

Combined Experimental and Computational Study of the Thermochemistry of the Fluoroaniline Isomers

Manuel A. V. Ribeiro da Silva,* Ana I. M. C. L. Ferreira, and José R. B. Gomes

Centro de Investigação em Química, Departamento de Química, Faculdade de Ciências, Universidade do Porto, Rua do Campo Alegre, 687, P-4169-007, Porto, Portugal

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The standard ($p^\circ = 0.1$ MPa) molar enthalpies of formation in the condensed phase of all the fluoroanilines, with the exception of the 2,3,5-trifluoroaniline compound, were derived from the standard molar energies of combustion in oxygen at $T = 298.15$ K, measured by rotating bomb combustion calorimetry. Calvet high-temperature vacuum sublimation experiments were performed to measure their enthalpies of vaporization or sublimation. These experiments allowed the determination of the standard molar enthalpies of formation in the gaseous phase and at $T = 298.15$ K. These values are also compared with estimates based on G3MP2B3 and BP86/6-31+G(d) computations, which have been extended also to the fluoroaniline that was not studied experimentally. The results are in close agreement with a mean deviation of ~ 3 kJ·mol⁻¹. The largest difference between experimental and G3MP2B3 values is found for the pentafluoroaniline (-7.0 kJ·mol⁻¹). For the three monofluoroanilines, the composite approach has been used also to compute gas-phase acidities, electron and proton affinities, ionization enthalpies and N–H bond dissociation enthalpies. The computed values compare well with available experimental results supporting the new computed data.

1. Introduction

Fluoroanilines constitute an important class of fluorinated compounds, since they show interesting biological activities and, consequently, are widely used as key intermediates in the manufacture of prominent pharmaceuticals and agrochemicals (pesticides, herbicides, and fungicides).^{1–3} Fluoroaniline isomers are used in the synthesis of fluorobenzofuroxans.⁴ In general, benzofuroxan derivatives present remarkable biological activities, such as antimicrobial, fungicidal, algicidal, herbicidal, nematocidal, muscle relaxant, and vasorelaxant activity and anticancer effects.⁵ 2-Fluoroaniline has also been used in the synthesis of pyrrolo[2,1-c][1,4]benzoxazine,⁶ a system with a possible therapeutic potential, which belongs to the family of 2-substituted 1,4-benzoxazine and that serves as a starting material in the production of several drugs, such as analgesics, central nervous depressants, and antibiotic compounds.

They have been extensively used also in the chemical industry for pigments, dyes, rubbers, and plastics.⁷ More recently, fluorinated anilines have been used in the synthesis of conducting polymers because of their stability in the presence of air and humidity and potentially attractive economics.^{8–10} Recent studies have shown good results on the development of a lactate biosensor¹¹ using polyaniline-*co*-fluoroaniline, of a glucose biosensor¹² synthesized with poly(2-fluoroaniline), and bacterial fuel cells¹³ using different fluoroaniline polymers.

As a consequence of their large use, they are common environmental pollutants,¹⁴ present in water and soil due to being directly released into the environment by effluent industries or indirectly as a result of degradation or biotransformation of agricultural agents. Some of these compounds are highly toxic, potentially mutagenic, and carcinogenic substances.¹⁵ The most frequently reported consequences associated with exposure to

halogenated aniline include methemoglobinemia, splenotoxicity, hepatotoxicity, and nephrotoxicity.¹⁶

In the present work, which is a part of a broad study on the thermochemistry of haloanilines, for which we already reported our studies on chloroanilines,^{17–21} bromoanilines,²² and iodoanilines,²³ we report now the standard molar enthalpies of formation in the gaseous state, at $T = 298.15$ K, of 18 isomers of fluoroaniline, obtained from measurements of the standard ($p^\circ = 0.1$ MPa) molar energies of combustion in oxygen at $T = 298.15$ K using a rotating bomb combustion calorimeter, in the condensed phase, and from the values of the enthalpies of vaporization or sublimation measured by high-temperature Calvet microcalorimetry. The standard molar enthalpies of formation, in the gaseous state, of mono-, di-, tri- tetra- and pentafluoroaniline isomers are also compared with values estimated using the Cox scheme²⁴ and using computational thermochemical methods.

2. Experimental Details

2.1. Materials and Purity Control. The 18 isomers of fluoroanilines and the 4-fluorobenzoic and pentafluorobenzoic acids were obtained commercially from Aldrich Chemical Co. and were purified by repeated vacuum distillation or sublimation, with the exception of 4-fluorobenzoic acid, which was purified by zone melting. The purity of liquid samples of the fluoroaniline isomers was checked by gas–liquid chromatography (GLC, HP-4890A), whereas for the crystalline samples, differential scanning calorimeter (DSC, Setaram DSC 141) experiments to check the purity of the samples, using the fractional fusion technique²⁵ were performed. The DSC was also used in this research to determine the temperatures and enthalpies of fusion of the 3,5-difluoroaniline; 2,4,5-, 2,4,6-, and 3,4,5-trifluoroaniline; 2,3,4,5- and 2,3,5,6-tetrafluoroaniline, and 2,3,4,5,6-pentafluoroaniline. The temperature scale of the calori-

* To whom correspondence should be addressed. Phone: +351 226082821. Fax: +351 226082822. E-mail: risilva@fc.up.pt.

TABLE 1: Specific Densities, Experimental and Literature Values of Enthalpies and Temperatures of Fusion of Crystalline Isomers of Fluoroaniline

compd	CAS ^g	ρ , g·cm ⁻³	$\Delta_{\text{cr}}^{\text{l}}H_{\text{m}}$ (exptl), kJ·mol ⁻¹	T_{fus} (exptl), K	T_{fus} (lit.), K
2-FC ₆ H ₄ NH ₂ (l)	348-54-9	1.151 ^b			244 ^b 244.6 ^c
3-FC ₆ H ₄ NH ₂ (l)	372-19-0	1.156 ^b			
4-FC ₆ H ₄ NH ₂ (l)	371-40-4	1.173 ^b			272.4 ^c 271.3 ^e
2,3-F ₂ C ₆ H ₃ NH ₂ (l)	4519-40-8	1.274 ^b			
2,4-F ₂ C ₆ H ₃ NH ₂ (l)	367-25-9	1.268 ^b			265.7 ^b
2,5-F ₂ C ₆ H ₃ NH ₂ (l)	367-30-6	1.288 ^b			284–286 ^b 286.4 ^e
2,6-F ₂ C ₆ H ₃ NH ₂ (l)	5509-65-9	1.199 ^b			
3,4-F ₂ C ₆ H ₃ NH ₂ (l)	3863-11-4	1.302 ^b			
3,5-F ₂ C ₆ H ₃ NH ₂ (cr)	372-39-4	1.29 ^a	16.49 ± 0.41	312.7 ± 0.16	310–314 ^b 313 ^e
2,3,4-F ₃ C ₆ H ₂ NH ₂ (l)	3862-73-5	1.393 ^b			
2,3,6-F ₃ C ₆ H ₂ NH ₂ (l)	67815-56-9	1.39 ^b			
2,4,5-F ₃ C ₆ H ₂ NH ₂ (cr)	367-34-0	1.32 ^a	23.11 ± 0.04	332.49 ± 0.10	332–336 ^b 333 ^e
2,4,6-F ₃ C ₆ H ₂ NH ₂ (cr)	363-81-5	1.51 ^b	16.91 ± 0.14	307.49 ± 0.04	306–310 ^b
3,4,5-F ₃ C ₆ H ₂ NH ₂ (cr)	163733-96-8	1.44 ^a	17.87 ± 0.11	335.55 ± 0.07	334–337 ^b
2,3,4,5-F ₄ C ₆ HNH ₂ (cr)	5580-80-3	1.45 ^a	19.01 ± 0.06	301.00 ± 0.08	300–302 ^b
2,3,4,6-F ₄ C ₆ HNH ₂ (l)	363-73-5	1.5 ^b			
2,3,5,6-F ₄ C ₆ HNH ₂ (cr)	700-17-4	1.47 ^a	8.19 ± 0.06	305.44 ± 0.13	304–305 ^b 296.7–299.7 ^f
2,3,4,5,6-F ₅ C ₆ NH ₂ (cr)	771-60-8	1.77 ^a	13.85 ± 0.05	308.06 ± 0.06	308–309 ^b 306.7–308.7 ^f

