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Enthalpies of Formation and Substituent Effects of *ortho*-, *meta*-, and *para*-Aminotoluenes from Thermochemical Measurements and from Ab Initio Calculations

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The molar enthalpies of vaporization of 2-amino-, 3-amino-, and 4-aminotoluenes were obtained from the temperature dependence of the vapor pressure measured by the transpiration method. The molar enthalpy of sublimation of 4-aminotoluene was measured in the same way. The standard ($p° = 0.1$ MPa) molar enthalpy of formation $\Delta_f H_m^\circ$(cr) at the temperature $T = 298.15$ K of crystalline 4-aminotoluene was measured using combustion calorimetry. The thermochemical investigations of aminotoluenes available in the literature were collected and combined with our own experimental results to obtain our own reliable standard molar enthalpies of formation at $T = 298.15$ K in the gaseous state. Ab initio calculations of aminotoluenes have been performed using the MP2Full/6-31G(d) and G3(MP2) basis sets, and the results from the bond separation method are in excellent agreement with the experiment. These new results help to resolve the uncertainty in the available thermochemical data on aminotoluenes. Weak mutual interactions of substituents in aminotoluenes have been realized using an isodesmic reaction procedure.

Introduction

In the course of our previous investigation of aliphatic[1,2] and aromatic amines,[2] we have revealed that the thermochemical literature on the title compounds is in disarray. Indeed, Draeger[3] reported the following gaseous enthalpies of formation, $\Delta_f H_m^\circ$(g): 54.8, 61.1, and 41.8 kJ·mol^{-1} for 2-, 3-, and 4-aminotoluenes at 298.15 K. These values assume noticeable interactions (over 20 kJ·mol^{-1}) between the methyl and amino group in aminotoluenes, which are dependent on their position on the benzene ring. However, this contradicts the thermochemical calculations performed later by Chao et al.,[4] which predicted nearly equal values of $\Delta_f H_m^\circ$(g), 56.4, 54.6.1, and 55.3 kJ·mol^{-1} for the 2-, 3-, and 4-aminotoluenes so that no noticeable substituent effects are expected in aminotoluenes. The enthalpy of formation in the gaseous phase of any compound is made up of two contributions: $\Delta_f H_m^\circ(g) = \Delta_f H_m^\circ(l) + \Delta_l^g H_m$ or $\Delta_f H_m^\circ(g) = \Delta_f H_m^\circ(cr) + \Delta_{cr}^g H_m$. Although the precise experimental value of the enthalpy of formation in the liquid state, $\Delta_f H_m^\circ$(l), of 2-aminotoluene and its vaporization enthalpy, $\Delta_l^g H_m$, are available from the recent literature,[5] thermodynamic data for 3- and 4-aminotoluenes are of low quality. For example, the $\Delta_f H_m^\circ$(l) values of 3-aminotoluene measured by combustion experiments[6,7] differ by over 30.0 kJ·mol^{-1}, necessitating new measurements on 3- and 4-aminotoluenes. Some available experimental data[8−13] on the vapor pressures of 3- and 4-aminotoluenes (see Table 1) were measured at elevated temperatures close to their boiling points, and enthalpies of vaporization at $T = 298.15$ K, $\Delta_l^g H_m$(298.15 K), were not derived by the authors. Thus, additional vapor pressure measurements on 3- and 4-aminotoluenes at the temperatures close to the reference temperature, $T = 298.15$ K, seemed desirable in order to derive the corresponding vaporization ($\Delta_l^g H_m$) or sublimation enthalpies ($\Delta_{cr}^g H_m$) at this temperature. In this work, we have measured the enthalpies of vaporization of all three isomers using the transpiration method. For the solid isomer, 4-aminotoluene, we have also measured its sublimation enthalpy using the transpiration method and its enthalpy of formation in the crystalline state, $\Delta_f H_m^\circ$(cr), by using combustion calorimetry. New experiments have allowed us to obtain reliable enthalpies of formation in the gaseous phase $\Delta_f H_m^\circ$(g) and have helped to resolve the uncertainty in the available thermochemical data on aminotoluenes. It has been shown recently that ab initio calculations show very good agreement with the experimental formation enthalpies of substituted benzenes.[14] For this reason, experimental investigations of the enthalpies of formation in the gaseous phase $\Delta_f H_m^\circ$(g) of all three isomers are accompanied with high-level MP2Full/6-31G(d) and G3(MP2) ab initio calculations.

Experimental Section

Materials. The liquid samples of aminotoluenes (purchased from Aldrich) having a mass-fraction purity of about 0.99 were purified by repeated distillation in vacuum. The solid sample of 4-aminotoluene (Aldrich) was purified by repeated sublimation in vacuum. Examination of the samples using GC showed no discernible amounts of impurities. The products were analyzed with a Hewlett-Packard gas chromatograph 5890 Series II equipped with a flame ionization detector and Hewlett-Packard 3390A integrator. A carrier gas (nitrogen) flow of 12.1 cm^3·s^{-1} was used in addition to an HP-5 capillary column (stationary phase cross-linked 5% PH ME silicone); the column length, inside diameter, and film thickness were 25 m, 0.32 mm, and 0.25 μm, respectively. The standard temperature program of the GC was $T = 323$ K, followed by a heating rate of 0.167 K·s^{-1} to $T = 523$ K.

