The Vaporization Enthalpies of 2- and 4-(N,N-Dimethylamino)pyridine, 1,5-Diazabicyclo[4.3.0]non-5-ene, 1,8-Diazabicyclo[5.4.0]undec-7-ene, Imidazo[1,2-a]pyridine and 1,2,4-Triazolo[1,5-a]pyrimidine by Correlation—Gas Chromatography

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S Supporting Information

ABSTRACT: The vaporization enthalpies of a series of heterocyclic compounds some suspected of showing evidence of a higher degree of self-association in comparison to many other nitrogen heterocycles have been measured both by correlation gas chromatography (CGC) and for comparison by transpiration. The compounds share some structural similarities. They include 2- and 4-(N,N-dimethylamino)pyridine, 1,5-diazabicyclo[4.3.0]non-5-ene, 1,8-diazabicyclo[5.4.0]undec-7-ene, 1,2,4-triazolo[1,5-a]pyrimidine and imidazo[1,2-a]pyridine. The vaporization enthalpies of the first three of the compounds are well reproduced by a standard series of reference compounds, mainly pyridine derivatives. The latter two compounds and 4-(N,N-dimethylamino)pyridine exhibit vaporization enthalpies approximately 7 kJ·mol^{-1} larger. Their values are reproduced by using standards previously shown to exhibit stronger but similar self-association properties. The crystal structure of 1,2,4-triazolo[1,5-a]pyrimidine has been determined in an effort to understand the nature of the self-association. The molecule crystallizes in planar stacks slightly offset with a stacking distance of 3.24 Å.

ΔH_{vap}
(kJ/mol)

54.9   69.0   72.5   67.3   61.5   69.5
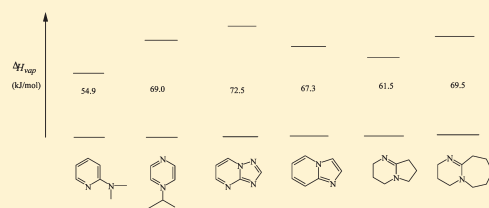
■ INTRODUCTION

Systems that self-assemble and the interactions responsible for assembly is an area that is reasonably well understood in the solid state but considerably less so in fluids. Recently we have been examining a series of heterocyclic compounds that by themselves are incapable of hydrogen bonding but do show evidence of a higher degree of self-association in comparison to most other nitrogen heterocycles previously examined by correlation—gas chromatography (CGC).[1−3] Pyridazine ($\Delta_l^g H_m$(298 K), 53.5 kJ·mol^{-1})[4] and 1-methylimidazole ($\Delta_l^g H_m$(298 K), 55.6 kJ·mol^{-1}),[5,6] for example have considerably larger vaporization enthalpies when compared to substances quite similar in size and structure such as pyrimidine ($\Delta_l^g H_m$(298 K) 41.0 kJ·mol^{-1}).[1] It has also recently been shown that the polycyclic aromatic 1,2-diazines, phthalazine and benzocinnoline show similar enhanced vaporization enthalpies when compared to their 1,3- and 1,4-structural isomers whereas *trans* azobenzene, the stereoisomer of *cis* azobenzene, an acyclic relative of benzocinnoline, does not.[2] This article reports the vaporization enthalpy of six compounds with some structural features similar to the N-alkylimidazoles previously examined.[3] The compounds include two N,N-dialkylaminopyridines: 2- and 4-(N,N-dimethylamino)pyridine; two 1,3-diazacyclohexanes: 1,5-diazabicyclo[4.3.0]non-5-ene and 1,8-diazabicyclo[5.4.0]undec-7-ene, and two pseudo aromatic heterocycles: imidazo[1,2-a]pyridine and 1,2,4-triazolo[1,5-a]pyrimidine.
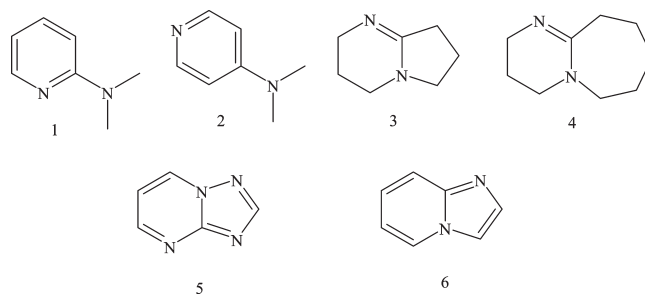

Figure 1. Compounds from left to right, top to bottom: 2-(N,N-dimethylamino)pyridine (**1**); 4-(N,N-dimethylamino)pyridine (**2**); 1,5-diazabicyclo[4.3.0]non-5-ene (**3**); 1,8-diazabicyclo[5.4.0]undec-7-ene (**4**); 1,2,4-trazolo[1,5-a]pyrimidine (**5**), and imidazo[1,2-a]pyridine (**6**).

Structures of these materials are provided in Figure 1. These materials have been evaluated by CGC using the heterocycles provided in Figure 2 as standards. Figure 2 also provides structures for the other materials mentioned above. Vaporization enthalpies for five of the six
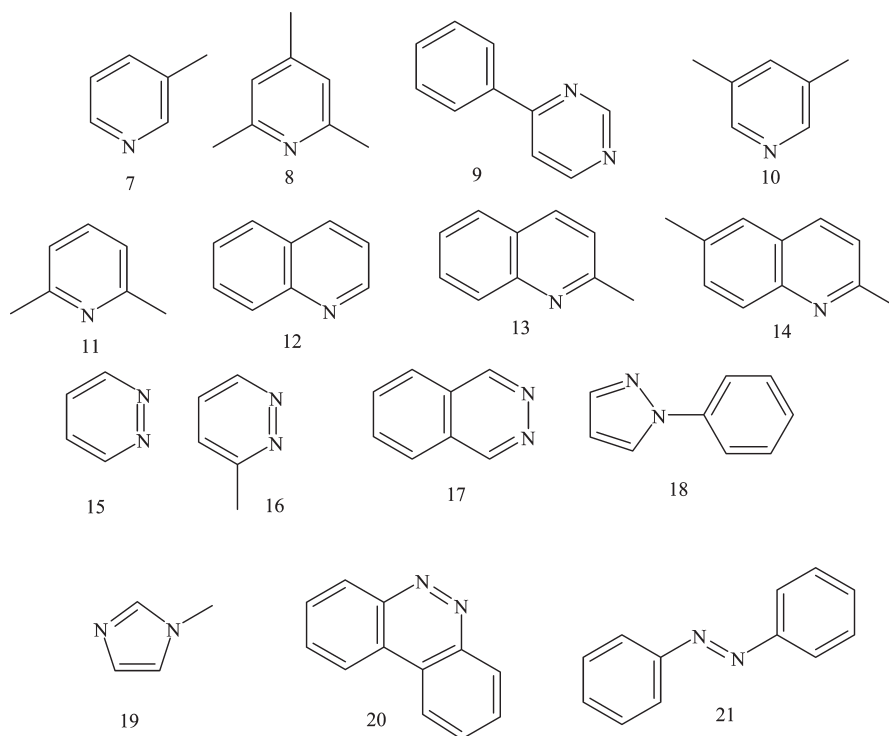
Figure 2. Compounds from left to right, top to bottom: 3-methylpyridine (**7**); 2,4,6-trimethylpyridine (**8**), 4-phenylpyrimidine (**9**); 3,5-dimethylpyridine (**10**); 2,6-dimethylpyridine (**11**); quinoline (**12**); 2-methylquinoline (**13**); 2,6-dimethylquinoline (**14**). The following compounds: pyridazine (**15**); 3-methylpyridazine (**16**); phthalazine (**17**); N-phenylpyrazole (**18**); N-methylimidazole (**19**); and benzo[c]cinnoline (**20**), among others, all exhibit anomalously larger vaporization enthalpies; *trans* azobenzene (**21**) does not.

compounds evaluated were not available in the literature. As an initial test of the quality of the results, the boiling temperatures were calculated from their predicted vapor pressures obtained by correlation as described below and illustrated by Table 5 and compared to their experimental values. The boiling temperatures of three of these compounds are within a few degrees of the literature values, while the predicted boiling temperature of two of other compounds are considerably lower. This is similar to the results observed previously for compounds exhibiting evidence of stronger self-association. The result for a sixth compound, 4-(N,N-dimethylamino)pyridine, was inconclusive. To confirm these conclusions, the vaporization enthalpies of 2-(N,N-dimethylamino)pyridine, 1,5-diazabicyclo[4.3.0]non-5-ene, 1,8-diazabicyclo[5.4.0]undec-7-ene and imidazo[1,2-a]pyridine and the sublimation enthalpy of 4-(N,N-dimethylamino)pyridine were also measured by transpiration. The vaporization enthalpies of three of the five compounds measured by transpiration are consistent with the results obtained by CGC using various pyridine heterocycles as standards. Transpiration results for the remaining three others reproduced results using derivatives of pyridazine and imidazoles as standards.

