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Experimental Enthalpies of Combustion of Organic Materials and The Correlation with Total Number of Bonds, Their Molecular Surface and Volume Properties

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Abstract

Experimentally determined heats of combustion of 21 random diverse organic materials are measured using traditional oxygen bomb calorimetry, as internal energy difference, ΔU, and enthalpy change, ΔH, reveal trends that correlate with their molecular properties which are calculated from the crystal structures. The R^2 values between ΔH and total number of covalent bonds, vdW volume, molecular volume, vdW surface area, molecular surface area, solvent accessible surface area and molecular weight are 0.95, 0.91, 0.91, 0.89, 0.87, 0.85 and 0.79, respectively. Oxygen content of the substances increases, rise of ΔH reflected whereas this pattern breaks down when another element is introduced instead. The linear correlations between ΔU, ΔH and the structure based molecular properties at molecule level described above are not limited, restricted or deviated by the type of elements, H, C, N, O, Cl that make up the materials or molecular class of substance.

Keywords

Combustion Energy, Material Matters, Bomb Calorimeter, Fibrate, Enthalpy Change, Heat, Internal Energy, Bonds, Molecular Properties

1. Introduction

Thermal decomposition of a material leads to the formation of its oxidized products in the presence of oxygen. For a given material, the thermal breakdown process corresponds to the overall outcome of chemical reactions, products formed, starting material, the elements that constitute the material, oxidation state of the

elements that are present in the material, kinds of bonds that make these materials and can correlate with the enthalpy change. The enthalpy of formation has been used to calculate the relative structural stability of isomers [1] and for the enthalpy contribution to functional groups of chemical materials manifested in methods for the prediction of thermal quantities [2]-[4]. Since active pharmaceutical ingredients (API) and excipients (inactive ingredients) go into drug compounding, the pharmaceutical industry for instance relies heavily on chemical characterizations of the above components. Solid state characterization sets the foundation for formulation development and aids in science-driven rational decisions in the development of a stable and manufacturable drug product with a realistic shelf life.

As of April 14, 2025, independent keyword or phrase searches for thermochemistry, theoretical studies of combustion, or combustion thermochemistry and molecular surface area and molecular properties, resulted in 948,267, 491,196 and 19 citations, respectively, whereas each of their earliest citation recorded in Scifinder was 1830, 1833, and 1976.

As highlighted, the few citations mentioned in this section for modeling and predicting efforts of conjecturing heat of combustion and along with that, which are referenced in them, provide a growing number of methods for a great many theoretical tryouts. Researchers [5]-[8] have hypothesized to predict the net heat of combustion of pure chemicals using models. A quantitative structure property relationship (QSPR) [9] based model was conceptualized to predict standard net heat of combustion of pure chemicals. Four parameters factored in this model are: Sv, the sum of the atomic van der Waals volumes (scaled on carbon atom); nC, the number of carbon atoms; SEige, the eigenvalue sum from the electronegativity weighted distance matrix; and Seig, the absolute eigenvalue sum on geometry matrix. Two models: a Multi-Variable Regression (MVR) centered on least squares and an Artificial Neural Network (ANN), based another QSPR approach predict the standard net heat of combustion for chemical compounds [10] constructed based only on their molecular structures. This is similar to using the QSPR attempt, a four-parameter factorization methodology that was reported previously by [9] [11] [12] for predicting the standard net heat of combustion of pure chemicals. The approach is focused primarily on petroleum fractions which are only hydrocarbons. The same author of [10] reported [13] predicting the standard net heat of combustion for pure hydrocarbons from their molecular structure where chemical functional groups, CH_3, CH_2 and Aromatic, are accounted in their model based calibration but the use of molecular volume, molecular surface area is not mentioned. In an alternative proposed technique [14], linear relationships between the molecular descriptors of similar compounds and that between their measured properties of related analogous compounds are demonstrated. Whereas the measured properties considered are the critical temperature, critical volume and compressibility factor, melting point, triple point temperature and pressure, normal boiling temperature, liquid molar volume, refractive index, flash point, lower and upper flammability limits, and lower flammability limit temperature

amongst homological compounds. Another model based approach was put forward by [15] for predicting the enthalpy of combustion of chemical compounds in which the model is an ANN that uses the group contributions for guesstimation. Quantum chemistry design that has electronic structure calculations factored in to compute thermochemical parameters ($\Delta_f H^0$(298K), S^0(298K), Cp), comparing with several published databases [16]. In this technique, bond additivity correction is included but molecular volume or surface area factors are not revealed as part of the model that is theorized to predict thermochemical parameters. Moreover, citations in the literature with the combination of surface area and heat of combustion are about contact, exposed, and transfer facts and do not refer to solid-state molecular concept that is the focus of this study. On the other hand, the references in the literature on molecular surface area and accessible area are all concentrated on solution investigations whereas this study tries to relate with the experimental solid-state heats of combustion results with molecular volume and surface area. This study is not about speculating heat of combustion of materials, theoretically or model based effort.

We have conducted the thermal combustion measurements for 21 materials experimentally and here report their corresponding thermal quantities and describe correlation trend discovered between the ΔU, ΔH and molecular properties of those materials. The study reported here differs from other computational trials stated above or any other experimental determination of heat of combustion for materials due to the following reasons. They are: 1) Experimentally determined heat of combustion by classical calorimetry method for 8 materials in solid-state and their results are not reported in the literature or found in the databases. 2) Experimentally determined heat of combustion for additional 13 independent/unrelated materials that were reported in literature to corroborate and prove our methods, procedures and analysis produce reliable, reproduceable and consistent results. 3) Discovered a strong correlation between the experimentally determined heat of combustion of all 21 materials and the total number of bonds, their molecular parameters, volume, surface area, compared to molecular weight. 4) Molecular parameters, vdW volume, molecular surface, accessible surface area are all calculated based on the crystal structures of the corresponding materials. 5) This is not a model based and/or regression type theoretical prediction method. 6) While a small number of materials comprised in the study to validate the experimental efforts, a highly diverse molecular classification is included in the dataset to establish the trend.

