5.81	21.25	0.13	76.55
347.9	34.0	15.93	4.14	24.39	-0.22	76.33
349.9	16.5	6.29	5.81	29.26	0.65	76.10
349.9	32.5	12.62	4.14	29.43	0.82	76.10
351.9	30.0	10.41	4.14	33.61	0.42	75.88
352.9	13.	4.06	5.81	34.96	-0.76	75.77
353.9	13.2	3.99	6.14	37.13	-1.29	75.66
354.9	42.0	11.67	4.07	41.10	-0.21	75.55
354.9	14.3	3.79	6.14	42.40	1.09	75.55
355.9	14.0	3.48	5.81	44.77	0.38	75.43
356.9	37.0	8.69	4.07	48.64	0.96	75.32
357.9	11.2	2.32	5.81	52.66	1.48	75.21
358.9	38.4	8.08	4.07	53.22	-1.68	75.10
359.9	12.4	2.42	5.81	57.08	-1.81	74.99
360.9	13.5	2.32	5.81	62.27	-0.84	74.88

^a Temperature of saturation. ^b Mass of transferred sample, condensed at $T = 243 \text{ K}$. ^c Volume of nitrogen used to transfer sample of mass m . ^d Parameter p_{calc} represents the vapor pressure at temperature T , calculated from sample mass m , and parameter p_{exp} represents the residual vapor pressure at the cooling temperature ($T = 243 \text{ K}$). ^e For this compound, the mass of the transferred sample was measured by weighing.

Table 2. Results of Typical Combustion Experiments at $T = 298.15$ K ($p^\circ = 0.1$ MPa) of the Acetates^a

compound	1,2-ethanediol monoacetate	1,2-ethanediol diacetate	1,2,3-propanetriol triacetate
$m(\text{substance})$ (g) ^b	0.432902	0.490975	0.539617
$m'(\text{cotton})$ (g) ^b	0.000859	0.001282	0.001106
$m''(\text{polyethylene})$ (g) ^b	0.31932	0.290231	0.273749
ΔT_c (K) ^c	1.58078	1.57579	1.57351
$(\epsilon_{\text{calor}})(-\Delta T_c)$ (J)	-23408.5	-23346.9	-23313.1
$(\epsilon_{\text{cont}})(-\Delta T_c)$ (J) ^d	-26.2	-25.98	-25.83
$\Delta U_{\text{decomp}}(\text{HNO}_3)$ (J)	40.91	41.81	41.51
ΔU_{corr} (J) ^e	8.84	9.76	10.37
$-m'\Delta_c u'$ (J)	14.56	21.72	18.74
$-m''\Delta_c u''$ (J)	14801.92	13453.51	12689.5
$\Delta_c u^\circ(l)$ (J/g)	-19793.2	-20054.0	-19604.3
$\Delta_c u^\circ(l)$ (J/g)	-19782.6 \pm 10.5	-20051.2 \pm 3.9	-19600.6 \pm 3.0

^a For the definition of the symbols, see ref 19. Values determined using a macrocalorimeter, under the following conditions: $T_h = 298.15$ K, $V(\text{bomb}) = 0.32$ dm³, $p'(\text{gas}) = 3.04$ MPa, and $m'(\text{H}_2\text{O}) = 1.00$ g.

^b Masses obtained from apparent masses. ^c $\Delta T_c = T^i - T^f + \Delta T_{\text{corr}}$.

^d $\epsilon_{\text{cont}}(-\Delta T_c) = \epsilon_{\text{cont}}^i(T^i - 298.15 \text{ K}) + \epsilon_{\text{cont}}^f(298.15 \text{ K} - T^f + \Delta T_{\text{corr}})$.

^e ΔU_{corr} is the correction to standard states; it is the sum of items 81–85, 87–90, 93, and 94 in ref 19.

molecules containing atoms of the first and second row of the periodic chart, based on ab initio molecular orbital theory. A modification of G3 theory that uses reduced orders of Møller–Plesset perturbation theory is G3MP2 theory.²¹ No corrections for internal rotors have been taken into account. The enthalpy values at $T = 298$ K were evaluated according to standard thermodynamic procedures.²²

3. Results and Discussion

The enthalpy of formation in the gaseous phase of any compound is composed of two contributions:

$$\Delta_f H_m^\circ(g) = \Delta_f^\circ H_m + \Delta_f H_m^\circ(l)$$

where $\Delta_f^\circ H_m$ is the enthalpy of vaporization and $\Delta_f H_m^\circ(l)$ is the enthalpy of formation in the liquid state. There is surprisingly little known about the $\Delta_f^\circ H_m$ and $\Delta_f H_m^\circ(l)$ values of ethanediol and propanetriol derivatives. Enthalpies of combustion in the liquid state only of several 1,2,3-propanetriol acetates were measured in 1956.²³ Available data on the vaporization enthalpies are collected in Table 3. In this context, a systematic study of thermochemistry of ethanediol and propanetriol acetyl derivatives seems to be highly desirable.

3.1. Vapor Pressures and Enthalpies of Vaporization. A summary of vapor pressures and vaporization enthalpies of acetates measured in this work has been presented in Table 1. A comparison of the vapor pressures measured in the present work with the literature is given in Figures S1–S3 in the Supporting Information. However, a proper comparison is hardly possible, because the literature data in most cases were measured at elevated temperatures close to the boiling point. The vaporization enthalpies reported in the literature are not always adjusted to the reference temperature (298 K). That is why we treated the primary experimental results from refs 24, 27, and 29, using eqs 2 and 3, and we calculated $\Delta_f^\circ H_m(298 \text{ K})$ for the sake of comparison with our results (see Table 3). Vaporization enthalpies $\Delta_f^\circ H_m(298 \text{ K})$ for 1,2-ethanediol diacetate and 1,2,3-propanetriol triacetate measured in this work are in close agreement with those values from the literature (see Table 3). The result for 1,2-ethanediol monoacetate ($\Delta_f^\circ H_m(298 \text{ K}) = 63.9 \pm 0.3$ kJ/mol) is somewhat higher than the value obtained from the ebulliometric measurements by Schmid et al.¹² The reason for such a disagreement could be due to the presence of a small amount of water (96.8 ppm) in the sample for ebulliometric study.¹²

