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Experimental and Computational Study on the Thermochemistry of Bromoanilines

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The standard ($p^\circ = 0.1\,\text{MPa}$) molar enthalpies of formation of 2-, 3-, and 4-bromoaniline, 2,4-, 2,5-, and 2,6-dibromoaniline, and 2,4,6-tribromoaniline were derived from the standard molar enthalpies of combustion, in oxygen, which yields $CO_2(g)$, $N_2(g)$, and $HBr{\cdot}600H_2O(l)$, at $T = 298.15\,\text{K}$, measured by using rotating-bomb calorimetry. The standard molar enthalpies of sublimation, or vaporization, of these compounds at $T = 298.15\,\text{K}$ were measured by using Calvet microcalorimetry, and so their standard molar enthalpies of formation in the gaseous state were derived. The enthalpies of fusion of the solid compounds were determined by DSC. The gas-phase enthalpies of formation were also estimated by density functional theory calculations performed at the BP86/6-31+G* level. As a result it is confirmed that thermodynamic data is consistent with intramolecular N–H···Br hydrogen bonding.

Aromatic amines are of great importance in biological and material sciences as well as in pharmaceutical and chemical industries. Halogenated anilines have gained the most focus of all of the aromatic amines, due to their high toxicity and wide uses. For example, they may be used as reagents or precursors for synthesizing organic dyes, in pigments, in agricultural agents, in pharmaceuticals and in the rubber industries.[1,2] Haloanilines are frequently found in both effluents of waste water treatment plants and surface water, due to chemical degradation or biotransformation of pesticides and herbicides, or due to accidental spills and illegal release of industrial and municipal wastewater.[3] These compounds have been determined to induce several kinds of toxicity, like methemoglobinemia, splenotoxicity, hepatotoxicity, and nephrotoxicity.[2,4]

Because of their stability in the presence of air and humidity, and potentially attractive economics,[5,6] aniline and haloanilines have been also used in the synthesis of conducting polymers with applications in rechargeable batteries, electromagnetic interference shielding, electrochromic display devices, sensors, and electrocatalysis.

The current work presents the results of calorimetric and computational thermochemistry studies on bromoanilines. The experimental investigation includes the determination of the standard massic energies of combustion in oxygen at $T = 298.15\,\text{K}$ of the different bromoanilines using a rotating-bomb combustion calorimeter, from which the values of the standard molar enthalpies of formation in the condensed phase were derived. The determination of the standard molar enthalpies of sublimation or vaporization at $T = 298.15\,\text{K}$ was done by using Calvet microcalorimetry with the high-temperature vacuum sublimation technique; these values allowed the derivation of the standard molar enthalpies of formation, in the gaseous state, of 2-, 3-, and 4-bromoaniline, 2,4-, 2,5-, and 2,6-dibromoaniline, and 2,4,6-tribromoaniline, which were compared with values estimated by the Cox scheme[7] and those obtained by density functional theory calculations.

Experimental

Materials. The three monobromoanilines, 2-bromoaniline [CAS 615-36-1], 3-bromaniline [CAS 591-19-5], and 4-bromoaniline [CAS 106-40-1]); the three dibromoanilines, 2,4-dibromoaniline [CAS 615-57-6], 2,5-dibromoaniline [CAS 3638-73-1], and 2,6-dibromoaniline [CAS 608-30-0]; the 2,4,6-tribromoaniline [CAS 147-82-0] compounds studied in this work were obtained commercially from Aldrich Chemical. 2-Bromoaniline, 4-bromoaniline, 2,4-dibromoaniline, 2,5-dibromoaniline, 2,6-dibromoaniline, and 2,4,6-tribromaniline were purified by vacuum sublimation, while 3-bromoaniline was purified by distillation under reduced pressure and was stored under nitrogen. The purities of the samples of the seven bromoanilines were checked by C, H, and N microanalyses, of which the results are presented in Table 1, together with the specific densities used to calculate the true mass from the apparent mass in air, and further checked by GLC.

Combustion Calorimetry. The energies of combustion of the seven bromoanilines were measured using a rotating-bomb calorimeter developed by Professor Stig Sunner at the University of Lund, Sweden. Both the apparatus and the operating technique have been described,[8–10] and only a brief description of the apparatus will be given here. The twin valve bomb with an internal volume of $0.258\,\text{dm}^3$ and wall thickness of 1 cm is made of stainless steel, internally lined with platinum, and all of the internal fittings are made entirely from platinum. In each experiment,

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Table 1. Specific Densities (ρ) and Mass Fractions (w) of C, H, and N

Compound	ρ	w					
		Expected			Found		
	$/\mathrm{g\,cm^{-3}}$	C	N	H	C	N	H
2-Bromoaniline[a)]	1.52	0.419	0.081	0.035	0.420	0.080	0.036
3-Bromoaniline[a)]	1.58				0.415	0.082	0.037
4-Bromoaniline[a)]	1.497				0.418	0.080	0.036
2,4-Dibromoaniline[b)]	2.260	0.287	0.056	0.020	0.290	0.054	0.019
2,5-Dibromoaniline[b)]	1.78				0.288	0.054	0.019
2,6-Dibromoaniline[b)]	1.76				0.286	0.055	0.020
2,4,6-Tribromoaniline[c)]	2.35	0.218	0.042	0.012	0.220	0.042	0.011

a) Molar mass of monobromoanilines: $M = 172.0225\,\mathrm{g\,mol^{-1}}$. b) Molar mass of dibromoanilines: $M = 250.9186\,\mathrm{g\,mol^{-1}}$. c) Molar mass of tribromoaniline: $M = 329.8147\,\mathrm{g\,mol^{-1}}$.

the bomb was suspended from the lid of the calorimeter can. Water was added to the calorimeter from a weighed perspex vessel; as the mass of water differed slightly 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.

