

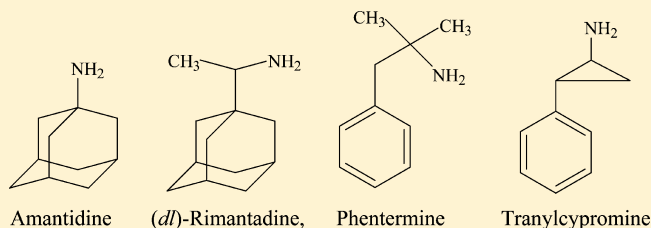
The Vaporization Enthalpies and Vapor Pressures of Some Primary Amines of Pharmaceutical Importance by Correlation Gas Chromatography

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Supporting Information

ABSTRACT: Vapor pressures, vaporization, and sublimation enthalpies of several pharmaceuticals have been evaluated by a combination of correlation chromatography experiments, differential calorimetry measurements with existing literature values. The compounds investigated and their properties include 1-adamantylamine [$\Delta_{\text{cr}}^1 H_{\text{m}}(T_{\text{fus}})/\text{kJ}\cdot\text{mol}^{-1} = (7.3 \pm 0.2)$; $T_{\text{fus}}/\text{K} = (477.4 \pm 0.9)$; $\Delta_{\text{l}}^{\text{s}} H_{\text{m}}(298.15 \text{ K})/\text{kJ}\cdot\text{mol}^{-1} = (59.9 \pm 2.5)$; $\Delta_{\text{cr}}^{\text{s}} H_{\text{m}}(298.15 \text{ K})/\text{kJ}\cdot\text{mol}^{-1} = (\sim 59.9 \pm 3.5)$; $p_{(l)}/\text{Pa} = (21 \pm 1)$; $p_{(\text{cr})}/\text{Pa} = (11.5 \pm 2.1)$]; 1-adamantylethanamine, [$\Delta_{\text{l}}^{\text{s}} H_{\text{m}}(298.15 \text{ K})/\text{kJ}\cdot\text{mol}^{-1} = (68.7 \pm 3.7)$; $p_{(l)}/\text{Pa} = (3 \pm 1)$]; α,α -dimethylphenethylamine [$\Delta_{\text{l}}^{\text{s}} H_{\text{m}}(298.15 \text{ K})/\text{kJ}\cdot\text{mol}^{-1} = (60.2 \pm 2.6)$; $p_{(l)}/\text{Pa} = (35 \pm 4)$]; *trans* 2-phenylcyclopropylamine [$\Delta_{\text{l}}^{\text{s}} H_{\text{m}}(298.15 \text{ K})/\text{kJ}\cdot\text{mol}^{-1} = (60.3 \pm 2.1)$, $p_{(l)}/\text{Pa} = (28 \pm 5)$]; 1-dodecanamine [$\Delta_{\text{cr}}^{\text{s}} H_{\text{m}}(298.15 \text{ K})/\text{kJ}\cdot\text{mol}^{-1} = (118.3 \pm 1.8)$; $p_{(\text{cr})}/\text{Pa} = 1.6 \pm 0.1$]; and 1-tetradecanamine [$\Delta_{\text{cr}}^{\text{s}} H_{\text{m}}(298.15 \text{ K})/\text{kJ}\cdot\text{mol}^{-1} = (134.5 \pm 2.1)$; $p_{(\text{cr})}/\text{Pa} = 0.12 \pm 0.04$]. Vapor pressure equations also derived from vapor pressure—retention time correlations as a function of temperature are reported for both standards and targets. The equations appear applicable from $T/\text{K} = 298.15$ to each compound's respective boiling temperature.



1. INTRODUCTION

A number of simple primary amines often prescribed as their salts have been of considerable pharmaceutical interest. Amantidine (1-aminoadamantane) has been used for the prevention of influenza A,¹ for treatment of dementia and other disorders of the central nervous system,^{1,2} and combined with other substances as a possible treatment for hepatitis C.^{3,4} Rimantadine (1-adamantylethanamine) has also been used for prevention of influenza A⁵ although the use of both rimantadine and amantidine are no longer recommended.⁶ Another simple amine, phentermine (α,α -dimethylphenethylamine), a substance with a pharmacology similar to amphetamine, is used medicinally as an appetite suppressant for patients who suffer from obesity.⁷ Tranlycypromine or *trans*-1-phenylcyclopropylamine, developed as an analogue of amphetamine, is a monoamine oxidase inhibitor and has been used in treatment of mood and anxiety disorders.⁸ The structures of these materials are shown in Figure 1. Despite their widespread use, information regarding the physical properties of many of these materials in the literature is relatively scarce. This work reports the vaporization enthalpies and vapor pressures of the amines as their free base. For those that are solids at room temperature, the vapor pressure of the subcooled liquid and the vapor pressure of the solid phase as evaluated by correlation gas chromatography and differential scanning calorimetry are also reported.

Recently the vaporization enthalpies and vapor pressures of a series of primary *n*-alkylamines including those of amphetamine have been reported.⁹ Measurements of these *n*-alkylamines were conducted using transpiration experiments, and properties of

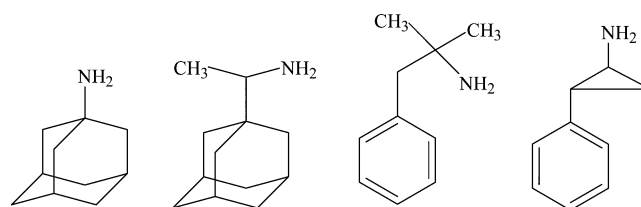


Figure 1. From left to right: amantidine; (*dl*)-rimantadine; phentermine; tranlycypromine.

amphetamine were obtained by correlation gas chromatography. The measurements reported in this previous work along with some additional results from the literature prompted a similar investigation of rimantidine, phentermine, and tranlycypromine, compounds with functional similarity to those previously used or studied. The vaporization enthalpies of these materials are reported as are their vapor pressures using a series of 1-alkanamines as standards. The vapor pressure results are compared to literature values and boiling temperatures when available. Sublimation enthalpies and vapor pressures are also evaluated for 1-dodecanamine and 1-tetradecanamine using either available or measured fusion enthalpies.

Thermochemical information for amantidine (1-adamantylamine) has been reported previously by Bazyleva et al.¹⁰ Our

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Table 1. Origin of the Standards and Targets and Their Analysis

compound	CAS RN	supplier	mass fraction	GC
benzylamine	100-46-9	MCB ^a	0.96	
1-heptanamine	111-68-2	Sigma Aldrich	0.99	
(<i>dl</i>) α -methylbenzylamine	618-36-0	Sigma Aldrich	0.99	> 0.99
2-phenethylamine	64-04-0	Fluka	AS ^b	> 0.99
1-octanamine	111-86-4	Sigma Aldrich	0.99	
(<i>dl</i>)-tranylcypromine (<i>trans</i> 2-phenylcyclopropylamine)	155-09-9	Sigma	0.97	
phentermine ^c (α,α -dimethylphenethylamine)	122-09-8	Supleco	0.99+	
amantadine (1-adamantylamine)	768-94-5	Sigma Aldrich	0.97	
1-decanamine	2016-57-1	Sigma Aldrich	0.95	
(<i>dl</i>)-rimantadine ^d (1-(1-adamantyl)ethylamine)	13392-28-4	Sigma Aldrich	0.99	
1-dodecanamine	124-22-1	Sigma Aldrich	0.98	
1-tetradecanamine	2016-42-4	Sigma Aldrich	0.95	

