

Experimental and Computational Investigation of the Energetics of the Three Isomers of Monochloroaniline

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The standard ($p^\circ = 0.1$ MPa) molar enthalpies of formation of 2-, 3-, and 4-chloroaniline were derived from the standard molar energies of combustion, in oxygen, at $T = 298.15$ K, measured by rotating bomb combustion calorimetry. The Calvet high-temperature vacuum sublimation technique was used to measure the enthalpies of vaporization or sublimation of the three isomers. These two thermodynamic parameters yielded the standard molar enthalpies of formation of the three isomers of chloroaniline, in the gaseous phase, at $T = 298.15$ K, as 53.4 ± 3.1 kJ·mol⁻¹ for 2-chloroaniline, 53.0 ± 2.8 kJ·mol⁻¹ for 3-chloroaniline, and 59.7 ± 2.3 kJ·mol⁻¹ for 4-chloroaniline. These values, which correct previously published data, were used to test the computational methodologies used. Therewith, gas-phase acidities, proton affinities, electron donor capacities, and N–H bond dissociation enthalpies were calculated and found to compare well with available experimental data for these parameters.

Introduction

The availability of thermodynamic data is of fundamental importance for the understanding of chemical properties, such as the energetics of chemical bonds, structural properties, and reactivity, and also the understanding and investigation of many problems associated with chemical industry, environmental chemistry, and medical and life sciences. Chloroanilines are widely used as chemical intermediates in the synthesis of agricultural agents (herbicides and pesticides), azo dyes, and pharmaceuticals and in the rubber and polymer industries. Exposure to chloroanilines occurs mainly during the manufacturing process. Environmental release can occur due to accidental spills during transport, release of effluents from manufacturing plants, seepage from waste sites, or the metabolism or degradation of some pesticides and herbicides used in agriculture. Due to their toxicity, both to invertebrates and vertebrates, and their high production rates, chloroanilines are listed by European Union as priority pollutants.¹ Chloroanilines induce numerous toxicities including hematotoxicity (methemoglobinemia, haemolytic anaemia), splenotoxicity, hepatotoxicity, and nephrotoxicity,^{2–5} and it was demonstrated that 4-chloroaniline, metabolite of the insecticide diflubenzuron⁶ and degradation product of triclocarban,⁷ has generally more toxicological potential than 2- or 3-chloroanilines. These last ones are usually used as chemical intermediates in the production of herbicides and are used to a lesser extent in the production of azo pigments in the textile and pharmaceutical industry.⁸ They are also used in the polymer industry.^{9–11}

Special interest in the chemistry of substituted anilines remains unabated due to their high toxicity to aquatic environments and soils and putative carcinogenicity and mutagenicity to living organisms.^{12–15} Rather interesting and in contradiction to these malefic effects caused by aniline derivatives, it was reported recently that this class of compounds may have an

important role in the prevention of DNA oxidation.¹⁶ Ly et al. showed that substituted anilines can actuate as reductive repair agents of DNA guanyl radicals due to the easy proton transfer and/or electron donation found in these species. They found also that anilines substituted with electron withdrawing groups such as $-\text{CF}_3$ were less reactive than those with electron donating groups such as $-\text{CH}_3$. The interesting chemistry of anilines and substituted anilines is also well evident from the controversy about which position—N, ortho, meta, or para—is the protonation site. This is due to the high dependence of the experimental and theoretical results on which protonation conditions and theoretical approaches, respectively, are used.¹⁷ The importance of the energetics of aniline and its derivatives is apparent from the number of works published recently in the literature.^{16–25} Although it is possible to derive some thermodynamic data by estimation schemes and theoretical methods of calculation, they should be based on reliable experimental values in order to ensure their accuracy.

For chloroanilines, the only experimental values for the standard molar enthalpies of formation, in the gaseous phase, known in the literature, are for 3-chloroaniline,^{26,27} 4-chloroaniline,^{26,28} and 2,3,4-, 2,4,5-, 2,4,6-, and 3,4,5-trichloroanilines.²⁹ The method used to measure the standard molar enthalpies of formation of 3- and 4-chloroaniline, in the condensed phase, is not very reliable, since they were determined by static bomb combustion calorimetry, a method that is well-known to be unsuitable for the combustion calorimetry of chlorine compounds.³⁰ These, in principle, wrong experimental results for 3- and 4-chloroanilines would lead to erroneous estimation procedures for this class of compounds, and will unable future theoretical estimates, for other compounds, which are based on isodesmic reactions involving these monochloroanilines. The other experimental values reported in the literature for the monochloroanilines are those concerning the gas-phase acidities³¹ and proton affinities³² for the meta and para derivatives. Similar to what happens with the standard enthalpies of formation, no values are found in the literature

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for the 2-chloroaniline species. In the literature, it is possible to find values of the N–H bond dissociation energy for the three monochloroaniline isomers.³³

In this work, we have measured the standard ($p^\circ = 0.1$ MPa) molar enthalpies of combustion, in oxygen, at $T = 298.15$ K, by rotating bomb combustion calorimetry, in the condensed phase, of the ortho, meta, and para isomers of chloroaniline, as well as their standard molar enthalpies of vaporization or sublimation at the temperature 298.15 K, using Calvet microcalorimetry. The derived standard molar enthalpies of formation, in the gaseous state, at $T = 298.15$ K, were compared with values estimated by the Cox scheme³⁴ and calculated by density functional theory methods.