2. Methods and Experimental

2.1. Oxygen Combustion Calorimeter

All materials studied are reagent grade and were utilized as supplied by their manufacturer. Benzoic acid (1 - 2 g) samples were used to calibrate the heat capacity of the Parr Constant Volume 1341 oxygen combustion calorimeter, with a 1108 stainless steel Container, and a 1672 Precision Thermometer. A Fisher 500 strip

chart recorder was used to develop the thermograms to assist in the data acquisition process, as outlined in both the Parr literature and the classic text [17]-[19]. Five trial runs for calibration and triplicate measurements for 21 materials each were repeated, respectively, with corrections for the fuse wire combustion contribution (typically less than 1 % of the total heat released), were conducted to assess the precision of the methods followed. A literature value of −26.43 kJ/g [17] [18] [20]-[22] for heat of combustion was accounted for the energy change at constant volume of the analytically weighed benzoic acid pellets. Similarly, the materials were likewise prepared and combusted individually following previously established procedures and methods [17] [19] [23].

2.2. Data Reduction to Determine Experimental Heat of Combustion

Following well-established procedures [17] [19] that are in practice universally, data were generated experimentally for all the materials and were reduced to determine their thermal quantities reported in the current study. Solid-state experimental combustion calorimetry applications on data generation, reduction and analysis have a long history, they are well described in many textbooks including "Experiments in Physical Chemistry" by [17] and "Laboratory Manual of Physical Chemistry" by [19] along with the necessary steps and equations for thorough calculations. The equations are shown below. The terms, $Ccal$, ΔH, q, U, ΔU, P, V and w represent heat capacity of the bomb calorimeter, enthalpy change, heat, internal energy, change in internal energy, pressure, volume and work, respectively. The magnitude and sign of Δn are determined as the change in the number of moles of substances in gas phase associated with the stoichiometric equation of the material that underwent combustion. Exact same data measurement steps, data processing routines were followed for all 21 materials that are included in this study.

As reported in the literature chemical composition of the final solution of combustion experiment was established by titrating the total acidity of aliquots with standard alkali in [24] for 3-Nitrobenzaldehyde and 4-Nitrobenzaldehyde. The heat of combustion values reported in the literature and that determined in this study for these materials are within the margin of error. No explicit information about product analysis mentioned by [25] for Acetylsalicylic Acid, [26] for Camphor and stated incomplete combustion of the sample may be a reason due to lower observed CO_2 values by [27] for Imidazole. Details about product analysis is unsaid in [28], however, the heats of combustion reported by [27] [28] are very comparable to that determined in this study for Imidazole. In another example, studies by [29], combustion products were examined for unburned C and CO and their heats of combustion are comparable to that reported by [24] and our values for 3-Nitrobenzaldehyde and 4-Nitrobenzaldehyde. Analysis of the combustion products composition for incompleteness in the combustion process was not conducted in this study because outcomes make relatively insignificant changes in comparison with that of the error due to partial oxidation in the procedure fol-

lowed. The Parr combustion instrument, the procedure and the quantity of the material used in every trial are based on well-established method in practice. The quantity of material used in every trial in this study for each material is well within the threshold of the instrument to undergo complete combustion. Furthermore, triplicate results produced for every material and pentaplicate measurements for benzoic acid standard support the complete combustion as if there was any incompleteness the results would fluctuate in the heat generated. The standardization of benzoic acid reported in [21] was conducted without the mention of product analysis for complete combustion. In addition, the heat of combustion generated with the benzoic acid standard used in this study is in agreement with the -26.43 kJ/g reported in literature [17] [18] [20]-[22] indicating and ensuring the complete combustion of the samples.

As described in many textbooks including "Experiments in Physical Chemistry" by [17] and "Laboratory Manual of Physical Chemistry" by [19] along with the necessary steps and (1 - 12), equations that are followed for thorough calculations, are summarized below on data reduction and analysis of solid state experimental combustion calorimetry study.

The heat capacity of the bomb calorimeter was determined through the combustion of benzoic acid. The equation for enthalpy is

$$\Delta H = \Delta U + \Delta(PV) = \Delta U + \Delta PV + P\Delta V - \quad (1),$$

where U, P and V represent internal energy, pressure and volume, respectively.

The change in internal energy, ΔU, is expressed as $q + w$, where q is heat and w is work. Substitution into the previous Equation (1), gives

$$\Delta H = q + w + \Delta PV + P\Delta V - \quad (2),$$

Equation (2) is further simplified to

$$w = -P\Delta V - \quad (3),$$

Since the volume of the bomb calorimeter is held constant, $\Delta V = 0$.

$$\text{Hence, } \Delta U = q \text{ and } P\Delta V = 0, \Delta H = \Delta U + \Delta PV - \quad (4),$$

Furthermore, substitution of ideal gas equation,

$$PV = nRT - \quad (5),$$

leads to

$$\Delta H = \Delta U + \Delta nRT - \quad (6),$$

where ΔU, n, R and T correspond to internal energy, moles, ideal gas constant (8.314 J/Kmol) and temperature, respectively.

To obtain q,

$$q = \left(\Delta U_{Benzoic\ Acid} + m_{Benzoic\ Acid}\right) + \left(\Delta U_{Fe} + m_{Fe}\right) - \quad (7),$$

where $\Delta U_{\text{Benzoic Acid}}$ is the energy of combustion of benzoic acid, 26.41 kJ/g, $m_{\text{Benzoic Acid}}$ is the mass of the pellet of benzoic acid, ΔU_{Fe} is the energy of combustion of iron, 6.68 kJ/g, and m_{Fe} is the mass of the iron wire burned. At constant volume,

$$q = Ccal \times \Delta T - \quad (8),$$

where $Ccal$ is the heat capacity of the bomb calorimeter and ΔT is the change in temperature,

$$Tmax - Tinital - \quad (9),$$

calculated experimentally from the graph of temperatures recorded before, during, and after the ignition of the bomb with time. The overall equation,

$$Ccal = \left[\left(\Delta U_{Benzoic\ Acid} + m_{Benzoic\ Acid}\right) + \left(\Delta U_{Fe} + m_{Fe}\right)\right] / \Delta T - \quad (10),$$

thus yields the heat capacity of the bomb calorimeter which will be used in calculation of heat of combustion for the desired compound.

$$\Delta T = Tmax - Tinital - \quad (11),$$

is determined from temperatures in the experimentally produced graph for the desired material being combusted. The value for q is obtained from the $Ccal$ value that is calculated using

$$q = Ccal \times \Delta T - \quad (12),$$

for benzoic acid.

