

Hypothetical Thermodynamic Properties. Subcooled Vaporization Enthalpies and Vapor Pressures of Polyaromatic Heterocycles and Related Compounds

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The vaporization enthalpies and vapor pressures of the liquid phase from $T = 298.15$ K to $T = 500$ K of a series of polyaromatic nitrogen heterocycles (PANH) have been derived using correlation gas chromatography. The vaporization enthalpies at $T = 298.15$ K measured in kilojoules per mole include: tri-*n*-butylamine (62.7 ± 1.3), 2-phenylpyridine (68.4 ± 1.9), 3-phenylpyridine (68.4 ± 1.6), quinazoline (58.9 ± 2.0), (–)-nicotine (63.9 ± 2.1), 4-phenylpyrimidine (68.8 ± 2.5), 2,2-dipyridine (67.0 ± 2.3), 2,4-dipyridine (70.9 ± 1.6), 4,4-dipyridine·1.7H₂O (70.7 ± 2.4), 4,4-dipyridine (anhydrous, 71.1 ± 2.6), 1,7-phenanthroline (79.4 ± 4.7), 4,7-phenanthroline (80.8 ± 4.8), 2-benzylpyridine (69.8 ± 2.8), and 9-methylcarbazole (79.4 ± 3.2). Fusion enthalpies ($\text{kJ}\cdot\text{mol}^{-1}$, T_{fus}/K) are also reported for 2,4-bipyridine (17.4 ± 0.4 , 332.8), 4,4-dipyridine (16.1 ± 1.0 , 377.5), 4,4-dipyridine·1.7H₂O (35.5 ± 0.5 , 341.3), 4-phenylpyrimidine (18.8 ± 0.3 , 334.1), 1,7-phenanthroline (18.2 ± 0.3 , 350.3), and 4,7-phenanthroline (21.8 ± 0.5 , 445.5). Vaporization enthalpy comparisons are made with available literature values by means of a thermochemical cycle; agreement is within the combined experimental uncertainties for all compounds except 4,4-dipyridine, for which evidence is provided that suggests that the current sublimation enthalpy value in the literature was measured on a hydrated form. Vapor pressures and normal boiling temperatures for the liquid phase are compared with available experimental literature values at elevated temperatures. Good agreement is found for most compounds.

Introduction

Polyaromatic hydrocarbons (PAHs) are an important group of environmental contaminants that are produced by a variety of incomplete combustion processes. Their heterocyclic nitrogen relatives, PANH, are also found environmentally in heavy petroleum. A significant amount of quality data have been reported on the thermodynamic properties of pyridine and its derivatives as a consequence of the increased demand for fuel, the subsequent use of heavier feedstocks, and the need to hydrodenitrogenate these feedstocks to meet current environmental requirements.¹ Far less data are available on the corresponding triazine, pyrazine, pyrimidine, and pyridazine derivatives. Recently we have reported on the vapor pressures and vaporization enthalpies of the parent heterocycles, 1,3,5-triazine, pyrazine, pyrimidine, and pyridazine, using correlation gas chromatography.² This work demonstrated that pyridine derivatives can serve as suitable reference standards for 1,3,5-triazines, pyrazines, and pyrimidines but were not suitable as reference standards for pyridazines. This article reports the vapor pressures and vaporization enthalpies of a series of aromatic heterocyclic tertiary amines, most of which have not been previously reported using a series of pyridine and its derivatives as standards.

The compounds whose vapor pressures and vaporization enthalpies have been evaluated in this study include 2- and 3-phenylpyridine, 2,2- and 4,4-bipyridine, quinazoline, (–)-nicotine, 2-benzylpyridine, 9-methylcarbazole, 4-phenylpyrimidine, and 1,7- and 4,7-phenanthroline. The structures of both the compounds used as standards and those evaluated are illustrated in Figure 1. Previous work on the phenylpyridine

isomers demonstrated that hydrocarbons can be used as standards for tertiary amines.³ In this previous study, however, the vapor pressures of the phenylpyridines were not evaluated. This current study reports both vaporization enthalpies and liquid vapor pressures for 2- and 3-phenylpyridines using heterocyclic amines as standards. (–)-Nicotine and 9-methylcarbazole both contain an aliphatic tertiary nitrogen atom. As a test on how well pyridine derivatives can serve as standards for aliphatic tertiary amines, the vaporization enthalpy and vapor pressure of tri-*n*-butylamine were also evaluated and the results compared with literature values.

A number of the materials studied are crystalline solids. Vaporization enthalpies of crystalline materials are also quite useful. Despite their hypothetical nature, vaporization enthalpies evaluated at $T = 298.15$ K when combined with fusion enthalpies can provide reasonable values for sublimation enthalpies, particularly for compounds that may be too nonvolatile to be measured by conventional methods but survive passage through a gas chromatograph.⁴ Since sublimation enthalpies of a few of the materials included in this study have been previously measured by other methods, the combination of fusion and vaporization enthalpies can provide additional validation of this work or identify sublimation enthalpy values that may be suspect.⁵ Examples of both of these circumstances are reported below.

Gas chromatography has been used in various ways to obtain vaporization enthalpies and vapor pressures of the subcooled liquid. Most of our previous work reported has been on hydrocarbons. Our group has been promoting correlation gas chromatography as a simple and reliable manner in which vapor pressures and vaporization enthalpies of the subcooled liquid can be derived.^{4,6,7} Since each analyte

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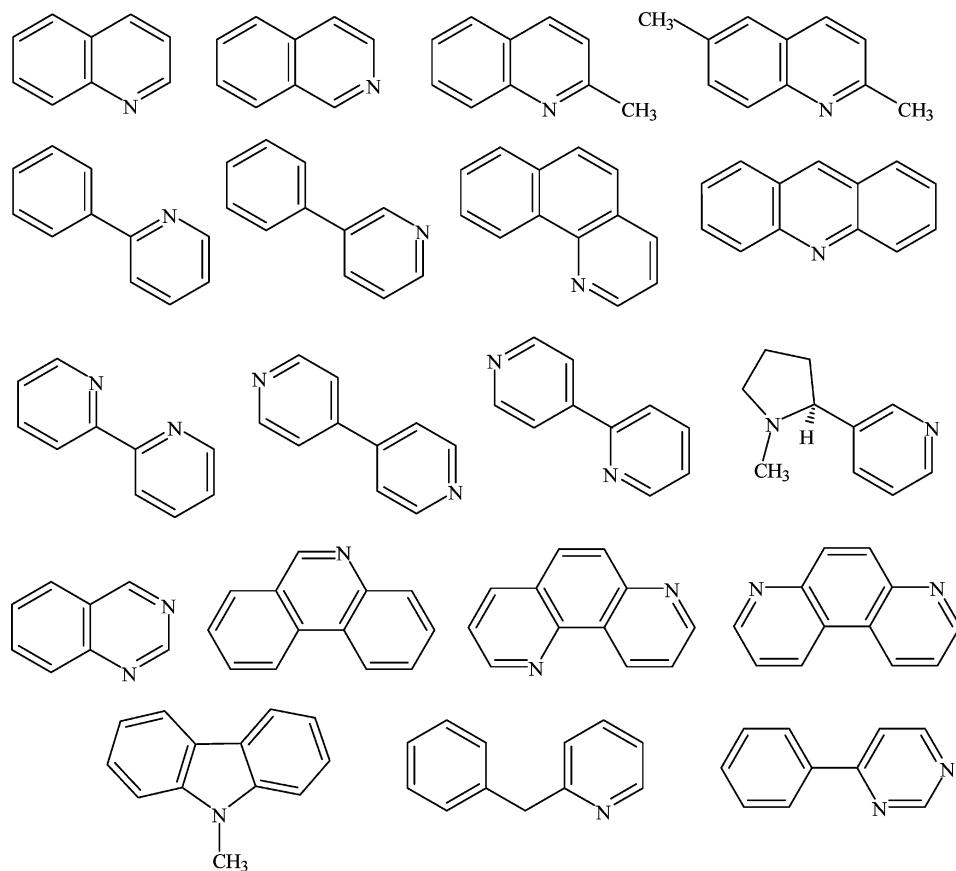


Figure 1. Structures of the standards and compounds investigated. From left to right, top to bottom: quinoline, isoquinoline, quinaldine, 2,6-dimethylquinoline, 2-phenylpyridine, 3-phenylpyridine, 7,8-benzoquinoline, acridine, 2,2-bipyridine, 4,4-bipyridine, 2,4-bipyridine, (–)-nicotine, quinazoline, phenanthridine, 1,7-phenanthroline, 4,7-phenanthroline, 9-methylcarbazole, 2-benzylpyridine, and 4-phenylpyrimidine.

gets adsorbed on the column and moves on the column according to its vapor pressure off the column, measurement of the temperature dependence of its elution time provides a convenient measure of the interaction of the analyte with the column. The magnitude of this interaction energy, referred to as the enthalpy of transfer from the stationary phase of the column to the gas phase, $\Delta_{\text{sln}}^{\text{g}}H_{\text{m}}(T_{\text{m}})$, is due mainly to the vaporization enthalpy of the compound. By using a series of standards with known vaporization enthalpies, the linear correlation observed between vaporization enthalpy and enthalpy of transfer provides a means of evaluating vaporization enthalpies of compounds also included in the mixture whose enthalpies of transfer can be measured but whose vaporization enthalpies are unknown. For compounds containing functional groups, it is generally necessary to include as standards compounds with similar functionality. Hydrocarbons have previously been demonstrated to act as suitable standards for tertiary amines.³ However, the best results are usually obtained when the standards are structurally more closely related to the compounds under evaluation. For the evaluation of vapor pressure, a similar linear relationship exists between the logarithm of vapor pressure and the corresponding logarithm of adjusted retention time as described below, presumably for the same reasons as why enthalpies correlate with each other.

A plot of $\ln(t_{\text{o}}/t_{\text{a}})$ versus $1/T$ over a $T = 30$ K range results in a linear relationship with the slope of the line equal to $-\Delta_{\text{sln}}^{\text{g}}H_{\text{m}}(T_{\text{m}})/R$ where R is the gas constant. The term t_{o} is a reference time, 1 min, and t_{a} represents the adjusted retention time. The adjusted retention time of an analyte is evaluated as the difference between the actual retention time

measured and the retention time of a reference that is not retained by the column. At elevated temperatures, this is usually the solvent or an added gas such as methane. A correlation coefficient (r^2) of less than 0.99 is usually indicative of some retention on the column of the nonretained reference. Additionally, $\ln(t_{\text{o}}/t_{\text{a}})$ of each analyte has also been found to correlate linearly with the logarithm of the vapor pressure of the liquid phase of each analyte, $\ln(p/p_{\text{o}})$ at a given temperature.^{4,6,7} The term p_{o} refers to a reference pressure; often $p_{\text{o}} = 101.325$ kPa. Thus the same series of experiments can be used to evaluate vapor pressures if the mixture also contains components with known vapor pressures.

