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Experimental study on the energetics of two indole derivatives

Standard molar enthalpies of formation of indole-2-carboxylic acid and indole-3-carboxaldehyde

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Abstract The standard ($p^\circ = 0.1$ MPa) molar energies of combustion, $\Delta_c H_m^\circ$, for indole-2-carboxylic acid and indole-3-carboxaldehyde, in the crystalline state, were determined, at $T = 298.15$ K, using a static bomb combustion calorimeter. For both compounds, the vapour pressures as function of temperature were measured, by the Knudsen effusion technique, and the standard molar enthalpies of sublimation, $\Delta_{cr}^\circ H_m^\circ$, at $T = 298.15$ K, were derived by the Clausius–Clapeyron equation. From the experimental results, the standard ($p^\circ = 0.1$ MPa) molar enthalpies of formation in the condensed and gaseous phases, at $T = 298.15$ K, of indole-2-carboxylic acid and indole-3-carboxaldehyde were derived. The results are analysed in terms of structural enthalpic increments.

Keywords Standard molar enthalpy of formation · Standard molar enthalpy of sublimation · Combustion calorimetry · Knudsen effusion technique · Vapour pressures · Indole-2-carboxylic acid · Indole-3-carboxaldehyde

Introduction

The study of compounds containing the indole nucleus has received special attention by the investigators since this moiety integrate a large number of compounds with important biological activity [1–3]. Consequently, the knowledge of the energetic properties of the indole derivatives plays an important contribution for the evaluation of their reactivity and this reason justify our interest on the extension of our previous thermochemical studies [4–7], studying the indole-2-carboxylic acid and the indole-3-carboxaldehyde (Fig. 1). In fact, indole-2-carboxylic acid derivatives have been used in a wide range of applications, since the motor dysfunction, cerebral edema formation or changes tissue brain [8], until its use as antihypertensive [9], antiarrhythmic [10], anticonvulsant [11, 12] or antifungal [13, 14]. On the other hand, indole-3-carboxaldehyde presents antimicrobial activity [15], beyond its use in the production of heterocyclic Schiff bases [16].

In this work, the standard ($p^\circ = 0.1$ MPa) molar enthalpies of combustion, $\Delta_c H_m^\circ$, in oxygen, at $T = 298.15$ K, were determined by static-bomb calorimetry, for indole-2-carboxylic acid and indole-3-carboxaldehyde.

The Knudsen mass-loss effusion technique was used to measure the vapour pressures as a function of temperature for both compounds. From the temperature dependence of the vapour pressure, the molar enthalpies and entropies of sublimation at the mean temperature of the experimental temperature range were derived. Standard molar enthalpies, entropies and Gibbs functions of sublimation, at the temperature of 298.15 K, were calculated.

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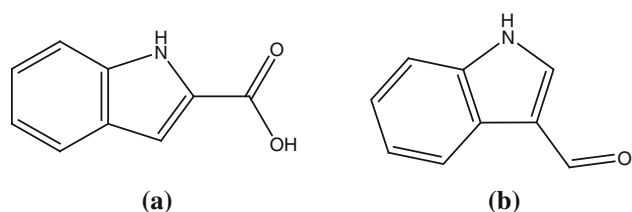


Fig. 1 Structural formulae indole-2-carboxylic acid (a) and indole-3-carboxaldehyde (b)

Experimental

Compounds and purity control

The indole-2-carboxylic acid [CAS 696-04-8] and the indole-3-carboxaldehyde [CAS 487-89-8] were obtained commercially from Aldrich Chemical Co, with initial purity of 0.98 and 0.97, mass fractions, respectively. The compounds were purified twice by sublimation under reduced pressure. The purity of both compounds has been checked by gas–liquid chromatography, performed on an Agilent 4890D Gas Chromatography equipped with an HP-5 column, cross-linked, 5 % diphenyl and 95 % dimethylpolysiloxane (15×0.530 mm i.d \times 1.5 μ m film thickness), and using nitrogen as carrier gas, as being ≥ 0.9998 mass fraction. Purity of the compounds was also checked by the consistent results obtained from the combustion experiments, as well as by the closeness to unity of the carbon dioxide recovery ratios for each compound. The average ratios of the mass of carbon dioxide recovered after combustion, to that calculated from the mass of sample, were (1.00064 ± 0.00022) and (0.99981 ± 0.00045) , respectively, for indole-2-carboxylic acid and indole-3-carboxaldehyde. The uncertainties are the standard deviations of the mean.