The calculated

$$q = \left(\Delta U_{Compound} + m_{Compound}\right) + \left(\Delta U_{Fe} + m_{Fe}\right) - \quad (13),$$

and is used to evaluate the change in internal energy, $\Delta U_{\text{Compound}}$. The change in enthalpy is determined for the heat of combustion using the equation,

$$\Delta H = \Delta U + \Delta nRT - \quad (14).$$

2.3. Molecular Properties

Values of molecular properties reported in this study are calculated by procedures described in [30]-[35] applying established methods utilizing crystal structures of the corresponding material available in Cambridge Structural Database (CSD) [33]. The vdW volume, molecular volume, vdW surface area, molecular surface area, solvent accessible surface area are molecule level properties using atomic parameters of the elements and not molar quantities. Atomic coordinates of entries found in CSD were used without additives, solvents, complexes corresponding only to reflect the chemical formula of a single monomeric molecule for the calculation of molecular properties of each material. As the molecular structures shown in **Table 1**, the total number of (covalent) bonds in every material is accounted, regardless of the elements making the bond. For single bond, double bonds and aromatic phenyl group, 1, 2 and 9 bonds are factored, respectively (substitutions are extra).

3. Results and Discussion

Variations in the energy released in thermal combustion process correspond partly due to the net energies of the chemical bonds that are broken in the starting material, leading to bonds created in the products formed as well as the oxidized forms of the elements in various stages of the process at exact temperature (exam-

ple 298 K). Critically, accounting phase (solid (s), liquid (l), gas (g)) changes in the evaluation would provide better estimation of the precise process under such conditions.

3.1. Thermodynamic Quantities of Materials

Combustion calorimeter constant utilized in this experiment was determined to be C_{cal} = 10.3693 kJ/g ˚C based on the benzoic acid standard. Randomly chosen materials that were considered for this study include chemically diverse, commercially available and accessible to the laboratory. In addition to the number of materials available, other factors, time requirement to perform multiplicate combustion experiments, costs and a minimum number of humans to conduct the experiment to reduce the variations, restricted full-text accessibility, make it impractical to explore thousands or hundreds of samples unlike in computational/theoretical centered prediction trials. Most of the citations reported experimental heats of combustion studies of one material with the exception of [29] recording maximum of six related compounds. Therefore, this study documenting experimental heats of combustion of 21 materials among which no such information is available for 8 will be the first to report in the literature.

Possible combustion reactions along with corresponding Δn (moles) and thermodynamic quantities for each material that underwent the decomposition process are shown alphabetically below and in Table 1.

3-Nitrobenzaldehyde:

$$C_7H_5NO_3\,(s) + 8\,O_2\,(g) \rightarrow 7\,CO_2\,(g) + 2\,H_2O\,(l) + 1\,HNO_3\,(l)$$

4-Hydroxybenzaldehyde:

$$C_7H_6O_2\,(s) + 7.5\,O_2\,(g) \rightarrow 7\,CO_2\,(g) + 3\,H_2O\,(l)$$

4-Nitrobenzaldehyde:

$$C_7H_5NO_3\,(s) + 8\,O_2\,(g) \rightarrow 7\,CO_2\,(g) + 2\,H_2O\,(l) + 1\,HNO_3\,(l)$$

4-Nitrobenzoic Acid:

$$C_7H_5NO_4\,(s) + 7.5\,O_2\,(g) \rightarrow 7\,CO_2\,(g) + 2\,H_2O\,(l) + 1\,HNO_3\,(l)$$

4-Nitrobenzyl Alcohol:

$$C_7H_7NO_3\,(s) + 8.5\,O_2\,(g) \rightarrow 7\,CO_2\,(g) + 3\,H_2O\,(l) + 1\,HNO_3\,(l)$$

Acetylsalicylic Acid:

$$C_9H_8O_4\,(s) + 9\,O_2\,(g) \rightarrow 9\,CO_2\,(g) + 4\,H_2O\,(l)$$

Benzimidazole:

$$C_7H_6N_2\,(s) + 11\,O_2\,(g) \rightarrow 7\,CO_2\,(g) + 2\,H_2O\,(l) + 2\,HNO_3\,(l)$$

Benzophenone:

$$C_{13}H_{10}O\,(s) + 15\,O_2\,(g) \rightarrow 13\,CO_2\,(g) + 5\,H_2O\,(l)$$

Bezafibrate:

$$C_{19}H_{20}ClNO_4\,(s) + 25\,O_2\,(g) \rightarrow 19\,CO_2\,(g) + 9\,H_2O\,(l) + 1\,HNO_3\,(l) + 1\,HClO_4\,(l)$$

Biphenyl:

$$C_6H_5C_6H_5\ (s) + 14.5\ O_2\ (g) \rightarrow 12\ CO_2\ (g) + 5\ H_2O\ (l)$$

Borneol:

$$C_{10}H_{18}O\ (s) + 14\ O_2\ (g) \rightarrow 10\ CO_2\ (g) + 9\ H_2O\ (l)$$

Camphor:

$$C_{10}H_{16}O\ (s) + 13.5\ O_2\ (g) \rightarrow 10\ CO_2\ (g) + 8\ H_2O\ (l)$$

Clofibric Acid:

$$C_{10}H_{11}ClO_3\ (s) + 13\ O_2\ (g) \rightarrow 10\ CO_2\ (g) + 5\ H_2O\ (l) + HClO_4\ (l)$$

