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Experimental and Computational Study on the Molecular Energetics of Indoline and Indole

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Static bomb calorimetry, Calvet microcalorimetry and the Knudsen effusion technique were used to determine the standard molar enthalpy of formation in the gas phase, at $T = 298.15$ K, of the indole and indoline heterocyclic compounds. The values obtained were 164.3 ± 1.3 $\text{kJ}\cdot\text{mol}^{-1}$ and 120.0 ± 2.9 $\text{kJ}\cdot\text{mol}^{-1}$, respectively. Several different computational approaches and different working reactions were used to estimate the gas-phase enthalpies of formation for indole and indoline. The computational approaches support the experimental results reported. The calculations were further extended to the determination of other properties such as bond dissociation enthalpies, gas-phase acidities, proton and electron affinities and ionization energies. The agreement between theoretical and experimental data for indole is very good supporting the data calculated for indoline.

1. Introduction

The indolic and indolinic (2,3-dihydroindolic) rings appear in a large number of compounds with biological and industrial importance. The indole structure can be found in many organic compounds such as in the amino-acid tryptophan, and in a large variety of alkaloids. Also, they are found in drugs or drugs candidates with interesting and promising therapeutic use, for central nervous system disorders, respiratory disorders, obesity, osteoporosis, neurodegenerative disorders and cerebellar disorders, acute and chronic pain, osteoarthritis, rheumatoid arthritis, cancer, asthma, bronchitis, Pick's disease and glaucoma, heart diseases, obesity or antithrombosis with potential for the treatment and prevention of thrombus-embolic diseases.[1−5] In industry, they are widely used especially in dyes and have potential as corrosion inhibitors.[6]

The thermochemical parameters, especially the enthalpies of formation, have a crucial importance, because they are needed, for example, to calculate the amount of energy involved in chemical reactions, to calculate other thermodynamic functions and to evaluate and interpret the stability of the molecules. Due to the several crucial applications of compounds containing the indolic and indolinic rings, several thermodynamic properties were determined for the parent compounds, i.e., indole and indoline (2,3-dihydroindole). Thermochemical data for these two compounds are scarce in the literature, especially in the case of indoline. The standard molar enthalpy of formation of indole, in the solid phase, was first determined in 1933 by Stern and Klebs[7] and reanalyzed by Cox and Pilcher[8] as 116.7 ± 0.7 $\text{kJ}\cdot\text{mol}^{-1}$. Three decades later, Zimmerman and Geisenfelder[9] performed new experiments and reached the result 92.02 $\text{kJ}\cdot\text{mol}^{-1}$, without the indication of the associated uncertainty. More recently, Good[10] obtained the value 86.7 ± 0.7 $\text{kJ}\cdot\text{mol}^{-1}$, which is the selected standard molar enthalpy of formation of indole, in the solid phase, in the NIST webbook.[11] There are several values for the enthalpy of sublimation of indole which differ both in the numerical result and in the temperature ranges at which they were determined. In chronological order, the enthalpies of sublimation published in the past were as follows: Serpinskii et al. reported the value of 74.9 $\text{kJ}\cdot\text{mol}^{-1}$ measured in the temperature interval 328−383 K,[12] which corrected to $T = 298.15$ K yields 77.8 $\text{kJ}\cdot\text{mol}^{-1}$. Aihara[13] published the value 69.87 ± 0.84 $\text{kJ}\cdot\text{mol}^{-1}$ at $T = 298.15$ K, whereas in the work due to Zimmerman et al.[9] a somewhat different result, 95.0 $\text{kJ}\cdot\text{mol}^{-1}$, was obtained. A decade later, Arshadi used a mass effusion technique to determine the enthalpy of sublimation of indole.[14] His value was 77.8 ± 1.6 $\text{kJ}\cdot\text{mol}^{-1}$, measured in the range of temperatures 275−303 K, which corrected to $T = 298.15$ K yields 77.4 ± 1.6 $\text{kJ}\cdot\text{mol}^{-1}$. Other data available in the literature are the ionization enthalpies, IE, for both compounds. In the case of indoline, the IE measured by Maier and Turner after photoelectron spectroscopy experiments is 689.9 ± 1.9 $\text{kJ}\cdot\text{mol}^{-1}$,[15] and that coming from the mass analyzed threshold ionization spectroscopy experiments due to Lee et al. is 697.0 ± 0.1 $\text{kJ}\cdot\text{mol}^{-1}$.[16] For indole, several values are available in the literature and range from 747 to 800 $\text{kJ}\cdot\text{mol}^{-1}$.[17] NIST's selected value for indole is 748.7 ± 0.1 $\text{kJ}\cdot\text{mol}^{-1}$,[18] which is identical to a more recent value due to Braun et al.[19] The reported proton affinities, PA, for indole and indoline are 933.4 ± [8] $\text{kJ}\cdot\text{mol}^{-1}$ and 957.1 ± [8] $\text{kJ}\cdot\text{mol}^{-1}$, respectively.[20] The experimental PA of indole is much higher than the calculated results available in the literature. At $T = 0$ K, the MPW1PW91/6-311+G(2d,2p)//MPW1PW91/6-31G* and MP2(full)/6-311+G(2d,2p)//MPW1PW91/6-31G* values, including the zero-point energy, calculated by Yang et al. for protonation at the most favorable C3 site are 892.2 $\text{kJ}\cdot\text{mol}^{-1}$ and 861.0 $\text{kJ}\cdot\text{mol}^{-1}$, respectively.[21] At $T = 298.15$ K, these PA values are more positive by 5.2 $\text{kJ}\cdot\text{mol}^{-1}$. Another computational PA ($T = 0$ K) available in the literature is that due to Somers et al.,[22] 888.7 $\text{kJ}\cdot\text{mol}^{-1}$, calculated at the B3LYP/6-31G* level of theory. More recently, the PAs computed by Otero et al.,[23] using the B3LYP/6-311++G(2d,2p) and MP2/6-31++G(d,p) approaches and considering thermal corrections for $T = 298.15$ K, were 891.6 and 884.2 $\text{kJ}\cdot\text{mol}^{-1}$, respectively. In the literature, there are additional experimental thermodynamic results for

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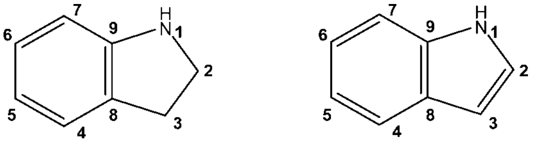


Indoline Indole

Figure 1. Structural formula of indoline and indole.

indole, i.e., the enthalpy of deprotonation (gas-phase acidity), namely, the value found by Meot-ner et al., 1472 ± 10 kJ·mol^{-1},[24] and the result reported by Taft and Bordwell, 1461 ± 9 kJ·mol^{-1},[25] the N−H bond dissociation enthalpy (BDE) due to Bordwell et al., 392.5 kJ·mol^{-1},[26] and the values compiled by Luo for the same property, i.e., N−H BDEs of 380 kJ·mol^{-1} and of 393.7 kJ·mol^{-1}.[27]