The samples of 4-aminotoluene did not appear to be hygroscopic, but the sublimed samples for combustion experiments were subjected to pellet-drying to remove traces of occluded water and were kept in desiccator under P_2O_5.

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TABLE 1: Compilation of Data on Enthalpies of Vaporization, $\Delta_l^g H_m$, of Aminotoluenes

	technique[a]	temperature range (K)	$\Delta_l^g H_m(T)$	$\Delta_l^g H_m$(298 K) kJ·mol^{-1} [b]	ref
2-aminotoluene (l)	E	313.2−473.2	50.4	56.2	8
	E	391.6−473.4	48.9 ± 0.3	57.6 ± 0.3	9
	M	473.2−690.2	44.6	63.1	10
				62.7 ± 0.5	4
	IP + E	289.9−516.8	51.50 ± 3	57.5 ± 0.3	5
	T	282.0−313.2	57.4 ± 0.2	57.3 ± 0.2	this work
3-aminotoluene (l)	E	313.2−473.2	50.7	56.4	8
	E	394.9−476.5	49.7 ± 0.3	58.6 ± 0.3	9
	M	476.4−704.2	45.1	64.1	10
				62.7 ± 0.5	4
	E	419.5−439.1	50.9 ± 0.3	59.6 ± 0.3	11
	T	281.7−312.9	58.4 ± 0.4	58.3 ± 0.4	this work
4-aminotoluene (l)	E	313.2−473.2	50.2	55.9	8
	E	315.0−473.5	52.2	57.7	12
	M	473.6−641.2	45.0	62.1	10
		393−474	49.6	58.4	13
	T	319.3−344.8	55.5 ± 0.3	57.8 ± 0.3	this work
4-aminotoluene (cr)				78.8 ± 0.5[c]	4
	T	284.0−313.2	76.2 ± 0.3[c]	76.2 ± 0.3[c]	this work

[a] Techniques: E = ebulliometry; M = static manometer; IP = inclined piston; T = transpiration. [b] Original vapor pressure available in the literature was treated using eqs 2 and 3 in order to evaluate the enthalpy of sublimation at 298.15 K in the same way as our own results in Table 3. [c] Enthalpy of sublimation $\Delta_{cr}^g H_m$.

Transpiration Method. The vapor pressures, enthalpies of vaporization, $\Delta_l^g H_m$, and enthalpies of sublimation, $\Delta_{cr}^g H_m$, of the aminotoluenes were determined by using the method of transference in a saturated stream of nitrogen. The method has been described before[15,16] and has proven to give results in agreement with other established techniques for determining the vapor pressures and enthalpies of vaporization of pure substances from the temperature dependence of the vapor pressure. About 0.5 g of the sample was mixed with glass beads and placed in a thermostated U tube 10 cm in length and 0.5 cm in diameter. A preheated nitrogen stream was passed through the U tube at constant temperature (±0.1 K). The flow rate of the nitrogen stream was measured using a soap-bubble flow meter (±0.2−0.3%) and optimized in order to reach the saturation equilibrium of the transporting gas at each temperature under study. We tested our apparatus at different flow rates of the carrier gas in order to check the lower boundary of the flow below which the contribution of the vapor condensed in the trap by diffusion becomes comparable to the transpired one. In our apparatus, the contribution due to diffusion was negligible at a flow rate down to 0.5 dm^3·h^{-1}. The upper limit for our apparatus was at a flow rate of 7.5 dm^3·h^{-1}. Thus, we carried out the experiments in the flow rate interval of (0.8−3.5) dm^3·h^{-1}, which has ensured that the transporting gas was in saturated equilibrium with the coexisting solid phase in the saturation tube. The amount of material transported was condensed in a cooled trap at 243 K. The amount of condensed substance was determined by GC analysis using an external standard (tridecane).

TABLE 2: Results for a Typical Combustion Experiment on 4-Aminotoluene at T = 298.15 K (p° = 0.1 MPa)

	4-aminotoluene
m(substance)/g[b]	0.470182
m'(cotton)/g[b]	0.003309
ΔT_c/K[c]	1.19523
$(\epsilon_{calor})(-\Delta T_c)$/J	−17703.95
$(\epsilon_{cont})(-\Delta T_c)$/J	−19.64
$\Delta U_{corr.}$/J	8.36
$-m'\Delta_c u'$/J[d]	56.07
ΔU (dec)/J	31.66
$\Delta_c u^\circ$(substance)/(J·g^{-1})	−37491.2

[a] For the definition of the symbols see ref 20. T_h = 298.15 K; V(bomb) = 0.3200 dm^3; p^i(gas) = 3.04 MPa; $m^i(H_2O)$ = 1.00 g; ΔU(ign) = 1.5 J; m(Pt) =9.64 g. [b] Masses obtained from apparent masses. [c] $\Delta T_c = T^f - T^i + \Delta T_{corr.}$; ϵ_{calor} = (14812.12 ± 0.74) J·K^{-1}; $(\epsilon_{cont})\cdot(-\Delta T_c) = (\epsilon^i_{cont})\cdot(T^i - 298.15\ K) + (\epsilon^f_{cont})\cdot(298.15\ K - T^f + \Delta T corr.)$. [d] ΔU_{corr}, the correction to standard state is the sum of items 81−85, 87−90, 93, and 94 in ref 20.

