

Experimental and Computational Study of the Thermochemistry of the Fluoromethylaniline Isomers

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The standard ($p^\circ = 0.1$ MPa) molar enthalpies of formation in the condensed phase of seven isomers of fluoromethylaniline were derived from the standard molar energies of combustion, in oxygen, to yield $\text{CO}_2(\text{g})$, $\text{N}_2(\text{g})$ and $\text{HF} \cdot 10\text{H}_2\text{O}(\text{l})$, at $T = 298.15$ K, measured by rotating bomb combustion calorimetry. The standard molar enthalpies of vaporization or sublimation of these compounds, also at $T = 298.15$ K, were determined using Calvet microcalorimetry, while the enthalpies of fusion of the solid compounds were determined by differential scanning calorimetry. The standard molar enthalpies of formation in the gaseous phase, at $T = 298.15$ K, were derived from the former two experimental quantities. G3MP2//B3LYP calculations were performed for all possible fluoromethylanilines allowing the estimation of data for the isomers that were not studied experimentally. The Cox scheme was applied with two different approaches for the estimation of the standard molar enthalpies of formation of all the isomers studied, and this led to the conclusion that the literature values for the enthalpies of formation of the *meta* and *para* isomers of methylaniline seem to be not reliable. Further G3MP2//B3LYPs calculations on the methylaniline isomers yielded new values for the standard molar enthalpies of formation of the isomers of methylaniline, which have been tested under the Cox scheme, resulting in better estimates.

1. Introduction

Haloanilines (halogenated benzenamines) are a very important family of organic compounds with a large relevance in the pharmaceutical and chemical industries. They are important intermediates in the manufacture of agricultural and pharmaceutical chemicals, dyes, pigments, drugs, rubbers, and other industrial chemical intermediates,¹ and for that reason, as well as for their known persistence and toxic characteristics, they became a class of organic chemicals of major environmental concern.² Introduction of halogenated anilines in the environment can be due to accidental release during the manufacturing process, or by the degradation of pesticides and herbicides. Some of these compounds are highly toxic, potentially mutagenic, and carcinogenic substances.^{3,4}

Fluoroanilines and their derivatives have revealed interesting biological activities, and consequently, are widely used as key intermediates in the manufacture of prominent pharmaceuticals and agrochemicals (pesticides, herbicides, and fungicides).^{5–7} In view of the generally high chemical stability demonstrated by organofluorine compounds, they have achieved enormous industrial importance, especially in the synthesis of conducting polymers.^{8–10}

Previously, we have presented thermochemical studies of fluoro,¹¹ chloro,^{12–16} bromo,¹⁷ and iodoaniline¹⁸ isomers. As a part of a broad thermochemical study on halogenated aniline derivatives and on the understanding of the energetic effect of halogen substitutions in the benzene ring, this paper reports on the thermochemistry of fluoromethylanilines: 2-fluoro-4-methylaniline (2-F-4-CH₃An, l); 2-fluoro-5-methylaniline (2-F-5-CH₃An, l); 3-fluoro-2-methylaniline (3-F-2-CH₃An, l); 3-fluoro-

4-methylaniline (3-F-4-CH₃An, cr); 4-fluoro-2-methylaniline (4-F-2-CH₃An, l); 4-fluoro-3-methylaniline (4-F-3-CH₃An, cr); and 5-fluoro-2-methylaniline (5-F-2-CH₃An, cr). The standard ($p^\circ = 0.1$ MPa) molar enthalpies of formation, in the condensed phase, of the seven fluoromethylaniline isomers, at $T = 298.15$ K, were obtained from measurements of their standard molar energies of combustion, in oxygen, at $T = 298.15$ K, using a rotating bomb combustion calorimeter, and their standard molar enthalpies of vaporization or sublimation were determined by high-temperature Calvet microcalorimetry. From these two sets of results, the standard molar enthalpies of formation, in the gaseous state, at $T = 298.15$ K, were derived. The measurements of the temperatures and enthalpies of fusion of the three crystalline fluoromethylanilines were done by differential scanning calorimetry (dsc).

Finally, the standard molar enthalpies of formation, in the gaseous state, of fluoromethylaniline isomers were compared with values estimated using the Cox scheme¹⁹ and with results derived from G3MP2//B3LYP calculations.

2. Experimental Details

2.1. Materials and Purity Control. The seven isomers of fluoromethylaniline were obtained commercially from Aldrich Chemical Co., and were purified by repeated vacuum distillations or sublimations. The purity of the liquid samples of fluoromethylaniline isomers was checked by gas–liquid chromatography (GLC, HP-4890A), while for the crystalline isomers the purity was checked by differential scanning calorimetry using a Setaram DSC 141, applying the fractional fusion technique.²⁰ The purity of the purified compounds is displayed in Table 1. The dsc was also used for the determination of the temperatures and enthalpies of fusion of the 3-fluoro-4-

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TABLE 1: Specific Densities and Purity of the Compounds. Experimental and Literature Values of Enthalpies and Temperatures of Fusion of Crystalline Isomers of Fluoromethylaniline.

compound	CAS	$\rho/\text{g}\cdot\text{cm}^{-3}$	purity	$\Delta_{\text{cr}}^{\text{f}}H_{\text{m}}(\text{exp})/\text{kJ}\cdot\text{mol}^{-1}$	$T_{\text{fus}}(\text{exp})/\text{K}$	$T_{\text{fus}}(\text{lit})/\text{K}$
2-F-4-CH ₃ An (l)	[452–80–2]	1.108 ^a	99.97%			
2-F-5-CH ₃ An (l)	[452–84–6]	1.109 ^a	99.98%			
3-F-2-CH ₃ An (l)	[443–86–7]	1.099 ^a	99.99%			
3-F-4-CH ₃ An (cr)	[452–77–7]	1.093 ^a	99.97%	17.71 ± 0.09	310.4 ± 0.07	303 – 305 ^a
4-F-2-CH ₃ An (l)	[452–71–1]	1.126 ^a	99.99%			
4-F-3-CH ₃ An (cr)	[452–69–7]	1.062 ^b	99.98%	18.02 ± 0.08	307.5 ± 0.10	307 – 311 ^a
5-F-2-CH ₃ An (cr)	[367–29–3]	1.028 ^b	99.97%	17.48 ± 0.06	311.3 ± 0.04	311 – 313 ^a