Calorimeter temperatures were measured within the bounds of $\pm 1 \times 10^{-4}$ K, with time intervals of 10 s using a Hewlett-Packard (HP-2804A) quartz crystal thermometer interfaced to an Olivetti M 250E microcomputer programmed to compute the adiabatic temperature change. At least 100 readings were taken for both the fore and after periods, whereas in the main period, the number of readings was about 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 rotating mechanism allows 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 about 63% of its final value and was continued throughout the experiment. Good et al.[11] have shown that by adopting this procedure, the frictional work due to 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 jacket consists of a thermostatic bath containing a cavity of exactly the same shape as the calorimeter can, but 1 cm larger in overall dimensions, enclosed by a hollow lid. The jacket and lid were filled with water maintained at a temperature of ca. 303.5 ± 10^{-4} K using a temperature controller (Tronac PTC 41).

In all experiments, data acquisition and control of the calorimeter was performed by means of the LABTERMO program.[12]

The energy equivalent of the calorimeter was determined by combustion of thermochemical standard benzoic acid (NIST Standard Reference Material 39i) having a massic energy of combustion under standard bomb conditions of $-26434 \pm 3\,\mathrm{J\,g^{-1}}$. From six calibration experiments, that were made in oxygen at $p = 3.04$ MPa with $1.00\,\mathrm{cm^3}$ of water added to the bomb, the value of energy equivalent of the calorimeter was found to be $\varepsilon(\text{calor}) = 25174.6 \pm 2.4\,\mathrm{J\,K^{-1}}$, where the uncertainty quoted is the standard deviation from the mean. For 2-bromoaniline, the energy equivalent of the calorimeter was determined as $\varepsilon(\text{calor}) = 25175.1 \pm 1.6\,\mathrm{J\,K^{-1}}$. The excellent agreement, previously obtained in this laboratory,[13] between the values of the energy equivalent $\varepsilon(\text{calor}) = 25177.7 \pm 2.3\,\mathrm{J\,K^{-1}}$, from combustion of benzoic acid with $1.00\,\mathrm{cm^3}$ of water added to the bomb, and from burning benzoic acid in the presence of $40.00\,\mathrm{cm^3}$ of an aqueous solution of composition similar to that resulting from the combustion of the bromine compounds, $25175.9 \pm 2.6\,\mathrm{J\,K^{-1}}$, means that the corrections for the standard state, (ΔU_Σ) do not lead to systematic errors in the values of the massic energies of combustion. Hence, in this work, the combustions of the isomers of bromoaniline were carried out in oxygen at a $p = 3.04$ MPa with 20 to $40\,\mathrm{cm^3}$ of an aqueous As_2O_3 ($0.08986\,\mathrm{mol\,dm^{-3}}$) in the bomb, which reduces all of the bromine produced in the combustion to hydrobromic acid. Within the precision of the analytical method, no evidence was found for oxidation of As_2O_3(aq) within about 5 h at room temperature in the presence of oxygen at $p = 3.04$ MPa. The extent of oxidation of As_2O_3(aq) was determined by titration with a standardized iodine solution. For the calculation of the energetic term $\Delta U(As_2O_3)$, corresponding to the energy of oxidation of As_2O_3(aq) to As_2O_5(aq) in aqueous solution, the procedure described by Hu et al.,[14] which uses the enthalpies of oxidation of As_2O_3(aq) by Br_2[15] and the thermal effects of mixing As_2O_5(aq) with strong acids,[16] was followed.

Crystalline compounds were burnt in pellet form. Both solid and liquid samples, with the exception of 2,4,6-tribromoaniline, were enclosed in sealed polyester bags made from Melinex® (0.025 mm thickness), using the technique described by Skinner and Snelson.[17] They determined the massic energy of combustion of dry Melinex® as $\Delta_c u^0 = -22902 \pm 5\,\mathrm{J\,g^{-1}}$; 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 from the Melinex® was calculated using a factor that was previously reported.[17]

Hexadecane (Aldrich Gold Label, mass fraction > 0.999), stored under nitrogen, was used as an auxiliary combustion aid in the combustion experiments of the crystalline 2,4,6-tribromoaniline, and its massic energy of combustion was $\Delta_c u^o = -47161.9 \pm 3.2\,\mathrm{J\,g^{-1}}$ in agreement with that of Fraser and Prosen[18] for a sample of mass fraction 0.9996, ($\Delta_c u^o = -47155.0 \pm 3.8\,\mathrm{J\,g^{-1}}$).

