



Experimental thermochemical study of 5-bromoindole and 5-bromoindoline

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ABSTRACT

The standard ($p^\circ = 0.1$ MPa) massic energies of combustion in oxygen of 5-bromoindole and 5-bromoindoline were determined at $T = 298.15$ K by rotating-bomb calorimetry. These values were used to derive the standard molar enthalpies of combustion and the standard molar enthalpies of formation, in the condensed phase, for these compounds. Further, the standard molar enthalpies of sublimation, at $T = 298.15$ K were determined by Calvet microcalorimetry. The combustion calorimetry results together with those from the Calvet microcalorimetry, were used to derive the standard molar enthalpies of formation, at $T = 298.15$ K, in the gaseous phase.

Compound	$-\Delta_c H_m^\circ / (\text{kJ} \cdot \text{mol}^{-1})$	$\Delta_{\text{cr}}^\circ H_m^\circ / (\text{kJ} \cdot \text{mol}^{-1})$
5-Bromoindole (cr)	4079.9 ± 2.3	92.3 ± 2.3
5-Bromoindoline (cr)	4321.1 ± 2.5	88.0 ± 1.9

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1. Introduction

Bromoindoles are compounds with high potential for applications in various domains, especially in the electrochemical industry as electrocatalysts, anode materials in batteries, anticorrosion coating, and fast response potentiometric sensors [1,2]. These compounds have also attracted great attention in pharmacology, mainly because of their ability to develop antifungal and antibacterial agents, but also as candidates for anti-oxidant, direct oxidation/reduction of biomolecules, and other biological activities [1–4]. Due to their presence in water and soil as persistent organic pollutants, these organobromine compounds have also been the focus of considerable research work to determine their toxicity effects on the environment [4].

In this work, the standard ($p^\circ = 0.1$ MPa) molar enthalpies of formation in the solid state, at $T = 298.15$ K, of 5-bromoindole and 5-bromoindoline, represented in figure 1, were determined from the values of the standard molar energies of combustion. The standard molar enthalpies of sublimation, at $T = 298.15$ K, were measured by Calvet microcalorimetry. From these two sets of results, the standard molar enthalpies of formation in the gaseous state, at the temperature 298.15 K, were derived.

The derived standard molar enthalpies of formation of these two bromo derivatives are discussed in terms of enthalpic increments and interpreted in terms of molecular structure.

2. Experimental

2.1. Compounds and purity control

5-Bromoindole [CAS 10075-50-0] and 5-bromoindoline [CAS 22190-33-6] were obtained commercially from Aldrich Chemical Co., with an initial mass fraction purity of 0.993 and 0.997, respectively. In order to assure a minimum mass fraction purity of 0.999, they were further purified by repeated sublimations under reduced pressure. No impurities were detected by g.l.c.

The relative atomic masses recommended by the IUPAC Commission in 2005 [5] were used in the calculations of all the molar quantities.

2.2. Combustion calorimetry

The standard massic energies of combustion of these two bromo derivatives were measured by rotating-bomb calorimetry, whose apparatus and operating technique were previously described in the literature [6–8].

The twin-valve bomb used, originally constructed at the University of Lund according to the design of Sunner [9], is made of stainless steel, has an internal volume of 0.258 dm^3 and it is internally lined with platinum with all the internal fittings made in platinum. Both compounds were burned in a pellet form. Due to its high volatility, it was necessary in the experiments with 5-bromoindole to enclose the pellets of this compound in sealed polyester bags made of melinex (0.025 mm of thickness) with massic energy of

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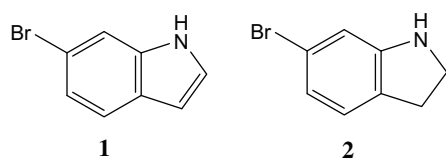


FIGURE 1. Structural formula of 5-bromoindole (1) and 5-bromoindoline (2).

combustion $\Delta_c u^\circ = -(22902 \pm 5) \text{ J} \cdot \text{g}^{-1}$ [10], a value confirmed in our laboratory. Since the combustion experiments of 5-bromoindoline yielded a small amount of carbon soot, in some of those experiments, dried *n*-hexadecane (Aldrich Gold Label, mass fraction > 0.999), stored under nitrogen, with massic energy of combustion $\Delta_c u^\circ = -(47150.4 \pm 1.3) \text{ J} \cdot \text{g}^{-1}$, a value determined in our laboratory, was used for auxiliary combustion.