Ethyl 4-Aminobenzoate:

$$C_9H_{11}NO_2\ (s) + 12\ O_2\ (g) \rightarrow 9\ CO_2\ (g) + 5\ H_2O\ (l) + 1\ HNO_3\ (l)$$

Fenofibrate:

$$C_{20}H_{21}ClO_4\ (s) + 25\ O_2\ (g) \rightarrow 20\ CO_2\ (g) + 10\ H_2O\ (l) + 1\ HClO_4\ (l)$$

Fenofibric Acid:

$$C_{17}H_{15}ClO_4\ (s) + 20.5\ O_2\ (g) \rightarrow 17\ CO_2\ (g) + 7\ H_2O\ (l) + 1\ HClO_4\ (l)$$

Gemfibrozil:

$$C_{15}H_{22}O_3\ (s) + 19\ O_2\ (g) \rightarrow 15\ CO_2\ (g) + 11\ H_2O\ (l)$$

Imidazole:

$$C_3H_4N_2\ (s) + 6.5\ O_2\ (g) \rightarrow 3\ CO_2\ (g) + 1\ H_2O\ (l) + 2\ HNO_3\ (l)$$

Salicylic Acid:

$$C_7H_6O_3\ (s) + 7\ O_2\ (g) \rightarrow 7\ CO_2\ (g) + 3\ H_2O\ (l)$$

trans-4-Hydroxy-L Proline:

$$C_5H_9NO_3\ (s) + 7\ O_2\ (g) \rightarrow 5\ CO_2\ (g) + 4\ H_2O\ (l) + 1\ HNO_3\ (l)$$

trans-Cinnamic Acid:

$$C_9H_8O_2\ (s) + 10\ O_2\ (g) \rightarrow 9\ CO_2\ (g) + 4\ H_2O\ (l)$$

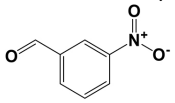
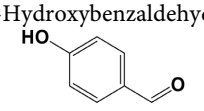
3.2. Experimentally Determined ΔU and ΔH

Very closely related materials, 3-Nitrobenzaldehyde and 4-Nitrobenzaldehyde, show noticeable difference in their ΔU and ΔH values though the difference between them originates from the position of substitution in the aromatic ring. Oxygen content is identical (31.8%) in these compounds. 4-Nitrobenzyl Alcohol, 4-Nitrobenzaldehyde, 4-Nitrobenzoic Acid share the identical substitution position in the aromatic ring but their oxidation state increases from first to last, however, their ΔU and ΔH decreases. The Oxygen content in 4-Nitrobenzyl Alcohol, 4-Nitrobenzaldehyde and 4-Nitrobenzoic Acid are 31.3%, 31.8% and 38.3%, respectively. Most oxidized molecules seem to release less energy. Borneol to Camphor, ΔU and ΔH increases from reduced to oxidized material, however, their oxygen content is correspondingly, 10.4% and 10.5%. Acetylation of Salicylic acid leads to an increase in the ΔU and ΔH, and this tendency is parallel with their molecular

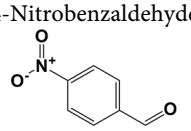
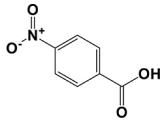
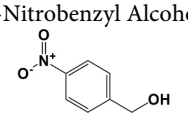
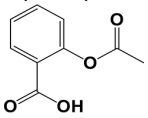
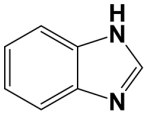
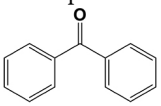
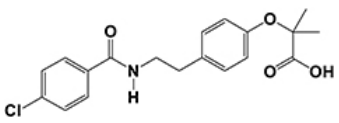
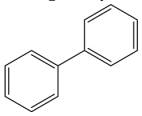
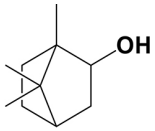
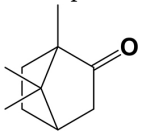
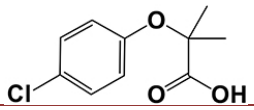
parameters, vdW volume, molecular volume, vdW surface, molecular surface area and molecular weight. Percentage of Carbon, Oxygen and Hydrogen contents are 60.0%, 35.5%, and 4.5% and 60.9%, 34.8%, and 4.4%, for acetylsalicylic acid and salicylic acid, respectively. Similar trend is seen from Biphenyl to Benzophenone with ΔU and ΔH increases and so are all the molecular parameters considered in this study. Elemental contents are 93.5%, 0, 6.5% and 85.7%, 8.8% and 5.5% for Carbon, Oxygen and Hydrogen in Biphenyl and Benzophenone, respectively. Another comparable review of Imidazole to Benzimidazole shows an increase in ΔU and ΔH with molecular parameters as well. The percentage of Carbon, Nitrogen and Hydrogen are 52.9%, 41.1% and 5.9% and 71.2%, 23.7% and 5.1% in them, correspondingly.

From Clofibric Acid, Gemfibrozil, Fenofibric Acid, Bezafibrate to Fenofibrate, ΔU and ΔH increases. The difference in ΔU and ΔH between Fenofibric acid and Fenofibrate is 447 kJ/mol and 345 kJ/mol, respectively and these differences in their thermodynamic quantities may be due to replacing H atom of the carboxylic acid by an isopropyl ester group. This chemical change results in increased molecular weight, vdW volume, vdW surface area, molecular volume, molecular surface area, percentage of Carbon and Hydrogen contents but reduces the Oxygen content. Comparison of Clofibric acid and Fenofibric acid shows the difference of 3919.6 kJ/mol, and 3920.8 kJ/mol in ΔU and ΔH, correspondingly. These changes imply the variations caused in their thermodynamic quantities and are due to incorporating benzoyl group either in between phenoxy and Cl bond or 4-chlorophenoxy and 2-methylpropanoic acid bond. The enthalpy of formation of this class of compounds are in the range from −5121.7 kJ/mol to −9572.3 kJ/mol. The negative nature of these values verifies their status of thermodynamic stability. In general, compared to their starting elements, the stability of these materials may be arranged in the following order, Fenofibrate > Bezafibrate > Fenofibric acid > Gemfibrozil > Clofibric acid in solid phase.