^a Estimated from the mass and the dimensions of the pellet. ^b Ref 27. ^c Ref 28. ^d Ref 29. ^e Ref 30. ^f Ref 31. ^g These registry numbers were supplied by the author.

meter was calibrated by measuring the melting temperatures of three high purity reference materials:²⁶ naphthalene (Aldrich 99.9%), benzoic acid (NIST Standard Reference Material 39i), and indium (Aldrich, mass fraction >0.999 99), and the power scale was calibrated with the high purity indium as reference material.²⁶ Thermograms of samples hermetically sealed in stainless steel crucibles were recorded in an air atmosphere. The crucibles and the samples of compounds were weighed on a Mettler UMT2 microbalance with a sensitivity of 1×10^{-7} g. For the experimental determinations, five or six samples weighing ≈ 6 mg were scanned in the temperature from $T = 298$ K to ~ 15 K above of the melting point using a heating rate of 1.67×10^{-2} K·s⁻¹. The recorded thermograms did not show any phase transitions between $T \approx 298$ K and the melting temperature of the samples. The enthalpies and temperatures of fusion were computed from the DSC thermograms and are presented in Table 1, together with the values of temperatures of fusion found in the literature,^{27–31} where the uncertainties assigned are the standard deviation of the mean. In that Table are also given the specific densities available in the literature²⁷ and the estimated ones from the mass and the dimensions of the pellet that were used to calculate the true mass from the apparent mass in air.

The relative atomic masses used throughout this paper were those recommended by the IUPAC Commission in 2001.³²

2.2. Combustion Calorimetry. The combustion experiments were performed with an isoperibol rotating-bomb calorimeter, originally constructed at the University of Lund according to the design of Sunner.³³ Both the apparatus and the operating technique have been described,^{34–36} so only a brief description of the apparatus will be given here. The stainless steel combustion bomb, internal volume 0.258 dm³ and wall thickness of 1 cm, is a twin-valve bomb platinum-lined with all the internal fittings machined from platinum. The bomb is suspended from the lid of the calorimeter can, to which a mass of near 5222.5 g of water, previously weighed in a perspex vessel, is added.

Calorimeter temperatures were measured to $\pm 10^{-4}$ K at intervals of 10 s using a Hewlett-Packard (HP-2804A) quartz crystal thermometer interfaced to an Olivetti M 250E micro-computer programmed to compute the adiabatic temperature change. At least 100 readings were taken for both the before and after periods, whereas in the main period, the number of readings was ~ 120 . For all experiments, the ignition was made so that the final temperature would be as close as possible to $T = 298.15$ K. The electrical energy for ignition was determined from the change in potential across a 1400 μ F condenser when discharged through a platinum wire of diameter 0.05 mm. The rotating mechanism allows the simultaneous axial and end-over-end rotation of the bomb. The rotation of the bomb was started when the temperature rise in the main period reached $\sim 63\%$ of its final value and was continued throughout the rest of the experiment. Good et al.³⁷ have adopted this procedure and showed that the frictional work due to the rotation of the bomb is automatically included in the temperature corrections for the work of stirring and heat exchanged with the surrounding isothermal jacket. This one 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 to $\pm 10^{-4}$ K using a temperature controller (Tronac PTC 41).

Data acquisition and control of the calorimeter was performed through the use of the LABTERMO program.³⁸

Benzoic acid (NIST Standard Reference Material 39i) was used for calibration of the calorimeter. Its mass-related energy of combustion is $-(26\,434 \pm 3)$ J·g⁻¹, under certificate conditions. Calibration experiments were carried out in oxygen at a pressure of 3.04 MPa, with 1.00 cm³ of water added to the bomb, according to the procedure suggested by Coops et al.³⁹ For each experiment, corrections were made to the energy equivalent of the calorimeter for the deviation from the mass of water used to the reference mass of 5222.5 g.

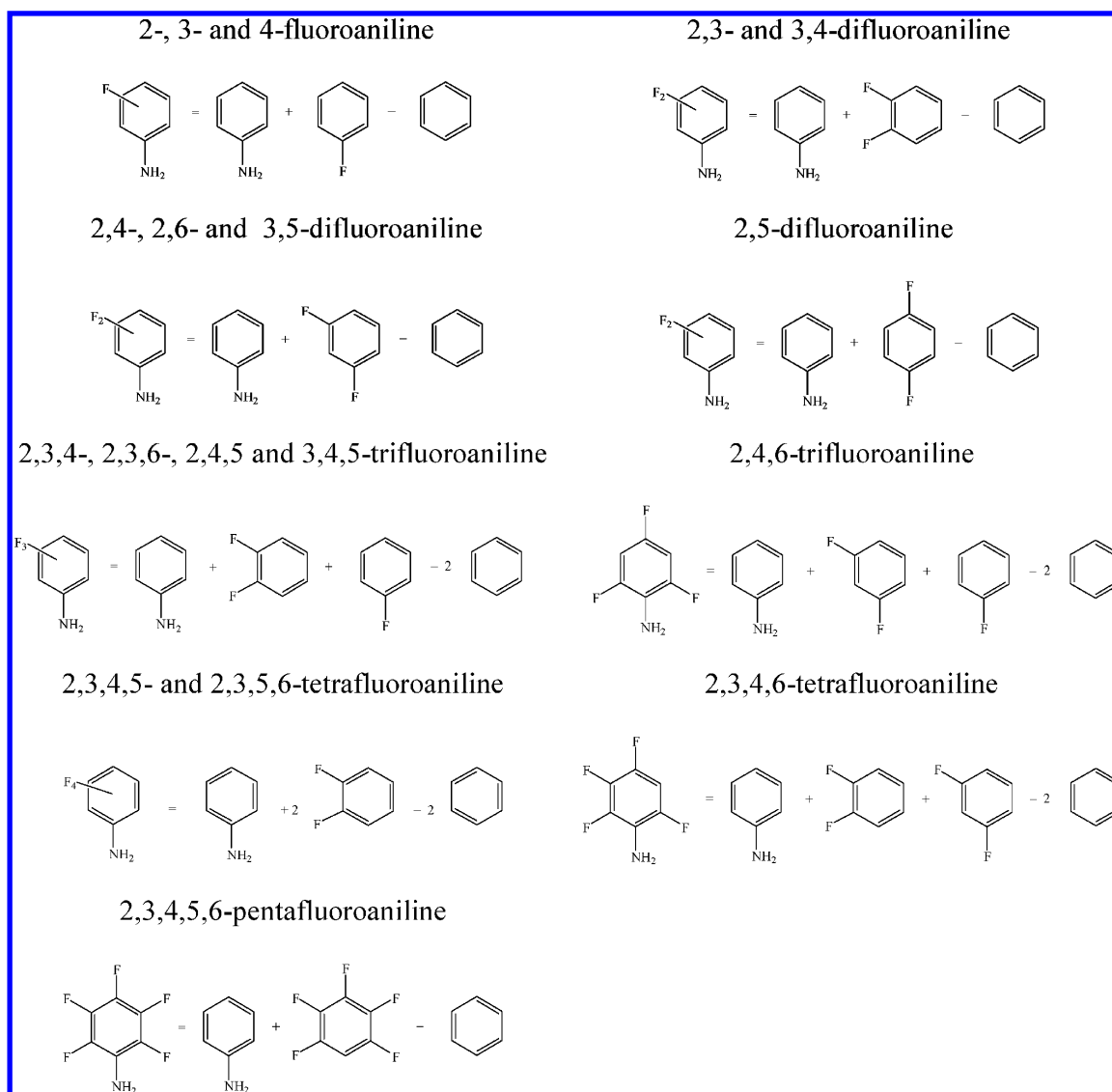


Figure 1. Molecular schemes for the estimation of the enthalpic corrections.