In all the experiments, the bomb was purged twice with oxygen to remove air, before being charged with 3.04 MPa of oxygen. Aqueous solutions (20.00 cm^3) of As_2O_3 with concentrations of $(0.09050 \text{ and } 0.09119) \text{ mol} \cdot \text{dm}^{-3}$ in the experiments with 5-bromoindole and of $0.09168 \text{ mol} \cdot \text{dm}^{-3}$ in the combustion of 5-bromoindoline were placed in the bomb to reduce all the bromine produced in the combustion to hydrobromic acid.

Water was added to the calorimeter from a weighed perspex vessel. As the mass of water was slightly different in each experiment, corrections were made to the energy equivalent of the calorimeter for the deviation from the average mass of 5222.5 g. The calorimeter temperatures were measured to $\pm(1 \cdot 10^{-4}) \text{ K}$, 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 when at least 100 readings at time intervals of 10 s were taken, after the start of the experiment, by the discharge of a $1400 \mu\text{F}$ capacitor through the platinum ignition wire, and using a cotton thread fuse, with an empirical formula $\text{CH}_{1.686}\text{O}_{0.843}$ and with $\Delta_c u^\circ(\text{cotton}) = -16250 \text{ J} \cdot \text{g}^{-1}$ [11], a value also previously confirmed in our laboratory. The temperature of the ignition was chosen so that the final temperature would be as close as possible to $T = 298.15 \text{ K}$. The rotation of the bomb was started when the temperature rise of the main period reached about 0.63 of its total value and was continued throughout the experiment. With this procedure, the frictional work due to the rotation of the bomb is automatically accounted in the temperature corrections for the work of water stirring and for the heat exchanged with the sur-

rounding isothermal jacket [12]. After ignition, 100 readings were taken for the main and for the after periods. In all the experiments, data acquisition was performed by means of the LABTHERMO program [13].

At the end of the experiment, the extent of the oxidation of $\text{As}_2\text{O}_3(\text{aq})$ was determined by titration with a standardized iodine solution, and the nitric acid formed was analysed by Devarda's alloy method [14]. The energy of oxidation of aqueous As_2O_3 to As_2O_5 , $\Delta U(\text{As}_2\text{O}_3)$, was calculated as described by Hu *et al.* [15], using the enthalpies of oxidation of $\text{As}_2\text{O}_3(\text{aq})$ by Br_2 [16] and the thermal effects of mixing $\text{As}_2\text{O}_5(\text{aq})$ with strong acids [17].

The corrections for nitric acid formation were based on $-59.7 \text{ kJ} \cdot \text{mol}^{-1}$, for the molar energy of formation of $0.1 \text{ mol} \cdot \text{dm}^{-3} \text{ HNO}_3(\text{aq})$ from $\text{N}_2(\text{g})$, $\text{O}_2(\text{g})$, and $\text{H}_2\text{O}(\text{l})$ [18].

The amount of $\text{H}_2\text{PtBr}_4(\text{aq})$ formed was determined from the mass loss of the platinum crucible and its supporting ring, and the corresponding energy correction was based on $\Delta_f H_m^\circ(\text{H}_2\text{PtBr}_4, \text{aq}) = -(368.2 \pm 0.1) \text{ kJ} \cdot \text{mol}^{-1}$ [18].

In the combustion experiments with carbon residue soot formation, if all the residue stayed inside the crucible and none was in the combustion solution, the carbon was quantified by weighing the crucible before and after calcinations, and the necessary energetic corrections for its formation were based on $\Delta_c u^\circ = -33 \text{ kJ} \cdot \text{g}^{-1}$ [19]. If the carbon residue was present on other parts of the bomb or in the solution, the experiment was discontinued. All the necessary weighing was made in a Mettler Toledo 240 balance, sensitivity $\pm(1 \cdot 10^{-5}) \text{ g}$, and corrections from apparent mass to true mass were made. For each compound an estimated pressure coefficient of massic energy, $(\partial u / \partial p)_T$, at $T = 298.15 \text{ K}$, was assumed to be $-0.2 \text{ J} \cdot \text{g}^{-1} \cdot \text{MPa}^{-1}$, a typical value for most organic compounds [20]. For both compounds, ΔU_{Σ} , the standard state corrections and the heat capacities of the bomb contents, ε_i and ε_f , were calculated by the procedure given by Bjellerup [21].