The saturated vapor pressure p_i^{sat} at each temperature, T_i, was calculated from the amount of product collected within a definite period of time. Assuming that Dalton's law of partial pressures applied to the nitrogen stream saturated with the substance (i) of interest is valid, values of p_i^{sat} were calculated

$$p_i^{sat} = \frac{m_i R T_a}{V M_i} \quad V = V_{N2} + V_i \quad (V_{N2} \gg V_i) \tag{1}$$

where R = 8.31447 J·K^{-1}·mol^{-1}, m_i is the mass of the transported compound, M_i is the molar mass of the compound, and V_i is its volume contribution to the gaseous phase. V_{N2} is the volume of the transporting gas, and T_a is the temperature of the soap-bubble meter. The volume of the transporting gas (V_{N2}) was determined from the flow rate and time measurements.

Combustion Calorimetry. An isoperibol bomb calorimeter was used for the measurement of the energy of combustion of 4-aminotoluene. Five successful experiments were carried out for this compound (see Table 2). The detailed procedure has been described previously.[17] The combustion products were examined for carbon monoxide (Dräger tube) and unburned carbon, but none was detected. The energy equivalent of the calorimeter ϵ_{calor} was determined with a standard reference sample of benzoic acid (sample SRM 39i, NIST). From nine experiments, ϵ_{calor} was measured to be (14 812.12 ± 0.74) J·K^{-1}. The correction for nitric acid formation was based on the titration with 0.1 mol·dm^{-3} NaOH(aq). The atomic weights used were those recommended by the IUPAC Commission.[18] The sample masses were reduced to vacuum, taking into consideration the density value ρ(293 K) = 1.13 g·cm^{-3} for solid 4-aminotoluene.[19] The energy of combustion of cotton thread

$\Delta_c u°(CH_{1.774}O_{0.887}) = -(16945.2 \pm 4.2)\ J{\cdot}g^{-1}$ was measured earlier. For converting the energy of the actual bomb process to that of the isothermal process and reducing to standard states, the conventional procedure[20] was applied.

Computations

Standard ab initio molecular orbital calculations were performed with the Gaussian 03 series of programs.[21] Energies were obtained at the G3MP2 level of theory. The G3 theory is a procedure for calculating the energies of molecules containing atoms of the first and second row of the periodic chart based on the ab initio molecular orbital theory. A modification of the G3 theory that uses reduced orders of the Moller–Plesset perturbation theory is the G3(MP2) theory.[22,23] This method saves considerable computational time compared to the G3 theory with some loss in accuracy, but it is much more accurate than the G2(MP2) theory. For all of the species included in this study, full geometry optimizations were carried out at the HF/6-31G(d) level. The corresponding harmonic vibrational frequencies were evaluated at the same level of theory to confirm that the optimized structures that were found correspond to potential energy minima and to evaluate the corresponding zero-point vibrational energies, ZPE, and the thermal corrections at 298 K. The ZPE values were scaled by the empirical factor, 0.9135. All of the minima found at the HF/6-31G(d) level were fully reoptimized again at the MP2(FULL)/6-31G(d) level. The G3MP2 theory uses geometries from the second-order perturbation theory and scaled zero-point energies from the Hartree–Fock theory followed by a series of single-point energy calculations at the MP2(Full), QCISD(T), and MP2/GTMP2Large levels of theory (for details see ref 22). The enthalpy value of the studied compounds at $T = 298$ K was evaluated according to standard thermodynamic procedures.[24] Aminotoluenes have many rotamers due to torsion around the C–CH$_3$ bond. However, the energy difference between these conformers has been found to be negligible (smaller than 0.1 kJ·mol^{-1}).[25–26]

Results and Discussion

Vapor Pressure Measurements. Our experimental vapor pressures of aminotoluenes have been measured in the temperature range of about 30 K and possibly close to ambient temperatures. The following equation was fitted to the experimental p, T data using a and b as adjustable parameters:

$$R \ln p_i^{sat} = a + \frac{b}{T} + \Delta_l^g C_p \ln\left(\frac{T}{T_0}\right) \qquad (2)$$

T_0 appearing in eq 2 is an arbitrarily chosen reference temperature (which has been chosen to be 298.15 K). Consequently, from eq 2, the expression for the vaporization enthalpy at temperature T is derived:

$$\Delta_l^g H_m(T) = -b + \Delta_l^g C_p\, T \qquad (3)$$

TABLE 3: Results from Measurements of the Vapor Pressure (*p*) of Aminotoluenes Using the Transpiration Method