For 2-, 3-, and 4-fluoroaniline and 2,4- and 2,6-difluoroaniline, the energy equivalent of the calorimeter was determined as $\epsilon(\text{calor}) = 25\,184.8 \pm 0.9 \text{ J}\cdot\text{K}^{-1}$, from seven calibration experiments, where the uncertainty quoted is the standard deviation of the mean. For 4-fluorobenzoic acid, pentafluorobenzoic acid, and the remaining 13 isomers of fluoroaniline, the energy equivalent of the calorimeter was found to be $\epsilon(\text{calor}) = 25\,165.6 \pm 1.5 \text{ J}\cdot\text{K}^{-1}$ from seven calibration experiments. Good et al.⁴⁰ and Cox et al.⁴¹ recommended 4-fluorobenzoic acid and pentafluorobenzoic acid, respectively, as test substances,²⁶ for bomb combustion calorimetry of organic fluorine compounds. For organic fluorine compounds in which the atomic ratio of hydrogen to fluorine is equal to or greater than unity, 4-fluorobenzoic acid serves as a test material, and the reactions of these compounds yield hydrogen fluoride as the sole fluorine-containing product. Pentafluorobenzoic acid is used as the test substance for compounds with an atomic ratio of hydrogen to fluorine less than unity, and in this case, the combustion reactions yield a mixture of hydrogen fluoride and carbon tetrafluoride as combustion products. To avoid the formation of carbon tetrafluoride in the combustion of highly fluorinated compounds, a hydrogen-containing auxiliary substance is used to ensure that the hydrogen-to-fluorine atomic ratio greatly exceeds unity and, therefore, to avoid the energy correction that would be necessary for this side reaction. In these

cases, it has been shown that the fluorine in the products was entirely in the form of hydrogen fluoride.⁴² The combustion experiments of 4-fluorobenzoic acid and pentafluorobenzoic acid were performed in oxygen at $p = 3.04 \text{ MPa}$ and in the presence of 10.00 cm^3 of water placed in the bomb. *n*-Hexadecane (Aldrich Gold Label, mass fraction >0.999), stored under nitrogen, was used in the combustion of pentafluorobenzoic acid, as the auxiliary material with a double purpose: to reduce the soot formation and to avoid the formation of carbon tetrafluoride. Its mass-related energy of combustion was found to be $\Delta_c u^0 = -(47\,160.8 \pm 4.1) \text{ J}\cdot\text{g}^{-1}$, in agreement with that of Fraser and Prosen⁴³ for a sample of mass fraction 0.9996, $\Delta_c u^0 = -(47\,155.0 \pm 3.8) \text{ J}\cdot\text{g}^{-1}$. The experimental values obtained for 4-fluorobenzoic acid, $\Delta_c u^0 = -(21\,865.1 \pm 2.0) \text{ J}\cdot\text{g}^{-1}$, and for pentafluorobenzoic acid, $\Delta_c u^0 = -(12\,059.2 \pm 3.6) \text{ J}\cdot\text{g}^{-1}$, are in agreement with the recommended values: $\Delta_c u^0 = -(21\,860 \pm 4) \text{ J}\cdot\text{g}^{-1}$ ²⁶ and $\Delta_c u^0 = -(12\,060.4 \pm 4.8) \text{ J}\cdot\text{g}^{-1}$,²⁶ respectively.

Sealed polyester bags made from Melinex (0.025 mm thickness) were used in combustion of crystalline isomers of fluoroaniline in pellet form, with the exception of pentafluoroaniline, which was burned enclosed in polyethylene bags. The bags were sealed using the technique described by Skinner and Snelson,⁴⁴ who determined the mass-related energy of combustion of dry Melinex as $\Delta_c u^0 = -(22\,902 \pm 5) \text{ J}\cdot\text{g}^{-1}$; this value

TABLE 2: Typical Combustion Results at $T = 298.15$ K^a

	calibration	4-FBA	PFBA	2-FAn	2,3-FAn	2,3,4-FAn	2,3,4,5-FAn	2,3,4,5,6-FAn
m (BA), g	1.004 05							
m' (cpd), g		1.094 81	1.200 62	0.618 16	0.585 41	0.718 53	1.023 00	1.163 01
m'' (fuse), g	0.002 85	0.003 28	0.003 04	0.003 16	0.003 17	0.003 32	0.003 53	0.003 10
m''' (<i>n</i> -hexadecane), g			0.239 50					
m'''' (polyethylene), g				0.235 45	0.162 27	0.163 32	0.260 89	0.253 52
T_i , K	297.0814	297.1851	297.1102	296.9864	297.2669	297.2564	296.9745	296.9979
T_f , K	298.1224	298.1549	298.1537	298.1543	298.1415	298.1504	298.1588	298.1591
ΔT_{ad} , K	1.055 46	0.952 62	1.025 81	1.150 66	0.857 93	0.877 33	1.166 71	1.143 87
ϵ_i , J·K ⁻¹	13.70	51.66	52.11	51.98	51.70	51.82	52.00	52.01
ϵ_f , J·K ⁻¹	14.79	53.52	53.38	54.37	53.26	53.17	53.95	53.59
ϵ (calor), J·K ⁻¹	25 183.24	25 166.0 ^c	25 163.9 ^c	25 182.7 ^d	25 171.5 ^c	25 163.5 ^c	25 159.7 ^c	25 168.9 ^c
Δm (H ₂ O), g	-0.5	0.1	-0.4	-0.5	1.4	-0.5	-1.4	0.8
$-\Delta U$ (IBP) ^b , J	26 592.14	24 021.53	25 865.54	29 035.22	21 638.37	22 120.85	29 423.24	28 848.20
ΔU (BA), J	26 542.81							
ΔU (fuse), J	46.28	53.27	49.37	51.32	51.48	53.92	57.33	50.34
ΔU (<i>n</i> -hexadecane), J			11 294.88					
ΔU (polyethylene), J				10 908.93	7518.62	7 566.86	12 087.59	11 746.19
ΔU (HNO ₃), J	1.74	4.54	4.30	42.86	34.51	36.42	41.79	38.21
ΔU (ign), J	1.30	1.31	1.30	1.30	1.29	1.29	1.29	1.29
ΔU_{Σ} , J		22.75	39.14	25.83	12.67	26.88	36.42	38.58
$-\Delta_c u^0$, J·g ⁻¹		21 867.69	12 058.64	29 128.83	23 950.89	20 092.09	16 979.38	14 595.64

^a $p^0 = 0.1$ MPa. m (BA) is the mass of benzoic acid; m' (cpd) is the mass of compound burned in each experiment; m'' (fuse) is the mass of the fuse (cotton) used in each experiment; m''' (*n*-hexadecane) is the mass of *n*-hexadecane used in each experiment; m'''' (polyethylene) is the mass of polyethylene used in each experiment; T_i is the initial temperature increase; T_f is the final temperature increase; ΔT_{ad} is the corrected temperature increase/variation of adiabatic temperature; ϵ_i is the energy equivalent of the contents in the initial state; ϵ_f is the energy equivalent of the contents in the final state; ϵ (calor) is the energy equivalent of the calorimeter; Δ (H₂O) is the deviation from 5222.5 g of the mass of water added to the calorimeter; ΔU (IBP) is the energy change for the isothermal combustion reaction under actual bomb conditions; ΔU (BA) is the energy of combustion of benzoic acid; ΔU (fuse) is the energy of combustion of the fuse (cotton); ΔU (*n*-hexadecane) is the energy of combustion of the *n*-hexadecane; ΔU (polyethylene) is the energy of combustion of the polyethylene; ΔU (HNO₃) is the energy correction for the nitric acid formation; ΔU (ign) is the electrical energy for ignition; ΔU_{Σ} is the standard state correction; $\Delta_c u^0$ is the standard mass-related energy of combustion. ^b ΔU (IBP) includes ΔU (ign). ^c ϵ (calor) = $25\,165.6 \pm 1.5$ J·K⁻¹. ^d ϵ (calor) = $25\,184.8 \pm 0.9$ J·K⁻¹.

TABLE 3: Values of Standard^a Mass-Related Energy of Combustion, $\Delta_c u^0$, of Fluoroanilines at $T = 298.15$ K

2-FAn	2,3-FAn	2,3,4-FAn	2,3,4,5-FAn	2,3,4,5,6-FAn
$-\Delta_c u^0$, J·g ⁻¹				
29 128.83	23 941.07	20 088.26	16 983.40	14 590.71
29 135.21	23 950.89	20 086.91	16 976.33	14 589.88
29 137.30	23 942.10	20 101.67	16 981.63	14 601.64
29 122.75	23 958.52	20 102.22	16 978.34	14 595.64
29 120.62	23 953.70	20 084.87	16 976.84	14 598.58
29 127.34	23 957.14	20 092.09	16 979.38	14 594.05
29 124.74				

$-\langle \Delta_c u^0 \rangle$, J·g⁻¹^b
 29 128.1 ± 2.4 23 950.6 ± 3.0 20 092.7 ± 3.1 16 979.3 ± 1.1 14 595.1 ± 1.9

^a $p^0 = 0.1$ MPa. ^b Mean value and standard deviation of the mean.