The energy equivalent of the calorimeter was determined by combustion of Thermochemical Standard benzoic acid, sample NBS 39j, with $\Delta_c u = -(26434 \pm 3) \text{ J} \cdot \text{g}^{-1}$ [22], without rotation of the bomb and following the same procedure described in the literature [11]. The energy equivalent of the calorimeter, for a reference mass of water of 5222.5 g, was found to be $\varepsilon_{\text{cal}} = (25164.0 \pm 2.1) \text{ J} \cdot \text{K}^{-1}$, as the average of six combustion experiments with benzoic acid, where the uncertainty quoted is the standard deviation of the mean.

TABLE 1
Combustion experiment data, at $T = 298.15 \text{ K}$, of 5-bromoindole

	1	2	3	4	5	6
$m(\text{cpd})/\text{g}$	0.94908	0.93446	0.97264	0.89428	0.90068	0.71480
$m'(\text{fuse})/\text{g}$	0.00320	0.00330	0.00350	0.00294	0.00347	0.00360
$m''(\text{melinex})/\text{g}$	0.04562	0.05004	0.04683	0.04275	0.03806	0.03973
T_i/K	297.2923	297.3006	297.2705	297.3412	297.3408	297.4987
T_f/K	298.1521	298.1524	298.1551	298.1524	298.1554	298.1560
$\Delta T_{\text{ad}}/\text{K}$	0.84408	0.83540	0.86666	0.79440	0.79705	0.64162
$\varepsilon_i/(\text{J} \cdot \text{K}^{-1})$	93.68	93.69	93.71	93.65	93.70	93.55
$\varepsilon_f/(\text{J} \cdot \text{K}^{-1})$	92.43	92.40	92.33	92.41	92.45	92.33
$\varepsilon(\text{calor})_{\text{corr}}/(\text{J} \cdot \text{K}^{-1})$	25173.2	25168.6	25172.8	25168.6	25156.9	25169.9
$\Delta m(\text{H}_2\text{O})/\text{g}$	2.2	1.1	2.1	1.1	-1.7	1.4
$-\Delta U(\text{IBP})/\text{J}$	21326.02	21102.84	21896.20	20067.12	20124.72	16208.34
$\Delta U(\text{fuse})/\text{J}$	51.97	53.59	56.84	47.75	56.35	58.46
$\Delta U(\text{melinex})/\text{J}$	1044.73	1145.94	1072.60	979.16	871.56	909.94
$\Delta U(\text{HNO}_3)/\text{J}$	36.54	30.21	31.46	28.89	37.01	31.64
$\Delta U(\text{As}_2\text{O}_3)/\text{J}$	406.85	394.31	444.59	356.84	387.33	302.83
$\Delta U(\text{ign})/\text{J}$	1.27	1.29	1.29	1.23	1.28	1.21
$\Delta U(\text{H}_2\text{PtBr}_4)/\text{J}$	0.00	0.12	0.04	0.03	0.01	0.00
$\Delta U(\text{carb})/\text{J}$	0	0	0	0	0	0
$\Delta U_{\Sigma}/\text{J}$	47.45	47.14	48.64	44.84	44.74	36.30
$-\Delta_c u^\circ/(\text{J} \cdot \text{g}^{-1})$	20797.49	20794.39	20811.43	20809.60	20792.87	20801.87
$-(\Delta_c u^\circ) = (20801.3 \pm 3.2) \text{ J} \cdot \text{g}^{-1}$						

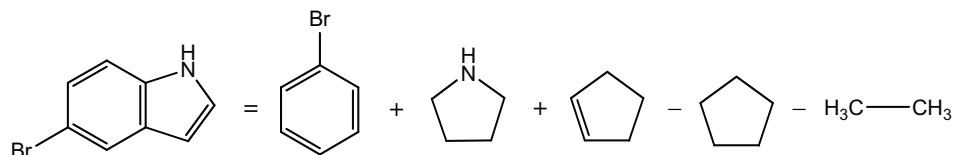
^a $\Delta U(\text{IBP})$ includes $\Delta U(\text{ign})$.