3.2. Correlation of the Enthalpies of Vaporization with the Number of Carbon Atoms in 1,2-Ethanediol Alkanoates. The correlation of enthalpies of vaporization with the number of C atoms in the series of homologues is a valuable test to check the internal consistency of the experimental results. The vaporization enthalpies $\Delta_f^\circ H_m$ appear to be a linear function of the number of C atoms of the aliphatic nitriles,³⁰ aliphatic esters,⁶ and diesters of carboxylic acids.⁸ The plot of $\Delta_f^\circ H_m(298 \text{ K})$ against the number of C atoms in the linear aliphatic chains of 1,2-ethanediol alkanoates $\text{R}-\text{CO}_2-\text{CH}_2-\text{CH}_2-\text{CO}_2-\text{R}$, with $\text{R} = \text{Me}$, Et , and Pr , is presented in Figure 1. The dependence of the vaporization enthalpy on the number of C atoms (N_C) is expressed by the following equation:

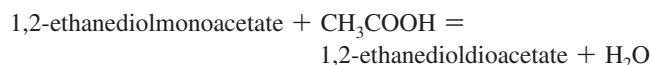
$$\Delta_f^\circ H_m(298 \text{ K}) (\text{kJ/mol}) = 5.9N_C + 55.6 \quad (4)$$

from which the $\Delta_f^\circ H_m(298 \text{ K})$ values of other representatives of this series can be easily calculated.

3.3. Enthalpies of Formation in the Liquid State. Results of typical combustion experiments for esters are summarized in Table 2 (extended experimental tables are given in Tables S2–S4 in the Supporting Information). The means of individual values of the standard specific energies of combustion ($\Delta_c u^\circ$) were derived as a rule from 4–6 independent experiments. To derive $\Delta_f H_m^\circ(l)$ from the molar enthalpy of combustion ($\Delta_c H_m^\circ$), the molar enthalpies of formation of $\text{H}_2\text{O}(l)$ (-285.830 ± 0.042 kJ/mol) and $\text{CO}_2(g)$ (-393.51 ± 0.13 kJ/mol) have been used as assigned by CODATA.³¹ Table 4 lists the derived standard molar enthalpies of combustion and the standard molar enthalpy of formation of the esters derived in this work. The total uncertainty was calculated according to the guidelines presented by Olofsson.³² The uncertainty assigned to $\Delta_f H_m^\circ$ is twice the overall standard deviation and includes the uncertainties from calibration, from the combustion energies of the auxiliary materials, and the uncertainties of the enthalpies of formation of the reaction products H_2O and CO_2 .

Only one previous experimental value of $\Delta_f H_m^\circ(l)$ for triacetin has been determined by Tavernier and Lamoroux,²³ using combustion calorimetry. Their value, $\Delta_f H_m^\circ(l) = -(1330.8 \pm 4.2)$ kJ/mol, is in disagreement, by 67 kJ/mol, with the result obtained in this work. We do not have any reasonable explanation for such a disagreement, but we intend to validate our value using ab initio calculations in the next chapter.

Schmid et al.¹² have recently published results on the esterification of 1,2-ethanediol with acetic acid via 1,2-ethanediol monoacetate to 1,2-ethanediol diacetate catalyzed by Amberlyst 36. We have used the enthalpy of reaction ($\Delta_r H_m^\circ = -3.2$ kJ/mol) of the reaction



reported in this work to derive the enthalpy of formation of 1,2-ethanediol monoacetate ($\Delta_f H_m^\circ(l) = -657.8$ kJ/mol), with the help of Hess's Law and the known enthalpies of formation of acetic acid,³³ 1,2-ethanediol diacetate (see Table 4) and water.³¹ The derived value is in excellent agreement with the direct calorimetric result measured in this work (see Table 4).

3.4. Calculation of the Gaseous Enthalpies of Formation. Values of the vaporization enthalpies of ethanediol and propanetriol acetates, derived in this work (see Table 1) have been used, together with the results from our combustion experiments (Table 2), for further calculation of the gaseous standard enthalpies of formation ($\Delta_f H_m^\circ(g)$ at 298 K). The resulting values of $\Delta_f H_m^\circ(g)$ are given in the last column in Table 4.

Table 3. Compilation of Data on Vaporization Enthalpies ($\Delta_f^g H_m$) of Compounds Studied in This Work

technique ^a	temperature range (K)	$\Delta_f^g H_m(T)$ (kJ/mol)	$-\Delta C_p^b$	$(C_p^l)^b$ (J mol ⁻¹ K ⁻¹)	$\Delta_f^g H_m(298\text{ K})$ (kJ/mol) ^c	ref
1,2-ethanediol monoacetate						
E	363.2–448.8	55.0	63.4	203.0 (from ref 56)	61.7 ± 0.3	12
T	301.3–346.3	62.3			63.9 ± 0.3	this work
1,2-ethanediol diacetate						
E	373–463	53.4			62.8 ± 0.8	24
C	298.15		80.6	269.2 (from ref 26)	61.0 ± 0.1	25
C	298.15				61.4 ± 0.2	26
T	291.2–334.2	60.3			61.4 ± 0.2	this work
1,2,3-propanetriol triacetate						
S	284.2–318.2	82.0	111.7	389.0 (from ref 26)	82.3 ± 0.2	27
C	298.15				83.4 ± 1.0	28
C	298.15				85.7 ± 0.3	26
E	439.5–590.2	59.7			83.8 ± 0.9	29
T	320.1–360.9	76.9			81.9 ± 0.3	this work

^a Techniques: E = ebulliometry; T = transpiration; S = static method (piston manometer). ^b Values of ΔC_p have been derived from the isobaric molar heat capacity of the liquid compounds (C_p^l), according to the procedure developed by Chickos and Acree.¹⁶ ^c Vapor pressure available in the literature were treated using eqs 2 and 3, to evaluate the enthalpy of vaporization at 298 K in the same way as our own results in Table 4.

