

Experimental and computational study on the thermochemistry of the isomers of iodoaniline and diiodoaniline

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Abstract

The gas-phase standard molar enthalpies of formation of the three monoiodoanilines were derived from the enthalpies of combustion in the condensed phases, measured by rotating-bomb calorimetry and their enthalpies of sublimation/vaporization obtained by Calvet microcalorimetry at $T = 298.15$ K. The standard enthalpies of formation for these compounds and for the diiodoaniline isomers were determined by DFT calculations. The theoretical calculations were performed with the B3LYP/6-31G(d):SBKJ-VDZ and B3LYP/6-311G(2d,2p):SBKJ-VDZ approaches. Estimated values are in excellent agreement with the reported experimental numbers derived in the present Letter.

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1. Introduction

The discovery and development of conducting polymers was one of the important achievements of Chemistry of the late decades of the XX Century, which was recognized by the attribution of the Nobel Prize of Chemistry in 2000 to A.G. MacDiarmid, H. Shirakawa and A.J. Heeger. Among the compounds showing such properties are the polyanilines which originate stable conjugated polymers. Halogenated anilines have also been used in the study of conducting polymers, which have important commercial applications such as sensors, batteries and chemically modified electrodes [1].

The polymers synthesized from iodoaniline are being applied [2] on steel surfaces by electrodeposition as a corrosion protection. These compounds are also frequently used in the manufacturing of pesticides and herbicides, dyes, pharmaceuticals and other industrial chemical intermediates, and some of them are highly toxic, potential mutagenic and carcinogenic substances. Their toxicity associated with exposure to halogenated aniline includes methemoglobinemia, splenotoxicity, hepatotoxicity, and nephrotoxicity [3].

Despite the large fields of application and interest of the iodoanilines, there are very few papers on its structure, energetics and spectroscopic characterization.

In this work, we have determined the standard molar enthalpies of formation, in gaseous state, at $T = 298.15$ K, of three isomers of monoiodoaniline. Those values were derived from the results of measurements of the standard ($p^0 = 0.1$ MPa) molar enthalpies of combustion, in oxygen, at $T = 298.15$ K, by rotating bomb combustion calorimetry, in condensed phase, and from the values for the standard molar enthalpies of vaporization or sublimation at the temperature of 298.15 K, measured by Calvet microcalorimetry. The obtained values of standard molar enthalpies of formation, in gaseous state, of 2-, 3- and 4-iodoaniline were compared with values estimated by the Cox scheme [4] and by Computational Thermochemical methods.

2. Experimental details

2.1. Materials and purity control

The 2-iodobenzoic acid [CAS 88-67-5] and the isomers of iodoanilines studied in this work were obtained commercially from Aldrich Chemical. 2-Iodoaniline [CAS 615-43-

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0], 4-iodoaniline [CAS 540-37-4] and 2-iodobenzoic acid were purified by vacuum sublimation; 3-iodoaniline [CAS 626-01-7] was purified by distillation under reduced pressure, and was stored under nitrogen. All the samples of iodoaniline isomers and 2-iodobenzoic acid were stored protected from light. The purities of the samples of 2-iodobenzoic acid and 2- and 4-iodoaniline were checked by DSC using the fractional fusion technique [5] and the one of 3-iodoaniline was checked by GLC. Details of the DSC experimental procedure are given in the [Supplementary Data](#). The recorded thermograms did not show any phase transitions between $T = 298$ K and the melting temperature of the samples. The enthalpies and temperatures of fusion were computed from the DSC thermograms, for 2-iodoaniline $\Delta_{\text{cr}}^{\text{f}} H_{\text{m}} (T_{\text{fus}} = 329.6 \pm 0.05 \text{ K}) = (19.38 \pm 0.07) \text{ kJ mol}^{-1}$ and for 4-iodoaniline $\Delta_{\text{cr}}^{\text{f}} H_{\text{m}} (T_{\text{fus}} = 336.0 \pm 0.09 \text{ K}) = (16.94 \pm 0.07) \text{ kJ mol}^{-1}$; the enthalpies and temperatures of fusion found in the literature are $\Delta_{\text{cr}}^{\text{f}} H_{\text{m}} (T_{\text{fus}} = 333.0 \text{ K}) = 18.4 \text{ kJ mol}^{-1}$ [6], $\Delta_{\text{cr}}^{\text{f}} H_{\text{m}} = 13.95 \text{ kJ mol}^{-1}$ [7] and $T_{\text{fus}} = 328\text{--}331 \text{ K}$ [8] for 2-iodoaniline, and $\Delta_{\text{cr}}^{\text{f}} H_{\text{m}} (T_{\text{fus}} = 334.0 \text{ K}) = 18.5 \text{ kJ mol}^{-1}$ [6], $\Delta_{\text{cr}}^{\text{f}} H_{\text{m}} = 15.10 \text{ kJ mol}^{-1}$ [7] and $T_{\text{fus}} = 334\text{--}336 \text{ K}$ [8] for 4-iodoaniline.