■ EXPERIMENTAL SECTION

Gas Chromatographic Studies. All compounds used in the study were obtained from Aldrich Chemical Co. except for 3,5-dimethylpyridine which was purchased from Acros and used as purchased. All were analyzed by gas chromatography and found to have purities of 98% mass fraction 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. CGC

experiments were performed on an HP 5890 Gas Chromatograph equipped with a flame ionization detector and run at a split ratio of approximately 100/1. Retention times were recorded on an HP Chemstation. The compounds were run isothermally either on a J&W 0.25 mm, 30 m DB5MS column or a Restek 0.5 mm, 30 m RTX-5 column. While enthalpies of transfer do depend on the nature of the column used, the results following the correlation remain independent of the nature of the column within the reproducibility of the results. 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 ±0.1 K. Helium was used as the carrier gas. The standards are injected simultaneously with the target substances along with an unretained analyte that measures the elution time without retention, t_e. At the temperatures used in these experiments, the retention time of the solvent, methanol, was used as a non-retained reference. Its retention time generally increased with increasing temperature as a consequence of the increase in viscosity of the carrier gas. Since each analyte moves on the column according to its vapor pressure on the column, measurement of the temperature dependence of its adjusted retention time, $t_a = t - t_e$, provides a convenient measure of both its volatility and interaction with the column. The term t_a is the time each analyte spends on the column. Since the vapor pressure of each analyte is inversely proportional to its adjusted retention time, t_a, a plot of $\ln(t_0/t_a)$ vs $1/T$ run isothermally, usually over a $T = 30$ K range, results in a linear relationship with a slope equal to the negative enthalpy of transfer of the analyte from the column to the gas phase, $-\Delta_{sln}^g H_m(T)/R$, divided by the gas constant. The term t_0 refers to the reference time, 1 min. All plots of $\ln(t_0/t_a)$, vs $1/T$ were characterized by correlation

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coefficients, r^2, >0.99. The retention times measured for all analytes are reported in the Supporting Information. The uncertainties ($\pm\sigma$) reported in the last column of Tables 4, 7 and 8 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.

The enthalpy of transfer measured from the temperature dependence of the negative logarithm of the adjusted retention time can be related to the following thermodynamic relationship:

$$\Delta_{sln}^g H_m(T_m) = \Delta_l^g H_m(T_m) + \Delta_{sln} H_m(T_m) \qquad (1)$$

where $\Delta_l^g H_m(T_m)$ refers to the vaporization enthalpy and $\Delta_{sln} H_m(T_m)$ refers to the interaction of each analyte with the column measured at some mean temperature, T_m. The enthalpy of transfer, $\Delta_{sln}^g H_m(T_m)$, has been found to correlate linearly with $\Delta_l^g H_m(T)$. Temperature T usually differs from T_m. The quality of the correlation obtained is determined both by the quality of data available for the standards and by selection of appropriate standards. Selection of the proper standards is of paramount importance. Previous work has shown that tertiary amines and even hydrocarbons could be used as standards for pyridine and its derivatives. Furthermore, with the exceptions previously noted above for the 1,2-diazines,[2,3] the N-alkylimidazoles and N-alkylpyrazoles,[3] other heterocycles not capable of hydrogen bonding with each other and containing up to 3 nitrogen atoms appear to correlate successfully with tertiary amines and a variety of other nitrogen heterocycles used as standards.[7] Additional details regarding the relationships between $\Delta_{sln}^g H_m(T_m)$, $\Delta_l^g H_m(T_m)$ and $\Delta_{sln} H_m(T_m)$ have been reported.[8]

Vapor pressure and Vaporization Enthalpies by Transpiration. The amines used for the transpiration experiments were of commercial origin with purity ≥99%. Prior to the experiments, the samples were purified by repeated vacuum distillation or vacuum fractional sublimation. The degree of purity of the samples was determined using a Hewlett-Packard gas chromatograph 5890 Series II equipped with a flame ionization detector and a Hewlett-Packard 3390A integrator. No impurities (greater than mass fraction 0.001) could be detected in the samples used for the measurements. Vapor pressures of the amines were determined using the method of transpiration[9,10] in a saturated nitrogen stream. About 0.5 g of the sample was mixed with glass beads and placed in a temperature controlled U-shaped tube having a length of 20 cm and a diameter of 0.5 cm. Glass beads with a diameter of the glass spheres of 1 mm provide surface large enough for rapid vapor—liquid equilibration. At constant temperature (±0.1 K), a nitrogen stream was passed through the U-tube and the transported amount of gaseous material was collected in a cooling trap. The flow rate of the nitrogen stream was measured using a soap bubble flow meter and was optimized in order to reach the saturation equilibrium of the transporting gas at each temperature under study. The amount of condensed substance was determined by GC analysis using an external standard (hydrocarbon $n\text{-}C_nH_{2n+2}$). The saturation vapor pressure p_i^{sat} at each temperature T_i was calculated from the amount of the product collected within a definite period of time. Assuming that Dalton's law of partial pressures applied to the nitrogen stream saturated with the substance i of interest is valid, values of p_i^{sat} were calculated with

$$p_i^{sat} = m_i \cdot R \cdot T_a / V \cdot M_i; V = V_{N2} + V_i \quad (V_{N2} \gg V_i) \qquad (2)$$

where $R = 8.314472\,\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$; m_i is the mass of the transported compound, M_i is the molar mass of the compound, and V_i its volume contribution to the gaseous phase. V_{N2} is the volume of the carrier gas and T_a is the temperature of the soap bubble meter. The volume of

the carrier gas V_{N2} was determined from the flow rate and the time measurement.

The vapor pressures and enthalpies of vaporization evaluated by this work were treated with eqs 3 and 4, respectively,

$$R \ln p_i^{sat} = a + \frac{b}{T} + \Delta_l^g C_p \ln\left(\frac{T}{T_0}\right) \qquad (3)$$

$$\Delta_l^g H_m(T) = -b + \Delta_l^g C_p T \qquad (4)$$

where p_i^{sat} is the vapor pressure; a and b are adjustable parameters; T_0 is an arbitrarily chosen reference temperature, $T_0 = 298.15$ K in this work; and $\Delta_l^g C_p$ is the difference of the molar heat capacities of the gaseous and the liquid phase. Values of $\Delta_l^g C_p$ were calculated using the group contribution method of Acree and Chickos.[11,12] Experimental results and parameters a and b are listed in Table 7 which will be discussed below. The experimental and calculational protocol was checked using vapor pressure measurements of the n-alcohols.[9] Vapor pressures derived by this method were reliable within 1−3% and their accuracy was governed by the reproducibility of the GC analysis. In order to assess the uncertainty of the vaporization enthalpy, the experimental data were approximated with the linear equation $\ln(p_i^{sat}) = f(T^{-1})$ using the method of least-squares. The uncertainty in the enthalpy of vaporization was assumed to be identical to the deviation of experimental $\ln(p_i^{sat})$ values from this linear correlation.