^a Ref 22. ^b Estimated from the mass and the dimensions of the pellet.

methylaniline, 4-fluoro-3-methylaniline, and 5-fluoro-2-methylaniline solids. The temperature scale of the calorimeter was calibrated by measuring the melting temperatures of three high purity reference materials:²¹ naphthalene (Aldrich 99.9%), benzoic acid (NIST Standard Reference Material 39i), and indium (Aldrich, mass fraction >0.99999), and the power scale was calibrated with the high purity indium as reference material.²¹ Thermograms of samples, hermetically sealed in stainless steel crucibles, were recorded in an air atmosphere. For the experimental determinations, five or six samples, weighing ≈ 6 mg, were scanned from $T = 298$ K to about 15 K above the melting point, using a heating rate of $(1.67 \times 10^{-2}) \text{ K}\cdot\text{s}^{-1}$. The crucibles and the samples of compounds were weighed on a Mettler UMT2 microbalance with a sensitivity of $\pm(1 \times 10^{-7})$ g. The recorded thermograms did not show any phase transitions between $T \approx 298$ K and the melting temperature of the samples.

The enthalpies and the onset temperatures of fusion were computed from the dsc thermograms. These temperatures are presented in Table 1 and the uncertainties assigned are the standard deviation of the mean. Table 1 also shows the temperatures of fusion and the specific densities found in the literature,²² together with the estimated ones used to calculate the true mass from the apparent mass in air, as well as the CAS numbers of the studied isomers.

The relative atomic masses used throughout this paper were those recommended by the IUPAC Commission in 2005.²³

2.2. Combustion Calorimetry. The standard molar enthalpies of combustion were determined with an isoperibol rotating-bomb calorimeter, originally constructed at the University of Lund according to the design of Sunner.²⁴ The apparatus and the operating technique have been described elsewhere.^{14,25,26} The bomb, whose internal volume is 0.258 dm³ and wall thickness of 1 cm, is a twin valve platinum lined bomb with all the internal fittings machined from platinum. Water was added to the calorimeter can from a weighed perspex vessel, and for each experiment, a correction to the energy equivalent was made for the difference between the mass of water used and the reference mass of 5222.5 g.

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. For each experiment, the ignition temperature was chosen so that the final temperature would be close to $T = 298.15$ K. For both the fore period and the after period, at least 100 readings were taken, whereas 120 readings are registered for the main period.

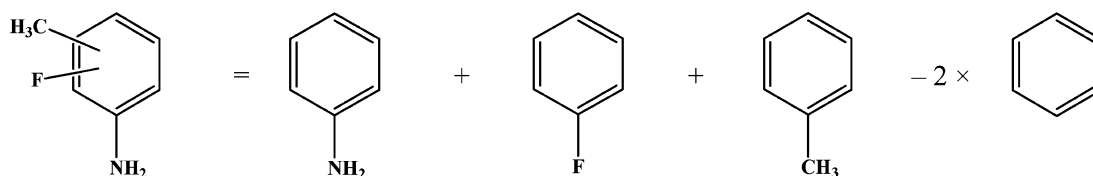
The rotating mechanism allowed simultaneous axial and end-over-end rotation of the bomb. Rotation of the bomb was started when the temperature rise in the main period reached about 0.63 of its total value and was continued throughout the rest of the experiment. By adopting this procedure, the frictional work of

the bomb rotation and stirring is automatically included in the temperature corrections for the work of water stirring and for the heat exchanged with the thermostated jacket as shown by Good et al.²⁷ This 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 ca. 303.5 K to $\pm 10^{-4}$ K using a temperature controller (Tronac PTC 41). Data acquisition and control of the calorimeter were performed using the program LABTERMO.²⁸ The energy equivalent of the calorimeter was determined from the combustion of benzoic acid (NIST Standard Reference Material 39j), having a massic energy of combustion under bomb conditions of $-(26434 \pm 3) \text{ J}\cdot\text{g}^{-1}$. 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.²⁹ One set of six calibration experiments was performed leading to the value of the energy equivalent of the calorimeter: $\epsilon(\text{calor}) = (25165.8 \pm 1.7) \text{ J}\cdot\text{K}^{-1}$, where the uncertainty quoted is the standard deviation of the mean.

For bomb combustion calorimetry of organic fluorine compounds in which the atomic ratio of hydrogen to fluorine is equal to or greater than unity, 4-fluorobenzoic acid was recommended as a test substance by Good et al.³⁰ where the combustion reaction of these compounds yields hydrogen fluoride as the sole fluorine-containing product. Hence, the accuracies of the experimental procedure and of the calorimeter were checked in our laboratory by measuring the energy of combustion of 4-fluorobenzoic acid. Samples were burned in the pellet form under oxygen, at $p = 3.04$ MPa, in the presence of 10.00 cm³ of water placed in the bomb. The standard massic energy of combustion obtained for 4-fluorobenzoic acid as the mean of six independent experiments was $\Delta_{\text{c}}u^{\circ} = -(21865.1 \pm 2.0) \text{ J}\cdot\text{g}^{-1}$, in good agreement with the recommended value: $\Delta_{\text{c}}u^{\circ} = -(21860 \pm 4) \text{ J}\cdot\text{g}^{-1}$.²¹

The combustion experiments of the seven isomers of fluoromethylaniline were also carried out in oxygen, at $p = 3.04$ MPa in the presence of 10.00 cm³ of water. The crystalline fluoromethylanilines were burnt in pellet form enclosed in sealed polyester bags made of Melinex (0.025 mm thickness) using the technique described by Skinner and Snelson,³¹ who determined the massic energy of combustion of dry Melinex as $\Delta_{\text{c}}u^{\circ} = -(22902 \pm 5) \text{ J}\cdot\text{g}^{-1}$; this value was confirmed in our laboratory. The mass of Melinex used in each experiment was corrected for the mass fraction of water (0.0032) and the mass of carbon dioxide produced in its combustion was calculated using the factor previously reported.³¹ The liquid isomers of fluoroaniline were burnt enclosed in polyethylene bags, for which we measured $\Delta_{\text{c}}u^{\circ} = -(46332.8 \pm 3.2) \text{ J}\cdot\text{g}^{-1}$, in good agreement with the literature³² value $\Delta_{\text{c}}u^{\circ} = -(46379.5 \pm 7.7) \text{ J}\cdot\text{g}^{-1}$. All the necessary weighing was made on a Mettler Toledo

SCHEME 1: Molecular Scheme for the Estimation of the Enthalpic Corrections



AE 240 balance, sensitivity of $\pm(1 \times 10^{-5})$ g, and corrections from apparent mass to true mass were introduced.