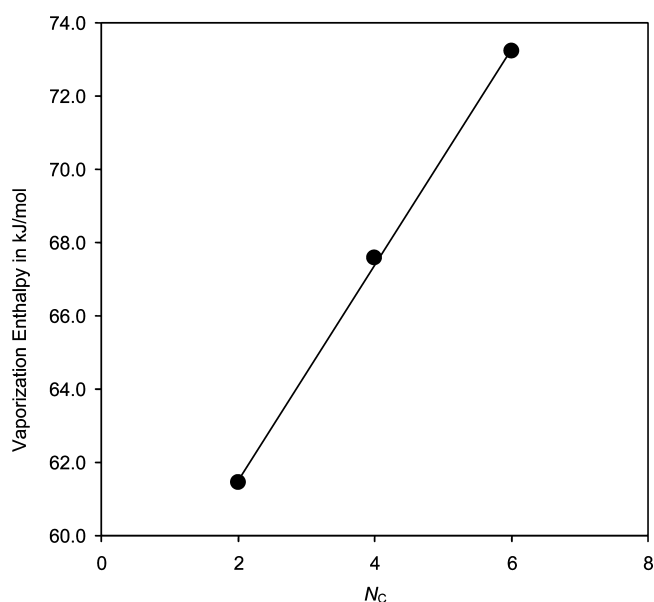


Figure 1. Correlation of the vaporization enthalpy of $\Delta_f^g H_m(298\text{ K})$ versus the number of C atoms (N_C) in the linear aliphatic chains for 1,2-ethanediol alkanates: $R-CO_2-CH_2-CH_2-CO_2-R$, with $R = \text{Me, Et, and Pr}$. Experimental data are given in Table S5 in the Supporting Information.

3.5. Quantum Chemical Calculations. Results of ab initio molecular orbital methods for the calculation of the enthalpy of formation of ethanediol and propanetriol acetates have not yet been reported in the literature. We have calculated the

gaseous enthalpies of formation with the help of the standard atomization reactions,³⁴ as well as through the use of bond separation reactions.³⁵ Using the enthalpies of these reactions that have been calculated by the G3MP2 method and the enthalpies of formation $\Delta_f H_m^o(g)$ for simple molecules as recommended by Pedley et al.,³³ the enthalpies of formation of ethanediol and propanetriol acetates have been calculated (see Tables 5–7).

3.5.1. Calculation of the Enthalpy of Formation of 1,2-Ethanediol Monoacetate. Study of the conformational equilibrium of 1,2-ethanediol monoacetate is important for correct calculation of its enthalpy of formation ($\Delta_f H_m^o(g)$). According to conformational analysis using the G3MP2 method, four possible arrangements were found in the 1,2-ethanediol monoacetate molecule, with regard to the double bond of the carbonyl group. Calculations have revealed a possibility of the intramolecular hydrogen bonding formation in conformers M2 and M3. Indeed, the distance between the hydrogen of the hydroxyl group and the oxygen in the chain is 2.33 Å in conformer M2. Also, the distance between the hydrogen of the hydroxyl group and the oxygen of the carbonyl group is 1.93 Å in M3. For comparison, in 1,2-ethanediol, where the intramolecular hydrogen bond is well-established, the very similar distance (2.24 Å) between the hydrogen of the hydroxyl and the oxygen of the second hydroxyl-group was calculated using the same G3MP2 method. The energy differences of the four conformers of 1,2-ethanediol monoacetate, which are related to the appropriate most-stable conformer M3, are given in Figure 2.

Table 4. Thermochemical Data at $T = 298.15\text{ K}$ ($p^\circ = 0.1\text{ MPa}$) for Compounds Studied in This Work

compound	state	$\Delta_c H_m^o$ (kJ/mol)	$\Delta_f H_m^o(l)$ (kJ/mol)	$\Delta_f^g H_m$ (kJ/mol)	$\Delta_f H_m^o(g)$ (kJ/mol)
1,2-ethanediol monoacetate	liquid	-2060.7 ± 2.2	-656.7 ± 2.3	63.9 ± 0.3	-592.8 ± 2.3
1,2-ethanediol diacetate	liquid	-2931.6 ± 1.3	-858.7 ± 1.6	61.4 ± 0.2	-797.3 ± 1.6
1,2,3-propanetriol triacetate	liquid	-4278.2 ± 1.6	-1264.2 ± 2.0	81.9 ± 0.3	-1182.3 ± 2.0

Table 5. Results of Calculation of the Standard Enthalpies of Formation ($\Delta_f H_m^o(g)$) of 1,2-Ethanediol Monoacetate at 298 K

conformer	Standard Enthalpy of Formation, $\Delta_f H_m^o$ (kJ/mol)					$\exp[-\Delta G_0/(RT)]$	x_i	$\Delta_f H_m^o(g)^a$ (kJ/mol)
	atomization	reaction R.1	reaction R.2	reaction R.3	average			
M1	-584.1	-591.8	-587.5	-589.1	-588.1	0.06	0.02	
M2	-592.6	-600.3	-595.9	-597.6	-596.6	1.00	0.66	
M3	-592.7	-600.4	-596.0	-597.7	-595.0	0.42	0.28	
M4	-584.3	-592.0	-587.7	-589.3	-588.3	0.05	0.04	-595.7 ± 2.5

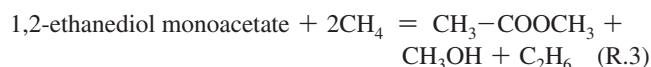
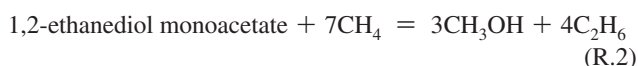
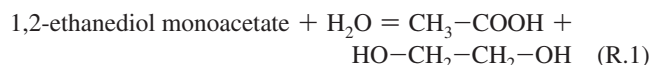
^a Calculated according to eq 5 as the average from atomization, bond separation, and isodesmic reactions.