X-ray Diffraction. Diffraction data collection was performed using a Bruker Kappa Apex II Charge Coupled Device (CCD) Detector system single crystal X-ray diffractometer equipped with an Oxford Cryostream LT device. Structure solution and refinement were carried out using the SHELXTL- PLUS software package

Vaporization Enthalpies and Vapor Pressures of the Standards. Available vaporization enthalpy values of the compound in this study from the literature are reported in Table 1. The vaporization enthalpies at $T = 298.15$ K of the standards are literature values and some were calculated from vapor pressure extrapolations of the Wagner and Cox equations, both known to extrapolate well over a limited temperature range and then fit to the Clapeyron eq. For comparison, vaporization enthalpies were also adjusted to this temperature using eq 5.

$$\Delta_l^g H_m(298.15\,\text{K})/(\text{kJ} \cdot \text{mol}^{-1}) = \Delta_l^g H_m(T_m)$$
$$+ [(10.58 + 0.26 C_p(l)/(\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}))(T_m/\text{K} - 298.15)]/1000 \qquad (5)$$

The heat capacity terms required for these temperature adjustments, values of $C_p(l)$, are reported in Table 1 and were evaluated by group additivity.[12] An uncertainty equal to 16 J·mol^{-1}·K^{-1} was associated with the temperature independent term of eq 5. Agreement between the two $\Delta_l^g H_m(298\,\text{K})$ values provided in the last two column of Table 1 are within the uncertainties reported. The literature vaporization enthalpy reported for 1,2, 4-triazolo[1,5-a]pyrimidine at $T = 298.15$ K was obtained by extrapolation of vapor pressures measured from $T = (370 -523)$ K using the Antoine eq and fit similarly.[13] Extrapolations of vapor pressures with temperature modeled by the Antoine eq are known to be more limited. We believe that the vaporization enthalpy calculated using eq 5, which is still within the experimental uncertainty cited in the literature, is a more reasonably value. To illustrate the applicability of eq 5 in adjusting vaporization enthalpies over this

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Table 1. Literature Vaporization Enthalpies

compound	$\Delta_l^g H_m(T_m)$ (kJ·mol^{-1})	T_m/K	$\Delta_l^g H_m$(440 K) (kJ·mol^{-1})	C_p(l) (J·mol^{-1}·K^{-1})	$\Delta_l^g H_m$(298 K) (kJ·mol^{-1}) [calcd][a]	$\Delta_l^g H_m$(298 K) (kJ·mol^{-1}) [lit]	ref
3-methylpyridine	36.07	440		158.1	43.4 ± 2.3	44.47 ± 0.1	14
2,6-dimethylpyridine	42.68 ± 0.1	340	32.77	186.5	45.15 ± 0.7	45.31 ± 0.1	15
3,5-dimethylpyridine	46.69 ± 0.1	340		186.5	49.16 ± 0.7	49.26 ± 0.1	15
2,4,6-trimethylpyridine	47.7 ± 0.6	357		214.9	51.5 ± 1.1		19
pyridazine						53.5 ± 0.4	4
3-methylpyridazine						56.1 ± 4.4	2
quinoline	50.74 ± 0.1	440	48.43	203.9	59.8 ± 2.2	59.31 ± 0.2	18
2-methylquinoline	53.01 ± 0.1	440	50.40	232.3	63.1 ± 2.2	62.64 ± 0.1	16
2,6-dimethylquinoline	57.05 ± 0.1	440	54.35	260.7	68.2 ± 2.2	67.07 ± 0.2	17
4-phenylpyrimidine						68.8 ± 2.5	7
phthalazine						72.8 ± 5.6	2
1-benzylimidazole						83.0 ± 1.0	3, 6
1,2,4-triazolo[1,5-a] pyrimidine	66.0 ± 2.5	440		185.3	74.2 ± 3.8	82.5 ± 13.1	13

[a] Literature data adjusted to T = 298.15 K using eq 5.

Table 2. Equation Parameters

			A. Parameters of the Wagner Equation				
Wagner equation[a]	A_W	B_W	C_W	D_W	T_c/K	p_c/kPa	φ/θ
3-methylpyridine[14]	−8.216 177	4.684 186	−4.363 634	−3.415 866	644.5	4680	2/4.8
2,6-dimethylpyridine[15]	−7.468 74	1.199 395	−1.029 95	−4.489 85	624	3850	2/4
3,5-dimethylpyridine[15]	−8.318 048	3.387 377	−2.542 684	−4.033 37	668	4050	2/4
2-methylquinoline[16]	−8.370 206	2.914 441	−3.761 685	−3.195 98	778	4030	2.5/5
2,6-dimethylquinoline[17]	−8.993 312	3.594 873	−4.631 73	−2.907 492	786	3480	2.5/5

			B. Parameters of the Cox Equation		
Cox equation[a]	A_o	A_1/T^{-1}	$A_2 \times 10^7/T^{-2}$	T_b/K[b]	range/K
quinoline[18]	2.854 61	−0.00 130	9.3118	510.298	298 to 559

		C. Parameters of the Third Order Polynomial, Equation 8			
	A/K^3	B/K^2	C/K	D	range/K
4-phenylpyrimidine[7]	82 739	−1191247.0	−3078.93	8.993	298 to T_b
2,4,6-trimethylpyridine[c]	−160 703	870547.8	−6636.067	12.401	287−423

[a] $T_r = T/T_c$. [b] T_b, boiling temperature at p = 101.325 kPa. [c] Experimental data from ref 19 fit to eq 8.

temperature range, the vaporization enthalpies of some of the other standards in Table 1 were adjusted over this same temperature range using eq 5 for comparison. Agreement between the two methods, columns 6 and 7 of Table 1 is within the uncertainties reported. The vaporization enthalpy of 1-benzylimidazole was calculated as the difference between the sublimation enthalpy[6] and fusion enthalpy as described previously.[3]

Liquid vapor pressures for 3-methylpyridine,[14] 2,6- and 3,5-dimethylpyridine,[15] 2-methylquinoline,[16] and 2,6-dimethylquinoline,[17] are available in various forms of the Wagner equation, eq 6. Liquid vapor pressures for quinoline[18] are available in the form of the Cox equation, eq 7. The parameters for these equations are reported in Table 2, parts A and B. Vaporization enthalpies at T = 298.15 K and vapor pressures for 4-phenylpyrimidine from T = 298.15 K to the boiling temperature (T_b), have been evaluated previously by CGC and fit to the third order polynomial, eq 8.[7] The constants for the calculation of liquid vapor pressure using eq 8 are provided in Table 2C. Experimental vapor pressures for 2,4,6-trimethylpyridine[19] were also previously fit to eq 8.[7] T_r refers to the reduced temperature,

T/T_c, p_c and T_c refer to the critical pressure and critical temperature, respectively and p_0 = 101.325 kPa.

$$\ln(p/p_c) = (1/T_r)[A_W(1 - T_r) + B_W(1 - T_r)^{1.5} + C_W((1 - T_r)^\varphi + D_W(1 - T_r)^\theta] \quad (6)$$

$$\ln(p/p_o) = (1 - T_b/T) \exp(A_o + A_1(T/K) + A_2(T/K)^2) \quad (7)$$

$$\ln(p/p_o) = A(T/K)^{-3} + B(T/K)^{-2} + C(T/K)^{-1} + D \quad (8)$$

■ RESULTS

The results of six correlations are reported in Table 3 and the resulting vaporization enthalpies of the substances targeted summarized in Table 4. The equations describing the correlations between $\Delta_l^g H_m$(298.15 K) and $\Delta_{sln}^g H_m(T_m)$, eqs 9−14, are reported under each respective table. The vaporization enthalpy of triazolo[1,5-a]pyrimidine reported in Table 1 is the only