Combustion calorimetry

The combustion experiments were performed with an isoperibol calorimetric system equipped with a twin valve static bomb (with an internal volume of 0.290 dm³). The apparatus and the detailed procedure have been described previously [17–19].

Combustion experiments with Thermochemical Standard benzoic acid, NBS Reference Material 39j, having a massic energy of combustion $\Delta_c u = -(26,434 \pm 3)$ J g^{−1}, under certificate conditions [20], were performed to calibrate the bomb. The calibration results were corrected to give the energy equivalent of the calorimeter, $\varepsilon_{\text{calor}}$, corresponding to the average mass of 2,900.0 g of water added to the calorimeter. From six experiments, it was found to be $\varepsilon_{\text{calor}} = (15,551.2 \pm 1.6)$ J K^{−1}.

The combustion experiments were carried out in oxygen at the pressure of 3.04 MPa with 1.00 cm³ of water added to the bomb. The bomb was purged twice to remove air, before being charged with 3.04 MPa of oxygen.

For all experiments, the calorimeter temperatures were measured to $\pm(1 \times 10^{-4})$ K, at time intervals of 10 s, with a S10 four wire calibrated ultra-stable thermistor probe (Thermometrics, Standard Serial No. 1030) and recorded by a high sensitivity nanovolt/microohm meter (Agilent 34420A) interfaced to a computer. Data acquisition and control of the calorimeter were performed using the programme LABTERMO [21]. At least 100 readings of the temperature, at time intervals of 10 s, were taken before the ignition of the samples which was made at $T = (298.150 \pm 0.001)$. After ignition, 100 readings were taken for each the main and after periods.

The crystalline samples were ignited in the pellet form. It was necessary to use *n*-hexadecane (Aldrich, mass fraction >0.999), stored under nitrogen as auxiliary combustion, with indole-3-carboxaldehyde combustion experiments. Its standard massic energy of combustion was determined in our laboratory as, $\Delta_c u^\circ = -(47,150.4 \pm 3.6)$ J g^{−1}. For the cotton thread fuse used, it was considered the empirical formula CH_{1.686}O_{0.843} and $\Delta_c u^\circ = -16,240$ J g^{−1} [22]. In the combustion experiments with a small residue of carbon soot formation inside the crucible, the necessary energetic correction for its formation was based on $\Delta_c u^\circ = -33$ J g^{−1} [22]. The electrical energy for ignition was determined from the change in potential difference across a 1,400 μ F condenser when discharged through the platinum ignition wire. The corrections for nitric acid formation were based on -59.7 kJ mol^{−1} [23], for the molar energy of formation of 0.1 mol dm^{−3} HNO₃(aq) from N₂, O₂, and H₂O(l). All the necessary weightings were made in a Mettler AE 240 balance and corrections from apparent mass to true mass were made. An estimated pressure coefficient of specific energy, $(\partial u/\partial p)_T = -0.2$ J g^{−1} MPa^{−1} at $T = 298.15$ K, a

Table 1 Areas and transmission probability factors for the platinum orifices of the Knudsen effusion apparatus; $l = 0.0125$ mm

	Orifice number	A_o/mm^2	w_o
Small orifices	A1	0.502	0.988
	A2	0.509	0.988
	A3	0.503	0.988
Medium orifices	B4	0.774	0.991
	B5	0.783	0.991
	B6	0.792	0.991
Large orifices	C7	1.099	0.992
	C8	1.125	0.992
	C9	1.131	0.992

typical value for most organic compounds [24], was assumed. For each compound, the massic energy of combustion, $\Delta_c u^\circ$, was calculated by the procedure given by Hubbard et al. [25]. The amounts of the compounds used in each experiment were determined from the total mass of carbon dioxide produced during the experiments,

taking into account that formed from the combustion of the cotton-thread fuse, *n*-hexadecane and that lost due to eventual carbon formation. The densities, at $T = 298.15$ K, were considered for indole-2-carboxylic acid as 1.133 g cm^{-3} [26], and for indole-3-carboxaldehyde as 1.278 g cm^{-3} [27].