The electrical energy for ignition was determined from the change in potential difference across a capacitor after discharge through the platinum ignition wire. For the cotton thread fuse with an empirical formula of $CH_{1.686}O_{0.843}$, $\Delta_c u^o = -16240\,\mathrm{J\,g^{-1}}$.[19] The nitric acid formed was determined using the Devarda's alloy method,[20] and corrections were based on $-59.7\,\mathrm{kJ\,mol^{-1}}$ for the standard molar energy of formation ($\Delta_f H_m^o$), in which 0.1 $\mathrm{mol\,dm^{-3}}$ HNO_3(aq) is formed from O_2(g), N_2(g), and H_2O(l).[21] The amount of H_2PtBr_4(aq) formed was determined from the mass loss of the platinum crucible and its supporting ring, which correlates to an energy correction based on $\Delta_f H_m^o(H_2PtBr_4, \text{aq}) = -368.2 \pm 0.1\,\mathrm{kJ\,mol^{-1}}$.[21] If the carbon soot which is formed due to incomplete combustion, stays on the walls of the platinum crucible, and not in the combustion solution or on the walls of the bomb, an energy correction for the carbon soot was done by weighing the crucible before and after calcinations. If the mass difference was greater than 1 mg, or if traces of soot were detected in any other part of the bomb, the experiments were discarded. Corrections for carbon soot formation were based on the standard massic energy of combustion of carbon ($\Delta_c u^o = -33\,\text{kJ}\,\text{g}^{-1}$).[22] An estimated pressure coefficient of massic energy, $(\partial u/\partial p)_T = -0.2\,\text{J}\,\text{g}^{-1}\,\text{MPa}^{-1}$, at $T = 298.15\,\text{K}$, which is a typical value for most organic compounds,[23] was used.

For each compound, ΔU_Σ and the heat capacities of the bomb contents, $\mathcal{E}_i$ and $\mathcal{E}_f$, were calculated by the procedure given by Bjellerup,[24] using the solubility constants and energies of solution of CO_2 and O_2, as given by Hu et al.[14]

All necessary weighing was done using a Mettler AE 240 balance with a sensitivity of $\pm 1 \times 10^{-5}$ g, and corrections from apparent mass to true mass were made.

Calvet Microcalorimetry. The enthalpies of sublimation, or vaporization, of the seven compounds were measured by using the drop-microcalorimetric technique for vacuum sublimation,[25] or vaporization.[26] For these measurements, a Calvet high-temperature microcalorimeter (Setaram HT 1000) was used. Both apparatus and technique have been recently described.[27]

Samples of about 3–5 mg of crystalline compound or 7–10 mg of the liquid 3-bromoaniline, contained in a small thin glass capillary tube that was sealed at one end, and a blank capillary were simultaneously dropped at room temperature into the hot reaction vessels, which were held at a convenient temperature T, and then removed from the hot zone by vacuum sublimation, or vaporization. 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 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 into each of the twin calorimeter cells.

From the experimental results, the standard molar enthalpies of sublimation, or vaporization at $T = 298.15\,\text{K}$, $\Delta_{\text{cr,l}}^{\text{g}} H_\text{m}^\text{o}$, were calculated using the $\Delta_{298.15\,\text{K}}^{T} H_\text{m}^\text{o}(\text{g})$ values estimated by a group method, based on the values of Stull et al.,[28] which take into account Chart 1.

The microcalorimeter was calibrated in situ using the reported standard molar enthalpies of sublimation of naphthalene ($72.6 \pm 0.6\,\text{kJ}\,\text{mol}^{-1}$),[29] for crystalline bromoanilines and of vaporization of *n*-undecane ($56.580 \pm 0.566\,\text{kJ}\,\text{mol}^{-1}$),[29] for liquid 3-bromoaniline.

Theoretical Calculations. The BP86 exchange-correlation functional and the 6-31+G* basis set were used for geometry optimization of the bromoanilines considered in this work. The calculations were performed by means of the Gaussian 98 suite of programs.[30] The BP86 functional is based on Becke's 1988 exchange[31] and on Perdew's 86 correlation functionals.[32] Vibrational frequencies have also been calculated at the same level of theory used in the optimization procedure. This is used to correct the computed electronic energy values for Zero-Point Energies, ZPE, as well as translational, rotational, and vibrational contributions to the enthalpy at $T = 298.15\,\text{K}$. The above mentioned exchange-correlation functional was chosen since, in previous works devoted to the thermochemistry of halogenated anilines,[10,33–35] it was found that the use of this functional permitted estimation of accurate gas-phase enthalpies of formation for this class of compounds. Atoms in Molecules calculations have been performed by means of the TOPMOD code.[36,37]

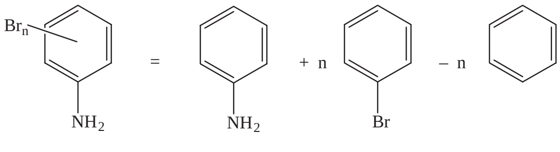


Chart 1.

Results

Purity Control. A differential scanning calorimeter, Setaram DSC 141, was used to determine the temperatures and enthalpies of fusion of 2- and 4-bromoanilines, of 2,4-, 2,5-, and 2,6-dibromoanilines, and of 2,4,6-tribromoaniline, and also to check the purity of these solid compounds, using the fractional fusion technique.[38] The temperature scale of the calorimeter was calibrated by measuring the melting temperatures of three high-purity reference materials: naphthalene (Aldrich 99.9%), benzoic acid (NIST Standard Reference Material 39i) and indium (Aldrich, mass fraction >0.99999),[29] whereas the power scale was calibrated with a highly pure indium sample as a reference.[29] Thermograms of samples hermetically sealed in stainless steel crucibles were recorded in air atmosphere. The crucibles and the samples of compounds were weighed on a Mettler UMT2 microbalance with a sensitivity of $\pm 1 \times 10^{-7}$ g. For experimental measurements, five to six samples weighing $\approx$6 mg were scanned in the temperature range from $T = 298\,\text{K}$ to about 15 K above of the melting point with a heating rate of $1.67 \times 10^{-2}\,\text{K}\,\text{s}^{-1}$. The recorded thermograms did not show any phase transitions between $T \approx 298\,\text{K}$ and the melting temperature of the samples. The enthalpies and temperatures of fusion were computed from the DSC thermograms, and are presented in Table 2 together with the published values of the temperatures of fusion,[39] where the uncertainties assigned to the temperature and enthalpies of fusion are the standard deviation from the mean. The relative atomic masses used throughout this paper were those recommended by the IUPAC Commission in 2001.[40]