^aMatheson, Coleman, and Bell. ^bAnalytical Standard. ^cSupplied in methylene chloride. ^dAvailable as the hydrochloride.

initial interest in using amantadine as a standard for our measurements was prompted by the similarity of its structure to that of rimantidine. On examining the properties of amantadine we were struck by the magnitude of its sublimation enthalpy. A careful study of this compound's vapor pressure as a function of temperature resulted in a sublimation enthalpy of only (61.7 ± 0.6) kJ·mol⁻¹.¹⁰ For a crystalline solid melting at $T/K = (479 \text{ to } 481)$, this value at first glance appeared remarkably small especially since a simple equation used to estimate this vaporization enthalpy predicted a vaporization enthalpy of approximately 60 kJ·mol⁻¹.¹¹ Details of this estimation are provided in the Experimental Section. As a consequence of the surprisingly low sublimation enthalpy, the vapor pressure and vaporization enthalpy of liquid amantadine were also evaluated by correlation gas chromatography. The sublimation enthalpy and vapor pressure of both the subcooled liquid and solid were likewise evaluated, and compared to existing values.¹⁰

2. EXPERIMENTAL SECTION

2.1. Materials. Table 1 lists the source of the amines used in this study and their composition. (*dl*)-Rimantadine was supplied as the hydrochloride salt which was neutralized with 1 M NaOH and extracted with hexane before use. The remainder of the amines were added to the hexane solution until comparable concentrations of all the amines were achieved. Analytical grade phentermine was purchased as a solution in methylene chloride and in the experiments where this substance was included, used as provided. The purity of this material was evaluated by gas chromatography. The retention time of each amine was also measured independently for identification purposes.

2.2. Fusion Enthalpies. The fusion enthalpy of 1-adamantylamine (amantadine) was measured on a Perkin-Elmer DSC 7 instrument using the Pyris Series Thermal Analysis software at a heating rate of rate of 5 K/60 s under a flow of nitrogen. The instrument was calibrated using high purity indium and tin samples provided by the manufacturer. The measurements of 1-adamantylamine (amantadine) were performed on samples as received from the supplier and also on material that was vacuum sublimed. As noted by Bazyleva et al.,¹⁰ 1-adamantylamine in contact with air reacts with either carbon dioxide or water vapor since the commercial sample exhibited broad peaks at approximately $T/K = (333, 410, \text{ and } 435)$. Only the peak due to fusion was found to be totally reproducible. Samples that were hermetically sealed in aluminum pans, examined after fusion exhibited some pan distortion likely due to the buildup of internal pressure. This distortion was probably responsible for

some peak abnormalities observed near the fusion temperature. These abnormalities were avoided by the use of high pressure sealable stainless steel capsules, (Perkin-Elmer, Product number: B0182902) capable of withstanding pressures up to 150 atm. Following sublimation of the sample, only a single peak at $T/K = 477$ was observed. The area of the fusion peak at $T/K = 477$ was sharp, and no additional peaks were observed. Experimental results recorded on both sets of sealed cells are summarized in Table 2. In addition to the fusion enthalpy exhibited by 1-

Table 2. Fusion Enthalpies of 1-Adamantylamine (Sublimed)

mass	T_{fus}	$\Delta_{\text{cr}}^{\text{1}}H_{\text{m}}(T_{\text{fus}})$	$\Delta_{\text{cr}}^{\text{1}}H_{\text{m}}(T_{\text{fus}})$
	K onset	J·g ⁻¹	kJ·mol ⁻¹
13.92	476.5	47.83	7.23
22.59	478.2	49.33	7.46
12.36	477.4	47.18	7.14
avg	477.4 ± 0.9	48.1 ± 1.1	7.3 ± 0.2

adamantylamine, solid–solid phase transitions below room temperature at $T_{\text{trs1}}/K = 241.4$ (1.72 ± 0.01) kJ·mol⁻¹ and $T_{\text{trs2}}/K = 284.6$ (5.31 ± 0.01) kJ·mol⁻¹ have also been reported.¹⁰

2.3. Powder Pattern: 1-Adamantylamine. Efforts to obtain a crystal structure of 1-adamantylamine at room temperature were unsuccessful. The material was not observed to diffract. The powder pattern of 1-adamantylamine at $T/K = 298.15$ indicated approximately 50% crystallinity. Details regarding the powder pattern are included in the Supporting Information. Powder XRD data were collected using a Rigaku Ultima IV powder diffractometer with Cu radiation. Scans were collected in 2theta–theta scanning mode at 40KV/44 mA power settings. JADE 9.3 software was used for data analysis.

2.4. Methods. Correlation gas chromatography experiments were conducted over a $T/K = 30$ temperature range at approximately $T/K = 5$ increments on an HP 5890 gas chromatograph running Chemstation and equipped with an FID detector using a 0.32 mm, 30 m DB5 column, and helium as the carrier gas. A split ratio of approximately 100/1 was used. The column temperature was maintained to $T/K = 0.1$ K as monitored by a Fluke digital thermometer. At the temperatures of the experiments, the solvents used (hexanes, methylene chloride) also served as the nonretained reference. Adjusted retention times, t_a , were calculated for each analyte by the difference between the measured retention time of each analyte and the nonretained reference. Plots of $\ln(t_o/t_a)$ against $1/T$ for each analyte, both standards and target, where t_o refers to the

Table 3. Thermodynamic Properties of the Primary Amines Used as Standards⁹

compounds	<i>T</i>	$\Delta_i^{\circ}H_m(T_m)(T_m/K)$	$C_p(l)$	$\Delta_i^{\circ}C\Delta T$	$\Delta_i^{\circ}H_m(298.15\text{ K})$	<i>p</i>	ref
	K range	kJ·mol ⁻¹	J·mol ⁻¹ ·K ⁻¹	kJ·mol ⁻¹	kJ·mol ⁻¹	Pa ^a 298.15 K	
benzylamine	293 to 363	52.7 ± 0.3 (328)	215.6	1.9 ± 0.5	54.6 ± 0.6	95	15
	302 to 458	48.96 (380)	215.6	5.4 ± 1.3	54.4 ± 1.3	110	16 17,
	276 to 313	54.5 ± 0.3 (295)	215.6	-0.2	54.3 ± 0.3	88	9
	277 to 316	54.4 ± 0.3 (297)			54.4 ± 0.3	87	9
(avg)					54.4 ± 0.6	95 ± 10	
1-heptanamine	298.15				50.0 ± 0.1		18
	327 to 430	43.4 ± 0.6 (379)	285.7	6.8 ± 1.3	50.2 ± 1.4	288	19
	280 to 306	50.2 ± 0.4 (293)	285.7	-0.4	49.8 ± 0.4	291	9
(avg)					50.0 ± 0.2	288¹⁹	
(dl) α-methyl-benzylamine	283 to 318	54.7 ± 0.3 (301)			55.0 ± 0.3	1.2	20
	284 to 323	54.9	241		55.3 ± 0.3	82	9
(avg)					55.2 ± 0.4	82	
2-phenethyl-amine	273 to 352	55.7 ± 0.2 (313)			56.8 ± 0.2	44	15
	285 to 323		247.5		57.5 ± 0.3	43	9
(avg)					57.2 ± 0.3	44 ± 1	
1-octanamine	308 to 453	47.8 ± 0.4 (381)	317.6		55.5 ± 2.3	136	19
	344 to 494	43.5 ± 0.4 (419)			54.6 ± 0.5	122	21
	274 to 313	55.3 ± 0.3 (294)			55.1 ± 0.3	108	9
(avg)					55.1 ± 0.5	122²¹	
1-decanamine	329 to 431	56.1 ± 0.6 (380)	381		65.1 ± 0.6	11	19
	299 to 343	64.9 (321)			64.9 ± 0.3	12	9
(avg)					65.0 ± 0.2	11¹⁹	
1-dodecanamine	367 to 444	61.3 ± 0.4 (406)	445.2		74.8 ± 1.8	2	19
	356 to 455	62.8 ± 0.7 (399)			75.5 ± 1.8	3	17
					75.2 ± 1.8	2¹⁹	
1-tetradecanamine	382 to 455	64.5 ± 1.0 (409)	509	15.9 ± 1.8	85.4 ± 2.0	0.03	19