The thermal population (p_i) of the conformers at $T = 298$ K is given by

$$p_i = \frac{\exp\left(-\frac{\Delta G_i}{RT}\right)}{1 + \sum_{i=1}^n \exp\left(-\frac{\Delta G_i}{RT}\right)} \quad (\Delta G_i = G_i - G_{M3}) \quad (5)$$

Results on p_i were used to calculate the energies and enthalpies of the equilibrium mixture of conformers and were finally applied to the calculation of $\Delta_f H_m^\circ(g)$ and of the gaseous enthalpy of formation of 1,2-ethanediol monoacetate.

We have calculated the gaseous enthalpy of formation of 1,2-ethanediol monoacetate with the aid of the standard atomization reaction, as well as through the use of the following isodesmic reaction (R.1) and bond separation reactions (R.2 and R.3):



The enthalpy of formation of 1,2-ethanediol monoacetate derived with the aid of the atomization procedure and reactions R.1–R.3 are very similar (see Table 5). The average values calculated from atomization, bond separation, and isodesmic reactions are also in agreement with the experimental result (see Table 4).

3.5.2. Calculation of the Enthalpy of Formation of 1,2-Ethanediol Diacetate. The most stable conformation of 1,2-ethanediol diacetate is presented in Figure 3. The energy differences of other less-stable conformers, related to the appropriate most stable conformer, exceeded 10 kJ/mol and were not taken into account. The enthalpy of formation of 1,2-ethanediol diacetate derived with the aid of the atomization procedure and reactions R.4–R.9 are in close agreement (see Table 6). Their average is also in agreement with our experimental result (see Table 4).

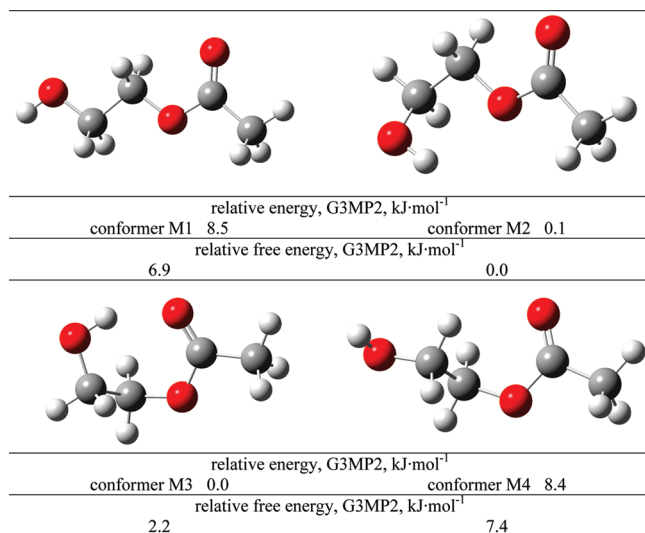
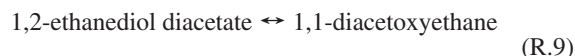
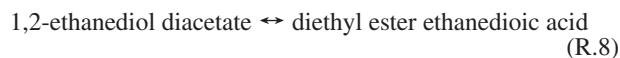
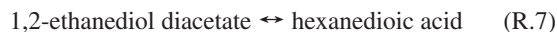
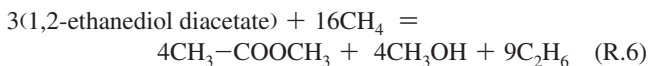
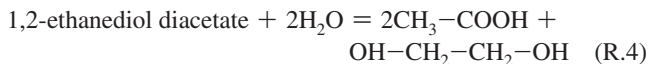
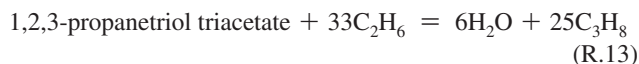
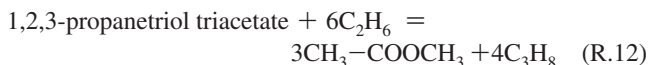
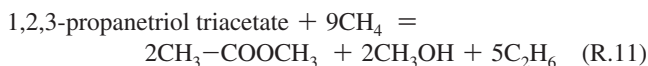
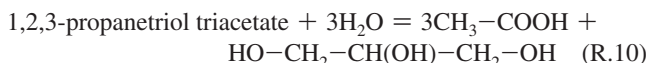


Figure 2. Stable conformations of 1,2-ethanediol monoacetate.



3.5.1.2. Calculation of the Enthalpy of Formation of 1,2,3-Propanetriol Triacetate. Ab initio calculations using the Hartree–Fock (HF) method revealed 109 rotamers within 12 kJ/mol from the global minimum of the 1,2,3-propanetriol triacetate.³⁶ The three most-stable conformers are presented in Figure 4. The thermal population p_i of these conformers at $T = 298$ K, according to eq 5, were taken into account by calculating $\Delta_f H_m^\circ(g)$ with the aid of reactions R.10–R.13.



In contrast to the ethanediol acetates, the enthalpy of formation of 1,2,3-propanetriol triacetate derived with the aid of the atomization procedure, as well as reactions R.10–R.13, have shown a large spread of values (see Table 7), apparently due to

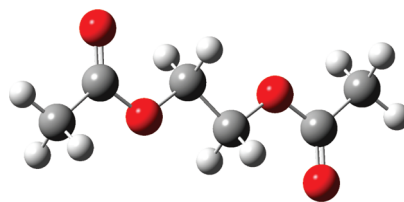


Figure 3. Depiction of the most-stable conformation of 1,2-ethanediol diacetate.

Table 6. Results of G3MP2 Calculations of the Standard Enthalpy of Formation ($\Delta_f H_m^\circ(g)$) of 1,2-Ethanediol Diacetate at 298 K

	$\Delta_f H_m^\circ(g)$ (kJ/mol)
atomization	−792.1
R.4	−802.3
R.5	−795.4
R.6	−797.6
R.7	−794.8
R.8	−792.4
R.9	−793.6
experiment	−797.3 ± 1.6
average ^a	−796.0 ± 3.0

^a Calculated as the average from bond separation and isomerization reactions.