Experimental Enthalpies of Formation. Results of a typical combustion experiment for each compound are given in Table 3, where the symbols have been defined elsewhere,[14,19,24] $\Delta m(\text{H}_2\text{O})$ is the deviation of the mass of water added to the calorimeter from 5222.5 g, which is the mass assigned to $\mathcal{E}$(calor). The values of the energy associated to the isothermal bomb process, $\Delta U(\text{IBP})$, were calculated using the expression:

$$\begin{aligned}\Delta U(\text{IBP}) = &-\{\mathcal{E}(\text{calor}) + \Delta m(\text{H}_2\text{O})c_p(\text{H}_2\text{O,l})\}\Delta T_\text{ad}\\ &+ \mathcal{E}_\text{i}(T_\text{i} - 298.15\,\text{K})\\ &+ \mathcal{E}_\text{f}(298.15\,\text{K} - T_\text{i} - \Delta T_\text{ad}) + \Delta U_\text{ign}, \qquad (1)\end{aligned}$$

where ΔT_ad is the adiabatic temperature rise and ΔT_corr is the

Table 2. Temperatures and Enthalpies of Fusion

Compound	$\Delta_\text{cr}^\text{l} H_{\text{m(exp)}}$ /kJ mol^{-1}	$T_{\text{fus(exp)}}$ /K	$T_{\text{fus(lit)}}$^{39} /K
2-Bromoaniline	16.14 ± 0.19	304.08 ± 0.12	302–304
4-Bromoaniline	16.75 ± 0.16	336.02 ± 0.13	335–337
2,4-Dibromoaniline	21.37 ± 0.15	351.36 ± 0.09	351–353
2,5-Dibromoaniline	20.47 ± 0.17	328.06 ± 0.17	324–326
2,6-Dibromoaniline	21.79 ± 0.18	355.54 ± 0.04	353–355
2,4,6-Tribromoaniline	25.75 ± 0.16	393.03 ± 0.05	393–395

Table 3. Typical Combustion Results at $T = 298.15\,\mathrm{K}$ ($p^\circ = 0.1\,\mathrm{MPa}$)[a)]

	2-Bromoaniline	3-Bromoaniline	4-Bromoaniline	2,4-Dibromoaniline	2,5-Dibromoaniline	2,6-Dibromoaniline	2,4,6-Tribromoaniline
m(cpd)/g	1.00415	1.18501	0.99088	1.48906	1.49718	1.48511	1.38655
m'(fuse)/g	0.00267	0.00272	0.00276	0.00317	0.00235	0.00277	0.00258
m''(melinex)/g	0.04420	0.04571	0.05465	0.05117	0.0418	0.03691	—
m'''(n-hex.)/g	—	—	—	—	—	—	0.20376
T_i/K	297.3141	297.1878	297.3314	297.3326	297.3305	297.3411	297.2255
T_f/K	298.1373	298.1546	298.1529	298.1544	298.1515	298.1489	298.1527
ΔT_ad/K	0.80633	0.94949	0.80513	0.80496	0.80387	0.79077	0.90911
$\mathcal{E}_\mathrm{i}/\mathrm{J\,K^{-1}}$	114.63	115.25	114.77	156.78	177.68	177.67	177.85
$\mathcal{E}_\mathrm{f}/\mathrm{J\,K^{-1}}$	113.11	113.33	113.03	153.28	173.64	173.71	173.97
$\mathcal{E}$(calor)/J K^{-1}	25178.9	25186.1	25170.0	25174.6	25171.3	25182.5	25172.1
$\Delta m(H_2O)$/g	0.9	0.3	−1.1	0.0	−0.8	−1.9	−0.6
$-\Delta U$(IBP)$^{b)}$/J	20393.65	24022.05	20363.67	20389.50	20376.03	20052.88	23044.66
ΔU(fuse)/J	43.36	44.17	44.82	51.48	38.16	44.98	41.90
ΔU(melinex)/J	1012.25	1046.75	1251.66	1171.94	1011.79	845.26	—
ΔU(n-hex.)/J	—	—	—	—	—	—	9609.82
$\Delta U(HNO_3)$/J	35.46	35.70	11.46	36.30	16.72	27.58	20.54
$\Delta U(As_2O_3)$/J	446.98	522.25	444.58	925.66	959.16	955.64	1036.01
ΔU(ign)/J	1.30	1.31	1.29	1.29	1.28	1.29	1.28
$\Delta U(H_2PtBr_4)$/J	0.19	0.03	0.13	0.35	0.28	0.19	0.31
ΔU(carb)/J	0.00	0.00	18.81	0.00	5.94	8.25	7.92
ΔU_Σ/J	50.79	59.36	51.22	66.77	76.10	74.61	76.15
$-\Delta_\mathrm{c}u^\circ$/J g^{-1}	18726.90	18830.04	18749.61	12180.17	12209.46	12196.32	8847.75