T K[a]	m mg[b]	$V_{(N2)}$ dm^3[c]	p Pa[d]	$(p_{exptl} - p_{calcd})$ Pa	$\Delta_l^g H_m$ or $\Delta_{cr}^g H_m$ kJ·mol^{-1}
2-aminotoluene; $\Delta_l^g H_m(298.15\ K) = (57.28 \pm 0.24)\ kJ{\cdot}mol^{-1}$					
$\ln(p/Pa) = \frac{289.97}{R} - \frac{77306.17}{R(T,K)} - \frac{67.17}{R}\ln\left(\frac{T,K}{298.15}\right)$					
282.0	1.08	2.394	10.53	0.04	58.37
283.3	1.10	2.170	11.86	0.11	58.28
285.9	1.59	2.544	14.53	−0.19	58.11
287.4	1.30	1.806	16.76	0.04	58.00
289.3	2.49	2.957	19.53	−0.08	57.88
291.3	1.18	1.209	22.72	−0.50	57.74
294.3	1.24	0.971	29.62	0.02	57.54
297.2	1.51	0.930	37.44	0.37	57.35
299.1	1.76	0.935	43.46	0.51	57.22
300.2	1.28	0.626	47.10	0.37	57.15
302.1	1.84	0.779	54.60	0.64	57.02
303.7	1.49	0.561	61.16	0.12	56.91
306.9	1.84	0.561	75.76	−1.14	56.70
310.3	1.71	0.405	97.26	−0.79	56.47
313.2	1.80	0.343	120.69	0.23	56.27
3-aminotoluene; $\Delta_l^g H_m(298.15\ K) = (58.34 \pm 0.41)\ kJ{\cdot}mol^{-1}$					
$\ln(p/Pa) = \frac{291.03}{R} - \frac{78224.88}{R(T,K)} - \frac{66.71}{R}\ln\left(\frac{T,K}{298.15}\right)$					
281.7	2.14	6.161	8.14	0.32	59.44
285.9	1.29	2.669	11.24	−0.10	59.16
289.1	2.17	3.359	14.98	0.06	58.94
291.4	1.96	2.601	17.50	−0.61	58.79
293.5	1.96	2.122	21.32	−0.22	58.65
296.9	1.76	1.474	27.64	−0.71	58.42
300.3	1.09	0.686	36.76	−0.28	58.20
303.3	2.68	1.305	47.40	0.76	58.00
305.3	1.22	0.514	54.86	0.64	57.86
308.2	2.62	0.893	67.65	0.49	57.67
312.1	1.58	0.411	88.22	−0.70	57.41
312.9	2.28	0.549	95.47	1.38	57.35
4-aminotoluene (l); $\Delta_l^g H_m(298.15\ K) = (57.78 \pm 0.29)\ kJ{\cdot}mol^{-1}$					
$\ln(p/Pa) = \frac{290.67}{R} - \frac{77803.88}{R(T,K)} - \frac{67.17}{R}\ln\left(\frac{T,K}{298.15}\right)$					
319.3	1.86	0.263	162.8	−0.4	56.36
323.0	2.21	0.245	207.3	−0.8	56.11
326.0	2.49	0.228	251.3	−0.9	55.91
329.2	2.60	0.193	310.9	2.9	55.69
332.2	3.11	0.193	370.8	0.7	55.49
335.2	4.08	0.210	447.0	4.1	55.29
338.5	4.48	0.193	535.2	−1.9	55.07
341.2	3.78	0.139	624.5	−2.4	54.89
344.8	4.59	0.138	764.6	−2.4	54.65
4-aminotoluene (cr); $\Delta_{cr}^g H_m(298.15\ K) = (76.22 \pm 0.30)\ kJ{\cdot}mol^{-1}$					
$\ln(p/Pa) = \frac{307.46}{R} - \frac{83760.49}{R(T,K)} - \frac{25.28}{R}\ln\left(\frac{T,K}{298.15}\right)$					
284.0	1.661	7.278	5.24	0.04	76.58
286.6	1.07	3.563	6.92	−0.10	76.52
287.2	1.75	5.497	7.35	−0.11	76.50
288.0	1.23	3.527	8.04	−0.12	76.48
290.4	1.68	3.636	10.66	0.03	76.42
292.8	1.62	2.645	14.08	0.23	76.36
295.3	1.61	2.079	17.82	−0.15	76.30
297.1	2.03	2.121	22.00	0.20	76.25
298.2	2.047	1.881	25.04	0.73	76.22
298.6	1.99	1.782	25.64	0.31	76.21
301.0	1.96	1.394	32.29	−0.06	76.15
302.2	1.39	0.891	35.81	−0.70	76.12
303.9	1.98	1.030	44.19	0.94	76.08
305.2	1.67	0.772	49.64	0.48	76.05
307.9	2.01	0.727	63.66	−0.28	75.98
308.2	1.84	0.653	64.67	−1.15	75.97
310.2	3.079	0.882	80.27	0.59	75.92
311.8	2.60	0.653	91.64	−1.03	75.88
313.2	2.70	0.594	104.64	−0.99	75.84

[a] Temperature of saturation. N2 gas flow 0.8–3.5 dm^3·h^{-1}. [b] Mass of transferred sample. Condensed at $T = 243$ K. [c] Volume of nitrogen. Used to transfer mass (m) of sample. [d] Vapor pressure at temperature T, calculated from m and the residual vapor pressure at $T = 243$ K.

Values of $\Delta_l^g C_p$ have been derived using the experimental values of the isobaric molar heat capacities C_p^l of aminotoluenes[27] according to a procedure developed by Chickos et al.[28] The value of $\Delta_{cr}^g C_p$ of solid 4-aminotoluene has been derived from the experimental isobaric molar heat capacity,[27] C_p^{cr}, according to a procedure developed by Chickos.[29] The experimental results and parameters a and b are listed in Table 3. The set of vapor pressures for 2-aminotoluene available from the literature[5,8–10] is remarkably consistent (see Figure 1), and we have performed measurements on this compound mostly for