^aExtrapolated to $T/K = 298.15$ if necessary from the temperature range noted in column 2, reference 9; only the values in bold were used in subsequent correlations.

reference time, 60 s, resulted in straight lines with slopes numerically equal to the enthalpy of transfer of each analyte from the condensed phase of the column to the gas phase, $-\Delta H_{tm}(T_m)$, divided by the gas constant R . Each plot was characterized by a correlation coefficient of $r^2 > 0.99$. All retention times are provided in the Supporting Information. The enthalpy of transfer, $-\Delta H_{tm}(T_m)$, is thermodynamically related to the vaporization enthalpy by eq 1 where $\Delta H_{intr}(T_m)$ represents the enthalpy of interaction of the analyte with the column.^{12,13} Correlation of the vaporization enthalpies of the standards, usually at $T/K = 298.15$ K with $\Delta H_{tm}(T_m)$ also results in a linear relationship provided the standards are appropriately selected. The selection of standards is usually dictated by the nature of the functional groups present and less so by the structure of the hydrocarbon portion of the molecule. Usually the best results are obtained when the structure of the standards closely resembles the structure of the targets.

$$\Delta H_{tm}(T_m) = \Delta_i^{\circ}H(T) + \Delta H_{intr}(T_m) \quad (1)$$

2.5. Estimation. The vaporization enthalpy of amantadine was estimated using eq 2. The terms in eq 2 refer to the number of carbon atoms, n_C , the number of sp^3 hybridized quaternary carbons, n_Q , and the contribution of a primary amine, b (14.8 kJ·mol⁻¹).¹¹ The carbon bearing the nitrogen was treated as a quaternary carbon. For amantadine, C₁₀H₁₇N, a vaporization enthalpy of 61.3 kJ·mol⁻¹ is estimated.

$$\begin{aligned} \Delta_i^{\circ}H(298K)/\text{kJ}\cdot\text{mol}^{-1} \\ = 4.69(n_C - n_Q) + 1.3n_Q + b + 3.0 \end{aligned} \quad (2)$$

2.6. Standards. The vaporization enthalpies used for the standards are summarized in Table 3. The values in bold are the average values used in the correlations. Additional details on their selection can be found in ref 9. Vapor pressures for the all of the standards are also available but some are available only over a limited temperature range. Vapor pressures over a larger temperature range have been reported for 1-octanamine by Steele et al.²¹ and for 1-heptanamine, 1-octanamine, 1-decanamine, 1-dodecanamine, and 1-tetradecanamine by Ralston et al.¹⁹ as noted in Table 3. Since the results from Ralston et al. are quite old, the vapor pressures for 1-octanamine reported by Ralston et al. were compared to those reported by Steele et al. and found to compare quite favorably. A visual comparison is available in the Supporting Information. Consequently, the vapor pressures measured for 1-heptanamine, 1-decanamine, and 1-dodecanamine by Ralston et al.¹⁹ and those reported by Steele et al. for 1-octanamine were used as standards in subsequent correlations. Only the vapor pressures for 1-tetradecanamine reported by Ralston et al. did not correlate well with the other 1-alkanamines at the lower temperatures, perhaps because of the large temperature extrapolation required. The vapor pressures of 1-tetradecanamine were not used as standards in the initial correlations. This compound's vapor pressures were treated as a target and evaluated by correlation for comparative purposes at the higher temperatures. The vapor pressures for 1-tetradecanamine evaluated in this work were used as a standard in one subsequent set of correlations. The experimental vaporization enthalpy of 1-tetradecanamine, evaluated at a mean temperature of $T/K = 409$ from literature vapor pressure measurements reported over the temperature range $T/K = (382 \text{ to } 454)$ and

Table 4. Constants for eq 3 Generated from Experimental Vapor Pressure—Temperature Data

	$A \cdot 10^{-8}/K^3$	$B \cdot 10^{-6}/K^2$	$C \cdot 10^{-3}/K$	D	T_b/K^a calc	$T_b/K^{a,b}$ lit
1-heptanamine ¹⁹	-10.395	7.611	-23.498	26.552	430	427–9
1-octanamine ²¹	0.134	-0.726	-2.167	8.207	452	448–50
1-decanamine ¹⁹	-3.300	1.802	-9.270	14.128	494	489–91
1-dodecanamine ¹⁹	3.301	-3.025	1.630	5.427	532	532

^anBT: normal boiling temperature. ^bSee Table 9 for boiling temperature references.

Table 5. Validation of the Vaporization Enthalpies of 1-Dodecanamine and 1-Tetradecanamine

run 1	-slope T		$\Delta H_{tm}(439\text{ K})$	$\Delta_i^{\circ}H_m(298\text{ K})$	$\Delta_i^{\circ}H_m(298\text{ K})$	$\Delta_i^{\circ}H_m(298\text{ K})$
	K	intercept	$\text{kJ}\cdot\text{mol}^{-1}$	$\text{kJ}\cdot\text{mol}^{-1}$ (lit)	$\text{kJ}\cdot\text{mol}^{-1}$ (calc)	$\text{kJ}\cdot\text{mol}^{-1}$ (lit)
1-heptanamine	4354.0	11.024	36.20	50.0 ± 0.2	50.1 ± 1.4	
1-octanamine	4750.6	11.375	39.49	55.1 ± 0.5	54.9 ± 1.5	
1-decanamine	5577.9	12.247	46.37	65.0 ± 0.2	65.0 ± 1.6	
1-dodecanamine	6451.6	13.277	53.64		75.7 ± 1.8	75.2 ± 1.8
1-tetradecanamine	7331.0	14.344	60.95		86.5 ± 1.9	85.4 ± 2.0

