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Vaporization and Sublimation Enthalpies of Acetanilide and Several Derivatives by Correlation Gas Chromatography

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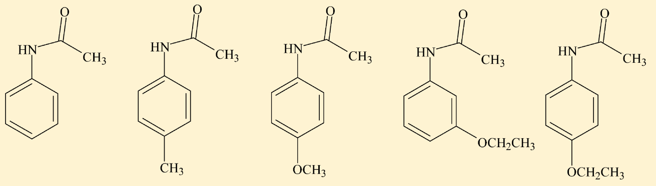
S *Supporting Information*



ABSTRACT: The vaporization and fusion enthalpies of acetanilide and several of its derivatives have been measured and combined to provide their corresponding sublimation enthalpies. Since all of the materials examined are solid at T = 298.15 K, the vaporization enthalpies measured by correlation gas chromatography at this temperature are for the subcooled liquid state. Fusion enthalpies have also been adjusted to T = 298.15 K. The compounds examined and their vaporization enthalpies measured at T = 298.15 K include the following values (in kJ·mol^{-1}): acetanilide (82.1 ± 3.0), 4-methylacetanilide (86.2 ± 3.2), 4-methoxyacetanilide (92.0 ± 3.4), 3-ethoxyacetanilide (94.1 ± 3.5), and 4-ethoxyacetanilide (94.8 ± 3.5). The following fusion enthalpies (kJ·mol^{-1}) and fusion temperatures (onset temperatures, K) were measured by differential scanning calorimetry (DSC): acetanilide (22.1 ± 0.1), (386.9 ± 0.1), 4-methylacetanilide (29.4 ± 0.2), (421.3 ± 0.3), 4-methoxyacetanilide (25.4 ± 0.3), (398.2 ± 1.2), 3-ethoxyacetanilide (28.9 ± 0.4), (368.0 ± 0.4), 4-ethoxyacetanilide (32.0 ± 0.1), (407 ± 0.1), and benzanilide (31.2 ± 0.7), (435 ± 0.3). Sublimation enthalpies calculated from vaporization and fusion enthalpies at T = 298.15 K compared favorably with available literature values.

■ INTRODUCTION

Acetanilide and some of its derivatives have found applications as analgesics and antipyretics.[1] The thermochemical properties of many of these materials have been the subject of numerous studies. This work complements existing measurements by reporting vaporization and fusion enthalpies of acetanilide and several of its derivatives at T = 298.15 K, allowing an evaluation of their sublimation enthalpies by completing thermochemical cycles as summarized by eq 1. The vaporization enthalpies were evaluated by correlation gas chromatography and the fusion enthalpies by differential scanning calorimetry (DSC). The compounds evaluated include acetanilide, 4-methylacetanilide, 4-methoxyacetanilide, 3-ethoxyacetanilide, and 4-ethoxyacetanilide (phenacetin). The structures of all the compounds included in this study are provided in Figure 1.

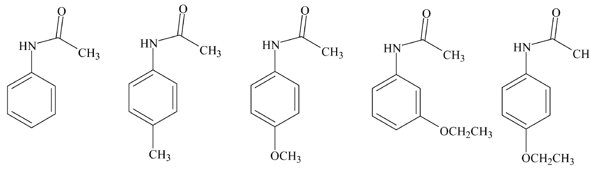


Figure 1. Structures of the compounds investigated.

$$\Delta H_{\mathrm{vap}}(298\ \mathrm{K}) = \Delta H_{\mathrm{sub}}(298\ \mathrm{K}) - \Delta H_{\mathrm{fus}}(298\ \mathrm{K}) \tag{1}$$