In the present work, both experimental and computational techniques were used to obtain additional thermochemical knowledge about the two title compounds. Experimentally, the standard molar energy of combustion of indoline, in liquid phase, at T = 298.15 K, was measured by static bomb calorimetry. The standard molar enthalpy of vaporization, at the same temperature, was measured by Calvet microcalorimetry. In the case of indole, only the standard molar enthalpy of sublimation, at T = 298.15 K, was redetermined as we decided to use the previously determined value of the standard enthalpy of formation in the condensed phase by Good.[10] Our decision is based on the fact that the result from Good is the selected value in the NIST webbook and also because, from previous experience, the results determined by this author are comparable to the ones determined in our laboratory.[28−30] Finally, the standard molar enthalpies of formation, in the gaseous phase, for indoline and indole were derived from the standard molar enthalpies of formation in the condensed phase and the standard molar enthalpy of vaporization or the standard molar enthalpy of sublimation, respectively. A computational chemistry approach was used to calculate the enthalpies of formation of both compounds under study using selected working reactions and also to compute the ionization enthalpies, proton and electron affinities, enthalpies of deprotonation and N−H and C−H bond dissociation enthalpies.

2. Experimental Section

2.1. Compounds and Purity Control. Indoline [CAS Registry No. 496-15-1, supplied by author] and indole [CAS Registry No. 120-72-9, supplied by author], whose structures are shown in Figure 1, were obtained commercially from Aldrich Chemical Co. Indoline was purified by repeated fractional distillation under reduced pressure. The carbon dioxide recovered from the combustion experiments was used as an indication of the purity of the purified compound. The average ratio of the mass of carbon dioxide recovered after combustion to that calculated from the mass of indoline used in each experiment was 99.983 ± 0.026%, where the uncertainties are twice the standard deviation of the mean. Indole was purified by repeated sublimation under reduced pressure. The purity of these two compounds was confirmed by gas−liquid chromatography.

2.2. Combustion Calorimetry. The energy of combustion of indoline was measured using an isoperibol static-bomb calorimeter, previously described in the literature.[31,32] Using the procedure of Coops et al.,[33] the energy equivalent of the calorimeter was determined as $\varepsilon_{\mathrm{cal}} = 15917.4 \pm 1.4$ J·K^{-1}, by combustion of thermochemical standard benzoic acid, sample NBS 39j, with massic energy of combustion, under bomb conditions, of $\Delta_{\mathrm{c}}u = -26434 \pm 3$ J·g^{-1},[34] and corrected to give the energy equivalent, $\varepsilon_{\mathrm{cal}}$, corresponding to the average mass of water added to the calorimeter, 3119.6 g.

In all combustion experiments, 1.00 cm^3 of water was introduced into a twin-valve combustion bomb type 1105 (Parr Instrument Company), with an internal volume of 0.340 dm^3. This bomb was purged twice to remove air, before being charged with oxygen at p = 3.04 MPa.

The liquid indoline was burnt enclosed in sealed polyester bags made of Melinex with 0.025 mm of thickness, previously weighed. The mass of Melinex used in each experiment was corrected for the mass fraction of water, w = 0.0032, and the mass of CO_2 resulted from the Melinex combustion was calculated using a factor previously reported.[35] The specific energy of combustion of dry Melinex, $\Delta_{\mathrm{c}}u^{\circ} = 22902 \pm 5$ J·g^{-1}, measured by Skinner and Snelson,[35] was confirmed in our laboratory.

For all experiments, the calorimeter temperatures were measured to $\pm 1 \times 10^{-4}$ K, at time intervals of 10 s, with a quartz crystal thermometer (Hewlett-Packard HP 2804A), interfaced to a PC. The ignition of the samples was made at T = 298.150 ± 0.001 K by the discharge of a 1400 μF capacitor through the platinum ignition wire. At least 100 readings were taken in each of the fore, main and after periods of each combustion experiment.

For the cotton thread fuse, with empirical formula $CH_{1.686}O_{0.843}$, the massic energy of combustion was assigned to $-\Delta_{\mathrm{c}}u^{\circ} = 16250$ J·g^{-1},[33] a value also confirmed in our laboratory.

The corrections for nitric acid formation were based on − 59.7 kJ·mol^{-1}, for the molar energy of formation of 0.1 mol·dm^{-3} HNO_3 (aq), from N_2 (g), O_2 (g) and H_2O (l).[36] All the necessary weighing was made in a Mettler Toledo 240 balance, sensitivity $\pm 1 \times 10^{-5}$ g, and corrections from apparent mass to true mass were made. For each compound an estimated pressure coefficient of massic energy, $(\partial u/\partial p)_T$, was assumed to be −0.2 J·g^{-1}·MPa^{-1}, at T = 298.15 K, a typical value for most organic compounds.[37] For each compound $\Delta_{\mathrm{c}}u^{\circ}$ was calculated by the procedure of Hubbard et al.[38] The amount of substance burnt in each experiment, and on which the energy of combustion was based, was determined from the mass of CO_2 produced during the experiments, taking into account that formed from the combustion of the cotton-thread fuse and the Melinex bags, with the weighings made in a Mettler Toledo AT 201 balance, sensitivity $\pm 1 \times 10^{-5}$ g.

The relative atomic masses used were those recommended by the IUPAC Commission in 2005.[39]

2.3. Calvet Microcalorimentry. The standard molar enthalpy of vaporization of indoline was determined with a Calvet High Temperature Microcalorimeter (Setaram, HT 1000D), using for this liquid a similar technique[40] to that described by Skinner et al.[41] for the sublimation of solids. The apparatus and the technique used are described in detail in the literature.[42]

In the experiments, samples of about 3−5 mg of compound, contained in a thin glass capillary tube sealed at one end, were dropped from room temperature into the hot zone of the calorimeter, held at T = 329 K, and then removed from the hot zone by vaporization under reduced pressure. The thermal corrections for the glass capillaries were made by dropping tubes of nearly equal mass into each of the twin cells. The observed standard molar enthalpies of phase transition, $\Delta_{\mathrm{l},\,298.15\,\mathrm{K}}^{\mathrm{g},\,329.1\,K}H_{\mathrm{m}}^{\circ}$, were corrected to T = 298.15 K using $\Delta_{298.15\mathrm{K}}^{T}H_{\mathrm{m}}^{\circ}(\mathrm{g})$ estimated by a group method based on the values of Stull et al.[43] The scheme used was: indoline = benzene + pyrrolidine − ethane, which yielded $\Delta_{298.15\mathrm{K}}^{329.1\mathrm{K}}H_{\mathrm{m}}^{\circ}(\text{indoline,g}) = 3.72$ kJ·mol^{-1}.