2.3. Calvet microcalorimetry

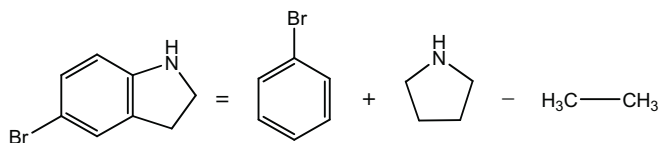
The standard molar enthalpies of sublimation of 5-bromoindole and 5-bromoindoline were measured using the “vacuum sublimation drop microcalorimetric method” of Skinner *et al.* [23]. The apparatus and technique have been recently described [24].

Samples of about 5 mg of each compound, contained in thin glass capillary tubes sealed at one end, were dropped from room temperature into the hot zone of the calorimeter, a Calvet High Temperature Microcalorimeter (Setaram, HT 1000D), held at $T = 360$ K for 5-bromoindole and at $T = 339$ K for 5-bromoindoline, and then removed from the hot zone by vacuum sublimation. 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 sublimation at the experimental temperature were corrected to $T = 298.15$ K using $\Delta_{298.15\text{ K}}^{\circ} H_{\text{m}}^{\circ}(\text{g})$ estimated by a group method based on the values of Stull *et al.* [25]. The scheme applied for 5-bromoindole was



and for 5-bromoindoline the following scheme was used:



which yield the following corrections: for 5-bromoindole, $\Delta_{298.15\text{ K}}^{360.0\text{ K}} H_{\text{m}}^{\circ}(\text{g}) = 8.23 \text{ kJ} \cdot \text{mol}^{-1}$, while for 5-bromoindoline, $\Delta_{298.15\text{ K}}^{339.4\text{ K}} H_{\text{m}}^{\circ}(\text{g}) = 6.17 \text{ kJ} \cdot \text{mol}^{-1}$.

The calorimeter was calibrated *in situ* with naphthalene, using the same experimental procedure as for the compounds, and using the value of $\Delta_{\text{cr}}^{\circ} H_{\text{m}}^{\circ} = (72.60 \pm 0.60) \text{ kJ} \cdot \text{mol}^{-1}$ [26] for the standard molar enthalpy of sublimation of naphthalene, at $T = 298.15$ K. The calibration constants of the calorimeter, k_{cal} , were obtained as the averages of six independent experiments at $T = 360$ K: $k_{\text{cal}} = 1.0049 \pm 0.0079$ and at $T = 339$ K: $k_{\text{cal}} = 0.9903 \pm 0.0037$.

3. Results and discussion

Tables 1 and 2 list the detailed combustion calorimetry experiment data for each compound, where the symbols have been defined elsewhere [15,21,27]. $\Delta m(\text{H}_2\text{O})$ is the deviation in the mass of water added to the calorimeter from 5222.5 g, which is the mass

assigned to $\varepsilon(\text{calor})$. The values of the energy associated with the isothermal bomb process, $\Delta U(\text{IBP})$, were calculated using the expression

$$\Delta U(\text{IBP}) = -\{\varepsilon(\text{calor}) + \Delta m(\text{H}_2\text{O})c_p(\text{H}_2\text{O}, \text{l})\}\Delta T_{\text{ad}} + \varepsilon_i(T_i - 298.15\text{ K}) + \varepsilon_f(298.15\text{ K} - T_i - \Delta T_{\text{ad}}) + \Delta U(\text{ign}),$$

where ΔT_{ad} is the adiabatic temperature rise.