Table 1 lists the sublimation, vaporization, and fusion enthalpies currently available in the literature for both the compounds under investigation and those used as standards. Tables 2, 3, and 4 adjust these phase enthalpies to T = 298.15 K when necessary. Equations 2 to 4 were used for these adjustments.[7] The quantities $C_p(\mathrm{l})$ and $C_p(\mathrm{cr})$ in these equations refer to the heat capacity of the liquid and solid phases, respectively, at T = 298.15 K. Both were estimated by group additivity.[7]

$$\begin{aligned}\Delta H_{\mathrm{sub}}&(298\ \mathrm{K})/\mathrm{kJ\cdot mol^{-1}}\\ &= \Delta H_{\mathrm{sub}}(T_{\mathrm{m}})/\mathrm{kJ\cdot mol^{-1}} + [0.75 + 0.15C_p(\mathrm{cr})\\ &\quad /(\mathrm{J\cdot K^{-1}\cdot mol^{-1}})][T_{\mathrm{m}}/\mathrm{K} - 298.15]/1000\end{aligned} \tag{2}$$

$$\begin{aligned}\Delta H_{\mathrm{fus}}&(298\ \mathrm{K})/\mathrm{kJ\cdot mol^{-1}}\\ &= \Delta H_{\mathrm{fus}}(T_{\mathrm{m}})/\mathrm{kJ\cdot mol^{-1}} + [(0.15C_p(\mathrm{cr}) - 0.26C_p(\mathrm{l}))\\ &\quad /(\mathrm{J\cdot K^{-1}\cdot mol^{-1}}) - 9.93][T_{\mathrm{fus}}/\mathrm{K} - 298.15]/1000\end{aligned} \tag{3}$$

$$\begin{aligned}\Delta H_{\mathrm{vap}}&(298\ \mathrm{K})/\mathrm{kJ\cdot mol^{-1}}\\ &= \Delta H_{\mathrm{vap}}(T_{\mathrm{m}})/\mathrm{kJ\cdot mol^{-1}} + (10.58 + 0.26C_p(\mathrm{l})\\ &\quad /(\mathrm{J\cdot K^{-1}\cdot mol^{-1}}))(T_{\mathrm{m}}/\mathrm{K} - 298.15)/1000\end{aligned} \tag{4}$$

Appropriate fusion enthalpies measured in this work are also included when literature values were unavailable. Further details for these experiments are provided in the Experimental Section. For acetanilide, several literature values for the fusion enthalpy

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Table 1. Literature Values of Phase Change Properties of Various Amides

	$\Delta H_{\mathrm{sub}}(T_{\mathrm{m}})$	T_{m}	$\Delta H_{\mathrm{fus}}(T_{\mathrm{fus}})$	T_{fus}	$\Delta H_{\mathrm{vap}}(T_{\mathrm{m}})$	T_{m}	
compounds studied	kJ·mol^{-1}	K	kJ·mol^{-1}	K (onset)	kJ·mol^{-1}	K	ref
acetanilide	99.5 ± 0.8	319.7	21.2 ± 0.5	386.1			1
	86.8	326					2
			21.44	386.9			3
			21.65 ± 0.02	387.5			4
			18.3 ± 0.8	389.3	53.4 ± 3.0	493	5
4-methylacetanilide			28.9	424			6, 7
4-methoxyacetanilide			27.8	400.3			8
4-ethoxyacetanilide	120 ± 3	298	30 ± 1	409.6	79 ± 1	459	9
					82 ± 1	476	9
	119.7	352.7					1
	115.5	349.5					10
			31.3	407.2			8
			21.4 ± 0.9	410	60.1 ± 3	522	5
Standards Used							
N-methylpropionamide					66.6 ± 0.2	298	11
2-pyrrolidinone					63.8 ± 1.2[a]	422	12
2-piperidone					74.5	302	13
caprolactam					75.1 ± 0.5	298	14
benzanilide	125.4 ± 2.3	298					15

[a] Calculated from the reported vapor pressures in the Supporting Information over the temperature range T = (406.6 to 438.3) K.