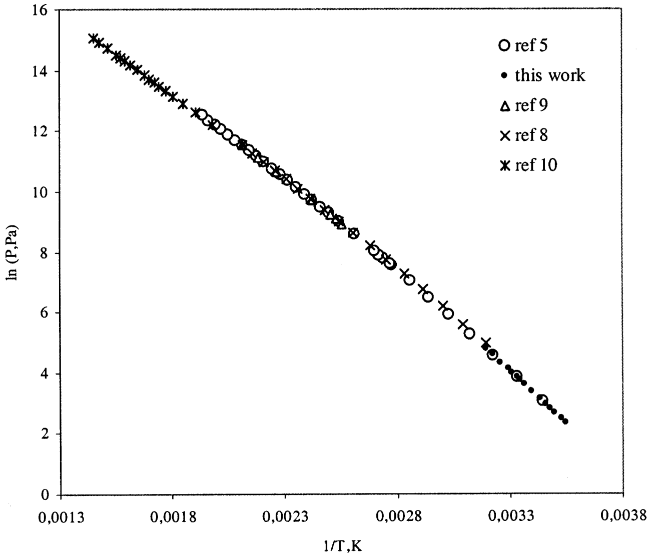


Figure 1. Experimental data of the vapor pressures of liquid 2-aminotoluene.

validation of the transpiration method toward the aromatic amines. As can be seen from Figure 1, our results are in excellent agreement with the old[8−10] measurements just as well as they are with the recent[5] measurements. This fact has encouraged our further investigation.

Enthalpies of Vaporization of Aminotoluenes. Although there are several reports of the dependence of vapor pressure on the temperature of aminotoluenes in the literature,[8−13] most authors did not calculate the enthalpies of vaporization at $T = 298.15$ K from their results. The original published experimental results[8−13] were treated in this work using eqs 2 and 3, and $\Delta_l^g H_m$(298.15 K) was calculated using the experimental isobaric molar heat capacities of aminotoluenes as described above for comparison with the results of this work. Our compilation of the data is presented in Table 1. Chao et al.[4] also provide a compilation of the experimental data on the vapor pressures of aminotoluenes. They selected data sets measured close to the boiling temperatures (mostly from refs 9 and 10) and derived enthalpies of vaporization of all three isomers (see Table 1). These values are about 4−5 kJ·mol^{-1} higher than those in other available data. The discrepancies are apparently due to the large temperature extrapolation of the results selected from refs 9 and 10. Analysis of the data gathered in Table 1 reveals that except for results derived at high temperatures by Glaser and Ruland,[10] the enthalpies of vaporization for each isomer from our measurements and those from the literature are consistent within ±1 kJ·mol.$^{-1}$

Another proof of the reliability of our measured enthalpies of vaporization for aminotoluenes provides a comparison among these values for ortho, meta and para isomers. Indeed, it is obvious from Table 1 that the vaporization enthalpies of 3- and 4-aminotoluenes are indistinguishable from each other within the boundaries of their experimental uncertainties. Such behavior is typical for most of the meta- und para-substituted benzenes.[30] The vaporization enthalpy of *ortho*-aminotoluene is slightly (about 1 kJ·mol^{-1}) lower than those of meta and para isomers, and such a decrease is also typical for substituted benzenes. Thus, the values of the vaporization enthalpies of aminotoluenes derived in this work possess a degree of internal consistency. As has been mentioned already, our results are very close to those reliable data available from the literature, however, our data have been measured around the reference temperature, $T = 298.15$ K, and less affected by the adjustment procedure according to eq 3. For these reasons, the values of $\Delta_l^g H_m$ (298.15 K) (see Table 3) have been selected for the further calculation of the standard enthalpies of formation, $\Delta_f H_m^\circ$(g), of the aminotoluenes.

TABLE 4: Compilation of Experimental Data on Enthalpies of Fusion, $\Delta_{cr}^{l} H_m$, of 4-Aminotoluene

ref	$\Delta_{cr}^{l} H_m$ at T_{fus} kJ·mol^{-1}	T_{fus} K	$\Delta_{cr}^{l} H_m$ at 298.15 K kJ·mol^{-1} [a]
43	17.30	316.6	
44	17.28	315.6	
27	17.19 ± 0.14	317.0 ± 0.5	
45	18.30		
46	18.12		
47	17.90	316.85	
31	18.91 ± 0.13	316.85	
	17.9 ± 0.3[b]	316.6[b]	17.1 ± 0.3

[a] The experimental enthalpies of fusion, $\Delta_{cr}^{l} H_m$, measured at T_{fus} and adjusted to 298.15 K (see text). [b] The average value.

Enthalpy of Sublimation of 4-Aminotoluene. This compound is solid at the reference temperature, 298.15 K. The melting temperature is 316 K (see Table 4). No experimental values of the enthalpies of the sublimation of 4-aminotoluene have been reported in the literature so far. The value reported by Chao et al.[4] (see Table 1) is an estimate from the vaporization enthalpy and the fusion enthalpy, $\Delta_{cr}^{l} H_m$. The value of $\Delta_{cr}^{g} H_m$(298.15 K) for 4-aminotoluene was obtained in this work from measurements in the temperature ranging from 284.0 K to 313.2 K. A valuable test of the consistency of the experimental data on the vaporization and sublimation enthalpies measured in this work is to compare the enthalpy of fusion, $\Delta_{cr}^{l} H_m$, of 4-aminotoluene obtained by difference to the experimental values. To do this, we investigated 4-aminotoluene by the method of transference above and below the temperature of fusion, and the values for $\Delta_{cr}^{g} H_m$(298.15 K) and $\Delta_l^g H_m$(298.15 K) were calculated. The enthalpy of fusion can be calculated as the difference $\Delta_{cr}^{l} H_m(298.15\ \text{K}) = \Delta_{cr}^{g} H_m - \Delta_l^g H_m$ (both values referring to $T = 298.15$ K) = (18.4 ± 0.4) kJ·mol^{-1}. The experimental enthalpy of fusion at the melting temperature, $T = 316.6$ K is $\Delta_{cr}^{l} H_m(T_{fus})$ = (17.9 ± 0.3) kJ·mol^{-1} (calculated as an average value from the data available in Table 4). Because of the deviation from $T = 298.15$ K, the experimental enthalpy of fusion of 4-aminotoluene had to be adjusted to the reference temperature. The adjustment was calculated from the equation[29,32]

