

A Study of the Vaporization Enthalpies of Some 1-Substituted Imidazoles and Pyrazoles by Correlation-Gas Chromatography

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The vaporization enthalpies of 1-methyl-, 1-ethyl-, 1-phenyl-, and 1-benzylimidazole, 1-methyl- and 1-phenylpyrazole, and *trans*-azobenzene are evaluated by correlation-gas chromatography (C-GC) using a variety of azines and diazines as standards. The vaporization enthalpies obtained by C-GC when compared to literature values are approximately $14 \text{ kJ}\cdot\text{mol}^{-1}$ smaller for the imidazoles and $6 \text{ kJ}\cdot\text{mol}^{-1}$ smaller for the pyrazoles. The literature vaporization enthalpies of 1-methylpyrrole and 1-methylindole, two closely related compounds with one less nitrogen, are reproduced by C-GC. These results suggest that the magnitude of the intermolecular interactions present in 1-substituted imidazoles and pyrazoles are significantly larger than the those present in the reference compounds and greater than or equal in magnitude to the enhanced intermolecular interactions observed previously in aromatic 1,2-diazines. The vaporization enthalpy and vapor pressure of a *trans*-1,2-diazine, *trans*-azobenzene, measured by C-GC using similar standards reproduced the literature values within experimental error.

The study of systems that self-assemble and the interactions responsible for self-assembly and recognition is an active area of science that ranges from crystal engineering in the solid state to liquid crystals and biology in the fluid states. Thermodynamically, a great deal is known about the magnitude of the strong intermolecular interactions such as hydrogen bonding. Considerably less is known experimentally, about the magnitude of weaker interactions at $T = 298.15 \text{ K}$, particularly in molecules found in biological systems. While the magnitude of the vaporization enthalpy can provide useful information regarding these interactions in isomeric systems, such studies are frequently hindered by the fact that many of the model compounds of interest are solids at the temperatures of interest and can only be studied in solution or at high temperatures. The presence of solvent obviously complicates any evaluation of the thermodynamics of self-association in solution.

Recently we examined the vaporization enthalpies of a series of aromatic diazines by correlation-gas chromatography (C-GC) and observed that compounds with adjacent nitrogens have anomalously larger vaporization enthalpies than other aromatic diazines.^{1–3} The 1,2-diazines examined included pyridazine and 3-methylpyridazine, both liquids, and phthalazine and benzo[*c*]cinnoline, two crystalline materials. The literature vaporization enthalpies of the latter two compounds were evaluated as the difference between their sublimation and fusion enthalpies at $T = 298.15 \text{ K}$ and compared to the vaporization enthalpy evaluated by correlation-gas chromatography using other tertiary aromatic amines as standards. A discrepancy of approximately $6 \text{ kJ}\cdot\text{mol}^{-1}$ was observed. The vaporization enthalpies of other isomeric diazines, quinazoline, quinoxaline, and phenazine, also crystalline solids, were successfully reproduced by correlation-gas chromatography using similar tertiary aromatic amines as standards. The results suggested that aromatic 1,2-diazines have