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.⁴⁴ The liquid isomers of fluoroaniline were burned while enclosed in polyethylene bags. In each experiment, it was ensured that the hydrogen-to-fluorine atomic ratio greatly exceeded unity. The combustion experiments of the 18 isomers of fluoroaniline were carried out in oxygen, at $p = 3.04$ MPa and in the presence of 10.00 cm³ of water.

All the necessary weighing was performed on a Mettler AE 240 balance with a sensitivity of 1×10^{-5} g, and corrections from apparent mass to true mass were made.

The nitric acid formed was determined using the Devarda's alloy method,⁴⁵ and corrections were based on -59.7 kJ·mol⁻¹ for the standard molar energy of formation in which 0.1 mol·dm⁻³ HNO₃ (aq) is formed from O₂ (g), N₂ (g), and H₂O (l).⁴⁶

The electrical energy for ignition was determined from the change in potential difference across a capacitor when dis-

charged through the platinum ignition wire. For the cotton thread fuse of empirical formula CH_{1.686}O_{0.843}, $\Delta_c u^0 = -16240$ J·g⁻¹.⁴⁷

Corrections to the standard state were made by the procedure given by Good and Scott,⁴⁸ including the values for the solubility of carbon dioxide in hydrofluoric acid solutions, as given by Cox et al.⁴¹ An estimated pressure coefficient of mass-related energy, $(\partial u/\partial p)_T = -0.2$ J·g⁻¹·MPa⁻¹, at $T = 298.15$ K, a typical value for most organic compounds,⁴⁹ was used for all compounds, with the exception of 4-fluorobenzoic acid, which was $(\partial u/\partial p)_T = -0.115$ J·g⁻¹·MPa⁻¹ at $T = 298.15$ K,⁴⁰ and of pentafluorobenzoic acid, which was $(\partial u/\partial p)_T = -0.12$ J·g⁻¹·MPa⁻¹ at $T = 298.15$ K.⁴¹

2.3. Microcalorimetry Calvet. The standard molar enthalpies of sublimation or vaporization of the 18 fluoroanilines were measured using the drop-microcalorimetric technique of vacuum sublimation of Skinner et al.⁵⁰ or of vaporization, as suggested by Ribeiro da Silva et al.⁵¹ For these measurements, a Calvet high-temperature microcalorimeter (Setaram HT 1000) with the vacuum promoted by a rotary vacuum pump and a vapor diffusion pump was used. Both apparatus and technique have been recently described.⁵²

Samples of about 3–5 mg of crystalline sample of compound and 7–10 mg of the liquid sample, contained in small, thin, glass capillary tubes sealed at one end, and blank capillaries were simultaneously dropped at room temperature into the hot reaction vessels, held at a predefined temperature, T , and then removed from the hot zone by vacuum sublimation or 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 ± 10 μ g, into each of the twin calorimeter cells. The samples of compounds and the glass capillary tubes were weighed on a Mettler CH-8608 analytical balance with a sensitivity of 1×10^{-6} g.

TABLE 4: Derived Standard^a Molar Values of Fluoroanilines in Condensed Phase, at $T = 298.15$ K

compd	$-\langle\Delta_c u^0\rangle, \text{J}\cdot\text{g}^{-1}$	$-\Delta_c U_m^0 (\text{cr/l}), \text{kJ}\cdot\text{mol}^{-1}$	$-\Delta_c H_m^0 (\text{cr/l}), \text{kJ}\cdot\text{mol}^{-1}$	$-\Delta_f H_m^0 (\text{cr/l}), \text{kJ}\cdot\text{mol}^{-1}$
2-FC ₆ H ₄ NH ₂ (l)	29 128.1 ± 2.4	3236.6 ± 0.8	3238.5 ± 0.8	159.2 ± 1.3
3-FC ₆ H ₄ NH ₂ (l)	29 028.6 ± 0.6	3225.6 ± 0.6	3227.4 ± 0.6	170.3 ± 1.2
4-FC ₆ H ₄ NH ₂ (l)	29 081.6 ± 2.9	3231.5 ± 0.9	3233.3 ± 0.9	164.4 ± 1.4
2,3-F ₂ C ₆ H ₃ NH ₂ (l)	23 950.6 ± 3.0	3092.2 ± 1.0	3092.8 ± 1.0	341.1 ± 1.8
2,4-F ₂ C ₆ H ₃ NH ₂ (l)	23 872.2 ± 1.5	3082.1 ± 0.7	3082.7 ± 0.7	351.2 ± 1.7
2,5-F ₂ C ₆ H ₃ NH ₂ (l)	23 884.2 ± 2.0	3083.6 ± 0.8	3084.3 ± 0.8	349.6 ± 1.7
2,6-F ₂ C ₆ H ₃ NH ₂ (l)	23 900.7 ± 1.5	3085.8 ± 0.7	3086.4 ± 0.7	347.5 ± 1.7
3,4-F ₂ C ₆ H ₃ NH ₂ (l)	23 963.0 ± 2.3	3093.8 ± 0.9	3094.4 ± 0.9	339.5 ± 1.8
3,5-F ₂ C ₆ H ₃ NH ₂ (cr)	23 678.9 ± 0.8	3057.1 ± 0.9	3057.7 ± 0.9	376.1 ± 1.7
2,3,4-F ₃ C ₆ H ₂ NH ₂ (l)	20 092.7 ± 3.1	2955.6 ± 1.1	2955.0 ± 1.1	515.1 ± 2.4
2,3,6-F ₃ C ₆ H ₂ NH ₂ (l)	19 992.1 ± 2.9	2940.8 ± 1.1	2940.2 ± 1.1	529.9 ± 2.4
2,4,5-F ₃ C ₆ H ₂ NH ₂ (cr)	19 883.6 ± 4.2	2924.8 ± 1.5	2924.2 ± 1.5	545.9 ± 2.6
2,4,6-F ₃ C ₆ H ₂ NH ₂ (cr)	19 848.6 ± 2.3	2919.7 ± 1.0	2919.1 ± 1.0	551.0 ± 2.3
3,4,5-F ₃ C ₆ H ₂ NH ₂ (cr)	19 961.3 ± 1.9	2936.3 ± 1.0	2935.7 ± 1.0	534.4 ± 2.3
2,3,4,5-F ₄ C ₆ HNH ₂ (cr)	16 979.3 ± 1.1	2803.1 ± 0.7	2801.2 ± 0.7	705.0 ± 2.8
2,3,4,6-F ₄ C ₆ HNH ₂ (l)	17 039.1 ± 2.9	2812.9 ± 1.1	2811.1 ± 1.1	695.2 ± 2.9
2,3,5,6-F ₄ C ₆ HNH ₂ (cr)	16 957.9 ± 2.0	2799.5 ± 0.9	2797.7 ± 0.9	708.6 ± 2.9
2,3,4,5,6-F ₅ C ₆ NH ₂ (cr)	14 595.1 ± 1.9	2672.1 ± 0.9	2669.0 ± 0.9	873.5 ± 3.5

^a $p^0 = 0.1$ MPa.

From the experimental results, the standard molar enthalpies of sublimation or vaporization at $T = 298.15$ K, $\Delta_{\text{cr,l}}^{\text{g}} H_m^0$ ($T = 298.15$ K), were calculated from $\Delta_{298.15\text{K}}^T H_m^0$ (g), estimated by a group method, on the basis of the values of Stull et al.,⁵³ taking into account the schemes of Figure 1.

For these measurements, the microcalorimeter was calibrated in situ using the reported standard molar enthalpies of sublimation of iodine, 62.440 ± 0.726 kJ·mol⁻¹,²⁶ for the 3,5-difluoroaniline; and naphthalene, 72.600 ± 0.600 kJ·mol⁻¹,²⁶ for all the others crystalline fluorinated compounds; and of the vaporization of *n*-decane, 51.420 ± 0.206 kJ·mol⁻¹,²⁶ for liquid isomers of fluoroaniline.