Experimental Section

All compounds used in the vaporization enthalpy study were obtained from various commercial sources and used as purchased. All were analyzed by gas chromatography and most found to have purities of 98 % or better. Since all were analyzed as mixtures which are separated by the chromatography, the initial purity of these materials is not as critical as in studies where the thermochemical properties are highly dependent on purity. Correlation gas chromatography experiments were performed on two different HP 5890 Gas Chromatographs equipped with split/splitless capillary injection ports and flame ionization detectors at a split ratio of approximately 100/1. Retention times were recorded to three significant figures following the decimal point using an HP 3396 Series III integrator or on an HP Chemstation. The compounds were run isothermally on 30 m SPB 5 columns. While enthalpies of transfer do depend on the nature of the column used, the results

Table 1. Vaporization Enthalpies in the Literature

compound [lit.]	$\Delta_f^\circ H_m(T_m/K)$ kJ·mol ⁻¹	T_m K	C_{pl} J·mol ⁻¹ ·K ⁻¹	$\Delta_f^\circ H_m(298.15\text{ K})$ kJ·mol ⁻¹ (calcd ^e)	$\Delta_f^\circ H_m(298.15\text{ K})$ kJ·mol ⁻¹ (lit.)	ref
tri- <i>n</i> -butylamine	62.75	318	413.8	65.0		9
	48.14	410	413.8	61.4		9
	49.3	447	413.8	66.9		10
quinoline					59.31 ± 0.2	11
isoquinoline					60.26 ± 0.12	11
quinaldine					62.64 ± 0.13	12
(<i>dl</i>)-nicotine ^b	50.5	463	285	64.5		9
nicotine ^b	53.1 ± 0.4	446	285	65.7 ± 2.7		13
nicotine ^b					67.4 ± 0.3 ^{c,d}	14
2,6-dimethylquinoline					67.07 ± 0.16	16
7,8-benzoquinoline	72.99 ± 0.3	360	278.1	78.11 ± 1.0	77.23 ^d	17
phenanthridine	74.31 ± 0.2	380	278.1	81.09 ± 1.3	80.14 ^d	17
acridine	72.94 ± 0.1	380	278.1	79.72 ± 1.3	78.63 ^d	17
2-phenylpyridine					68.7 ± 4.6	3
3-phenylpyridine					67.4 ± 4.5	3
9-methylcarbazole					81.1 ± 0.3 ^d	21

^a Literature data adjusted to $T = 298.15\text{ K}$ using eq 2. ^b Chirality not specified. ^c Calculated from the parameters of the Cox equation using data from ref 15 as reported by Basarova et al.¹⁵ ^d Calculated from the slope of the line by plotting $\ln(p)$ vs $1/T$ using extrapolating vapor pressures calculated from either the Cox or Wagner equations at a mean temperature of $T = 298.15\text{ K}$ using the parameters of Table 2A or 2B as described in the text.

Table 2. Parameters (A) of the Cox Equation Used as Standards and for Reference Parameters (B) of the Wagner Equation, and (C) of the Antoine Equation

(A)	A_0	A_1 T^{-1}	$A_2 \cdot 10^7$ T^{-2}	T_b K	range K		
Cox equation ^f							
quinoline ¹¹	2.85461	-0.00130236	9.3118	510.298	298 to 559		
isoquinoline ¹¹	2.85183	-0.00126768	8.8569	516.391	313 to 566		
acridine ¹⁷	2.89594	-0.00111538	6.486	618.059	383 to 637		
phenanthridine ¹⁷	2.90928	-0.00113569	6.7834	623	383 to 473		
7,8-benzoquinoline ¹⁷	2.88454	-0.00111802	6.6824	614.49	373 to 662		
9-methylcarbazole ^{21,b}	2.94053	-0.73537	2679200	616.966	362 to 890		
(B)	A_w	B_w	C_w	D_w	T_c K	p_c kPa	range /K
Wagner equation ^f							
quinaldine ¹²	-8.370206	2.914441	-3.761685	-3.195981	778	4030	320 to 570
2,6-dimethylquinoline ¹⁶	-8.993312	3.594873	-4.63173	-2.907492	786	3480	337 to 592
nicotine ^{15,d}	-8.83376	3.40331	-5.13787	-6.91787	756.3	3059	300 to 520
(C)	A	B	C	range K			
Antoine equation							
tri- <i>n</i> -butylamine ^{9,e}	4.96696	1088.83	-134.511	298 to 337			
tri- <i>n</i> -butylamine ^{9,e}	7.169	2515	0	333 to 487			
tri- <i>n</i> -butylamine ^{10,f}	16.2878	3865.58	-86.15	362 to 531			
(<i>dl</i>)-nicotine ^{9,e}	5.91387	1650.347	-96.779	406 to 520			

^a $p_0 = 101.325\text{ kPa}$. ^b Calculated from the Cox equation in the form: $\ln(p/p_0) = [1 - 1/(T/T_b)]\exp[A_0 + A_1(T/T_b) + A_2(T/T_b)^2]$. ^c $T_r = T/T_c$. ^d Stereochemistry not specified. ^e $\log(p) = A - B/(T + C)$, $p = \text{kPa}$. ^f $\ln(p) = A - B/(T + C)$, $p = \text{mm Hg}$.

following the correlation remain independent of the nature of the column within the reproducibility of the results. Helium was used as the carrier gas. At the temperatures of the experiments, the retention time of methane or of the solvents used, cyclopentane or cyclohexane, generally increased with increasing temperature. This is a consequence of the increase in viscosity of the carrier gas with temperature; it is the criterion that has been used to confirm that the reference was not being retained on the column. The retention time of the reference was used to determine the dead volume of the column. 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, generally over a 30 K range. Column temperatures were controlled by the gas chromatograph and were monitored independently by using a Fluke digital thermometer. Temperature maintained by the gas chromatograph was constant to $\pm 0.1\text{ K}$. Enthalpies of transfer were calculated as the negative product of the slope of the line obtained by plotting $\ln(t_0/t_a)$ vs $1/T$ and the gas constant, R . All plots of $\ln(t_0/t_a)$ vs $1/T$, where $t_0 = 1\text{ min}$, were characterized

by correlation coefficients, r^2 , > 0.99 . Unless noted otherwise, $p_0 = 101.325\text{ kPa}$. The retention times measured for all analytes are reported in the Supporting Information. The uncertainties ($\pm \sigma$) reported in the last column of Tables 3, 7, and 12 were calculated from the uncertainty in the slope and intercept of the equations listed at the bottom of each respective table. These uncertainties reflect the potential error in the absolute value of the vaporization enthalpy.

Fusion enthalpies were measured on a Perkin-Elmer DSC-7. Each fusion enthalpy reported is the mean of three measurements. Sample sizes varied from (8 to 11) mg of sample. Each was hermetically sealed in aluminum pans. The calibration of the instrument was checked using indium. Uncertainties are reported as two standard deviations. Fusion enthalpies were measured on commercial samples, purchased from Aldrich Chemical Co. with the following purities: 2,2-dipyridine, 99 %; 4,4-dipyridine·H₂O, 98 %; 4,4-dipyridine (anhydrous), 98 %; 4-phenylpyrimidine, 96 %; 4,7-phenanthroline, 98 %; 1,7-phenanthroline, 99 %. Anhydrous 2,4-dipyridine, 97 %, was purchased from Alpha Aesar. Analysis

by gas chromatography (FID detection) confirmed the analyses of the commercial samples as minimum purities. Excluding water, analysis of the volatile components in all the samples, including 4-phenylpyrimidine, resulted in purities of 98.8+ %. No transitions other than melting were observed for all materials examined over the temperature range $T = 305$ K to T_{fus} except for 4,4-dipyridine and its hydrate. The results for 4,4-dipyridine and 4,4-dipyridine·H₂O are discussed in the text. The crystal structure of dipyridine·2H₂O has been reported, but apparently it decomposes rather quickly at room temperature to an amorphous powder according to X-ray powder diffraction.⁸ The water content in the 4,4-dipyridine·H₂O sample was determined by integration of the ¹H NMR spectrum on a Bruker 300 MHz instrument in deuteriochloroform. Both DSC and NMR detected a small amount of water in the anhydrous form. The ratio of water to 4,4-dipyridine in the hydrated form was approximately 1.7/1.

Vapor Pressures and Vaporization Enthalpies

Vaporization enthalpies of all the standards and compounds used for comparison at $T = 298.15$ K are reported in Table 1. Vaporization enthalpies for tri-*n*-butylamine were calculated from three sets of vapor pressure data reported in the literature, all of which were calculated from the Antoine constants at the mean temperature of measurement using eq 1.^{9,10} Temperature adjustments to $T = 298.15$ K were performed using eq 2.¹⁸ The C_{pl} term in eq 2 refers to the heat capacity at $T = 298.15$ K and was estimated by group additivity.¹⁹ The vaporization enthalpies of acridine and 7,8-benzoquinoline are available at $T = (380 \text{ and } 360)$ K, respectively; these values were also adjusted to $T = 298.15$ K using eq 2 and are reported in column 5 of Table 1. In these cases, the vapor pressures, reported from $T = (383 \text{ to } 637)$ K for acridine and $T = (373 \text{ to } 672)$ K for 7,8-benzoquinoline, are available in the form of the Cox equation, eq 3. Since the Cox equation is known to extrapolate reasonably well over a limited temperature range, vapor pressures were first extrapolated and then fit to the Clausius–Clapeyron equation over the temperature range $T = (283 \text{ to } 313)$ K to provide a mean value at $T = 298.15$ K. The resulting vaporization enthalpies are reported in the sixth column of Table 1. These values are in good agreement with the values calculated using eq 2. Since the vapor pressures of acridine and 7,8-benzoquinoline calculated from the Cox equation were the values used in subsequent vapor pressure correlations, the vaporization enthalpy values reported in column 6, Table 1, were the vaporization enthalpy standards used in all subsequent correlations. Vapor pressures for nicotine have been measured by Lencka et al.¹⁴ and made available in the form of the Wagner equation (eq 4) from $T = (300 \text{ to } 520)$ K by Basarova et al.¹⁵ A similar extrapolation and calculation was performed for nicotine to provide a vaporization enthalpy at $T = 298.15$ K; this is reported as the third nicotine entry in Table 1. The resulting vaporization enthalpies calculated at $T = 298.15$ K are also shown in columns 5 and 6 of Table 1. Vaporization enthalpies derived from both methods are in reasonable agreement with each other. Two of the three literature values reported for nicotine do not indicate which form, chiral or racemic, was measured. In the third case, the report indicated that the measurements were reported on the racemic form.⁹ In view of the ambiguity in stereochemistry, (–)-nicotine was treated as an unknown in this work. Parameters of the Cox (eq 3), Wagner (eq 4),

and Antoine (Table 2, footnote e and f) equations used to calculate vapor pressures of all the standards are reported in Table 2A to 2C.

$$\Delta_1^{\text{g}}H_{\text{m}}(T_{\text{m}}) = 2.303RB[T_{\text{m}}/(T_{\text{m}} + C)]^2 \quad (1)$$

$$\Delta_1^{\text{g}}H_{\text{m}}(298.15 \text{ K})/\text{kJ} \cdot \text{mol}^{-1} = \Delta_1^{\text{g}}H_{\text{m}}(T_{\text{m}}) + [(10.58 + 0.26C_p(1))(T_{\text{m}} - 298.15 \text{ K})]/1000 \quad (2)$$

$$\ln(p/p_o) = (1 - T_b/T)\exp(A_o + A_1(T/K) + A_2(T/K)^2) \quad (3)$$

$$\ln(p/p_c) = (1/T_r)[A_w(1 - T_r) + B_w(1 - T_r)^{1.5} + C_w(1 - T_r)^{2.5} + D_w(1 - T_r)^5] \quad (4)$$

Results

To test how well aromatic nitrogen compounds can serve as standards for tertiary aliphatic amines, a mixture of several aromatic heterocyclic compounds was used to evaluate the vaporization enthalpy of tri-*n*-butylamine. Also included as unknowns were 2- and 3-phenylpyridine. The latter two compounds were included since previous measurements of these compounds by correlation gas chromatography did not evaluate their vapor pressures and included several aromatic hydrocarbons as standards. It was of some interest to determine the consistency in values evaluated using only aromatic heterocyclic amines as standards.