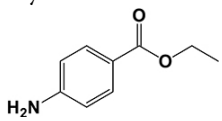
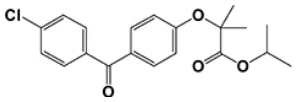
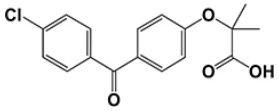
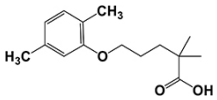
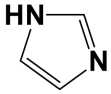
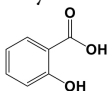
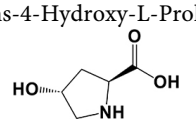
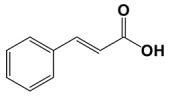
Table 1. Experimentally determined thermal quantities (along with the error) for 21 materials used in the current study along with that is full-text accessible in the literature and corresponding citations.

Material Information	Average ΔU (kJ/mol)[a,b]	Δn (mol)	Average ΔH (kJ/mol)[a,b]	Literature ΔH (kJ/mol)[c]	Citation[c]
3-Nitrobenzaldehyde 	−3055.62 ± 28.17	−1	−3058.1 ± 28.17	−3330.09 ± 0.61 −3334.9 ± 1.5	[29] [24]
4-Hydroxybenzaldehyde 	−2654.34 ± 6.32	−0.5	−2655.58 ± 6.32	Not available	

Continued

4-Nitrobenzaldehyde 	−3452.49 ± 14.38	−1	−3454.97 ± 14.38	−3331.86 ± 0.91 −3339.8 ± 1.3 −3316 ± 6	[29] [24] [36]
4-Nitrobenzoic Acid 	−2827.68 ± 48.13	−0.5	−2828.91 ± 48.13	Not available	
4-Nitrobenzyl Alcohol 	−3545.44 ± 25.72	−1.5	−3549.16 ± 25.72	−3548.49 ± 1.47	[37]
Acetylsalicylic Acid 	−3891.10 ± 36.99	0	−3891.1 ± 36.99	−3926.71 ± 0:34	[25]
Benzimidazole 	−3462.6 ± 31.32	−4	−3472.51 ± 31.32	−3691.6 ± 1.0	[28]
Benzophenone 	−6554.23 ± 26.75	−2	−6559.19 ± 26.75	−6512.0[c] −6510.3 ± 2.1	[38] [39]
Bezafibrate 	−9557.41 ± 12.84	−6	−9572.27 ± 12.84	Not available	
Biphenyl 	−6188.90 ± 31.04	−2.5	−6195.09 ± 31.04	−6245.84 ± 0.33 −6248.02 ± 2 −6251.8 ± 1.4	[40] [41] [42]
Borneol 	−5899.01 ± 2.16	−4	−5908.92 ± 2.82	−6136.1 −6145.9	[23]
Camphor 	−6012.73 ± 34.65	−3.5	−6021.4 ± 34.65	−5902.5 ± 2.9 5910.7 5904.2	[26]
Clofibric Acid 	−5114.23 ± 16.64	−3	−5121.66 ± 16.64	Not available	

Continued

Ethyl-4-Aminobenzoate 	−4718.18 ± 14.39	−3	−4725.61 ± 14.39	−4694.9 ± 0.8 −4695.4 ± 1.2	[43] [44]
Fenofibrate 	−9904.68 ± 48.78	−5	−9917.07 ± 48.78	Not available	
Fenofibric Acid 	−9033.80 ± 119.60	−3.5	−9042.47 ± 119.60	Not available	
Gemfibrozil 	−8412.97 ± 47.00	−4	−8422.88 ± 47.00	Not available	
Imidazole 	−1833.07 ± 4.15	−3.5	−1841.74 ± 4.15	−1801.9 ± 0.5 −1810.6 ± 3.3	[28] [27]
Salicylic Acid 	−3014.53 ± 22.90	0	−3014.53 ± 22.90	−3022.9[d] −3020.3 ± 1.0	[45] [46]
trans-4-Hydroxy-L-Proline 	−2587.31 ± 14.11	−2	−2592.26 ± 14.11	Not available	
trans-Cinnamic Acid 	−3933.4 ± 25.20	−1	−3935.88 ± 25.20	−4348 ± 2	[47]

[a]Substances available in our laboratory and that are chemically diverged were included in this experimental combustion study for validation of our experimental particulars (ΔH and ΔU). Thirteen materials that were previously studied by exact same combustion calorimetry method of solid-state experiments and their values that are in the literature[b] with full-text accessibility are included in this study. [b]Statistical treatment used to obtain error (± values) of the experimental results are for mean $\bar{x}$, standard deviation (s) and errors, $\bar{x} = \sum_{i=1}^{n} x_i / n$ $s = \sqrt{\sum_{i=1}^{n} \left((xi - \bar{x})^2 / (n-1) \right)}$ error = s/√n for mean $\bar{x}$, standard deviation (s) and errors, respectively for (samples) results *x*1, *x*2, *x*3, number of sample size, *n*. [c]Heat of combustion values (with error) as in literature and corresponding citations are shown in the table to establish the agreement between the results produced in this study (shown under column a) and the corresponding full-text citation that reported the details in the literature. [d]Error not reported in the corresponding citation in the literature.

ΔH and ΔU values determined in this study experimentally for the 21 compounds are between −3913.99 and −6160.65 and −3909.11 and −6153.15 kJ/mol, respectively with the 95% Confidence interval. Some of the materials included in this study may have been explored previously by other investigations for experimental combustion calorimetry examination, however, to minimize the fluctuations, those are repeated here. This approach is expected to avoid changes due to

the use of different instruments, procedures, conditions, temperature under which the experiments may have been conducted and lessen factors and errors. Review of the experimentally determined heats of combustion values documented in the literature that are full-text accessible [23]-[29] [30] [36]-[47] for 13 materials are included and those are within 0% to 10% from that determined in this study (Figure 1, Table 1). Without full-text accessibility specifics of the conditions under which experiment is conducted, outcomes, or conclusions cannot be verified for comparation or validation. The agreement between the experimentally determined heat of combustion of 13 materials studied here and those found in the literature is $R^2 = 0.99$ that implies the reproducibility of the process followed in the study. Furthermore, the comparable ΔH values produced in this study for overlapping 13 materials for which heat of combustion is reported in the literature act as controls too, validating and strengthening the method and approach that is applied for other materials that are studied by experimental combustion calorimetry for the first time.