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Table 3. Results of the Correlations of Runs 1−6

run 1	slope, T/K	intercept	$\Delta_{sln}^{g}H_m(431\ K)$, $kJ\cdot mol^{-1}$	$\Delta_f^g H_m(298\ K)$, $kJ\cdot mol^{-1}$ (lit.)	$\Delta_f^g H_m(298\ K)$, $kJ\cdot mol^{-1}$ (calcd)
3-methylpyridine	−3466.4	9.728	28.82	44.47 ± 0.1	44.9 ± 2.5
2,4,6-trimethylpyridine	−4044.3	10.474	33.62	51.5 ± 1.1	50.9 ± 2.6
2-(N,N-dimethylamino)pyridine	−5773.9	10.691	36.56		54.6 ± 2.7
1,5-diazabicyclo[4.3.0]non-5-ene	−4397.9	11.377	41.57		60.9 ± 2.9
4-(N,N-dimethylamino)pyridine	−4999.6	11.36	41.91		61.3 ± 2.9
1,8-diazabicyclo[5.4.0]undec-7-ene	−5041.6	12.043	46.91		67.6 ± 3.1
4-phenylpyrimidine	−5642.9	12.182	48	68.8 ± 2.5	68.9 ± 3.2

$$\Delta_l^g H_m(298\ K)/kJ\cdot mol^{-1} = (1.25 \pm 0.05)\Delta_{sln}^g H_m(431\ K)/kJ\cdot mol^{-1} + (8.792 \pm 2.0);\quad r^2 = 0.9982 \tag{9}$$

run 2	slope, T/K	intercept	$\Delta_{sln}^{g}H_m(415\ K)$, $kJ\cdot mol^{-1}$	$\Delta_f^g H_m(298\ K)$, $kJ\cdot mol^{-1}$ (lit.)	$\Delta_f^g H_m(298\ K)$, $kJ\cdot mol^{-1}$ (calcd)
2,6-dimethylpyridine	−3680.59	10.219	30.60	45.31 ± 0.1	45.7 ± 1.7
3,5-dimethylpyridine	−3975.98	10.376	33.05	49.26 ± 0.1	48.9 ± 1.7
2-(N,N-dimethylamino)pyridine	−4486.06	10.941	37.3		54.5 ± 1.8
1,5-diazabicyclo[4.3.0]non-5-ene	−5104.98	11.663	42.44		61.2 ± 1.9
4-(N,N-dimethylamino)pyridine	−5114.02	11.573	42.52		61.3 ± 2.0
2-methylquinoline	−5201.07	11.592	43.24	62.64 ± 0.1	62.3 ± 2.0
1,8-diazabicyclo[5.4.0]undec-7-ene	−5722.8	12.272	47.58		68.0 ± 2.1
4-phenylpyrimidine	−5825.55	12.345	48.43	68.8 ± 2.5	69.1 ± 2.1

$$\Delta_l^g H_m(298\ K)/kJ\cdot mol^{-1} = (1.31 \pm 0.033)\Delta_{sln}^g H_m(415\ K)/kJ\cdot mol^{-1} + (5.56 \pm 1.33);\quad r^2 = 0.9986 \tag{10}$$

run 3	slope, T/K	intercept	$\Delta_{sln}^{g}H_m(430\ K)$, $kJ\cdot mol^{-1}$	$\Delta_f^g H_m(298\ K)$, $kJ\cdot mol^{-1}$ (lit.)	$\Delta_f^g H_m(298\ K)$, $kJ\cdot mol^{-1}$ (calcd)
2,6-dimethylpyridine	−3663.7	9.926	30.46	45.31 ± 0.1	45.6 ± 2.3
quinoline	−4841.0	10.797	40.25	59.31 ± 0.1	58.8 ± 2.6
imidazo[1,2-a]pyridine	−5000.0	11.063	41.57		60.5 ± 2.6
2-methylquinoline	−5173.6	11.27	43.01	62.64 ± 0.2	62.5 ± 2.7
triazolo[1,5-a]pyrimidine	−5279.4	11.43	43.89		63.7 ± 2.7
2,6-dimethylquinoline	−5623.2	11.818	46.75	67.07 ± 0.2	67.5 ± 2.8

$$\Delta_l^g H_m(298\ K)/kJ\cdot mol^{-1} = (1.348 \pm 0.045)\Delta_{sln}^g H_m(430\ K)/kJ\cdot mol^{-1} + (4.51 \pm 1.84);\quad r^2 = 0.9977 \tag{11}$$

run 4	slope, T/K	intercept	$\Delta_{sln}^{g}H_m(432\ K)$, $kJ\cdot mol^{-1}$	$\Delta_f^g H_m(298\ K)$, $kJ\cdot mol^{-1}$ (lit.)	$\Delta_f^g H_m(298\ K)$, $kJ\cdot mol^{-1}$ (calcd)
pyridazine	−3587.5	9.493	29.83	53.5 ± 0.4	53.1 ± 2.2
3-methylpyridazine	−3943.2	9.937	32.78	56.1 ± 4.8	56.5 ± 2.3
imidazo [1,2-a] pyridine	−4980.9	11.022	41.41		66.5 ± 2.5
1,2,4-triazolo [1,5-a] pyrimidine	−5250.5	11.369	43.65		69.1 ± 2.6
phthalazine	−5628.0	11.573	46.79	72.8 ± 5.6	72.7 ± 2.7

$$\Delta_l^g H_m(298\ K)/kJ\cdot mol^{-1} = (1.15 \pm 0.046)\Delta_{sln}^g H_m(432\ K)/kJ\cdot mol^{-1} + (18.7 \pm 1.7);\quad r^2 = 0.9984 \tag{12}$$

run 5	slope, T/K	intercept	$\Delta_{sln}^{g}H_m(415\ K)$, $kJ\cdot mol^{-1}$	$\Delta_f^g H_m(298\ K)$, $kJ\cdot mol^{-1}$ (lit.)	$\Delta_f^g H_m(298\ K)$, $kJ\cdot mol^{-1}$ (calcd)
pyridazine	−3702.1	10.011	30.78	53.5 ± 0.4	52.7 ± 6.0
3-methylpyridazine	−4045.5	10.427	33.63	56.1 ± 4.8	56.5 ± 6.2
imidazo [1,2-a] pyridine	−5072	11.484	42.17		67.8 ± 6.8
1,2,4-triazolo [1,5-a] pyrimidine	−5361.1	11.877	44.57		71.0 ± 7.0
phthalazine	−5717.1	12.03	47.53	72.8 ± 5.6	75.0 ± 7.3
1-benzylimidazole	−6283.9	13.039	52.24	83.0 ± 1.0	81.2 ± 6.3

$$\Delta_l^g H_m(298\ K)/kJ\cdot mol^{-1} = (1.33 \pm 0.11)\Delta_{sln}^g H_m(415\ K)/kJ\cdot mol^{-1} + (11.7 \pm 4.8);\quad r^2 = 0.9854 \tag{13}$$

run 6	slope, T/K	intercept	$\Delta_{sln}^{g}H_m(415\ K)$, $kJ\cdot mol^{-1}$	$\Delta_f^g H_m(298\ K)$, $kJ\cdot mol^{-1}$ (lit.)	$\Delta_f^g H_m(298\ K)$, $kJ\cdot mol^{-1}$ (calcd)
pyridazine	−3859	9.672	32.08	53.5	52.8 ± 3.3
3-methylpyridazine	−4219.7	10.119	35.08	56.1	56.9 ± 3.4
4-N,N-dimethylaminopyridine	−5333.2	11.337	44.34		69.6 ± 3.8
1,2,4-triazolo [1,5-a] pyrimidine	−5541.9	11.537	46.07		71.9 ± 3.9
1-benzylimidazole	−6506.4	12.778	54.09	83	82.9 ± 4.3

$$\Delta_l^g H_m(298\ K)/kJ\cdot mol^{-1} = (1.37 \pm 0.06)\Delta_{sln}^g H_m(415\ K)/kJ\cdot mol^{-1} + (8.95 \pm 2.6);\quad r^2 = 0.9978 \tag{14}$$

Table 4. Summary of the Vaporization Enthalpies Evaluated in Runs 1−6[a]

	$\Delta_f^g H_m$(298 K)/kJ·mol^{-1}		
	run 1	run 2	average (runs 1 and 2)
2-(N,N-dimethylamino)pyridine	54.6 ± 2.7	54.5 ± 1.8	54.6 ± 2.3
1,5-diazabicyclo[4.3.0]non-5-ene	60.9 ± 2.9	61.2 ± 1.9	61.1 ± 2.4
4-(N,N-dimethylamino)pyridine	61.3 ± 2.9	61.3 ± 2.0	61.3 ± 2.5
1,8-diazabicyclo[5.4.0]undec-7-ene	67.6 ± 3.1	68.0 ± 2.1	67.8 ± 2.6
		run 3	
imidazo[1,2-a]pyridine		60.5 ± 2.6	
triazolo[1,5-a]pyrimidine		63.7 ± 2.7	

	run 4	run 5	run 6	average
imidazo[1,2-a]pyridine	66.5 ± 2.5	67.8 ± 6.8		67.1 ± 4.6
triazolo[1,5-a]pyrimidine	69.1 ± 2.6	71.0 ± 7.0	71.9 ± 3.9	70.7 ± 4.5
4-(N,N-dimethylamino)pyridine			69.6 ± 3.8	69.6 ± 3.8

[a] The uncertainty reported is an average of the deviations reported in columns 2−4.