This concern over the proper choice of standards arose when it was observed that pyridine and its derivatives, appropriate and successful standards for the evaluation of pyrazines, pyrimidines, and 1,3,5-triazines, appeared to be unsuccessful in the evaluation of these properties in pyridazine and its derivatives as noted above.² Since 2- and 3-phenylpyridine have similar retention times, duplicate runs of two separate mixtures were evaluated. The results of four runs are reported in Table 3. The correlations between enthalpies of transfer and vaporization enthalpies are provided below each run in Table 3 as eqs 5 to 8.

The results of the four experiments are summarized in Table 4. The vaporization enthalpies for tri-*n*-butylamine fall in between the three literature values. Given the large temperature adjustment necessary for two of the three measurements reported in Table 1, agreement between the different sets of measurements in Table 4 can be considered reasonably satisfactory. Similarly, the vaporization enthalpies measured for 2- and 3-phenylpyridine are within the experimental uncertainties reported previously. As might be expected, the use of aromatic heterocyclic amine standards instead of aromatic hydrocarbons provided somewhat better correlations, as indicated by a comparison of the relative uncertainties obtained by the two sets of measurements. In subsequent correlations that use 2-phenylpyridine and/or tri-*n*-butylamine as standards, the values evaluated by this work were used. The mean values of the vaporization enthalpies derived for the compounds used as standards in these correlations are also reported in this instance for comparison of reproducibility and congruence with literature values. These values are reported in italics in Table 4.

As a test of how well the slopes and intercepts obtained from the gas chromatographic retention times are capable of reproducing experimental vapor pressures, values of $\ln(t_r/t_s)$ calculated from the slopes and intercepts of Table 3 were correlated with $\ln(p/p_o)$ values calculated from the Cox and Wagner equations. Vapor pressures near ambient temperatures were extrapolated values in some cases. The correlation obtained at

Table 3. Vaporization Enthalpies Results of Runs 1 to 4

run 1	slope		$\Delta_{\text{sln}}^{\text{g}}H_{\text{m}}(439 \text{ K})$	$\Delta_{\text{l}}^{\text{g}}H_{\text{m}}(298.15 \text{ K})$	$\Delta_{\text{l}}^{\text{g}}H_{\text{m}}(298.15 \text{ K})$
	T/K	intercept	$\text{kJ}\cdot\text{mol}^{-1}$	$\text{kJ}\cdot\text{mol}^{-1}$ (lit.)	$\text{kJ}\cdot\text{mol}^{-1}$ (calcd)
tri- <i>n</i> -butylamine	-5076.2	11.583	42.202		62.7 ± 1.6
quinoline	-4760.6	10.455	39.578	59.31	59.5 ± 1.5
isoquinoline	-4819.4	10.487	40.067	60.26	60.1 ± 1.5
quinaldine	-5079.8	10.892	42.231	62.64	62.7 ± 1.6
2,6-dimethylquinoline	-5506.5	11.385	45.779	67.07	67.1 ± 1.7
2-phenylpyridine	-5636.3	11.517	46.858		68.4 ± 1.8

$$\Delta_{\text{l}}^{\text{g}}H_{\text{m}}(298.15 \text{ K})/\text{kJ}\cdot\text{mol}^{-1} = (1.225 \pm 0.038)\Delta_{\text{sln}}^{\text{g}}H_{\text{m}}(439 \text{ K}) + (10.96 \pm 0.18) \quad r^2 = 0.9981 \quad (5)$$

run 2	slope		$\Delta_{\text{sln}}^{\text{g}}H_{\text{m}}(439 \text{ K})$	$\Delta_{\text{l}}^{\text{g}}H_{\text{m}}(298.15 \text{ K})$	$\Delta_{\text{l}}^{\text{g}}H_{\text{m}}(298.15 \text{ K})$
	T/K	intercept	$\text{kJ}\cdot\text{mol}^{-1}$	$\text{kJ}\cdot\text{mol}^{-1}$ (lit)	$\text{kJ}\cdot\text{mol}^{-1}$ (calcd)
tri- <i>n</i> -butylamine	-5300.3	12.099	44.065		62.6 ± 1.8
quinoline	-4984.6	10.971	41.440	59.31	59.4 ± 1.7
isoquinoline	-5046	11.009	41.950	60.26	60.0 ± 1.7
quinaldine	-5317.3	11.439	44.206	62.64	62.8 ± 1.8
2,6-dimethylquinoline	-5738.2	11.918	47.705	67.07	67.0 ± 2.0
3-phenylpyridine	-5878.5	12.074	48.872		68.4 ± 2.0

$$\Delta_{\text{l}}^{\text{g}}H_{\text{m}}(298.15 \text{ K})/\text{kJ}\cdot\text{mol}^{-1} = (1.213 \pm 0.041)\Delta_{\text{sln}}^{\text{g}}H_{\text{m}}(439 \text{ K}) + (9.17 \pm 0.20) \quad r^2 = 0.9977 \quad (6)$$

run 3	slope		$\Delta_{\text{sln}}^{\text{g}}H_{\text{m}}(440 \text{ K})$	$\Delta_{\text{l}}^{\text{g}}H_{\text{m}}(298.15 \text{ K})$	$\Delta_{\text{l}}^{\text{g}}H_{\text{m}}(298.15 \text{ K})$
	T/K	intercept	$\text{kJ}\cdot\text{mol}^{-1}$	$\text{kJ}\cdot\text{mol}^{-1}$ (lit)	$\text{kJ}\cdot\text{mol}^{-1}$ (calcd)
tri- <i>n</i> -butylamine	-5023.8	11.54	41.766		62.6 ± 0.9
quinoline	-4706.2	10.408	39.126	59.31	59.5 ± 0.9
isoquinoline	-4766.5	10.444	39.627	60.26	60.1 ± 0.9
quinaldine	-5034.7	10.866	41.857	62.64	62.7 ± 0.9
2,6-dimethylquinoline	-5456.4	11.346	45.362	67.07	67.0 ± 1.0
2-phenylpyridine	-5590.8	11.487	46.480		68.3 ± 1.0
7,8-benzoquinoline	-6532.3	12.259	54.307	77.23	77.7 ± 1.2
acridine	-6580.3	12.325	54.706	78.63	78.2 ± 1.2

$$\Delta_{\text{l}}^{\text{g}}H_{\text{m}}(298.15 \text{ K})/\text{kJ}\cdot\text{mol}^{-1} = (1.202 \pm 0.022)\Delta_{\text{sln}}^{\text{g}}H_{\text{m}}(440 \text{ K}) + (12.43 \pm 0.36) \quad r^2 = 0.9986 \quad (7)$$

run 4	slope		$\Delta_{\text{sln}}^{\text{g}}H_{\text{m}}(440 \text{ K})$	$\Delta_{\text{l}}^{\text{g}}H_{\text{m}}(298.15 \text{ K})$	$\Delta_{\text{l}}^{\text{g}}H_{\text{m}}(298.15 \text{ K})$
	T/K	intercept	$\text{kJ}\cdot\text{mol}^{-1}$	$\text{kJ}\cdot\text{mol}^{-1}$ (lit)	$\text{kJ}\cdot\text{mol}^{-1}$ (calcd)
tributylamine	-4917.2	11.295	40.880		62.7 ± 1.0
quinoline	-4591.6	10.145	38.173	59.31	59.4 ± 1.0
isoquinoline	-4656.8	10.192	38.715	60.26	60.1 ± 1.0
quinaldine	-4926.6	10.617	40.958	62.64	62.8 ± 1.0
2,6-dimethylquinoline	-5342.5	11.084	44.415	67.07	67.0 ± 1.1
3-phenylpyridine	-5485.5	11.244	45.604		68.5 ± 1.1
7,8-benzoquinoline	-6394.8	11.944	53.164	77.23	77.7 ± 1.3
acridine	-6438.6	12.001	53.528	78.63	78.2 ± 1.3

$$\Delta_{\text{l}}^{\text{g}}H_{\text{m}}(298.15 \text{ K})/\text{kJ}\cdot\text{mol}^{-1} = (1.22 \pm 0.023)\Delta_{\text{sln}}^{\text{g}}H_{\text{m}}(440 \text{ K}) + (12.75 \pm 0.36) \quad r^2 = 0.9985 \quad (8)$$

Table 4. Summary of the Vaporization Enthalpies and Enthalpies of Transfer of Runs 1 to 4

	$\Delta_{\text{l}}^{\text{g}}H_{\text{m}}(298.15 \text{ K})/\text{kJ}\cdot\text{mol}^{-1}$				average ^a	$\Delta_{\text{l}}^{\text{g}}H_{\text{m}}(298.15 \text{ K})$ [lit.]
	run 1	run 2	run 3	run 4		$\text{kJ}\cdot\text{mol}^{-1}$
tri- <i>n</i> -butylamine	62.7	62.6	62.6	62.7	62.7 ± 1.3	65.0; 61.4, 66.9
quinoline	59.5	59.4	59.5	59.4	59.5 ± 1.3	59.31 ± 0.2
isoquinoline	60.1	60.0	60.1	60.1	60.1 ± 1.3	60.26 ± 0.12
quinaldine	62.7	62.8	62.7	62.8	62.8 ± 1.3	62.64 ± 0.13
2,6-dimethylquinoline	67.1	67.0	67.0	67.0	67.0 ± 1.5	67.07 ± 0.16
7,8-benzoquinoline			77.7	77.7	77.7 ± 1.3	78.11 ± 1.0; 77.23
acridine			78.2	78.2	78.2 ± 1.3	79.72 ± 1.3; 78.63
2-phenylpyridine	68.4	68.4			68.4 ± 1.9	68.7 ± 4.6
3-phenylpyridine			68.3	68.5	68.4 ± 1.6	67.4 ± 4.5

^a The uncertainty is the average uncertainty associated with each run as reported in Table 3.

$T = 298.15 \text{ K}$ is illustrated in Table 5 for runs 1 to 4. The correlation is characterized by eq 9 reported below the table.