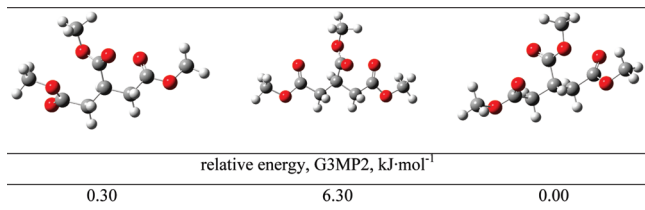


Figure 4. Depictions of the most-stable conformations of 1,2,3-propanetriol triacetate.

the large size of this molecule. However, the average $\Delta_f H_m^\circ(g)$ value that is calculated from all four ab initio results is still in acceptable agreement with our experimental result (see Table 4).

3.6. Additive Calculations of Thermodynamic Properties of Model Compounds Related to Biofuels. The enthalpies of formation of the model compounds such as ethanediol and propanetriol acetates could be predicted successfully using the high-level ab initio method. However, note that the composite G3MP2 method used in this work is quite a time-consuming method. For small molecules, such as ethanediol monoacetate, a required job CPU time was only 4 h for the longest step (step 4 with QCISD(T)/6-31G(d)). For medium-sized molecules, such as ethanediol diacetate, the required job CPU time was already 36 h. (The calculations were performed at the university computational center with a Dual Core AMD Opteron 2220 SE, using two processors and 2500 Mb RAM). However, for 1,2,3-propanetriol triacetate, it already was possible to complete our calculations within 120 h. Following this, an alternative group additivity procedure is required to predict the thermochemical properties of large molecules related to glycerol derivatives and other model compounds for biofuels.

The group additivity methods^{37–40} serve as a valuable tool for many scientists and engineers whose work involves the thermodynamic characterization of elementary and overall reaction processes. Benson's group additivity method⁴⁰ presently seems to have the most widespread acceptance, and the overall best record for reliability of estimation techniques. A group is defined by Benson³⁷ as "a polyvalent atom (ligancy ≥ 2) in a molecule together with all of its ligands". In this work, we endorse and follow Benson's methodology.

3.6.1. Additive Calculations of the Enthalpies of Formation of Aliphatic Esters in the Liquid and in the Gaseous State. Our approach for evaluating the group additivity values (GAVs) was similar to that of others,^{40,41} in that we began by deriving GAVs for the alkane groups, using, as a database, the set of thermodynamic properties for 68 compounds, as has been used by Cohen.⁴⁰ The polyfunctional least-squares method was used to evaluate the additivity parameters. The group contribution values, which are specific for alkanes $C-(C)(H_3)$, $C-(C_2)(H_2)$, $C-(C_3)(H)$, $C-(C_4)$ and the correction for 1–4 C–C interactions $(C-C)_{1-4}$, are well-established⁴¹ (see Table

Table 7. Results of G3MP2 Calculations of the Standard Enthalpies of Formation ($\Delta_f H_m^\circ(g)$) for 1,2,3-propanetriol triacetate at 298 K

	$\Delta_f H_m^\circ(g)$ (kJ/mol)
atomization	–1156.4
R.10	–1183.1
R.11	–1164.3
R.12	–1168.4
R.13	–1170.7
experiment	–1182.3 \pm 2.0
average	–1171.6 \pm 8.1 ^a

^a Calculated as the average from the isodesmic and bond separation reactions.

Table 8. Group Additivity Values for the Calculation of the Enthalpy of Formation ($\Delta_f H_m^\circ$), and the Enthalpy of Vaporization ($\Delta_v H_m^\circ$) for Aliphatic Esters at $T = 298$ K

increment	$\Delta_f H_m^\circ(g)$ (kJ/mol)	$\Delta_f^\circ H_m$ (kJ/mol)	$\Delta_v H_m^\circ(l)$ (kJ/mol)
Hydrocarbons			
$C-(C)(H)_3$	–41.80	6.33	–48.50
$C-(C)_2(H)_2$	–23.06	4.52	–27.23
$C-(C)_3(H)$	–10.49	1.24	–10.37
$C-(C)_4$	–3.17	–2.69	1.90
$(C-C)_{1-4}$	2.56	0.26	2.01
$C_d(C)(H)$	36.0	3.8	32.2
$C-(C_d)(C)(H)_2$	–18.8	3.8	–23.9
Esters			
$(CO_2)-(C)_2$	–327.6	18.82	–346.3
$C-(C)(H)_2(CO_2)$	–20.96	4.38	–25.60
$C-(C)_2(H)(CO_2)$	–13.46	1.56	–15.36
$C-(C)_3(CO_2)$	0.83	–0.53	0.43
$C-(C)(H)_2(O)$	–33.31	3.13	–36.44
$C-(C)_2(H)(O)$	–28.67	–0.51	–27.09
$C-(C)_3(O)$	–21.67	–6.01	–14.19
$(C-CO)_{1-4}$	0.83	–1.57	3.19
$(C-Oe)_{1-4}$	0.16	–0.27	–0.14
Alcohols^a			
$C-(C)(H)_2(OH)$	–29.03	6.90	–32.25
$OH-(C)$	–158.6	31.80	–190.4
Biofuels			
C_{EDM}	–551.0	57.6	–608.2
C_{EDD}	–713.7	48.7	–761.7
C_{PDT}	–1056.9	62.9	–1118.7

^a Increments for alcohols were taken from our previous work.⁴¹

8). With these values fixed, we then turned to esters to derive GAVs necessary for those compounds: the carboxyl group $(CO_2)-(C)_2$ and the alkyl chain attached to the carbonyl side $C-(C)(H)_2(CO_2)$, $C-(C)_2(H)(CO_2)$, $C-(C)_3(CO)$, and for the alkyl chain attached to the oxygen of the carboxyl group: $C-(C)(H)_2(O)$, $C-(C)_2(H)(O)$, $C-(C)_3(O)$. Similar to alkanes, a correction for the interaction between the C atom of the alkane chain with the double-bonded oxygen of the carbonyl group $(C-CO)_{1-4}$ and a correction for the interaction between the C atom of the alkane chain with the oxygen on the other side of the carbonyl group $(C-Oe)_{1-4}$ was introduced. For example, to predict the enthalpy of formation of butyl acetate, the following contributions should be taken into account:

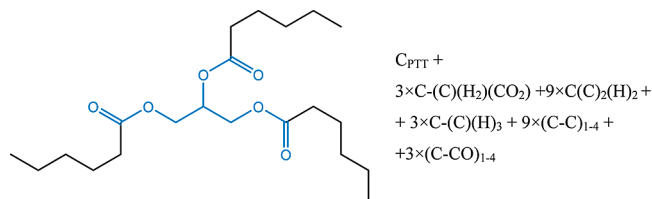
$$(CO_2)-(C)_2 \times 1 + C-(C)(H)_2(O) \times 1 + C-(C)(H_3) \times 2 + C-(C)_2(H)_2 \times 2 + (C-C)_{1-4} \times 1 + (C-Oe)_{1-4} \times 1$$

For deriving GAVs for the aliphatic esters we have collected a series of compounds with the secondary, tertiary and quaternary branching of the alkyl substituents. These compounds have constituted a matrix (see Table S6 in the Supporting Information) which has been solved using the polyfunctional least-squares method, and the group additivity parameters have been evaluated (see Table 8).

3.6.2. Extension of Benson's Methodology for the Prediction of Vaporization Enthalpies. Original works by Benson³⁷ and an updated compilation⁴⁰ do not provide GAVs for the calculation of vaporization enthalpies ($\Delta_v H_m^\circ$) at 298 K. This is not the fault of the empirical and half-empirical methods for estimating the vaporization enthalpies of organic compounds.^{41–43,60,61} However, it seems to be logical to follow Benson's methodology for this thermodynamic property as well. In this work, to predict the vaporization enthalpies of aliphatic esters, we have applied the same definition of groups and the same evaluation procedure as

those used for the formation enthalpies. The evaluation of the GAVs to predict the vaporization enthalpies ($\Delta_f^g H_m$) was based on experimental data (see Table S7 in the Supporting Information). Group additivity parameters have been evaluated using the least-squares method, and they are given in Table 8. Results for the predicted data presented in Table S7 of the Supporting Information show that the average standard deviations of the selected data taken into correlation and the predicted values are also at the level of 1–2 kJ/mol.

3.6.3. Additive Calculations of the Formation Enthalpies and the Vaporization Enthalpies of Compounds Relevant to Biofuels. The main parts of biofuels are glycerol derivatives with long alkyl chains. Having established experimental formation enthalpies and vaporization enthalpies of 1,2-ethanediol and 1,2,3-propanetriol acetates, it is reasonable to develop a general group additivity procedure for predicting these thermochemical properties for similar compounds with long alkyl chains. In our previous work,⁴⁵ we applied an incremental scheme to the alkylurea derivatives, which consists of the determination of increments for the substitution of H atoms by CH₃ groups in the standard series starting with urea itself. This procedure has been shown to provide consistent results. In this work, we suggest a similar procedure, where the acetyl-substituted units of the 1,2-ethanediol monoacetate (EDM), 1,2-ethanediol diacetate (EDD), and 1,2,3-propanetriol triacetate (PTT) have been taken as the starting points. Subtracting an appropriate number of CH₃ increments from EDM, EDD, and PTT, the values for the starting units (C_{EDM} , C_{EDD} , and C_{PTT}) have been introduced. For example, to predict the formation enthalpy or the vaporization enthalpy of 1,2,3-propanetriol trihexanoate, the following calculations should be performed:



The C_{PDT} fragment consists of the following increments:

$$C_{PDT} = 3 \times (CO_2)-(C)_2 + 2 \times C-(C)(H)_2(O) + 1 \times C-(C)_2(H)(O) + 2 \times (C-O)_{1-4}$$

However, this fragment has been considered as the special unit, C_{PDT} , and its value was derived from the experimental properties of 1,2,3-propanetriol triacetate (see Table 8). For the hydrocarbon chains that are attached to the C_{PDT} , the further additional contributions $3 \times C-(C)(H_2)(CO_2) + 9 \times C(C_2)(H)_2 + 3 \times C-(C)(H)_3 + 9 \times (C-C)_{1-4} + 3 \times (C-CO)_{1-4}$ have been taken into account. Group contribution values, which are specific for alkanes and alkanols are well established.⁴¹ The group additive parameters specific for aliphatic esters have just been derived in the previous section. Now, using the new GAVs (C_{EDM} , C_{EDD} , and C_{PDT}), the gaseous or liquid enthalpy of formation of any arbitrarily large ester or triglyceride could be predicted.

3.7. Validation of the Experimental Results Available for Biofuel Components. A large number of experimental enthalpies of combustion of compounds parent to biofuels—fatty esters and triglycerides—were measured in 1989 by Freeman and Bagby.⁴⁶ Vapor pressures and vaporization enthalpies for a large number of triglycerides with saturated and unsaturated alkyl chains were measured using the pendulum–tensimeter method.⁴⁷ Goodrum and co-workers measured the vapor pres-

sure of large esters and triglycerides using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC).^{48–51} Compilations of the available experimental data on these compounds are listed in Tables 9 and 10. Unfortunately, the purities and water contents of samples used in those studies are ill-defined. Thus, one needs a criterion to assess the reliability of the experimental results available for biofuel components in the literature. One of the best indicators for possible experimental errors is a large discrepancy between experimental and calculated values—especially if other, closely related compounds show no such discrepancy. In this context, it was interesting to check archival data that are available for the triglycerides.^{45–51} Calculations of the $\Delta_f^g H_m$ for triglycerides (Table 9) with the aid of parameters listed in Table 8 have provided values that mostly deviate 10–90 kJ/mol from our predictions (except for the calorimetric measurements by Nilsson and Wadsö²⁶). Calculations of the $\Delta_f H_m(l)$ value for triglycerides (Table 10) have shown values that deviate 60–800 kJ/mol from our predictions. In our opinion, the thermochemistry for triglycerides required the extended additional experimental measurements.