The electrical energy for ignition was determined from the change in potential difference across a 1400 μF condenser when discharged through a platinum ignition wire of diameter 0.05 mm. For the cotton thread fuse of empirical formula $\text{CH}_{1.686}\text{O}_{0.843}$, $\Delta_c u^0 = -16240 \text{ J}\cdot\text{g}^{-1}$,³³ a value that has been confirmed in our laboratory. Corrections for nitric acid formation were based on $-59.7 \text{ kJ}\cdot\text{mol}^{-1}$ for the standard molar energy of formation in which $0.1 \text{ mol}\cdot\text{dm}^{-3}$ $\text{HNO}_3(\text{aq})$ is formed from $\text{O}_2(\text{g})$, $\text{N}_2(\text{g})$, and $\text{H}_2\text{O}(\text{l})$.³⁴ The nitric acid formed was determined using the Devarda's alloy method.³⁵ For the experiments with a small carbon residue soot formed during the combustion, totally on the walls of the platinum crucible, the necessary energetic correction for its formation was based on $\Delta_c u^0 = -33 \text{ kJ}\cdot\text{g}^{-1}$.²⁹ This correction was needed in one combustion experiment of 3-fluoro-4-methylaniline, one experiment of 4-fluoro-3-methylaniline, and two combustion experiments with 5-fluoro-2-methylaniline being, at the most, of 13 J.

An estimated pressure coefficient of massic energy: $(\partial u/\partial p)_T = -0.2 \text{ J}\cdot\text{g}^{-1}\cdot\text{MPa}^{-1}$, at $T = 298.15 \text{ K}$, a typical value for most organic compounds,³⁶ was used for all compounds, with the exception of 4-fluorobenzoic acid for which $(\partial u/\partial p)_T = -0.115 \text{ J}\cdot\text{g}^{-1}\cdot\text{MPa}^{-1}$ at $T = 298.15 \text{ K}$.³⁰

Corrections to the standard state were made by the procedure given by Good and Scott³⁷ including the values for the solubility of carbon dioxide in hydrofluoric acid solutions, as given by Cox et al.³⁸

2.3. Calvet Microcalorimetry. The standard molar enthalpies of sublimation or vaporization of the seven fluoromethylanilines were measured using the Calvet microcalorimetry drop-method.^{39,40} For these measurements a high-temperature Calvet microcalorimeter (Setaram HT 1000) was used with the vacuum promoted by a rotatory vacuum pump and a vapor diffusion pump. Both the apparatus and the technique have been recently described.⁴¹

Samples of about 3–5 mg and 7–10 mg of crystalline and liquid fluoromethylaniline, respectively, contained in thin glass capillary tubes sealed at one end, and blank reference 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 near equal mass, to within $\pm 10 \mu\text{g}$, into each of the twin calorimeter cells.⁴¹ The samples of compounds and the glass capillary tubes were weighed on a Mettler CH-8608 analytical balance with a sensitivity of $\pm(1 \times 10^{-6})$ g.

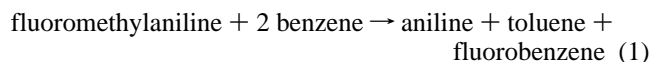
The observed standard molar enthalpies of sublimation or vaporization, $\Delta_{\text{cr},1,298.15\text{K}}^{\text{g},T} H_{\text{m}}^0$, have been corrected to $T = 298.15 \text{ K}$ using $\Delta_{298.15\text{K}}^T H_{\text{m}}^0(\text{g})$ estimated by a group method, based on the values of Stull et al.,⁴² taking into account the equation shown in Scheme 1.

For these measurements, the microcalorimeter was calibrated in situ making use of the reported standard molar enthalpy of

sublimation of naphthalene (72.600 ± 0.600) $\text{kJ}\cdot\text{mol}^{-1}$,²¹ at $T = 298.15 \text{ K}$, for the three crystalline fluoromethylanilines, and of the enthalpy of vaporization of *n*-decane (51.420 ± 0.206) $\text{kJ}\cdot\text{mol}^{-1}$,²¹ at $T = 298.15 \text{ K}$, for the liquid isomers of fluoromethylaniline. The calibrations constants, k , of the calorimeter were obtained as the average of six independent experiments for each working temperature: $k(T = 324 \text{ K}) = 0.9891 \pm 0.0025$ and $k(T = 324 \text{ K}) = 1.0163 \pm 0.0017$, respectively for the sublimation and vaporization experiments, where the uncertainties quoted are the standard deviations of the means.

2.4. Theoretical Calculations. The enthalpies of formation of all possible simultaneously single fluorinated and single methylated anilines were estimated using a similar strategy to that used in a very recent work devoted to the thermochemistry of the complete set of fluorinated anilines.¹¹ In that work, it was found that the G3MP2⁴³ approach based on B3LYP optimized geometries (G3MP2B3 keyword in Gaussian code⁴⁴) together with the consideration of the atomization reaction yield excellent estimates of the standard molar enthalpies of formation for the 18 fluoroanilines that were also studied experimentally. The mean absolute deviation between experimental and computational derived results was of only $3.3 \text{ kJ}\cdot\text{mol}^{-1}$ with the largest deviation, $7.0 \text{ kJ}\cdot\text{mol}^{-1}$, found for the completely substituted pentafluoroaniline. Therefore, the same computational method has been used in the present study. The G3MP2B3 composite approach uses 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.⁴⁵ The energies computed at $T = 0 \text{ K}$ were thermally corrected for $T = 298.15 \text{ K}$ 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.