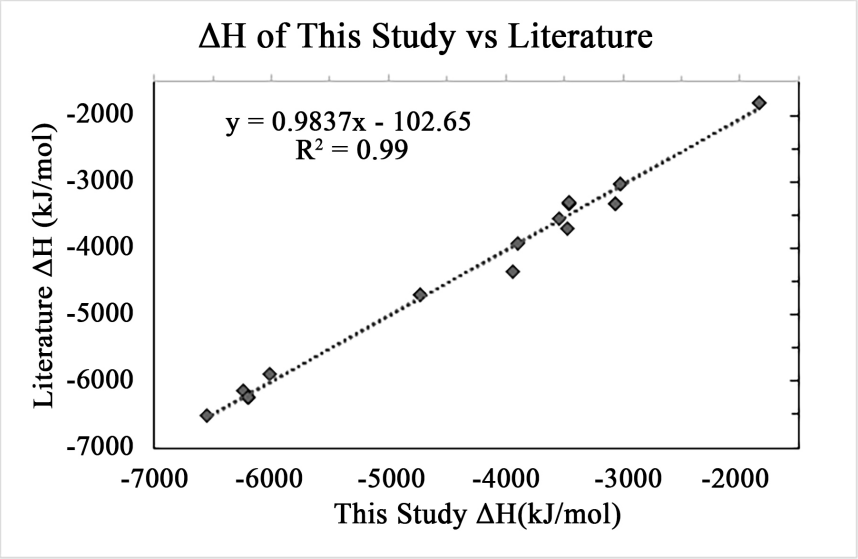


Figure 1. Experimentally determined heats of combustion reproducibility as reflected by R^2 of 0.99 between the 13 materials studied here and that reported in the literature. Some materials have more than one reported value in literature (Table 1) accessible in full-text. The thirteen materials for which experimentally determined heat of combustion not available in the literature are: 1) Imidazole, 2) 3-Nitrobenzaldehyde, 3) Salicylic Acid, 4) Benzimidazole, 5) 4-Nitrobenzaldehyde, 6) 4-Nitrobenzyl Alcohol, 7) Acetylsalicylic Acid, 8) trans-Cinnamic Acid, 9) Ethyl-4-Aminobenzoate, 10) Camphor, 11) Borneol, 12) Biphenyl, and 13) Benzophenone.

3.2. Molecular Properties of Materials

In order to perform a chemical synthesis, a specific starting material is needed and its molecular properties define the suitability of it. This aptness evolves from molecular nature which is constituted by elements, the chemical structure character and the phase it exits. Here several properties that are based on the molecular basis

of the materials are scrutinized in the analysis.

For combustion process, comparison of ΔU with total number of bonds and molecular parameters total number of bonds reflected the highest correlation (0.95) and on the other hand Molecular Weight showed the lowest R^2 value (0.80) (Figure 2). Based on R^2 the order is total number of bonds (0.95) > vdW Volume (0.92) > Molecular Volume (0.91) > vdW Surface Area (0.89) > Molecular Surface Area (0.89) > Solvent Accessible Surface Area (0.85) > Molecular Weight (0.80) with ΔU. As R^2 indicates the linear fit of 0.99 between experimentally determined ΔU and ΔH quantities for random the 21 materials reported in this study.