The specific densities were $\rho = 1.73 \text{ g cm}^{-3}$, $\rho = 1.821 \text{ cm}^{-3}$ [8], $\rho = 1.71 \text{ g cm}^{-3}$ [8] for 2-, 3- and 4-iodoaniline, respectively, and $\rho = 2.25 \text{ cm}^{-3}$ [8] for 2-iodobenzoic acid.

The relative atomic masses used throughout this Letter were those recommended by the IUPAC Commission in 2001 [9].

2.2. Combustion calorimetry

The combustion of the isomers of iodoaniline was made as suggested by Carson et al. [10] who applied the rotating-bomb calorimetry to the combustion of four iodomethanes using a technique in which the iodine produced in the combustion process is dissolved in aqueous potassium iodide. This procedure was also previously used in our Laboratory in the combustion of 2- and 4-iodobenzoic acids [11,12] by rotating-bomb calorimetry.

The rotating-bomb calorimeter used in these experiments was developed by Sunner at the University of Lund, Sweden. Both the apparatus and the operating technique have been previously described [13,14] and are presented in detail in the [Supplementary Data](#).

The energy equivalent of the calorimeter, determined from six combustion experiments of benzoic acid (NIST Standard Reference Material 39j), in oxygen at $p = 3.04 \text{ MPa}$, with 1.00 cm^3 of water added to the bomb, was $\varepsilon(\text{calor}) = (25165.8 \pm 1.7) \text{ J K}^{-1}$. The calorimeter was recalibrated by combustion of benzoic acid in the presence of a mass of 1.0 g of solid iodine contained in sealed polyester bags made from Melinex[®] (0.025 mm thickness) and a volume of 10.00 cm^3 of an aqueous solution of KI 0.8995. From seven calibration experiments, the value of energy effective equivalent with its standard deviation of the mean was $\varepsilon(\text{calor})_{\text{ef.}} = (25166.5 \pm 1.5) \text{ J K}^{-1}$. The calibration

results were corrected to give the energy equivalent, $\varepsilon(\text{calor})$, corresponding to the average mass of water added to the calorimeter: 5222.5 g .

The accuracy of the combustion calorimetry for organic iodine compounds was checked, by measuring the energy of combustion of the recommended test substance [15], 2-iodobenzoic acid, in the presence of an aqueous solution of KI $0.8995 \text{ mol dm}^{-3}$, yielding $\Delta_{\text{c}} u^{\circ} = -(12772.5 \pm 1.7) \text{ J g}^{-1}$ in good agreement with the recommended value $\Delta_{\text{c}} u^{\circ} = -(12771.3 \pm 2.4) \text{ J g}^{-1}$ [15].

The solid 2- and 4-iodoanilines in the pellet form, and the liquid 3-iodoaniline were burnt enclosed in Melinex[®] bags using the technique described by Skinner and Snelson [16], who determined the massic energy of combustion of dry Melinex[®] as $\Delta_{\text{c}} u^{\circ} = -(22902 \pm 5) \text{ J g}^{-1}$; this value was confirmed in our Laboratory. The mass of Melinex[®] used in each experiment was corrected for the mass fraction of water (0.0032) and the mass of carbon dioxide produced from the Melinex[®] was calculated using the factor previously reported [16]. The combustion experiments of the three isomers of iodoaniline were carried out in oxygen at the pressure of 3.04 MPa and with 10.00 cm^3 of an aqueous solution of KI $0.8995 \text{ mol dm}^{-3}$, placed in the bomb. For all the combustion experiments with iodine-compounds, the final solution was titrated against $\text{Na}_2\text{S}_2\text{O}_3$ (aq) and the amount of iodine found, within the precision of the analytical method, was the expected one. A value of $\Delta_{\text{sol}} U_{\text{m}}(\text{I}_2) = (3.7 \pm 0.1) \text{ kJ mol}^{-1}$ [10] was used for the molar energy of solution of $\text{I}_2(\text{cr})$ in aqueous KI solution.