Table 2. Temperature Adjusted Sublimation and Fusion Enthalpies

	$\Delta H_{\mathrm{sub}}(T_{\mathrm{m}})$	T_{m}	$\Delta H_{\mathrm{fus}}(T_{\mathrm{m}})$	T_{fus}	$C_p(\mathrm{l})/C_p(\mathrm{cr})$	ΔH(298 K)/kJ·mol^{-1}	
compounds studied	kJ·mol^{-1}	K	kJ·mol^{-1}	K	J·mol^{-1}·K^{-1}	ΔH_{sub}	ΔH_{fus}
acetanilide	99.5 ± 0.8	319.7	21.2 ± 0.5	386.1	239.1/177	100.0 ± 1.0	12.4 ± 1.2
	86.8	326			239.1/177	87.6 ± 0.2	
			21.4	386.9	239.1/177		17.4 ± 1.2
			21.65 ± 0.02	387.5	239.1/177		17.6 ± 1.2
			18.3 ± 0.8	389.3	239.1/177		14.2 ± 1.5
			22.1 ± 0.1[a]	386.9	239.1/177		18.1 ± 1.2
						value used	17.6 ± 1.2
4-methylacetanilide			28.9	424	267.5/204.6		22.8 ± 1.8
			29.4 ± 0.2[a]	421	267.5/204.6		23.5 ± 1.8
						average	23.2 ± 1.8
4-methoxyacetanilide			27.8	400.3	297.3/254.4		22.8 ± 1.5
			25.4 ± 0.3[a]	398.2	297.3/254.4		20.5 ± 1.5
						average	21.7 ± 1.5
3-ethoxyacetanilide			28.9 ± 0.4[a]	368	329.2/281.3		25.1 ± 1.2
4-ethoxyacetanilide	120 ± 3	298	30	409.6	329.2/281.3	120 ± 3	24.1 ± 1.8
	119.7 ± 0.7	352.7			329.2/281.3	121.7 ± 0.9	
	115.5 ± 2.7	349.5			329.2/281.3	117.4 ± 2.8	
			21.4 ± 0.9	410.2	329.2/281.3		15.4 ± 2.0
			32.0 ± 0.1[a]	407.0	329.2/281.3		26.2 ± 1.8
						average	25.2 ± 1.8
Standards Used							
benzanilide	125.4 ± 2.3	298			328.5/236.4	125.4 ± 2.3	
			31.2 ± 0.7[a]	435	328.5/236.4		24.2 ± 2.6

[a] This work, see Table 4.

are available. In this case, the value measured by adiabatic calorimetry was used for evaluating the vaporization enthalpy of this compound.[4] Adiabatic calorimetric results are generally more accurate than those obtained by DSC. One of the fusion enthalpy values reported in the literature for both acetanilide and 4-ethoxyacetanilide differs significantly from the rest,[5] suggesting the possibility of polymorphism. To remove this ambiguity for the samples investigated in this work, the fusion enthalpies of both were also determined.

■ EXPERIMENTAL SECTION

Materials and Methods. All compounds used in this study were commercial samples. Additional details are summarized in Table 5. No analysis was available from the supplier for the samples of acetanilide and 4-methylacetanilide used. These were analyzed by gas chromatography and both found to be 99+ %.

Correlation gas chromatography experiments were performed on an HP 5890 gas chromatograph, equipped with a flame