As stated above, the enthalpies of formation for all the fluoromethylanilines have been estimated after the computation of the reaction of atomization at $T = 298.15 \text{ K}$ with the G3MP2//B3LYP approach and the experimental gas-phase enthalpies of formation at $T = 298.15 \text{ K}$ for carbon, $\Delta_f H_{\text{m}}^0(\text{g}) = 716.67 \text{ kJ}\cdot\text{mol}^{-1}$, hydrogen, $\Delta_f H_{\text{m}}^0(\text{g}) = 218.00 \text{ kJ}\cdot\text{mol}^{-1}$, nitrogen, $\Delta_f H_{\text{m}}^0(\text{g}) = 472.68 \text{ kJ}\cdot\text{mol}^{-1}$, and fluorine, $\Delta_f H_{\text{m}}^0(\text{g}) = 79.39 \text{ kJ}\cdot\text{mol}^{-1}$.⁴⁶ An alternative approach has also been employed and considers the calculation of the enthalpy, at $T = 298.15 \text{ K}$, of the gas-phase reaction described by the eq 1 below:



and the experimental standard gas-phase enthalpies of formation, $\Delta_f H_{\text{m}}^0(\text{g})$, for benzene, aniline, toluene, and fluorobenzene. The $\Delta_f H_{\text{m}}^0(\text{g})$ for these compounds are $(82.6 \pm 0.7) \text{ kJ}\cdot\text{mol}^{-1}$, $(87.1 \pm 1.1) \text{ kJ}\cdot\text{mol}^{-1}$, $(50.5 \pm 0.5) \text{ kJ}\cdot\text{mol}^{-1}$ and $-(115.9 \pm 1.4)$

TABLE 2: Typical Combustion Results at $T = 298.15$ K ($p^\circ = 0.1$ MPa)^a

	calibration	2-F-4-CH ₃ An	2-F-5-CH ₃ An	3-F-2-CH ₃ An	3-F-4-CH ₃ An	4-F-2-CH ₃ An	4-F-3-CH ₃ An	5-F-2-CH ₃ An
$m(\text{BA})/\text{g}$	0.99705							
$m'(\text{cpd})/\text{g}$		0.51364	0.54303	0.58418	0.69834	0.59917	0.70738	0.71805
$m''(\text{fuse})/\text{g}$	0.00322	0.00388	0.00358	0.00375	0.00386	0.00337	0.00360	0.00330
$m'''(\text{polyethylene})/\text{g}$		0.17599	0.18168	0.20162		0.16292		
$m''''(\text{Melinex})/\text{g}$					0.04660		0.04628	0.04586
T_i/K	297.0961	297.1718	297.1246	297.0427	297.2296	297.0933	297.2365	297.2128
T_f/K	298.1617	298.1472	298.1465	298.1515	298.1462	298.1511	298.1649	298.1533
$\Delta T_{\text{ad}}/\text{K}$	1.04937	0.95829	1.00521	1.09170	0.90029	1.04037	0.91127	0.92352
$\epsilon_i/\text{J}\cdot\text{K}^{-1}$	13.68	51.67	51.73	51.84	51.42	51.80	51.43	51.44
$\epsilon_f/\text{J}\cdot\text{K}^{-1}$	14.75	53.74	53.91	54.21	53.43	54.00	53.47	53.50
$\epsilon(\text{calor})/\text{J}\cdot\text{K}^{-1}$	25165.99	25166.6	25165.8	25161.2	25165.8	25160.8	25162.0	25163.7
$\Delta m(\text{H}_2\text{O})/\text{g}$	0.1	0.2	0.0	-1.1	0.0	-1.2	-0.9	-0.5
$-\Delta U(\text{IBP})^b/\text{J}$	26423.22	24165.12	25347.58	27523.75	22701.50	26229.08	22974.98	23285.37
$\Delta U(\text{BA})/\text{J}$	26357.59							
$\Delta U(\text{fuse})/\text{J}$	52.29	63.01	58.14	60.90	62.69	54.73	58.46	53.59
$\Delta(\text{polyethylene})/\text{J}$		8154.10	8417.57	9341.57		7548.77		
$\Delta U(\text{Melinex})/\text{J}$					1067.33		1060.00	1050.37
$\Delta U(\text{HNO}_3)/\text{J}$	12.06	31.04	37.25	39.88	40.36	39.88	40.83	40.83
$\Delta U(\text{ign})/\text{J}$	1.28	1.29	1.29	1.29	1.27	1.29	1.29	1.29
$\Delta U_\Sigma/\text{J}$	----	28.73	28.624	28.77	22.41	27.39	22.26	22.09
$-\Delta_c u^0/\text{J}\cdot\text{g}^{-1}$	----	30932.64	30948.57	30902.51	30799.77	30973.36	30808.66	30803.55

^a $m(\text{BA})$ is the mass of benzoic acid; $m'(\text{cpd})$ is the mass of compound burnt in each experiment; $m''(\text{fuse})$ is the mass of fuse (cotton) used in each experiment; $m'''(\text{polyethylene})$ is the mass of polyethylene used in each experiment; $m''''(\text{Melinex})$ is the mass of Melinex used in each experiment; T_i is the initial temperature rise; T_f is the final temperature rise; ΔT_{ad} is the corrected temperature rise/variation of adiabatic temperature; ϵ_i is the energy equivalent of contents in the initial state; ϵ_f is the energy equivalent of contents in the final state; $\epsilon(\text{calor})$ is the energy equivalent of the calorimeter; $\Delta m(\text{H}_2\text{O})$ is the deviation of mass of water added to the calorimeter from 5222.5 g; $\Delta U(\text{IBP})$ is the energy change for the isothermal combustion reaction under actual bomb conditions; $\Delta U(\text{BA})$ is the energy of combustion of the benzoic acid; $\Delta U(\text{fuse})$ is the energy of combustion of the fuse (cotton); $\Delta U(\text{polyethylene})$ is the energy of combustion of the polyethylene; $\Delta U(\text{Melinex})$ is the energy of combustion of the Melinex; $\Delta U(\text{HNO}_3)$ is the energy correction for the nitric acid formation; $\Delta U(\text{ign})$ is the electrical energy for ignition; ΔU_Σ is the standard state correction; $\Delta_c u^0$ is the standard massic energy of combustion. ^b $\Delta U(\text{IBP})$ includes $\Delta U(\text{ign})$.

