Experimental and Computational Investigation of the Thermochemistry of the Six Isomers of Dichloroaniline

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The standard ($p^o = 0.1$ MPa) molar enthalpies of formation of 2,3-, 2,4-, 2,5-, 2,6-, 3,4- and 3,5-dichloroanilines were derived from the standard molar energies of combustion, in oxygen, to yield CO_2(g), N_2(g) and $HCl\cdot 600H_2O$(l), 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 sublimation of the six isomers. These two thermodynamic parameters yielded the standard molar enthalpies of formation of the six isomers of dichloroaniline, in the gaseous phase, at $T = 298.15$ K. The gas-phase enthalpies of formation were also estimated by G3MP2B3 calculations, which were further extended to the computation of gas-phase acidities, proton affinities, and ionization enthalpies.

Introduction

Chloroanilines or chlorobenzenamines are important for the manufacture of many interesting materials such as paints, pesticides, plastics and pharmaceuticals, but they have also strong impact due to their environmental problems and toxicity when spoiled into soils and water.[1] These chlorinated heterocycles may result in nature also from soil microbial metabolism of other organic molecules such as phenylureas, phenylcarbamates and acylanilides.[2,3] Therefore, it is not surprising that several works concerning the removal or diminution of chloroanilines from soils and water are found in the literature.[4−6] Unfortunately, these compounds have resistance to biodegradation that is due to their toxicity to microorganisms, which is dependent on the number and position of chlorine atoms on the aromatic ring.[6] Further, they were found also to adsorb strongly on soils, making their extraction by modern separation techniques difficult.[4] Therefore, the best way to remove these compounds from industrial wastes is incineration, which needs to be well-controlled and complete to avoid the formation of other new air pollutants. Knowledge of the thermochemical properties of these halogenated compounds is crucial for the security of complete combustion processes.

To provide new thermochemical date for this important class of compounds, the present work presents a detailed experimental and computational study that permitted us to obtain the standard molar enthalpies of formation, in gaseous state, at $T = 298.15$ K, of the six isomers of dichloroaniline. Standard ($p^o = 0.1$ MPa) molar enthalpies of combustion of the dichloroanilines, in oxygen, at $T = 298.15$ K, have been determined by rotating bomb combustion calorimetry, in condensed phase, whereas their standard molar enthalpies of sublimation at the temperature 298.15 K, have been obtained by using Calvet microcalorimetry. Computational methods have also been used to obtain values for other properties that are important for the description of several reaction mechanisms. These thermodynamic properties were the ionization enthalpies, the gas-phase acidities and the proton affinities of the six dichloroaniline isomers.

Experimental Details

The compounds studied in this work were obtained commercially from Aldrich Chemical Co., and were purified by repeated sublimation at reduced pressure. The specific densities used to calculate the mass from apparent mass in air were $\rho = 1.554\ g\cdot cm^{-3}$ [7] for 2,3- and 2,6-dichloroaniline, $\rho = 1.564\ g\cdot cm^{-3}$ for 2,4- and 2,5-dichloroaniline , $\rho = 1.543\ g\cdot cm^{-3}$ for 3,4-dichloroaniline, and $\rho = 1.603\ g\cdot cm^{-3}$ for 3,5-dichloroaniline.

The combustion experiments were performed with an isoperibol rotating-bomb calorimeter, developed by Sunner[8] at the University of Lund, Sweden. The apparatus and the technique have been described in the literature.[9,10] The bomb, whose internal volume is 0.258 dm^3, is of stainless steel lined with platinum, and the internal fittings are machined from platinum. In each experiment, the bomb is suspended from the lid of the calorimeter can, to which 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 of 5222.5 g.

Calorimeter temperatures were measured to $\pm 10^{-4}$ 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 corrected temperature change. 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. Data acquisition and control of the calorimeter was performed through the use of the LABTERMO program.[11]

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 total value and was continued throughout the

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rest of the experiment. By adopting this procedure, described by Good et al.,[12] the frictional work due to the rotation of the bomb is automatically included in the temperature corrections for the work of water stirring and for the heat exchanged with the surrounding isothermal jacket.