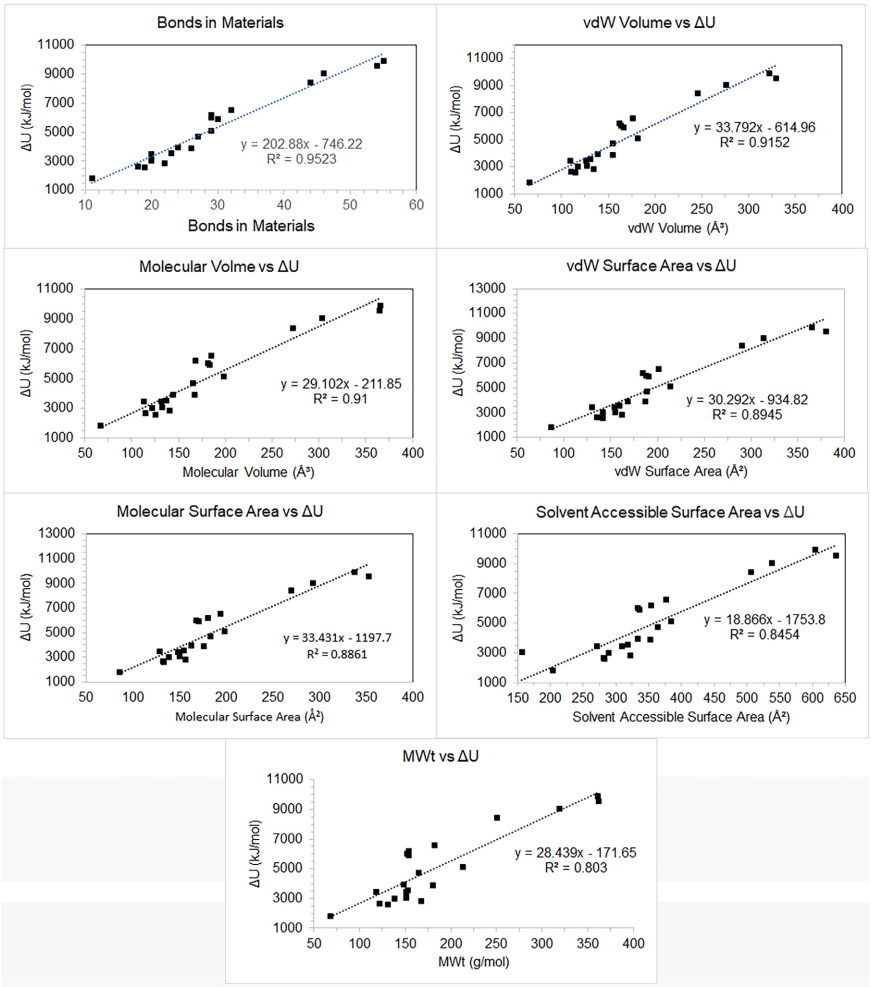


Figure 2. Trends between molecular parameters, total number of bonds, vdW Volume (Å^3), Molecular Volume (Å^3), vdW Surface Area (Å^2), Molecular Surface Area (Å^2), Solvent Accessible Surface Area (Å^2), Molecular Weight (g/mol) for 21 materials and their corresponding ΔU (kJ/mol) along with the linear fit line, equation and R^2 values are shown.

Materials included in Figure 2 are numbered according to increasing molecular weight. They are: 1) Imidazole, 2) trans-4-Hydroxy-L-Proline, 3) 4-Hydroxybenzaldehyde, 4) 4-Nitrobenzoic Acid, 5) 3-Nitrobenzaldehyde, 6) Salicylic Acid, 7)

Benzimidazole, 8) 4-Nitrobenzaldehyde, 9) 4-Nitrobenzyl Alcohol, 10) Acetyl-salicylic Acid, 11) trans-Cinnamic Acid, 12) Ethyl-4-Aminobenzoate, 13) Clofibric, 14) Camphor, 15) Borneol, 16) Biphenyl, 17) Benzophenone, 18) Gemfibrozil, 19) Fenofibric acid, 20) Bezafibrate, and 21) Fenofibrate.

Among the molecular parameters analyzed, total number of bonds (0.95) reflected the highest and Molecular Weight showed the lowest (0.79) R^2 value trends with ΔH for combustion process for these 21 materials. Based on R^2, the order is total number of bonds (0.95) > vdW Volume (0.91) > Molecular Volume (0.91) > vdW Surface Area (0.89) > Molecular Surface Area (0.89) > Solvent Accessible Surface Area (0.85) > Molecular Weight (0.79) for 21 random materials reported in the current study (Figure 3). Molecular properties except molecular weight, vdW volume, molecular volume, vdW surface area, molecular surface area, solvent accessible surface area are molecule level properties using atomic parameters of the elements that constitute the substance/material rather than the molar scale property.

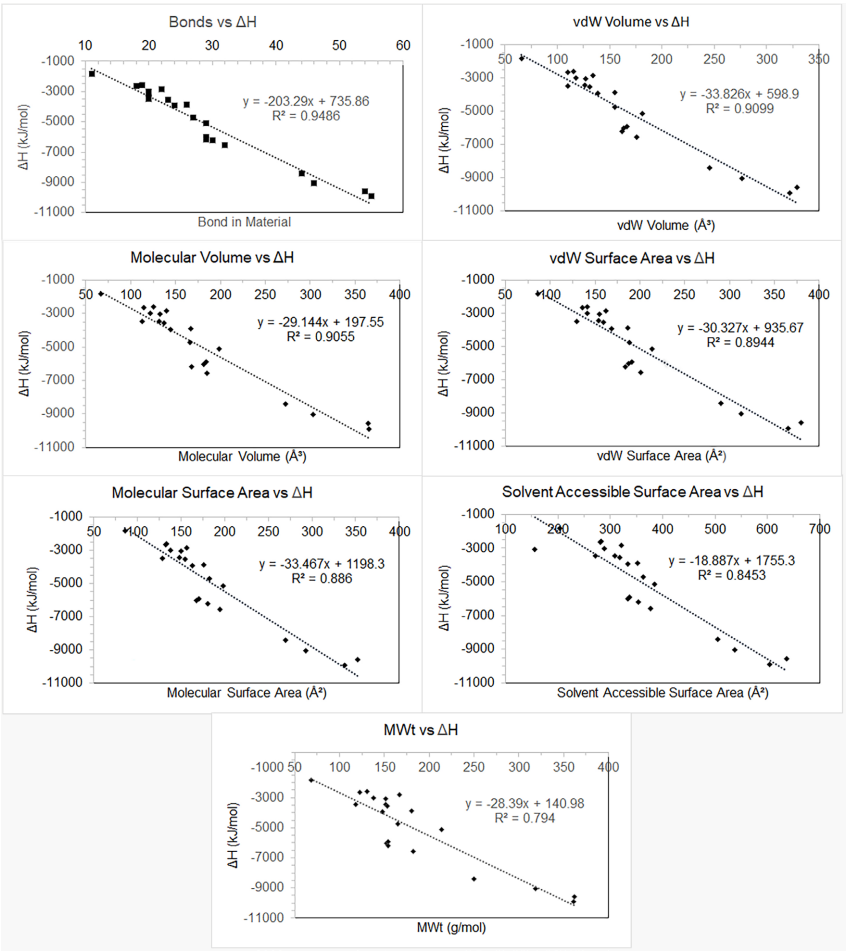


Figure 3. Trends between molecular parameters, total number of bonds, vdW Volume (Å^3), Molecular Volume (Å^3), vdW Surface Area (Å^2), Molecular Surface Area (Å^2), Solvent Accessible Surface Area (Å^2) and Molecular Weight (g/mol) for 21 materials and their corresponding ΔH (kJ/mol) along with the linear fit line, equation and R^2 values are shown. Materials included in **Figure 3** are numbered according to increasing molecular weight.

When Polar ASA and MSA examined with ΔU or ΔH individually for all the materials the linear fit R^2 values are significantly very low for the above molecular properties. In addition to the linear relationship, exponential, logarithmic or polynomial trend between these quantities were explored. These attempts suggest there is no significantly noticeable correlation between combustion energy parameters and polar molecular properties could be established.