TABLE 2
Combustion experiment data, at $T = 298.15$ K, of 5-bromoindoline

	1	2	3	4	5	6
$m(\text{cpd})/\text{g}$	0.75758	0.69215	0.76703	0.90928	0.48810	0.62299
$m'(\text{fuse})/\text{g}$	0.00330	0.00283	0.00299	0.00293	0.00332	0.00298
$m''(\text{hexad.})/\text{g}$					0.08736	0.12066
T_i/K	297.5206	297.521	297.4541	297.3264	297.5475	297.3669
T_f/K	298.2078	298.1502	298.1491	298.1468	298.1596	298.1604
$\Delta T_{\text{ad}}/\text{K}$	0.67200	0.61260	0.67869	0.80414	0.59673	0.77756
$\varepsilon_i/(\text{J} \cdot \text{K}^{-1})$	92.12	93.55	93.62	93.75	93.56	93.75
$\varepsilon_f/(\text{J} \cdot \text{K}^{-1})$	90.95	92.37	92.43	92.67	92.67	93.01
$\varepsilon(\text{calor})_{\text{corr}}/(\text{J} \cdot \text{K}^{-1})$	25166.9	25173.6	25172.8	25174.5	25167.3	25148.1
$\Delta m(\text{H}_2\text{O})/\text{g}$	0.7	2.3	2.1	2.5	0.8	−3.8
$-\Delta U(\text{IBP})/\text{J}$	16972.71	15477.40	17146.80	20317.94	15072.63	19625.78
$\Delta U(\text{fuse})/\text{J}$	53.59	45.96	48.56	47.58	53.92	48.40
$\Delta U(\text{hexad.})/\text{J}$					4118.41	5689.16
$\Delta U(\text{HNO}_3)/\text{J}$	33.31	29.13	24.48	38.27	26.33	28.14
$\Delta U(\text{As}_2\text{O}_3)/\text{J}$	346.59	310.10	329.29	387.49	215.35	257.58
$\Delta U(\text{ign})/\text{J}$	1.30	1.28	1.29	1.29	1.29	1.28
$\Delta U(\text{H}_2\text{PtBr}_4)/\text{J}$	0.05	0.01	0.02	0.02	0.02	0.10
$\Delta U(\text{carb})/\text{J}$	13.20	26.40	9.90	29.70	19.80	14.85
$\Delta U_{\Sigma}/\text{J}$	34.52	31.60	35.13	41.29	28.70	37.26
$-\Delta_c u^{\circ}/(\text{J} \cdot \text{g}^{-1})$	21803.44	21797.30	21797.35	21811.75	21818.68	21798.09
$-(\Delta_c u^{\circ}) = (21804.4 \pm 3.6) \text{ J} \cdot \text{K}^{-1}$						

$m(\text{cpd})$, $m'(\text{fuse})$, $m''(\text{melinex})$, and $m'''(\text{hexad.})$ are the mass of compound burnt, the mass of fuse (cotton) used, the mass of melinex and the mass of *n*-hexadecane, respectively, used in each experiment; T_i is the initial temperature rise; T_f is the final temperature rise; ΔT_{ad} is the corrected temperature rise; ε_i is the energy equivalent of contents in the initial state; ε_f is the energy equivalent of contents in the final state; $\varepsilon(\text{calor})_{\text{corr}}$ is the energy equivalent of the calorimeter corrected to the mass of water used; $\Delta m(\text{H}_2\text{O})$ is the deviation of mass of water added to the calorimeter from 5222.5 g; $\Delta U(\text{IBP})$ is the energy change for the isothermal combustion reaction under actual bomb conditions; $\Delta U(\text{fuse})$ is the energy of combustion of the fuse (cotton); $\Delta U(\text{melinex})$ is the energy combustion of the melinex; $\Delta U(\text{hexad.})$ is the energy of combustion of the *n*-hexadecane; $\Delta U(\text{HNO}_3)$ is the energy correction for the nitric acid formation; $\Delta U(\text{As}_2\text{O}_3)$ is the energy of oxidation of the aqueous solution of As_2O_3 ; $\Delta U(\text{ign})$ is the electrical energy for ignition; $\Delta U(\text{H}_2\text{PtBr}_4)$ is the energy correction for the formation of the platinum complex; $\Delta U(\text{carb})$ is the energy correction for carbon soot formation; ΔU_{Σ} is the standard state correction and $\Delta_c u^{\circ}$ is the standard massic energy of combustion.

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

In these tables, the mean values of the standard massic energies of combustion of the compounds under study are also registered, $\langle \Delta_c u^\circ \rangle$, where the uncertainties represent the standard deviation of the means. The results refer to the combustion reaction (1) for 5-bromoindole and (2) for 5-bromoindoline:



Table 3 lists the derived standard ($p^\circ = 0.1$ MPa) molar energies and enthalpies of combustion, and standard molar enthalpies of formation, in condensed phase, at $T = 298.15$ K. In accordance with the normal thermochemical practice, the uncertainties assigned are twice the overall standard deviation of the mean and include the uncertainties in calibration and in the values of the auxiliary quantities used. To derive $\Delta_f H_m^\circ$ from $\Delta_c H_m^\circ$, the values $\Delta_f H_m^\circ(\text{H}_2\text{O}, \text{l}) = -(285.830 \pm 0.04) \text{ kJ} \cdot \text{mol}^{-1}$ [19], $\Delta_f H_m^\circ(\text{CO}_2, \text{g}) = -(393.51 \pm 0.13) \text{ kJ} \cdot \text{mol}^{-1}$ [19], and $\Delta_f H_m^\circ(\text{HBr} \cdot 600\text{H}_2\text{O}, \text{l}) = -(120.924 \pm 0.005) \text{ kJ} \cdot \text{mol}^{-1}$ [18,19] are used.

The values of the standard molar enthalpies of sublimation at $T = 298.15$ K, obtained by Calvet microcalorimetry, and the respective uncertainties, which are twice the standard deviation from the mean and include the uncertainties in calibration, are given in table 4.

Table 5 summarizes the values of the standard molar enthalpies of formation in gaseous phase, $\Delta_f H_m^\circ(\text{g})$, derived from the standard molar enthalpies of formation in the condensed phases and the standard molar enthalpies of sublimation.

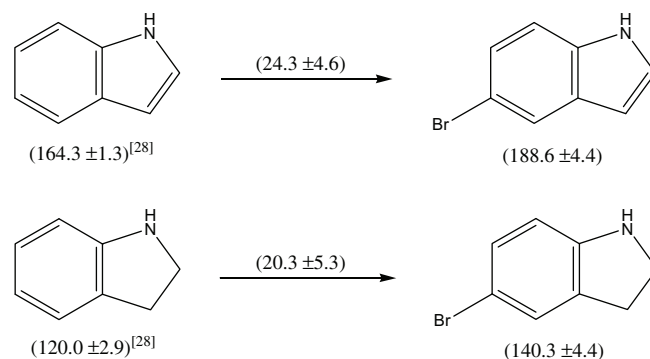
The standard molar enthalpies of formation obtained in this work, together with the literature values for indole $\Delta_f H_m^\circ(\text{indole}) = (164.3 \pm 1.3) \text{ kJ} \cdot \text{mol}^{-1}$ [28], and indoline, $\Delta_f H_m^\circ(\text{indoline}) = (120.0 \pm 2.9) \text{ kJ} \cdot \text{mol}^{-1}$ [28], enable us to establish the enthalpic increment for the –Br substitution in position 5 of indole and indoline molecules. As shown in Scheme 1, the

enthalpic increment due to the introduction of the bromo in indole is (24.3 ± 4.6) and for indoline is (20.3 ± 5.3) , which can be considered identical within the experimental uncertainties.

These results are in agreement with the enthalpic increment found for the introduction of the –Br in other aromatic rings, as

shown in Scheme 2 with the available literature data for bromobenzene [29], bromoanilines [30], and bromopyridines [31,32].

Scheme 3 shows that the enthalpies of hydrogenation, in the gaseous phase, of indole to indoline and of 5-bromoindole to 5-bromoindoline are the same, within the associated uncertainties, showing internal consistency of the experimental results obtained in this work.



Scheme 1. Enthalpic effect due to the introduction of a bromo atom in position 5 of the indole and indoline.

TABLE 3

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, $\Delta_f H_m^\circ$, in condensed phase, at $T = 298.15$ K

Compound	$-\Delta_c U_m^\circ / (\text{kJ} \cdot \text{mol}^{-1})$	$-\Delta_c H_m^\circ / (\text{kJ} \cdot \text{mol}^{-1})$	$\Delta_f H_m^\circ(\text{cr}) / (\text{kJ} \cdot \text{mol}^{-1})$
5-Bromoindole (cr)	4078.0 ± 2.3	4079.9 ± 2.3	96.3 ± 3.7
5-Bromoindoline (cr)	4318.6 ± 2.5	4321.7 ± 2.5	52.3 ± 4.0