Table 2 Combustion experiments of indole-2-carboxylic acid, at $T = 298.15$ K

	1	2	3	4	5	6	7
$m(\text{cpd})/\text{g}$	0.69350	0.72613	0.71651	0.73393	0.74083	0.73686	0.73573
$m'(\text{fuse})/\text{g}$	0.00226	0.00237	0.00287	0.00213	0.00249	0.00249	0.00281
$\Delta T_{\text{ad}}/\text{K}$	1.16784	1.22281	1.20747	1.23615	1.24914	1.24180	1.24080
$\varepsilon_f/\text{JK}^{-1}$	14.13	14.21	14.19	14.23	14.23	14.22	14.22
$\Delta m(\text{H}_2\text{O})/\text{g}$	−4.2	−4.0	−4.7	−6.3	−5.7	−5.5	−7.8
$-\Delta U(\text{IBP})^a/\text{J}$	18,156.71	19,012.48	18,770.38	19,207.96	19,412.96	19,299.98	19,272.46
$\Delta U(\text{fuse})/\text{J}$	36.70	38.49	46.61	34.59	40.44	40.44	45.63
$\Delta U(\text{HNO}_3)/\text{J}$	32.76	31.59	31.77	31.35	33.81	32.91	32.79
$\Delta U(\text{ign})/\text{J}$	0.58	0.59	0.62	0.66	0.65	0.58	0.62
$\Delta U(\text{Carbon})/\text{J}$	0.00	0.00	0.00	0.00	0.00	0.00	0.00
$\Delta U_\Sigma/\text{J}$	14.44	15.21	14.94	15.36	15.56	15.46	15.44
$-\Delta_c u^\circ/\text{J g}^{-1}$	26,060.29	26,065.84	26,066.71	26,060.61	26,083.11	26,071.67	26,067.44
$-\langle \Delta_c u^\circ \rangle = 26,068.0 \pm 2.9 \text{ J g}^{-1}$							

^a $\Delta U(\text{IBP})$ already includes $\Delta U(\text{ign})$

Table 3 Combustion experiments of indole-3-carboxaldehyde, at $T = 298.15$ K

	1	2	3	4	5	6
$m(\text{cpd})/\text{g}$	0.49178	0.49194	0.49872	0.50096	0.49601	0.52643
$m'(\text{fuse})/\text{g}$	0.00246	0.00246	0.00224	0.00226	0.00257	0.00240
$m''(n\text{-hex})/\text{g}$	0.18950	0.22573	0.24084	0.18451	0.19769	0.18492
$\Delta T_{\text{ad}}/\text{K}$	1.55520	1.66485	1.72246	1.55635	1.58808	1.60649
$\varepsilon_f/\text{J K}^{-1}$	14.83	15.05	15.11	14.84	14.91	14.91
$\Delta m(\text{H}_2\text{O})/\text{g}$	−13.5	−11.7	−10.8	−9.6	−11.6	−8.8
$-\Delta U(\text{IBP})^a/\text{J}$	24,119.86	25,833.45	26,733.96	24,163.11	24,642.57	24,947.13
$\Delta U(n\text{-hex})/\text{J}$	8,935.22	10,643.24	11,355.62	8,699.65	9,321.39	8,719.01
$\Delta U(\text{fuse})/\text{J}$	39.95	39.95	36.38	36.70	41.74	38.98
$\Delta U(\text{HNO}_3)/\text{J}$	31.76	29.43	32.84	29.55	29.07	29.01
$\Delta U(\text{ign})/\text{J}$	0.59	0.52	0.55	0.58	0.58	0.52
$\Delta U(\text{Carbon})/\text{J}$	6.93	0.00	17.49	1.32	0.00	21.78
$\Delta U_\Sigma/\text{J}$	13.23	13.83	14.20	13.40	13.49	14.05
$-\Delta_c u^\circ/\text{J g}^{-1}$	30,718.27	30,709.03	30,703.42	30,711.29	30,718.90	30,712.27
$-\langle \Delta_c u^\circ \rangle = 30,712.2 \pm 2.4 \text{ J g}^{-1}$						

^a $\Delta U(\text{IBP})$ already includes $\Delta U(\text{ign})$

$m(\text{cpd})$ is the mass of compound burnt in each experiment; $m'(\text{fuse})$ is the mass of the fuse (cotton) used in each experiment; $m''(n\text{-hex})$ is the mass of the *n*-hexadecane used in each experiment; ΔT_{ad} is the corrected temperature rise; ε_f is the energy equivalent of the contents in the final state; $\Delta m(\text{H}_2\text{O})$ is the deviation of mass of water added to the calorimeter from 2,900.0 g; $\Delta U(\text{IBP})$ is the energy change for the isothermal combustion reaction under actual bomb conditions; $\Delta U(n\text{-hex})$ is the energy of combustion of *n*-hexadecane; $\Delta U(\text{fuse})$ is the energy of combustion of the fuse (cotton); $\Delta U(\text{HNO}_3)$ is the energy correction for the nitric acid formation; $\Delta U(\text{ign})$ is the electric energy for the ignition; $\Delta U(\text{Carbon})$ is the energy correction for the carbon residue soot formation; ΔU_Σ is the standard state correction; $\Delta_c u^\circ$ is the standard massic energy of combustion

The relative atomic masses used were those recommended by the IUPAC Commission in 2009 [28].