The electrical energy for ignition was determined from the change in potential difference across a capacitor when discharged through the platinum ignition wire. For the cotton thread fuse of empirical formula $\text{CH}_{1.686}\text{O}_{0.843}$, $\Delta_{\text{c}} u^{\circ} = -16240 \text{ J g}^{-1}$ [17]. The nitric acid formed was determined using the Devarda's alloy method [18] and corrections were based on $-59.7 \text{ kJ mol}^{-1}$ for the molar energy of formation in which 0.1 mol dm^{-3} $\text{HNO}_3(\text{aq})$ is formed from $\text{O}_2(\text{g})$, $\text{N}_2(\text{g})$ and $\text{H}_2\text{O}(\text{l})$ [19]. An estimated pressure coefficient of massic energy: $(\partial u / \partial p)_T = -0.2 \text{ J g}^{-1} \text{ MPa}^{-1}$ at $T = 298.15 \text{ K}$, a typical value for most organic compounds [20].

2.3. Microcalorimetry Calvet

The enthalpies of transition from the condensed phase to the gaseous one were measured by a calorimetric method, using the drop-microcalorimetric technique of vacuum sublimation [21,22], or vaporization [23]. The samples contained in small thin glass capillary tubes were dropped at room temperature into the hot reaction vessel in the Calvet High-Temperature Microcalorimeter (Setaram HT1000) held at a convenient T and then removed from the hot zone by vacuum sublimation/vaporization. The observed enthalpy of sublimation/vaporization was corrected to $T = 298.15 \text{ K}$ using $\Delta_{298.15 \text{ K}}^T H_{\text{m}}^{\circ}(\text{g})$ estimated by a Group Method, based on the values of Stull et al. [24]. The microcalorimeter was calibrated in situ for these

measurements using the reported enthalpy of sublimation/vaporization of reference compounds. Details of the experimental procedure are given in the [Supplementary Data](#).

2.4. Theoretical calculations

The B3LYP hybrid method [25] as included in the GAUSSIAN 98 computer code [26] has been used in all calculations. Due to the size of the iodine atom, 46 inner electrons were included in the SKBJ relativistic effective core potential and the SKBJ-VDZ basis set was employed to describe the $5s^2 5p^5$ valence electrons [27]. Two sets of calculations with two different basis sets, 6-31G(d) and 6-311+G(2d,2p), for the smaller elements, hydrogen, carbon and nitrogen have been carried out to study the influence of extra polarization and diffuse functions on the calculated thermochemical parameters. The B3LYP/6-31G(d):SBKJ-VDZ and the B3LYP/6-311+G(2d,2p):SBKJ-VDZ approaches have been used for the optimization and calculation of frequencies of the three iodoaniline derivatives, of benzene, aniline and iodobenzene. Hereafter and throughout the Letter, these two theoretical approaches will be named SBS and LBS, respectively.

3. Results

3.1. Experimental enthalpies of formation

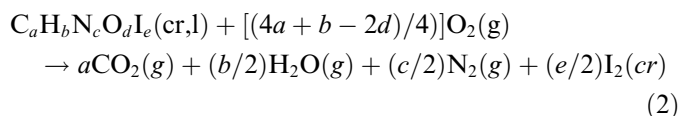
Results for a typical combustion experiment of each compound are given in [Table 1](#), where $\Delta m(\text{H}_2\text{O})$ is the deviation of the mass of water added to the calorimeter from 5222.5 g, the mass assigned to $\varepsilon(\text{calor})_{\text{ef}}$, and ΔU_{Σ} is the energy correction to the standard state. The remaining quantities are as previously defined [17]. The values of

the energy associated to the isothermal bomb process, $\Delta U(\text{IBP})$, were calculated using the expression:

$$\begin{aligned} \Delta U(\text{IBP}) = & \{ \varepsilon(\text{calor})_{\text{ef}} + \Delta m(\text{H}_2\text{O})c_p(\text{H}_2\text{O}, l) \} \Delta T_{\text{ad}} \\ & + \varepsilon_i(T_i - 298.15 \text{ K}) + \varepsilon_f(298.15 \text{ K} - T_i) \\ & + \Delta T_{\text{corr}} + \Delta U_{\text{ign}} \end{aligned} \quad (1)$$

where ΔT_{ad} is the adiabatic temperature raise and ΔT_{corr} is the correction for the heat exchange, work of stirring and the frictional work of bomb rotation.