$$\frac{\Delta_{cr}^{l} H_m\left(\frac{T_{fus}}{K}\right) - \Delta_{cr}^{l}(298.15\ \text{K})}{\text{J}\cdot\text{mol}^{-1}} = \left\{(0.75 + 0.15 C_p^{cr})\left[\left(\frac{T_{fus}}{K}\right) - 298.15\right]\right\} - \left\{(10.58 + 0.26 C_p^{l})\left[\left(\frac{T_{fus}}{K}\right) - 298.15\right]\right\} \quad (4)$$

where the value of $\Delta_{cr}^{l} C_p$ has been derived from the experimental isobaric molar heat capacity of liquid 4-aminotoluene, C_p^{l}= 216.2 J·mol^{-1}·K^{-1}, and the isobaric molar heat capacities of the solid 4-aminotoluene, C_p^{cr} = 163.5 J·mol^{-1}·K^{-1}, are reported in ref 27. With this adjustment (the uncertainty of the correlation was not taken into account), the standard enthalpy of fusion at $T = 298.15$ K, $\Delta_{cr}^{l} H_m$(298.15 K) = (17.1 ± 0.3) kJ·mol^{-1} was calculated (see Table 4). Thus, the enthalpy of fusion $\Delta_{cr}^{l} H_m^\circ$ calculated from the difference $\Delta_{cr}^{g} H_m - \Delta_l^g H_m$ measured in this work differs from those measured by calorimetry (and adjusted to $T = 298.15$ K) only by 1.3 kJ·mol^{-1}. The agreement could be considered as acceptable taking into

TABLE 5: Summary of Experimental Specific Energies of Combustion and Standard Molar Thermodynamic Functions at T = 298.15 K ($p°$ = 0.1 MPa) for 4-Aminotoluene

4-aminotoluene; $[(\Delta_c u°)\{$4-aminotoluene, cr, 298.15 K$\}]/(\mathrm{J{\cdot}g^{-1}})$				
−37485.9	−37493.8	−37497.0	−37484.6	−37491.4
$\langle\Delta_c u°\rangle/(\mathrm{J{\cdot}g^{-1}})$				−37490.5 ± 5.2
$\Delta_c H_m°(\mathrm{cr})/(\mathrm{kJ{\cdot}mol^{-1}})$				−4021.6 ± 1.3
$\Delta_f H_m°(\mathrm{cr})/(\mathrm{kJ{\cdot}mol^{-1}})$				−19.2 ± 1.3

TABLE 6: Total Energies at 0 K and Enthalpies at 298.15 K (in Hartree) of the Molecules Studied in This Work

	G3MP2		MP2Full /6-31G (d)	TCH
compounds	E_0	H_{298}	E_0	with scaling
2-aminotoluene	−326.353429	−326.344918	−325.860159	0.149184
3-aminotoluene	−326.353026	−326.344139	−325.859091	0.148940
4-aminotoluene	−326.352140	−326.343211	−325.858728	0.148970
benzene	−231.829758	−231.824309	−231.487188	0.102963
amino-benzene	−287.113824	−287.106878	−286.683433	0.120578
toluene	−271.068985	−271.061629	−270.662873	0.131314
methane	−40.422100	−40.418284		
ammonia	−56.470142	−56.466333		
ethene	−78.434778	−78.430777		
ethane	−79.651199	−79.646714		

TABLE 7: Results of Calculation of the Standard Enthalpy of Formation $\Delta_f H_m°(g)$ for Aminotoluenes in the Gaseous Phase at 298.15 K in kJ·mol^{-1}

	G3MP2			MP2Full	
		bond separation			
compounds	atomization	reaction 1	reaction 2	reaction 2	exptl
2-aminotoluene	50.7	57.7	53.1	52.8	52.6 ± 1.0
3-aminotoluene	52.7	59.7	55.2	55.0	57.0
4-aminotoluene	55.2	62.1	57.6	56.0	57.0 ± 1.3

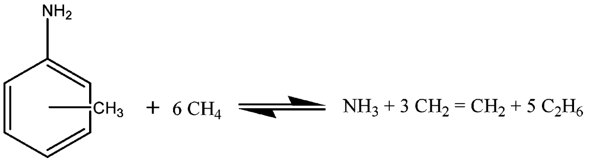
account the spread of the experimental values, $\Delta_{cr}^{l}H_m(T_{fus})$, collected in Table 4. Thus, our results for the vaporization and sublimation enthalpies of 4-aminotoluene have been proven to be consistent.