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 303.5 K $\pm \approx 10^{-4}$ K using a temperature controller (Tronac PTC 41), so that the calorimeter was completely surrounded by a constant-temperature.

Benzoic acid (Bureau of Analyzed Samples, Thermochemical Standard CRM-190) was used for the calibration of the bomb. Its massic energy of combustion is $-26\,435.1 \pm 3.5$ J·g^{-1}, under certificate conditions. Calibration experiments were carried out in oxygen, at the pressure of 3.04 MPa, with 1.00 cm^3 of water added to the bomb. From six calibration experiments the value of energy equivalent of the calorimeter was found to be ϵ(calor) $= 25\,185.6 \pm 2.3$ J·K^{-1}, where the uncertainty quoted is the standard deviation of the mean.

The crystalline compounds were burnt in pellet form. The combustion experiments were carried out in oxygen at a pressure of 3.04 MPa in the presence of an aqueous solution of As_2O_3, to reduce to hydrochloric acid all the free chlorine produced by the combustion. For the compounds 2,3- and 3,4-dichloroaniline, 25.00 cm^{-3} of aqueous As_2O_3 0.08934 mol·dm^{-3} were used, and for the compounds 2,4-, 2,5-, 2,6- and 3,5-dichloroaniline 25.00 cm^{-3} of aqueous As_2O_3 0.08959 mol·dm^{-3} were used. The extent of oxidation of As_2O_3(aq) was determined by titration with standardized iodine solution. For the calculation of the energetic term $\Delta U(As_2O_3)$, 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.[13] as well as the enthalpies of oxidation of As_2O_3(aq) by Cl_2,[14] and the thermal effects of mixing As_2O_5(aq) with strong acids.[15] 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.[10,16]

The electrical energy for ignition was determined from the change in potential difference across a 1400 μF condenser discharge through a platinum wire of diameter 0.05 mm.

The amount of H_2PtCl_6(aq) was determined from the loss of mass from the platinum crucible and it supporting parts of the system and the energy correction was based on $\Delta_f H_m^o(H_2PtCl_6,aq) = -676.1 \pm 0.1$ kJ·mol^{-1}.[17] For the cotton thread fuse with empirical formula $CH_{1.686}O_{0.843}$, $\Delta_c u^o = -16\,240$ J·g^{-1} was used,[18] a value previously confirmed in our laboratory.

The nitric acid formed was determined using the Devarda's alloy method[19] and corrections were based on -59.7 kJ·mol^{-1} for the molar energy of formation in which 0.1 mol·dm^{-3} HNO_3(aq) was formed from O_2(g), N_2(g) and H_2O(l).[17] An estimated value of the pressure coefficient of massic energy was $(\partial u/\partial p)_T = -0.2$ J·g^{-1}·MPa^{-1} at $T = 298.15$ K, a typical value for most organic compounds,[20] was assumed for all dichloroanilines. 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.,[18] using the solubility constants and energies of solution of CO_2 and O_2 as given by Hu et al.[13]

The relative atomic masses used throughout this paper were those recommended by the IUPAC Commission in 2001.[21]

The standard molar enthalpies of sublimation of the compounds were measured using the vacuum sublimation drop-microcalorimetric technique.[22,23] Samples of about 3−5 mg of crystalline compound, 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. 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 ± 10 μg, into each of the twin calorimeter cells.