The individual values of $-\Delta_c u^\circ$ together with the mean value, $\langle \Delta_c u^\circ \rangle$, and its standard deviation are given, for each compound, in [Table 2](#). Here, $\Delta_c u^\circ$ refers to the idealized combustion reaction:



[Table 3](#) lists the derived standard molar energies and enthalpies of combustion and standard molar enthalpies of formation for the iodoanilines in the condensed phase at $T = 298.15 \text{ K}$. In accordance with normal thermochemical practice [28,29], the uncertainties assigned to the standard molar enthalpies of combustion 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. To derive $\Delta_f H_m^\circ(\text{cr}/l)$ from $\Delta_c H_m^\circ(\text{cr}/l)$, the standard molar enthalpies of formation of $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O}(l)$, at $T = 298.15 \text{ K}$, $-(393.51 \pm 0.13) \text{ kJ mol}^{-1}$ [30] and $-(285.830 \pm 0.004) \text{ kJ mol}^{-1}$ [30], respectively, were used.

Measurements of the standard molar enthalpies of sublimation/vaporization of iodoanilines, by microcalorime-

Table 1
Typical combustion results at $T = 298.15 \text{ K}$ ($p^0 = 0.1 \text{ MPa}$)

	Comparison experiment	2-Iodobenzoic acid	2-Iodoaniline	3-Iodoaniline	4-Iodoaniline
$m(\text{BA})/\text{g}$	0.60149				
$m'(\text{cpd})/\text{g}$		1.33595	1.05431	1.09870	1.09764
$m''(\text{fuse})/\text{g}$	0.00333	0.00340	0.00318	0.00320	0.00310
$m'''(\text{melinex})/\text{g}$	0.04238		0.04450	0.03930	0.04382
$m''''(\text{I}_2)/\text{g}$	1.05404				
T_i/K	297.4679	297.4572	297.4567	297.4341	297.4322
T_f/K	298.1006	298.1545	298.1483	298.1505	298.1488
$\Delta T_{\text{ad}}/\text{K}$	0.67180	0.68000	0.67486	0.69987	0.69971
$\varepsilon_i/\text{J K}^{-1}$	51.58	51.43	51.32	51.61	51.35
$\varepsilon_f/\text{J K}^{-1}$	60.97	59.18	58.86	59.00	59.01
$\varepsilon(\text{calor})/\text{J K}^{-1}$					
$\varepsilon(\text{calor})_{\text{ef}}/\text{J K}^{-1}$	25166.8	25168.4	25174.4	25169.81	25169.4
$\Delta m(\text{H}_2\text{O})/\text{g}$	−1.1	0.2	1.9	0.8	0.7
$-\Delta U(\text{IBP})^\circ/\text{J}$	16938.41	17146.82	17022.40	17650.30	17645.78
$\Delta U(\text{BA})/\text{J}$	15887.53				
$\Delta U(\text{fuse})/\text{J}$	54.08	55.22	51.64	51.97	50.34
$\Delta U(\text{melinex})/\text{J}$	970.48		1019.14	900.12	1003.61
$\Delta U(\text{I}_2)/\text{J}$	15.37	9.97	8.91	9.28	9.27
$\Delta U(\text{HNO}_3)/\text{J}$	14.18	10.60	36.27	38.66	42.24
$\Delta U(\text{ign})/\text{J}$	1.28	1.28	1.29	1.29	1.29
$\Delta U_{\Sigma}/\text{J}$	26.23	26.65	19.92	20.57	20.67
$-\Delta_c u^\circ/\text{J g}^{-1}$		12773.17	15085.20	15152.38	15067.06

Table 2

Individual values of standard ($p^0 = 0.1$ MPa) massic energies of combustion $\Delta_c u^\circ$ of iodoanilines at $T = 298.15$ K

2-Iodoaniline	3-Iodoaniline	4-Iodoaniline
15087.66	15152.38	$-\Delta_c u^\circ / \text{J} \cdot \text{g}^{-1}$
15085.20	15152.52	15064.87
15085.62	15155.51	15067.93
15085.62	15152.43	15071.60
15083.87	15158.36	15067.06
15084.05	15150.59	15062.82
		15061.65
		$-\langle \Delta_c u^\circ \rangle / (\text{J} \cdot \text{g}^{-1})^a$
15084.9 ± 0.7	15153.6 ± 1.1	15066.0 ± 1.5

^a Mean value and standard deviation of the mean.