Table 6. Correlation of Vaporization Enthalpies with Enthalpies of Transfer of Some Primary Amines

run 3	-slope T		$\Delta H_{tm}(449\text{ K})$	$\Delta_i^{\circ}H_m(298\text{ K})$	$\Delta_i^{\circ}H_m(298\text{ K})$
	K	intercept	$\text{kJ}\cdot\text{mol}^{-1}$	$\text{kJ}\cdot\text{mol}^{-1}$ (lit)	$\text{kJ}\cdot\text{mol}^{-1}$ (calc)
1-heptanamine	4187.9	10.619	34.82	50.0 ± 0.2	51.7 ± 3.2
1-octanamine	4565.9	10.934	37.96	55.1 ± 0.5	56.0 ± 3.4
(dl) α -methylbenzylamine	4356.7	10.314	36.22	55.2 ± 0.4	53.6 ± 3.3
2-phenethylamine	4540.9	10.462	37.75	57.2 ± 0.3	55.8 ± 3.3
α,α -dimethylphenethylamine	4801.1	10.73	39.91		58.8 ± 3.4
1-decanamine	5382.3	11.783	44.75	65.0 ± 0.2	65.4 ± 3.6
1-adamantylamine	4852.5	10.369	40.34		59.3 ± 3.4
1-dodecanamine	6242.9	12.784	51.9	75.5 ± 1.8	75.3 ± 3.9
(dl) 1-(1-adamantyl)ethylamine	5661.9	11.225	47.07		68.6 ± 3.7
1-tetradecanamine	7129.9	13.87	59.28	85.4 ± 2.0	85.5 ± 4.3
run 5	-slope T		$\Delta H_{tm}(403\text{ K})$	$\Delta_i^{\circ}H_m(298\text{ K})$	$\Delta_i^{\circ}H_m(298\text{ K})$
	K	intercept	$\text{kJ}\cdot\text{mol}^{-1}$	$\text{kJ}\cdot\text{mol}^{-1}$ (lit)	$\text{kJ}\cdot\text{mol}^{-1}$ (calc)
benzylamine	4422.9	10.659	36.77	54.4 ± 0.6	54.2 ± 1.6
(dl) α -methylbenzylamine	4569.2	10.832	37.99	55.2 ± 0.4	55.4 ± 1.7
2-phenethylamine	4774.7	11.03	39.7	57.2 ± 0.3	57.2 ± 1.7
α,α -dimethylphenethylamine	5267.8	11.853	43.79		61.5 ± 1.8
1-decanamine	5662.7	12.456	47.08	65.0 ± 0.2	65.0 ± 1.9
trans 2-phenylcyclopropylamine	5256.3	11.527	43.7		61.4 ± 1.8
1-adamantylamine	5098.1	10.965	42.38		60.0 ± 1.8
run 7	-slope T		$\Delta H_{tm}(469\text{ K})$	$\Delta_i^{\circ}H_m(298\text{ K})$	$\Delta_i^{\circ}H_m(298\text{ K})$
	K	intercept	$\text{kJ}\cdot\text{mol}^{-1}$	$\text{kJ}\cdot\text{mol}^{-1}$ (lit)	$\text{kJ}\cdot\text{mol}^{-1}$ (calc)
(dl) α -methylbenzylamine	4274.8	10.151	35.54	55.2 ± 0.4	55.0 ± 2.3
2-phenethylamine	4430.4	10.238	36.83	57.2 ± 0.3	56.7 ± 2.3
α,α -dimethylphenethylamine	4687.5	10.498	38.97		59.7 ± 2.4
trans 2-phenylcyclopropylamine	4637.9	10.169	38.56		59.1 ± 2.4
1-decanamine	5246.8	11.502	43.62	65.0 ± 0.2	66.1 ± 2.5
1-adamantylamine	4741.6	10.143	39.42		60.3 ± 2.4
1-dodecanamine	6058.0	12.396	50.36	75.5 ± 1.8	75.4 ± 2.7
1-tetradecanamine	6902.0	13.389	57.38	85.4 ± 2.0	85.1 ± 2.9

adjusted to $T/K = 298.15$, did correlate well with the other 1-alkanamines as determined in the trial runs described below and was used as a vaporization enthalpy standard. The literature vapor pressures reported for the C_7 , C_8 , C_{10} , and C_{12} 1-alkanamines,^{19,21} reported over the temperature ranges cited in Table 3 were all fit to a third order polynomial, eq 3, found to extrapolate well with temperature.^{9,14} The constants of eq 3, A to D , are summarized in Table 4; p represents the vapor pressure and p_0 refers to 101325 Pa. Equation 3 was then used to predict

the normal boiling temperature of the C_7 , C_8 , C_{10} , and C_{12} 1-alkanamines which are also reported in Table 4. As noted in the last two columns of this table, the predicted boiling temperatures reproduce the experimental values within a few degrees. As a consequence of this agreement, the vapor pressures calculated using eq 3 were used as standards.

$$\ln(p/p_0) = A(T/K)^{-3} + B(T/K)^{-2} + C(T/K)^{-1} + D \quad (3)$$

2.7. Temperature Adjustments. The vaporization enthalpies reported in Table 3 were adjusted from the mean temperature of measurement, T_m , cited in column 3 of Table 3 using eq 4. The $C_p(l)$ term in this equation refers to the liquid heat capacity at $T/K = 298.15$ which was estimated by group additivity. Similarly, the fusion enthalpy of 1-adamantylamine was adjusted from $T/K = (T_{fus} + 298.15)$ using eq 5. The $C_p(cr)$ term in this equation also refers to the heat capacity at $T/K = 298.15$. For reasons discussed below, the experimental heat capacity of the solid was used in this instance. These equations have been previously shown by means of thermochemical cycles to provide reliable temperature adjustments.²²

$$\begin{aligned} \Delta_1^8 H_m(298.15 \text{ K}) / (\text{kJ} \cdot \text{mol}^{-1}) \\ = \Delta_1^8 H_m(T_m) / \text{kJ} \cdot \text{mol}^{-1} \\ + [(10.58 + 0.26 \cdot C_p(l) / (\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})) \\ (T_m / \text{K} - 298.15 \text{ K})] / 1000 \end{aligned} \quad (4)$$

$$\begin{aligned} \Delta_{cr}^1 H(298.15 \text{ K}) / (\text{kJ} \cdot \text{mol}^{-1}) \\ = \Delta_{cr}^1 H(T_{fus}) / \text{kJ} \cdot \text{mol}^{-1} \\ + [(0.15 C_p(cr) - 0.26 C_p(l) / (\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}) - 9.83)] \\ [T_{fus} / \text{K} - 298.15] / 1000 \end{aligned} \quad (5)$$

2.8. Uncertainties. Uncertainties in the temperature adjustment of vaporization enthalpy, eq 4, were calculated using an uncertainty of $\pm 16 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ for $C_p(l)$. The uncertainty in the temperature adjustment of the fusion enthalpy, eq 5, has been estimated as 30% of the total adjustment.²² Potential uncertainties in results from correlations were evaluated from both the uncertainty in the slope and intercept evaluated as $(u_1^2 + u_2^2 + \dots)^{0.5}$. Uncertainties in derived results were evaluated similarly unless noted otherwise.

3. RESULTS

3.1. Vaporization Enthalpies. As mentioned in a previous section, since the vapor pressures reported by Ralston et al.¹⁹ are somewhat dated, the vaporization enthalpies for 1-dodecanamine and 1-tetradecanamine were both treated as unknowns and their vaporization enthalpies were evaluated using enthalpies of transfer measured by gas chromatography and the experimental vaporization enthalpies of the C_7 , C_8 , and C_{10} 1-alkanamines reported previously.⁹ Equations 6 and 7 describe the correlation obtained in runs 1 and 2 by correlating enthalpies of transfer with the experimental vaporization enthalpies provided in the table. Equation 6 characterizes the correlation obtained for run 1. Similar details for run 2 characterized by eq 7 are available in the Supporting Information. The vaporization enthalpies measured in run 1 are well within the experimental uncertainty of the literature values for 1-dodecanamine and 1-tetradecanamine which are reported in the last column of Table 5 and not used in either correlation.