2.4. Theoretical Calculations. The enthalpies of formation of all fluorinated anilines, mono-, di-, tri-, tetra and pentafluoroaniline, were estimated after Gaussian-3 based G3MP2B3 computations and the consideration of the atomization reaction. The computations carried out with the G3MP2B3 composite approach⁵⁴ use the B3LYP method and the 6-31G(d) basis set for both the optimization of geometry and calculation of frequencies. Introduction of high-order corrections to the B3LYP/6-31G(d) enthalpy is done in a manner that follows the Gaussian-3 philosophy, albeit using a second-order Moller–Plesset perturbation instead of MP4, as in the original G3 method.⁵⁵ The composite calculations were carried out by means of the Gaussian 03 computer code.⁵⁶ The energies computed at $T = 0$ K were thermally corrected for $T = 298.15$ K by introducing the vibrational, translational, rotational, and the pV terms. The vibrational term is based on the vibrational wave numbers calculated at the B3LYP/6-31G(d) level.

These computations have also been extended to the cationic, anionic, and radical species obtained from the three neutral fluoroaniline isomers to determine a few other thermodynamic properties for the latter compounds; namely, their ionization and N–H bond dissociation enthalpies, their gas-phase acidities, and finally, their electron and proton affinities.

For comparison purposes, the enthalpies of formation for all fluoroanilines have also been estimated from thermally corrected energies computed at the BP86/6-31+G(d) level of theory, that is, the BP86/6-31+G(d) has been used both for structure optimization and for the calculation of the vibrational frequencies. In this situation, a reaction of group substitution involving aniline, benzene, and fluorobenzene has been considered for all fluoroanilines, as revealed in Subsection 3.2.

3. Results

3.1. Experimental Enthalpies of Formation. Results for a typical combustion experiment of each compound are given in Table 2, where Δm (H₂O) 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 energy correction to the standard state. The remaining quantities are as previously defined.^{47,48} The values of the energy associated to the isothermal bomb process, ΔU (IBP), were calculated using the expression

$$\Delta U (\text{IBP}) = -\{\epsilon (\text{calor}) + \Delta m (\text{H}_2\text{O}) c_p (\text{H}_2\text{O}, \text{l})\} \Delta T_{\text{ad}} + \epsilon_i (T_i - 298.15 \text{ K}) + \epsilon_f (298.15 \text{ K} - T_f + \Delta T_{\text{corr}}) + \Delta U_{\text{ign}} \quad (1)$$

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

The individual values of $\Delta_c u^0$ together with the mean value, $\langle\Delta_c u^0\rangle$, and its standard deviation, are given for the test substances, each mono-, di-, tri-, and tetrafluoroaniline and pentafluoroaniline, in Table 3. These values of $\Delta_c u^0$ referred to the idealized combustion reaction of fluoroaniline isomers, yielding HF·10H₂O (l) as the only fluorine-containing product in the final state, accordingly to eq 2.

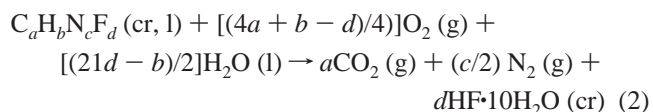


Table 4 lists the derived mean values of mass-related energy, together with the values of standard molar energies of combustion, $\Delta_c U_m^0$ (cr, l), and enthalpies of combustion, $\Delta_c H_m^0$ (cr, l), as well as the standard molar enthalpies of formation, $\Delta_f H_m^0$ (cr, l), for all the fluoroaniline isomers in the condensed phase at $T = 298.15$ K. In accordance with normal thermochemical practice,^{57,58} 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 $\Delta_f H_m^0$ (cr/l) from $\Delta_c H_m^0$ (cr/l) the standard molar enthalpies of formation of CO₂ (g), H₂O (l), and HF·10H₂O (l), $T = 298.15$ K, $-(393.51 \pm 0.13)$ kJ·mol⁻¹,⁵⁹ $-(285.830 \pm 0.040)$ kJ·mol⁻¹,⁵⁹ and $-(322.034 \pm 0.650)$ kJ·mol⁻¹,⁶⁰ respectively, were used.

TABLE 5: Standard^a Molar Enthalpies of Sublimation and Vaporization, $\Delta_{\text{cr,l}}^{\text{g}} H_{\text{m}}^{\circ}$, for the 17 Fluoroanilines, at 298.15 K, Determined by Microcalorimetry

compd	no. experiments	<i>T</i> , K	$\Delta_{\text{cr,l}}^{\text{g},T} H_{\text{m}}^{\circ}$ kJ·mol ⁻¹	$\Delta_{298.15\text{K}}^T H_{\text{m}}^{\circ}$ (g) kJ·mol ⁻¹	$\Delta_{\text{cr,l}}^{\text{g}} H_{\text{m}}^{\circ}$ (298.15 K) kJ·mol ⁻¹
2-FC ₆ H ₄ NH ₂ (l)	5	344.7	59.5 ± 0.1	7.5	52.0 ± 0.6
3-FC ₆ H ₄ NH ₂ (l)	6	344.8	62.2 ± 0.2	7.5	54.7 ± 0.6
4-FC ₆ H ₄ NH ₂ (l)	5	344.8	62.3 ± 0.3	7.5	54.8 ± 0.8
2,3-F ₂ C ₆ H ₃ NH ₂ (l)	6	344.6	57.4 ± 0.2	8.1	49.3 ± 0.5
2,4-F ₂ C ₆ H ₃ NH ₂ (l)	6	344.7	60.2 ± 0.1	8.1	52.1 ± 0.5
2,5-F ₂ C ₆ H ₃ NH ₂ (l)	6	344.5	60.6 ± 0.1	8.1	52.5 ± 0.5
2,6-F ₂ C ₆ H ₃ NH ₂ (l)	5	344.7	55.6 ± 0.1	8.1	47.5 ± 0.5
3,4-F ₂ C ₆ H ₃ NH ₂ (l)	5	344.6	61.4 ± 0.1	8.1	53.3 ± 0.5
3,5-F ₂ C ₆ H ₃ NH ₂ (l)	6	309.1	73.6 ± 0.1	1.9	71.7 ± 1.7
2,3,4-F ₃ C ₆ H ₂ NH ₂ (l)	5	326.8	59.1 ± 0.1	5.4	53.7 ± 0.5
2,3,6-F ₃ C ₆ H ₂ NH ₂ (l)	5	326.8	55.5 ± 0.1	5.4	50.1 ± 0.5
2,4,5-F ₃ C ₆ H ₂ NH ₂ (cr)	5	326.7	79.1 ± 0.1	5.4	73.7 ± 1.2
2,4,6-F ₃ C ₆ H ₂ NH ₂ (cr)	6	323.8	70.9 ± 0.3	4.9	66.0 ± 1.2
3,4,5-F ₃ C ₆ H ₂ NH ₂ (cr)	5	323.6	79.5 ± 0.1	4.8	74.6 ± 1.3
2,3,4,5-F ₄ C ₆ HNH ₂ (cr)	5	323.8	79.5 ± 0.1	5.2	74.3 ± 1.3
2,3,4,6-F ₄ C ₆ HNH ₂ (l)	5	324.1	55.7 ± 0.2	5.3	50.4 ± 0.6
2,3,5,6-F ₄ C ₆ HNH ₂ (cr)	5	323.8	67.7 ± 0.2	5.2	62.5 ± 1.1
2,3,4,5,6-F ₅ C ₆ NH ₂ (cr)	5	323.8	69.2 ± 0.1	5.5	63.7 ± 1.1