Table 5. Correlation of $\ln(p/p_o)$ (Lit.) with $\ln(t_o/t_a)$ at T = 298.15 K for Run 2[a]

run 2	slope, T/K	intercept	$\ln(t_0/t_a)$	$\ln(p/p_0)$ lit	$\ln(p/p_0)$ (calcd)
2,6-dimethylpyridine	−3680.59	10.219	−2.13	−4.86	−4.92
3,5-dimethylpyridine	−3975.98	10.376	−2.96	−6.1	−6.02
2-(N,N-dimethylamino)pyridine	−4486.06	10.941	−4.11		−7.53
1,5diazabicyclo[4.3.0]non-5-ene	−5104.98	11.663	−5.46		−9.31
4-(N,N-dimethylamino)pyridine	−5114.02	11.573	−5.58		−9.47
2-methylquinoline	−5201.07	11.592	−5.85	−9.78	−9.83
1,8-diazabicyclo[5.4.0]undec-7-ene	−5722.8	12.272	−6.92		−11.23
4-phenylpyrimidine	−5825.55	12.345	−7.19	−11.61	−11.59

[a] p_0 = 101.325 kPa.

$$\ln(p/p_o)_{calc} = (1.316 \pm 0.019)\ln(t_o/t_a) - (2.12 \pm 4.09); \quad r^2 = 0.9996 \quad (15)$$

Table 6. Constants of Equation 5^{,a} and Experimental and Predicted Boiling Temperatures

						T_b/K[b]	
compound	A/K^3	B/K^2	C/K	D	p/kPa	lit	calcd
1,5-diazabicyclo[4.3.0]non-5-ene							
run 1	32198211.83	−754501.37	−3352.01	9.262	1.47	370.2	379.2
run 2	59025623.51	−963598.05	−2898.689	9.027	1.47	370.2	379.2
1,8-diazabicyclo[5.4.0]undec-7-ene							
run 1	61193659.29	−1025298.42	−3315.72	9.155	0.4	354.2	351.9
					0.08	370.2	380.4
run 2	78641023.30	−1167533.73	−3000.657	8.996	0.4	354.2	352.1
					0.08	370.2	380.4
2-N,N-(dimethylamino)pyridine							
run 1	8721128.07	−535375.08	−3277.644	9.164	101.3	469.2	476.1
					2.0	361.2	359.0
run 2	45110792.05	−814218.84	−2620.39	8.720	101.3	469.2	474.3
					2.0	361.2	359.1
4-N,N-(dimethylamino)pyridine							
run 1	*37602851.35*	*−805105.12*	−3245.291	9.064	6.67	435.2	420
run 2	64357070.84	−1014884.62	−2745.262	8.730	6.67	435.2	419.1
imidazo [1,2-a] pyridine							
run 3[b]	69729011.12	−1073486.71	−2412.080	8.259	0.133	376.2[b]	335.3
					3.6	426	401.3
					0.033	370.2	314.7

[a] Constants in italics are considered unreliable. [b] Boiling temperatures and pressures were taken from either the Aldrich Catalog or from SciFinder Scholar. Boiling temperatures are at the pressures noted in column 6.

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Table 7. Experimental Vapor Pressures and Enthalpies of Vaporizations by Transpiration

T^a/ K	m^b/ mg	$V_{(N2)}{}^c$/dm^3	flow of N$_2$/dm$^3 \cdot$h^{-1}	p^d/Pa	$(p_{exp} - p_{calc})$/ Pa	$\Delta_l^g H_m$/ kJ·mol^{-1}

A. 2-(N,N-Dimethylamino)pyridine (1); $\Delta_l^g H_m(298.15\,K) = (55.15 \pm 0.10)\,kJ\cdot mol^{-1}$

$$\ln(p/p_o) = \frac{285.36}{R} - \frac{74972.37}{(R \cdot T/K)} - \frac{66.5}{R}\ln\left(\frac{T/K}{298.15}\right)$$

T^a/ K	m^b/ mg	$V_{(N2)}{}^c$/dm^3	flow of N$_2$/dm$^3 \cdot$h^{-1}	p^d/Pa	$(p_{exp} - p_{calc})$/ Pa	$\Delta_l^g H_m$/ kJ·mol^{-1}
288.1	3.89	2.90	2.56	27.4	0.4	55.86
291.5	3.13	1.80	3.04	35.4	−0.1	55.62
295.3	3.97	1.70	2.54	47.6	0.1	55.37
298.7	3.39	1.12	3.04	61.1	−0.3	55.14
302.2	4.14	1.06	2.54	79.5	0.1	54.90
305.5	6.35	1.26	3.02	101.6	0.8	54.67
309.1	4.00	0.640	2.56	126.6	−2.5	54.43
312.7	7.41	0.911	3.04	163.5	−0.6	54.19
316.2	6.50	0.636	2.54	206.6	−0.6	53.95
319.7	5.65	0.444	1.07	257.2	−2.1	53.71
323.2	7.13	0.449	1.08	321.2	−1.4	53.47
326.7	7.00	0.356	1.07	397.3	−2.5	53.23
330.2	6.45	0.266	1.06	490.4	−0.6	52.99
333.7	7.93	0.266	1.06	599.6	−1.2	52.76
337.2	10.49	0.288	1.07	735.0	4.2	52.52
340.6	10.94	0.249	1.07	884.6	2.9	52.29
344.2	10.14	0.191	1.07	1071.1	4.9	52.04
347.6	11.27	0.178	1.07	1285.5	9.0	51.81

B. 4-(N,N-Dimethylamino)pyridine; $\Delta_{cr}^g H_m(298.15\,K) = (87.02 \pm 0.19)\,kJ\cdot mol^{-1}$

$$\ln(p/p_o) = \frac{313.49}{R} - \frac{95610.41}{(R \cdot T/K)} - \frac{28.8}{R}\ln\left(\frac{T/K}{298.15}\right)$$

T^a/ K	m^b/ mg	$V_{(N2)}{}^c$/dm^3	flow of N$_2$/dm$^3 \cdot$h^{-1}	p^d/Pa	$(p_{exp} - p_{calc})$/ Pa	$\Delta_l^g H_m$/ kJ·mol^{-1}
323.2	0.79	2.50	4.29	6.35	0.02	86.30
325.7	0.86	2.14	4.27	8.08	−0.01	86.23
328.2	0.91	1.79	4.29	10.23	−0.09	86.16
330.7	1.25	1.92	4.27	13.08	−0.02	86.09
333.2	1.16	1.43	4.28	16.29	−0.20	86.02
338.2	2.25	1.70	2.38	26.46	0.25	85.87
343.1	2.62	1.28	2.40	41.16	0.63	85.73
348.1	2.07	0.673	2.38	61.76	−0.62	85.59
353.1	2.85	0.594	2.38	96.21	1.43	85.44
358.1	2.02	0.285	1.14	142.2	0.3	85.30
360.6	2.36	0.272	1.13	174.5	0.8	85.22
363.1	3.32	0.317	1.13	211.4	0.9	85.15
365.6	3.06	0.244	1.13	252.8	−3.0	85.08
368.1	3.73	0.245	1.13	306.5	−2.9	85.01

C. 1,5-Diazabicyclo[4.3.0]non-5-ene (3); $\Delta_l^g H_m(298.15\,K) = (61.88 \pm 0.21)\,kJ\cdot mol^{-1}$

$$\ln(p/p_o) = \frac{290.62}{R} - \frac{80635.25}{(R \cdot T/K)} - \frac{62.9}{R}\ln\left(\frac{T/K}{298.15}\right)$$