Vapour pressures measurements

The vapour pressures of the crystalline indole-2-carboxylic acid and indole-3-carboxaldehyde were measured, at several temperatures, by the mass-loss Knudsen-effusion technique. This apparatus allows the simultaneous operation of nine aluminium effusion cells and has been tested by measuring vapour pressures between 0.1 and 1 Pa, over

temperature ranges of ca. 20 K, of benzoic acid, phenanthrene, anthracene, benzanthrone and 1,3,5-triphenylbenzene [29]. Both, the measured vapour pressures and the derived enthalpies of sublimation of the test substances, are in excellent agreement with the literature results for those compounds. The nine effusion cells are contained in cylindrical holes inside three aluminium blocks, three cells per block. Each block is kept at a constant temperature, different from the other two blocks. For each compound, the measurements were extended through a chosen temperature interval corresponding to measured vapour pressures in the range 0.1–1.0 Pa.

Table 4 Derived standard ($p^\circ = 0.1$ MPa) molar energies of combustion, $\Delta_c U_m^\circ$, standard molar enthalpies of combustion, $\Delta_c H_m^\circ$, and standard molar enthalpies of formation, $\Delta_f H_m^\circ$, for the crystalline compounds at $T = 298.15$ K

Compound	$-\Delta_c U_m^\circ(\text{cr})/\text{kJ mol}^{-1}$	$-\Delta_c H_m^\circ(\text{cr})/\text{kJ mol}^{-1}$	$-\Delta_f H_m^\circ(\text{cr})/\text{kJ mol}^{-1}$
Indole-2-carboxylic acid	$4,201.1 \pm 1.3$	$4,201.7 \pm 1.3$	340.9 ± 1.8
Indole-3-carboxaldehyde	$4,458.2 \pm 1.4$	$4,460.1 \pm 1.4$	81.9 ± 1.8

Table 5 Knudsen effusion results for indole-2-carboxylic acid and indole-3-carboxaldehyde

T/K	t/s	Orifices	m/mg			p/Pa		
			m_{A}	m_{B}	m_{C}	p_{A}	p_{B}	p_{C}
Indole-2-carboxylic acid								
360.11	21,815	A1-B4-C7	3.05	4.58	6.39	0.096	0.094	0.092
362.18	21,815	A2-B5-C8	3.87	5.72	7.92	0.121	0.116	0.111
364.18	21,815	A3-B6-C9	4.55	7.02	9.71	0.146	0.141	0.136
366.12	18,559	A1-B4-C7	5.14	7.60	10.98	0.192	0.184	0.187
368.17	18,559	A2-B5-C8	6.21	9.41	13.25	0.230	0.226	0.221
370.18	18,559	A3-B6-C9	7.29	11.39	16.07	0.277	0.271	0.267
372.12	12,603	A1-B4-C7	6.16	9.16	13.23	0.342	0.329	0.334
374.16	12,603	A2-B5-C8	7.50	11.36	15.89	0.412	0.405	0.393
376.18	12,603	A3-B6-C9	8.60	13.52	19.03	0.485	0.478	0.470
378.12	10,419	A1-B4-C7	9.49	14.42	20.18	0.642	0.632	0.622
380.17	10,419	A2-B5-C8	11.68	17.89	24.75	0.782	0.777	0.747
382.18	10,419	A3-B6-C9	13.59	21.07	29.46	0.935	0.907	0.887
Indole-3-carboxaldehyde								
372.16	25,647	A3-B6-C9	4.50	6.81	9.67	0.126	0.124	0.123
374.14	25,647	A2-B5-C8	5.51	8.52	11.8	0.157	0.157	0.151
376.13	25,647	A1-B4-C7	6.41	10.03	14.28	0.185	0.188	0.188
378.16	22,718	A3-B6-C9	7.30	11.08	15.72	0.233	0.229	0.227
380.16	22,718	A2-B5-C8	8.96	13.89	19.00	0.290	0.291	0.277
382.12	22,718	A1-B4-C7	10.55	16.23	22.60	0.347	0.346	0.338
384.15	10,361	A3-B6-C9	6.28	9.74	13.54	0.442	0.446	0.433
386.14	10,361	A2-B5-C8	7.75	11.89	16.03	0.554	0.551	0.517
388.12	10,361	A1-B4-C7	8.86	13.73	18.95	0.644	0.646	0.627
390.15	10,258	A3-B6-C9	10.26	15.42	21.57	0.736	0.718	0.702
392.16	10,258	A2-B5-C8	12.31	18.99	25.73	0.896	0.896	0.844
394.13	10,258	A1-B4-C7	14.54	22.05	30.73	1.075	1.057	1.035