a) m(cpd), m'(fuse), m''(melinex), and m'''(n-hex.) are the mass of compound burnt, the mass of fuse (cotton) used, the mass of melinex and the mass of n-hexadecane respectively 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; $\mathcal{E}_\mathrm{i}$ is the energy equivalent of contents in the initial state; $\mathcal{E}_\mathrm{f}$ is the energy equivalent of contents in the final state; $\mathcal{E}$(calor) is the energy equivalent of the calorimeter; $\Delta m(H_2O)$ is the deviation of mass of water added to the calorimeter from 5222.5 g; ΔU(IBP) is the energy change for the isothermal combustion reaction under actual bomb conditions; ΔU(fuse) is the energy combustion of the fuse (cotton); ΔU(melinex) is the energy combustion of the melinex; ΔU(n-hex.) is the energy of combustion of the n-hexadecane; $\Delta U(HNO_3)$ is the energy correction for the nitric acid formation; $\Delta U(As_2O_3)$ is the energy of oxidation of the aqueous solution of As_2O_3; ΔU(ign) is the electrical energy for ignition; $\Delta U(H_2PtBr_4)$ is the energy correction for the formation of the platinum complex; ΔU(carb) is the correction energy for carbon soot formation; ΔU_Σ is the standard state correction; $\Delta_\mathrm{c}u^0$ is the standard massic energy of combustion. b) ΔU(IBP) includes ΔU(ign).

Table 4. Individual Values of $\Delta_c u^o$ of the Compounds at $T = 298.15$ K and $p^\circ = 0.1$ MPa

2-Bromoaniline	3-Bromoaniline	4-Bromoaniline	2,4-Dibromoaniline	2,5-Dibromoaniline	2,6-Dibromoaniline	2,4,6-Tribromoaniline
			$-\Delta_c u^o/\mathrm{J\,g^{-1}}$			
18726.90	18823.53	18757.54	12181.80	12198.68	12184.23	8852.59
18738.46	18818.42	18759.71	12177.94	12209.12	12200.39	8847.79
18724.32	18835.77	18741.64	12180.17	12205.63	12196.32	8850.31
18742.13	18839.44	18757.80	12190.50	12202.74	12192.12	8844.57
18738.01	18836.07	18749.61	12189.26	12216.84	12206.73	8846.57
18716.45	18830.04	18734.96	12189.14	12209.46	12201.51	8847.75
		18737.93		12218.07		
			$-\langle\Delta_c u^o\rangle/(\mathrm{J\,g^{-1}})$[a)]			
18731.0 ± 3.8	18830.5 ± 3.3	18748.5 ± 4.2	12184.8 ± 2.2	12208.6 ± 2.7	12196.9 ± 3.2	8848.3 ± 1.2

a) Mean value and standard deviation of the mean.

Table 5. Derived Standard ($p^\circ = 0.1$ MPa) Molar Values of Bromoanilines in the Condensed Phase at $T = 298.15$ K

Compound	$-\Delta_c U^o_m$(cr/l) /kJ mol^{-1}	$-\Delta_c H^o_m$(cr/l) /kJ mol^{-1}	$\Delta_f H^o_m$(cr/l) /kJ mol^{-1}
2-Bromoaniline (cr)	3222.2 ± 1.6	3224.0 ± 1.6	27.5 ± 1.8
3-Bromoaniline (l)	3239.3 ± 1.5	3241.1 ± 1.5	44.6 ± 1.7
4-Bromoaniline (cr)	3225.2 ± 1.8	3227.0 ± 1.8	30.5 ± 1.9
2,4-Dibromoaniline (cr)	3057.4 ± 1.5	3058.0 ± 1.5	26.4 ± 1.7
2,5-Dibromoaniline (cr)	3063.4 ± 1.7	3064.0 ± 1.7	32.3 ± 1.8
2,6-Dibromoaniline (cr)	3060.4 ± 1.9	3061.0 ± 1.9	29.4 ± 2.0
2,4,6-Tribromoaniline (cr)	2918.3 ± 1.1	2917.7 ± 1.1	50.9 ± 1.3

Table 6. $\Delta^{g}_{cr,l}H^o_m$ ($p^\circ = 0.1$ MPa) for the Seven Bromoanilines, at $T = 298.15$ K, Determined by Calvet Microcalorimetry

Compound	Number of experiments	T /K	$\Delta^{g,T}_{cr,l}H^o_m$ /kJ mol^{-1}	$\Delta^{T}_{298.15\,\mathrm{K}}H^o_m$(g) /kJ mol^{-1}	$\Delta^{g}_{cr,l}H^o_m$(298.15 K) /kJ mol^{-1}
2-Bromoaniline (cr)	6	324.2	79.3 ± 0.2	4.3	75.0 ± 1.4
3-Bromoaniline (l)	6	344.8	71.0 ± 0.2	7.6	63.4 ± 1.5
4-Bromoaniline (cr)	5	334.3	85.3 ± 0.4	5.9	79.4 ± 1.7
2,4-Dibromoaniline (cr)	6	355.0	98.3 ± 0.2	10.3	88.0 ± 1.5
2,5-Dibromoaniline (cr)	6	344.7	94.2 ± 0.3	8.5	85.7 ± 1.9
2,6-Dibromoaniline (cr)	6	355.0	91.0 ± 0.2	10.3	80.7 ± 1.4
2,4,6-Tribromoaniline (cr)	5	391.1	113.6 ± 0.1	16.9	96.7 ± 1.7

correction for the heat exchange, work of stirring and the frictional work of bomb rotation.