The observed enthalpies of sublimation $\Delta_{cr,298.15K}^{g,T} H_m^o$, were corrected to $T = 298.15$ K using values of $\Delta_{298.15K}^{T} H_m^o$(g) estimated by a group-additivity method based on data of Stull et al.,[24] where T is the temperature of the hot reaction vessel. The microcalorimeter was calibrated in situ for these measurements using the reported standard molar enthalpy of sublimation of naphthalene of 72.6 ± 0.6 kJ·mol^{-1}.[25]

Computational Details

In the present work, G3MP2B3 composite[26] calculations have been carried out to compute the energies of all compounds under study. This approach uses the B3LYP method and the 6-31G(d) basis set for both the optimization of geometry and calculation of frequencies. The calculation of frequencies permitted us also to correct energies for $T = 298.15$ K by introduction of the vibrational, translational, rotational and the pV terms. Then, high-order corrections to the B3LYP/6-31G(d) enthalpy were successively introduced by following the Gaussian-3 philosophy, albeit using a second-order Moller−Plesset perturbation instead of MP4 as in the original G3 method.[27] These composite calculations were carried out by means of the Gaussian 98 computer code.[28] The enthalpies computed for each compound were used to estimate standard enthalpies of formation and to compute ionization enthalpies, proton affinities and gas-phase acidities of the six dichloroanilines.

In a previous work, concerning the thermochemistry of monochloroanilines,[29] it was found that the BP86/DZVP level of theory was capable of reproducing gas-phase standard molar enthalpies more accurately than the composite method. Therefore, this approach was used again in the present work. The geometry of the dichloroanilines, and of benzene, chlorobenzene, dichlorobenzenes and aniline, were optimized within the Kohn−Sham formalism at the BP86/DZVP levels of theory. The BP86 method is based on Becke's 1988 exchange and on the Perdew's 86 correlation functionals.[30,31] The atomic electron density was described by the standard polarized double-ζ split valence basis set DZVP.[32] Calculation of frequencies was carried out at the same level of theory used in the optimization procedure. This was done to guarantee that optimized structures are minima on the PES and to obtain thermal corrections to the energy at $T = 298.15$ K. These calculations were performed by means of the GAMESS-UK suite of programs.[33,34]

Results

Combustion Experiments. Detailed results for a typical combustion experiment of each compound are given in Table 1, were $\Delta m(H_2O)$ is the deviation of the mass of water added to the calorimeter from 5222.5 g, the mass assigned to ϵ(calor), and ΔU_Σ is the correction to the standard state. The remaining terms have been previously described.[18,35] Table 2 lists the

TABLE 1: Results of a Typical Combustion Experiment at $T = 298.15$ K

	2,3-Clan	2,4-Clan	2,5-Clan	2,6-Clan	3,4-Clan	3,5-Clan
m(cpd)/g	0.98692	1.07447	1.06583	0.99788	0.99162	0.99325
m'(fuse)/g	0.00239	0.00261	0.00236	0.00326	0.00291	0.00300
ΔT_{ad}/K	0.76663	0.83444	0.82607	0.77225	0.77025	0.76860
$\epsilon_i/(J \cdot K^{-1})$	114.86	114.96	114.95	114.88	114.87	114.88
$\epsilon_f/(J \cdot K^{-1})$	110.63	110.63	110.58	110.75	110.58	110.77
$\Delta m(H_2O)$/g	0.4	−1.2	−1.4	0.5	0.6	−2.1
$-\Delta U$(IBP)/J[a]	19396.17	21106.44	20894.01	19538.71	19488.40	19437.99
$-\Delta U$(fuse)/J	38.81	42.39	38.33	52.94	47.26	48.72
$-\Delta U(HNO_3)$/J	12.78	32.36	32.60	13.25	9.07	17.07
$-\Delta U(As_2O_3)$/J	573.20	625.75	646.54	531.36	583.83	538.40
$-\Delta U$(ign)/J	1.28	1.26	1.27	1.27	1.28	1.27
$-\Delta U(H_2PtCl_6)$/J	2.03	2.32	2.54	2.22	1.72	2.66
$-\Delta U_\Sigma$/J	43.20	46.28	45.89	43.73	43.45	43.47
$-\Delta_c u^o/J \cdot g^{-1}$	18974.33	18946.40	18884.92	18935.35	18961.97	18915.35