The calibration was made with n-undecane, 99+, supplied by Aldrich Chemical Co., using the value of $\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}^{\circ}(n\text{-undecane}) = 56.580 \pm 0.566$ kJ·mol^{-1} for the standard molar enthalpy of vaporization of the n-undecane at T = 298.15 K.[44] The value of the enthalpy of vaporization of n-undecane, at the temperature

TABLE 1: Areas and Transmission Probability Factors of the Effusion Orifices

orifice no.	A_o/mm^2	w_o
1	0.5027	0.9884
2	0.6627	0.9899
3	0.7854	0.9907

of the calibration experiments, was calculated from their value at $T = 298.15$ K, using literature values of $\Delta^{T}_{298.15\mathrm{K}}H^{\circ}_{\mathrm{m}}(\mathrm{g})$ from Stull et al.[43] The experimental procedure for the calibration experiments was the same as that used in the experiments with indoline. At this working temperature, $T = 329$ K, the value of the calibration constant was found to be k_{cal} ($T = 329$ K) $= 1.0089 \pm 0.0012$.

2.4. Knudsen-Effusion Technique. The Knudsen mass-loss effusion technique was used to measure the vapor pressures as a function of temperature of indole. An apparatus was used that enables the simultaneous operation of three Knudsen cells, with three different effusion holes. The detailed description of the apparatus, procedure, and technique can be found elsewhere.[45]

The temperature interval was chosen to make possible the measurements of vapor pressures in the range 0.1−1.0 Pa. In each effusion experiment, the mass loss, Δm during the effusion period t, is determined by weighing the effusion cells in a Mettler AE 163 balance, sensitivity ± 0.01 mg, before and after the effusion time in a system evacuated to a pressure near 1×10^{-4} Pa. At the temperature T of the experiment, the vapor pressure p is calculated by eq 1,

$$p = \left(\frac{\Delta m}{A_o w_o t}\right)\sqrt{\frac{2\pi RT}{M}} \tag{1}$$

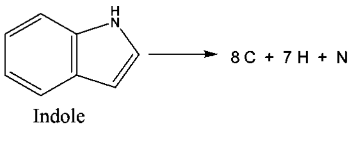
where M is the molar mass of the effusing vapor, R is the gas constant, A_o is the area of the effusion hole and w_o is the respective Clausing factor calculated by eq 2,

$$w_o = \left\{1 + \left(\frac{3l}{8r}\right)\right\}^{-1} \tag{2}$$

where l is the thickness of the effusion orifice and r its radius.

The thicknesses of the effusion orifices made on a thin platinum foil are 0.0125 mm; their areas and Clausius factors are registered in Table 1.

2.4. Computational Thermochemistry. The G3MP2B3 composite approach was used throughout this work.[46] The enthalpy of formation of indole was estimated after the consideration of the following gas-phase working reactions:



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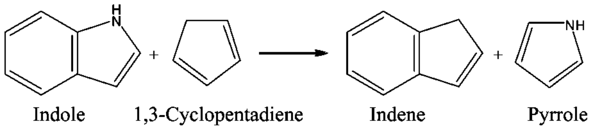

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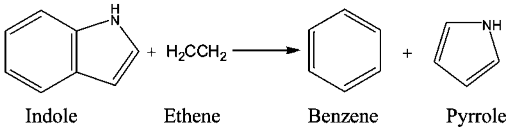

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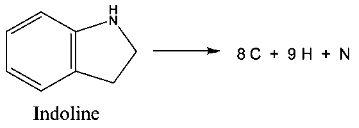
The gas-phase reactions shown below were used to estimate the enthalpy of formation of indoline:



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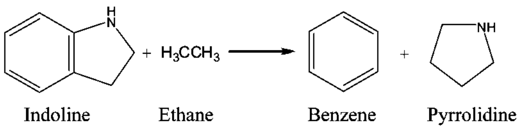

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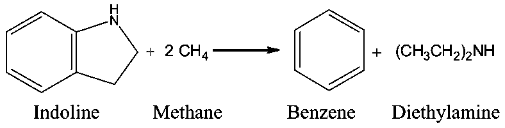

(8)

These reactions have been chosen on the basis of the available experimental thermochemical data for the compounds there used. It must be noticed that some of the reactions are not isodesmic and that some errors due to the consideration of different bonds in the reactants and in the products may not be compensated.

The computations carried out with the G3MP2B3 composite approach use the B3LYP method and the 6-31G(d) basis set for both the optimization of geometry and calculation of frequencies. Introduction of high-order corrections to the B3LYP/6-31G(d) enthalpy is done in a manner that follows the Gaussian-3 philosophy, albeit using a second-order Moller−Plesset perturbation instead of MP4 as in the original G3 method.[47] The composite calculations were carried out by means of the Gaussian 03 computer code[48] The energies computed at $T = 0$ K were thermally corrected for $T = 298.15$ K by introducing the vibrational, translational, rotational and the pV terms. The vibrational term is based on the vibrational wave numbers calculated at the B3LYP/6-31G(d) level. The same computational approach was used to calculate also the ionization enthalpies, proton and electron affinities, gas-phase acidities and C−H and N−H bond dissociation enthalpies. For that purpose, the G3MP2B3 computations were also extended to cationic, anionic and radicalar species obtained from indole and indoline.

Finally, to clarify some data, additional calculations were performed with other computational approaches, namely the CBS-QB3 composite method,[49] the B3LYP[50,51] and BP86[52,53] approaches based on the density functional theory and the MP2 method, i.e., Moller−Plesset perturbation theory second-order corrections to the Hartree−Fock energy.[54] The 6-311+G(2d,2p) basis set was used in the noncomposite calculations.[55]

3. Results and Discussion

3.1. Indoline in the Condensed Phase. Detailed results of all combustion experiments for indoline are listed in Table 2. In this table, $\Delta m(\mathrm{H_2O})$ is the deviation of the mass of water added to the calorimeter from 3119.6 g, ΔU(IPB) is the energy change for the isothermal combustion reaction under bomb conditions and ΔU_{Σ} is the correction to the standard state calculated by the procedure of Hubbard et al.;[38] the remaining

TABLE 2: Combustion Experiments, at T = 298.15 K, of Indoline[a]

	experiment					
	1	2	3	4	5	6
m(CO$_2$, total)/g	2.40768	2.33233	2.12738		2.12114	
m (cpd)/g	0.77097	0.73962	0.67681	0.79939	0.67490	0.83520
m(Melinex)/g	0.05455	0.06215	0.05344	0.05299	0.05327	0.05527
m(fuse)/g	0.00300	0.00291	0.00328	0.00297	0.00316	0.00287
ΔT_{ad}/K	1.90823	1.84552	1.68290	1.97190	1.67939	2.06115
ε_f/J·K^{-1}	16.54	16.55	16.36	16.64	16.31	16.78
Δm(H$_2$O)/g	0.0	0.0	0.0	0.0	+ 0.1	0.0
$-\Delta U$(IBP)^b/J	30404.78	29405.74	26813.76	31419.52	26758.87	32842.07
ΔU(Melinex)/J	1249.38	1423.46	1223.79	1213.51	1219.91	1265.83
ΔU(fuse)/J	48.72	47.26	53.27	48.23	51.32	46.61
ΔU(HNO$_3$)/J	50.92	46.03	43.22	49.01	42.03	53.01
ΔU (ign)/J	0.84	0.68	1.16	0.81	0.75	0.67
ΔU_Σ/J	17.37	16.83	15.13	18.06	15.11	18.96
$-\Delta_c u°$/J·g^{-1}	37664.75	37684.43	37644.76	37642.09	37680.40	37664.82
% CO$_2$	99.975	99.946	100.057	(99.983)	99.953	(99.983)