The results of all the combustion experiments for each compound together with the mean value, $\langle\Delta_c u^o\rangle$ and its standard deviation are given in Table 4. The values of $\Delta_c u^o$ are related to the idealized combustion reaction of mono-, di-, and tribromoaniline, yielding $\mathrm{HBr{\cdot}600H_2O(l)}$ as the only bromine-containing product in the final state, as described by Eq. 2:

$$\begin{aligned}&\mathrm{C_aH_bN_cBr_d(cr,l)}\\&\quad+ [(4a + b - d)/4]\mathrm{O_2(g)} + [(1200d - b + d)/2]\mathrm{H_2O(l)}\\&\quad\rightarrow a\mathrm{CO_2(g)} + (c/2)\mathrm{N_2(g)} + d\mathrm{HBr{\cdot}600H_2O(l)}.\end{aligned} \tag{2}$$

Table 5 lists the derived standard molar energies of combustion, $\Delta_c U^o_m$(cr,l), and enthalpies of combustion, $\Delta_c H^o_m$(cr,l), as well as the $\Delta_f H^o_m$(cr,l) for the seven studied bromoanilines in the condensed phase at $T = 298.15$ K. All of the uncertainties assigned to the standard molar enthalpies of combustion, in accordance with normal thermochemical practice,[41,42] are twice the overall standard deviation of the mean and include the uncertainties in calibration and those from the auxiliary quantities used. The values of $\Delta_f H^o_m$(cr,l) were derived from $\Delta_c H^o_m$(cr,l), using the values of the $\Delta_f H^o_m$ of $\mathrm{CO_2(g)}$, $\mathrm{H_2O(l)}$, and $\mathrm{HBr{\cdot}600H_2O(l)}$, at $T = 298.15$ K, which are -393.51 ± 0.13 kJ mol^{-1},[43] -285.830 ± 0.042 kJ mol^{-1},[43] and -120.294 ± 0.005 kJ mol^{-1}, respectively.[21,43]

The values of $\Delta^{g}_{cr}H^o_m$ or $\Delta^{g}_{l}H^o_m$ of the bromoanilines obtained by Calvet microcalorimetry, and the respective uncertainties, which are twice the standard deviation from the mean and include the uncertainties in calibration, are given in Table 6.

$\Delta_f H^o_m$(cr,l), together with $\Delta^{g}_{cr}H^o_m$ or $\Delta^{g}_{l}H^o_m$ yield the standard molar enthalpies of formation in the gaseous phase, $\Delta_f H^o_m$(g), of the seven bromoanilines, being all values summarized in Table 7.

Table 7. $\Delta_f H_m^o$ ($p^o = 0.1\,\text{MPa}$) in Both Condensed and Gaseous Phase, and $\Delta_{cr,l}^{g} H_m^o$ at $T = 298.15\,\text{K}$

Compound	$\Delta_f H_m^o$(cr,l) /kJ mol^{-1}	$\Delta_{cr,l}^{g} H_m^o$(298.15 K) /kJ mol^{-1}	$\Delta_f H_m^o$(g) /kJ mol^{-1}
2-Bromoaniline (cr)	27.5 ± 1.8	75.0 ± 1.4	102.5 ± 2.3
3-Bromoaniline (l)	44.6 ± 1.7	63.4 ± 1.5	108.0 ± 2.3
4-Bromoaniline (cr)	30.5 ± 1.9	79.4 ± 1.7	109.9 ± 2.5
2,4-Dibromoaniline (cr)	26.4 ± 1.7	88.0 ± 1.5	114.4 ± 2.3
2,5-Dibromoaniline (cr)	32.3 ± 1.8	85.7 ± 1.9	118.0 ± 2.6
2,6-Dibromoaniline (cr)	29.4 ± 2.0	80.7 ± 1.4	110.1 ± 2.4
2,4,6-Tribromoaniline (cr)	50.9 ± 1.3	96.7 ± 1.7	147.6 ± 2.1

Table 8. Experimental and Estimated (Cox Scheme and DFT Calculations) $\Delta_f H_m^o$(g) of the Bromoanilines

Compound	$\Delta_f H_m^o$(g)/kJ mol^{-1}			$\Delta^{a)}$/kJ mol^{-1}	
	Experimental	Cox scheme	DFT	Cox scheme	DFT
2-Bromoaniline	102.5 ± 2.3	113.9 ± 4.3	101.9	+11.4 ± 4.9	−0.6
3-Bromoaniline	108.0 ± 2.3	109.9 ± 4.3	104.8	+1.9 ± 4.9	−3.2
4-Bromoaniline	109.9 ± 2.5	109.9 ± 4.3	108.1	0.0 ± 5.0	−1.8
2,3-Dibromoaniline	—	144.7 ± 6.0	124.5	—	—
2,4-Dibromoaniline	114.4 ± 2.3	136.7 ± 6.0	120.7	+22.1 ± 6.4	+6.3
2,5-Dibromoaniline	118.0 ± 2.6	136.7 ± 6.0	119.7	+18.5 ± 6.5	+1.7
2,6-Dibromoaniline	110.1 ± 2.4	144.7 ± 6.0	116.3	+34.4 ± 6.5	+6.2
3,4-Dibromoaniline	—	136.7 ± 6.0	130.7	—	—
3,5-Dibromoaniline	—	132.7 ± 6.0	121.2	—	—
2,4,6-Tribromoaniline	147.6 ± 2.1	167.5 ± 7.3	134.4	+19.6 ± 7.6	−13.2

a) Difference between the estimated and the experimental estimated values.