[a] ΔU (IBP) already includes the ΔU (ign). ΔT_{ad} is the corrected temperature rise; ϵ_i and ϵ_f are the energy equivalents of contents in the initial and final states, respectively; $\Delta m(H_2O)$ is the deviation of mass of water added to the calorimeter from 5222.5 g; ΔU(IBP) is the energy change for the isothermal combustion reaction under actual bomb conditions; ΔU(fuse) is the energy of combustion of the fuse (cotton); $\Delta U(HNO_3)$ is the energy correction for the nitric acid formation; ΔU(ign) is the electrical energy for ignition; ΔU_Σ is the standard state correction; $\Delta_c u^o$ is the standard massic energy of combustion.

individual values of massic energy of combustion together with its mean $\langle \Delta_c u^o \rangle$ and its standard deviation. These values of $\Delta_c u^o$ refer to the combustion reaction:

$$C_6H_5NCl_2(cr) + (6.75)O_2(g) + (1198.5)H_2O(l) \rightarrow 6CO_2(g) + (1/2)N_2(g) + 2HCl \cdot 600H_2O(aq) \quad (1)$$

in which reactants and products are in the thermodynamic standard states at $T = 298.15$ K (with $HCl \cdot 600H_2O(aq)$ as the chlorine-containing product in the final state).

The energies of combustion that appear in the last row of Table 2 are converted to standard molar units in the first column of Table 3, $\Delta_c U_m^o(cr)$. Then, from these values, the standard molar enthalpies of combustion, $\Delta_c H_m^o(cr)$, are calculated by introduction of the ΔnRT term, being $\Delta n = -0.25$ as calculated from the number of gas-phase species appearing in eq 1. In accordance with normal thermochemical practice,[36,37] 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. Then, to derive the standard molar enthalpies of formation for the dichloroanilines, $\Delta_f H_m^o(cr)$, in the condensed phase and at $T = 298.15$ K, from $\Delta_c H_m^o(cr)$ values for the reaction described by eq 2, the standard molar enthalpies of formation of $CO_2(g)$, -393.51 ± 0.13 kJ·mol^{-1};[38] $H_2O(l)$, -285.830 ± 0.004 kJ·mol^{-1},[38] and HCl in $600H_2O(l)$, -166.540 ± 0.005 kJ·mol^{-1},[17,38] were used. The $\Delta_f H_m^o(cr)$ results show that the compounds with two adjacent chlorine atoms are less stable than the other isomers whereas 2,5-dichloroaniline is the isomer that releases less heat during the combustion experiment. The literature reports only the value of the standard molar enthalpy of formation, in the crystalline phase, of 3,4-dichloroaniline, as -89.12 kJ·mol^{-1},[39] a value that is substantially different from the one presented in this work. This was to be expected because Masalitinova et al.[39] used static bomb combustion calorimetry for chlorine compounds, as we have already stressed in ref 29. As it will be seen later in the text, our experimental results are in good agreement with those coming from modern computational approaches.

Phase-Change Experiments. Measurements of the enthalpies of sublimation of dichloroanilines, 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

$$\Delta_{cr}^{g} H_m^o(T{=}298.15\ K) = \Delta_{cr,298.15K}^{g,T} H_m - \Delta_{298.15K}^{T} H_m^o(g) \quad (2)$$

using $\Delta_{298.15K}^{T} H_m^o(g)$ estimated by a group-additivity method, i.e., (dichloroaniline = aniline + 2(chlorobenzene − benzene), based on the values of Stull et al.[24]

The higher $\Delta_{cr}^{g} H_m^o$ values clearly show that the intermolecular forces are larger in the case of the 3,4- and 3,5-dichloroanilines and that the presence of a chlorine atom in position 2 diminishes those forces, possibly due to the formation of intramolecular N−H···Cl bonds as previously reported for 2-chloroaniline based on microwave and infrared experiments.[40,41] In fact, the enthalpy of phase transition is much lower for the isomer with chlorines in positions 2 and 6, suggesting that the presence of chlorine atoms disable the formation of intermolecular hydrogen bonds.