$<\Delta_c u^o> = -(37663.5 \pm 7.2)$ J·g^{-1} (0.019%)

[a] m(CO$_2$, total) is the total mass of carbon dioxide recovered in the combustion; m(cpd) is the mass of compound burnt in each experiment; m(Melinex) is the mass of Melinex used to enclose the compound; m(fuse) is the mass of the cotton thread fuse; ΔT_{ad} is de adiabatic temperature rise; ε_f is the energy equivalent of the calorimeter including the contents of the bomb in the final state; Δm(H$_2$O) is the deviation of the mass of water added to the calorimeter from 3119.6 g; ΔU(IBP) is the energy change for isothermal combustion reaction under actual bomb conditions; ΔU(Melinex) is the energy of combustion of the Melinex used in each experiment; ΔU(fuse) is the energy of combustion of the fuse (cotton); Δ(HNO$_3$) is the energy correction for the nitric acid formation; ΔU(ign) is the electrical energy supplied for ignition; ΔU_Σ is the standard state correction; $\Delta_c u^o$ is the massic energy of combustion of the compound. [b] ΔU(IBP) already includes ΔU(ign).

TABLE 3: Derived Standard ($p°$ = 0.1 MPa) Molar Energy of Combustion, $\Delta_c U^o_m$, Standard Molar Enthalpy of Combustion, $\Delta_c H^o_m$, and the Standard Molar Enthalpy of Formation of Indoline in Liquid Phase, $\Delta_f H^o_m$, at T = 298.15 K

compound	$-\Delta_c U^o_m$/kJ·mol^{-1}	$-\Delta_c H^o_m$/kJ·mol^{-1}	$\Delta_f H^o_m$/kJ·mol^{-1}
indoline (l)	4488.1 ± 2.2	4492.4 ± 2.2	58.1 ± 2.4

quantities are as previously defined.[38] As the samples were ignited at T = 298.150 ± 0.001 K,

$$\Delta U(\mathrm{IPB}) = -\{\varepsilon_{cal} + \Delta m(\mathrm{H_2O})c_p(\mathrm{H_2O,l}) + \varepsilon_f)\Delta T_{ad} + \Delta U(\mathrm{ign}) \quad (9)$$

The derived standard molar values for the energy ($\Delta_c U^o_m$) and enthalpy ($\Delta_c H^o_m$) of the combustion reactions according to eq 10 are given in Table 3.

$$\mathrm{C_8H_9N(l)} + \frac{41}{2}\mathrm{O_2(g)} \rightarrow 8\mathrm{CO_2(g)} + \frac{9}{2}\mathrm{H_2O(l)} + \frac{1}{2}\mathrm{N_2(g)} \quad (10)$$

The uncertainty assigned to the standard molar enthalpy of combustion, in accordance with the normal thermochemical practice, is twice the overall standard deviation of the mean and includes the uncertainty in the calibration.[56,57] The value of the standard molar enthalpy of formation in the liquid phase, $\Delta_f H^o_m$(l), registered in Table 3, was derived from $\Delta_c H^o_m$, using the values, at T = 298.15 K, of the standard molar enthalpies of formation of liquid water and gaseous carbon dioxide, respectively as $\Delta_f H^o_m$(H$_2$O,l) = −285.830 ± 0.042 kJ·mol^{-1} [58] and $\Delta_f H^o_m$(CO$_2$,g) = −393.51 ± 0.13 kJ·mol^{-1}.[58]

3.2. Phase Transition of Indoline. Results of the microcalorimetric determination of the enthalpy of vaporization of indoline are reported in Table 4. The enthalpy of vaporization at the temperature T corresponds to the mean value of five independent experiments with the uncertainty given as the standard deviation. The uncertainty associated to the standard molar enthalpy of vaporization, at T = 298.15 K, is twice the standard deviation and includes the uncertainty associated to the calibration procedure.

3.3. Phase Transition of Indole. The integrated form of the Clausius−Clapeyron equation, ln(p/Pa) = $a - b$·(T/K)$^{-1}$, where a is a constant and $b = \Delta^g_{cr}H^o_m(\langle T\rangle)/R$, was used to derive the standard molar enthalpy of sublimation of indole, at the mean temperature of the experimental range of temperatures. The experimental results obtained from each effusion cell, together with the residuals of the Clausius−Clapeyron equation, derived from the least-squares adjustments are presented in Table 5.

The entropy of sublimation at equilibrium was calculated as

$$\Delta^g_{cr}S_m\{\langle T\rangle, p(T{=}\langle T\rangle)\} = \frac{\Delta^g_{cr}H^o_m(\langle T\rangle)}{\langle T\rangle} \quad (11)$$

Table 6 presents for each orifice used and for the global treatment of all the (p,T) points obtained for indole, the detailed parameters of the Clausius−Clapeyron equation together with the calculated standard deviation and the standard molar enthalpy of sublimation at the mean temperature of the experiments $T = \langle T\rangle$. The equilibrium pressure at this temperature $p(T{=}\langle T\rangle)$ and the entropy of sublimation, at equilibrium conditions, are also reported in Table 6. The plot of ln p vs 1/T for the data obtained experimentally gives a good straight line. The (p, T) values calculated from the (p, T) equations within the range of experimental pressures between 0.1 and 1 Pa are compiled in Table 7.

The sublimation enthalpy, at T = 298.15 K, was derived from the same quantity at the mean temperature $\langle T\rangle$ using eq 12,

$$\Delta^g_{cr}H^o_m(T{=}298.15\ \mathrm{K}) = \Delta^g_{cr}H^o_m(\langle T\rangle) + \Delta^g_{cr}c^o_{p,m}(298.15\ \mathrm{K} - \langle T\rangle) \quad (12)$$

where $\Delta^g_{cr}c^o_{p,m} = -50$ J·K^{-1}·mol^{-1}, a value estimated by other authors and tested for organic compounds.[59]

Finally, in Table 8 the values, at T = 298.15 K, of the standard molar enthalpy, entropy and Gibbs energy of sublimation for indole are presented. The enthalpy of sublimation