Experimental Details

The isomers of chloroanilines studied in this work were obtained commercially from Aldrich Chemical. Both 2- [CAS 95-51-2] and 3-chloroaniline [CAS 108-42-9] were purified by distillation at a reduced pressure and were stored under nitrogen. The sample of 4-chloroaniline [CAS 106-47-8] was purified by vacuum sublimation. The purities of the samples of 2- and 3-chloroaniline were checked by gas–liquid chromatography (GLC), and the one of 4-chloroaniline was checked by differential scanning calorimetry (DSC). The specific densities, used to calculate the mass from the apparent mass in air, were $\rho = 1.213 \text{ g}\cdot\text{cm}^{-3}$,³⁵ $\rho = 1.206 \text{ g}\cdot\text{cm}^{-3}$,³⁵ and $\rho = 1.429 \text{ g}\cdot\text{cm}^{-3}$ ³⁶ for 2-, 3-, and 4-chloroaniline, respectively. The measured melting point of 4-chloroaniline was $T = 344.78$ K (the temperature interval found in the literature³⁶ is 341–344 K).

The relative atomic masses used throughout this paper were those recommended by the IUPAC Commission in 2001.³⁷

The combustion experiments were performed with an isoperibol rotating bomb calorimeter, described in the literature,^{38,39} which was originally constructed at the University of Lund, Sweden, according to the design of Professor Stig Sunner.⁴⁰ The stainless steel combustion bomb, internal volume of 0.258 dm^3 and wall thickness of 1 cm, is a twin valve bomb lined with platinum, and the internal fittings are machined from platinum. The bomb is suspended from the lid of the calorimeter can, to which a mass of nearly 5222.5 g of water, previously weighed in a Perspex vessel, is added. For each experiment, a correction to the energy equivalent was made for the deviation of the mass of water used to the reference mass 5222.5 g.

Calorimeter temperatures were measured within the bounds of $\pm 10^{-4}$ K, at time intervals of 10 s, using a Hewlett-Packard (HP-2804A) quartz thermometer interfaced to an Olivetti M 250E microcomputer programmed to compute the adiabatic temperature change.

The isothermal jacket consists of a thermostatic bath containing a cavity of exactly the same shape as the calorimeter can, but 1 cm larger in overall dimensions, enclosed by a hollow lid. The jacket and lid were filled with water maintained at a temperature of ~ 303.5 K to $\pm 10^{-4}$ K using a temperature controller (Tronac PTC 41), so that the calorimeter was completely surrounded by a constant temperature.

The electrical energy for ignition was determined from the change in potential difference across a $1400 \mu\text{F}$ condenser discharge through a platinum wire of diameter 0.05 mm. For each experiment, the ignition temperature was chosen so that the final temperature would be close to $T = 298.15$ K. Fore-period and after-period readings were taken for about 20 min, and the main period was about 25 min. The rotating mechanism allows the simultaneous axial and end-over-end rotation of the bomb. Rotation of the bomb was started when the temperature

rise in the main period reached about 0.63 of its final value and was continued throughout the rest of the experiment. Using this procedure, described by Good et al.,⁴¹ the frictional work of bomb rotation is automatically included in the temperature corrections for the work of stirring and heat exchanged with the surrounding thermostat. Data acquisition and control of the calorimeter was performed through the use of the LABTERMO program.⁴²

The energy equivalent of the calorimeter was determined, in the conventional way without rotation, by combustion of benzoic acid (Bureau of Analysed Samples, thermochemical standard CRM-190) having a massic energy of combustion under standard bomb conditions of $-26\,435.1 \pm 3.5 \text{ J}\cdot\text{g}^{-1}$. Calibration experiments were carried out in oxygen, at a pressure of 3.04 MPa, with 1.00 cm^3 of water added to the bomb. From six calibration experiments, the value of the energy equivalent of the calorimeter was found to be $\epsilon(\text{calor}) = (25\,174.6 \pm 2.4) \text{ J}\cdot\text{K}^{-1}$, where the uncertainty quoted is the standard deviation of the mean.

For bomb combustion calorimetry of organic chlorine compounds, 4-chlorobenzoic acid was recommended as a test substance.⁴³ Hence, the accuracy of the calorimeter was checked in our laboratory by measuring the energy of combustion of 4-chlorobenzoic acid in the presence of 20.00 cm^3 of an aqueous solution of As_2O_3 . The standard molar enthalpy of combustion obtained was $\Delta_c U_m^\circ = -3064.5 \pm 1.2 \text{ kJ}\cdot\text{mol}^{-1}$ ⁴⁴ and $\Delta_c U_m^\circ = -3063.92 \pm 0.91 \text{ kJ}\cdot\text{mol}^{-1}$,⁴⁵ in good agreement with the values of Hu et al.⁴³ and with the recently recommended value $\Delta_c U_m^\circ = -3063.48 \pm 0.23 \text{ kJ}\cdot\text{mol}^{-1}$.⁴⁶ The values of $\Delta_c U_m^\circ$ refer to the reaction with $\text{HCl}\cdot 600\text{H}_2\text{O}(\text{l})$ as the chlorine-containing product in the final state.