TABLE 3: Values of Standard ($p^\circ = 0.1$ MPa) Massic Energy of Combustion, $\Delta_c u^0$, of Fluoromethylanilines, at $T = 298.15$ K

2-F-4-CH ₃ An	2-F-5-CH ₃ An	3-F-2-CH ₃ An	3-F-4-CH ₃ An	4-F-2-CH ₃ An	4-F-3-CH ₃ An	5-F-2-CH ₃ An
			$-\Delta_c u^0/\text{J}\cdot\text{g}^{-1}$			
30938.46	30942.52	30902.51	30803.79	30980.69	30813.03	30804.10
30939.83	30951.99	30894.59	30797.60	30977.18	30810.29	30803.55
30932.64	30948.57	30900.02	30794.96	30973.36	30808.66	30813.32
30945.70	30943.02	30897.76	30809.48	30969.74	30795.60	30799.75
30925.11	30944.12	30903.69	30789.72	30964.63	30799.69	30796.88
30931.50	30958.22	30912.12	30799.77	30977.23	30813.43	30798.32
			$-\Delta_c u^0/(\text{J}\cdot\text{g}^{-1})^a$			
30935.5 ± 3.0	30948.1 ± 2.5	30901.8 ± 3.0	30799.2 ± 2.8	30973.8 ± 2.4	30806.8 ± 3.0	30802.7 ± 2.4

^a Mean value and standard deviation of the mean.

$\text{kJ}\cdot\text{mol}^{-1}$, respectively, and were all taken from the compilation due to Pedley.⁴⁷

3. Results

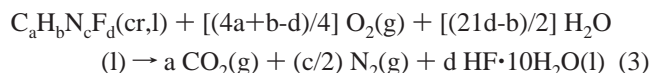
3.1. Experimental Enthalpies of Formation. Detailed results for a typical combustion experiment of each isomer of fluoromethylaniline are given in Table 2, where $\Delta m(\text{H}_2\text{O})$ is the deviation of the mass of water added to the calorimeter from 5222.5 g, the mass assigned to $\epsilon(\text{calor})$, and ΔU_Σ is the energy correction to the standard state. The remaining quantities are as previously defined.^{33,37} The values of the energy associated to the isothermal bomb process, $\Delta U(\text{IBP})$, were calculated using the following expression:

$$\Delta U(\text{IBP}) = -\{\epsilon(\text{calor}) + \Delta m(\text{H}_2\text{O}) c_p(\text{H}_2\text{O}, \text{l})\} \Delta T_{\text{ad}} + (T_i - 298.15 \text{ K}) \epsilon_i + (298.15 \text{ K} - T_i - \Delta T_{\text{ad}}) \epsilon_f + \Delta U_{\text{ign}} \quad (2)$$

where ΔT_{ad} is the calorimeter temperature change corrected for the heat exchange, work of stirring, and the frictional work of bomb rotation.

The values of the standard massic energy of combustion, $\Delta_c u^0$, refer to the idealized combustion reaction of fluoromethylaniline

isomers, yielding $\text{HF}\cdot 10\text{H}_2\text{O}(\text{l})$ as the only fluorine-containing product in the final state, according to eq 3.



The individual values of $\Delta_c u^0$ together with the mean value, $\langle \Delta_c u^0 \rangle$, and its standard deviation, are registered in Table 3.

Table 4 lists the derived mean values of massic energy of combustion, together with the values of standard molar energies and enthalpies of combustion, $\Delta_c U_m^0(\text{cr}, \text{l})$ and $\Delta_c H_m^0(\text{cr}, \text{l})$, as well as the standard molar enthalpies of formation, $\Delta_f H_m^0(\text{cr}, \text{l})$, for the seven isomers of fluoromethylaniline in the condensed phase, at $T = 298.15$ K. In accordance with normal thermochemical practice,^{48,49} 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 the auxiliary quantities used. To derive $\Delta_f H_m^0(\text{cr}, \text{l})$ from $\Delta_c H_m^0(\text{cr}, \text{l})$ the standard molar enthalpies of formation of $\text{CO}_2(\text{g})$, $\text{H}_2\text{O}(\text{l})$ and $\text{HF}\cdot 10\text{H}_2\text{O}(\text{l})$, at $T = 298.15$ K, respectively, $-(393.51 \pm 0.13) \text{ kJ}\cdot\text{mol}^{-1}$,⁵⁰ $-(285.830 \pm 0.040) \text{ kJ}\cdot\text{mol}^{-1}$,⁵⁰ and $-(322.034 \pm 0.650) \text{ kJ}\cdot\text{mol}^{-1}$,⁵¹ were used.

TABLE 4: Derived Standard ($p^0 = 0.1$ MPa) Molar Thermodynamic Properties for Fluoromethylanilines in the Condensed Phase, at $T = 298.15$ K

compound	$-\langle \Delta_c U_m^0 \rangle / \text{J} \cdot \text{g}^{-1}$	$-\Delta_c U_m^0(\text{cr/l}) / \text{kJ} \cdot \text{mol}^{-1}$	$-\Delta_c H_m^0(\text{cr/l}) / \text{kJ} \cdot \text{mol}^{-1}$	$-\Delta_c H_m^0(\text{cr/l}) / \text{kJ} \cdot \text{mol}^{-1}$
2-F-4-CH ₃ An (l)	30935.5 \pm 3.0	3871.4 \pm 1.1	3874.5 \pm 1.1	202.5 \pm 1.6
2-F-5-CH ₃ An (l)	30948.1 \pm 2.5	3873.0 \pm 1.1	3876.1 \pm 1.1	201.0 \pm 1.6
3-F-2-CH ₃ An (l)	30901.8 \pm 3.0	3867.2 \pm 1.1	3870.3 \pm 1.1	206.8 \pm 1.6
3-F-4-CH ₃ An (cr)	30799.2 \pm 2.8	3854.3 \pm 1.3	3857.4 \pm 1.3	219.6 \pm 1.7
4-F-2-CH ₃ An (l)	30973.8 \pm 2.4	3876.2 \pm 1.1	3879.3 \pm 1.1	197.7 \pm 1.5
4-F-3-CH ₃ An (cr)	30806.8 \pm 3.0	3855.3 \pm 1.3	3858.4 \pm 1.2	218.6 \pm 1.7
5-F-2-CH ₃ An (cr)	30802.7 \pm 2.4	3854.8 \pm 1.2	3857.9 \pm 1.2	219.2 \pm 1.7