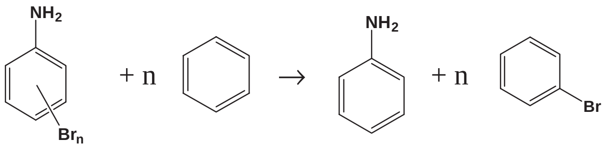
Enthalpies Estimated with the Cox Scheme. The values of $\Delta_f H_m^o$(g) are compared (Table 8) with values estimated using the Cox scheme[7] by assuming that the enthalpy increment for substitution of bromine in the different positions of aniline will be the same as for substitution of bromine in benzene with a correction term of 4 kJ mol^{-1} that was applied for the *ortho*-pair of substituents and another additional correction of 4 kJ mol^{-1} for every set of three substituents in three consecutive carbon atoms of the aromatic ring.

To obtain the estimated values, $\Delta_f H_m^o$(g) of benzene 82.6 ± 0.7 kJ mol^{-1},[44] bromobenzene 105.4 ± 4.1 kJ mol^{-1}, and aniline 87.1 ± 1.1 kJ mol^{-1}, at $T = 298.15\,\text{K}$, were used. Thus, based on the Cox scheme, the characteristic increment in $\Delta_f H_m^o$(g) calculated for the introduction of a bromine atom in a benzene ring is 22.8 ± 4.1 kJ mol^{-1}, and the $\Delta_f H_m^o$(g) for the different isomers of bromoaniline can be estimated.

The values of $\Delta_f H_m^o$(g) estimated by the Cox scheme are in excellent agreement with the experimental ones only in the case of 3-bromoaniline and 4-bromoaniline, this is for the bromine mono substitution in the positions *meta* and *para* with respect to the NH_2 group. However, large deviations are found when the substituent is at an *ortho* position, which is the cases of 2-bromoaniline, the 2,4-, 2,5-, 2,6-dibromoanilines, and the 2,4,6-tribromoaniline, for which experimental results are available. For these compounds, experimental results are lower than the estimated ones by the Cox scheme, suggesting an unexpected stabilization of these compounds. This is a result of the interaction between the bromine atoms in the *ortho* positions and the amino group, i.e. intramolecular hydrogen bonding may occur. To check the consistency of this hypothesis and the quality of the experimental results, density-functional theory based calculations were carried out to estimate the gas-phase standard enthalpies of formation of all the bromoaniline compounds.

Computed Enthalpies of Formation. The BP86/6-31+G* optimized geometric parameters for the different bromoanilines are identical to those computed for unsubstituted aniline when the bromine atoms are at *meta* and/or *para* positions, with the obvious exception of the C–Br bond length. Similar findings were obtained from calculations performed at the B3LYP/6-31+G* level of theory. Results from this hybrid DFT approach are not given since they are identical to those computed by the BP86/6-31+G* method. When bromine is at the *ortho* position the differences are easily identified by an increase in the planarity of the amino group (from 131.7° in aniline to 136.2° in 2-bromoaniline or 141.6° in 2,6-dibromoaniline), accompanied by a slight decrease in the C–N bond length and a slight increase in the N–H bond length. In addition, the H–N–H angle increases by 2 or 4.3° for 2-bromoaniline or 2,6-dibromoaniline, respectively. The calculated differences for the compounds with bromine atom(s) attached to the ring at the *ortho* positions mean that there is some interaction between the halogen atoms and the amino group's hydrogen atoms. The formation of halogen–hydrogen bonds has been previously reported for 2-chloroaniline based on results from microwave and infrared experiments.[45,46] The presence of halogen–hydrogen bonds in 2-chloro and 2-bromoanilines was determined by the use of a topological analysis using wave functions resulting from B3LYP/6-31G(d) calculations, I enable direct comparison with previous results for compounds containing weak hydrogen bonds[47,48] available in the literature, that were computed using the same theoretical approach. A critical point appears in the region between the halogen and the amino group's hydrogen atom with the following parameters: in 2-chloroaniline, electron density (ρ) = 0.013, laplacian of the electron density ($\nabla^2\rho$) = 0.059, electron localization function, (η) = 0.030 and Core Valence Bifurcation Index (CVB) = 0.042; in 2-bromoaniline, $\rho = 0.014$, $\nabla^2\rho = 0.067$, $\eta = 0.026$, and CVB = 0.112. The comparison of the CVB indices with those reported by Silvi et al. for a series of complexes bonded by an intermolecular hydrogen bond suggests that the energy of the internal hydrogen bond in 2-chloroaniline is 10–15 kJ mol^{-1} while for 2-bromoaniline the N–H···Br bond strength is less than one half of the energy of the N–H···Cl bond in 2-chloroaniline.