Within the precision of the analytical method, no evidence was found for the oxidation of the aqueous solution of As_2O_3 after the bomb had been charged with oxygen at $p = 3.04$ MPa and left up to 5 h at room temperature.^{39,44,47}

The liquid 2- and 3-chloroanilines were burnt in sealed polyester bags made of Melinex (0.025 mm thickness) using the technique described by Skinner and Snelson,⁴⁸ who determined the massic energy of combustion of dry Melinex as $\Delta_c u^\circ = -22\,902 \pm 5 \text{ J}\cdot\text{g}^{-1}$. This value was confirmed in our laboratory and used in this work. 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.⁴⁸ The 4-chloroaniline was burnt in pellet form. For all compounds, the combustion experiments were carried out in oxygen at a pressure of 3.04 MPa and with 20 cm^3 of an aqueous $0.08986 \text{ mol}\cdot\text{dm}^{-3}$ As_2O_3 solution placed in the bomb, to reduce to hydrochloric acid all the free chlorine produced by the combustion. The extent of oxidation of $\text{As}_2\text{O}_3(\text{aq})$ was determined by titration with a standardized iodine solution. For the calculation of the energetic term $\Delta U(\text{As}_2\text{O}_3)$ corresponding to the energy of oxidation of As_2O_3 to As_2O_5 in aqueous solution, we used the procedure described by Hu et al.,⁴³ as well as the enthalpies of oxidation of $\text{As}_2\text{O}_3(\text{aq})$ by Cl_2 ,⁴⁹ and the thermal effects of mixing $\text{As}_2\text{O}_5(\text{aq})$ with strong acids.⁵⁰ The amount of $\text{H}_2\text{PtCl}_6(\text{aq})$ was determined from the loss of mass from the platinum crucible and the supporting parts of the system, and the energy correction was based on $\Delta_f H_m^\circ(\text{H}_2\text{PtCl}_6, \text{aq}) = -676.1 \pm 0.1 \text{ kJ}\cdot\text{mol}^{-1}$.⁵¹ For the cotton thread fuse whose empirical formula is $\text{CH}_{1.686}\text{O}_{0.843}$, $\Delta_c u^\circ = -1650 \text{ J}\cdot\text{g}^{-1}$ was used,⁵² a value previously confirmed in our laboratory.

The nitric acid formed was determined using Devarda's alloy method,⁵³ and corrections were based on $-59.7 \text{ kJ}\cdot\text{mol}^{-1}$ for

the molar energy of formation in which $0.1 \text{ mol} \cdot \text{dm}^{-3} \text{ HNO}_3$ (aq) is formed from $\text{O}_2(\text{g})$, $\text{N}_2(\text{g})$, and $\text{H}_2\text{O}(\text{l})$.⁵¹ An estimated value of the pressure coefficient of massic energy of $(\partial u/\partial p)_T = -0.2 \text{ J} \cdot \text{g}^{-1} \cdot \text{MPa}^{-1}$ at $T = 298.15 \text{ K}$, a typical value for most organic compounds,⁵⁴ was assumed for all chloroanilines. For each compound, the standard state corrections, ΔU_Σ , and the heat capacities of the bomb contents, ϵ_i and ϵ_f , were calculated by the procedure given by Hubbard et al.⁵² using the solubility constants and energies of solution of CO_2 and O_2 as given by Hu et al.⁴³

The standard molar enthalpies of phase transition of chloroanilines were measured using the vacuum sublimation drop-microcalorimetric technique,^{55,56} and the same method was employed in the determination of the enthalpies of vaporization.⁵⁷ Samples of about 3–5 mg of crystalline compound and of 7–10 mg of the liquid chloroanilines, contained in a small thin glass capillary tube sealed at one end, and a blank capillary were simultaneously dropped at room temperature into the hot reaction vessels in the Calvet high-temperature microcalorimeter (Setaram, Lyon, France), held at the convenient temperature T , and were removed from the hot zone by vacuum sublimation/vaporization. The thermal corrections for the glass capillary tubes were determined in separate experiments and were minimized, as far as possible, by dropping tubes of nearly equal mass, to within $\pm 10 \mu\text{g}$, into each of the twin calorimeter cells.

The observed enthalpies of sublimation or vaporization, $\Delta_{\text{cr,l},298.15\text{K}}^{g,T} H_m^\circ$, were corrected to $T = 298.15 \text{ K}$ using values of $\Delta_{298.15\text{K}}^{g,T} H_m^\circ(\text{g})$ estimated by a group-additivity method based on data of Stull et al.,⁵⁸ where T is the temperature of the hot reaction vessel. The microcalorimeter was calibrated in situ for these measurements, using the reported standard molar enthalpies of sublimation of naphthalene $72.6 \pm 0.6 \text{ kJ} \cdot \text{mol}^{-1}$,⁴⁶ for 4-chloroaniline and of vaporization of *n*-decane $51.420 \pm 0.206 \text{ kJ} \cdot \text{mol}^{-1}$,⁴⁶ for liquid 2- and 3-chloroanilines.

The experimental strategies followed in this paper have been successfully applied in the research of other chlorinated aromatic compounds.^{44,45,47,59,60}

Computational Details

The enthalpies of formation of the three chloroaniline isomers were estimated from density functional theory (DFT) or Gaussian-3 based G3MP2B3 computations and the consideration of an appropriate working reaction.