TABLE 5: Standard ($p^0 = 0.1$ MPa) Molar Enthalpies of Vaporization and Sublimation, $\Delta_{\text{cr,l}}^g H_m^0$, for the Seven Isomers of Fluoromethylaniline, at 298.15 K, Determined by Calvet Microcalorimetry

compound	number of experiments	T/K	$\Delta_{\text{cr,l}}^g H_m^0(298.15 \text{ K}) / \text{kJ} \cdot \text{mol}^{-1}$	$\Delta_{298.15 \text{ K}}^T H_m^0(\text{g}) / \text{kJ} \cdot \text{mol}^{-1}$	$\Delta_{\text{cr,l}}^g H_m^0(298.15 \text{ K}) / \text{kJ} \cdot \text{mol}^{-1}$
2-F-4-CH ₃ An (l)	5	323.8	61.5 \pm 0.1	4.9	56.6 \pm 0.6
2-F-5-CH ₃ An (l)	5	323.9	61.8 \pm 0.1	4.9	56.9 \pm 0.5
3-F-2-CH ₃ An (l)	5	324.1	62.7 \pm 0.2	4.9	57.8 \pm 0.6
3-F-4-CH ₃ An (cr)	5	324.0	81.1 \pm 0.2	4.9	76.2 \pm 1.4
4-F-2-CH ₃ An (l)	5	323.9	64.7 \pm 0.1	4.9	59.8 \pm 0.8
4-F-3-CH ₃ An (cr)	5	324.1	82.0 \pm 0.1	4.9	77.1 \pm 1.3
5-F-2-CH ₃ An (cr)	5	324.1	80.0 \pm 0.1	4.9	75.1 \pm 1.3

TABLE 6: Experimental and Estimated (Cox Scheme and G3MP2//B3LYP Calculations) Gas-Phase Enthalpies of Formation of the Fluoromethylanilines

compound	experimental	$-\Delta_f H_m^0(\text{g}) / \text{kJ} \cdot \text{mol}^{-1}$			$\Delta^a / \text{kJ} \cdot \text{mol}^{-1}$		
		Cox scheme		G3MP2//B3LYP	Cox scheme		G3MP2//B3LYP
		approach I ^b	approach II ^c	R. atom./R.Eq.1 ^d	approach I ^b	approach II ^c	R. Atom./R.Eq.1 ^d
2-F-3-CH ₃ An		125.4 \pm 1.6 ^e 133.1 \pm 1.6 ^f	131.5 \pm 2.7	144.7/142.8			
2-F-4-CH ₃ An	145.9 \pm 1.7	152.7 \pm 1.6 ^e 140.2 \pm 1.6 ^f	139.5 \pm 2.7	140.8/138.9	6.8 \pm 2.3	-6.4 \pm 3.2	-5.1/-7.0
2-F-5-CH ₃ An	144.1 \pm 1.7	133.4 \pm 1.6 ^e 141.1 \pm 1.6 ^f	139.5 \pm 2.7	141.2/139.3	-10.7 \pm 2.3	-4.6 \pm 3.2	-2.9/-4.8
2-F-6-CH ₃ An		137.3 \pm 2.2 ^e 137.3 \pm 2.2 ^f	139.5 \pm 2.7	145.9/144.0			
3-F-2-CH ₃ An	149.0 \pm 1.7	137.3 \pm 2.2 ^e 137.3 \pm 2.2 ^f	131.5 \pm 2.7	147.2/145.3	-11.7 \pm 2.8	-17.5 \pm 3.2	-1.7/-3.7
3-F-4-CH ₃ An	143.4 \pm 2.2	152.7 \pm 1.6 ^e 140.2 \pm 1.6 ^f	139.5 \pm 2.7	145.3/143.4	9.3 \pm 2.7	-3.9 \pm 3.5	1.9/0.0
3-F-5-CH ₃ An		137.4 \pm 1.6 ^e 145.1 \pm 1.6 ^f	143.5 \pm 2.7	145.4/143.5			
4-F-2-CH ₃ An	137.9 \pm 1.7	145.3 \pm 2.2 ^e 145.3 \pm 2.2 ^f	139.5 \pm 2.7	146.5/140.0	7.4 \pm 2.8	1.6 \pm 3.2	3.9/2.1
4-F-3-CH ₃ An	141.5 \pm 2.1	133.4 \pm 1.6 ^e 141.1 \pm 1.6 ^f	139.5 \pm 2.7	141.4/139.5	-8.1 \pm 2.6	-2.0 \pm 3.4	-0.1/-2.0
5-F-2-CH ₃ An	144.1 \pm 2.1	145.3 \pm 2.2 ^e 145.3 \pm 2.2 ^f	139.5 \pm 2.7	146.5/144.6	1.2 \pm 3.0	-4.6 \pm 3.4	2.4/0.5

^a Difference between the experimental and the estimated values. ^b Approach I: values estimated using the methylaniline isomers as the starting compounds. ^c Approach II: values estimated using the aniline as the starting compound. ^d Values estimated from the atomization reaction or by the reaction shown by Equation 1s. ^e Values estimated using the values of $\Delta_f H_m^0$ (methylanilines, g) from ref 53. ^f Values estimated using the values of $\Delta_f H_m^0$ (methylanilines, g) calculated in this paper.

Results of the measurements of the enthalpies of sublimation or vaporization for fluoromethylanilines, obtained by Calvet microcalorimetry, are given in Table 5, with the respective uncertainties, taken as twice the standard deviations of the mean which include the uncertainties in calibration.

The values of the standard molar enthalpies of formation in the gaseous phase, at $T = 298.15$ K, of the seven fluoromethylanilines derived from the values of standard molar enthalpies

of formation in the condensed phase (Table 4) and the standard molar enthalpies of sublimation or vaporization (Table 5), are summarized in Table 6.