Gas-Phase Enthalpies. Combining the standard molar enthalpies of formation in the condensed phase, $\Delta_f H_m^o(cr)$, with the standard molar enthalpies of sublimation, $\Delta_{cr}^{g} H_m^o$(298.15 K), it is possible to derive the standard molar enthalpies of formation in the gaseous state, $\Delta_f H_m^o(g)$, for the six dichloroaniline isomers, which are compiled in Table 5.

Other strategies, such as the empirical method proposed by Cox[42] or ab initio based computations, may also be used to obtain standard molar enthalpies of formation. Cox suggested a method to estimate the standard molar enthalpies of formation of gaseous benzene derivatives,[42] by assuming that each group, when substituted into a benzene ring, produces a characteristic increment in $\Delta_f H_m^o(g)$ 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 on three adjacent carbon atoms of the aromatic ring. From the standard molar gas-phase enthalpies of formation given in the literature[43] for benzene, $\Delta_f H_m^o = 82.6 \pm 0.7$ kJ·mol^{-1}, for 1,2-dichlorobenzene, $\Delta_f H_m^o = 30.2 \pm 2.1$ kJ·mol^{-1}, for 1,3-dichlorobenzene, $\Delta_f H_m^o = 25.7 \pm 2.1$ kJ·mol^{-1}, for 1,4-dichlorobenzene, $\Delta_f H_m^o = 22.5 \pm 1.5$ kJ·mol^{-1} and for aniline, $\Delta_f H_m^o = 87.1 \pm 1.1$ kJ·mol^{-1}, it is possible to estimate, following the suggestions of Cox, the $\Delta_f H_m^o(g)$ for the different dichloroanilines. The estimated values coming from the application of the Cox method are also reported in Table 5. These estimated $\Delta_f H_m^o(g)$ are in good agreement with the experimental determination if one considers the limit of acceptance of 10 kJ·mol^{-1} indicated by Cox for his scheme.[42] However, for one of the compounds, namely, 2,6-dichloroaniline a large difference is found, $\Delta = -22.0 \pm 3.0$ kJ·mol^{-1}, which is not surprising because the intramolecular N−H···Cl bonds are completely neglected by the Cox scheme. For the other five isomers, positive and negative differences between estimated and experimental do not have a simple explanation.

The use of first-principles calculations are known to provide accurate estimations for the gas-phase enthalpies of formation if the computations are combined with precise experimental enthalpies of formation for all species appearing in a well-chosen working reaction, except the one we are interested in. In the present work, BP86/DZVP and G3MP2B3 calculations have been carried out to estimate the enthalpy of formation of the six dichloroanilines. The latter method was tuned to provide excellent estimates of this property for small and medium sized

TABLE 2: Individual Values of the Massic Energy of Combustion $-\Delta_c u^o$ of the Compounds at $T = 298.15$ K

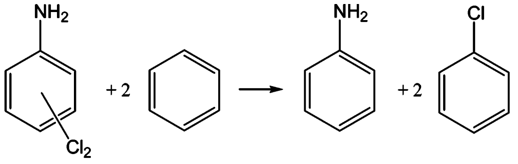
2,3-dichloroaniline	2,4-dichloroaniline	2,5-dichloroaniline	2,6-dichloroaniline	3,4-dichloroaniline	3,5-dichloroaniline
			$\Delta_c u^o$/J·g^{-1}		
18974.33	18956.19	18884.92	18935.35	18961.97	18915.35
18982.64	18946.40	18889.33	18940.70	18970.00	18919.81
18969.04	18931.80	18897.29	18929.19	18972.53	18915.23
18979.88	18955.43	18902.56	18937.86	18964.26	18904.36
18973.97	18960.97	18890.80	18944.22	18967.41	18919.07
18962.33	18934.48	18879.12	18940.09	18969.54	18911.33
	18943.95				18919.98
			$-\langle\Delta_c u^o\rangle$/J·g^{-1} [a]		
18973.7 ± 3.0	18947.0 ± 4.2	18890.7 ± 3.4	18937.9 ± 2.1	18967.6 ± 1.6	18915.0 ± 2.1

[a] Mean value and standard deviation of the mean.