T^a/ K	m^b/ mg	$V_{(N2)}{}^c$/dm^3	flow of N$_2$/dm$^3 \cdot$h^{-1}	p^d/Pa	$(p_{exp} - p_{calc})$/ Pa	$\Delta_l^g H_m$/ kJ·mol^{-1}
320.2	4.23	1.33	3.20	62.69	0.80	60.63
327.2	6.24	1.23	3.20	100.47	−0.07	60.14
334.2	6.36	0.798	3.19	157.37	−2.08	59.66
341.2	3.61	0.291	1.03	244.79	−1.70	59.17
348.1	5.31	0.283	1.01	369.87	−3.35	58.69
351.6	6.55	0.285	1.01	453.03	−3.48	58.45
355.1	12.29	0.434	1.01	558.62	2.90	58.21
358.6	8.78	0.252	1.01	687.08	13.72	57.96
362.1	10.72	0.262	1.01	808.49	−3.75	57.72

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Table 7. Continued

T^a/ K	m^b/ mg	$V_{(N2)}{}^c$/dm^3	flow of N$_2$/dm^3·h^{-1}	p^d/Pa	$(p_{exp} - p_{calc})$/ Pa	$\Delta_f^g H_m$/ kJ·mol^{-1}

D. 1,8-Diazabicyclo[5.4.0]undec-7-ene (4); $\Delta_f^g H_m$(298.15 K) = (70.72 ± 0.15) kJ·mol^{-1}

$$\ln(p/p_o) = \frac{318.26}{R} - \frac{92872.52}{(R\cdot T/K)} - \frac{74.3}{R}\ln\left(\frac{T/K}{298.15}\right)$$

T^a/ K	m^b/ mg	$V_{(N2)}{}^c$/dm^3	flow of N$_2$/dm^3·h^{-1}	p^d/Pa	$(p_{exp} - p_{calc})$/ Pa	$\Delta_f^g H_m$/ kJ·mol^{-1}
328.2	4.12	2.23	3.35	29.69	0.28	68.65
330.7	4.02	1.81	3.35	35.79	0.23	68.45
333.1	4.08	1.52	3.35	43.05	0.36	68.25
335.7	3.92	1.23	3.35	51.58	0.11	68.03
338.1	3.77	1.00	3.35	60.28	−1.12	67.83
343.1	4.47	0.837	3.35	86.17	−1.01	67.42
348.1	3.90	0.518	2.07	121.59	−0.53	67.00
353.2	3.91	0.378	1.33	166.91	−3.18	66.58
358.1	5.08	0.353	1.33	231.89	−0.61	66.18
360.6	5.59	0.331	1.32	273.04	1.88	65.97
363.1	6.50	0.331	1.32	317.36	2.29	65.76
365.6	5.95	0.264	1.32	364.98	−0.40	65.56
368.1	7.01	0.265	1.32	427.83	4.17	65.35

E. Imidazo[1,2-a]pyridine (6); $\Delta_f^g H_m$(298.15 K) = (67.41 ± 0.23) kJ·mol^{-1}

$$\ln(p/p_o) = \frac{292.77}{R} - \frac{85716.18}{(R\cdot T/K)} - \frac{61.4}{R}\ln\left(\frac{T/K}{298.15}\right)$$

T^a/ K	m^b/ mg	$V_{(N2)}{}^c$/dm^3	flow of N$_2$/dm^3·h^{-1}	p^d/Pa	$(p_{exp} - p_{calc})$/ Pa	$\Delta_f^g H_m$/ kJ·mol^{-1}
318.2	2.15	4.36	5.23	10.33	0.00	66.21
323.2	1.97	2.75	5.24	14.95	−0.21	65.90
328.2	2.80	2.61	5.22	22.41	0.40	65.59
333.2	2.78	1.84	5.22	31.50	−0.04	65.27
338.1	2.77	1.31	5.24	44.22	−0.13	64.96
343.2	3.92	1.30	5.22	62.90	0.64	64.65
348.2	5.25	1.30	5.22	84.35	−1.78	64.33
353.2	7.45	1.30	5.22	119.66	1.76	64.02
358.1	4.82	0.639	2.56	158.16	−0.90	63.71
360.6	5.58	0.632	2.53	185.19	0.51	63.55
363.1	6.47	0.639	2.56	212.37	−1.29	63.39
368.1	8.60	0.635	2.54	284.24	0.74	63.08

[a] Saturation temperature. [b] Mass of transferred sample condensed at T = 243 K. [c] Volume of nitrogen used to transfer mass m of sample. [d] Vapor pressure at temperature T, calculated from m and the residual vapor pressure at the cooling temperature T = 243 K; p_0 = 1 Pa.

experimental value currently available in the literature for comparison. The use of pyridine and quinoline derivatives as standards, run 3, results in a vaporization enthalpy of (63.7 ± 2.7) kJ·mol^{-1}, considerably less than either experimental value reported in Table 1 for this compound. This suggests that the standards used for this material are inappropriate. The use of pyridazine derivatives and N-benzylimidazole, compounds previously shown to exhibit anomalously larger vaporization enthalpies, runs 4, 5 and 6, results in an averaged vaporization enthalpy value of (70.7 ± 4.5) kJ·mol^{-1} for triazolo[1,5-a]pyrimidine, a value that does fall within the literature value cited in Table 1 or calculated using eq 5. On the basis of these results, triazolo[1,5-a]pyrimidine appears to have intermolecular interactions comparable to those found in pyridazines, N-substituted imidazoles and pyrazoles, approximately 7 kJ·mol^{-1} larger than found in pyridines, pyrimidines and derivatives.

In addition to vaporization enthalpies, the equations obtained from the CGC results are capable of providing vapor pressures as well, provided vapor pressures of the standards are available over a broad temperature range. Table 5 illustrates a typical correlation at between $\ln(p/p_0)_{lit}$ and $\ln(t_0/t_a)$ at T = 298.15 K for run 2.

Since different standards were used for each run, separates correlations were performed for runs 1, 2, and 3 at T = 10 K intervals from T = (298.15 to 440) K. Vapor pressures as a function of temperature in terms of $\ln(p/p_0)$ were calculated by correlations similar to the one illustrated in Table 5 and fit to eq 8. The constants of eq 8 are reported in Table 6 along with predicted boiling temperatures at various experimental pressures. As noted in the table, the boiling temperatures for the first three entries are predicted within an absolute average error of less than 6 K. The boiling temperatures of 1,5-diazabicyclo[4.3.0]non-5-ene and 1,8-diazabicyclo[5.4.0]undec-7-ene are predicted to be slightly larger than the experimental values. The results calculated for 4-(N,N-dimethylamino)pyridine are just the opposite. The boiling temperature is under-predicted by 16 K which makes the vapor pressures calculated by these correlations and the vaporization enthalpy suspect. The boiling temperature calculated for imidazo[1,2-a]pyridine under-predicts the experimental value by 40 K at 3.6 kPa and 25 K at 0.133 kPa. This is similar to what was previously observed for various pyridazine and imidazoles using inappropriate standards. We conclude from this that the vaporization enthalpies

Table 8. Comparison of Vaporization Enthalpies

	$\Delta_l^g H_m(298\ K)/kJ\cdot mol^{-1}$		
	transpiration	correlation gas chromatography	$\Delta\Delta_l^g Hm(298\ K)$
		Runs 1−2	
2-(N,N-dimethylamino)pyridine	55.2 ± 0.10	54.6 ± 2.3	0.6 ± 2.3
1,5-diazabicyclo[4.3.0]non-5-ene	61.9 ± 0.21	61.1 ± 2.4	0.8 ± 2.4
4-(N,N-dimethylamino)pyridine	68.4 ± 0.9[a]	61.3 ± 2.5	7.1 ± 2.7
1,8-diazabicyclo[5.4.0]undec-7-ene	70.7 ± 0.15	67.8 ± 2.6	2.9 ± 2.6
		Run 3	
imidazo[1,2-a]pyridine	67.4 ± 0.2	60.5 ± 2.6	6.9 ± 2.6
triazolo[1,5-a]pyrimidine	74.2 ± 3.8[b]	63.7 ± 2.7	10.5 ± 4.7
		Runs 4−6	
imidazo[1,2-a]pyridine	67.4 ± 0.23	67.1 ± 4.6	0.3 ± 4.6
triazolo[1,5-a]pyrimidine	74.2 ± 3.8[b]	70.7 ± 4.5	3.5 ± 5.9
4-(N,N-dimethylamino)pyridine	68.4 ± 0.9[a]	69.6 ± 3.8	1.2 ± 3.9