In the DFT calculations, the geometry of all compounds was optimized within the Kohn–Sham formalism at the B3LYP/DZVP or BP86/DZVP levels of theory. The B3LYP three-parameter hybrid method was proposed by Becke⁶¹ and comprises an exchange-correlation functional that mixes the nonlocal Fock exchange with the gradient-corrected form of Becke⁶² and adds the correlation functional proposed by Lee et al.⁶³ The BP86 method is based on Becke's 1988 exchange and on Perdew's 86 correlation functionals.^{62,64} The atomic electron density was described by the standard polarized double- ζ split valence basis set (DZVP).⁶⁵ Calculation of frequencies was carried out at the same level of theory as that used in the optimization procedure. This was done in order to guarantee that optimized structures are minima on the potential energy surface (PES) and to obtain thermal corrections to the energy at $T = 298.15 \text{ K}$. These calculations were performed by means of the GAMESS-UK suite of programs.^{66,67}

The calculations employing the G3MP2B3 composite approach⁶⁸ use the B3LYP method and the 6-31G(d) basis set for both the optimization of geometry and calculation of frequencies. Successive introduction of high-order corrections to the B3LYP/

TABLE 1: Typical Combustion Results at $T = 298.15 \text{ K}$ ($p^\circ = 0.1 \text{ MPa}$) for the Three Different Chloroanilines^a

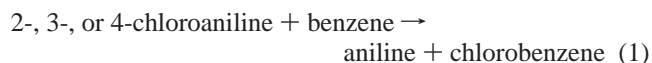
	calibration	2-chloro-aniline	3-chloro-aniline	4-chloro-aniline
$m(\text{BA})/\text{g}$	1.080 89			
$m'(\text{cpd})/\text{g}$		0.966 34	0.945 54	0.802 55
$m''(\text{fuse})/\text{g}$	0.003 00	0.002 99	0.002 89	0.002 66
$m'''(\text{Melinex})/\text{g}$		0.045 08	0.043 24	
T_i/K	297.0960	297.1533	297.1251	297.3152
T_f/K	298.2460	298.1955	298.1440	298.1460
$\Delta T_{\text{ad}}/\text{K}$	1.137 18	1.028 62	1.001 88	0.814 00
$\epsilon_f/\text{J} \cdot \text{K}^{-1}$	13.82	94.49	94.45	93.84
$\epsilon_i/\text{J} \cdot \text{K}^{-1}$	14.98	91.97	92.08	91.91
$\epsilon(\text{calor})/\text{J} \cdot \text{K}^{-1}$	25 174.57	25 167.1	25 185.1	25 174.6
$\Delta m(\text{H}_2\text{O})/\text{g}$	2.1	−1.8	2.5	0.0
$-\Delta U(\text{IBP})^\circ/\text{J}$	28 653.82	25 999.96	25 306.13	20 568.55
$\Delta U(\text{BA})/\text{J}$	28597.62			
$\Delta U(\text{fuse})/\text{J}$	48.72	48.56	46.93	43.20
$\Delta U(\text{Melinex})/\text{J}$		1032.35	990.32	
$\Delta U(\text{HNO}_3)/\text{J}$	6.21	13.49	5.49	0.72
$\Delta U(\text{As}_2\text{O}_3)/\text{J}$		325.78	252.19	213.47
$\Delta U(\text{ign})/\text{J}$	1.28	1.29	1.30	1.31
$\Delta U(\text{H}_2\text{PtCl}_6)/\text{J}$		0.74	0.71	0.74
$\Delta U_\Sigma/\text{J}$		52.28	51.38	41.88
$-\Delta_c u^\circ/\text{J} \cdot \text{g}^{-1}$		25 379.75	25 337.70	25 253.54

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

6-31G(d) enthalpy follows the Gaussian-3 philosophy albeit using a second-order Moller–Plesset perturbation instead of MP4 as in the original G3 method.⁶⁹ The composite calculations were carried out by means of the Gaussian 98 computer code.⁷⁰

The energies computed by each of three approaches, at $T = 0 \text{ K}$, were thermally corrected for $T = 298.15 \text{ K}$ by introducing the vibrational, translational, rotational, and pV terms. The vibrational term is based on the vibrational wavenumbers calculated by each of the three DFT approaches as explained above.

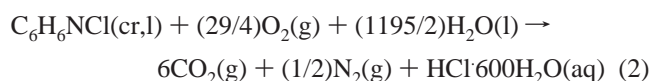
The enthalpies of formation in the gas phase for the three isomers were estimated considering the computed enthalpy of the following working reaction, at $T = 298.15 \text{ K}$,



and the experimental standard gas-phase enthalpies of formation, at $T = 298.15 \text{ K}$, of benzene, $\Delta_f H_m^\circ = 82.7 \pm 0.7 \text{ kJ} \cdot \text{mol}^{-1}$,⁷¹ aniline, $\Delta_f H_m^\circ = 87.1 \pm 1.1 \text{ kJ} \cdot \text{mol}^{-1}$,⁷¹ and chlorobenzene, $\Delta_f H_m^\circ = (52.0 \pm 1.3) \text{ kJ} \cdot \text{mol}^{-1}$.⁷¹ The present computational procedure was found to yield accurate enthalpies of formation for similar organic compounds, namely, dichlorophenols,⁷² chloronitroanilines,⁶⁰ and aminophenols.²⁴