TABLE 4

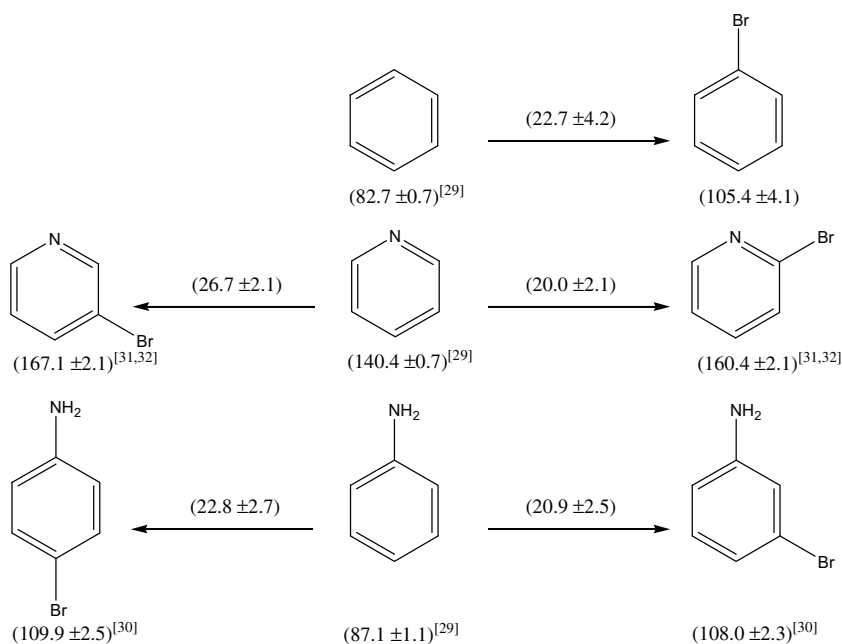
Standard ($p^\circ = 0.1$ MPa) molar enthalpies of sublimation, at $T = 298.15$ K, determined by microcalorimetry

Compound	Number of experiments	T/K	$\Delta_{\text{cr}}^{g,T} H_m^\circ / (\text{kJ} \cdot \text{mol}^{-1})$	$\Delta_{298.15\text{K}}^{g,T} H_m^\circ(\text{g}) / (\text{kJ} \cdot \text{mol}^{-1})$	$\Delta_f H_m^\circ(T = 298.15\text{ K}) / (\text{kJ} \cdot \text{mol}^{-1})$
5-Bromoindole	5	360.0	100.55 ± 0.47	8.23	92.3 ± 2.3
5-Bromoindoline	5	339.4	93.70 ± 0.57	5.70	88.0 ± 1.9

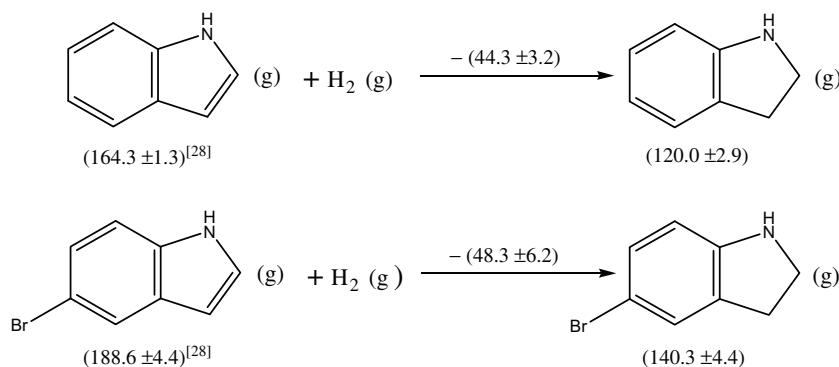
TABLE 5

Derived standard ($p^\circ = 0.1$ MPa) molar enthalpies of formation, and of phase transition, at $T = 298.15$ K

Compound	$\Delta_f H_m^\circ(\text{cr}) / (\text{kJ} \cdot \text{mol}^{-1})$	$\Delta_{\text{cr}}^{g,T} H_m^\circ / (\text{kJ} \cdot \text{mol}^{-1})$	$\Delta_f H_m^\circ(\text{g}) / (\text{kJ} \cdot \text{mol}^{-1})$
5-Bromoindole	96.3 ± 3.7	92.3 ± 2.3	188.6 ± 4.4
5-Bromoindoline	52.3 ± 4.0	88.0 ± 1.9	140.3 ± 4.4



Scheme 2. Enthalpic effect due to introduction of a bromo atom in benzene, pyridine, and aniline.



Scheme 3. Enthalpies of hydrogenation of indole and of indoline.

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