TABLE 4: Microcalorimetric Standard ($p° = 0.1$ MPa) Molar Enthalpy of Vaporization of Indoline, at $T = 298.15$ K

compound	no. of experiments	T/K	$\Delta_{\mathrm{l},\,298.15\mathrm{K}}^{\mathrm{g},T}H_{\mathrm{m}}^{\mathrm{o}}$/kJ·mol^{-1}	$\Delta_{298.15\mathrm{K}}^{T}H_{\mathrm{m}}^{\mathrm{o}}$(g)/kJ·mol^{-1}	$\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}(T = 298.15\mathrm{K})$/kJ·mol^{-1}
indoline (l)	5	329.1	65.58± 0.61	3.72	61.9 ± 1.7

TABLE 5: Knudsen Effusion Results for Indole

		p/Pa			$10^2\cdot\Delta\ \ln(p/Pa)$		
T/K	t/s	orifice 1	orifice 2	orifice 3	orifice 1	orifice 2	orifice 3
275.15	25334	0.1594	0.1471	0.1438	8.1	0.1	− 2.2
277.17	23626	0.1902	0.1862	0.1773	0.8	− 1.2	− 6.2
279.15	23293	0.2551	0.2376	0.2311	6.2	− 1.1	− 3.8
281.16	21359	0.3146	0.2964	0.2842	2.9	− 3.0	− 7.2
283.17	18714	0.4001	0.3804	0.3680	3.1	− 1.9	− 5.2
285.14	15803	0.5186	0.4912	0.4852	6.0	0.6	− 0.6
287.14	14268	0.6637	0.6304	0.6060	7.7	2.5	− 1.4
289.15	12217	0.8228	0.7868	0.7596	6.4	1.9	− 1.6
291.14	10187	0.9900	0.9112	0.8910	2.7	− 5.7	− 7.9

TABLE 6: Experimental Results for Indole, Where *a* and *b* Are from the Clausius−Clapeyron Equation $\ln(p/\mathrm{Pa}) = a - b\cdot(K/T)$, and $b = \Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}(\langle T\rangle)/R$; $R = 8.314472$ J·mol^{-1}·K^{-1}

orifice number	a	b	$\langle T\rangle$/K	$p(\langle T\rangle)$/ Pa	$\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}(\langle T\rangle)$/ kJ·mol^{-1}	$\Delta_{\mathrm{cr}}^{\mathrm{g}}S_{\mathrm{m}}(\langle T\rangle, p(\langle T\rangle))$/ J·mol^{-1}·K^{-1}
1	32.4147	9433.32	283.15	0.3867	78.4 ± 1.1	276.8 ± 4.0
2	32.2697	9409.53	283.15	0.3833	78.2 ± 1.2	276.3 ± 4.1
3	32.3578	9442.44	283.15	0.3714	78.5 ± 1.2	277.2 ± 4.4
global	**32.3474**	**9428.09**	**283.15**	**0.3867**	**78.4** ± **1.4**	**276.8** ± 4.0

TABLE 7: Values of (p, T) from the Vapor Pressure Equation for Indole

p/Pa	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
T/K	271.1	277.6	281.0	283.4	285.3	286.9	288.3	289.5	290.5	291.5

TABLE 8: Derived Standard ($p° = 0.1$ MPa) Molar Enthalpy, $\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}$, Entropy, $\Delta_{\mathrm{cr}}^{\mathrm{g}}S_{\mathrm{m}}^{\mathrm{o}}$ and Gibbs Energy, $\Delta_{\mathrm{cr}}^{\mathrm{g}}G_{\mathrm{m}}^{\mathrm{o}}$, of Sublimation, at $T = 298.15$ K

compound	$\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}$/kJ·mol^{-1}	$\Delta_{\mathrm{cr}}^{\mathrm{g}}S_{\mathrm{m}}^{\mathrm{o}}$/kJ·mol^{-1}	$\Delta_{\mathrm{cr}}^{\mathrm{g}}G_{\mathrm{m}}^{\mathrm{o}}$/kJ·mol^{-1}
indole	77.6 ± 1.1	170.6 ± 4.0	26.8± 1.7

measured in the present work, $\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}} = 77.6 \pm 1.1$ kJ·mol^{-1}, in very good agreement with the results reported by Serpinskii et al.[12] and by Arshadi[14] but it is in clear disagreement with the value reported by Aihara[13] and, especially, with the result due to Zimmerman et al.[9]

3.4. Indole and Indoline in the Gas Phase. The experimental values of the standard molar enthalpy of formation, in the condensed phase and of the standard molar enthalpy of vaporization of indoline, at $T = 298.15$ K, obtained respectively by combustion calorimetry and Calvet microcalorimetry, were used to derive the standard molar enthalpy of formation of indoline in the gas phase. As already written above, the standard molar enthalpy of formation in the gaseous phase for indole was derived from the standard molar enthalpy of formation in the condensed phase due to Good,[7] together with the standard molar enthalpy of sublimation determined in the present work. All these quantities are summarized in Table 9.

The standard molar enthalpies of formation of indole and indoline were estimated by using eqs 8 and their enthalpies of reaction calculated with the G3MP2B3 computational approach. The enthalpies of reaction were combined with the experimental standard molar enthalpies of formation of all the intervening species, with the exception of indole and indoline, to obtain the gas-phase standard molar enthalpies of formation, $T = 298.15$ K, of indole and indoline. The experimental gas-phase enthalpies of formation at $T = 298.15$ K used: carbon atom, $\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\mathrm{o}}(\mathrm{g}) = 716.67$ kJ·mol^{-1};[60] hydrogen atom, $\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\mathrm{o}}(\mathrm{g}) = 218.00$ kJ·mol^{-1}; nitrogen atom, $\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\mathrm{o}}(\mathrm{g}) = 472.68$ kJ·mol^{-1};[60] indene, $\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\mathrm{o}}(\mathrm{g}) = 163.4 \pm 2.0$ kJ·mol^{-1};[61] 1,3-cyclopentadien, $\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\mathrm{o}}(\mathrm{g}) = 134.3 \pm 1.5$ kJ·mol^{-1};[61] pyrrole, $\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\mathrm{o}}(\mathrm{g}) = 108.4 \pm 0.6$ kJ·mol^{-1};[61] ethene, $\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\mathrm{o}}(\mathrm{g}) = 52.5 \pm 0.3$ kJ·mol^{-1};[61] benzene, $\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\mathrm{o}}(\mathrm{g}) = 82.6 \pm 0.7$ kJ·mol^{-1};[61] ethane, $\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\mathrm{o}}(\mathrm{g}) = -83.8 \pm 0.3$ kJ·mol^{-1};[61] pyrrolidine, $\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\mathrm{o}}(\mathrm{g}) = -3.4 \pm 1.0$ kJ·mol^{-1};[61] methane, $\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\mathrm{o}}(\mathrm{g}) = -74.4 \pm 0.4$ kJ·mol^{-1};[61] and diethylamine, $\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\mathrm{o}}(\mathrm{g}) = -72.2 \pm 1.2$ kJ·mol^{-1}.[61]

TABLE 9: Derived Standard ($p° = 0.1$ MPa) Molar Enthalpies of Formation, and of Phase Transition, at $T = 298.15$ K