Results

Detailed results for a typical combustion experiment of chloroanilines are given in Table 1, in which $\Delta m(\text{H}_2\text{O})$ is the deviation of the mass of water added to the calorimeter from 5222.5 g, the mass assigned to $\epsilon(\text{calor})$, and ΔU_Σ is the correction to the standard state. The remaining quantities are as previously defined.^{52,73} Table 2 lists the individual values of massic energy of combustion together with its mean $\langle \Delta_c u^\circ \rangle$ and its standard deviation. $\Delta_c u^\circ$ refers to the combustion reaction



in which reactants and products are in the thermodynamic standard states at $T = 298.15 \text{ K}$ (with $\text{HCl} \cdot 600\text{H}_2\text{O}(\text{aq})$ as the

TABLE 2: Individual Values of Standard ($p^\circ = 0.1$ MPa) Massic Energies of Combustion, $\Delta_c u^\circ$, of the Three Chloroaniline Isomers at $T = 298.15$ K

2-chloroaniline	3-chloroaniline	4-chloroaniline
	$-\Delta_c u^\circ / \text{J} \cdot \text{g}^{-1}$	
25 384.25	25 347.40	25 253.54
25 372.55	25 330.13	25 243.92
25 370.12	25 337.70	25 246.30
25 380.87	25 342.57	25 251.15
25 379.75	25 333.55	25 266.36
25 372.22	25 329.29	25 266.67
	$-(\Delta_c u^\circ)^a / (\text{J} \cdot \text{g}^{-1})$	
25 376.6 ± 2.3	25 336.8 ± 2.9	25 254.7 ± 4.0

^a Mean value and standard deviation of the mean.**TABLE 3: Derived Standard 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 Three Chloroanilines at $T = 298.15$ K, with $p^\circ = 0.1$ MPa**

compound	$-\Delta_c U_m^\circ(\text{cr/l}) / \text{kJ} \cdot \text{mol}^{-1}$	$-\Delta_c H_m^\circ(\text{cr/l}) / \text{kJ} \cdot \text{mol}^{-1}$	$-\Delta_f H_m^\circ(\text{cr/l}) / \text{kJ} \cdot \text{mol}^{-1}$
2-chloroaniline (l)	3237.3 ± 1.4	3239.2 ± 1.4	3.0 ± 1.6
3-chloroaniline (l)	3232.3 ± 1.5	3234.1 ± 1.5	8.1 ± 1.7
4-chloroaniline (cr)	3221.8 ± 1.5	3223.6 ± 1.5	18.5 ± 1.7

chlorine-containing product in the final state). Table 3 lists the derived standard molar energies and enthalpies of combustion and standard molar enthalpies of formation for the chloroanilines in the condensed phase at $T = 298.15$ K. In accordance with normal thermochemical practice,^{74,75} 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 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 $\text{CO}_2(\text{g})$, -393.51 ± 0.13 $\text{kJ} \cdot \text{mol}^{-1}$,⁷⁶ $\text{H}_2\text{O}(\text{l})$, -285.830 ± 0.004 $\text{kJ} \cdot \text{mol}^{-1}$,⁷⁶ and HCl in $600\text{H}_2\text{O}(\text{l})$, -166.540 ± 0.005 $\text{kJ} \cdot \text{mol}^{-1}$,^{51,76} were used.

The results of the measurements of the enthalpies of transition phase of chloroanilines, by microcalorimetry, as well as the respective uncertainties, taken as twice the standard deviations of the mean, are given in Table 4. The standard molar enthalpies of phase transition, at the temperature $T = 298.15$ K, were calculated by eq 3

$$\Delta_{\text{cr}}^g H_m^\circ(T = 298.15 \text{ K}) = \Delta_{\text{cr}, 298.15 \text{ K}}^{g, T} H_m^\circ - \Delta_{298.15 \text{ K}}^T H_m^\circ(\text{g}) \quad (3)$$

using $\Delta_{298.15 \text{ K}}^T H_m^\circ(\text{g})$ estimated by the group-additivity method, that is, chloroaniline = aniline + chlorobenzene – benzene, based on the values of Stull et al.⁵⁸

The literature values for the standard molar enthalpies of formation of the three isomers of monochloroaniline, in the condensed state, determined by Masalatinova et al.,²⁶ are for 2-chloroaniline, -4.64 $\text{kJ} \cdot \text{mol}^{-1}$, for 3-chloroaniline, -20.3 $\text{kJ} \cdot \text{mol}^{-1}$, and for 4-chloroaniline, -33.3 $\text{kJ} \cdot \text{mol}^{-1}$, which are very different from the ones determined in the present work (last column of Table 3). This was to be expected, since Masalatinova et al. used the static bomb combustion calorimetry, a method that is not appropriate for halogenated compounds.³⁰ Also, the literature values of Zalikin and co-workers²⁷ for the standard enthalpy of vaporization of 3-chloroaniline, 54.0 ± 0.2 $\text{kJ} \cdot \text{mol}^{-1}$, and of Stephenson and Malanowski²⁸ for the standard enthalpy of sublimation of 4-chloroaniline, 90.7 $\text{kJ} \cdot \text{mol}^{-1}$, are quite different from the ones obtained in the present work (last column of Table 4).