3.8. Strength of Intramolecular Hydrogen Bond in 1,2-Ethanediol Monoacetate. According to the conformational analysis presented in Section 3.5.1, there are two conformers of 1,2-ethanediol monoacetate (see Figure 2) where hydrogen bonding is possible. There are some spectroscopic observations of an intramolecular hydrogen bond in this compound.⁵² Although spectroscopic data can provide qualitative evidence of the intramolecular hydrogen bonding, it has been proven to be difficult to determine the hydrogen bond strength quantitatively.^{53,54} One of the ways to accomplish this is ab initio calculation. Hydrogen bond strength in 1,2-ethanediol monoacetate could be defined as the energetic difference of the hydrogen-bonded conformers (see Figure 2) and an appropriate conformer obtained by a 180° rotation of the hydroxyl group around the C–O single bond with subsequent geometry optimization. Our G3MP2 calculations of hydrogen bond strength of both conformers (M2 and M3), performed in this way, provided values of 7.1 and 7.0 kJ/mol, respectively. Another simple way to assess hydrogen bond strength is to consider the enthalpy differences between hydrogen-bonded and non-hydrogen-bonded conformers M1 and M2 or M4 and M3, which are also ~8.5 kJ/mol. Thus, the hydrogen bond strength on the level of 7–8 kJ/mol could be predicted using two procedures based on ab initio calculations.

We recently have shown that thermochemistry is also able to contribute to the quantification of hydrogen bond strength.⁵⁵ The group additivity procedure is conventionally applied for this purpose. According to this method, special effects (e.g., hydrogen bond strength) of a compound could be obtained as the difference between the observed enthalpy of formation in the gaseous state, $\Delta_f H_m^o(g)$, and a value calculated with GAVs. Similarly, we have recently discussed substituent effects of benzene derivatives.^{53–55} In this work, for the quantitative analysis of hydrogen bond strength, we have used the group additivity parameters developed in the present work (see Table 7). Indeed, we can summarize the 1,2-ethanediol monoacetate (EDM) molecule from the following increments:

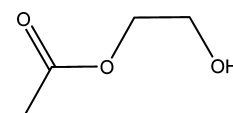


Table 9. Compilation of Data on Enthalpies of Vaporization of Triglycerides

technique ^a	temperature range (K)	$\Delta_f^s H_m$			Δ^d	$-\Delta C_p^b$ (J mol ⁻¹ K ⁻¹)	ref
		at <i>T</i> -mean	at 298 K	additive ^c			
Tripropin, C3, CAS No. [139-45-7]							
C			91.4±0.4	90.3	1.1	126.1	26
Tributyrin, C4, CAS No. [60-01-5]							
C			107.1±1.0	104.7	2.4	159.3	26
S	325–366	81.4	88.5		−16.2		47
TGA	464–591	62.4	97.5		−7.2		48
TGA	323–583	78.4	99.1		−5.6		49
Tricaproin, C6, CAS No. [621-70-5]							
TGA	358–633	92.8	128.6	133.4	−4.7	209.0	49
TGA	511–641	78.0	135.5		2.1		50
S	356–406	94.8	111.3		−22.1		47
Tricaprylin, C8, CAS No. [538-23-8]							
TGA	398–653	117.2	170.7	162.0	8.7	258.8	49
TGA	552–658	104.0	182.7		20.7		50
S	396–453	116.4	147.7		−14.3		47
Tricaprin, C10, CAS No. [621-71-6]							
TGA	586–668	146.6	248.1	190.7	57.4	308.6	48
TGA	438–668	138.6	212.3		21.6		49
S	437–485	124.7	173.3		−17.4		47
Trilaurin, C12, CAS No. [538-24-9]							
TGA	621–675	221.1	346.5	219.4		358.3	4
S	458–520	136.1	202.4		−17.0		8
Trimyristin, C14, CAS No. [555-45-3]							
TGA	629–676	199.0	343.7	248.1	95.6	408.1	51
S	488–551	147.8	235.8		−12.3		47
Tripalmitin, C16, CAS No. [555-44-2]							
TGA	647–672	474.3	640.0	276.8		457.9	51
S	506–572	160.7	268.5		−8.3		47
Tristearin, C18, CAS No. [555-43-1]							
TGA	625–778	220.8	400.2	305.4	94.8	507.6	51
S	521–588	167.4	294.9		−10.5		47
Triarachidin, C20, CAS No. [620-64-4]							
				334.1		357.0	
Tribehenin, C22, CAS No. [18641-57-1]							
				362.8		387.0	
Tribenzoin, CAS No. [614-33-5]							
S	423–476	123.5	153.1	153.3	−0.2	206.5	47
1-Capryl-2-lauryl-3-myristin, CAS No. [30283-10-4]							
S	464–526	131.9	197.1	209.8	−12.7	341.7	47
1-Lauryl-2-myristyl-3-palmitin, CAS No. [60138-25-2]							
S	491–551	147.8	236.4	248.1	−11.7	408.1	47
1-Myristyl-2-palmityl-3-stearin; CAS No. [60183-20-7]							
S	508–572	158.2	266.4	276.8	−10.4	457.9	47
1-Myristyl-2-capryl-3-stearin							
S	491–551	148.2	233.1	238.5	−5.4	391.5	47
1-Myristyl-2-lauryl-3-stearin							
S	493–559	150.7	245.1	257.6	−12.5	424.7	47
1-Palmityl-2-capryl-3-stearin							
S	506–558	154.9	247.9	248.1	−0.2	408.1	47
1-Palmityl-2-lauryl-3-stearin							
S	506–566	159.9	262.4	267.2	−4.8	474.4	47
2-Oleyl-1,3-distearin, CAS No. [2846-04-0]							
S	523–593	165.8	294.4	287.4	7.0	505.5	47