			$\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\mathrm{o}}$(g)/kJ·mol^{-1}	
compound	$\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\mathrm{o}}$(l,cr)/ kJ·mol^{-1}	$\Delta_{\mathrm{l,cr}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}$/ kJ·mol^{-1}	experimental	computational[a]
indoline (l)	58.1 ± 2.4	61.9 ± 1.7	120.0 ± 2.9	116.5 (6) 116.9 (7) 119.6 (8)
indole (cr)	86.7 ± 0.7[b]	77.6 ± 1.1	164.3 ± 1.3 181.6[c] 156.3 ± 1.0[d]	158.8 (3) 165.1 (4) 158.8 (5)

[a] G3MP2B3 approach was used to calculate the enthalpy of the working reactions indicated in parenthesis. [b] Experimental result taken from ref 10. [c] Value from the NIST webbook, ref 11. [d] Value from the compilation due to Pedley.[61]

The calculated enthalpies of formation are listed and compared with the experimental results in Table 9. As can be seen in that table, the agreement between the reported experimental data and the computational values is excellent. In the case of indoline, the result calculated with eq 8 is almost identical to the experimental result. Those calculated with eq 6 or 7 are outside but close to the interval defined by the uncertainty associated with the experimental result. It is encouraging that three different working reactions lead to estimated results that are in close agreement with the experimental value supporting the experimental result. In the case of indole, the enthalpic difference between the results calculated with eqs 3−5, $\Delta\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\mathrm{o}}(\mathrm{g}) = 6.3$ kJ·mol^{-1}, doubles that found for indoline using also three different working reactions, $\Delta\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\mathrm{o}}(\mathrm{g}) = 3.1$ kJ·mol^{-1}. Even though it is not a significantly large difference, the calculated results introduce an interesting question, that is, which is the experimental result that must be selected in future compilations of thermochemical data? The result is already published in the compilation due to Pedley, $\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\mathrm{o}}(\mathrm{g}) = 156.3 \pm 1.0$ kJ·mol^{-1}, or that reported in the present work, $\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\mathrm{o}}(\mathrm{g}) = 164.3 \pm 1.3$ kJ·mol^{-1}. This question arises from the fact that two of the calculated values ($\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\mathrm{o}}(\mathrm{g}) = 158.8$ kJ·mol^{-1}) are closer to the former experimental result and another

TABLE 10: Comparison of Estimated Standard Molar Enthalpies of Formation for Indole Obtained with Several Computational Approaches[a]

working reaction	G3MP2B3	CBS-QB3	B3LYP[b]	BP86[b]	MP2[b]
3	158.8	169.4			
4	165.1	167.5	165.2	163.6	171.3
5	158.8	160.3	166.4	165.2	162.5

[a] All values are in kJ·mol^{-1}. Experimental results are: 164.3 ± 1.3, ref 10 and this work; 181.6, ref 11; 156.3 ± 1.0, ref . [b] The 6-311+G(2d,2p) basis set was used for geometry optimization and calculation of thermal corrections.

TABLE 11: G3MP2B3 Computed Electron (EA) and Proton (PA) Affinities, Ionization Enthalpies (IE), Gas-Phase Acidities ($\Delta H_{\mathrm{acidity}}$) and Bond Dissociation Enthalpies (BDE) for Indole and Indoline

compound	EA	PA	IE	$\Delta H_{\mathrm{acidity}}$	Y−H BDE
indoline	−84.2[b]	921.5 (N)	714.0	1531.7 (N)	363.8 (N)
		957.1 ± [8][c]	*689.9 ± 1.9*[d]	1607.2 (C3)	366.5 (C3)
			697.0 ± 0.1[e]		
indole	−86.9	889.1 (C3)	763.4	1460.8 (N)	392.2 (N)
		933.4 ± [8][c]	*747−800* [f]	1608.0 (C2)	*380* [j] *(N)*
			748.7 ± 0.1[g]	*1472 ± 10*[h]	*393.7* [j] *(N)*
				1461 ± 9[i]	*392.5*[k] *(N)*

[a] All values in kJ·mol^{-1} and experimental results are in italic. [b] B3LYP/6-311+G(2d,2p) value due to convergence problems in G3MP2B3 calculations for the anion. [c] Reference 20. [d] Reference 15. [e] Reference 16. [f] Range of experimental values in ref 17. [g] Reference 18. Selected value in ref 17. [h] Reference 24. [i] Reference 25. [j] Reference 27. [k] Reference 26.

calculated value ($\Delta_f H_m^o(g) = 165.1$ kJ·mol^{-1}) is closer to the result based on the enthalpy of sublimation reported in the present work. The value reported on the Pedley's compilation was based on the enthalpy of formation reported by Good[10] and on the enthalpy of sublimation determined by Aihara.[13] As the sublimation enthalpy value of Aihara is quite different from the other enthalpies of sublimation reported by Serpinskii et al., by Arshadi and also from our value, all in close agreement with each other, recalculating the value of Pedley using the latter enthalpies of sublimation, the agreement would be excellent. Because the difference between these two available experimental results is small and the computational approach has an associated uncertainty,[62] some other computational approaches were used to go a step further in supporting the new value obtained in this work. The approaches considered were the CBS-QB3 method, which is also a composite approach, the B3LYP and BP86 functionals and the MP2 approach. In the latter three noncomposite methodologies, the electrons were described by the 6-311+G(2d,2p) basis set. The calculated enthalpies of formation of indole with these approaches, and considering the reactions in eqs 3−5, are reported in Table 10. As it can be seen in this table, the lowest estimated enthalpy of formation for indole is that obtained from the use of the CBS-QB3 method and the reaction described by eq 5. The calculated value is 160.3 kJ·mol^{-1}, which is right between the two experimental results that seem more reliable. All the other combinations of methods and reactions yield values that are closer to the experimental gaseous enthalpy of formation reported in the present work, i.e., 164.3 ± 1.3 kJ·mol^{-1}. Importantly, the enthalpies of formation estimated for indoline by the use of the B3LYP/6-311+G(2d,2p) and the reactions described by eqs 8 are 117.0 kJ·mol^{-1} and 120.0 kJ·mol^{-1}, respectively, which are in very nice agreement with the experimental result reported here, 120.0 ± 2.9 kJ·mol^{-1}, which further supports the $\Delta_f H_m^o(g) = 164.3 \pm 1.3$ kJ·mol^{-1} determined for indole.