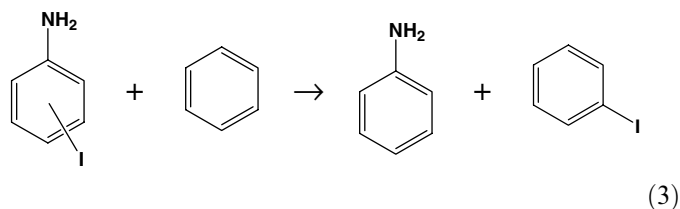
try, as well as the respective uncertainties, taken as twice the standard deviations of the mean and include the uncertainties in calibration, are given in Table 4. The derived standard molar enthalpies of formation in the condensed phase, Table 3, and the standard molar enthalpies of transition phase, Table 4, yield the standard molar enthalpies of formation in the gaseous phase of the three isomers of iodoaniline which are summarized in Table 5.

3.2. Computed enthalpies of formation

Fig. 1 presents selected geometrical parameters for iodobenzene, aniline and iodoanilines. *Ortho*, *meta* or *para* substitution in aniline with one iodine atom seems to have a tiny influence on the geometrical parameters of the corresponding iodoanilines. It is noticed that the influence vanishes from the *ortho* to the *para* derivative, i.e., the C–NH₂

bond length and the H–N–H angle are more similar to aniline in the case of 4-iodoaniline. The geometrical variations between the iodoanilines and aniline are similar to those reported recently between the three monochloroanilines and aniline [31].

The $\Delta_f H_m^\circ(g)$ of the three monoiodoanilines were estimated by considering the enthalpy of the following working reaction



calculated with the SBS or the LBS energies of each species, corrected for $T = 298.15$ K, and the experimental $\Delta_f H_m^\circ(g)$ of benzene, $\Delta_f H_m^\circ(g) = (82.6 \pm 0.7) \text{ kJ mol}^{-1}$ [32], of aniline, $\Delta_f H_m^\circ(g) = (87.1 \pm 1.1) \text{ kJ mol}^{-1}$ [32], and of iodobenzene, $\Delta_f H_m^\circ(g) = (164.9 \pm 5.9) \text{ kJ mol}^{-1}$ [32].

The DFT estimated $\Delta_f H_m^\circ(g)$ for 2-iodoaniline are $169.8 \text{ kJ mol}^{-1}$ (SBS) and $168.2 \text{ kJ mol}^{-1}$ (LBS), for 3-iodoaniline are $170.3 \text{ kJ mol}^{-1}$ (SBS) and $167.8 \text{ kJ mol}^{-1}$ (LBS) and for 4-iodoaniline are $171.1 \text{ kJ mol}^{-1}$ (SBS) and $169.4 \text{ kJ mol}^{-1}$ (LBS), c.f. Table 5. The small differences between the enthalpies of formation of the three monoiodoanilines are in agreement with the minor structural changes between them. The average deviation between the computed SBS or LBS and the experimental values is of 1.1 or 1.5 kJ mol^{-1} , respectively. This is an important result since it shows that very good estimates are possible

Table 3

Derived standard ($p^0 = 0.1$ MPa) molar values of iodoanilines in condensed phase, at $T = 298.15$ K

Compound	$-\Delta_c U_m^\circ(\text{cr/l}) / \text{kJ mol}^{-1}$	$-\Delta_c H_m^\circ(\text{cr/l}) / \text{kJ mol}^{-1}$	$\Delta_f H_m^\circ(\text{cr/l}) / \text{kJ mol}^{-1}$
2-IC ₆ H ₄ NH ₂	3303.9 ± 0.9	3306.4 ± 0.9	87.9 ± 1.2
3-IC ₆ H ₄ NH ₂	3319.0 ± 1.0	3301.5 ± 1.0	102.9 ± 1.3
4-IC ₆ H ₄ NH ₂	3299.8 ± 1.1	3302.3 ± 1.1	83.7 ± 1.4