Table 6 Experimental results for indole-2-carboxylic acid and indole-3-carboxaldehyde, where a and b are from Clausius–Clapeyron equation

Orifices	a	b	$\langle T \rangle / \text{K}$	$p(\langle T \rangle) / \text{Pa}$	$\Delta_{\text{cr}}^{\text{g}} H_{\text{m}}^{\circ}(\langle T \rangle) / \text{kJ mol}^{-1}$	$\Delta_{\text{cr}}^{\text{g}} S_{\text{m}}^{\circ}(\langle T \rangle, p(\langle T \rangle)) / \text{J K}^{-1} \text{mol}^{-1}$
Indole-2-carboxylic acid						
A1-A2-A3	36.41 ± 0.45	$14,135 \pm 166$				
B4-B5-B6	37.24 ± 0.44	$14,267 \pm 163$				
C7-C8-C9	37.18 ± 0.55	$14,251 \pm 204$				
Global results	37.11 ± 0.31	$14,218 \pm 115$	371.14	0.301	118.2 ± 1.0	318.5 ± 2.7
Indole-3-carboxaldehyde						
A1-A2-A3	36.69 ± 0.52	$14,422 \pm 199$				
B4-B5-B6	36.54 ± 0.61	$14,368 \pm 232$				
C7-C8-C9	36.06 ± 0.48	$14,195 \pm 184$				
Global results	36.43 ± 0.33	$14,328 \pm 125$	383.14	0.381	119.1 ± 1.0	310.9 ± 2.6

$\ln(p/\text{Pa}) = a - b(\text{K}/T)$ and $b = \Delta_{\text{cr}}^{\text{g}} H_{\text{m}}^{\circ}(\langle T \rangle) / R$; $R = 8.314472 \text{ J K}^{-1} \text{mol}^{-1}$

In the present work, the vapour pressure was measured between 360 and 382 K for indole-2-carboxylic acid and 372–394 K for indole-3-carboxaldehyde.

In each effusion experiment the loss of mass, Δm , of the samples, during a convenient effusion time period, t , is determined by weighing the effusion cells to $\pm 0.01 \text{ mg}$ before and after the effusion period in a system evacuated to a pressure near $(1 \times 10^{-4}) \text{ Pa}$. At the temperature T of the experiment, the vapour pressure p is calculated by the Eq. (1) where M is the molar mass of the effusing vapour, R is the gas constant, A_0 is the area of the effusion hole and w_0 is the Clausing factor. This factor is calculated by Eq. (2), where l is the thickness of the effusion hole and r its radius.

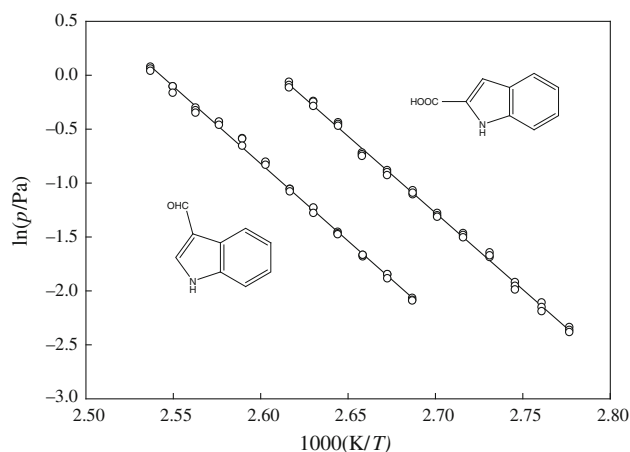
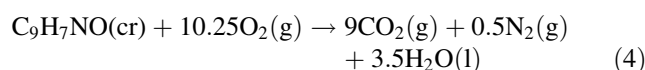
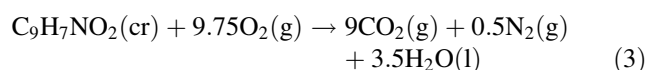
$$p = (\Delta m / A_0 w_0 t) (2\pi RT / M)^{1/2}, \quad (1)$$

$$w_0 = \{1 + (3l/8r)\}^{-1}. \quad (2)$$

The areas and Clausing factors of the effusion orifices, made in platinum foil of 0.0125 mm thickness, are register in Table 1.