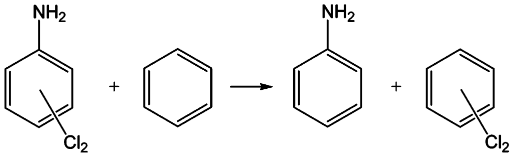
TABLE 3: Derived Standard Molar Energies of Combustion $\Delta_c U_m^o$, Standard Molar Enthalpies of Combustion $\Delta_c H_m^o$, and Standard Molar Enthalpies of Formation $\Delta_f H_m^o$, for the Compounds at $T = 298.15$ K, with $p^o = 0.1$ MPa

compound	$-\Delta_c U_m^o$(cr)/ kJ·mol^{-1}	$-\Delta_c H_m^o$(cr)/ kJ·mol^{-1}	$-\Delta_f H_m^o$(cr)/ kJ·mol^{-1}
2,3-dichloroaniline	3074.1 ± 1.2	3074.7 ± 1.2	48.2 ± 1.4
2,4-dichloroaniline	3069.8 ± 1.5	3070.4 ± 1.5	52.5 ± 1.7
2,5-dichloroaniline	3060.6 ± 1.3	3061.2 ± 1.3	61.7 ± 1.5
2,6-dichloroaniline	3068.3 ± 1.0	3068.9 ± 1.0	54.0 ± 1.3
3,4-dichloroaniline	3073.1 ± 0.9	3073.7 ± 0.9	49.2 ± 1.2
3,5-dichloroaniline	3064.6 ± 1.0	3065.2 ± 1.0	57.7 ± 1.3

molecules,[26,27] whereas the former approach was found to yield excellent estimates for the three monochloroaniline isomers[29] and also for the six dichlorophenol isomers.[44] These two approaches have been used to compute the enthalpy of the following reactions:



(3)



(4)

considering the energies of all species, thermally corrected for $T = 298.15$ K. Then, using the latter value and the experimental enthalpies of formation of the other compounds appearing in reaction 3 or reaction 4 with the exception of the dichloroaniline (values for benzene, aniline, and the three dichloroaniline appear above; for chlorobenzene, $\Delta_f H_m^o = 52.0 \pm 1.3$ kJ·mol^{-1}),[43] the estimated $\Delta_f H_m^o$ are obtained. The use of the composite method to calculate the enthalpy of the reaction of atomization for the dichloroanilines, which would permit us to estimate their $\Delta_f H_m^o$ from the experimental values of H, C, N, and Cl atoms was not considered here because it would provide poorer estimates.[29] The values estimated with the G3MP2B3 approach and reaction 4 are reported in Table 5. Results are in excellent agreement with experimental values and the mean of their deviations to experimental data is only 1.5 kJ·mol^{-1}. This mean value increases to 3.3 kJ·mol^{-1} (results not shown) if the working reaction 3 is used. Interestingly, this difference is smaller if the BP86/DZVP approach is used; it is of 2.2 kJ·mol^{-1} if reaction 4 is used and it is of 2.7 kJ·mol^{-1} if reaction 3 is considered (results not shown).

Other Thermodynamic Properties. In a previous work, the G3MP2B3 approach was found to be an excellent choice for the calculation of some other gas-phase properties of other chlorinated anilines.[29] In fact, proton affinities and gas-phase acidities almost matched available experimental values.[45,46] Considering the six experimental values available for aniline, 3-chloroaniline and 4-chloroaniline, the mean deviation is 3.4 kJ·mol^{-1}, well within the ~4 kJ·mol^{-1} aimed for the computational methods. In the case of the ionization enthalpies, there are three values for the 4-chloroaniline compounds, and the G3MP2B3 adiabatic result is within the experimental values[47] and differs by only 5.0 kJ·mol^{-1} for the lowest experimental result. The agreement is even better for 3-chloroaniline, −3.7 kJ·mol^{-1}, whereas for 2-chloroaniline it is of 10.5 kJ·mol^{-1}, but being inside the interval defined by the two experimental values. From what is exposed above, it seems that G3MP2B3 values are excellent estimations for these properties. Therefore, in the present work, these properties have been also evaluated for the six dichloroanilines. In the literature, only the experimental ionization energy of the 2,6-dichloroaniline compound is available, its value being 733.3 ± 1.9 kJ·mol^{-1}.[48,49]