Table 4

Standard ($p^0 = 0.1$ MPa) molar enthalpies of sublimation and vaporization, $\Delta_{\text{cr,l}}^g H_m^\circ$, for the three iodoanilines, at 298.15 K, determined by microcalorimetry

Compound	Number experiments	T/K	$\Delta_{\text{cr,l}}^{g,T} H_m^\circ / \text{kJ mol}^{-1}$	$\Delta_{298.15 \text{ K}}^T H_m^\circ(g) / \text{kJ mol}^{-1}$	$\Delta_{\text{cr,l}}^g H_m^\circ(298.15 \text{ K}) / \text{kJ mol}^{-1}$
2-IC ₆ H ₄ NH ₂	5	333.0	87.1 ± 0.1	5.8	81.3 ± 1.4
3-IC ₆ H ₄ NH ₂	6	364.9	78.7 ± 0.3	11.2	67.5 ± 1.4
4-IC ₆ H ₄ NH ₂	5	333.0	90.6 ± 0.2	5.8	84.8 ± 1.4

Table 5

Experimental and estimated (Cox scheme and DFT calculations) gas-phase enthalpies of formation of the iodoanilines

Compound	$\Delta_f H_m^\circ(g) / \text{kJ mol}^{-1}$			$\Delta^a / \text{kJ mol}^{-1}$	
	Experimental	Cox scheme	Calculated SBS; LBS ^b	Cox scheme	Calculated SBS; LBS ^b
2-IC ₆ H ₄ NH ₂	169.2 ± 1.8	173.4 ± 6.0	169.8; 168.2	-4.2 ± 6.2	-0.6 ; 1.0
3-IC ₆ H ₄ NH ₂	170.4 ± 1.9	169.4 ± 6.0	170.3; 167.8	1.0 ± 6.3	0.1 ; 2.6
4-IC ₆ H ₄ NH ₂	168.5 ± 2.0	169.4 ± 6.0	171.1; 169.4	-0.9 ± 6.3	-2.6 ; -1.0

^a Difference between the experimental and the estimated values.

^b SBS and LBS stand for DFT calculations with the small and large basis sets, respectively. See text for more details.

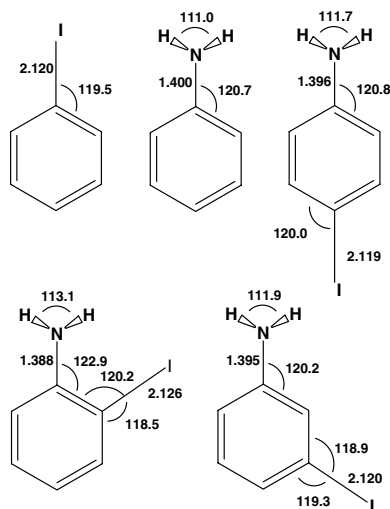
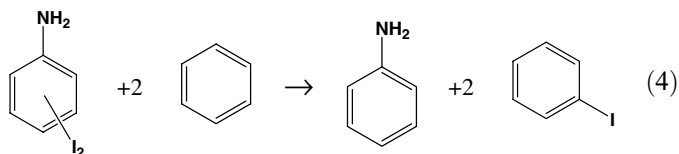


Fig. 1. Selected geometric parameters for iodobenzene, aniline and monoiodoanilines.

even if the inner electrons of the heavier elements are treated with pseudopotentials, and it suggests that calculations may be extended to the estimation of enthalpies of formation of larger molecules if accurate experimental results are available for similar compounds.

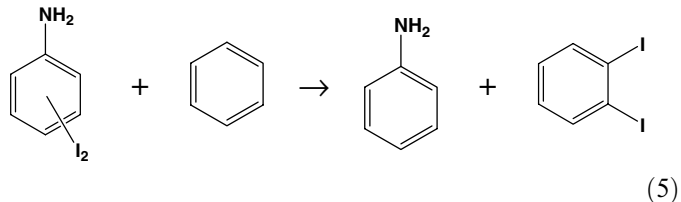
Since the SBS approach seems to be accurate enough for the prediction of the standard molar enthalpies of formation of iodoanilines, these calculations have been extended to the six isomers of diiodoaniline. The $\Delta_f H_m^\circ(\text{g})$ was estimated by considering the enthalpy of the following working reaction



following a similar procedure to that used with the monoiodoanilines. The SBS results are compiled in Table 6. The enthalpies of formation clearly show that the two isomers with iodine substitution in two adjacent carbon atoms, namely 2,3-diiodoaniline and 3,4-diiodoaniline, are more unstable than the other diiodoanilines. This reflects the unstable steric influence due to the proximity of two bulky

substituents. Interestingly, the enthalpies of formation for the other four compounds are almost the same, suggesting that iodine substituents do not exert any significant effect on the stability of the aniline structure referred above.