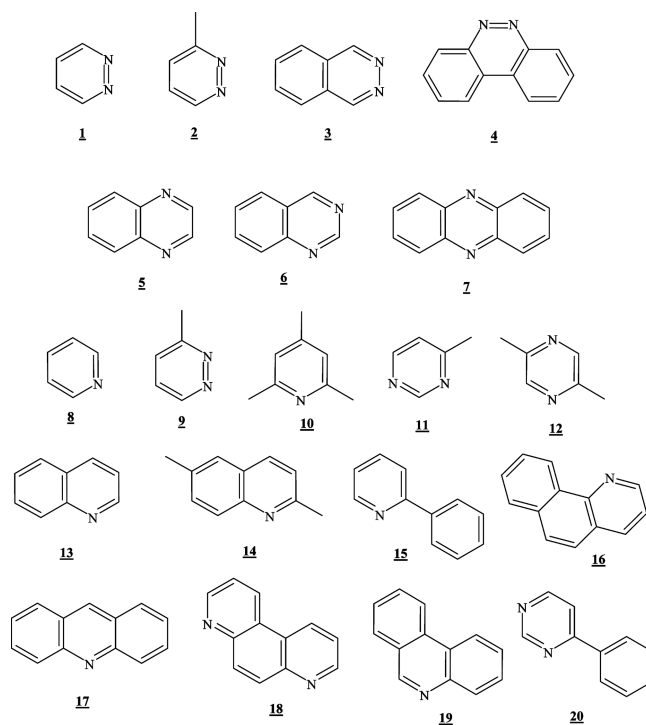


Figure 1. Compounds used as standards or discussed in the text; from left to right, top to bottom: pyridazine (1), 3-methylpyridazine (2), phthalazine (3), benzo[*c*]cinnoline (4), quinoxaline (5), quinazoline (6), phenazine (7), pyridine (8), 3-picoline (9), 2,4,6-trimethylpyridine (10), 4-methylpyrimidine (11), 2,5-dimethylpyrazine (12), quinoline (13), 2,6-dimethylquinoline (14), 2-phenylpyridine (15), 7,8-benzoquinoline (16), acridine (17), 4,7-phenanthroline (18), phenanthridine (19), and 2-phenylpyrimidine (20).

substantially larger intermolecular interactions than other isomeric diazines. The structures of the heterocycles just discussed and those used as standards in this work are illustrated in Figure 1.

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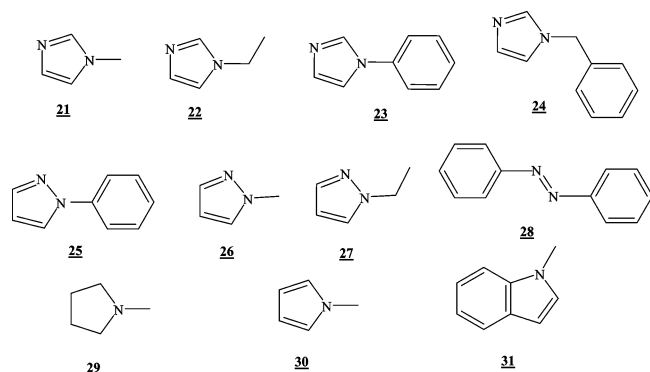


Figure 2. Vaporization enthalpies $\Delta_{\text{cr}}^{\text{L}}H_{\text{m}}(298 \text{ K})$ evaluated in this study: 1-methylimidazole (21), 1-ethylimidazole (22), 1-phenylimidazole (23), 1-benzylimidazole (24), 1-phenylpyrazole (25), 1-methylpyrazole (26), 1-ethylpyrazole (27), *trans*-azobenzene (28), 1-methylpyrrolidine (29), 1-methylpyrrole (30), and 1-methylindole (31).

Aromatic 1,2-diazines are not found commonly in biological systems. Observance of an effect such as found in the aromatic 1,2-diazines suggests that correlation-gas chromatography experiments might be useful in identifying strong intermolecular interactions and hence systems prone to self-assemble. While not providing an absolute measure of the magnitude of the interaction, the results can provide a measure of the relative difference in the magnitude of interaction between the systems of interest and those of the reference compounds chosen as standards.