This process was repeated for each compound over the temperature range $T = 298.15 \text{ K}$ to $T = 500 \text{ K}$ at 10 K intervals

Table 5. Correlation between $\ln(t_o/t_a)$ and $\ln(p/p_o)$ at $T = 298.25$ K for Runs 1 to 4

$T = 298.15$ K	$\ln(t_o/t_a)$				average	$\ln(p/p_o)_{\text{exp}}$	$\ln(p/p_o)_{\text{calc}}$
	run 1	run 2	run 3	run 4			
tri- <i>n</i> -butylamine	-5.44	-5.68	-5.31	-5.2	-5.39	-9.1	-8.95
quinoline	-5.51	-5.75	-5.38	-5.26	-5.46	-9.4	-9.04
isoquinoline	-5.68	-5.92	-5.54	-5.43	-5.62	-9.78	-9.26
quinaldine	-6.15	-6.4	-6.02	-5.91	-6.1	-10.96	-9.89
2,6-dimethylquinoline	-7.08	-7.33	-6.95	-6.83	-7.03	-14.44	-11.13
7,8-benzoquinoline			-9.65	-9.5	-9.57	-14.75	-14.5
acridine			-9.75	-9.59	-9.67		-14.62
2-phenylpyridine	-7.39		-7.26		-7.32		-11.51
3-phenylpyridine		-7.64		-7.15	-7.37		-11.57

$$\ln(p/p_o) = (1.326 \pm 0.034) \ln(t_o/t_a) - (1.80 \pm 0.148) \quad r^2 = 0.9973 \quad (9)$$

Table 6. Constants of Equation 9 and Corresponding Estimated and Experimental Boiling Temperatures Derived from Runs 1 to 4

	A	B	C	D	BT_{calc}^a	BT_{lit}^b
	K^3	K^2	K		K	K
tri- <i>n</i> -butylamine	30767110.1	-712464.53	-3836.038	10.769	481.3	486.2
quinoline	70264429.1	-1071875.28	-2317.095	8.142	509.6	510.3 ^c
isoquinoline	73060204.0	-1098099.34	-2313.099	8.095	515	516.4 ^c
quinaldine	70559084.1	-1076785.25	-2717.977	8.676	521.3	521.2
2,6-dimethylquinoline	77271221.9	-1140593.21	-3053.545	9.029	542.1	540.2
7,8-benzoquinoline	117024769.3	-1520001.94	-3074.300	8.498	615.8	614.5 ^c
acridine	117215491.1	-1521846.26	-3126.912	8.566	617	618.1 ^c
2-phenylpyridine	82334650.2	-1199538.89	-2988.675	8.899	550.2 ^d	543.2 ^d
3-phenylpyridine	78066389.6	-1137160.48	-3293.956	9.322	547.4 ^e	543.2 ^e

^a Calculated boiling temperature using eq 10. ^b Literature boiling temperature from ref 9 unless noted otherwise. ^c See Table 2A. ^d 2007–8 Aldrich Catalog. ^e Boiling temperature at 99.8 kPa, 2007–8 Aldrich Catalog.

(not shown). The resulting $\ln(p/p_o)$ values were then fit to eq 10, resulting in the parameters reported in Table 6.

$$\ln(p/p_o) = A(T/K)^{-3} + B(T/K)^{-2} + C(T/K)^{-1} + D \quad (10)$$

As noted above, three sets of vapor pressure values are available for tri-*n*-butylamine in the form of the Antoine equation over the following range of temperatures: from $T = (298 \text{ to } 337)$ K,⁹ a second from $T = (333 \text{ to } 487)$ K,⁹ and a third from $T = (362 \text{ to } 531)$ K.¹⁰ Vapor pressures reproduced from these equations are reported as solid circles, circles, and squares at 10 K increments in Figure 2. The circles and squares represent vapor pressures calculated from the Antoine equation at temperatures offset by $T = 5$ K. The line represents the results from this study over the same temperature interval calculated using eq 10 and the constants from Table 6. The correlation observed between this work and the literature values appears to improve with increasing temperature.

As a further test of how well vapor pressures calculated by eq 10 are capable of reproducing experimental values, the normal boiling temperatures of all of the compounds involved in the correlation were estimated by extrapolation. The results are compared to experimental values in the last two columns of Table 6. The average absolute deviation is 3.2 K with the largest difference of 7 K measured for 2-phenylpyridine.

The success in using aromatic heterocyclic compounds for reproducing the vaporization enthalpy and vapor pressure of tri-*n*-butylamine encouraged us to evaluate the vaporization enthalpies of a series of other aromatic nitrogen heterocyclic compounds including (-)-nicotine and 9-methylcarbazole, both of which contain a tertiary aliphatic nitrogen atom using the compounds just discussed as standards. With the exception of (-)-nicotine and benzylpyridine which are liquids at ambient temperatures, quinazoline, 2,2-dipyridine, and 4,4-dipyridine·

$x\text{H}_2\text{O}$, 9-methylcarbazole and 1,7- and 4,7-phenanthroline are solids at $T = 298.15$ K. The vaporization enthalpies of these materials at $T = 298.15$ K would correspond to the subcooled liquid and as such are hypothetical thermodynamic properties. While the vaporization enthalpy for 9-methylcarbazole at $T = 298.15$ K has not been reported, critically evaluated vapor pressure data for the liquid form are available at elevated temperatures in the form of the Cox equation.²¹ Extrapolation of the vapor pressures calculated from the Cox equation to a mean temperature of $T = 298.15$ K as described above for acridine and 7,8-benzoquinoline resulted in the vaporization enthalpy reported in the last column of Table 1. As a test of how well the standards chosen were capable of reproducing both vapor pressure and vaporization enthalpy, 9-methylcarbazole was treated as an unknown in these experiments. Additionally, the sample of 4,4-dipyridine in the form of a hydrate was initially examined. Since water does not produce a signal in the FID detector, it was expected that the presence of water in the crystal would not interfere with the retention time of 4,4-dipyridine. As is described below, this was found to be the case. All runs that included 2-phenylpyridine and tri-*n*-butylamine as standards evaluated in this work also included a number of other vaporization enthalpies from the literature.

The results of six additional experiments are reported in Table 7 as runs 5 to 10. The compounds evaluated include quinazoline, (-)-nicotine, 2,2-dipyridine, 4,4-dipyridine·1.7H₂O, 1,7- and 4,7-phenanthroline, 2-benzylpyridine, and 9-methylcarbazole. Equations 11 to 16 describe the correlation measured between enthalpies of transfer of the standards and their corresponding vaporization enthalpies at $T = 298.15$ K. The resulting vaporization enthalpies obtained for duplicate runs are summarized in Table 8. The results are reproducible, and for two of the compounds, (-)-nicotine and 9-methylcarbazole, the results are in good agreement with literature values.

Table 7. Vaporization Enthalpies and Enthalpies of Transfer of Runs 5 to 10

run 5	slope		$\Delta_{\text{sln}}^{\text{g}}H_{\text{m}}(465 \text{ K})$ kJ·mol ⁻¹	$\Delta_{\text{f}}^{\text{g}}H_{\text{m}}(298.15 \text{ K})$ kJ·mol ⁻¹ (lit.)	$\Delta_{\text{f}}^{\text{g}}H_{\text{m}}(298.15 \text{ K})$ kJ·mol ⁻¹ (calcd)
	T/K	intercept			
tri- <i>n</i> -butylamine	-5238.3	11.618	43.549	62.70	62.9 ± 1.7
quinazoline	-4904.9	10.352	40.778		59.3 ± 1.6
(-)-nicotine	-5355.1	10.945	44.520		64.1 ± 1.7
2,6-dimethylquinoline	-5608.4	11.178	46.626	67.07	66.9 ± 1.8
2,2-dipyridine	-5634.4	11.133	46.842		67.1 ± 1.8
2-phenylpyridine	-5746.5	11.309	47.774	68.40	68.3 ± 1.9
4,4-dipyridine·1.7H ₂ O	-5980.4	11.535	49.719		70.8 ± 1.9
7,8-benzoquinoline	-6624.8	11.892	55.076	77.23	77.7 ± 2.1
acridine	-6672.3	11.953	55.471	78.63	78.2 ± 2.2

$$\Delta_{\text{f}}^{\text{g}}H_{\text{m}}(298.15 \text{ K})/\text{kJ} \cdot \text{mol}^{-1} = (1.287 \pm 0.038)\Delta_{\text{sln}}^{\text{g}}H_{\text{m}}(465 \text{ K}) + (6.85 \pm 0.41) \quad r^2 = 0.9974 \quad (11)$$

run 6	slope		$\Delta_{\text{sln}}^{\text{g}}H_{\text{m}}(464 \text{ K})$ kJ·mol ⁻¹	$\Delta_{\text{f}}^{\text{g}}H_{\text{m}}(298.15 \text{ K})$ kJ·mol ⁻¹ (lit.)	$\Delta_{\text{f}}^{\text{g}}H_{\text{m}}(298.15 \text{ K})$ kJ·mol ⁻¹ (calcd)
	T/K	intercept			
tri- <i>n</i> -butylamine	-5272.4	11.686	43833	62.70	63.2 ± 2.5
quinazoline	-4830.0	10.178	40154		58.5 ± 2.3
(-)-nicotine	-5315.7	10.850	44192		63.7 ± 2.5
2,6-dimethylquinoline	-5578.9	11.105	46380	67.07	66.5 ± 2.7
2,2-dipyridine	-5612.1	11.076	46657		66.9 ± 2.7
2-phenylpyridine	-5741.6	11.290	47733	68.40	68.3 ± 2.7
4,4-bipyridine·1.7H ₂ O	-5961.6	11.486	49562		70.6 ± 2.8
7,8-benzoquinoline	-6631.0	11.898	55128	77.23	77.8 ± 3.1
acridine	-6675.0	11.951	55493	78.63	78.3 ± 3.2

$$\Delta_{\text{f}}^{\text{g}}H_{\text{m}}(298.15 \text{ K})/\text{kJ} \cdot \text{mol}^{-1} = (1.29 \pm 0.056)\Delta_{\text{sln}}^{\text{g}}H_{\text{m}}(464 \text{ K}) + (6.6901 \pm 0.59) \quad r^2 = 0.9944 \quad (12)$$

run 7	slope		$\Delta_{\text{sln}}^{\text{g}}H_{\text{m}}(464 \text{ K})$ kJ·mol ⁻¹	$\Delta_{\text{f}}^{\text{g}}H_{\text{m}}(298.15 \text{ K})$ kJ·mol ⁻¹ (lit.)	$\Delta_{\text{f}}^{\text{g}}H_{\text{m}}(298.15 \text{ K})$ kJ·mol ⁻¹ (calcd)
	T/K	intercept			
tri- <i>n</i> -butylamine	-5092.5	11.23	42.337	62.70	62.2 ± 3.6
2,2-dipyridine	-5585.7	10.997	46.437	67.00	67.4 ± 3.9
2-phenylpyridine	-5681.0	11.14	47.229	68.40	68.4 ± 3.9
4,4-dipyridine·1.7H ₂ O	-5935.8	11.414	49.348	70.70	71.1 ± 4.1
7,8-benzoquinoline	-6606.7	11.833	54.925	77.23	78.2 ± 4.5
phenanthridine	-6660.6	11.913	55.374	80.14	78.8 ± 4.6
1,7-phenanthroline	-6712.8	11.936	55.808		79.4 ± 4.6
4,7-phenanthroline	-6849.6	12.098	56.945		80.8 ± 4.7