Enthalpy of Formation of 4-Aminotoluene. The results of a typical combustion experiment for 4-aminotoluene are summarized in Table 2. The values of the standard specific energies of combustion, $\Delta_c u°$, together with their mean, are given in Table 5. To derive $\Delta_f H_m°(\mathrm{cr})$ from $\Delta_c H_m°$, the molar enthalpies of formation of H_2O(l): −(285.830 ± 0.042) kJ·mol^{-1} and CO_2(g): −(393.51 ± 0.13) kJ·mol^{-1} were taken, as assigned by CODATA.[33] Table 5 lists the derived standard molar enthalpy of combustion and the standard molar enthalpy of formation of 4-aminotoluene. The total uncertainty was calculated according to the guidelines presented by Olofsson.[34] The uncertainty assigned to $\Delta_f H_m°$ is twice the overall standard deviation and includes the uncertainties from calibration, from the combustion energies of the auxiliary materials, and the uncertainties of the enthalpies of formation of the reaction products, H_2O and CO_2.

Previous determinations of the standard molar enthalpy of formation $\Delta_f H_m°(\mathrm{cr})$ of 4-aminotoluene were made by Swarts[6] and Pushin[7] by combustion calorimetry. Their values of 18.2 and 20.6 kJ·mol^{-1} are in close agreement with each other, but they are about 40 kJ·mol^{-1} less negative than our value −(19.2 ± 1.3) kJ·mol^{-1}. We do not have a reasonable explanation for such a discordance, but a rough estimation performed by Chao et al.[4] using the enthalpies of formation of aniline, toluene, and 1,4-dimethylbenzene provided the value of $\Delta_f H_m°(\mathrm{cr}) = -23.5$ kJ·mol^{-1} for 4-aminotoluene, and this value is in reasonable agreement with our new combustion results.

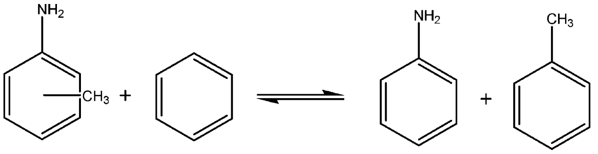
Calculation of the Gaseous Enthalpies of Formation. The values of the vaporization enthalpies of aminotoluenes, as well as the enthalpy of sublimation of 4-aminotoluene, derived in this work possess internal consistency. These values (see Table 3) can now be used for further calculation of the standard enthalpies of formation, $\Delta_f H_m°(g)$ at 298.15 K, of the aminotoluenes. For this purpose, we selected the following enthalpies of formation from the literature: $\Delta_f H_m°(l) = -(4.7 \pm 1.0)$ kJ·mol^{-1} of 2-aminotoluene, derived from the combustion results by Steele et al.[3] and $\Delta_f H_m°(l) = -1.3$ kJ·mol^{-1} of 3-aminotoluene[35,36] and $\Delta_f H_m°(\mathrm{cr}) = -(19.2 \pm 1.3)$ kJ·mol^{-1} of 4-aminotoluene, measured in this work. The resulting values of the standard molar enthalpies of formation, $\Delta_f H_m°(g)$, of aminotoluenes are given in the last column of Table 7.

Quantum Chemical Calculations for Aminotoluenes. Ab initio molecular orbital methods for the calculation of the enthalpy of formation of aminotoluenes have not been yet reported in the literature. Our results are presented in Table 6. In standard Gaussian-n theories, theoretical enthalpies of formation are calculated through atomization reactions.[37] Raghavachari et al.[38] have proposed to use a set of isodesmic reactions, the “bond separation reactions”, to derive theoretical enthalpies of formation. We calculated the enthalpies of formation of aminotoluenes with the help of both atomization and bond-separation methods. For the latter method, two sets of isodesmic reactions were used to determine the enthalpies of formation of the aminotoluenes via a theoretical calculation of the reaction enthalpies. The first scheme is based on the reaction of aminotoluene with methane to form simple molecules:



(1)

The second scheme is based on the distribution reaction of aminotoluene with benzene:



(2)

Isodesmic reactions rely on the similarity of bonding environments in the reactants and products that leads to the cancellation of systematic errors in the ab initio calculations.[37] Using the enthalpies of reactions 1 and 2, calculated by G3(MP2) and MP2Full/6-31G(d), together with the enthalpies of formation, $\Delta_f H_m°(g)$, for benzene, toluene, aniline, ammonia, methane, ethane, and ethene recommended by Pedley et al.,[39] we calculated the enthalpies of formation of all three isomeric aminotoluenes (see Table 7). Although the enthalpies of formation of the aminotoluenes were calculated with help of isodesmic reaction 2, for both the G3(MP2) and the MP2Full/6-31G(d) method, they are in excellent agreement with the experimental values derived in this work; the enthalpies of formation of the aminotoluenes were estimated with the help of the atomization procedure, and bond-separation reaction 1 systematically deviates from the experimental results by about 3−4 kJ·mol.$^{-1}$ Because the G3(MP2) method is more sophisticated in comparison to MP2Full/6-31G(d), the enthalpies of

TABLE 8: Results of Calculation of the Standard Enthalpies of Reactions, $\Delta_r H^\circ_m$ for Reactions Involving Aminotoluenes in the Gaseous Phase at 298.15 K in kJ·mol^{-1}

	$-\Delta_r H^\circ_m$/kJ·mol^{-1}		
reaction 2	MP2Full6-31G (d)	G3MP2	exptl
2-aminotoluene	−2.2	−1.9	−2.4
3-aminotoluene	0.0	+0.2	+0.2
4-aminotoluene	+1.0	+2.6	+2.0

formation calculated by G3(MP2) are considered to be more reliable for the analysis of substituent effects in aminotoluenes.