The full set of computed proton affinities, gas-phase acidities and ionization enthalpies are reported in Table 6. Starting with the ionization enthalpies and with the comparison between theory and experiment, it is found that the difference between the G3MP2B3 and the experimental value is ~54 kJ·mol^{-1}. Obviously, so large a difference must be dissected because the confidence on the present theoretical results is dependent on this issue. As written above for the monochloroanilines, several experimental values are reported in the literature and only some of them are close to the computed values. Interestingly enough and when more than one value is available, only the lowest result is close to the G3MP2B3 number.[29,48] For example, in the case of the 2-chloroaniline isomer, the highest experimental value is ~47 kJ·mol^{-1} higher than the G3MP2B3 result, a difference that is comparable to that calculated for the 2,6-dichloroaniline compound. Because the experimental results compiled by Rosenstock et al.[47] come from several different works and experimental techniques, one could not easily attribute the difference to any possible source of errors. Further, it is not possible for us to decide which is the most accurate experimental number, unless, as performed by Hunter and Lias[46] in their review of proton affinities, we choose the value that is closer to a computationally derived result. With that procedure, and as referred above, the G3MP2B3 and the lowest experimental results are within 10 kJ·mol^{-1}. Therefore, the computed ionization enthalpy for 2,6-dichloroaniline should be used in future compilations of ionization enthalpies. Curiously, as happened with the standard enthalpies of formation, the ionization enthalpies could be divided in three groups: the lowest ionization enthalpies are calculated for 2,4- and 3,4-dichloroa-

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

compound	no. of experiments	T/K	$\Delta_{cr}^{g,T}H_{m}^{o}$/ kJ·mol^{-1}	$\Delta_{298.15K}^{T}H_{m}^{o}$(g)/ kJ·mol^{-1}	$\Delta_{cr}^{g}H_{m}^{o}$(298.15 K)/ kJ·mol^{-1}
2,3-dichloroaniline	6	355		9.1	82.2 ± 1.0
2,4-dichloroaniline	5	356	91.3 ± 1.0	9.2	84.7 ± 1.3
2,5-dichloroaniline	5	355	93.9 ± 0.3	9.1	83.4 ± 1.3
2,6-dichloroaniline	6	355	92.5 ± 1.3	9.1	74.2 ± 0.9
3,4-dichloroaniline	5	355	83.3 ± 0.9	9.1	87.5 ± 0.2
3,5-dichloroaniline	6	356	96.6 ± 0.2	9.2	86.7 ± 0.7
			95.9 ± 0.7		

TABLE 5: Comparison between Experimental Derived Standard Molar Enthalpies of Formation, $\Delta_{f}H_{m}^{o}$, at T = 298.15 K, for the Six Isomers and Those Estimated from DFT[a] Calculations and from the Cox Scheme[a]

isomer	experimental	G3MP2B3	BP86/DZVP	Cox
2,3-dichloroaniline	34.0 ± 1.7	31.9 (2.1)	35.8 (−1.8)	42.7 ± 2.5 (−8.7 ± 3.0)
2,4-dichloroaniline	32.2 ± 2.1	33.9 (−1.7)	28.5 (3.7)	34.2 ± 2.5 (−2.0 ± 3.3)
2,5-dichloroaniline	21.7 ± 2.0	22.7 (−1.0)	25.4 (−3.7)	31.0 ± 2.0 (−9.3 ± 2.8)
2,6-dichloroaniline	20.2 ± 1.6	22.3 (−2.1)	24.6 (−4.4)	42.2 ± 2.5 (−22.0 ± 3.0)
3,4-dichloroaniline	38.3 ± 1.2	38.0 (0.3)	39.1 (−0.8)	34.7 ± 2.5 (3.6 ± 2.8)
3,5-dichloroaniline	29.0 ± 1.5	30.7 (−1.7)	27.2 (1.8)	30.2 ± 2.5 (−1.1 ± 2.9)

[a] Enthalpic differences with respect to the experimental values are given in parentheses. All units in kJ·mol^{-1}.