^a *p*^o = 0.1 MPa.**TABLE 6: Experimental and Estimated (Cox Scheme and DFT Calculations) Gas-Phase Enthalpies of Formation of the Fluoroanilines**

compd	$-\Delta_{\text{f}} H_{\text{m}}^{\circ}$ (g), kJ·mol ⁻¹			$\Delta_{\text{f}}^{\text{a}}$, kJ·mol ⁻¹		
	exptl	Cox scheme	calcd	Cox scheme	calcd	
2-FC ₆ H ₄ NH ₂	107.2 ± 1.4	107.5 ± 1.9	110.5 ^b	109.3 ^c	0.3 ± 2.4	3.3 ^b
3-FC ₆ H ₄ NH ₂	115.6 ± 1.3	111.5 ± 1.9	112.8 ^b	112.6 ^c	-4.1 ± 2.3	-2.8 ^b
4-FC ₆ H ₄ NH ₂	109.6 ± 1.6	111.5 ± 1.9	106.4 ^b	106.2 ^c	1.9 ± 2.5	-3.2 ^b
2,3-F ₂ C ₆ H ₃ NH ₂	291.8 ± 1.9	281.3 ± 1.6	290.4 ^b	288.4 ^c	10.5 ± 2.5	-1.4 ^b
2,4-F ₂ C ₆ H ₃ NH ₂	299.1 ± 1.8	300.8 ± 1.6	299.9 ^b	299.6 ^c	1.7 ± 2.4	0.8 ^b
2,5-F ₂ C ₆ H ₃ NH ₂	297.1 ± 1.8	298.3 ± 1.6	303.9 ^b	304.0 ^c	1.2 ± 2.4	6.8 ^b
2,6-F ₂ C ₆ H ₃ NH ₂	300.0 ± 1.8	292.8 ± 1.6	303.4 ^b	302.3 ^c	7.2 ± 2.4	3.4 ^b
3,4-F ₂ C ₆ H ₃ NH ₂	286.2 ± 1.9	289.3 ± 1.6	286.9 ^b	286.2 ^c	3.1 ± 2.5	0.7 ^b
3,5-F ₂ C ₆ H ₃ NH ₂	304.4 ± 2.4	304.8 ± 1.6	308.3 ^b	308.9 ^c	0.4 ± 2.9	3.9 ^b
2,3,4-F ₃ C ₆ H ₂ NH ₂	461.4 ± 2.5	488.7 ± 2.9	462.2 ^b	459.6 ^c	27.3 ± 3.8	0.8 ^b
2,3,5-F ₃ C ₆ H ₂ NH ₂		496.7 ± 2.9	481.1 ^b	480.2 ^c		
2,3,6-F ₃ C ₆ H ₂ NH ₂	479.8 ± 2.5	488.7 ± 2.9	479.0 ^b	477.0 ^c	8.9 ± 3.8	-0.8 ^b
2,4,5-F ₃ C ₆ H ₂ NH ₂	472.2 ± 2.9	500.7 ± 2.3	475.3 ^b	474.9 ^c	28.5 ± 4.1	3.1 ^b
2,4,6-F ₃ C ₆ H ₂ NH ₂	485.0 ± 2.6	496.7 ± 2.9	489.3 ^b	488.8 ^c	11.7 ± 3.9	4.3 ^b
3,4,5-F ₃ C ₆ H ₂ NH ₂	459.8 ± 2.6	496.7 ± 2.9	464.4 ^b	463.0 ^c	36.9 ± 3.9	4.6 ^b
2,3,4,5-F ₄ C ₆ HNH ₂	630.7 ± 3.1	679.3 ± 3.3	635.6 ^b	632.3 ^c	48.6 ± 4.5	4.9 ^b
2,3,4,6-F ₄ C ₆ HNH ₂	644.8 ± 3.0	679.3 ± 3.3	647.5 ^b	644.5 ^c	34.5 ± 4.5	2.7 ^b
2,3,5,6-F ₄ C ₆ HNH ₂	646.1 ± 3.1	679.3 ± 3.3	651.4 ^b	649.1 ^c	33.2 ± 4.5	5.3 ^b
2,3,4,5,6-F ₅ C ₆ NH ₂	809.8 ± 3.7	802.1 ± 2.1	802.8 ^b	797.8 ^c	7.7 ± 4.3	7.0 ^b

^a Difference between the experimental and the estimated values. ^b G3MP2B3. ^c BP86/6-31+G*.

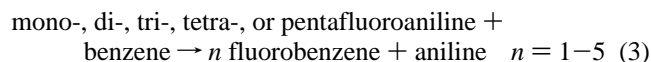
The present results may be compared with the values concerning fluorinated derivatives of aniline that have already been published in the literature. The only results found are the $\Delta_{\text{f}} H_{\text{m}}^{\circ}$ (cr/l) reported by Swartz in 1919,⁶¹ for the three monofluorinated anilines. The results of Swartz are positive and with values 44.56 kJ·mol⁻¹, 48.33 kJ·mol⁻¹ and 27.0 kJ·mol⁻¹, respectively, for the *ortho*-, *meta*-, and *para*-fluoroanilines. The older values differ from the present results by ~200 kJ·mol⁻¹, which is a consequence of having been determined by static bomb combustion calorimetry, a technique that is not appropriate for combustion calorimetry of halogenated compounds.

Table 5 registers the measurements of the standard molar enthalpies of sublimation or vaporization of the fluoroanilines by Calvet microcalorimetry, as well the respective uncertainties, taken as twice the standard deviations of the mean, which include the uncertainties in calibration. The derived standard molar enthalpies of formation in the condensed phase, Table 4, and the standard molar enthalpies of sublimation or vaporization, Table 5, yield the standard molar enthalpies of formation in

the gaseous phase of the 18 isomers of fluoroaniline, which are summarized in Table 6.

3.2. Computed Enthalpies of Formation. The enthalpies of formation for all the fluoroanilines, including that for 2,3,5-trifluoroaniline, which was not studied experimentally, since it was not possible to obtain a pure sample of this compound, have been estimated after the computation of the reaction of atomization at *T* = 298.15 K with the G3MP2B3 approach and the experimental gas-phase enthalpies of formation at *T* = 298.15 K: for carbon, $\Delta_{\text{f}} H_{\text{m}}^{\circ}$ (g) = 716.67 kJ·mol⁻¹; hydrogen, $\Delta_{\text{f}} H_{\text{m}}^{\circ}$ (g) = 218.00 kJ·mol⁻¹; nitrogen, $\Delta_{\text{f}} H_{\text{m}}^{\circ}$ (g) = 472.68 kJ·mol⁻¹; and fluorine, $\Delta_{\text{f}} H_{\text{m}}^{\circ}$ (g) = 79.39 kJ·mol⁻¹.⁶² Please note that the present strategy differs from that used by other authors, that is, the computation of the enthalpy of atomization at *T* = 0 K and then the combination of this value at *T* = 0 K with a theoretical estimate for the enthalpic difference between *T* = 298.15 K and *T* = 0 K for the species we are interested in and experimental temperature corrections for the elements, in their standard states, which compose that species.^{63,64} Other

authors prefer a mixture of computational and experimental corrections for the elements.⁶⁵ In the case of the computations with the BP86/6-31+G(d) approach, the estimates are based on the computed enthalpy for the following working reaction



and the experimental gas-phase enthalpies of formation of benzene, $\Delta_f H_m^\circ(\text{g}) = 82.7 \pm 0.7 \text{ kJ}\cdot\text{mol}^{-1}$; aniline, $\Delta_f H_m^\circ(\text{g}) = 87.1 \pm 1.1 \text{ kJ}\cdot\text{mol}^{-1}$; and fluorobenzene, $\Delta_f H_m^\circ(\text{g}) = -(115.9 \pm 1.4) \text{ kJ}\cdot\text{mol}^{-1}$.⁶⁶ The enthalpies estimated for all the fluoroanilines with both approaches introduced above are also collected in Table 6 and compared directly with the experimental results. Globally, the agreement between experimental and computational enthalpies of formation is excellent. Importantly, confirming previous conclusions obtained for other halogenated anilines,^{20,22,23,67} the use of the BP86 or B3LYP exchange-correlation functionals together with a group substitution reaction yields very good estimates for the gas-phase enthalpies of formation of substituted anilines. Here, the mean absolute deviation to the experimental results, that is, the sum of all Δ 's in Table 6 divided by 18, is $3.2 \text{ kJ}\cdot\text{mol}^{-1}$ for the BP86 values and $3.3 \text{ kJ}\cdot\text{mol}^{-1}$ for the G3MP2B3 estimates. All estimates deviate from the experimental values by $<5 \text{ kJ}\cdot\text{mol}^{-1}$, except the results computed for 2,5-difluoroaniline and pentafluoroaniline. In the former case, the differences are of $\sim 7 \text{ kJ}\cdot\text{mol}^{-1}$ for both computational approaches, whereas for the latter compound, differences are 7.0 and $12.0 \text{ kJ}\cdot\text{mol}^{-1}$ for G3MP2B3 and BP86 approaches, respectively. Since these two compounds are substantially different both in number and in positioning of fluorine atoms attached to the aromatic ring, it is not possible to advance any easy justification for the larger deviations found for these two compounds.