$$\Delta_{\text{f}}^{\text{g}}H_{\text{m}}(298.15 \text{ K})/\text{kJ} \cdot \text{mol}^{-1} = (1.276 \pm 0.081)\Delta_{\text{sln}}^{\text{g}}H_{\text{m}}(464 \text{ K}) + (8.18 \pm 0.92) \quad r^2 = 0.9841 \quad (13)$$

run 8	slope		$\Delta_{\text{sln}}^{\text{g}}H_{\text{m}}(464 \text{ K})$ kJ·mol ⁻¹	$\Delta_{\text{f}}^{\text{g}}H_{\text{m}}(298.15 \text{ K})$ kJ·mol ⁻¹ (lit.)	$\Delta_{\text{f}}^{\text{g}}H_{\text{m}}(298.15 \text{ K})$ kJ·mol ⁻¹ (calcd)
	T/K	intercept			
tri- <i>n</i> -butylamine	-5163.9	11.397	42930	62.70	62.2 ± 3.7
2,2-dipyridine	-5649.2	11.146	46965	67.0	67.4 ± 4.0
2-phenylpyridine	-5750.6	11.302	47809	68.4	68.5 ± 4.1
4,4-dipyridine·1.7H ₂ O	-5995.1	11.553	49841	70.7	71.1 ± 4.2
7,8-benzoquinoline	-6668.9	11.979	55443	77.23	78.3 ± 4.7
phenanthridine	-6715.6	12.043	55831	80.14	78.8 ± 4.7
1,7-phenanthroline	-6770.3	12.072	56285		79.4 ± 4.8
4,7-phenanthroline	-6902.7	12.223	57386		80.8 ± 4.9

$$\Delta_{\text{f}}^{\text{g}}H_{\text{m}}(298.15 \text{ K})/\text{kJ} \cdot \text{mol}^{-1} = (1.286 \pm 0.083)\Delta_{\text{sln}}^{\text{g}}H_{\text{m}}(464 \text{ K}) + (7.00 \pm 0.94) \quad r^2 = 0.9834 \quad (14)$$

run 9	slope		$\Delta_{\text{sln}}^{\text{g}}H_{\text{m}}(464 \text{ K})$ kJ·mol ⁻¹	$\Delta_{\text{f}}^{\text{g}}H_{\text{m}}(298.15 \text{ K})$ kJ·mol ⁻¹ (lit.)	$\Delta_{\text{f}}^{\text{g}}H_{\text{m}}(298.15 \text{ K})$ kJ·mol ⁻¹ (calcd)
	T/K	intercept			
tri- <i>n</i> -butylamine	-4949.8	11.022	41.150	62.70	62.6 ± 2.4
2-benzylpyridine	-5645.5	11.132	46.935		70.0 ± 2.7
7,8-benzoquinoline	-6396.3	11.488	53.176	77.23	78.0 ± 3.0
acridine	-6429.5	11.522	53.452	78.63	78.3 ± 3.0
9-methylcarbazole	-6539.1	11.709	54.364		79.5 ± 3.1
4,7-phenanthroline	-6625.9	11.726	55.085	80.80	80.4 ± 3.1

$$\Delta_{\text{f}}^{\text{g}}H_{\text{m}}(298.15 \text{ K})/\text{kJ} \cdot \text{mol}^{-1} = (1.276 \pm 0.056)\Delta_{\text{sln}}^{\text{g}}H_{\text{m}}(464 \text{ K}) + (10.12 \pm 0.063) \quad r^2 = 0.9960 \quad (15)$$

run 10	slope		$\Delta_{\text{sln}}^{\text{g}}H_{\text{m}}(488 \text{ K})$ kJ·mol ⁻¹	$\Delta_{\text{f}}^{\text{g}}H_{\text{m}}(298.15 \text{ K})$ kJ·mol ⁻¹ (lit.)	$\Delta_{\text{f}}^{\text{g}}H_{\text{m}}(298.15 \text{ K})$ kJ·mol ⁻¹ (calcd)
	T/K	intercept			
tri- <i>n</i> -butylamine	-5081.1	11.320	42.242	62.70	62.7 ± 2.6
2-benzylpyridine	-5712.8	11.301	47.494		69.5 ± 2.9
7,8-benzoquinoline	-6473.9	11.677	53.822	77.23	77.7 ± 3.3
acridine	-6527.7	11.751	54.269	78.63	78.2 ± 3.3
9-methylcarbazole	-6629.4	11.923	55.114		79.3 ± 3.4
4,7-phenanthroline	-6721.7	11.951	55.881	80.80	80.3 ± 3.4

$$\Delta_{\text{f}}^{\text{g}}H_{\text{m}}(298.15 \text{ K})/\text{kJ} \cdot \text{mol}^{-1} = (1.292 \pm 0.06)\Delta_{\text{sln}}^{\text{g}}H_{\text{m}}(488 \text{ K}) + (8.09 \pm 0.58) \quad r^2 = 0.9978 \quad (16)$$

Table 8. Summary of the Vaporization Enthalpies and Enthalpies of Transfer of Runs 5 to 10

	$\Delta_{\text{tr}}^{\text{g}}H_{\text{m}}(298.15 \text{ K})/\text{kJ}\cdot\text{mol}^{-1}$						average ^a	$\Delta_{\text{tr}}^{\text{g}}H_{\text{m}}(298.15 \text{ K}) [\text{lit.}]/\text{kJ}\cdot\text{mol}^{-1}$
	run 5	run 6	run 7	run 8	run 9	run 10		
quinazoline	59.3	58.5					58.9 ± 2.0	65.7 ± 2.7; ^b 64.5 ^c 67.4 ± 0.3 ^b
(-)-nicotine	64.1	63.7					63.9 ± 2.1	
2,2-dipyridine	67.1	66.9					67.0 ± 2.3	
4,4-dipyridine · 1.7H ₂ O	70.8	70.6					70.7 ± 2.4	
1,7-phenanthroline			79.4	79.4			79.4 ± 4.7	
4,7-phenanthroline			80.8	80.8			80.8 ± 4.8	
2-benzylpyridine					70.0	69.5	69.8 ± 2.8	
9-methylcarbazole					79.5	79.3	79.4 ± 3.2	
							81.1 ± 0.3	

^a The uncertainty is the average uncertainty associated with each run in Table 7. ^b Stereochemistry not specified.^{13,15} ^c Racemic form.

Table 9. Constants of Equation 10 and Corresponding Estimated and Experimental Normal Boiling Temperatures Derived from Runs 5 to 10

runs 5 and 6	A	B	C	D	BT_{calc}^a	BT_{lit}^b
	K ³	K ²	K		K	K
tri- <i>n</i> -butylamine					479.8	486.2
quinazoline	62950221.9	-1019157.75	-2388.439	8.073	512.4	516.2
(-)-nicotine	69850065.0	-1084705.54	-2782.671	8.667	528.8	520.2 ^c
2,6-dimethylquinoline					543.6	540.2
2,2-dipyridine	81725945.6	-1192649.71	-2825.351	8.6	549.4	546.2
2-phenylpyridine					551	543.2
4,4-dipyridine · 1.7H ₂ O	89520224.09	-1264611.026	-3050.209	8.891	563.7	578.2
7,8-benzoquinoline					614.6 ^d	611.2 ^d
acridine					615.9	618.1
runs 7 and 8	A	B	C	D	BT_{calc}^a	BT_{lit}^b
	K ³	K ²	K		K	K
tri- <i>n</i> -butylamine					480.6	486.2
2,2-dipyridine	82980265.7	-1197572.80	-2914.488	8.767	549.6	546.2
2-phenylpyridine					551.6	543.2
4,4-dipyridine · 1.7H ₂ O	88090511.1	-1246867.02	-3194.165	9.087	564.2	578.2
7,8-benzoquinoline					617.9 ^d	614.5 ^d
phenanthridine					618.7 ^d	623 ^d
1,7-phenanthroline	121578810.4	-1558844.12	-3192.849	8.625	623.7	633.2
4,7-phenanthroline	123705709.5	-1579329.77	-3296.579	8.741	628.7	na
runs 9 and 10	A	B	C	D	BT_{calc}^a	BT_{lit}^b
	K ³	K ²	K		K	K
tri- <i>n</i> -butylamine					481.3	486.2
7,8-benzoquinoline					618.1 ^d	614.5 ^d
Acridine					619.4	618.1
4,7-phenanthroline					620.7	na
2-benzylpyridine	79549255.1	-1163591.12	-3291.65	9.325	551.2	549.2
9-methylcarbazole	119137844.7	-1531860.0	-3317.94	8.855	619 d	617 ^d

^a Calculated boiling temperature using eq 10. ^b Literature boiling temperature from ref 9 unless noted otherwise. ^c Reported to decompose. ^d See Table 2A.

Table 10. Fusion Enthalpies of the Compounds Studied

	$\Delta_{\text{cr}}^{\text{l}}H_{\text{m}}(T_{\text{fus}})$	T_{fus}	$C_p(\text{l})$	$C_p(\text{cr})$	$\Delta_{\text{cr}}^{\text{l}}H_{\text{m}}(298 \text{ K})$	ref
	$\text{kJ}\cdot\text{mol}^{-1}$	K ^a	$\text{J}\cdot\text{mol}^{-1}$	K ⁻¹	$\text{kJ}\cdot\text{mol}^{-1}$	
quinazoline	16.95	320.8	202.8	149.8	16.0	20
2,2-dipyridine	20.4	345.2	246.4	184.8	18.3 ± 0.7	23
9-methylcarbazole	17.15	362.5	299.1	211.7	13.56	24
4,7-phenanthroline	21.8 ± 0.5	445.5	277	202	14.3 ± 2.3	this work
1,7-phenanthroline	18.2 ± 0.3	350.3	277	202	15.5 ± 0.8	this work
4,4-dipyridine · 1.7H ₂ O	35.5 ± 0.5	341.3	≈374.4 ^b	≈247 ^b	≈31.4 ± 1.6	this work

^a Onset temperature. ^b Estimated by adding the estimated molar heat capacity of the anhydrous form to the heat capacity of 1.7 moles of water (75.3 and 36.6) $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ for liquid and solid water, respectively.

Vapor pressures were similarly obtained by correlating $\ln(t_o/t_a)$ with $\ln(p/p_o)$ of the standards. For runs 5 through 10, with the exceptions of tri-*n*-butylamine and 2-phenylpyridine, the compounds used as standards were literature values using the parameters given in Tables 2A and 2B. Vapor pressures for tri-*n*-butylamine and 2-phenylpyridine were values calculated using eq 10 evaluated in runs 1 to 4, and vapor pressures calculated for 4,7-phenanthroline in runs 7 and 8 were used as standards in runs 9 and 10. The protocol followed was the same as described above and illustrated in Table 5. Correlations were performed from $T = (298.15 \text{ to } 500) \text{ K}$ at 10 K intervals. The constants of eq 10 calculated for quinazoline, (-)-nicotine, 2,2-dipyridine, 4,4-dipyridine, phenanthridine, 1,7- and 4,7-phenanthroline, 2-benzylpyridine, and 9-methylcarbazole are summa-

rized in Table 9. Vapor pressures for 9-methylcarbazole calculated from the Cox equation were not used in the correlations. Constants for eq 10 obtained for the compounds used as standards are not included in Table 9. As a means of evaluating the quality of the vapor pressures obtained by these correlations, the boiling temperatures calculated using the constants of eq 10 are included in column 6 of the table for both standards and unknowns. A normal boiling temperature for 4,7-phenanthroline could not be located.