[a] Calculated as the difference between $\Delta_{cr}^g H_m(298.15)$ and $\Delta_{cr}^l H_m(298.15)$; see Supporting Information. [b] Measured by ebulliometry.[13]
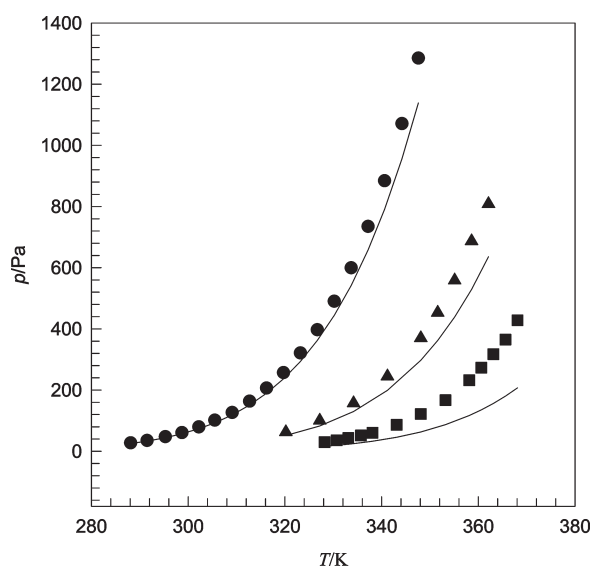

Figure 3. The vapor pressures measured by transpiration (symbols) and those calculated by correlation eq 8 (line) for 2-(N,N-dimethyla-mino)pyridine (circles), 1,5-diazabicyclo[4.3.0]non-5-ene (triangles), and 1,8-diazabicyclo[5.4.0]undec-7-ene (squares).

and vapor pressures of 1,5-diazabicyclo[4.3.0]non-5-ene, 1,8-diazabicyclo[5.4.0]undec-7-ene and 2-N,N-dimethylaminopyridine evaluated by runs 1−3 are relatively accurate. The vaporization enthalpy results for 4-(N,N-dimethylamino)pyridine and imidazo[1,2-a]pyridine using the standards of runs 1 through 3 are clearly more problematic. Consequently, both of these materials were evaluated also using pyridazine and imidazole derivatives, runs 4−6. Since vapor pressures of the standards used for these runs are not available, no definite conclusion regarding the vaporization enthalpies of imidazo[1,2-a]pyridine and 4-(N,N-dimethylamino)pyridine is warranted.

As a test of the results of the two sets of correlations, runs 1−3 and 4−6, the vaporization enthalpies of 2- and 4-(N,N-dimethylamino)pyridine, 1,5-diazabicyclo[4.3.0]non-5-ene, 1,8-diazabicyclo[5.4.0]undec-7-ene, and imidazo[1,2-a]pyridine have also

been measured by transpiration. The results for these five compounds are reported in Table 7 and the results of the two methods compared in Table 8 and Figure 3. With the exception of 4-(N,N-dimethylamino)pyridine, both vaporization enthalpies and vapor pressures measured by transpiration compare favorably with those of runs 1 and 2 for 2-(N,N-dimethylamino)pyridine, 1,5-diazabicyclo[4.3.0]non-5-ene, and 1,8-diazabicyclo[5.4.0]undec-7-ene. The vapor pressures calculated by correlation eq 8 using the constants for run 1 in Table 6 are compared with the values measured by transpiration in Figure 3. Comparisons appear best for 2-(N,N-dimethylamino)pyridine and show somewhat increasing divergence between the two methods for 1,5-diazabicyclo[4.3.0]non-5-ene, and 1,8-diazabicyclo[5.4.0]undec-7-ene. The vapor pressure comparison for 4-(N,N-dimethylamino)pyridine, not shown, showed the largest divergence. The vaporization enthalpy of 4-(N,N-dimethylamino)-pyridine obtained from the transpiration experiments was calculated as the difference between the sublimation enthalpy ((87.02 ± 0.19) kJ·mol^{-1})[20] and the fusion enthalpy,[20] ($\Delta_{cr}^g H_m(T_{fus})$= 21.63 kJ·mol^{-1}). Information detailing the temperature adjustment of the fusion enthalpy to $T = 298.15$ K is provided in the Supporting Information. The vaporization enthalpy of 4-(N,N-dimethylamino)pyridine obtained in this manner does compare favorably with the results of run 6 using pyridazine and imidazole derivatives as standards.

■ DISCUSSION OF RESULTS

In an effort to gain some understanding as to why the use of some standards in CGC result in vaporization enthalpies that are smaller in magnitude than measured by other means, both structural and polar effects have been considered. 2-(N,N-Dimethylamino)-pyridine, 1,5-diazabicyclo[4.3.0]non-5-ene, and 1,8-diazabicyclo-[5.4.0]undec-7-ene are compounds that have some structural features similar to 1-substituted imidazoles. The vaporization enthalpies of these materials are well reproduced by CGC using pyridines as standards while those of 1-substituted imidazoles using similar standards were not.[3] This suggests that having two conjugated nitrogens in a 1,3-relationship is not a sufficient structural criterion to identify the differences observed. Extensive conjugation appears to also be important requirement. In an effort to examine the role that polarity may play, Table 9 lists a series of compounds, many used as

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Table 9. Experimental and C-GC Vaporization Enthalpies and Their Relation to Dipole Moments (μ)

		$\Delta_l^g H_m$(298 K) (kJ·mol^{-1})				
		lit.	CGC	ref[a]	$\Delta\Delta_l^g H_m$(298 K) (kJ·mol^{-1})	μ (D)[b]
				A		
C_5H_5N	pyridine	40.2 ± 0.1	40.0 ± 2.3[c]	1, 25	0.2 ± 2.3	2.19 B
C_5H_7N	N-methylpyrrole	40.6 ± 0.8	40.3 ± 2.5	3, 26	0.3 ± 2.6	1.96 B
$C_5H_{11}N$	N-methylpyrrolidine	34.2 ± 0.7	36.6 ± 2.4	3, 27	−2.4 ± 2.5	1.1 B
C_6H_7N	3-methylpyridine	44.5 ± 0.2	44.5 ± 2.0[c]	1, 14	0 ± 2.0	2.4 B
$C_7H_{10}N_2$	2-N,N-dimethylamino-pyridine	55.2 ± 0.1	54.6 ± 2.3	tw	0.6 ± 2.3	1.92 B
$C_8H_6N_2$	quinoxaline	56.5 ± 2.0	58.7 ± 1.9	2, 30	−2.2 ± 2.8	0.51 B
$C_8H_{11}N$	2,4,6-trimethylpyridine	51.0 ± 1.0	50.4 ± 2.9	11, 19	−0.6 ± 3.0	2.26 C
C_9H_7N	quinoline	59.3 ± 0.2	59.5 ± 1.3	7, 18	−0.2 ± 1.3	2.24 B
C_9H_7N	isoquinoline	60.3 ± 0.12	60.1 ± 1.3	7, 18	−0.2 ± 1.3	2.53 B
$C_{10}H_8N_2$	2,2-bipyridyl	67.0 ± 2.3	63.5 ± 3.2	7	3.5 ± 3.9	0.69 B
$C_{10}H_9N$	2-methylquinoline	62.6 ± 0.1	62.8 ± 1.3	7, 17	−0.2 ± 1.3	2.07 B
$C_{12}H_{10}N_2$	trans azobenzene	74.7 ± 1.6	74.9 ± 0.7	3, 28	−0.2 ± 1.7	0 B
$C_{13}H_9N$	phenanthridine	80.14	79.3 ± 5.5	7, 29	0.8 ± 5.5	2.39 B
$C_{13}H_9N$	acridine	78.63	78.2 ± 1.3	7, 29	0.4 ± 1.3	2.29 B
				B		
$C_4H_4N_2$	pyridazine	53.5 ± 0.4	46.5 ± 2.2	11, 4	7.0 ± 2.2	4.1 B
$C_4H_6N_2$	N-methylimidazole	55.6 ± 0.6	48.8 ± 3.5	3, 5, 6	6.8 ± 3.6	3.7[d] B
$C_4H_6N_2$	N-methylpyrazole	48.0 ± 1.3	41.6 ± 2.9	tw,[e] 6	6.4 ± 3.2	2.29 B
$C_7H_{10}N_2$	4-N,N-dimethylamino-pyridine	68.4 ± 0.9	61.3 ± 2.5	tw	7.1 ± 2.7	4.33 B
$C_9H_8N_2$	N-phenylpyrazole	70.2 ± 3.4	63.5 ± 2.9	3, 25	6.7 ± 4.5	2.0 B
$C_9H_8N_2$	N-phenylimidazole	84.6 ± 3.7	67.7 ± 2.1	3, 25	16.9 ± 4.3	3.5 B
$C_{12}H_8N_2$	benzo[c]cinnoline	89.2 ± 2.3	81.9 ± 1.1	2, 28	7.3 ± 2.5	4.1 B