In fact, if we consider the BP86 estimates for the difluoroanilines, it is found that for two of the six isomers, the Δ values are smaller than $1 \text{ kJ}\cdot\text{mol}^{-1}$. In addition, the BP86 values for the tetrafluoroanilines are also in excellent agreement with experimental results, with the largest deviation found for 2,3,5,6-tetrafluoroaniline and of only $3.0 \text{ kJ}\cdot\text{mol}^{-1}$. Also interesting, for the monofluoroanilines, the two computational approaches yield the following order of stability, meta > ortho > para, whereas from the experimental determinations, it is found that the meta is the most stable monofluoroaniline and that the ortho is the least stable. However, if we take into account the uncertainties associated with the experimental results, it is possible to suggest the following order of stability: meta > ortho = para. Other changes in relative stability determined by computational and experimental methods are found for 2,5- and 2,6-difluoroanilines and for 2,3,4- and 3,4,5-trifluoroanilines. The interaction between fluorine atoms attached to adjacent carbon atoms in the ring is found to be largely destabilizing. For example, the difference between the enthalpy of formation of 3,4- and 3,5-difluoroanilines is of $\sim 18 \text{ kJ}\cdot\text{mol}^{-1}$. A stabilizing interaction is found when fluorine atoms appear in positions 2 or 6 or both due to the formation of internal hydrogen bonds.

The variation of the standard experimental gas-phase enthalpies of formation for the mono fluoro-, chloro-,²⁰ bromo-²² and iodoanilines²³ is illustrated in Figure 2. The consideration of the experimental values together with the experimental uncertainties yields the following conclusions: (i) the meta compound is the most stable isomer only when the halogen element is fluorine; (ii) the enthalpic differences between the most and least stable isomers diminish with the size of the halogen atom; (iii) the enthalpies of formation for the three iodoanilines are

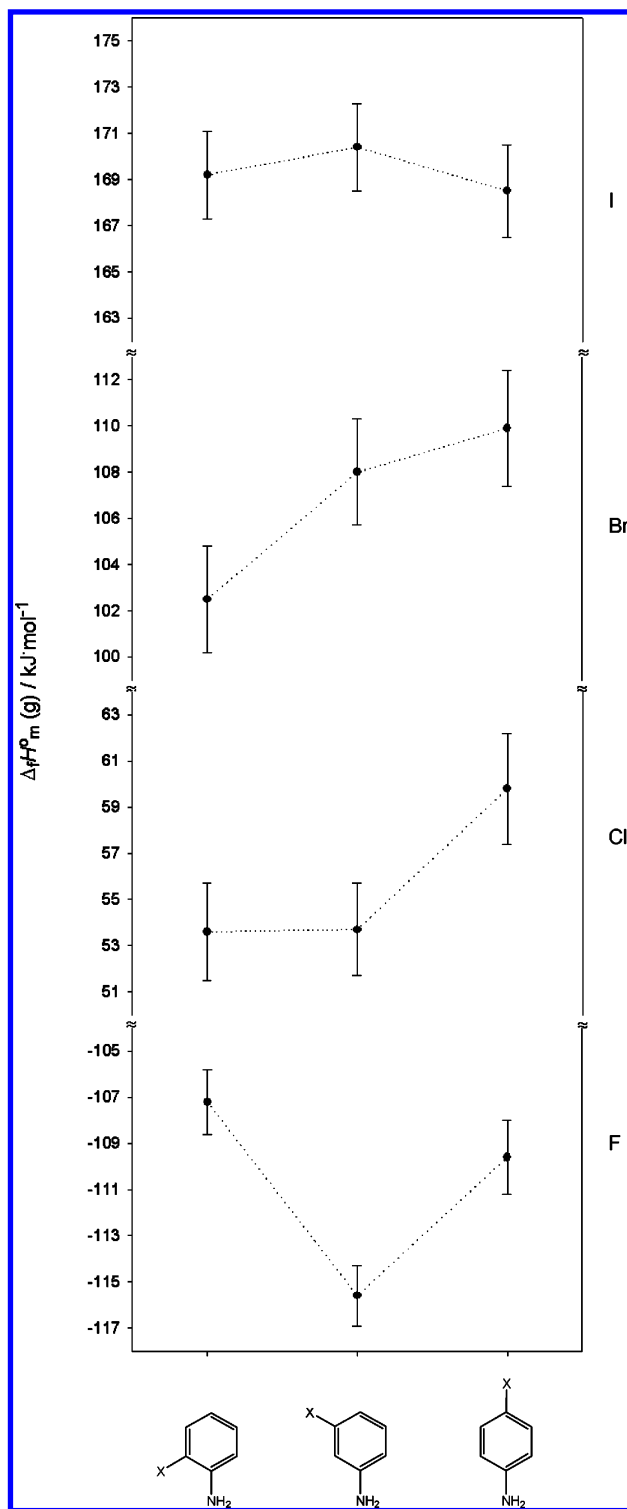


Figure 2. Variation of the standard molar enthalpy of formation in the monohalogenated anilines. Experimental results for the chloro-, bromo-, and iodoanilines have been taken from refs 20, 22, and 23, respectively.

almost degenerate; (iv) there is not any similar trend for the enthalpic variation when going from the ortho to the para isomers with the size of the halogen atom.

The plotting of the experimental gas-phase enthalpy of formation of aniline and pentafluoroaniline and also of each of the most stable mono-, di-, tri-, and tetrafluoroaniline with $0 < n < 5$ follows an almost linear correlation with $R^2 = 0.9996$ and slope $-178.0 \text{ kJ}\cdot\text{mol}^{-1}$. Very recently, we have found a similar slope for the computed enthalpies of formation for all

TABLE 7: G3MP2B3 Computed Electron (EA) and Proton (PA) Affinities, Ionization Enthalpies (IE), Gas-Phase Acidities ($\Delta H_{\text{acidity}}$) and N–H Bond Dissociation Enthalpies (BDE) for the Three Fluoroanilines

compd	EA, kJ·mol ⁻¹	PA, kJ·mol ⁻¹	IE, kJ·mol ⁻¹	$\Delta H_{\text{acidity}}$, kJ·mol ⁻¹	N–H BDE, kJ·mol ⁻¹
2-fluoroaniline	90.7	866.7 (N)	773.5 820.1 ^a ; 789.2 ^b	1519.3 1517. ± 9.2 ^c	397.3
3-fluoroaniline	94.4	867.9 (C4) 867.3 ^d	779.9 803.7 ^b	1513.8 1511. ± 8.8 ^c	401.3
4-fluoroaniline	80.6	870.3 (N) 871.5 ^d	760.0 762.2 9. ± 6 ^c ; 789.2 ^b	1530.3 1524. ± 8.8 ^c	393.4

^a Ref 70. ^b Refs 71–73, vertical value. ^c Ref 74. ^d Ref 69. ^e Ref 75.

fluorobenzenes ($R^2 = 0.9964$ and slope -174.2 kJ·mol⁻¹), suggesting that the effects of introducing fluorine atoms in the parent aniline compound are similar to that found for benzene.⁶⁸

3.3. Enthalpies Estimated with the Cox Scheme. Cox²⁴ suggested a method to estimate the standard molar enthalpies of formation of gaseous aromatic compounds by assuming that each group, when substituted into a benzene ring, produces a characteristic increment in $\Delta_f H_m^0$ (g) and that each ortho pair of substituents leads to an enthalpy increment of 4 kJ·mol⁻¹, with another additional increment of 4 kJ·mol⁻¹ for every set of three substituents in three consecutive carbon atoms of the aromatic ring. From the values of $\Delta_f H_m^0$ (g), at $T = 298.15$ K, for benzene and for fluorobenzene available in the literature,⁶⁶ the calculated enthalpic increments of a fluorine atom in a benzene ring is $-(198.6 \pm 1.6)$ kJ·mol⁻¹, which together with the enthalpy of formation of aniline allows the estimation of the standard molar enthalpies of formation of the three isomers of monofluoroaniline. The values estimated by following the ideas of Cox²⁴, which are in very good agreement with the experimental $\Delta_f H_m^0$ (g), are registered in Table 6. For the estimation of the $\Delta_f H_m^0$ (g) for the six isomers of difluoroanilines, the enthalpic increments for the introduction of two fluorine atoms in the relative positions ortho, meta, and para were calculated using the $\Delta_f H_m^0$ (g) available in the literature⁶⁶ for 1,2-difluorobenzene, 1,3-difluorobenzene, and 1,4-difluorobenzene: $-(293.7 \pm 10.9)$, $-(309.2 \pm 1.0)$, and $-(306.7 \pm 1.0)$ kJ·mol⁻¹, respectively. These increments were used in the estimations of $\Delta_f H_m^0$ (C₆H₃NH₂F₂, g) by means of eq 4.

$$\Delta_f H_m^0(\text{C}_6\text{H}_3\text{NH}_2\text{F}_2, \text{g}) = \Delta_f H_m^0(\text{C}_6\text{H}_5\text{NH}_2, \text{g}) + [\Delta_f H_m^0(\text{C}_6\text{H}_4\text{F}_2, \text{g}) - \Delta_f H_m^0(\text{C}_6\text{H}_6, \text{g})] \quad (4)$$

The estimated values are also included in Table 6 and are in generally good agreement with the experimental ones, except for the 2,3-C₆H₃NH₂F₂ and 2,6-C₆H₃NH₂F₂, for which the large deviations are a result of the molecular interactions of three substitutions in three consecutive carbon atoms of the benzenic ring.