For the remaining primary amines evaluated in this study, the retention times of some of the amines overlapped with some of the standards. It was therefore necessary to perform duplicate evaluations using separate correlations. Runs 3 to 8 reported in Table 6 resulted in correlation eqs 8 to 13. Details for only one set of correlations are provided in Table 6. Complete details are available in the Supporting Information. The amines in these tables are listed in order of their elution off the column. Table 7

Table 7. A Summary and Comparison of the Vaporization Enthalpies ($\text{kJ} \cdot \text{mol}^{-1}$) with Literature Values at $T/K = 298.15$

	run 1	run 2	run 3	run 4	run 5	run 6	run 7	run 8	avg ^a	lit
benzylamine					54.2 ± 1.6	54.2 ± 1.6			54.2 ± 1.6	54.6 ± 0.6
1-heptanamine	50.1 ± 0.7	50.5 ± 1.4	51.7 ± 3.2	51.6 ± 3.2					51.0 ± 2.1	50.0 ± 0.2
(dl) α-methyl- benzylamine			53.6 ± 3.3	53.7 ± 3.2	55.4 ± 1.7	55.4 ± 1.7	55.0 ± 2.3	55.0 ± 2.3	54.7 ± 2.4	55.2 ± 0.4
2-phenethylamine			55.8 ± 3.3	55.8 ± 3.3	57.2 ± 1.7	57.2 ± 1.7	56.7 ± 2.3	56.7 ± 2.3	56.6 ± 2.4	57.2 ± 0.3
1-octanamine	54.9 ± 0.7	54.9 ± 1.5	56.0 ± 3.4	56.0 ± 3.3					55.5 ± 2.2	55.1 ± 0.5
trans 2-phenyl-cyclopropylamine					61.4 ± 1.8	61.4 ± 1.8	59.1 ± 2.4	59.2 ± 2.4	60.3 ± 2.1	
α,α-dimethyl- phenethylamine			58.8 ± 3.4	58.8 ± 3.4	61.5 ± 1.8	61.7 ± 1.8			60.2 ± 2.6	
1-adamantylamine			59.3 ± 3.4	59.4 ± 3.4	60.0 ± 1.8	60.1 ± 1.7	60.3 ± 2.4	60.3 ± 2.4	59.9 ± 2.5	
1-decanamine	65.0 ± 0.7	64.6 ± 1.6	65.4 ± 3.6	65.5 ± 3.6	65.0 ± 1.9	65.0 ± 1.8	66.1 ± 2.5	66.1 ± 2.5	65.3 ± 2.3	65.0 ± 0.2
1-dodecanamine	75.5 ± 0.8	75.1 ± 1.7	75.3 ± 3.9	75.3 ± 3.9			75.4 ± 2.7	75.4 ± 2.7	75.3 ± 2.6	75.2 ± 1.8
(dl) 1-(1-adamantyl)- ethylamine			68.6 ± 3.7	68.7 ± 3.7					68.7 ± 3.7	
1-tetradecanamine	86.2 ± 0.9	85.8 ± 1.8	85.5 ± 4.3	85.5 ± 4.2			85.1 ± 2.9	85.1 ± 2.9	85.5 ± 2.8	85.4 ± 2.0

^aThe uncertainties are also averages.

Table 8. Correlation between $\ln(t_o/t_a)_{\text{avg}}$ and Literature $\ln(p/p_o)$ Values for Runs 3 and 4 at $T/K = 298.15$

	$\ln(t_o/t_a)_{\text{run 3}}$	$\ln(t_o/t_a)_{\text{run 4}}$	$\ln(t_o/t_a)_{\text{avg}}$	$\ln(p/p_o)_{\text{lit}}$	$\ln(p/p_o)_{\text{calc}}$
1-heptanamine	-3.427	-3.443	-3.435	-5.868	-5.867
(dl) α -methylbenzylamine	-4.300	-4.323	-4.311		-6.785
1-octanamine	-4.380	-4.400	-4.39	-6.723	-6.868
2-phenethylamine	-4.768	-4.790	-4.779		-7.277
1-decanamine	-6.269	-6.291	-6.28	-9.139	-8.852
α,α -dimethylphenethylamine	-5.373	-5.395	-5.384		-7.912
1-adamantylamine	-5.907	-5.930	-5.918		-8.472
(dl) 1-(1-adamantyl)ethylamine	-7.765	-7.785	-7.775		-10.42
1-dodecanamine	-8.155	-8.174	-8.165	-10.686	-10.829
1-tetradecanamine	10.044	10.056	-10.05		-12.807
$\ln(p/p_o) = (1.049 \pm 0.69)\ln(t_o/t_a)_{\text{avg}} - (2.26 \pm 0.40)$				$r^2 = 0.9915$	14

Table 9. A to D Constants of eq 3, Liquid Vapor Pressures at $T/K = 298.15$ and Normal Boiling Temperatures (T_b/K) Evaluated from Runs 3 and 4, 5 and 6, and 7 and 8

	$A \cdot 10^{-8}/K^3$	$B \cdot 10^{-6}/K^2$	$C \cdot 10^{-3}/K$	D	$p_{(l)}/\text{Pa}$ 298.15 K calc	T_b/K calc
Runs 3 and 4						
1-heptanamine	-7.22	5.039	-16.688	20.657	287	429
(dl) α -methylbenzylamine	-4.76	3.083	-11.701	15.743	115	461
2-phenethylamine	-3.693	2.249	-9.737	14.025	70	473
1-octanamine	-5.062	3.353	-12.734	17.217	105	453
α,α -dimethylphenethylamine	-2.379	1.226	-7.383	12.04	37	488
1-adamantylamine	-0.732	-0.093	-3.926	8.506	21	515
1-decanamine	-0.969	0.17	-5.417	11.065	15	495
1-dodecanamine	2.99	-2.901	1.534	5.375	2	532
1-(1-adamantyl)ethylamine	3.275	-3.209	3.224	2.512	3	566
1-tetradecanamine	6.886	-5.917	8.307	-0.081	0.3	570
Runs 5 and 6						
benzylamine	-5.306	3.503	-12.619	16.486	160	453
α,α -dimethylphenethylamine	-2.298	1.192	-7.623	12.7	30	483
<i>trans</i> 2-phenylcyclopropylamine	-1.114	0.219	-4.927	9.86	23	500
1-adamantylamine	-0.372	-0.416	-2.947	7.534	22	517
Runs 7 and 8						
α,α -dimethylphenethylamine	-2.400	1.248	-7.457	12.12	37	487
<i>trans</i> 2-phenylcyclopropylamine	-1.756	0.730	-6.019	10.521	31	500
1-adamantylamine	-0.805	-0.018	-4.190	8.802	21	514

summarizes the vaporization enthalpies evaluated using eq 6 to 13 for both standards and target molecules. The last two columns in the table compare the results obtained for the standards with their literature values.