Table 3. Temperature Adjusted Vaporization Enthalpies

	ΔH(298 K)/kJ·mol^{-1}		$\Delta H_{vap}(T_m)$	T_m	C_p(l)	ΔH_{vap}(298 K)
compounds studied	ΔH_{sub}	ΔH_{fus}	kJ·mol^{-1}	K	J·mol^{-1}·K^{-1}	kJ·mol^{-1}
acetanilide	100.0 ± 1.0	17.6 ± 1.2[a]				82.4 ± 1.6
	87.6 ± 0.2	17.6 ± 1.2[a]				70.0 ± 1.2
4-ethoxyacetanilide	120 ± 3	25.1 ± 1.8[b]				94.9 ± 3.5
			79 ± 1	459	329.2	94.5 ± 2.8
	121.7 ± 0.9	25.1 ± 1.8[b]			329.2	96.6 ± 2.0
	117.4 ± 2.8	25.1 ± 1.8[b]			329.2	92.3 ± 3.3
Standards Used						
N-methylpropionamide						66.6 ± 0.2
2-pyrrolidinone			63.8 ± 1.2	422	169.7	70.7 ± 2.3
2-piperidone			74.5	302	195.6	74.8 ± 0.1
caprolactam						75.1 ± 0.5
benzanilide	125.4 ± 2.3	24.2 ± 2.6				101.2 ± 3.5

[a] Value measured by adiabatic calorimetry (ref 4). [b] Average of (24.1 + 26.2) kJ·mol^{-1} from Table 2.

Table 4. Fusion Enthalpies of Some of the Amides Studied in This Work

		$\Delta H_{fus}(T_m)$	T_{fus}	$\Delta H_{fus}(T_{fus})_{avg}$	T_{fus}
	mg	kJ·mol^{-1}	K (onset)	kJ·mol^{-1}	K$_{avg}$ (onset)
acetanilide	8.66	22.0	386.8	22.1 ± 0.1	386.9 ± 0.1
	8.19	22.2	387.0		
	8.22	22.1	386.8		
4-methylacetanilide	8.82	29.4	421.3	29.4 ± 0.2	421.3 ± 0.3
	8.57	29.3	421.5		
	8.73	29.6	421.0		
4-methoxyacetanilide	6.55	25.7	399.4	25.4 ± 0.3	398.2 ± 1.2
	7.17	25.4	398.1		
	7.78	25.2	397.1		
3-ethoxyacetanilide	4.03	29.0	368.1	28.9 ± 0.4	368.0 ± 0.4
	4.14	29.2	368.4		
	4.26	28.4	367.6		
4-ethoxyacetanilide	6.14	32.0	406.9	32.0 ± 0.1	407 ± 0.1
	5.83	32.1	407		
	6.84	31.9	407.2		
benzanilide	9.63	30.9	434.9	31.2 ± 0.7	435 ± 0.3
	9.66	30.7	434.7		
	9.55	32.0	435.3		

Table 5. Suppliers of the Amides Studied

	supplier	purity
N-methylpropionamide	Sigma-Aldrich	98 %
2-pyrrolidinone	Sigma-Aldrich	99 %
2-piperidone	Sigma-Aldrich	99 %
caprolactam	Sigma-Aldrich	99 %
acetanilide	Eastman	white label
4-methylacetanilide	Eastman	white label
4-methoxyacetanilide	Alfa Aesar	98+ %
3-ethoxyacetanilide	Alfa Aesar	99+ %
4-ethoxyacetanilide	Alfa Aesar	97 %
benzanilide	Sigma-Aldrich	98 %

ionization detector and run at a split ratio of approximately 100:1. Retention times were recorded on an HP Chemstation. Retention times measured for the compounds in this study are available as Supporting Information. The compounds were run isothermally as a mixture on a 0.25 mm, 30 m DB5MS column at 10 psi using helium as the carrier gas. Loading on the column was kept to a minimum by injecting 1 μL of a dilute solution of the analytes in methanol. At the temperatures of these experiments, the retention time of methanol also functioned as the nonretained reference. Adjusted retention times, t_a, were calculated by subtracting the measured retention time of the nonretained reference from the retention time of each analyte as a function of temperature, at T = 5 K intervals over a T = 30 K range. Column temperatures were controlled by the gas chromatograph and were monitored independently by using a Fluke 50S K/J digital thermometer. The temperature maintained by the gas chromatograph was constant to ± 0.1 K. Enthalpies of transfer were calculated as the product of the slope of the line obtained by plotting $\ln(t_o/t_a)$ vs $1/T$ and the gas constant, R. All plots of $\ln(t_o/t_a)$ vs $1/T$, where t_o = 1 min, were characterized by correlation coefficients, r^2, > 0.99. The uncertainties (± σ) reported in the last column of the correlation tables below were calculated from the uncertainty in the slope and intercept of the equations listed at the bottom of each respective run. These uncertainties reflect the potential error in the absolute value of the vaporization enthalpy and are a measure of the precision of the measurements. Although the results are highly reproducible, the absolute error is also dependent on the quality of the data used as reference and the choice of appropriate standards. Generally, standards containing the same