Figure 3 provides a qualitative means of judging the reproducibility and quality of the vapor pressures obtained from these correlations. The top curve compares the vapor pressures of (-)-nicotine from this work (line) with literature values for (*dl*)-nicotine (triangles⁹) and for nicotine of unspecified stere-

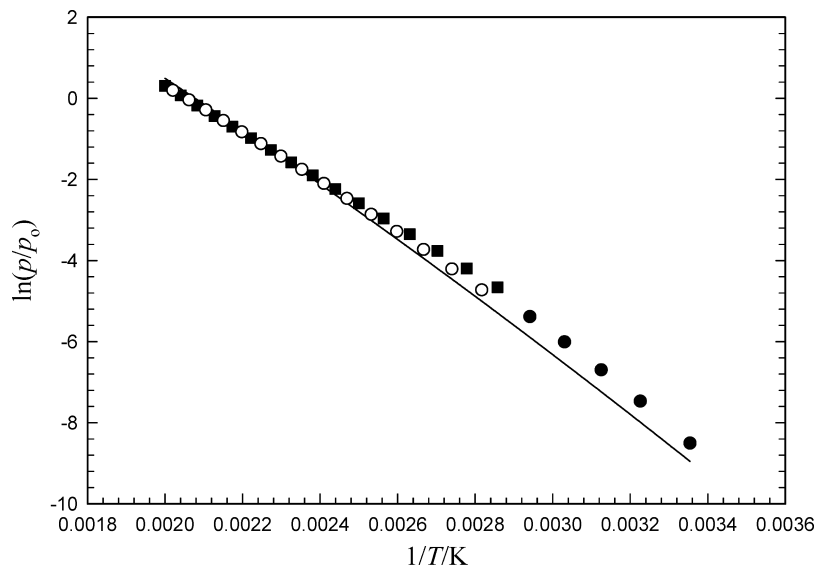


Figure 2. Comparison of $\ln(p/p_0)$ values for tri-*n*-butylamine ($p_0 = 101.325$ kPa) obtained in this work, eq 10, with literature values: —, this work; ●, ref 9; ■, ref 9; ○, ref 10. The ○ and ■ values are calculated at 10 K intervals offset by 5 K.

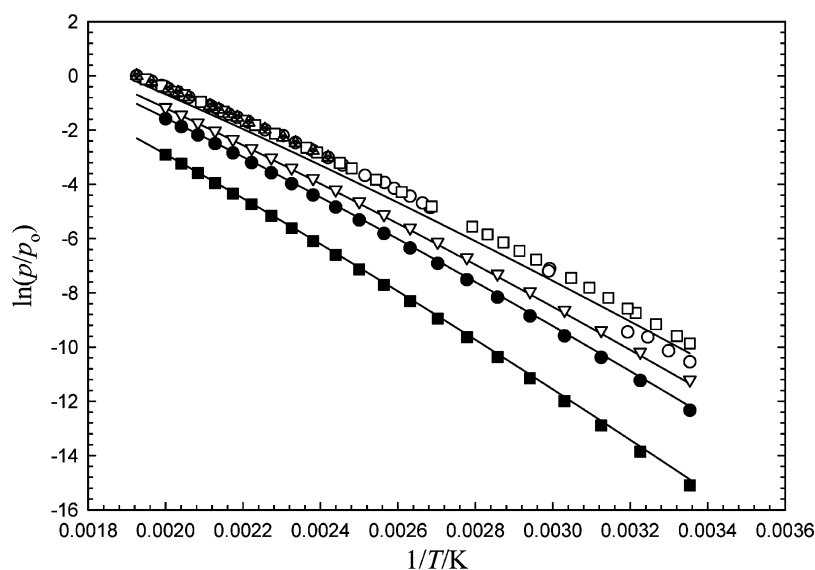


Figure 3. From top to bottom: a comparison of $\ln(p/p_0)$ of (—) nicotine obtained by correlation (line) from $T = (298.15$ to $500)$ K with literature values for nicotine (○, ref 13; □, ref 15; and △, ref 9) over the temperature range $T = (298.15$ to $520)$ K. Upper middle: a comparison of $\ln(p/p_0)$ for 2,2-dipyridine from duplicate runs 5 and 6 (▽) to the corresponding values obtained in duplicate runs 7 and 8 (line) from $T = (298.15$ to $500)$ K. Lower middle: a similar comparison for 4,4-dipyridine for duplicate runs 5 and 6 (●) to runs 7 and 9 (—). Bottom: calculated vapor pressures for 9-methylcarbazole from the Cox equation²¹ (■) with the results from this work, duplicate runs 9 and 10 (—).

ochemistry (squares^{14,15} and circles¹³). The middle two curves compare the vapor pressures of 2,2-dipyridine and 4,4-dipyridine calculated by averaging runs 5 and 6 (triangle and solid circles, respectively) to those obtained by averaging runs 7 and 8 (lines) using somewhat different standards. The lower curve compares vapor pressures calculated for 9-methylcarbazole from this work (line) with values calculated with the Cox equation (solid squares) using the parameters given in Table 2A. The comparisons for the most part are quite good suggesting that both the vapor pressure equations and vaporization enthalpies generated for those compounds are reasonably accurate.

As noted above, despite their hypothetical nature, vaporization enthalpies of solids combined with fusion enthalpies at $T = 298.15$ K can provide reliable sublimation enthalpy values. A number of the compounds used in this study have had their sublimation enthalpies reported in the literature. The fusion enthalpies of a few of these materials have also been reported. Table 10 lists fusion enthalpies reported in the literature along

with some of the values measured in this work. Since fusion enthalpies are measured at temperatures other than $T = 298.15$ K, it is necessary to adjust these values for temperature. Equation 17 has been used for these purposes.⁵ Additionally, eq 18 is the thermodynamic equality that relates sublimation, vaporization, and fusion enthalpies.

$$\Delta_{\text{cr}}^1 H_{\text{m}}(298.15 \text{ K}) = \Delta_{\text{cr}}^1 H_{\text{m}}(T_{\text{fus}}) + \{[0.15C_p(\text{cr}) - 0.26C_p(\text{l})/J - 9.83]/J \cdot \text{mol}^{-1}\}[(T_{\text{fus}}/\text{K} - 298.15)]/1000 \quad (17)$$

$$\Delta_{\text{l}}^{\text{g}} H_{\text{m}}(298.15 \text{ K}) = \Delta_{\text{cr}}^{\text{g}} H_{\text{m}}(298.15 \text{ K}) - \Delta_{\text{cr}}^1 H_{\text{m}}(298.15 \text{ K}) \quad (18)$$

The temperature adjustments of fusion enthalpies to $T = 298.15$ K are summarized in Table 10. Adjustment of the fusion enthalpy of the hydrated form of 4,4-dipyridine to $T = 298.15$ K, however, is problematic. Equation 17 was derived for pure

Table 11. Comparison of Vaporization Enthalpies Using Equation 18 With This Work

	$\Delta_{cr}^{\circ}H_m(298\text{ K})$	$\Delta_{cr}^1H_m(298\text{ K})$	$\Delta_1^{\circ}H_m(298\text{ K})/\text{kJ}\cdot\text{mol}^{-1}$	
	$\text{kJ}\cdot\text{mol}^{-1}$	$\text{kJ}\cdot\text{mol}^{-1}$	calcd ^a	this work
quinazoline	77.6 ^b , 76.6 ± 1.4 ^c	16.0	61.6, 60.6	58.9 ± 2.0
9-methylcarbazole	95.5 ± 4.0 ^d	13.56 ^e	81.94; 81.1 ^f	79.4 ± 3.2
2,2-dipyridine	81.8 ± 2.3 ^g	18.3 ± 0.7 ^h	63.5 ± 3.2	67.0 ± 2.3
4,4-dipyridine·1.7H ₂ O	106.3 ± 2.8 ^g	≈31.4 ± 1.6	≈74.9 ± 3.4	70.7 ± 2.4

^a Calculated using eq 18. ^b Ref 20. ^c Ref 26. ^d Ref 21 and 25. ^e Ref 24. ^f See Table 1. ^g Reference 22. ^h Reference 23.

Table 12. Vaporization Enthalpies and Enthalpies of Transfer of Runs 11 to 14

run 11	slope		$\Delta_{sln}^{\circ}H_m(489\text{ K})$	$\Delta_1^{\circ}H_m(298.15\text{ K})$	$\Delta_1^{\circ}H_m(298.15\text{ K})$
	T/K	intercept	$\text{kJ}\cdot\text{mol}^{-1}$	$\text{kJ}\cdot\text{mol}^{-1}$ (lit.)	$\text{kJ}\cdot\text{mol}^{-1}$ (calcd)
tri- <i>n</i> -butylamine	-4894.2	10.877	40.688	62.70	62.6 ± 2.4
4-phenylpyrimidine	-5488.5	10.781	45.629		68.8 ± 2.5
4,4-bipyridine (anhy)	-5715.2	11.02	47.514		71.1 ± 2.6
7,8-benzoquinoline	-6375.6	11.421	53.005	77.23	78.0 ± 3.0
acridine	-6416.2	11.469	53.342	78.63	78.4 ± 3.0
4,7-phenanthroline	-6605.8	11.66	54.918	80.80	80.4 ± 3.1

$$\Delta_1^{\circ}H_m(298.15\text{ K})/\text{kJ}\cdot\text{mol}^{-1} = (1.246 \pm 0.055)\Delta_{sln}^{\circ}H_m(489\text{ K}) + (11.9 \pm 0.64) \quad r^2 = 0.9960 \quad (19)$$

run 12	slope		$\Delta_{sln}^{\circ}H_m(489\text{ K})$	$\Delta_1^{\circ}H_m(298.15\text{ K})$	$\Delta_1^{\circ}H_m(298.15\text{ K})$
	T/K	intercept	$\text{kJ}\cdot\text{mol}^{-1}$	$\text{kJ}\cdot\text{mol}^{-1}$ (lit.)	$\text{kJ}\cdot\text{mol}^{-1}$ (calcd)
tri- <i>n</i> -butylamine	-4965.2	11.025	41.279	62.70	62.6 ± 2.2
4-phenylpyrimidine	-5547.4	10.902	46.119		68.7 ± 2.4
4,4-bipyridyl (anhy)	-5769.4	11.131	47.965		71.1 ± 2.5
7,8-benzoquinoline	-6418.3	11.509	53.359	77.23	77.9 ± 2.7
acridine	-6465.4	11.57	53.751	78.63	78.4 ± 2.8
4,7-phenanthroline	-6659.6	11.77	55.365	80.80	80.4 ± 2.8