This article examines a series of model compounds, derivatives of which are found in biological systems. The structures of the compounds that are the subject of this study are provided in Figure 2. The compounds of this study include some 1-substituted imidazoles and pyrazoles, and an acyclic 1,2-diazine. All of the materials examined are incapable of hydrogen bonding with each other. A comparison of the differences observed between the vaporization enthalpies evaluated by correlation-gas chromatography and by other methods can provide a differential measure of the intermolecular interactions associated with the heterocyclic core relative to the compounds chosen for reference. The compounds included in this study are 1-methyl-, 1-ethyl-, 1-phenyl-, and 1-benzylimidazole, 1-phenyl- and 1-methylpyrazole, and *trans*-azobenzene. The 1-substituted imidazoles were chosen because some physical properties available for these materials also suggest the presence of strong intermolecular interactions. For example, the boiling temperatures of 1-methyl and 1-ethylimidazole ($\text{C}_4\text{H}_6\text{N}_2$ and $\text{C}_5\text{H}_8\text{N}_2$), $T_{\text{b}} = (478 \text{ and } 481) \text{ K}$, respectively, are very similar to the boiling temperatures of two compounds previously found to behave anomalously, pyridazine ($\text{C}_4\text{H}_4\text{N}_2$, $T_{\text{b}} = 481 \text{ K}$) and 3-methylpyridazine ($\text{C}_5\text{H}_6\text{N}_2$, $T_{\text{b}} = 487 \text{ K}$), compounds with the same number of heavy atoms and roughly similar surface areas. *trans*-Azobenzene was studied as an example of a *trans*-1,2-diazine related to the *cis*-1,2-diazine, benzo[*c*]cinnoline, studied previously to determine if stereochemistry and/or cyclization plays any role affecting vaporization enthalpy. Evaluation of the vaporization enthalpies of 1-methylpyrrolidine, 1-methylpyrrole, and 1-methylindole by correlation-gas chromatography was prompted by the results obtained for the corresponding imidazoles.

Vaporization enthalpies for the 1-substituted imidazoles studied are available in the literature and in cases where comparisons are made, the differences observed between the literature values and those obtained by correlation-gas chromatography are found to be even larger than what has been

observed previously for the aromatic 1,2-diazines. The literature values for 1-methyl- and 1-phenylpyrazole were also found to be larger than the values calculated by correlation but comparable in magnitude to those found for the aromatic 1,2-diazines. Differences between the vaporization enthalpies obtained by gas chromatography and by other methods for the 1,2- and 1,3-diazacyclopentadiene compounds studied appear to be real. These results illustrate how correlation-gas chromatography experiments can be used to quantitatively evaluate anomalous intermolecular interactions. They also emphasize the importance of careful selection of reference compounds when vaporization enthalpies are evaluated by C-GC.

Correlation-gas chromatography is a simple method for evaluating both vaporization enthalpy and vapor pressure regardless of whether the target substance is a solid or liquid provided appropriate standards are used with reliable vaporization enthalpies and liquid vapor pressures.^{1–4} The standards are injected simultaneously with the target substances along with an unretained analyte that measures the elution time, t_{e} . 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, $t_{\text{a}} = t - t_{\text{e}}$, provides a convenient measure of both its volatility and interaction with the column. Since the vapor pressure of each analyte is inversely proportional to its adjusted retention time, t_{a} , a plot of $\ln(t_0/t_{\text{a}})$ vs $1/T$ run isothermally, usually over a $T = 30 \text{ K}$ 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, $-\Delta_{\text{sin}}^{\text{g}}H_{\text{m}}(T)$, divided by the gas constant. The term t_0 refers to a reference time, 1 min, and t_{a} is the time each analyte spends on the column. As described above, it is evaluated as the difference between the measured retention time of each analyte, t , and that of a nonretained reference, t_{e} . The enthalpy of transfer can be related to the following thermodynamic relationship:

$$\Delta_{\text{sin}}^{\text{g}}H_{\text{m}}(T_{\text{m}}) = \Delta_{\text{f}}^{\text{g}}H_{\text{m}}(T_{\text{m}}) + \Delta_{\text{sin}}H_{\text{m}}(T_{\text{m}}) \quad (1)$$