The energies of all bromoanilines, and those of aniline, benzene, and bromobenzene, which were all corrected for $T = 298.15$ K, were used to compute the energy of the reaction described by the following equation:



(3)

Combining those enthalpies of reaction with the experimental $\Delta_\mathrm{f}H^\mathrm{o}_\mathrm{m}$(g) of benzene, aniline, and bromobenzene given above, it was possible to estimate the $\Delta_\mathrm{f}H^\mathrm{o}_\mathrm{m}$(g) of the bromoanilines. The DFT estimated values for all monobromoanilines, all dibromoanilines, and the 2,4,6-tribromoaniline are summarized in Table 8. The deviations from the experimental values are now much smaller when compared with those from the Cox scheme, suggesting that a reparametrization of values from the Cox scheme is needed. The BP86/6-31+G* values computed for the monobromoanilines agree with experimental values, and the deviations increase with an increase in the number of attached bromine atoms. These errors would be less if dibromobenzene or tribromobenzenes were used in Eq. 3 instead of multiplying $\Delta_\mathrm{f}H^\mathrm{o}_\mathrm{m}$ of bromobenzene by 2 or 3, respectively. However, this is not possible because of experimental $\Delta_\mathrm{f}H^\mathrm{o}_\mathrm{m}$ values for the dibromobenzenes and tribromobenzenes have not been published in the literature. Although an excellent agreement between theoretical and experimental results was obtained for the entire series of dichlorophenols, based on BP86 calculations and on the experimental enthalpies of formation of aniline, benzene and of 1,2-, 1,3-, and 1,4-dichlorobenzenes,[33] the DFT results for the dibromoanilines given in Table 8 must be used with caution. An uncertainty of ±6 kJ mol^{-1} is proposed. Nevertheless, it should be pointed out here that similar uncertainties are associated with the results from computations using composite methods, such as the different Gaussian-N approaches. The full set of results for the tribromoanilines are: $\Delta_\mathrm{f}H^\mathrm{o}_\mathrm{m}$(2,3,4-tribromoaniline) = 150.0 kJ mol^{-1}; $\Delta_\mathrm{f}H^\mathrm{o}_\mathrm{m}$(2,3,5-tribromoaniline) = 140.8 kJ mol^{-1}; $\Delta_\mathrm{f}H^\mathrm{o}_\mathrm{m}$(2,3,6-tribromoaniline) = 140.5 kJ mol^{-1}; $\Delta_\mathrm{f}H^\mathrm{o}_\mathrm{m}$(2,4,5-tribromoaniline) = 143.6 kJ mol^{-1}; $\Delta_\mathrm{f}H^\mathrm{o}_\mathrm{m}$(2,4,6-tribromoaniline) = 134.4 kJ mol^{-1}; $\Delta_\mathrm{f}H^\mathrm{o}_\mathrm{m}$(3,4,5-tribromoaniline) = 153.4 kJ mol^{-1}. Since only a single experimental result is available for the tribromoanilines and the deviation between the DFT and the experimental $\Delta_\mathrm{f}H^\mathrm{o}_\mathrm{m}$ is ≈13 kJ mol^{-1} the BP86 numbers may be used only to extract the order of stability. 2,4,6-Tribromoaniline is the most stable while the least stable is the 3,4,5-isomer. This is easily explained by the fact that bromines are not adjacently placed in 2,4,6-tribromoaniline, which prevents Br···Br destabilizing interactions and also that two stabilizing N–H···Br bonds are possible in this isomer, as explained above. In the least stable isomer N–H···Br bonds are not possible and all bromine atoms are placed in three adjacent positions, i.e., in the case of the 3,4,5-tribromoaniline species.

The mono and dibromoanilines follow a similar trend in stability. In the case of the mono derivatives, the most stable compound is 2-bromoaniline while the 3- and 4-isomers are less stable. Interestingly, experimental $\Delta_\mathrm{f}H^\mathrm{o}_\mathrm{m}$ suggest that 3-bromoaniline and 4-bromoaniline are almost degenerate while the DFT calculations put the 3-bromoaniline in the middle of the other two isomers. Turning our attention to the dibromoanilines, 2,6-dibromoaniline is the most stable and the 3,4-isomer is the least stable, giving further support to the discussion above concerning the tribromoanilines.

Conclusion

Rotating-bomb calorimetry and Calvet microcalorimetry experiments have been performed to obtain the $\Delta_\mathrm{c}H^\mathrm{o}$ in the condensed phase and the enthalpies of phase-transition to the gaseous state of the three monobromoanilines, of three of the six dibromoanilines and of one of the six tribromoanilines. The derived $\Delta_\mathrm{f}H^\mathrm{o}_\mathrm{m}$(g) have been compared with DFT estimated values and those obtained by application of the Cox scheme. It was found that the Cox scheme yields excellent estimates for the 3- and the 4-bromoaniline but fails completely in the case of the *ortho* isomer since it does not include the stabilizing effects of the internal N–H···Br bond. Confirmation of the presence of N–H···Br bonds has been accomplished by the use of topological approaches. It is proposed that their strength is about one-half of the energy of internal N–H···Cl bonds. Since the compounds with two or three bromine atoms studied experimentally have at least one Br atom in *ortho* position, it is not surprising that estimates for these compounds are also poor. The use of DFT calculations together with a working reaction employing aniline, benzene, and bromobenzene yields excellent estimates for the monobromoanilines, good estimates for the dibromoanilines and a fair estimate for the 2,4,6-tribromoaniline. In other words for the theoretical prediction of the standard molar enthalpies of the other bromoanilines, accurate experimental $\Delta_\mathrm{f}H^\mathrm{o}_\mathrm{m}$(g) of the three tribromobenzenes, three tetrabromobenzenes, and of pentabromobenzene are needed, and therefore, future experimental work should focus on these compounds. These studies should be extended to the other halogenated benzenes as well.

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Supporting Information

Geometries of all bromoanilines in PDF format. This material is available free of charge on the Web at: http://www.csj.jp/journals/bcsj/.

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