The gas-phase enthalpy of formation of 1,2-diiodobenzene, $\Delta_f H_m^\circ(\text{g}) = (251.7 \pm 5.9) \text{ kJ mol}^{-1}$ [32], is also available in the literature, which permits the use of another working reaction, Eq. (5), and permits one to assure if the more positive values estimated for 2,3-diiodoaniline and 3,4-diiodoaniline are influenced by a bad description of the $\text{I} \cdots \text{I}$ interaction.



The new estimated values are somewhat lower but in good agreement with those calculated with Eq. (4), and therefore, supporting all other results reported in Table 6.

3.3. Enthalpies estimated with the Cox scheme

Cox suggested [4] a method to estimate the standard molar enthalpies of formation of gaseous benzene derivatives, by assuming that each group, when substituted into a benzene ring, produces a characteristic increment in $\Delta_f H_m^\circ(\text{g})$ and that each *ortho*-pair of substituents leads to an enthalpy increment of 4 kJ mol^{-1} , with another additional correction of 4 kJ mol^{-1} for every set of three substituents in three consecutive carbon atoms of the aromatic ring. From the literature values [32] of $\Delta_f H_m^\circ(\text{g})$ of benzene, iodobenzene and aniline, the calculated enthalpic increment for the introduction of an iodine atom in a benzene ring is of $(82.3 \pm 5.9) \text{ kJ mol}^{-1}$. So, according to the Cox scheme, the estimated value for the standard molar enthalpies of formation, in the gaseous state, of *ortho*-iodoaniline is $(173.3 \pm 6.0) \text{ kJ mol}^{-1}$, whereas the estimated value for both the *meta*- and the *para*-isomers is $(169.3 \pm 6.0) \text{ kJ mol}^{-1}$, c.f. Table 5. These estimated values, although with a larger deviation from the experimental data than the computational values, differ from the experimental ones by $0.9\text{--}4.2 \text{ kJ mol}^{-1}$; this is, very well within the limit of acceptance of $\pm 10 \text{ kJ mol}^{-1}$ indicated by Cox for his scheme. In view of the relative differences of the computational values and the estimated ones by the Cox Scheme in relation to the experimental values, the computational thermochemistry yields better estimations for the compounds of which no experimental results are known.

4. Conclusions

Rotating-bomb calorimetry and Calvet microcalorimetry experiments have been performed to obtain the enthalpies of combustion in the condensed phase and the enthalpies of phase-transition to the gaseous state. The

Table 6
DFT/SBS estimated gas-phase enthalpies of formation of the diiodoanilines

Compound	$\Delta_f H_m^\circ(\text{g})/\text{kJ mol}^{-1}$
2,3- $\text{I}_2\text{C}_6\text{H}_4\text{NH}_2$	260.9 ^a ; 257.9 ^b
2,4- $\text{I}_2\text{C}_6\text{H}_4\text{NH}_2$	242.4 ^a
2,5- $\text{I}_2\text{C}_6\text{H}_4\text{NH}_2$	241.6 ^a
2,6- $\text{I}_2\text{C}_6\text{H}_4\text{NH}_2$	242.1 ^a
3,4- $\text{I}_2\text{C}_6\text{H}_4\text{NH}_2$	259.4 ^a ; 256.4 ^b
3,5- $\text{I}_2\text{C}_6\text{H}_4\text{NH}_2$	242.4 ^a

^a Calculated from Eq. (4).

^b Calculated from Eq. (5).

derived gas-phase enthalpies of formation have been compared with DFT estimated values with an excellent agreement among them. The computations were further extended to the diiodoanilines. It was found that the three monoisomers are almost energetically degenerate, showing the absence of important stabilizing effects with position of the iodine in the aromatic ring. The same applies for the diiodoanilines, except for those with iodine atoms attached to adjacent carbons due to I·····I destabilizing steric effects.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.cplett.2006.03.004](https://doi.org/10.1016/j.cplett.2006.03.004).

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