Table 6. Evaluation of the Vaporization Enthalpies of Various Acetanilide Derivatives

	slope		ΔH_{trn}(459 K)	ΔH_{vap}(298 K)	ΔH_{vap}(298 K)
run 1	T/K	intercept	kJ·mol^{-1}	kJ·mol^{-1} (lit)	kJ·mol^{-1} (calc)
N-methylpropionamide	−3753.4	9.647	31.2	66.6 ± 0.2	65.8 ± 2.3
2-pyrrolidinone	−4289.1	9.929	35.66	70.7 ± 2.3	70.7 ± 2.4
2-piperidone	−4690.3	10.265	38.99	74.8 ± 0.1	74.4 ± 2.5
caprolactam	−4939.1	10.463	41.06	75.1 ± 0.5	76.6 ± 2.5
acetanilide	−5552.4	11.4	46.16		82.2 ± 2.7
4-methylacetanilide	−5987.7	11.912	49.78		86.2 ± 2.8
4-methoxyacetanilide	−6610.2	12.654	54.95		91.9 ± 3.0
3-ethoxyacetanilide	−6867.8	13.054	57.1		94.2 ± 3.0
4-ethoxyacetanilide	−6944.1	13.127	57.73		94.9 ± 3.1
benzanilide	−7596.5	13.514	63.15	101.2 ± 3.5	100.9 ± 3.2

$$\Delta H_{vap}(298.15\,\text{K})/\text{kJ}\cdot\text{mol}^{-1} = (1.10 \pm 0.04)\Delta H_{trn}(459\,\text{K}) + (31.6 \pm 1.8)$$
$$r^2 = 0.9955 \qquad (5)$$

	slope		ΔH_{trn}(459 K)	ΔH_{vap}(298 K)	ΔH_{vap}(298 K)
run 2	T/K	intercept	kJ·mol^{-1}	kJ·mol^{-1} (lit)	kJ·mol^{-1} (calc)
N-methylpropionamide	−3792.4	9.725	31.53	66.6 ± 0.2	65.3 ± 2.9
2-pyrrolidinone	−4413.8	10.198	36.69	70.7 ± 2.3	70.9 ± 3.0
2-piperidone	−4835.9	10.581	40.2	74.8 ± 0.1	74.7 ± 3.2
caprolactam	−5077.2	10.762	42.21	75.1 ± 0.5	76.9 ± 3.2
acetanilide	−5665.9	11.643	47.1		82.0 ± 3.4
4-methylacetanilide	−6106.9	12.168	50.77		86.2 ± 3.6
4-methoxyacetanilide	−6770	13.001	56.28		92.1 ± 3.8
3-ethoxyacetanilide	−6970.8	13.273	57.95		93.9 ± 3.9
4-ethoxyacetanilide	−7053.6	13.361	58.64		94.7 ± 3.9
benzanilide	−7714.2	13.766	64.13	101.2 ± 3.5	100.6 ± 4.1

$$\Delta H_{vap}(298.15\,\text{K})/\text{kJ}\cdot\text{mol}^{-1} = (1.08 \pm 0.05)\Delta H_{trn}(459\,\text{K}) + (31.1 \pm 2.3)$$
$$r^2 = 0.9929 \qquad (6)$$

functional groups as the materials under investigation provide the best correlations. Certain substitutions have also been found to provide reliable results. Substitution of an oxygen for carbon as found in 3- and 4-ethoxyacetanilide has previously been shown to be acceptable.[16,17]