Thermodynamic quantities are crucial for establishing the reaction energies of synthesis, understanding their mechanisms of reactions them, calculating the chemical equilibrium in processes engaging the material of interest, and many more practical applications. Experimentally determined thermodynamic data for a class of materials with significantly diverse functionalities would provide statistics for the purpose of benchmarking, standardizing and parametrization of future computational methods [48]-[51] as well as estimating their values when not available in literature. When solid materials undergo thermal treatment, they not only undergo physical transformation, but also chemical changes including disruption of intermolecular and intramolecular interactions and cleavage of bonds that make up their molecular identity. Depending on the material, any, some or all the above events are likely to emerge in some order. Moreover, material matters can be processed for better outcomes with the knowledge of molecular properties, for example, choosing the best substrate, agonists, inhibitors, etc., that are reactive or unreactive thermodynamically under specific conditions. This study may lay a foundation to expand the future use of thermodynamic quantities of materials that are stable, show enhanced absorption, and are transported better through membrane barriers, to stay the least. Overall, experimentally-determined thermodynamic quantities from this study correlate better with the molecular properties, volume and surface that comprise the structural parameters of the substances studied. The molecular properties, volume and surface area can be factored into heat of combustion perdition trials. Most interestingly, this study connects molecular structural properties with their heat of combustion, and may help establish links between different aerobic processes including human physiology, respiration, perspiration, metabolism and toxicity in the future.

These materials are used in chemical, biological, pharmacological, medical studies and clinical applications as starting materials in organic synthesis, agonists, inhibitors, in *in vivo* and *in vitro* experiments and as therapeutic regiments, respectively. Therefore, the information obtained from this study is of interest for technical assessment of pertinent practices. Furthermore, thermodynamic quantities obtained from combustion calorimetry experiments provide an opportunity to compare those values for a wider class of materials. With additional time and resources more materials can be included in the expansion of the correlation trend between experimentally determined heat of combustion and molecular parameters, molecular volumes and surfaces.

The correlation between the heats of combustion and molecular properties may have become clear because the study is conducted in solid phase and in such state,

materials have rigid volume, surface area and shape. When the temperature increases the atoms, ions, molecules that make a material undergo increased vibrational, rotational and bending motions in solid state due to heat that is transferred in the form of kinetic energy. If the material is in liquid or gas phase translational motions also reflect the relative change in energy. When the motions are significantly higher than that in the ground state of the material it echoes in their molecular parameters. Until the parent material starts to undergo chemical changes to smaller degradative substance due to increased energy, volume, surface area reflects variations taking place due to bonding distance, bonding angles, torsion and conformation. Until the energy is less than the heat of enthalpy, conformational change shift from lower energy, stable form to higher energy, unstable form which is similar to folded, native form to denatured, unwound forms in macromolecules, proteins, DNA, RNA and sugars/glycans. Such shifts result in inter and intra molecular interaction, electrostatic interaction, columbic, dipole, hydrogen bonding, hydrophobic attraction or repugnance, ionic, pi, van der Waals force to breakdown. When such conformational changes take place in small size molecules, it can induce changes in macromolecules in their presence. This is in addition to the changes that take place in macromolecules on their own. This phenomenon can be classified as native/denature or folding/unwinding events that are known to take place in nature. In biological phase under physiological conditions such shifts take place without or with small or larger complex molecules' presence or due to other factors including hydration/solvation. When the material undergoes combustion the molecular mass weight of the parent material is distributed across the resulting remains along with oxygen. At that stage of combustion process covalent bonds of parent material start to break. That causes the total number of bonds to outperform other parameters, especially molecular weight, and reflect stronger correlation with heat of combustion (ΔH and/or ΔU) as the phenomenon is associated to the event at molecule level.

Molecules are tightly packed with static volume, surface and shape with less degrees of freedom in solid and crystal phases compared to liquid or gas forms. For materials in gas phase, n, the number of moles depends on the molecular mass/weight and may show a pronounced correlation with $\Delta H/U$ like molecular properties though pressure can alter the relationship with volume and surface. In liquid phase, concentration may play a role and concentration depends on the molecular mass/weight. This may cause the correlation between molecular mass and $\Delta H/U$ to be weaker. In aggregate, solid and crystalline phases concentration doesn't change significantly and the role of molecular mass/weight reflects less correlation with $\Delta H/U$ compared to other molecular parameters. In biophase due to the presence of other materials that coexist and factors that cause cross interference, correlation between molecular mass/weight and $\Delta H/U$ may show complex phenomenon.

4. Conclusion

This study produced experimentally determined heat of combustion for 8 mate-

rials, trans-4-Hydroxy-L-Proline, 4-Hydroxybenzaldehyde, 4-Nitrobenzoic Acid, Clofibric, Gemfibrozil, Fenofibric acid, Bezafibrate, and Fenofibrate as their experimental values are not existing. Experimentally determined heat of combustion in this study for 21 random materials shows a strong trend with the total number of bonds and their molecular properties vdW Volume, Molecular Volume, vdW Surface Area, Molecular Surface Area, Solvent Accessible Surface Area but a weaker tendency is seen with their molecular weight. The trends revealed by volume and surface area with heat of combustion change and internal energy differences are independent of the type of elements that constitute the material. Furthermore, molecular classification of material doesn't alter the trend between internal energy differences, ΔU or enthalpy changes, ΔH and molecular volume and surface properties.

Acknowledgements

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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Abbreviations and Acronyms

Molecular Weight (MWt) (g/mol),
Van der Waals (vdW) Volume ($Å^3$),
Molecular Volume ($Å^3$),
Accessible Surface Area (ASA) ($Å^2$),
Molecular Surface Area (MSA) ($Å^2$),
Internal Energy Change (ΔU) (kJ/mol),
Enthalpy Change (ΔH) (kJ/mol),
Number of Moles Change (Δn),
Calorimeter Constant (C_{cal}),
Solid (s),
Liquid (l),
Gas (g),
Heat (q),
Work (w),
Artificial Neural Network (ANN),
Multi-Variable Regression (MVR),
Quantitative Structure Property Relationship (QSPR).