$$\Delta_1^{\circ}H_m(298.15\text{ K})/\text{kJ}\cdot\text{mol}^{-1} = (1.264 \pm 0.05)\Delta_{sln}^{\circ}H_m(489\text{ K}) + (10.46 \pm 0.57) \quad r^2 = 0.9968 \quad (20)$$

run 13	slope		$\Delta_{sln}^{\circ}H_m(490\text{ K})$	$\Delta_1^{\circ}H_m(298.15\text{ K})$	$\Delta_1^{\circ}H_m(298.15\text{ K})$
	T/K	intercept	$\text{kJ}\cdot\text{mol}^{-1}$	$\text{kJ}\cdot\text{mol}^{-1}$ (lit.)	$\text{kJ}\cdot\text{mol}^{-1}$ (calcd)
tri- <i>n</i> -butylamine	-4946.8	11.008	41.126	62.70	62.7 ± 1.4
2-benzylpyridine	-5605.7	11.04	46.603	69.80	69.7 ± 1.5
2,4-bipyridine	-5721.2	11.013	47.564		70.9 ± 1.6
7,8-benzoquinoline	-6383.2	11.443	53.068	77.23	77.9 ± 1.7
acridine	-6428.4	11.499	53.443	78.63	78.4 ± 1.7
9-methylcarbazole	-6531.4	11.673	54.299	79.40	79.4 ± 1.8
4,7-phenanthroline	-6623.5	11.7	55.066	80.80	80.5 ± 1.8

$$\Delta_1^{\circ}H_m(298.15\text{ K})/\text{kJ}\cdot\text{mol}^{-1} = (1.272 \pm 0.033)\Delta_{sln}^{\circ}H_m(490\text{ K}) + (10.28 \pm 0.40) \quad r^2 = 0.9974 \quad (21)$$

run 14	slope		$\Delta_{sln}^{\circ}H_m(490\text{ K})$	$\Delta_1^{\circ}H_m(298.15\text{ K})$	$\Delta_1^{\circ}H_m(298.15\text{ K})$
	T/K	intercept	$\text{kJ}\cdot\text{mol}^{-1}$	$\text{kJ}\cdot\text{mol}^{-1}$ (lit.)	$\text{kJ}\cdot\text{mol}^{-1}$ (calcd)
tri- <i>n</i> -butylamine	-5030.2	11.177	41.819	62.7	62.7 ± 1.4
2-benzylpyridine	-6452.6	11.583	47.243	69.8	69.7 ± 1.6
2,4-bipyridine	-5682.7	11.194	48.165		70.9 ± 1.6
7,8-benzoquinoline	-6503.1	11.65	53.644	77.2	77.9 ± 1.8
acridine	-6599.6	11.81	54.064	78.6	78.4 ± 1.8
9-methylcarbazole	-6693	11.84	54.867	79.4	79.4 ± 1.8
4,7-phenanthroline	-5793.5	11.159	55.643	80.8	80.5 ± 1.8

$$\Delta_1^{\circ}H_m(298.15\text{ K})/\text{kJ}\cdot\text{mol}^{-1} = (1.285 \pm 0.032)\Delta_{sln}^{\circ}H_m(490\text{ K}) + (8.96 \pm 0.39) \quad r^2 = 0.9976 \quad (22)$$

materials, and there is no guarantee that it can be applied to hydrates or amorphous materials. However since the fusion temperature is close to $T = 298.15\text{ K}$, this insures a small temperature adjustment. Using adjusted heat capacities derived as noted in footnote b of Table 10 and as is discussed below, a fusion enthalpy at $T = 298.15\text{ K}$ of $31.4\text{ kJ}\cdot\text{mol}^{-1}$ is estimated for 4,4-dipyridine hydrate. Accepting this value for the moment,

the vaporization enthalpies measured in this work can be compared to the literature values calculated using eq 18. This comparison is documented in Table 11. Most vaporization enthalpy comparisons are within experimental error of each other. As noted in this table, the vaporization enthalpy value calculated for 4,4-dipyridine hydrate is remarkably close to the value previously reported for the anhydrous material.²² Since

Table 13. Vaporization Enthalpies and the Constants of Equation 10 and Corresponding Estimated and Experimental Normal Boiling Temperatures Derived from Runs 11 to 14

runs 11 and 12	$\Delta_{\text{f}}^{\ominus}H_{\text{m}}(298.15 \text{ K})$ kJ·mol ⁻¹	A K ³	B K ²	C K	D	BT_{calc}^a K	BT_{lit}^b K
tri- <i>n</i> -butylamine						481.0	486.2
4-phenylpyrimidine	68.8 ± 2.5	82739965.41	-1191247.386	-3078.925	8.993	392.0	390.2 ^c
4,4-dipyridine (anhyd)	71.1 ± 2.6	87876825.41	-1240023.916	-3205.124	9.104	563.4	578.2 ^e
7,8-benzoquinoline						615.4	614.5 ^e
acridine						616.7	618.1 ^e
4,7-phenanthroline						623.5	na
runs 13 and 14	$\Delta_{\text{f}}^{\ominus}H_{\text{m}}(298.15 \text{ K})$ kJ·mol ⁻¹	A K ³	B K ²	C K	D	BT_{calc}^a K	BT_{lit}^b K
tri- <i>n</i> -butylamine						482.4	486.2
2-benzylpyridine						549.8	549.2
2,4-bipyridine	70.9 ± 1.6	89785140.71	-1256837.408	-3110.722	8.95	564.7	554.2 ^f
7,8-benzoquinoline						614.1	614.5 ^e
acridine						615.4	619.5
9-methylcarbazole						615.2	617 ^e
4,7-phenanthroline						624.5	na

^a Calculated boiling temperature using eq 10. ^b Literature boiling temperature from ref 9 unless noted otherwise. ^c Boiling temperature at 0.53 kPa, experimental data: SciFinder Scholar. ^d Boiling temperature at 0.53 kPa, experimental data: SciFinder Scholar. ^e See Table 2A. ^f Experimental data, SciFinder Scholar.

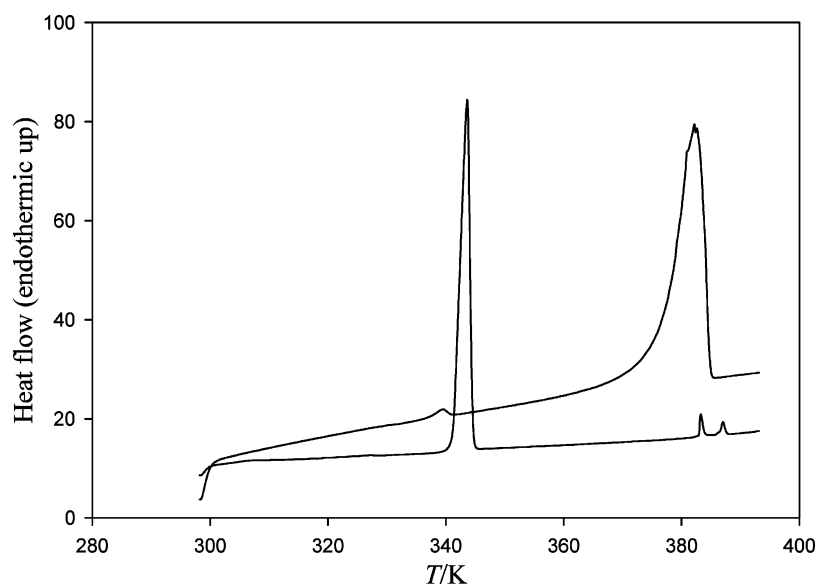


Figure 4. DSC trace of dipyrindine·1.7H₂O (lower) and anhydrous dipyrindine (upper). There is some evidence of a very weak transition at $T = 327 \text{ K}$ in dipyrindine·1.7H₂O not evident on this scale. The weak peaks at approximately $T = 386 \text{ K}$ in dipyrindine·1.7H₂O varied in relative intensity from run to run, and a third peak was also observed in one run between the two.

the sublimation enthalpy of 4,4-dipyridine was subsequently used in calculating the gas phase enthalpy of formation of 4,4-dipyridine,²² a concern immediately arose concerning the possibility that either the sublimation enthalpy reported in the literature was for a hydrated form of 4,4-dipyridine or that the hydrated form used in our measurements somehow affected the retention times of 4,4-dipyridine. Consequently, both the vaporization and fusion enthalpies of the anhydrous form of 4,4-dipyridine were also measured. As an added precaution, the vaporization and fusion enthalpies of a related compound, 2,4-bipyridine, for which an experimental sublimation enthalpy and condensed phase enthalpy of formation value is available,²² were also measured. An additional compound that became available to us, 4-phenylpyrimidine, was also included in the mixture. Due to the similarity in retention times of the two dipyridines, two sets of duplicate mixtures were used. The retention times of the gas chromatographic experiments are available in the Supporting Information, and the resulting correlations are reported in Table 12, eqs 19 to 22. Table 13 summarizes the

vaporization enthalpy and vapor pressure results obtained using the protocol describe above for runs 11 to 14. The parameters of eq 10 generated for 4-phenylpyrimidine, 4,4-dipyridine, and 2,4-dipyridine in the liquid state along with the predicted boiling temperatures for each of the compounds in the mixture are also provided in this table. Although the extrapolated boiling temperatures of both the anhydrous and hydrated form differ from the literature value by approximately 15 K, the two differ from each other by less than 1 K in temperature. Similarly, the extrapolated value for 2,4-dipyridine differs by approximately 10 K from the experimental value, while its vaporization enthalpy is consistent with experimental sublimation and fusion enthalpy results.

The heat flow diagrams obtained for the solid to liquid transition of both the hydrated and anhydrous forms of crystalline 4,4-dipyridine are compared in Figure 4. The anhydrous form melted at $T = 377.5 \text{ K}$ (onset temperature) with a fusion enthalpy of $(102.4 \pm 3.0) \text{ J} \cdot \text{g}^{-1}$. It also exhibited a smaller peak at $T = 337 \text{ K}$ [$(1.5 \pm 0.3) \text{ J} \cdot \text{g}^{-1}$]. Unlike the hydrated form,

Table 14. Fusion Enthalpies of 4-Phenylpyrimidine and the Dipyridines

	$\Delta_{cr}^1H_m$ kJ·mol ⁻¹	T_{fus} K ^a	$C_p(l)$ J·mol ⁻¹ ·K ⁻¹	$C_p(cr)$ J·mol ⁻¹ ·K ⁻¹	$\Delta_{cr}^1H_m(298\text{ K})$ kJ·mol ⁻¹	ref
4-phenylpyrimidine	18.8 ± 0.3	334.1	246.4	184.8	17.1 ± 0.6	this work
2,2-dipyridine	20.4	345.2	246.4	184.8	18.3 ± 0.7	23 ^b
2,4-dipyridine	17.4 ± 0.4	332.8	264.4	184.8	15.8 ± 0.6	this work
4,4-dipyridine (anhyd)	16.1 ± 1.0	377.5	264.4	184.8	12.3 ± 1.5	this work

^a Onset temperature. ^b Estimated by adding the estimated molar heat capacity of the anhydrous form to the heat capacity of 1.7 moles of water; (75.3 and 36.6) J·mol⁻¹·K⁻¹ for liquid and solid water, respectively.