Run 1:

$$\Delta_1^{\text{g}}H_m(298.15 \text{ K})/\text{kJ}\cdot\text{mol}^{-1} = (1.47 \pm 0.03)\Delta H_{\text{tm}}(439 \text{ K}) - (3.1 \pm 1.1) \quad r^2 = 0.9997 \quad (6)$$

Run 2:

$$\Delta_1^{\text{g}}H_m(298.15 \text{ K})/\text{kJ}\cdot\text{mol}^{-1} = (1.54 \pm 0.04)\Delta H_{\text{tm}}(439 \text{ K}) - (5.7 \pm 1.7) \quad r^2 = 0.9993 \quad (7)$$

3.2. Liquid Vapor Pressures. In addition to vaporization enthalpies, retention times in the form $\ln(t_o/t_a)$ have been found to correlate well with vapor pressures expressed in similar form as $\ln(p/p_o)$. The results of the correlation at $T/K = 298.15$ for the compounds in runs 3 and 4 of Table 6 using the vapor pressures of the primary alkyl amines of Table 4 as standards are summarized in Table 8. Values of (t_o/t_a) calculated from each pair of runs in Table 6 were averaged and plotted as $\ln(t_o/t_a)_{\text{avg}}$.

Vapor pressures were generated from available experimental values using eq 3 and the constants of Table 4 and plotted as $\ln(p/p_o)$.^{19,21} Equation 14 listed below Table 8 describes the quality of the correlation obtained at $T/K = 298.15$. Correlations were repeated at $T/K = 10$ increments from ambient temperature to $T/K = 500$. The resulting correlation coefficients, r^2 exceeded 0.99 at all temperatures and approached 1.0 at the higher temperatures. The vapor pressures resulting from each correlation as a function of temperature were then also fit to a third order polynomial in temperature, eq 3. The A–D constants of eq 3 and estimated vapor pressures at $T/K = 298.15$ for both standards and target substances used in runs 3 and 4 are summarized in Table 9. Predicted normal boiling temperatures using eq 3 are also included in the last column of the table. Also included in this table, are the coefficients of eq 3 for all the target substances evaluated in subsequent correlations, runs 5 to 8. Coefficients for eq 3 evaluated in runs 5 to 8 as well as predicted vapor pressures at $T/K = 298.15$ and normal boiling temperatures are available for both standards and targets in the Supporting Information.

Table 10. A Summary of Liquid/Subcooled Liquid Vapor Pressures and Normal Boiling Temperatures (T_b /K) in Table 9 and Comparison with Experimental or Estimated Values

	$p_{(l)}/\text{Pa}$ 298.15 K calc	$p_{(l)}/\text{Pa}$ 298.15 K exp ^a	T_b/K calc	T_b/K lit ^b
benzylamine	160	87 to 110	453	457 to 458
1-heptanamine	287	288	429	427 to 429
(dl) α -methylbenzylamine	115/116/114	1.2 to 82	461/461/461	458
2-phenethylamine	70/70/71	43 to 44	473/473/473	470 to 473
1-octanamine	105	122	453	448–50
trans 2-phenylcyclopropylamine	31/23/31	15.6 ^c	500/500	494 ^c
α,α -dimethylphenethylamine	37/30/37	32 ^c	488/483/487	478 ^d
1-adamantylamine	21/22/21	21.8 ^c	515/517/514	501 ^c
1-decanamine	15/15/15	11	495/494/494	489 to 491
1-dodecanamine	2/2	2	532/532	532 ^f
1-(1-adamantyl)ethylamine	3	6 ^c	566	513 ^c
1-tetradecanamine	0.3/0.3	0.03 ^g /0.5 ^h	570/569	565 ^e

^aData and references available in Table 3 unless noted otherwise. ^bNormal boiling temperatures from the 2012–2014 Handbook of Fine Chemicals, Sigma-Aldrich, unless noted otherwise. ^cEstimate from ref 24. ^dFrom reference 25. ^eFrom reference 26. ^fLide, D. R. *CRC Handbook of Chemistry and Physics*, 76th ed; CRC Press: Boca Raton FL; 1995; p 3–147. ^gExtrapolated from $T/\text{K} = 382$; the vapor pressures for this material did not correlate well with the other 1-alkanamines; ref 19. ^hFrom an experimental database; literature reference not provided, ref 24.

Run 3:

$$\Delta_1^{\text{g}}H_{\text{m}}(298.15 \text{ K})/\text{kJ}\cdot\text{mol}^{-1} = (1.38 \pm 0.06)\Delta H_{\text{tm}}(449 \text{ K}) + (3.51 \pm 2.5) \quad r^2 = 0.9913 \quad (8)$$

Run 4

$$\Delta_1^{\text{g}}H_{\text{m}}(298.15 \text{ K})/\text{kJ}\cdot\text{mol}^{-1} = (1.38 \pm 0.06)\Delta H_{\text{tm}}(449 \text{ K}) + (3.25 \pm 2.5) \quad r^2 = 0.9917 \quad (9)$$

Run 5:

$$\Delta_1^{\text{g}}H_{\text{m}}(298.15 \text{ K})/\text{kJ}\cdot\text{mol}^{-1} = (1.05 \pm 0.03)\Delta H_{\text{tm}}(403 \text{ K}) + (15.6 \pm 1.2) \quad r^2 = 0.9983 \quad (10)$$

Run 6:

$$\Delta_1^{\text{g}}H_{\text{m}}(298.15 \text{ K})/\text{kJ}\cdot\text{mol}^{-1} = (1.05 \pm 0.03)\Delta H_{\text{tm}}(403 \text{ K}) + (15.7 \pm 1.2) \quad r^2 = 0.9984 \quad (11)$$

Run 7:

$$\Delta_1^{\text{g}}H_{\text{m}}(298.15 \text{ K})/\text{kJ}\cdot\text{mol}^{-1} = (1.38 \pm 0.04)\Delta H_{\text{tm}}(469 \text{ K}) + (5.95 \pm 1.8) \quad r^2 = 0.9975 \quad (12)$$

Run 8:

$$\Delta_1^{\text{g}}H_{\text{m}}(298.15 \text{ K})/\text{kJ}\cdot\text{mol}^{-1} = (1.37 \pm 0.04)\Delta H_{\text{tm}}(469 \text{ K}) + (6.28 \pm 1.8) \quad r^2 = 0.9975 \quad (13)$$

A comparison of the coefficients of eq 3 obtained for the standards in Table 9 bear little resemblance to those reported in Table 4. Nevertheless, a comparison of the predicted boiling temperatures for the standards in both tables show differences of only a degree. The following vapor pressure predictions at $T/\text{K} = 298.15$ were obtained using the two sets of constants reported in Tables 4 and 9, respectively (p/Pa): 1-heptylamine (288, 286), 1-octanamine (122, 105), 1-decanamine (10.8, 8.8), and 1-dodecanamine (2.3, 2.0). This suggests that the constants reported in Tables 3 and 9 would probably be reasonably accurate for providing vapor pressures over the temperature range $T/\text{K} = (298.15 \text{ to } T_b)$, from room temperature to each compound's respective boiling temperature.

Similar correlations as those reported in Table 8 were repeated for runs 5 and 6 and for runs 7 and 8 over the temperature range $T/\text{K} = (298.15 \text{ to } 500)$ also at $T/\text{K} = 10$ increments. Details similar to Table 8 for these runs are available in the Supporting Information. Standards used for runs 5 and 6 included 1-decanamine and the results from runs 3 and 4 for (dl) α -methylbenzylamine and 2-phenethylamine. Standards used for runs 7 and 8 included 1-decanamine, 1-dodecanamine, and the results for α -methylbenzylamine, 2-phenethylamine, and 1-tetradecanamine also obtained from runs 3 and 4. Correlation coefficients, r^2 exceeded 0.999 at all temperatures. The A to D constants for eq 3, liquid vapor pressures at $T/\text{K} = 298.15$, and predicted boiling temperatures for only the compounds treated as unknowns are included for runs 5 and 6 and 7 and 8 in Table 9. Complete details for all the compounds are available in the Supporting Information. The results of all correlations are discussed below.