The sum of the standard molar enthalpies of formation in the condensed state, $\Delta_f H_m^\circ(\text{cr/l})$, and the standard molar en-

thalpies of sublimation/vaporization, $\Delta_{\text{cr}, \text{l}}^g H_m^\circ(298.15 \text{ K})$, taken from the last columns of Tables 3 and 4, respectively, yields the standard molar enthalpies of formation in the gaseous state for the three chloroaniline isomers, which are summarized in Table 5. The DFT and G3MP2B3 estimated enthalpies of formation are also reported in Table 5. The theoretical values are in excellent agreement with the experimental enthalpies of formation. All computed values lie within the experimental uncertainties.

As referred to in the Introduction section, some other thermodynamic properties, such as the ability for electron donation, proton transfer, and N–H bond scission, are important for many applications involving aniline derivatives. Therefore, and taking in mind the excellent agreement between the calculated and experimental enthalpies of formation, the computational approaches were used to extract these quantities in order to compare it with previously reported data and to fulfill some gaps. The computed gas-phase acidities, proton affinities, electron donor capacities, and N–H bond dissociation enthalpies, at $T = 298.15$ K, for aniline and the three chloroaniline isomers are reported in Table 6 and compared with experimental data if available.

Discussion

Cox suggested³⁴ 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 $\text{kJ} \cdot \text{mol}^{-1}$, with another additional correction of 4 $\text{kJ} \cdot \text{mol}^{-1}$ for every set of three substituents on three adjacent carbon atoms of the aromatic ring. From the literature values⁷¹ of $\Delta_f H_m^\circ(\text{g})$ of benzene, chlorobenzene, and aniline, the calculated enthalpic increment for the introduction of a chlorine atom in a benzene ring is of -30.7 ± 1.5 $\text{kJ} \cdot \text{mol}^{-1}$. Thus, according to the Cox scheme, the estimated value for the standard molar enthalpies of formation, in the gaseous state, of *ortho*-chloroaniline is 60.4 ± 1.9 $\text{kJ} \cdot \text{mol}^{-1}$, whereas the estimated value for both the meta and para isomers is 56.4 ± 1.9 $\text{kJ} \cdot \text{mol}^{-1}$ (cf. Table 5). These estimated values differ from the experimental ones by 7 $\text{kJ} \cdot \text{mol}^{-1}$ in the case of the ortho isomer and by 3.4 and 3.3 $\text{kJ} \cdot \text{mol}^{-1}$ in the cases, respectively, of the meta and para isomers, which is very well within the limit of acceptance of 10 $\text{kJ} \cdot \text{mol}^{-1}$ indicated by Cox for his scheme.³⁴ The Cox scheme fails completely in the differentiation between the 3- and 4-chloroaniline isomers, since the same value is predicted for these two isomers and also predicts the 2-chloroaniline to be the least stable compound. The former effect was expected, since Cox did not provide any correction to differentiate substitution at aromatic ring positions 3 or 4 due to the possibility of different resonance/inductive effects depending on the substituent, which could increase or decrease the overall compound stability. The wrong prediction of 2-chloroaniline as the least stable isomer strongly suggests that a reparametrization of the Cox scheme is still needed in order to ensure reliable results.

The problems found with the Cox scheme disappear if accurate computations are combined with precise experimental enthalpies of formation for all species appearing in a well-chosen working reaction, except that we are interested in. The results reported in Table 5 show that the three theoretical approaches are well-suited for the estimation of gas-phase standard enthalpies of formation of aromatic compounds containing chlorine atoms. All numbers are in excellent agreement with the experimental value, but a closer inspection of the results shown

TABLE 4: Standard ($p^\circ = 0.1$ MPa) Molar Enthalpies of Sublimation or Vaporization, $\Delta_{\text{cr,l}}^{\text{g}} H_{\text{m}}^\circ$, at $T = 298.15$ K Determined by Microcalorimetry for the Isomers of Monochloroanilines

compound	no. of experiments	T/K	$\Delta_{\text{cr,l}}^{\text{g}} H_{\text{m}}^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\Delta_{298.15\text{K}}^{\text{g}} H_{\text{m}}^\circ(\text{g})/\text{kJ}\cdot\text{mol}^{-1}$	$\Delta_{\text{cr,l}}^{\text{g}} H_{\text{m}}^\circ(298.15\text{ K})/\text{kJ}\cdot\text{mol}^{-1}$
2-chloroaniline (l)	6(l)	370.2	68.4 ± 1.9	12.0	56.4 ± 1.6
3-chloroaniline (l)	8	370.3	73.1 ± 1.2	12.0	61.1 ± 2.8
4-chloroaniline (cr)	6	335.5	84.9 ± 0.9	6.7	78.2 ± 1.5

TABLE 5: Comparison between Experimentally Derived Standard Molar Enthalpies of Formation, $\Delta_f H_{\text{m}}^\circ$, at $T = 298.15$ K, for the Three Chloroaniline Isomers and Those Estimated from DFT and G3MP2B3 Calculations and from the Cox Scheme^a (All Units in $\text{kJ}\cdot\text{mol}^{-1}$)

isomer	experimental	BP86/DZVP	B3LYP/DZVP	G3MP2B3	Cox
2-chloroaniline	53.4 ± 3.1	$54.1 (+0.7)$	$54.5 (+1.1)$	$51.5 (-1.9)$	$60.4 \pm 1.8 (+7.6 \pm 3.6)$
3-chloroaniline	53.0 ± 2.8	$55.0 (+2.0)$	$54.9 (+1.9)$	$55.4 (+2.4)$	$56.4 \pm 1.8 (+3.4 \pm 3.3)$
4-chloroaniline	59.7 ± 2.3	$57.7 (-2.0)$	$57.5 (-2.2)$	$57.9 (-1.8)$	$56.4 \pm 1.8 (+3.3 \pm 2.9)$

^a Enthalpic differences with respect to the experimental values are given in parantheses.