Results

Detailed results of all combustion experiments performed for indole-2-carboxylic acid and indole-3-carboxaldehyde are given in Tables 2 and 3, respectively, together with the mean value, $\langle \Delta_c u^{\circ} \rangle$, and its standard deviation. Here, $\Delta_c u^{\circ}$ refers to the idealized combustion reaction described by Eqs. (3) for indole-2-carboxylic acid and (4) for indole-3-carboxaldehyde, $\Delta m(\text{H}_2\text{O})$ is the deviation of the mass of water added to the calorimeter from 2,900.0 g, the mass assigned for $\varepsilon_{\text{calor}}$, ΔU_{Σ} is the correction to the standard state and the remaining terms are as previously described [25].

**Fig. 2** Plots of $\ln(p/\text{Pa})$ against $1/T$ for indole-2-carboxylic acid and indole-3-carboxaldehyde**Table 7** Values of the standard ($p^{\circ} = 0.1 \text{ MPa}$) molar enthalpies, $\Delta_{\text{cr}}^{\text{g}} H_{\text{m}}^{\circ}$, entropies, $\Delta_{\text{cr}}^{\text{g}} S_{\text{m}}^{\circ}$, and Gibbs energies, $\Delta_{\text{cr}}^{\text{g}} G_{\text{m}}^{\circ}$, of sublimation, at $T = 298.15 \text{ K}$, for indole-2-carboxylic acid and indole-3-carboxaldehyde

Compound	$\Delta_{\text{cr}}^{\text{g}} H_{\text{m}}^{\circ} / \text{kJ mol}^{-1}$	$\Delta_{\text{cr}}^{\text{g}} S_{\text{m}}^{\circ} / \text{kJ mol}^{-1}$	$\Delta_{\text{cr}}^{\text{g}} G_{\text{m}}^{\circ} / \text{kJ mol}^{-1}$
Indole-2-carboxylic acid	120.3 ± 1.0	218.0 ± 2.7	55.3 ± 1.3
Indole-3-carboxaldehyde	121.9 ± 1.0	213.1 ± 2.6	58.4 ± 1.3

For the static bomb measurements, as the samples were ignited at $T = (298.150 \pm 0.001)$ K,




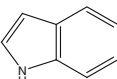
$$\Delta U(\text{IBP}) = -\{\varepsilon_{\text{calor}} + c_p(\text{H}_2\text{O}, \text{l}) \cdot \Delta m(\text{H}_2\text{O}) + \varepsilon_{\text{f}}\} \times \Delta T_{\text{ad}} + \Delta U(\text{ign}), \quad (5)$$

where $\Delta U(\text{IBP})$ is the energy associated to the isotherm bomb process, ε_{f} is the energy of the bomb contents after ignition, $\Delta U(\text{ign})$ is the ignition energy and ΔT_{ad} is the adiabatic temperature rise.

Table 8 Standard ($p^\circ = 0.1$ MPa) molar enthalpies of formation for indole-2-carboxylic acid and indole-3-carboxaldehyde in both crystalline and gaseous phases and standard molar enthalpy of sublimation at $T = 298.15$ K

Compound	$-\Delta_{\text{f}}H_{\text{m}}^\circ(\text{cr})/\text{kJ mol}^{-1}$	$\Delta_{\text{cr}}H_{\text{m}}^\circ/\text{kJ mol}^{-1}$	$\Delta_{\text{f}}H_{\text{m}}^\circ(\text{g})/\text{kJ mol}^{-1}$
Indole-2-carboxylic acid	340.9 ± 1.8	120.3 ± 1.0	-220.6 ± 2.0
Indole-3-carboxaldehyde	81.9 ± 1.8	121.9 ± 1.0	40.0 ± 2.0

Table 9 Experimental standard molar enthalpies of formation in the gaseous state, at $T = 298.15$ K, and enthalpic increments for $-\text{CHO}$ or $-\text{COOH}$ substitution in those heterocycles