The G3MP2B3 approach was used to compute some other thermodynamic properties for indole and indoline. The calculated values for the gas-phase acidity, enthalpy of ionization, electron and proton affinity as well as C−H or N−H bond dissociation enthalpies are reported in Table 11. The electron affinity obtained for the two title compounds is almost the same, i.e., ~85 kJ·mol^{-1}. The introduction of one electron in indole or indoline is almost 100 kJ·mol^{-1} less demanding than on pyrrole.[63] The insertion of a proton into each of these compounds does not occur at the same position in the ring. In the case of indoline, the most favorable position is at the nitrogen atom, PA of 921.5 kJ·mol^{-1}, whereas in the case of indole the proton enters at the C3 position with a calculated PA of 889.1 kJ·mol^{-1}. Either of these two calculated results is ~40 kJ·mol^{-1} less positive than the values appearing in the compilation of Hunter and Lias.[20] Interestingly, the value calculated for pyrrole, 872.9 kJ·mol^{-1}, with the same computational approach almost matches the experimental result.[63] Similar concordance between G3MP2B3 and experimental data was observed in a previous work,[28] which suggests that the present PAs should be introduced in future compilations of thermodynamic data. The calculated adiabatic ionization enthalpies are ~15 kJ·mol^{-1} higher than the selected results for indoline and indole but included in the interval defined by the large number of available experimental values.[17] The gas-phase acidity calculated for indole almost matches one of the experimental results available and is almost included in the uncertainty interval associated with the other experimental result,[25] suggesting that the calculated gas-phase acidity for indoline is reliable. The calculated acidities show that the deprotonation of indole ($\Delta H_{\mathrm{acidity}} = 1461$ kJ·mol^{-1}) is much easier than the removal of a single proton in indoline ($\Delta H_{\mathrm{acidity}} = 1532$ kJ·mol^{-1}). Nevertheless, the removal of a proton from a carbon atom of the two rings costs the same, i.e., ~1608 kJ·mol^{-1}. Finally, the calculated N−H BDE in the case of indole is 392.2 kJ·mol^{-1}, which is in perfect agreement with two of the experimental results available.[26,27] This gives additional confidence for the calculated N−H BDE for indoline, 363.8 kJ·mol^{-1}, showing that compounds containing the indolinic ring may be better antioxidants than those containing the indolic moiety. Interestingly, the enthalpy required to remove a hydrogen atom from the N position in the indolinic ring is almost degenerate with that needed to retrieve a hydrogen atom from the C3 position.

4. Final Remarks

A combined experimental and theoretical study was performed and the standard molar enthalpies of formation in the gas phase of indole and indoline were obtained. The experimental result determined in the present work for indoline, 120.0 ± 2.9 kJ·mol^{-1}, is in excellent agreement with the results calculated using the G3MP2B3 approach, whereas for indole, calculations with several different approaches support the experimental value presented in this work, i.e., 164.3 ± 1.3 kJ·mol^{-1}. Other thermodynamic properties of indole and indoline were also calculated and compared with literature values. The calculation of the N−H BDE shows that compounds with the indolinic ring may be better antioxidants than those containing the indolic moiety.

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References and Notes

(1) Torrens Jover, A.; Yenes Minguez, S. EP Patent 1849784-A1, 2007.

(2) Boyd, M.; Colucci, J. WO Patent 143825-A1, 2007.

(3) Lee, S.; Yang Yi, K.; Kim, S.; Suh, J.; Kim, N. J.; Yoo, S.; Lee, B. H.; Seo, H. W.; Kim, S.; Lim, H. *Eur. J. Med. Chem.* **2003**, *38*, 459.

(4) Bentley, J. M.; Adams, D. R.; Bebbington, D.; Benwell, K. R.; Bickerdike, M. J.; Davidson, E. P.; Dawson, C. E.; Dourish, C. T.; Duncton, M. A. J.; Gaur, S.; George, A. R.; Giles, R.; Hamlyn, R. J.; Kennett, G. A.; Knight, A. R.; Malcolm, C. S.; Mansell, H. L.; Misra, A.; Monck, N. J. T.; Pratt, R. M.; Quirk, K.; Roffey, J. R. A.; Vickers, S. P.; Cliffe, I. A. *Bioorg. Med. Chem. Lett.* **2004**, *14*, 2367.

(5) Noguchi, T.; Tanaka, N.; Nishimata, T.; Goto, R.; Hayakawa, M.; Sugidachi, A.; Ogawa, T.; Asai, F.; Matsui, Y.; Fujimoto, K. *Chem. Pharm. Bull.* **2006**, *54*, 163.

(6) Sundaraganesan, N.; Umamaheswari, H.; Dominic Joshua, B.; Meganathan, C.; Ramalingam, M. *J. Mol. Struct. (THEOCHEM)* **2008**, *850*, 84.

(7) Stern, A.; Klebs, G. *Justus Liebigs Ann. Chem.* **1933**, *504*, 287.

(8) Cox, J. D.; Pilcher, G. *Thermochemisdtry of Organic and Organometallic Compounds*; Academic Press: London, 1970.

(9) Zimmerman, H.; Geisenfelder, H. *Z. Electrochem.* **1961**, *65*, 368.

(10) Good, W. *J. Chem. Eng. Data* **1972**, *17*, 28.

(11) Afeefy, H. Y.; Liebman, J. F.; Stein, S. E. *Neutral Thermochemical Data in NIST Chemistry WebBook, NIST Standard Reference Database Number 69*; Linstrom, P. J., Mallard, W. G., Eds.; National Institute of Standards and Technology: Gaithersburg, MD, 2005. (http://webbook.nist.gov).

(12) Serpinskii, V. V.; Voitkevich, S. A.; Lyuboshits, N. Y. *Zh. Fiz. Khim.* **1954**, *28*, 810.

(13) (a) Aihara, A. *J. Chem. Soc. (Japan)* **1955**, *76*, 492. (b) Pedley, J. B. *Thermochemical Data and Structures of Organic Compounds*; TRC Data Series: College Station, TX, 1994; Vol. 1.

(14) Arshadi, M. R. *J. Chem. Soc., Faraday Trans. I* **1974**, *70*, 1569.

(15) Maier, J. P.; Turner, D. W. *J. Chem. Soc., Faraday Trans.* **2 1973**, *2*, 521.

(16) Lee, J.; Lin, J.; Wu, R. H.; Tzeng, B. *J. Chem. Phys.* **2003**, *118*, 10034.

(17) Lias, S. G. *Ionization Energy Evaluation in NIST Chemistry WebBook, NIST Standard Reference Database Number 69*; Linstrom, P. J.; Mallard, W. G., Eds.; National Institute of Standards and Technology: Gaithersburg, MD, 2005; 20899 (http://webbook.nist.gov).

(18) Hager, J. W.; Wallace, S. C. *Anal. Chem.* **1988**, *60*, 5.

(19) Braun, J. E.; Grebner, Th. L.; Neusser, H. J. *J. Phys. Chem. A* **1998**, *102*, 3273.

(20) Hunter, E. P. L.; Lias, S. G. *J. Phys. Chem. Ref. Data* **1998**, *27*, 413.

(21) Yang, Z.; Ruan, C.; Ahmed, H.; Rodgers, M. T. *Int. J. Mass Spectrom.* **2007**, *265*, 388.

(22) Somers, K. R. F.; Kryachko, E. S.; Ceulemans, A. *Chem. Phys.* **2004**, *301*, 61.