The uncertainties associated with the temperature adjustments are as follows. A potential uncertainty equal to 30 % of the correction is usually associated with the use of eqs 2 and 3. While this value has been chosen arbitrarily, the combination of eqs 2 and 3 have been shown to generally fit experimental sublimation enthalpies within an uncertainty of approximately ± 4 kJ·mol^{-1}.[7] The uncertainty associated with eq 6, described below, has an uncertainty of ± 16 J·mol^{-1} assigned to the temperature-independent term of the equation.[7] Equations 2, 3, and 6 have proven reliable up to approximately 500 K, although the uncertainties associated with temperature adjustments near the upper limit are probably larger.

Fusion Enthalpies. Fusion enthalpies were measured on a Perkin-Elmer DSC 7 instrument using the Pyris Series Thermal Analysis software. The experiments were conducted under an atmosphere of nitrogen at a flow rate of 20 mL·min^{-1} at a ramp rate of 5 °C·min^{-1} from T = (298 K to T_{fus}) in hermetically sealed aluminum pans. The instrument was calibrated using indium metal, 99.999 %, as a standard. The results are summarized in Table 4. Fusion temperatures are reported as onset temperatures. No mass loss was observed following fusion. The fusion enthalpies of acetanilide and 4-ethoxyacetanilide were measured to confirm the identity of material used in the event the samples exhibit polymorphism. It should be pointed out that although 4-ethoxyacetanilide was the least pure material studied, 97 %, the purity of this material did not seem to seriously affect its fusion enthalpy relative to literature values. The results obtained suggest that the samples investigated were crystallographically identical to those previously reported by the majority of studies.

RESULTS

The results of duplicate correlation gas chromatography runs are reported in Table 6 and in Figure 2. Experimental retention

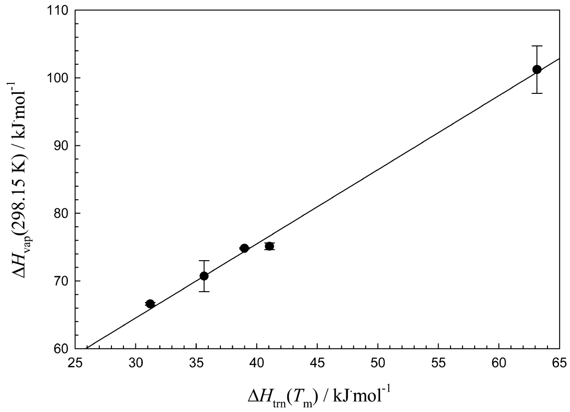

Figure 2. Plot of vaporization enthalpy of the standards at T = 298.15 K versus the enthalpies of transfer measured at T = 459 K for the results reported in Table 6, run 1.

Table 7. Sublimation Enthalpies of Acetanilide and Several Derivatives

	ΔH_{vap}(298 K)/kJ·mol^{-1}		ΔH_{fus}(298 K)	ΔH_{sub}(298 K)^{a}/kJ·mol^{-1}		
	runs 1, 2	average^{a}	kJ·mol^{-1}	this work	lit.	ref
acetanilide	82.2 ± 2.7	82.1 ± 3.0	17.6 ± 1.2	99.7 ± 3.3	100.0 ± 1.0	1
	82.0 ± 3.4				87.6 ± 0.2	2
4-methylacetanilide	86.2 ± 2.8	86.2 ± 3.2	23.2 ± 1.8	109.4 ± 3.5		
	86.2 ± 3.6					
4-methoxyacetanilide	91.9 ± 3.0	92.0 ± 3.4	21.7 ± 1.5	113.7 ± 3.7		
	92.1 ± 3.8					
3-ethoxyacetanilide	94.2 ± 3.0	94.1 ± 3.5	25.1 ± 1.2	119 ± 3.7		
	93.9 ± 3.9					
4-ethoxyacetanilide	94.9 ± 3.1	94.8 ± 3.5	25.2 ± 1.8	120.0 ± 3.9	120.0 ± 3.0	9
	94.7 ± 3.9				121.7 ± 0.9	1
					117.4 ± 2.8	10

[a] An average vaporization enthalpy and uncertainty was used in the calculation of sublimation enthalpy.