TABLE 6: G3MP2B3 Computed Proton Affinities, PAs, Gas-Phase Acidities, $\Delta H_{\text{acidity}}$, Electron Donor Capacity, EDC, and N–H Bond Dissociation Enthalpies, N–H BDEs, at $T = 298.15$ K, for Aniline and the Three Chloroaniline Isomers (All Units in $\text{kJ}\cdot\text{mol}^{-1}$)

compound	PA		$\Delta H_{\text{acidity}}$		EDC	N–H BDE		
	calcd	exptl ^a	calcd	exptl ^b	calcd	calcd	calcd ^c	exptl ^d
aniline	881.1 ^e	882.5	1536.4	1533 ± 8.8	757.9	396.7	385.8	386.2
2-chloroaniline	870.5 ^e		1507.3		772.7	401.6	388.7	389.5
3-chloroaniline	866.7 ^f	868.1	1505.7	1502 ± 8.8	777.8	402.5	390.8	387.4
4-chloroaniline	866.3 ^e	873.8	1511.6	1508 ± 8.8	757.6	396.9	383.7	386.6

^a Taken from ref 32. ^b Taken from ref 31. ^c Taken from ref 19. ^d Taken from ref 33. ^e N-protonation. ^f C4-protonation.

in Table 5 yields some interesting findings. The experimental enthalpies of formation for the 2- and 3-chloroaniline compounds are almost energetically degenerate ($\Delta < 1$ $\text{kJ}\cdot\text{mol}^{-1}$), in agreement with the DFT computed values. However, all computational approaches give a reversed order of stability. Interestingly enough, the, in principle, more accurate G3MP2B3 approach gives an enthalpic difference between the 2- and 3-isomers of ~ 4 $\text{kJ}\cdot\text{mol}^{-1}$. This larger difference is due to the much more stable 2-chloroaniline isomer predicted by the composite approach when compared with the other methods. Further, the enthalpic difference between the least and the most stable isomers determined experimentally is ~ 7 $\text{kJ}\cdot\text{mol}^{-1}$, in agreement with that retrieved from the composite approach but larger than that found for the DFT estimated values. The enthalpies of formation for the three chloroanilines may be compared with the enthalpies of formation of the corresponding pyridines. The experimental gas-phase enthalpies of formation are available for 2-chloropyridine, $\Delta_f H_{\text{m}}^\circ = 104.5 \pm 1.8$ $\text{kJ}\cdot\text{mol}^{-1}$, and 3-chloropyridine, $\Delta_f H_{\text{m}}^\circ = 107.6 \pm 1.7$ $\text{kJ}\cdot\text{mol}^{-1}$.⁵⁹ The enthalpic difference between these two derivatives is 3.1 $\text{kJ}\cdot\text{mol}^{-1}$, somewhat larger than the experimental and DFT computed differences found between the $\Delta_f H_{\text{m}}^\circ$ values of 2-chloroaniline and 3-chloroaniline but in better agreement with the computed G3MP2B3 enthalpic difference.

Finally, the average deviation between calculated and experimental $\Delta_f H_{\text{m}}^\circ$ values shows that BP86/DZVP gives the best estimates for the three chloroanilines; the mean deviation is 1.6 $\text{kJ}\cdot\text{mol}^{-1}$. The mean deviations of the two other theoretical approaches considered in the present work are 1.7 and 2.0 $\text{kJ}\cdot\text{mol}^{-1}$ for the B3LYP/DZVP and G3MP2B3 methodologies, respectively. These findings are in agreement with previous works devoted to the study of chlorinated aromatic compounds.^{45,72} The G3MP2B3-corrected energies, the atomization reaction for each compound, and the experimental enthalpies^{76,77} of hydrogen, $\Delta_f H_{\text{m}}^\circ = 218.00$ $\text{kJ}\cdot\text{mol}^{-1}$, of carbon, $\Delta_f H_{\text{m}}^\circ = 716.67$ $\text{kJ}\cdot\text{mol}^{-1}$, of nitrogen, $\Delta_f H_{\text{m}}^\circ = 472.68$ $\text{kJ}\cdot\text{mol}^{-1}$, and of chlorine, $\Delta_f H_{\text{m}}^\circ = 121.30$ $\text{kJ}\cdot\text{mol}^{-1}$, were used also to estimate the gas-phase enthalpies of formation of the three chloroaniline

isomers. The estimated values are 46.5, 50.3, and 52.9 $\text{kJ}\cdot\text{mol}^{-1}$ for 2-, 3-, and 4-chloroaniline, respectively, corresponding to a mean deviation of 5.5 $\text{kJ}\cdot\text{mol}^{-1}$.