^a Techniques: TGA = thermogravimetry; S- static pendulum-tensimetric method. ^b Values of ΔC_p have been derived from the isobaric molar heat capacity of the liquid compounds (C_p^l) or solid compounds (C_p^s), according to the procedure developed by Chickos and Acree.¹⁶ ^c Calculated using group additive values (GAVs) from Table 8. ^d Difference between the experimental value and those calculated with increments from Table 8.

$$\Delta_f H_m^\circ(g)_{\text{add}} = 1 \times \text{C}-(\text{C})(\text{H})_3 + 1 \times (\text{CO}_2)(\text{C})_2 + 1 \times \text{C}-(\text{C})(\text{H})_2(\text{O}) + 1 \times \text{C}-(\text{C})(\text{H})_2(\text{OH}) + 1 \times \text{O}-(\text{C})(\text{H}) = -590.3 \text{ kJ/mol}$$

and the difference between the experimental and the additive value could be a measure of the hydrogen bonding strength (HB):

$$(\text{HB})_{\text{EDM}} = \Delta_f H_m^\circ(g)_{\text{exp}} - \Delta_f H_m^\circ(g)_{\text{add}} = -(592.8 + 590.3) \text{ kJ/mol} = -(2.5 \pm 2.3) \text{ kJ/mol}$$

As can be seen, this value is in accordance (within the boundaries of experimental uncertainties) with the strength $-(8.5 \pm 4.9) \text{ kJ/mol}$ obtained above from the ab initio calculations (see Figure 2).

To assess the consistency of this result, it is interesting to calculate the hydrogen bonding strength of the 1,2-ethanediol (ED), using its enthalpy of formation, $\Delta_f H_m^\circ(g) = -(388.0 \pm 2.0) \text{ kJ/mol}$ (from ref 55) and the same group additivity method:

$$\Delta_f H_m^\circ(g)_{\text{add}} = 2 \times \text{O}-(\text{C})(\text{H}) + 2 \times \text{C}-(\text{C})(\text{H})_2(\text{OH}) = -(375.3 \pm 2.0) \text{ kJ/mol}$$

The difference between the experimental and the additive value could be a measure of the hydrogen bonding strength (HB) in the 1,2-ethanediol (ED):

$$(\text{HB})_{\text{ED}} = \Delta_f H_m^\circ(g)_{\text{exp}} - \Delta_f H_m^\circ(g)_{\text{add}} = -(388.0 + 375.3) \text{ kJ/mol} = -(12.7 \pm 2.0) \text{ kJ/mol}$$

As expected, the strength of the hydrogen bond in 1,2-ethanediol monoacetate is somewhat lower than that in 1,2-ethanediol. Such a similarity of hydrogen bond strength in ethanediol derivatives

Table 10. Standard Enthalpies of Formation, $\Delta_f H_m^\circ(298 \text{ K})$, for the Triglycerides in the Liquid and Crystal State

T_m (from ref ⁵⁷)	ΔH_m^a	$\Delta_f H_m^\circ(\text{cr})$	$\Delta_f H_m^\circ(\text{l})^b$	additive ^c	Δ
Triacetin, C1 (liq.), CAS No. [102-76-1]					
			-1330.8	-1264.2	-66.2
Tributylin, C4 (liq.), CAS No. [60-01-5]					
			-1496.0	-1407.1	-88.9
Tricaproin, C6 (liq.), CAS No. [621-70-5]					
				-1558.4	
Tricaprylin, C8 (liq.), CAS No. [538-23-8]					
			-2501.3	-1709.7	-791.6
Tricaprin, C10 (cr), CAS No. [621-71-6]					
304.8	3.0	-1971.8	-1968.8	-1861.1	-107.7
Trilaurin, C12 (cr), CAS No. [538-24-9]					
318.9	10.8	-2175.1	-2164.3	-2012.4	-151.9
Trimyristin, C14 (cr), CAS No. [555-45-3]					
330.3	19.0	-2336.5	-2317.5	-2163.7	-153.8
Tripalmitin, C16 (cr), CAS No. [555-44-2]					
339.1	27.2	-2447.6	-2420.4	-2315.0	-105.4
Tristearin, C18 (cr), CAS No. [555-43-1]					
345.7	35.1	-2320.1	-2285.0	-2466.3	181.3
Triarachidin, C20 (cr), CAS No. [620-64-4]					
351.0	42.9	-2732.7	-2689.8	-2617.7	-72.1
Tribehenin, C22 (cr), CAS No. [18641-57-1]					
354.9	50.3	-3065.7	-3015.4	-2769.0	-246.4

^a Enthalpy of melting at 298 K calculated from the experimental values measured at the fusion temperature (T_m ; from ref 57), according to the procedure by Chickos and Acree.¹⁶ ^b Obtained from the sum of $\Delta_f H_m^\circ(\text{cr}) + \Delta H_m$. ^c Estimated using the GAVs given in Table 8.

proves the consistency of the procedure and the experimental data involved in the interpretation.

4. Conclusions and Outlook

The purpose of this work was to establish a consistent set of experimental thermochemical quantities for aliphatic esters of carboxylic acids, 1,2-ethanediol and 1,2,3-propanetriol acetates, which are parent compounds of the main components of biofuels. Group additive values (GAVs) derived in this work provide a further improvement on the group contribution methodology for predicting the thermodynamic properties of a broad range of compounds relevant to biodiesel. The derived values of increments can be applied to the prediction of the energy content of biofuels, to the modeling and the simulation of the thermochemistry and kinetics of the decomposition reactions of biofuels. For a complete and thorough analysis, the standard enthalpies of formation of *unsaturated* methyl esters of long-chain fatty acids are needed. These data will be determined in a future project.

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Supporting Information Available: Results from combustion calorimetry (Tables S1–S4); experimental data for compounds used in the thermochemical calculations (Table S5); data involved in the calculation of the group additivity values (Tables S6 and S7); total energies at 0 K and enthalpies at 298.15 K (given in units of Hartrees) of the molecules studied in this work (Table S8); and synthesis of 1,2-ethanediol monoacetate. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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