[a] Where references to both CGC and literature values and can be found; tw: this work. [b] Key: B, benzene; C, CCl$_4$.[21] [c] Average of two or more runs. [d] Reference 22 [e] See run 7 in the Supporting Information.

standards in various correlations, their literature vaporization enthalpies measured by various methods, their vaporization enthalpy obtained by CGC, and their corresponding dipole moments if available, most measured in benzene Only compounds whose dipole moments could be located are included in Table 9. Also included in column 6 of Table 9 is the error associated with the measurement as judged by the uncertainty in both the literature value and the corresponding value obtained by correlation. The dipole moments of the compounds in Table 9A vary from 0 to 2.5 D. Most of these compounds have been used as standards in various correlations, including for those compounds listed in Table 9B. The enthalpy difference between most of the literature values and those measured by correlation in Table 9B appears to be a constant 7 kJ·mol^{-1} larger. Only N-phenylimidazole shows a larger deviation.[3] A recent redetermination of the vaporization enthalpy of 1-methylimidazole,[5] resulted in a new value considerably smaller than the 64.7 kJ·mol^{-1} reported earlier[6] and also results in a 7 kJ·mol^{-1} difference. Most of the dipole moments of these materials are greater than 2.5 D, the N-substituted pyrazoles being the notable exceptions. Solely on the basis of dipole moments, both pyrazoles would be expected to correlate with the compounds in Table 9A. Either one of the experimental numbers for these materials is in error or polarity, at least as measured by the magnitude of the dipole moment, does not seem to completely correlate with the vaporization enthalpy behavior exhibited by the compounds in Table 9. It is not clear why there appears to be a discontinuity in vaporization enthalpy obtained by correlation with compounds exhibiting a dipole moment above and below a dipole moment of about 2.5 D

Polarity, extensive conjugation and planarity appear to be important structural features of all the compounds in Table 9B. Planarity is observed in the crystal structure of 4-N,N-(dimethylamino)pyridine[23] and all the ring atoms of N-alkyl and N-aryl substituted pyrazoles listed in the Cambridge Database likewise lie in the same plane. The tertiary nitrogen adjacent to the methylene group in N-benzyl-imidazole, another compounds found to exhibit a larger vaporization enthalpy than expected (10.8 ± 5.3 kJ·mol^{-1}), is likewise planar.[24] While a number of the compounds exhibiting larger vaporization enthalpy are liquids whose crystal structures have not been determined, the crystal structure of 1,2,4-triazolo[1,5-a]pyrimidine seemed like a another good test case to determine whether planarity is an important structural feature. Like 4-N,N-(dimethylamino)pyridine, 1,2,4-triazolo[1,5-a]pyrimidine is another material that formally contains an sp^3 hybridized bridgehead nitrogen.

The crystal structure of 1,2,4-triazolo[1,5-a]pyrimidine is shown in Figure 4 and the packing in the crystal is provided in Figure 5. Additional details regarding the structure are available in the Supporting Information. The molecule in the solid state is planar and the packing in the crystal shows stacking in which the molecular planes are separated by (3.24 ± 0.01) Å. Calculation of this distance is discussed in the Supporting Information. Other additional short contacts include a separation of 2.428 Å between the hydrogen on C5 and N4′ of adjacent stacks. Short contacts in the solid state have also been observed in some of the crystalline materials found in Table 9A and many are likewise planar.

The combination of planarity, polarity and extensive conjugation are common to all the systems that appear to exhibit anomalously
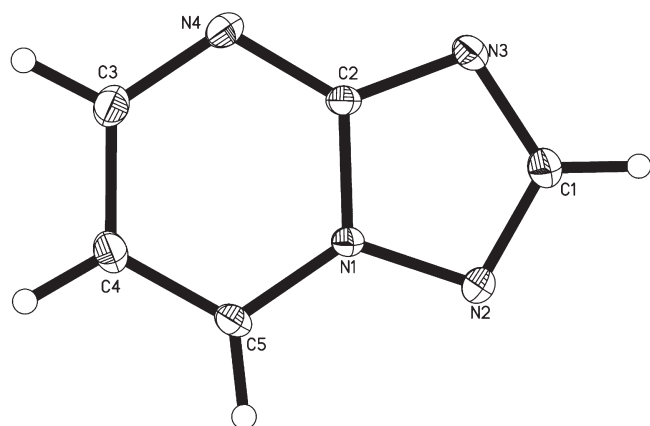
Figure 4. Crystal structure of 1,2,4-trazolo[1,5-*a*]pyrimidine. A projection view with 50% thermal ellipsoids.
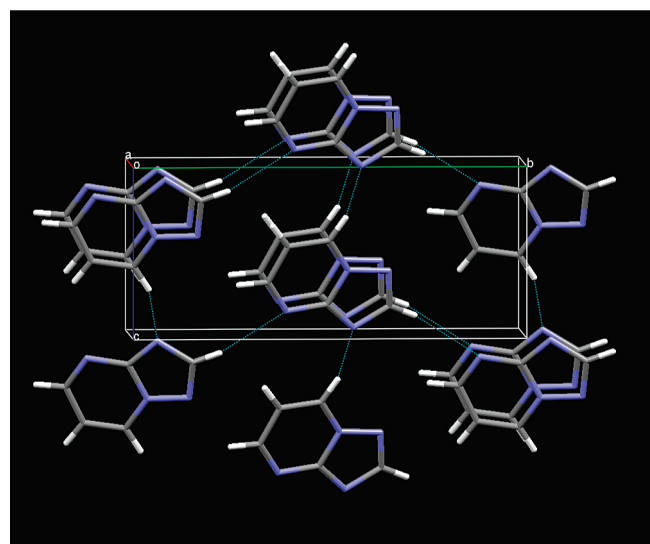

Figure 5. Molecular packing of 1,2,4-trazolo[1,5-*a*]pyrimidine down the *a* axis.

larger vaporization enthalpies. Perhaps π-π stacking interactions as suggested by the short stacking distance in the crystal structure of 1,2,4-triazolo[1,5-*a*]pyrimidine also plays an important role in the liquid state of the compounds of Table 9B. It is presently unclear whether the relatively constant discrepancy of 7 kJ·mol^{-1} characterizing the compounds of Table 9B, among others, is simply fortuitous or if it represents the contribution of a specific interaction not universally found in the other nitrogen heterocycles examined thus far.

■ ASSOCIATED CONTENT

ⓢ Supporting Information. Tables of retention times, the temperature adjustment of fusion enthalpy, and crystal and structure refinement data for triazolo[1,5-*a*]pyrimidine. This material is available free of charge via the Internet at http://pubs.acs.org.

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