4. DISCUSSION

4.1. Vaporization Enthalpies. As indicated by the compounds in Table 7, the major structural feature in common is that they are all primary alkyl amines. It has been previously observed that primary aromatic amines such as the anilines generally do not correlate as well with their aliphatic counterparts. On the basis of the result of this work, vaporization enthalpies for phenyl substituted alkyl amines appear to be well reproduced by primary aliphatic amines provided the amino group is not directly attached to the aromatic ring. The correlation coefficients, r^2 , exceeded 0.99 for all runs. The uncertainty reported in the second to last column of Table 7 is an average of the uncertainty associated with each run and is considerably less than $4 \text{ kJ}\cdot\text{mol}^{-1}$. The standard deviation associated with the reproducibility of each value generated in runs 1 to 8 ranged from $0.44 \text{ kJ}\cdot\text{mol}^{-1}$ for 1-adamantylamine to $1.6 \text{ kJ}\cdot\text{mol}^{-1}$ for 2-phenethylamine. The vaporization enthalpies of the compounds used as standards are well within the experiment error of the values reported in the literature. As commented in the introduction, the vaporization enthalpy of 1-adamantylamine of $(59.9 \pm 2.5) \text{ kJ}\cdot\text{mol}^{-1}$ is in good agreement with the $60 \text{ kJ}\cdot\text{mol}^{-1}$ estimated using eq 1.

4.2. Liquid Vapor Pressures and Boiling Temperatures. Table 10 compares the predicted vapor pressures at $T/\text{K} =$

Table 11. A Comparison of $C_p(\text{cr})$ Estimations with Experimental Values at $T/K = 298.15$ for Some Polycyclic Compounds with and without Multiple Solid–Solid Phase Changes

	$T_{\text{trsl}}/K/T_{\text{trsl}}/K$	$\Delta_{\text{trsl}}H(T_{\text{trsl}})$	T_{fus}	$\Delta_{\text{cr}}^1H(T_{\text{fus}})$	$C_p(\text{cr})_{\text{est}}^a/C_p(\text{cr})_{\text{exp}}$	ref
		$\text{kJ}\cdot\text{mol}^{-1}$	K	$\text{kJ}\cdot\text{mol}^{-1}$	$\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	
1-adamantylamine	241/285	1.72/5.31	477.4	7.3	210/266	10
adamantane	209	3.38	543	14.0	194/190	27/28
<i>endo</i> -tricyclo[5.2.1.0 ^{2,6}]decane	204	2.57	345	3.07	194/205	29
hexamethylenetetramine				na	152/154	25
1-adamantanol	357	11.3	553	12.4	212/197	30
2-adamantanol	238/322/389	0.16/2.3/8.0	569	11.9	205/207	30

^aCalculated using the following group values for crystalline materials: ²³ $-\text{NH}_2$ ($21.6 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$); $-\text{OH}$ ($23.5 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$); cyclic $\text{N}(\text{C}_3)$ ($1.2 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$); cyclic $\text{C}(\text{C}_2)(\text{H}_2)$; ($24.6 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$); cyclic $\text{C}(\text{C}_3)(\text{H})$ ($11.7 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$); cyclic $\text{C}(\text{C}_3)(\text{N})$, $\text{C}(\text{C}_3)(\text{O})$ ($6.1 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$).

Table 12. Fusion, Vaporization and Sublimation Enthalpies at $T/K = 298.15$

	T_{fus}	$\Delta_{\text{cr}}^1H(T_{\text{fus}})$	$C_p(\text{l})_{\text{est}}/C_p(\text{cr})_{\text{est}}$	$\Delta C_p\Delta T$	$\Delta_{\text{cr}}^1H(298 \text{ K})$	$\Delta_{\text{f}}^{\text{H}}(298 \text{ K})$	$\Delta_{\text{cr}}^{\text{H}}(298 \text{ K})$
	K	$\text{kJ}\cdot\text{mol}^{-1}$	$\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	$\text{kJ}\cdot\text{mol}^{-1}$	$\text{kJ}\cdot\text{mol}^{-1}$	$\text{kJ}\cdot\text{mol}^{-1}$	$\text{kJ}\cdot\text{mol}^{-1}$
1-adamantylamine	477	7.3 ± 0.2^a	$266^b/295$	-8.3 ± 2.5	-1.0 ± 2.5	59.9 ± 2.5	$\sim 59.9 \pm 3.5^d$
1-dodecanamine	301.5	43.5^c	$445.2/354.1$	-0.42 ± 0.1	43.1 ± 0.1	75.2 ± 1.8	118.3 ± 1.8
1-tetradecanamine	311.3	51.0^c	$509/407.9$	-1.88 ± 0.6	49.1 ± 0.6	85.4 ± 2.0	134.5 ± 2.1

^aEnthalpy for solid–liquid conversion of a partially crystalline phase, ref 10. ^bExperimental value. ^cFrom reference 33. ^dSee discussion in text.

298.15 and boiling temperature results of the correlations summarized in Table 9 to literature values or in a few cases to estimated values. The entries in columns 2 and 4 refer to predicted vapor pressures and boiling temperatures calculated for up to three sets of independent correlations obtained from runs 3 to 8. The first of up to three entries is the value estimated using the material as a target, and the subsequent values are those obtained using the same material as a standard. Despite the fact that the three sets of correlations used some different compounds as standards, vapor pressures and boiling temperatures are quite reproducible. Vapor pressures at $T/K = 298.15$ appear to be best reproduced for the aliphatic amines, while the vapor pressures for those primary amines containing a phenyl group generally appear to be somewhat overestimated. Normal boiling temperatures appear to be slightly over predicted but otherwise well reproduced regardless of structure. The largest discrepancies are observed with values that are estimated.

4.3. Fusion Enthalpies. Fusion enthalpies are available in the literature for both 1-dodecanamine and 1-tetradecanamine. Equation 5 described previously has generally been successful in providing appropriate temperature adjustments of fusion enthalpies. The equation relies on estimation of the heat capacities of both the solid and liquid phases at $T/K = 298.15$ by group additivity. For 1-adamantylamine, the heat capacity has been measured experimentally as $266 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$. This value can be compared to $210 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$, estimated by group additivity for the crystalline phase and $294.6 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ estimated for the liquid at $T/K = 298.15$. As noted above, the powder pattern of 1-adamantylamine suggests 50% crystallinity. The estimated value in this case is significantly different from the experimental value which is nearly midway between the value predicted for the solid and liquid phases of 1-adamantylamine. For comparison, Table 11 lists estimated and experimental heat capacities of some other polycyclic compounds of similar structure. Adamantane exhibits a substantial phase transition below room temperature but is sufficiently crystalline for X-ray analysis. Single crystal data suggests a disordered structure.³² *endo*-Tricyclo[5.2.1.0^{2,6}]decane, whose crystal structure is not available, also exhibits a substantial phase transition below room temperature, whereas the phase transitions exhibited by the two adamantanols occur