Table 8. Comparison of Estimated and Experimental Fusion and Vaporization Enthalpies

	$\Delta S_{tpce}(T_{fus})$		ΔH_{fus}(298 K)		ΔH_{vap}(298 K)	
	J·K·mol^{-1}	T_{fus}	kJ·mol^{-1}		kJ·mol^{-1}	
	est^{a}	K	est	exp	est^{b}	exp
N-methylpropionamide					64.3	66.6 ± 0.2
2-pyrrolidinone					68.0	70.7 ± 2.3
2-piperidone					73.6	74.8 ± 0.1
caprolactam					78.3	75.1 ± 0.5
N-methylbenzamide^{c}	48.6	352	17.1	19.6 ± 0.2	83.0	84.9 ± 0.5
acetanilide	48.6	386.9	18.8	22.1 ± 0.1	83.0	82.1 ± 3.2
4-methylacetanilide	49.2	421.3	20.7	29.4 ± 0.2	87.7	86.2 ± 3.2
4-methoxyacetanilide	56.0	398.2	22.3	25.4 ± 0.3	92.7/103.9	92.0 ± 3.4
3-ethoxyacetanilide	63.1	368	23.2	28.9 ± 0.4	97.4/107.2	94.1 ± 3.5
4-ethoxyacetanilide	63.1	407	25.7	32.0 ± 0.1	97.4/107.2	94.8 ± 3.5
benzanilide	60.5	435	26.3	31.2 ± 0.7	106.5	100.6 ± 4.1

[a] Group values used for the estimation of total phase change entropy: primary sp^3 carbon (CH_3−), 17.6; secondary sp^3 carbon (−CH_2−), 7.1; tertiary benzenoid carbon (=CH−), 7.4; quaternary benzenoid carbon (=C−R adjacent to an sp^2 carbon or heteroatom with lone pairs, −7.5; quaternary benzenoid carbon (=C−R adjacent to an sp^2 carbon, −9.6; ether (−O−), 4.71; secondary amide (−CONH−), 1.5 J·K·mol^{-1} (ref 20). [b] The group value for a secondary amide, b_i: 42.5 kJ·mol^{-1}; b_i ether: 5.0 kJ·mol^{-1}; F_i (ether) in 4-methoxyacetanilide: (1.62 + 0.85)/2; F_i (ether) in both ethoxyacetanilides: (1.08 + 0.85)/2; F_i (−CONH−) value for all alkoxyacetanilides: (1.62 + 0.85)/2; ref 21. [c] Reference 18.

Table 9. Comparison of Estimated and Experimental Sublimation Enthalpies

	ΔH_{fus}	ΔH_{vap}(298 K)	ΔH_{sub}(298 K)^{a}	
	kJ·mol^{-1}	kJ·mol^{-1}	kJ·mol^{-1}	
	est	est	est	exp
N-methylbenzamide^{b}	17.1	83.0	101.1	101.0 ± 0.2
acetanilide	18.8	83.0	101.8	100.0 ± 1.0
4-methylacetanilide	20.7	87.7	108.4	109.4 ± 3.5
4-methoxyacetanilide	22.3	92.7/103.9	115.0/126.2	113.7 ± 3.7
3-ethoxyacetanilide	23.2	97.4/107.2	120.6/130.4	119 ± 3.7
4-ethoxyacetanilide	25.7	97.4/107.2	123.1/132.9	120.0 ± 3.0
				121.7 ± 0.9
benzanilide	26.3	106.5	132	125.4 ± 2.3