The estimation of $\Delta_f H_m^0$ (C₆NH₂F₅, g) was based on the enthalpic increment for the entrance of the five fluorine atoms into the benzene ring. The $\Delta_f H_m^0$ (C₆HF₅, g) = $-(40.0 \pm 8.7)$ kJ·mol⁻¹,⁶⁶ taken from the literature has been used in a similar way similar to that described by eq 4, yielding $\Delta_f H_m^0$ (C₆NH₂F₅, g) = -802.1 ± 2.1 kJ·mol⁻¹. This result is in reasonable agreement with the experimental one, especially for such a highly substituted compound.

On the absence of reliable values for the standard molar enthalpies of formation of trifluorobenzenes and tetrafluorobenzenes, the estimation of the $\Delta_f H_m^0$ (g) for the isomers of trifluoroaniline and tetrafluoroaniline was made on the basis of the enthalpic increments derived from fluorobenzene, yielding the estimations compiled in Table 6, which differ largely from the experimental values.

3.4. Other Thermochemical Properties. The G3MP2B3 computations have also been performed for the compounds obtained by the removal or introduction of electrons or H⁺ from or into the neutral fluoroanilines and also to the radicals formed by abstraction of a hydrogen atom from each of these three isomers. The whole set of results obtained are reported in Table 7. The electron affinities shown in this Table have been calculated from the enthalpic differences between the anionic and neutral forms, showing that the introduction of a single electron into the fluorinated anilines is much more favorable in the case of the para isomer. The proton affinities, computed as $\text{PA}[\text{C}_6\text{H}_4\text{FNH}_2] = H[\text{C}_6\text{H}_4\text{FNH}_2] - H[\text{C}_6\text{H}_4\text{FNH}_3]^+ + 5RT/2$, are compared with available experimental data in Table 7. The G3MP2B3 values for the 3- and 4-fluoroanilines are in close agreement with the experimental results given in the compilation due to Hunter and Lias.⁶⁹ This means that the new result computed for the 2-fluoroaniline should be used in future compilations of results. As already found for the monochloroanilines,²² the protonation in the meta compound is more favorable by ~ 6 kJ·mol⁻¹ with respect to N-protonation if it occurs at the C4 atom, that is, in the carbon atom positioned adjacently to the carbon atom to which the fluorine atom is bonded, but N-protonation is preferred for 2- and 4-fluoroanilines. In the case of the ortho isomer, the cation formed after N-protonation is almost 12 kJ·mol⁻¹ more stable than that formed after C4-protonation. In the case of the para isomer, this difference increases to ~ 45 kJ·mol⁻¹, since in 4-fluoroaniline, C4-protonation involves the deviation from the planarity of the fluorine atom, and consequently, a large destabilization is found. The entire set of computed proton affinities, N- or C_x protonation, is given in the Supporting Information.

The computed adiabatic ionization enthalpies, a property that measures the capacity of these compounds to act as electron-donor species, are also included in Table 7. The G3MP2B3 results are compared with available experimental data. At first glance, it seems that this computational approach cannot be employed to obtain this kind of information, since the deviation between computed and experimental results for 2- and 3-fluoroaniline and also between the computed and two of the three experimental results available for 4-fluoroaniline are too high (16–30 kJ·mol⁻¹). However, these experimental results are vertical and cannot be directly compared with the present computed results. In a single case and for 4-fluoroaniline, the difference between the G3MP2B3 result and the experimental value due to Farrell and Newton⁷⁵ is only 2.2 kJ·mol⁻¹. Therefore, it seems that the G3MP2B3 composite approach yields accurate ionization enthalpies for this class of compounds and that the computed IE values for the other two isomers are accurate. Similarly, the same method also yields very good gas-phase acidities, as also shown in Table 7: the G3MP2B3 values are almost inside the interval defined by the uncertainties associated with the experimental results of Bartmess et al.⁷⁴ The G3MP2B3 values have been calculated as $H[\text{C}_6\text{H}_4\text{XNH}_2] - H[\text{C}_6\text{H}_4\text{XNH}_3] + 5RT/2$.

The computed N–H BDEs for the three fluoroanilines are similar to the computed N–H BDE for aniline, 396.7 kJ·mol⁻¹. If one considers only this property, the N–H BDEs reported in Table 7 mean that these compounds have similar antioxidant properties. The meta derivative will be a slightly poorer antioxidant, and the para compound will be a slightly more effective antioxidant.

4. Conclusions

The gas-phase standard molar enthalpies of formation for all fluoroanilines, except 2,3,5-trifluoroaniline, have been determined by a combination of rotating-bomb combustion calorimetry and Calvet microcalorimetry experiments. The former technique was used to obtain the enthalpies of combustion, in oxygen and at $T = 298.15$ K, and the latter was used to get the standard molar enthalpies for phase transition. The results show that the meta position is clearly the most stable, contrasting with the results found previously for the other halogenated anilines. Then it is not surprising to find that the 3,5-difluoroaniline is the most stable of the six twice fluorine-substituted anilines. However, in the trifluoroanilines, the most stable isomer is that with fluorine substitution at positions 2-, 4-, and 6-, since the two isomers with fluorine atoms at positions 3 and 5 have one or two pairs of fluorine atoms attached to adjacent carbon atoms of the aromatic ring, in the 2,3,5- and 3,4,5-trifluoroanilines, respectively, which contribute as a source of destabilization. Thus, the most stable trifluoroaniline is the 2,4,6-trifluoro derivative in which the fluorine atoms are not attached to adjacent carbon atoms, showing that the interaction with neighboring fluorine atoms is much more destabilizing than with the amino group. Finally, the most stable tetrafluoroaniline is the derivative with fluorine substitution at positions 2-, 3-, 5-, and 6-.

The standard molar enthalpies of formation of all fluoroanilines have also been estimated by the Cox method and by G3MP2B3 or BP86/6-31+G(d) computational approaches. The Cox method was found to yield rather satisfactory estimates when the enthalpic increments were obtained from the experimental fluorobenzenes with fluorine substitution at positions similar to those found in the fluoroanilines. The Cox method yield estimates for the mono-, di-, and pentafluoroanilines that are not far from the experimental values. As a consequence of the nonavailability of accurate experimental gas-phase enthalpies of formation for the tri- and tetrafluorobenzenes, the estimated values for the tri- and tetrafluoroaniline have been estimated with the consideration of the enthalpy for the fluorobenzene compound, yielding estimates that are too far from the experimental results. These problems were not found when the composite approach or the density functional theory method were used. In fact, it was found that the two computational approaches yield estimates that are in excellent agreement with the experimental results. Importantly, the calculated mean deviations are lower than 3.5 kJ·mol⁻¹. This shows that the nonconsideration of a working reaction that compares the fluoroanilines with the fluorobenzenes does not introduce any significant errors into the final estimates. However, the largest absolute difference between computed and experimental enthalpies of formation was found for the pentafluoroaniline.

Finally, the G3MP2B3 approach has been used also to compute gas-phase acidities, electron and proton affinities, ionization enthalpies, and N–H bond dissociation enthalpies. In some cases, the computed values were found to be in excellent agreement with available experimental data, suggesting that when the experimental results were not known or were

rather different, the computational values should be used in future compilations of thermochemical data.

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Supporting Information Available: Table S1 with 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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