(23) Otero, N.; Moa, M. J. G.; Mandado, M.; Mosquera, R. A. *Chem. Phys. Lett.* **2006**, *428*, 249.

(24) Meot-ner, M.; Liebman, J. F.; Kafafi, S. A. *J. Am. Chem. Soc.* **1988**, *110*, 5937.

(25) Taft, R. W.; Bordwell, F. G. *Acc. Chem. Res.* **1988**, *21*, 463.

(26) Bordwell, F. G.; Zhang, X.; Cheng, J.-P. *J. Org. Chem.* **1991**, *56*, 3216.

(27) Luo, Y. R. *Comprehensive Handbook of Chemical Bond Energies*; CRC Press, Taylor & Francis Group: Boca Raton, FL, 2007.

(28) Ribeiro da Silva, M. A. V.; Ferreira, A. I. M. C. L.; Gomes, J. R. B. *J. Phys. Chem. B* **2007**, *111*, 2052.

(29) Ribeiro da Silva, M. A. V.; Ferreira, A. I. M. C. L.; Gomes, J. R. B. *J. Phys. Chem. B* **2007**, *111*, 6444.

(30) Santos, C. P. F. Ph.D. Thesis, University of Porto, 2004.

(31) Ribeiro da Silva, M. A. V.; Ribeiro da Silva, M. D. M. C.; Pilcher, G. *Rev. Por. Quím.* **1984**, *26*, 163.

(32) Ribeiro da Silva, M. A. V.; Ribeiro da Silva, M. D. M. C.; Pilcher, G. *J. Chem. Thermodyn.* **1984**, *16*, 1149.

(33) Copps, J.; Jessup, R. S.; Van Nes, K. In *Experimental Termochemistry*; Rossini, F. D., Ed.; Interscience: New York, 1956; Vol. 1, Chapter 3.

(34) *Certificate of Analysis Standard Reference Material 39j Benzoic Acid Calorimetric Standard*; NBS, Washington, DC, 1995.

(35) Skinner, H. A.; Snelson, A. *Trans. Faraday Soc.* **1960**, *56*, 1776.

(36) Wagman, D. D.; Evans, W. H.; Parker, V. B.; Shum, R. H.; Halow, F.; Bailey, S. M.; Churney, K. L.; Nuttall, R. L. *J. Phys. Chem. Ref. Data*, **1982**, 11 Supplement 2.

(37) Washburn, E. W. *J. Res. Nalt. Bur. Stand. (U.S.)* **1933**, *10*, 525.

(38) Hubbard, W. N.; Scott, D. W.; Waddington, G. In *Experimental Thermochemistry*; Rossini, F. D., Ed.; Interscience: New York., 1956; Chapter 5; Vol. 1.

(39) Wieser, M. E. *Pure Appl. Chem.* **2006**, *78*, 2051.

(40) Ribeiro da Silva, M. A. V.; Matos, M. A. R.; Amaral, L. M. P. F. *J. Chem. Thermodyn.* **1995**, *27*, 565.

(41) Adedeji, F. A.; Brown, D. L. S.; Connor, J. A.; Leung, M.; Paz-Andrade, M.I.; Skinner, H. A. *J. Organomet. Chem.* **1975**, *97*, 221.

(42) Santos, L. M. N. B. F.; Schröder, B.; Fernandes, O. O. P.; Ribeiro da Silva, M. A. V. *Thermochim. Acta* **2004**, *415*, 15.

(43) Stull, R. D.; Westrum, E. F.; Sinke, G. C. *The Chemical Thermodynamics of Organic Compounds*; Wiley: New York, 1969.

(44) Sabbah, R.; Xu-wu, A.; Chickos, J. D.; Planas Leitão, M. L.; Roux, M. V.; Torres, L. A. *Thermochim. Acta* **1999**, *331*, 93.

(45) Ribeiro da Silva, M. A. V.; Monte, M. J. *Thermochim. Acta* **1990**, *171*, 169.

(46) Baboul, A. G.; Curtiss, L. A.; Redfern, P. C.; Raghavachari, K. *J. Chem. Phys.* **1999**, *110*, 7650.

(47) Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Rassolov, V.; Pople, J. A. *J. Chem. Phys.* **1998**, *109*, 7764.

(48) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision C.01; Gaussian, Inc.: Wallingford, CT, 2004.

(49) Montgomery, J. A., Jr.; Frisch, M. J.; Ochterski, J. W.; Petersson, G. A. *J. Chem. Phys.* **2000**, *112*, 6532.

(50) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(51) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1980**, *37*, 785.

(52) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098.

(53) Perdew, J. P. *Phys. Rev. B* **1986**, *33*, 8822.

(54) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618.

(55) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650.

(56) Rossini, F. D. In *Experimental Thermochemistry*; Rossini, F. D., Ed. Interscience: New York, 1956; Vol. 1,Chapter 14.

(57) Olofsn, G. In *Combustion Calorimetry*; Sunner, S.; Månsson M., Eds.; Pergamon: Oxford, 1979; Chapter 6.

(58) Cox, J. D.; Wagman, D. D.; Medvedev, V. A. *CODATA Key Values for Thermodynamics*; Hemisphere: New York, 1989.

(59) Burkinshaw, P. M.; Mortimer, C.T. *J. Chem. Soc., Dalton Trans* **1984**, 75.

(60) Chase, M. W., Jr. *J. Phys. Chem. Ref. Data* **1998**, 1, Monograph 9.

(61) Pedley, J. B. *Thermochemical Data and Structures of Organic Compounds*; TRC Data Series: College Station, TX, 1994; Vol. 1.

(62) The G3MP2B3 approach and the atomization reaction were used to estimate the gas-phase enthalpies of formation of other compounds used in this work, namely, indene, $\Delta_f H_m^\circ(g) = 153.3$ kJ·mol^{-1}, toluene, $\Delta_f H_m^\circ(g) = 44.5$ kJ·mol^{-1}, pyrrole, $\Delta_f H_m^\circ(g) = 109.5$ kJ·mol^{-1}, 1-methylpyrrole, $\Delta_f H_m^\circ(g) = 103.8$ kJ·mol^{-1}, 2,5-dimethylpyrrole, $\Delta_f H_m^\circ(g) = 40.5$ kJ·mol^{-1}, pyrrolidine, $\Delta_f H_m^\circ(g) = 1.3$ kJ·mol^{-1}. Experimental results for these compounds with the exception of 1-methylpyrrole and 2,5-dimethylpyrrole are given in the text. The experimental $\Delta_f H_m^\circ(g)$ for 1-methylpyrrole and 2,5-dimethylpyrrole are 103.1 ± 0.5 and 39.8 ± 0.8 kJ·mol^{-1}, respectively. The differences between calculated and experimental results are 10.1, 6.0, −1.1,−0.8,−0.7 and−4.7 kJ·mol^{-1}.

(63) Santos, A. F. L. O. M.; Gomes, J. R. B.; Ribeiro da Silva, M. A. V. Manuscript in preparation.

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