3.2. Computed Enthalpies of Formation. The enthalpies of formation in the gas-phase for all fluoromethylanilines, even those that were not studied experimentally due to the lack of high-purity samples, were estimated by using the reaction of atomization or the reaction of group substitution given in eq 1

and the G3MP2//B3LYP energies of all compounds there included corrected for $T = 298.15$ K. The fully optimized structures of all compounds are given in the Supporting Information while the estimated enthalpies of formation are compiled in Table 6 and compared with the experimental results. The values estimated with either of the approaches chosen here are in clear agreement with the experimental results. It is found that the use of the atomization reaction provides the best estimates with a maximum deviation of $5.1 \text{ kJ}\cdot\text{mol}^{-1}$ and a mean deviation of only $2.6 \text{ kJ}\cdot\text{mol}^{-1}$. Interestingly, the maximum deviation between experimental and estimated results with the reaction of group substitution is also obtained for the 2-fluoro-3-methylaniline compound, but in this case, it is $7.0 \text{ kJ}\cdot\text{mol}^{-1}$. When the reaction of group substitution is used, the mean deviation is equal to $2.9 \text{ kJ}\cdot\text{mol}^{-1}$. Therefore, due to the excellent agreement between experimental and G3MP2//B3LYP data, one is able to suggest, and with a quite large confidence, that the estimated values for the three isomers that were not studied experimentally, namely, 2-fluoro-6-methylaniline, 3-fluoro-5-methylaniline, and 3-fluoro-6-methylaniline, should be used in future compilations of thermochemical data.

A close analysis of the enthalpies of formation shows that the position of the fluoro and methyl does not exert any significant influence on the stability of the fluoromethylanilines. In fact, the computed enthalpic difference between the most and less stable isomers is of only $6.4 \text{ kJ}\cdot\text{mol}^{-1}$. The picture arising from the experimental values, even the series of fluoromethylanilines is not complete, is somewhat different since the experimental enthalpy of the 4-fluoro-2-methylaniline is not as negative as that determined for the other isomers; in this case, the enthalpic difference between the most and less stable isomers increases to $11.1 \text{ kJ}\cdot\text{mol}^{-1}$. The stability of the isomers is not easily analyzed since it is dependent on several factors linked with the ability of the fluoro and methyl substituents to act as electron acceptor or electron donor, respectively, and mixed with the differences in the inductive effects of those groups inserted at the ortho, meta, and para positions.

3.3. Enthalpies Estimated with the Cox Scheme. Cox¹⁹ suggested a method to estimate the standard molar enthalpies of formation of gaseous aromatic compounds based on the transferability of group enthalpic contributions by assuming that each group, when substituted into a benzene ring, produces a characteristic increment in $\Delta_f H_m^0(\text{g})$ and that each ortho-pair of substituents leads to an enthalpic increment of $4 \text{ kJ}\cdot\text{mol}^{-1}$; an additional correction of $4 \text{ kJ}\cdot\text{mol}^{-1}$ must also be considered for every set of three substituents in three consecutive carbon atoms of the aromatic ring. From the literature values of $\Delta_f H_m^0(\text{g})$, at $T = 298.15$ K, for *o*-, *m*-, and *p*-methylaniline (toluidine), respectively, $(53.2 \pm 0.5) \text{ kJ}\cdot\text{mol}^{-1}$,^{52,53} $61.1 \text{ kJ}\cdot\text{mol}^{-1}$,^{53,54} and $41.8 \text{ kJ}\cdot\text{mol}^{-1}$,^{53,54} for benzene, $(82.6 \pm 0.7) \text{ kJ}\cdot\text{mol}^{-1}$,⁴⁷ and for fluorobenzene, $-(115.9 \pm 1.4) \text{ kJ}\cdot\text{mol}^{-1}$,⁴⁷ the calculated enthalpic increment for the introduction of a fluorine atom in a benzene ring is $-(198.5 \pm 1.6) \text{ kJ}\cdot\text{mol}^{-1}$. So, following the Cox scheme,¹⁹ the estimated values for standard molar enthalpies of formation in the gaseous phase of the eleven isomers of fluoromethylaniline could be calculated introducing the enthalpic increment of a fluorine atom in the methylaniline ring, according to eq 4:

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

This approach is named from now on as approach I. Based on this approach the estimated values differ largely from the

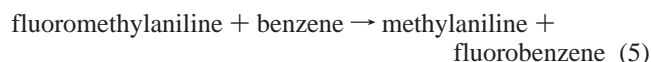
experimental values as shown in Table 6. This huge difference between experimental and estimated values could only be explained by the absence of reliable literature values for the standard molar enthalpies of formation of the isomers of methylaniline. In fact, as discussed below, only the value reported for the *o*-methylaniline is based on experimental determinations, while those available for the *m*- and *p*-methylaniline are based on empirical treatment of data existing in the literature. Another approach, from now on named as approach II, considers aniline, $\Delta_f H_m^0(\text{g}) = (87.1 \pm 1.1) \text{ kJ}\cdot\text{mol}^{-1}$,⁴⁷ as the starting compound and adds the enthalpic increment of $-(198.5 \pm 1.6) \text{ kJ}\cdot\text{mol}^{-1}$ for the introduction of a fluorine atom in the aromatic ring and $-(32.1 \pm 0.9) \text{ kJ}\cdot\text{mol}^{-1}$ for the introduction of a $-\text{CH}_3$ group, derived from the $\Delta_f H_m^0(\text{toluene}, \text{g}) = (50.5 \pm 0.5) \text{ kJ}\cdot\text{mol}^{-1}$.⁴⁷ The estimated values for the standard molar enthalpies of formation of the fluoromethylanilines based on this approach II, shown in Table 6, are in much better agreement with the experimental ones than those obtained with approach I, with the exception of the 3-fluoro-2-methylaniline. Since the first approach considers the enthalpies of the three methylanilines as the starting species for the application of the Cox scheme, instead of separated groups as in approach II, the former was expected to give much better estimates than the later. The results given in Table 6 seem to suggest exactly the opposite. However, as already stated above, only the standard gas-phase enthalpy of formation of the *o*-methylaniline is based on experimental determinations (enthalpy of formation of the liquid, $-(4.72 \pm 0.96) \text{ kJ}\cdot\text{mol}^{-1}$, and the enthalpy of vaporization, $(57.9 \pm 0.24) \text{ kJ}\cdot\text{mol}^{-1}$) due to Steele et al.⁵² These experimental results, based on rotating-bomb combustion calorimetry and vapor pressure measurements, corrected previous values due to Pushin and to Glaser and Ruland, respectively.⁵³ In the case of the two other isomers, Draeger⁵⁴ used standard statistics on previously determined spectroscopic quantities and the previously reported values of Kudchadker et al.⁵⁵ for the standard enthalpies of formation at $T = 298.15$ K of *o*-, *m*-, and *p*-methylanilines to derive several thermochemical properties. This author assumed several approximations, such as that the barrier restricting internal rotation of the amino substituent was the same as that found in aniline, that the vibrational assignments made by other authors were satisfactory, that the structure of the aniline ring remained unperturbed after introduction of a methyl group, and that the amino group lied in the plane of the aromatic ring. The value derived for the *o*-methylaniline, $\Delta_f H_m^0 = 54.8 \text{ kJ}\cdot\text{mol}^{-1}$, was found to be close to the experimental value reported later by Steele et al.,⁵² since Draeger considered, even in an approximated way, the barrier for internal rotation of the methyl group. For the other two isomers, namely, *m*- and *p*-methylaniline, the methyl group was assumed to rotate freely and rather different values of $\Delta_f H_m^0$ have been calculated; for the *m*-methylaniline, $\Delta_f H_m^0 = 61.1 \text{ kJ}\cdot\text{mol}^{-1}$, while for *p*-methylaniline $\Delta_f H_m^0 = 41.8 \text{ kJ}\cdot\text{mol}^{-1}$.⁵⁴ In a more recent work, Verevkin reported the ortho interactions in alkyl substituted anilines.⁵⁶ After analysis of data available in the literature noticed the large enthalpic difference between the experimental $\Delta_f H_m^0$ for the *o*-methylaniline compound and that reported in the NIST Webbook for the *p*-methylaniline compound since it was not expected as it seemed from the absence of an evident stabilization on going from *o*-methylaniline, to 2,4-dimethylaniline.⁵⁶ Based also on an empiric treatment of literature data, Verevkin proposed that a much more acceptable estimate for the gas-phase enthalpies of formation of both *m*- and *p*-methylanilines would be close to $55.0 \text{ kJ}\cdot\text{mol}^{-1}$.