TABLE 6: G3MP2B3 Computed Proton Affinities, PA, Gas-Phase Acidities, $\Delta H_{acidity}$, Ionization Enthalpies, IE, at T = 298.15 K, for the Six Dichloroaniline Isomers[a]

compound	PA		$\Delta H_{acidity}$	IE
2,3-dichloroaniline	858.5[b]	4.3[d]	1484.6	786.8
2,4-dichloroaniline	857.6[b]		1484.8	771.8
2,5-dichloroaniline	853.8[b]	5.4[d]	1479.1	788.9
2,6-dichloroaniline	860.2[b]	22.5[d]	1489.9	787.2
3,4-dichloroaniline	853.9[b]		1487.5	771.8
3,5-dichloroaniline	861.5[c]	−12.0[d]	1478.2	796.7

[a] All units in kJ·mol^{-1}. [b] N-protonation. [c] C4-protonation. [d] Difference between N-protonation and C4-protonation affinities.

nilines; the highest value is calculated for 3,5-dichloroaniline; the other three isomers have almost the same ionization enthalpy.

No experimental gas-phase enthalpies or proton affinities were found for the dichloroanilines and, using a reasoning similar to that performed for experimental and G3MP2B3 computed values for the monochloroanilines, it is possible to ensure that the gas-phase acidities and proton affinities that appear in Table 6 would be accurate enough to prevent future experimental work on these compounds because an uncertainty interval of ±5 kJ·mol^{-1} is suggested for these computed properties. As found for the 3-chloroaniline,[29] the protonation in 3,5-dichloroaniline is more favorable if it occurs at the C4-site (para position), and for the other five isomers, protonation occurs at the nitrogen atom. However, for 2,3-dichloroaniline, protonation at the nitrogen atom is only 4.3 kJ·mol^{-1} more favorable than protonation at the C4-position; cf. Table 6. Protonation at the other carbon atoms without chlorine substitution is unfavorable by more than 20 kJ·mol^{-1}.

Conclusions

The standard molar gas-phase enthalpies of formation, at T = 298.15 K, of the six dichloroanilines have been obtained both by experimental and by computational techniques. The enthalpies of formation were indirectly retrieved from rotating bomb combustion calorimetry and Calvet microcalorimetry experiments, and their values show that the 2,6-dichloroaniline is the most stable isomer whereas the 3,4-dichloroaniline is the least stable species. The former observation comes possibly from the enhanced stabilization of the 2,6-dichloroaniline compound due to the formation of two N−H···Cl bonds similarly to that previously observed experimentally for 2-chloroaniline. In the case of the 3,4-dichloroaniline species, there are two chlorine atoms in adjacent positions that destabilize this compound when compared with the other isomers except 2,3-dichloroaniline. Nevertheless, in the latter case, the chlorine substitution in position 2 permits some stabilization due to the formation of internal hydrogen bond.

The $\Delta_{f}H_{m}^{o}$ values have been also 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 and, in the case of the Gaussian-3 theory based calculations, maximum deviation is lower than 2.1 kJ·mol^{-1}. The composite calculations have also been extended for the calculation of other thermodynamic properties, namely proton affinities, gas-phase acidities and ionization enthalpies. The excellent agreement between experimental and computational data previously reported for monochloroanilines, and also due to the excellent description of the gas-phase enthalpies of the dichloroanilines, the new computed proton affinities, gas-phase acidities and ionization enthalpies values seem to be of great confidence.

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Supporting Information Available: Tables listing the geometries and the G3MP2B3 and BP86/DZVP enthalpies at T = 298.15 K, for all compounds considered in the theoretical calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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