Table 15. Comparison of Vaporization Enthalpies Using Equation 18 With This Work

	$\Delta_{cr}^2H_m(298\text{ K})$ kJ·mol ⁻¹	$\Delta_{cr}^1H_m(298\text{ K})$ kJ·mol ⁻¹	$\Delta_1^2H_m(298\text{ K})/\text{kJ}\cdot\text{mol}^{-1}$	
			calcd ^a	this work
4-phenylpyrimidine	85.9 ± 2.6 ^b	17.1 ± 0.6		68.8 ± 2.5
2,2-dipyridine	81.8 ± 2.3 ^c	18.3 ± 0.7	63.5 ± 3.2	67.0 ± 2.3
2,4-dipyridine	87.9 ± 1.7 ^c	15.8 ± 0.6	72.1 ± 1.8	70.9 ± 1.6
4,4-dipyridine (anhyd)	106.3 ± 2.8 ^c	12.4 ± 1.4	93.9	71.1 ± 2.6
4,4-dipyridine·1.7H ₂ O	106.3 ± 2.8 ^c	≈31.4 ± 1.6	≈74.9 ± 3.4	70.7 ± 2.4

^a Calculated using eq 18. ^b Sum of the fusion and vaporization enthalpies. ^c From ref 22.

Table 16. Comparison of Enthalpies of Formation of 2,2-, 2,4-, and 4,4-Dipyridine in kJ·mol⁻¹ at T = 298.15 K

	$\Delta_fH_m(cr)$ lit. ^a	$\Delta_{cr}^2H_m^b$	$\Delta_fH_m^o(g)^b$	$\Delta_fH_m^o(g)$ lit. ^a	$\Delta_fH_m^o(g)$ lit. ^a	
					ab initio	PM3
2,2-bipyridine	186.1 ± 2.0	85.3 ± 2.4	271.4 ± 3.1	267.9 ± 3.0	276.3	261.8
2,4-bipyridine	196.3 ± 2.1	86.7 ± 1.9	283.0 ± 2.8	284.4 ± 2.8	304.5	261.1
4,4-bipyridine	186.8 ± 2.2	83.5 ± 3.0 ^c	270.2 ± 3.6	293.1 ± 3.7	318.6	260.6

^a Ref 22. ^b Sum of $\Delta_{cr}^1H_m + \Delta_1^2H_m$; this work. ^c Average of runs 11 and 12.

Table 17. Summary of The Vaporization and Fusion Enthalpies and Constants of Equation 10 Evaluated in the Study

	$\Delta_1^2H_m(298\text{ K})$ kJ·mol ⁻¹	$\Delta_{cr}^1H_m(T_{fus})$ kJ·mol ⁻¹	A	B	C	D
			K ₃	K ₂	K	
tri- <i>n</i> -butylamine	62.7 ± 1.3		30767110.1	-712464.53	-3836.038	10.769
2-phenylpyridine	68.4 ± 1.9		82334650.2	-1199538.89	-2988.675	8.899
3-phenylpyridine	68.4 ± 1.6		78066389.6	-1137160.48	-3293.956	9.322
quinazoline	58.9 ± 2.0		62950221.9	-1019157.75	-2388.439	8.073
(-)-nicotine	63.9 ± 2.1		69850065.0	-1084705.54	-2782.671	8.667
4-phenylpyrimidine	68.8 ± 2.5	18.8 ± 0.3	82739965.4	-1191247.39	-3078.925	8.993
4,4-dipyridine (anh)	71.1 ± 2.6	16.1 ± 1.0	87876825.4	-1240023.92	-3205.124	9.104
4,4-dipyridine·1.7H ₂ O	70.7 ± 2.4	35.5 ± 0.5	88090511.1	-1246867.02	-3194.165	9.087
2-benzylpyridine	69.8 ± 2.8		79549255.1	-1163591.12	-3291.65	9.325
2,4-bipyridine	70.9 ± 1.6	17.4 ± 0.4	89785140.7	-1256837.41	-3110.722	8.950
2,2-dipyridine	67.0 ± 2.3		81725945.6	-1192649.71	-2825.351	8.600
9-methylcarbazole	79.4 ± 3.2		119137844.7	-1531860.00	-3317.940	8.855
1,7-phenanthroline	79.4 ± 4.7	18.2 ± 0.3	121578810.4	-1558844.12	-3192.849	8.625
4,7-phenanthroline	80.8 ± 4.8	21.8 ± 0.5	123705709.5	-1579329.77	-3296.579	8.741

fusion of the anhydrous form appears to be characterized by several overlapping transitions. The hydrated form melted sharply at $T = 341.3\text{ K}$ with a fusion enthalpy of $(187.2 \pm 2.2)\text{ J}\cdot\text{g}^{-1}$. The figure also shows two, and in one case (not shown) three weak peaks in repeated runs, two of which were not clearly resolved, at $T = (382\text{ and }386)\text{ K}$ with transition enthalpies of $[(2.85 \pm 1.5)\text{ and } (2.7 \pm 0.2)]\text{ J}\cdot\text{g}^{-1}$, respectively. It should also be noted that the hydrated form also shows a very weak peak at approximately $T = 327\text{ K}$ which is too weak to be observed in Figure 4. The simplest explanation of the multiple peaks observed in both forms is that the hydrated form contains a small amount of the anhydrous material and the anhydrous material contains a small amount of water. The enthalpy ratio of the hydrated to anhydrous form on a mass basis is approximately 1.82/1. Using this ratio to correct for the heat flow of the hydrated form suggests an anhydrous composition of 0.993 (top curve). Adjusting the experimental enthalpies per gram of the anhydrous form of 4,4-dipyridine for this composition results in a fusion enthalpy of $(16.1 \pm 1.0)\text{ kJ}\cdot\text{mol}^{-1}$ as reported as the last entry in Table 14. Similarly, a composition

of 0.984 is calculated for the hydrated form which adjusts to a value of $190.4\text{ J}\cdot\text{g}^{-1}$ for the pure hydrated form, 4,4-dipyridine· $x\text{H}_2\text{O}$. Converting the value for the hydrated form from a mass basis to a molar basis is problematic. An ¹H NMR analysis in CDCl₃ of the hydrated form suggested a ratio of water/4,4-dipyridine of approximately 1.7/1. Assuming a molecular weight on this basis, $186.8\text{ g}\cdot\text{mol}^{-1}$, results in a fusion enthalpy of $35.5\text{ kJ}\cdot\text{mol}^{-1}$, reported in column 2, Table 10, as the last entry. As noted above, adjusting this value to $T = 298.15\text{ K}$ using eq 17 is equally problematic. However, since the fusion temperature is close to $T = 298.15\text{ K}$, this insures a small temperature adjustment. Using adjusted heat capacities derived as noted in footnote b of Table 10, a fusion enthalpy of approximately $31.4\text{ kJ}\cdot\text{mol}^{-1}$ is estimated.

The vaporization enthalpy results measured and calculated for all the dipyridines and the sublimation enthalpy obtained from the sum of the vaporization and fusion enthalpy of 4-phenylpyrimidine are summarized in Table 15. The similarity in vaporization enthalpy obtained for both the hydrate and anhydrous forms of 4,4-dipyridine, the last column in this table,

implies that the sublimation enthalpy reported for 4,4-dipyridine in the literature is likely for a hydrated form.²² If this conclusion is correct, several additional comments apply. The sublimation enthalpies of 2,2-, 2,4-, and 4,4-dipyridine were all measured by drop calorimetry.²² Since the enthalpy measured by this apparatus includes the enthalpy associated with heating the sample from $T = 298.15$ K to the temperature of the calorimeter, $T = 368$ K, a sizable heat capacity adjustment must be applied. In this case, it was estimated to be $12.8 \text{ kJ}\cdot\text{mol}^{-1}$ for all the dipyridine isomers.²² The vaporization enthalpies for 2,2- and 2,4-dipyridine calculated from the sublimation enthalpies reported²² and the values measured in this work are within experimental error of each other as noted in Table 15. If the sublimation enthalpy of the sample of 4,4-dipyridine was in fact accidentally measured on a hydrated form, as these results suggest, the heat capacity correction for the hydrated form should probably be somewhat larger than $12.8 \text{ kJ}\cdot\text{mol}^{-1}$, resulting in a somewhat larger temperature adjustment. This could bring the vaporization enthalpy calculated, ($\approx 74.9 \pm 3.4$) $\text{kJ}\cdot\text{mol}^{-1}$, even closer in line with the value measured in this work, (70.7 ± 2.4) $\text{kJ}\cdot\text{mol}^{-1}$.

Accepting for the moment that the sublimation enthalpy measured by drop calorimetry was in fact for a hydrated form of 4,4-dipyridine, the gas phase enthalpy of formation of 4,4-dipyridine would need to be revised. Ribeiro da Silva et al.²² point out that 4,4-dipyridine was repeatedly sublimed before the samples were burned and that good carbon dioxide recoveries were obtained. Whether similar precautions were followed prior to the sublimation enthalpy measurements is not clear. What is also of some concern is that combustion of the samples was performed in a bomb calorimeter in the presence of 1 mL of water. If anhydrous 4,4-dipyridine absorbs water on standing, given the fact that the fusion enthalpy of the hydrate is greater than that of the anhydrous material, this could also have had some impact on the resulting enthalpy of combustion, resulting in a combustion enthalpy somewhat lower than for the truly anhydrous form.

Table 16 lists the condensed and gas phase enthalpies of formation of the dipyridines reported by Ribeiro da Silva et al.²² and those calculated using the sublimation enthalpies calculated in this work using eq 18. The sublimation enthalpies of 2,2- and 2,4-dipyridine measured in this work (column 4) are well within experimental error of each other and with the results reported by Ribeiro da Silva et al.²² (column 5). Our results also suggest that the sublimation enthalpy of 4,4-dipyridine is also within experimental error of the 2,2- and 2,4-isomers. The condensed phase enthalpy of formation of the 2,4-isomer is some $10 \text{ kJ}\cdot\text{mol}^{-1}$ larger than the value measured for 2,2- and 4,4-isomers.²² This makes the 2,4-isomer the least stable of the three isomers. Also included in Table 15 are the results of theoretical calculations previously performed on the three isomers.²² If 4,4-bipyridine is kinetically very hydroscopic, partial formation of a hydrate in the combustion calorimeter prior to combustion would result in a smaller condensed phase enthalpy of formation. The ab initio calculations would appear to most closely parallel the experimental results in this case. Otherwise the PM3 results appear most consistent with the enthalpy of formation for at least two of the three isomers.

For convenience to the reader, the vaporization and fusion enthalpies and constants of eq 10 for all the compounds evaluated in this study are summarized in Table 17.

Summary

Vapor pressures and vaporization enthalpies of a series of heterocyclic polyaromatic hydrocarbons have been evaluated by correlation gas chromatography. The vaporization enthalpy results for the most part appear in good agreement with literature values. The only discrepancy encountered is with 4,4-dipyridine. Our results suggest that the sublimation enthalpy in the literature is most consistent with the hydrated form of 4,4-dipyridine.

Supporting Information Available:

Tables including the experimental retention times described in the text and literature references of the standards used. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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