Internal rotation of the CH3 and NH2 tops has been considered on the basis of the corresponding potential energy functions in evaluation of the thermal part of the enthalpies of formation from quantum-chemical calculations. The values of the frequencies of normal vibrations and the moments of inertia for the molecules of the aminotoluenes are given in the tables of the Supporting Information.

Analysis of Substituent Effects. The inclusion of the amino substituent in toluene leads to the variation of charge distribution in the molecule, and consequently, this affects the structural, electronic, and vibrational parameters. The methyl and amino groups are generally referred to as electron-donating substituents in an aromatic system. The CH_3 interacts with nearby π systems via hyperconjugation, whereas the NH_2 shares its lone-pair electrons with p electrons in the ring. Both mechanisms imply electronic delocalization, with the energetics expected to be small. But how can these energetics be assessed properly? The total energetics of the substituent effects can be examined in several different ways. The following two approaches are generally used:

(a) Group additivity procedures are conventionally applied to derive substituent effects (or strain enthalpies) as the differences between the observed enthalpies of formation in the gaseous state and the values calculated by applying anyone of a number of group-additivity schemes.[40,41] We have discussed the substituent effects of alkyl-anilines recently[1,2] in such a manner.

(b) Isodesmic reactions involving aminotoluene can be also used to obtain the effects of the interaction of CH_3 and NH_2 by attaching them to the separate benzene rings (according to the scheme presented by reaction 2 above). This will allow the total substituent effect to be evaluated for each species studied. This way is especially convenient for benzene derivatives because the enthalpy of the distribution reaction like that in reaction 2 expresses the energetics of the mutual interaction of substituents on the benzene ring directly. For instance, from the enthalpy of reaction 2, one can distinguish the strain (or substituent effects) of 2-aminotoluene in comparison to benzene, toluene, and aniline, or in other words, this amount of interaction is caused by the steric and electronic interactions of methyl and amino substituents. We calculated the substituent effects in aminotoluenes with the help of reaction 2 using the experimental enthalpies of formation, $\Delta_f H^\circ_m$(g), of the participants.[39] These calculations (see Table 8) reveal that 2-aminotoluene is stabilized slightly by about 2.4 kJ·mol^{-1}. In contrast, a weak destabilization of about 2 kJ·mol^{-1} is calculated in 4-aminotoluene. 3-Aminotoluene is observed to be about strainless. These effects are very small, but they are in accordance with the structural alterations observed in aminotoluenes in comparison with toluene and aniline. The amino group in aniline and its derivatives are known to have a pyramidalized geometry resulting from a balance between opposing forces: the stability gained by the molecule as a whole arising from p−π conjugation of the nitrogen lone pair with the aromatic system versus that gained by the amine using highly directed sp^3 orbitals for bond formation.[25,26] This asymmetric interaction between the amino group and the aromatic ring produces a small displacement of the nitrogen atom out of the benzene ring. However, this delicate interplay between geometrical and electronic factors in 2-aminotoluene results in a very weak stabilization of 2.4 kJ·mol^{-1}. The calculated structure for 4-aminotoluene shows that the minimum energy conformation has a hydrogen atom of the methyl group perpendicular to the plane of the ring. The aromatic ring in 4-aminotoluene is clearly distorted from a regular hexagon (as that in benzene); however, the angle between the ring and the NH_2 plane in 4-aminotoluene is calculated to be 42°, which is very close to that in aniline.[42] This shows that the interaction of the CH_3 substituent with the amino group is not large and the destabilization of 4-aminotoluene by 2.0 kJ·mol^{-1} obtained in this work seems to be reasonable in size.

A substantial advantage of ab initio calculations toward benzene derivatives is that this method allows for the estimation of substituent effects directly from enthalpies H_{298} (see Table 6). Indeed, the latter values result from ab initio calculations directly. One can derive the substituent effects on the benzene ring using these values, H_{298}, with the help of an isodesmic reaction such as that in Scheme 2. In the case of aminotoluenes, the enthalpy of the reaction in Scheme 2 is, in general, equivalent to the interaction between the amino and methyl groups. Thus, the substituent effects in aminotoluenes were derived (Table 8) as the enthalpies of reaction 2 and using only the ab initio values of the enthalpies, H_{298}, of reactions of the participants from Table 6. For validation of this procedure, we have also calculated the standard enthalpies of reaction 2, $\Delta_r H^\circ_m$, using the experimental $\Delta_f H^\circ_m$(g) of the reaction participants selected in this work. The results are compared in Table 8. They show that $\Delta_r H^\circ_m$, derived experimentally or calculated by MP2Full/6-31G(d) or G3(MP2), are in excellent agreement.

Conclusions

This investigation was undertaken to establish a consistent set of experimental thermochemical quantities for isomeric aminotoluenes. Our own results, together with a large number of experimental results from the literature have been used to derive reliable values for the enthalpy of formation of aminotoluenes at the reference temperature, 298.15 K. This collection, together with our own results helps to resolve the previous contradictions in the experimental thermochemistry of aminotoluenes.

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Supporting Information Available: The values of the frequencies of normal vibrations and the moments of inertia for the molecules of the aminotoluenes. This material is available free of charge via the Internet at http://pubs.acs.org.

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