Compound	$\Delta_{\text{f}}H_{\text{m}}^\circ(\text{g})/\text{kJ mol}^{-1}$	$\Delta\{\Delta_{\text{f}}H_{\text{m}}^\circ(\text{g})\}/\text{kJ mol}^{-1}$ $-\text{COOH}$	$\Delta\{\Delta_{\text{f}}H_{\text{m}}^\circ(\text{g})\}/\text{kJ mol}^{-1}$ $-\text{CHO}$
Thiophene 	115.0 ± 1.0 [35]		
2-Thiophenecarboxylic acid	-259.2 ± 1.9 [36]	-374.2 ± 2.1	
3-Thiophenecarboxylic acid	-261.8 ± 1.7 [36]	-376.8 ± 2.0	
2-Thiophenecarboxaldehyde	-7.1 ± 1.9 [37]		-122.1 ± 2.1
3-Thiophenecarboxaldehyde	-7.4 ± 1.9 [37]		-122.4 ± 2.1
Furan 	-34.8 ± 0.7 [38]		
2-Furancarboxylic acid	-410.3 ± 2.1 [39]	-375.5 ± 2.2	
3-Furancarboxylic acid	-415.8 ± 1.7 [39]	-381.0 ± 1.8	
2-Furancarboxaldehyde	-151.0 ± 4.6 [38]		-116.2 ± 4.6
3-Furancarboxaldehyde	-151.9 ± 1.1 [40]		-117.1 ± 1.3
Pyrrole 	108.3 ± 0.5 [41]		
2-Pyrrolecarboxylic acid	-286.3 ± 1.7 [42]	-394.6 ± 1.8	
2-Pyrrolecarboxaldehyde	-31.3 ± 1.8 [43]		-139.6 ± 1.9
Indole 	164.3 ± 1.3 [4]		
Indole-2-carboxylic acid	$-220.6 \pm 2.0^{\text{a}}$	-384.9 ± 2.4	
Indole-3-carboxaldehyde	$40.0 \pm 2.0^{\text{a}}$		-124.3 ± 2.4

^a This work

Table 4 lists the derived standard molar energy, $\Delta_{\text{c}}U_{\text{m}}^\circ(\text{cr})$, and enthalpy, $\Delta_{\text{c}}H_{\text{m}}^\circ(\text{cr})$, of combustion and the standard molar enthalpy of formation in condensed state, $\Delta_{\text{f}}H_{\text{m}}^\circ(\text{cr})$, for each one of the two compounds studied, at $T = 298.15$ K. These values are derived taking into account the Eqs. (3) and (4). To obtain $\Delta_{\text{f}}H_{\text{m}}^\circ(\text{cr})$ from $\Delta_{\text{c}}H_{\text{m}}^\circ(\text{cr})$ the standard molar enthalpies of formation of $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O}(\text{l})$, at $T = 298.15$ K, $-(393.51 \pm 0.13)$ kJ mol⁻¹ [30], and $-(285.830 \pm 0.040)$ kJ mol⁻¹ [30], respectively, were used. In accordance with normal thermochemical practice [31, 32], the uncertainties assigned to the standard molar enthalpies of formation are, in each case, twice the overall standard deviation of the mean and include the uncertainties in calibration and in the values of auxiliary quantities used.

The experimental results obtained through the effusion experiments are compiled in Table 5. The subscripts A, B, C of the variables m and p stand, respectively, for the results obtained through the small (A1, A2, A3), the medium (B4, B5, B6), and the large (C7, C8, C9) effusion orifices. The integrated form of the Clausius–Clapeyron equation, $\ln(p/\text{Pa}) = a - b(T/\text{K})^{-1}$, where a is a constant

and $b = \Delta_{\text{cr}}^{\text{g}} H_{\text{m}}^{\circ}(\langle T \rangle)/R$, was used to derive the standard molar enthalpies of sublimation, $\Delta_{\text{cr}}^{\text{g}} H_{\text{m}}^{\circ}(\langle T \rangle)$, at the mean temperature of the experimental temperature range. Table 6 presents, for each series of effusion orifices (A, B, C) and for the global treatment of all results, the parameters of the Clausius–Clapeyron equation, together with the calculated standard deviation and the standard molar enthalpies of sublimation at the mean temperature of the experimental range $T = \langle T \rangle$. The equilibrium pressure at this temperature $p(T = \langle T \rangle)$ and the entropies of sublimation, calculated through the Eq. (6), are also registered in this table.

$$\Delta_{\text{cr}}^{\text{g}} S_{\text{m}}\{\langle T \rangle, p(T = \langle T \rangle)\} = \Delta_{\text{cr}}^{\text{g}} H_{\text{m}}^{\circ}(\langle T \rangle)/\langle T \rangle. \quad (6)$$

The plots of $\ln p = f(1/T)$ for the two compounds studied experimentally are presented in Fig. 2.