TABLE 7: Estimated Enthalpies of Formation for the Three Toluidines (methylanilines).^{a,b}

reaction ^c	compound		
	<i>o</i> -TLD	<i>m</i> -TLD	<i>p</i> -TLD
atomization	51.0	53.5	54.4
2-F-3-CH ₃ An + BNZ → <i>o</i> -TLD + F-BNZ	50.6		
4-F-2-CH ₃ An + BNZ → <i>o</i> -TLD + F-BNZ	56.3		
5-F-2-CH ₃ An + BNZ → <i>o</i> -TLD + F-BNZ	54.8		
2-F-5-CH ₃ An + BNZ → <i>m</i> -TLD + F-BNZ		52.0	
4-F-3-CH ₃ An + BNZ → <i>m</i> -TLD + F-BNZ		54.8	
2-F-4-CH ₃ An + BNZ → <i>p</i> -TLD + F-BNZ			50.7
3-F-4-CH ₃ An + BNZ → <i>p</i> -TLD + F-BNZ			57.7
mean	53.2; 53.2 ± 0.5 ^d	53.4	54.3

^a $\Delta_f H_m^\circ$ of the elements taken from ref 46. $\Delta_f H_m^\circ$ for benzene and fluorobenzene taken from ref 47. $\Delta_f H_m^\circ$ for the fluoromethylanilines were taken from Table 6. ^b All values in kJ·mol⁻¹. ^c TLD and BNZ stand for methylaniline and benzene, respectively. ^d Experimental value taken from ref 52.

Here, we have used the same G3MP2//B3LYP approach and the atomization reaction or that given below,



for the estimation of the standard molar gas-phase enthalpies of formation of the three methylanilines; the values are reported in Table 7. The $\Delta_f H_m^\circ$ for the three methylanilines are almost degenerate, but the 2-methyl isomer seems to be the most stable. Further, the values based on the Gaussian-3 approach are in clear agreement with the experimental result due to Steele et al.⁵² and also with the estimates of Verevkin.⁵⁶

Using these new $\Delta_f H_m^\circ$ for the methylanilines as starting parameters for the application of the Cox scheme following approach I, the estimated results, which are also registered in Table 6, are in good agreement with the experimental and with the computational ones, which suggest that the actual values in the literature for the standard molar enthalpies of formation of the isomers meta and para of the methylaniline are not the correct ones.

4. Conclusions

The standard molar enthalpies of formation, in the condensed phases, of seven isomers of fluoromethylaniline have been experimentally measured by rotating bomb combustion calorimetry, whereas the standard molar enthalpies of phase transitions to the gaseous state of the same isomers were measured by a direct calorimetric method using high-temperature Calvet microcalorimetry. By the combination of those results, the standard molar enthalpies of formation of those isomers, in the gaseous phase, at $T = 298.15$ K, were derived.

The standard molar enthalpies of formation of all fluoromethylanilines have been also estimated by the Cox method and by G3MP2//B3LYP computational approach and were found to be in good agreement with the experimental derived values. The Cox method was found to yield rather unsatisfactory estimates when the standard molar enthalpies of formation were estimated starting from the literature values of the methylanilines and introducing the enthalpic increment of a fluorine atom in a benzene ring, derived from the enthalpy of formation of fluorobenzene. On the other hand, if the Cox Scheme was used starting from the aniline, and introducing the enthalpic increments of the entrance of a fluorine atom and a methyl group, calculated from the standard molar enthalpies of formation of, respectively, fluorobenzene and toluene, the estimated values were in good agreement with the ones derived from computational thermochemistry, a thing that would not be expected on these type of estimations. This fact led us to perform additional computations on the standard molar enthalpies of

formation of the three isomers of methylaniline. It was found that the literature values for the meta and para isomers were not reliable. This was confirmed by applying again the Cox scheme, starting from the new values of the standard molar enthalpies of formation of methylaniline, which yields estimates for the standard molar enthalpies of formation of the fluoromethylanilines that are now in good agreement with the experimentally derived results in this paper. As a result of these findings, we propose new values for the gaseous standard molar enthalpies of formation of the meta and para isomers of methylaniline.

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Supporting Information Available: Details of all the combustion calorimetry experiments for the seven fluoromethylaniline studied, as well as the fully optimized structures of all compounds are given in the Supporting Information. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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