[a] $\Delta H_{sub}(298\ \mathrm{K}) = \Delta H_{fus} + \Delta H_{vap}(298\ \mathrm{K})$. [b] Reference 21.

times are available as Supporting Information. Uncertainties indicated in Figure 2 are a combination of the literature value and that associated with the temperature adjustment. Equations 5 and 6 below each run characterize the quality of each correlation. The correlation coefficient (r^2) of both runs exceeds 0.99. It should be pointed out that acetanilide and all of its derivatives are solids at T = 298.15 K. The vaporization enthalpies reported in Table 6 and in Figure 2, therefore, are for the subcooled liquid and therefore should be considered as hypothetical thermodynamic properties. Despite this fact, it is possible to evaluate their quality by combining them with experimental fusion enthalpies evaluated at T = 298.15 K and comparing their sum to experimental sublimation enthalpies measured directly. This is possible for two of the compounds examined, acetanilide and 4-ethoxyacetanilide. The comparisons are reported in column 5 of Table 7 along with the sublimation enthalpies for the other compounds examined. The comparisons for acetanilide and 4-ethoxyacetanilide are within the experimental uncertainties in all but one case. The earlier work reported by Aihara[2] for acetanilide is the only outlier. Sublimation enthalpies for the remaining acetanilide derivatives in Table 7 are not currently available.

Estimations. Estimation methods provide an approximate value that can be useful in several ways. Depending on the property, they can provide guidance in selecting experimental conditions such as an appropriate range of temperature for study. Additionally, they can be helpful in identifying outliers or questionable results, and they can provide an approximate value in cases where measurement is not possible either due to instrumental limitations or compound instability. The compounds included in the estimations described below are those of this study and literature values of *N*-methylbenzamide.[18]

An indirect method for estimating fusion enthalpy has been reported provided the experimental fusion temperature is known.[18] The method consists of estimating the total phase change entropy of the substance. The total phase change entropy in this context refers to the total entropy change in going from $T = 0$ K to the liquid at $T = T_{\text{fus}}$. Provided there are no significant undetected phase transitions occurring in the solid within this temperature range, along with the fusion temperature, an approximate fusion enthalpy can be evaluated as $T_{\text{fus}}\Delta S_{\text{tpce}}$.[19] The estimation is best described as a group additive method.[20] The group values used in the estimations summarized in Table 8 are provided in footnote *a* below the table. The estimated and experimental fusion enthalpies are compared in columns 4 and 5 of Table 8. While some estimations are more accurate than others, all can be considered to be in qualitative agreement with the experimental results.

The estimation used for vaporization enthalpy is described by eq 7.[21]

$$\Delta H_{\text{vap}}(298\text{ K})/\text{kJ}\cdot\text{mol}^{-1} = 4.69(n_{\text{C}} - n_{\text{Q}}) + 1.3n_{\text{Q}} + \sum_i n_i F_i B_i + 3.0 \qquad (7)$$

The term n_{C} refers to the total number of carbon atoms, n_{Q} refers to the number of quaternary sp^3 hybridized carbon atoms, n_i refers to the number of functional groups of type i, F_i is a coefficient whose value is dependent on the location of the function group in the molecule, and b_i refers to the group contribution of functional group i. In instances where only one functional group is present, F_i is numerically equal to 1. For compounds with multiple functional groups, setting $F_i = 1$ is the simplest approximation. For the alkoxyamides of this study, both values are provided in the fifth column of Table 8. In this case, the simplest approximation ($F_i = 1$) provides the best fit, primarily because of the large contribution of the amide functional group to the vaporization enthalpy. The group values used and additional details concerning the estimations are provided in a footnote of Table 8.

Finally, it is possible to also estimate and compare the sublimation enthalpies of the solid amides of this study by combining estimated vaporization and fusion enthalpies. As indicated in Table 9, errors often cancel. The estimated sublimation enthalpies obtained compare quite well to experimental values in most cases.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Tables of the experimental retention times described in the text. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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