Sublimation enthalpies, at $T = 298.15$ K, were derived from the sublimation enthalpies calculated at the mean temperature $\langle T \rangle$ of the experiments, by the Eq. (7).

$$\Delta_{\text{cr}}^{\text{g}} H_{\text{m}}^{\circ}(T = 298.15 \text{ K}) = \Delta_{\text{cr}}^{\text{g}} H_{\text{m}}^{\circ}(\langle T \rangle) + \Delta_{\text{cr}}^{\text{g}} C_{\text{p,m}}^{\circ}(298.15 \text{ K} - \langle T \rangle). \quad (7)$$

The $\Delta_{\text{cr}}^{\text{g}} C_{\text{p,m}}^{\circ}$ values were calculated as -28.44 and $-33.15 \text{ J K}^{-1} \text{ mol}^{-1}$ for indole-2-carboxylic acid and indole-3-carboxaldehyde, respectively, using Eq. (8) proposed by Chickos et al. [33]:

$$\Delta_{\text{cr}}^{\text{g}} C_{\text{p,m}}^{\circ} = -\{0.75 + 0.15 C_{\text{p,m}}^{\circ}(\text{cr})\}. \quad (8)$$

The values of $C_{\text{p,m}}^{\circ}(\text{cr})$ were derived from data of Chickos et al. [34] using an additivity approach.

For each compound, the values, at $T = 298.15$ K, of the standard molar enthalpies of sublimation, the standard molar entropies of sublimation calculated by the Eq. (9), were $p^{\circ} = 10^5$ Pa, and the standard molar Gibbs energies of sublimation, are reported in Table 7.

$$\Delta_{\text{cr}}^{\text{g}} S_{\text{m}}^{\circ}(T = 298.15 \text{ K}) = \Delta_{\text{cr}}^{\text{g}} S_{\text{m}}\{\langle T \rangle, p(\langle T \rangle)\} + \Delta_{\text{cr}}^{\text{g}} C_{\text{p,m}}^{\circ} \ln(298.15 \text{ K}/\langle T \rangle) - R \ln\{p^{\circ}/p(\langle T \rangle)\} \quad (9)$$

The standard molar enthalpies of formation in the gaseous state, at $T = 298.15$ K, were obtained for each compound by the addition of the derived standard molar enthalpies of formation in the crystalline state and the standard molar enthalpies of sublimation. The results are summarized in Table 8.

Discussion

Considering the experimental values obtained for the standard molar enthalpies of formation, in the gaseous phase, of indole-2-carboxylic acid and indole-3-carboxaldehyde and

the available literature values for other five member heterocyclic compounds (N, O, S heteroatoms), it is possible to calculate the enthalpic effects due to the presence of the functional groups $-\text{CHO}$ or $-\text{COOH}$ in those rings.

Table 9 summarizes the experimental values of the standard molar enthalpies of formation, in the gaseous state, available in the literature for thiophene, furan, pyrrole, indole and their carboxaldehyde and carboxylic acid derivatives, as well as the calculated enthalpic increments for the insertion of the $-\text{CHO}$ or $-\text{COOH}$ groups.

The aldehyde group produces, within the experimental uncertainties ascribed to then, similar effects in both positions, 2- and 3-, for furan, thiophene and indole. For pyrrole, the introduction of the $-\text{CHO}$ group in the position 2- of the ring produces a higher stabilizing effect, compared with the other heterocyclic rings, as a consequence of an intramolecular N–H–O bond [42].

Comparing the enthalpic increments inherent to the presence of the substituent $-\text{COOH}$ in the different heterocyclic rings, we can see that for 2-substituted furan and thiophene and 3-substituted thiophene, the enthalpic increments are the same, within experimental uncertainties associated. The presence of this group in the 3-position of furan or in position 2 of pyrrole and indole has a higher stabilizing enthalpic contribution, being this effect much more pronounced for the pyrrole, probably due to a stronger interaction between the pyrrolic NH and the $-\text{COOH}$ group.

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