As concluded above, the computational approaches used in the present work seem well suited to deal with this family of compounds. Therefore, they were used to compute some other properties difficult to be measured experimentally. The G3MP2B3 results together with available experimental data are compiled in Table 6. Experimental proton affinities are known for aniline, 3-chloroaniline, and 4-chloroaniline. In the first review of Lias et al., the proton affinity for aniline was reported to be 876 $\text{kJ}\cdot\text{mol}^{-1}$.⁷⁸ More recently, this value was updated to be 882.5 $\text{kJ}\cdot\text{mol}^{-1}$.³² The list of proton affinities included in these works uses both experimental and computational information to tune the final suggested value. The proton affinity computed for aniline, $\text{PA}[\text{C}_6\text{H}_4\text{XNH}_2] = H[\text{C}_6\text{H}_4\text{XNH}_2] - H[\text{C}_6\text{H}_4\text{XNH}_3]^+ + 5RT/2$, with X = H or Cl, almost matches the experimentally derived number given above. An excellent agreement is also verified for the 3-chloroaniline species, while for the para isomer the comparison between G3MP2B3 and experimental values is not so good. The excellent agreement found for aniline and 3-chloroaniline seems to support the adequacy of the G3MP2B3 approach to compute proton affinities and, therefore, suggests that the computed value for 2-chloroaniline, 870.5 $\text{kJ}\cdot\text{mol}^{-1}$, is a good estimate. In fact, this approach yields much more accurate results, when compared with the experimental values available, than those computed by the B3LYP, MP2, or CCSD(T) methods.⁷⁹ The computed proton affinities show that nitrogen protonation is preferred for all species except for 3-chloroaniline. In the latter, protonation in the para position is preferred by ~ 3.5 $\text{kJ}\cdot\text{mol}^{-1}$; please see the Supporting Information. Further, for aniline and 3-chloroaniline, the proton affinity differences between protonation at nitrogen and C4 positions is small enough to suggest that protonation may occur at both sites. The B3LYP/DZVP and BP86/DZVP approaches were also used to compute proton affinities, but the computed values are 4–9 $\text{kJ}\cdot\text{mol}^{-1}$ lower than the G3MP2B3 values given in Table 6 and, thus, much farther from the experimental numbers

available. The computed values show that N-protonation is easier for aniline than for the monochloroaniline derivatives.

Gas-phase acidities calculated as $H[C_6H_4XNH]^- - H[C_6H_4XNH_2] + 5RT/2$, with $X = H$ or Cl , at the G3MP2B3 level are 3–4 kJ·mol⁻¹ systematically smaller than the available experimental values, but all values fall within the interval defined by experimental uncertainty.

We could not find any experimental value regarding the capacity of these compounds to act as electron donors, which is the same as the electron affinities for the corresponding anilinium cations, that is, $C_6H_4XNH_2^+$, with $X = H$ or Cl . Therefore, trusting the excellent G3MP2B3 computed standard enthalpies of formation, proton affinities, and gas-phase acidities, it is possible to conclude that aniline and 4-chloroaniline have the same electron donor capacity and that the meta derivative has the lowest capacity to donate electrons.

Another important parameter with particular interest for the design of new antioxidants is the energy required for homolytic cleavage of the N–H bonds. There is an enormous interest in an accurate definition of antioxidant strength, as is evident from the large number of recent computational studies devoted to this field.^{80–83} However, the majority of these studies are devoted to O–H bond dissociation energies and less attention is given to what happens with antioxidants containing N–H bonds. As previously reported,¹⁹ there are some examples of compounds containing N–H bonds that dissociate at a lower energy than common antioxidants based on phenol derivatives. The G3MP2B3 computed values are compared with available experimental N–H bond dissociation enthalpies and (RO)-B3LYP/6-311+G(2d,2p)/(U)B3LYP/6-31G(d) computed values in Table 6. It is found that the composite methodology is not adequate to compute this property with values being systematically larger than reported experimental bond dissociation enthalpies, which contrasts with the excellent results computed for the other thermodynamic properties.

Conclusions

A combined experimental and computational study permitted the standard gas-phase enthalpies of formation, at $T = 298.15$ K, for the three possible chloroaniline isomers to be obtained. Experimentally, the enthalpies of formation were indirectly retrieved from rotating bomb combustion calorimetry and Calvet microcalorimetry experiments, which yielded the enthalpies of combustion and the enthalpies of vaporization or sublimation, respectively. The final experimental $\Delta_f H_m^\circ$ values are 53.4 ± 3.1 , 53.0 ± 2.8 , and 59.7 ± 2.3 kJ·mol⁻¹ for 2-, 3-, and 4-chloroaniline isomers, respectively.

The $\Delta_f H_m^\circ$ values have also been estimated by DFT and G3MP2B3 calculations and by considering a pertinent working reaction. All computed values are in excellent agreement with the experimental data herewith reported, all falling within experimental uncertainty. This good agreement between the present experimental and computational results does support that the values previously reported in the literature are not reliable. Importantly, when compared with experimental data, the BP86/DZVP approach was shown to provide the best estimates of $\Delta_f H_m^\circ$ in agreement with previous works devoted to the study of chlorinated aromatic compounds.

When compared with available experimental data, it is shown that the use of the composite G3MP2B3 approach yields accurate proton affinities and gas-phase acidities but gives poor N–H bond dissociation enthalpies. Finally, from the computed N–H bond dissociation enthalpies, it is found that aniline and monochloroanilines have almost the same antioxidant power,

but from the computed gas-phase acidities, it is suggested that chlorinated anilines are more effective than aniline if the mechanism of reduction involves proton transfer.

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Supporting Information Available: Table listing proton affinities for aniline and monochloroanilines. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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