above $T/K = 298.15$, and hexamethylenetetramine does not appear to exhibit any solid–solid phase transitions. The heat capacities of all these compounds are well reproduced by estimation. The discrepancy in $C_p(\text{cr})(298.15 \text{ K})$ observed for 1-adamantylamine suggests either greater motion and/or disorder in the solid state as compared to *endo*-tricyclo[5.2.1.0^{2,6}]decane, or the group value used for a solid aliphatic primary amines needs re-evaluation. The current group value was evaluated on the basis of 38 entries, all of which were either amino acids or aromatic amines, all of which were effectively modeled with the current value for a primary amine.²³ In addition to 1-adamantylamine, 6-aminohexanol appears to be the only other solid primary aliphatic amine to our knowledge whose $C_p(\text{cr})(298.15 \text{ K})$ has been measured.³³ The heat capacity reported, $230 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ compares with an estimated value of $207 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$. While the estimated value is some $23 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ lower than the value reported, this result is within 10% of the experimental value and not sufficient to justify adjustment of the current value at the present time. Consequently, temperature adjustments of the fusion enthalpies to $T/K = 298.15$ of 1-adamantylamine used the experimental heat capacity for the solid while similar adjustments for 1-dodecanamine, and 1-tetradecanamine used estimated values. All $C_p(\text{l})$ values were estimated. The results are summarized in Table 12. Uncertainties for the fusion enthalpies of 1-dodecanamine and 1-tetradecanamine are not available.³³ Although a slightly negative fusion enthalpy is calculated for 1-adamantylamine at $T/K = 298.15$, taking into account the uncertainty in the temperature adjustment, a possible fusion enthalpy of up to $1.5 \text{ kJ}\cdot\text{mol}^{-1}$ is still consistent with the temperature adjustments.³⁴

4.4. Sublimation Enthalpies. The sublimation enthalpy is related to the vaporization enthalpy and fusion enthalpy by eq 14 provided that both enthalpies are adjusted to the same temperature, T .

$$\Delta_{\text{cr}}^{\text{H}}(T) = \Delta_{\text{f}}^{\text{H}}(T) + \Delta_{\text{cr}}^1H(T) \quad (14)$$

Combining the fusion enthalpies adjusted to $T/K = 298.15$ with the vaporization enthalpies from Table 7, the sublimation enthalpies calculated for the three solid amines are summarized

Table 13. Solid Vapor Pressures

T/K	1-adamantylamine $p_{(cr)}/\text{Pa}^a$	1-adamantylamine $p_{(cr)}/\text{Pa}$ (lit) ^b	1-dodecanamine $p_{(cr)}/\text{Pa}^c$	1-tetradecanamine $p_{(cr)}/\text{Pa}^c$
298.15	11.5 ± 2.1		1.6 ± 0.1	0.12 ± 0.04
293.6	8.0 ± 1.6	7.8 (KE)		
297.1	10.6 ± 2.0	10.7 (T)		

^aVapor pressures calculated from runs 3 and 4, 5 and 6, and 7 and 8, respectively; the uncertainty represents two standard deviations of the results. ^bKE, Knudsen effusion; T, transpiration, ref 10. ^cVapor pressures calculated from runs 3 and 4 and 7 and 8, respectively; the same value resulted from both runs.

in the last column of Table 12. Of the three primary amines, the sublimation enthalpy of only 1-adamantylamine has been measured. Combined with a possible fusion enthalpy of up to 1.5 kJ·mol⁻¹ results in a sublimation enthalpy of $\sim 61.4 \pm 3.5$ kJ·mol⁻¹, in good agreement with the experimental sublimation enthalpy of (61.7 ± 0.6) kJ·mol⁻¹.¹⁰ Sublimation enthalpies of 118.3 ± 1.8 and 134.5 ± 2.1 kJ·mol⁻¹ at $T/K = 298.15$ are calculated for 1-dodecanamine and 1-tetradecanamine, respectively by combining the vaporization enthalpies measured in this work with fusion enthalpies available in the literature and adjusted subsequently for temperature.

4.5. Sublimation Vapor Pressures. As an independent check on the validity of both the vapor pressures evaluated for 1-adamantylamine, and its fusion enthalpy, it is also possible to evaluate the vapor pressure of the solid material and compare it to literature values. The constants for eq 3 reported in Table 9 for all three sets of runs were used to independently calculate the vapor pressures of 1-adamantylamine over a $T/K = 30$ range centered at $T_{\text{fus}}/K = 477.4$. The Clausius–Clapeyron equation was then used to calculate the vaporization enthalpy for each set of runs. A mean value for $\Delta_{\text{cr}}^{\text{g}}H(T_{\text{fus}})$ of (43.8 ± 0.6) kJ·mol⁻¹ was calculated. The vaporization enthalpy from each set of runs was then combined with the fusion enthalpy of (7.3 ± 0.2) kJ·mol⁻¹ resulting in a mean value for $\Delta_{\text{cr}}^{\text{g}}H(T_{\text{fus}})$ of (51.1 ± 0.7) kJ·mol⁻¹. Using the vapor pressure calculated by eq 3 at $T_{\text{fus}}/K = 477.4$, used to approximate the triple point, a second application of the Clausius–Clapeyron equation modified by including a heat capacity adjustment term for the sublimation enthalpy, eqs 15 and 16, resulted in a mean vapor pressure of the solid phase at $T/K = 298.15$ of 11 ± 1 Pa.^{31,14} The individual vapor pressures resulting from each set of runs are listed in Table 13. As summarized in Table 13, the literature value measured by Knudsen effusion at $T/K = 293.6$ is 7.5 Pa and compares with a value of (8.1 ± 0.7) Pa obtained using eq 15; the vapor pressure evaluated by transpiration at $T/K = 297.1$ is reported as 10.7 Pa and the value obtained in this work is (10.8 ± 0.8) Pa. Despite our initial concern regarding the use of 1-adamantylamine as a standard, the results from previous work reported by Bazyleva et al.¹⁰ are totally consistent with our own and the agreement observed serves as a form of validation of our own results.

$$\ln(p_{298}/\text{Pa}) = [\Delta_{\text{cr}}^{\text{g}}H(T_{\text{fus}}) + \Delta_{\text{cr}}^{\text{g}}C_p\Delta T] \\ [1/T_{\text{fus}}/K - 1/298.15]/R + \ln(p_{477}/\text{Pa}) \quad (15)$$

where

$$\Delta_{\text{cr}}^{\text{g}}C_p\Delta T = [0.75 + 0.15C_p(\text{cr})][(T_{\text{fus}}/K - 298.15)/2] \quad (16)$$

Application of the same protocol resulted in solid vapor pressures of 1.6 and 0.12 Pa for 1-dodecanamine and 1-tetradecanamine, respectively. Although vapor pressures for the solid phase of these materials are not available, the agreement

observed above for 1-adamantylamine suggests that these results are likely to be reliable as well. Application of this protocol to a variety of other organic compounds have reproduced vapor pressures measured by other means well within a factor of 3.^{14,31} As suggested by this study and others,^{14,35,36} the accuracy of this protocol is very likely related to the quality of data available and the appropriateness of the compounds chosen as standards.

■ ASSOCIATED CONTENT

📄 Supporting Information

Tables of the experimental retention times for runs 1 to 8, tables of correlation between $\ln(t_o/t_a)$ and literature $\ln(p/p_o)$ values. For runs 5 and 6 and 7 and 8 vapor pressure parameters for all runs described in the text, powder X-ray pattern and other details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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