where $\Delta_{\text{f}}^{\text{g}}H_{\text{m}}(T_{\text{m}})$ refers to the vaporization enthalpy and $\Delta_{\text{sin}}H_{\text{m}}(T_{\text{m}})$ refers to the interaction of each analyte with the column measured at some mean temperature, T_{m} . The enthalpy of transfer, $\Delta_{\text{sin}}^{\text{g}}H_{\text{m}}(T_{\text{m}})$, has been found to correlate linearly with $\Delta_{\text{f}}^{\text{g}}H_{\text{m}}(T)$. 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 as is demonstrated below 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 noted above for the 1,2-diazines, heterocycles containing up to three nitrogen atoms appear to correlate successfully with other tertiary amines and other nitrogen heterocycles used as standards.^{1–4} Additional details regarding the relationships between $\Delta_{\text{sin}}^{\text{g}}H_{\text{m}}(T_{\text{m}})$, $\Delta_{\text{f}}^{\text{g}}H_{\text{m}}(T_{\text{m}})$, and $\Delta_{\text{sin}}H_{\text{m}}(T_{\text{m}})$ have been reported.⁵

Experimental Section

All compounds used in this study were obtained from Aldrich Chemical Co. with the exception of benzo[*c*]cinnoline, which was purchased from Alpha Aesar, and were used as purchased. Unless noted otherwise, all were analyzed by gas chromatography and found to have purities of 97% mass fraction or better. Since all were analyzed as mixtures separated by the chroma-

TABLE 1: Fusion Enthalpies Measured by DSC

	mass (mg)	$\Delta_{\text{cr}}^{\text{l}}H_{\text{m}}(T_{\text{fus}})$ ($\text{J}\cdot\text{g}^{-1}$)	T_{fus} (K)	$\Delta_{\text{cr}}^{\text{l}}H_{\text{m}}(T_{\text{fus}})$ ($\text{kJ}\cdot\text{mol}^{-1}$)	$\Delta_{\text{cr}}^{\text{l}}H_{\text{m}}(T_{\text{fus}})$ ($\text{kJ}\cdot\text{mol}^{-1}$) [avg]	T_{fus} (K) ^a [avg]
1-benzylimidazole ²⁹	21.87	135.96	344.1	21.51	21.5 ± 0.5	343.9
	16.06	134.58	344	21.29		
	13.17	137.47	343.7	21.75		

^a Onset temperature.

TABLE 2: Literature Vaporization Enthalpies

compound	$\Delta_{\text{f}}^{\text{g}}H_{\text{m}}(T_{\text{m}})$ ($\text{kJ}\cdot\text{mol}^{-1}$)	T_{m} (K)	$C_p(\text{l})$ ($\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$)	$\Delta_{\text{f}}^{\text{g}}H_{\text{m}}(298\text{ K})$ ($\text{kJ}\cdot\text{mol}^{-1}$) [calc] ^a	$\Delta_{\text{f}}^{\text{g}}H_{\text{m}}(298\text{ K})$ ($\text{kJ}\cdot\text{mol}^{-1}$) [lit.]	ref
pyridine					40.21 ± 0.1	26
3-picoline					44.47 ± 0.07	27
2,5-dimethylpyrazine	43.6 ± 0.4	357	185.4	48.0 ± 1.0		11
2,4,6-trimethylpyridine	47.7 ± 0.6	357	214.9	51.5 ± 1.1		11
quinoline					59.31 ± 0.21	8
2,6-dimethylquinoline					67.07 ± 0.16	10
2-phenylpyridine					68.4 ± 1.9	4
7,8-benzoquinoline	73.0 ± 0.3	360	278.1	78.11 ± 1.0	77.23 ^b	9
acridine					78.63 ^b	9
4,7-phenanthroline					80.8 ± 4.8	4
phenanthridine					80.14	9
4-phenylpyrimidine					68.8 ± 2.5	4
pyridazine					53.5 ± 0.4	28
3-methylpyridazine					56.1 ± 4.4	3
phthalazine					72.8 ± 5.6	3
benzo[c]cinnoline					89.2 ± 2.3	3
1-methylpyrrolidine					34.2 ± 0.7	22
1-methylpyrrole	37.7 ± 0.05	353	150.7	40.4 ± 0.8		23
1-methylpyrrole	38.8 ± 0.1	339	150.7	40.8 ± 0.7		24
1-methylindole					62.2 ± 1.6	25

^a Literature data adjusted to $T = 298.15\text{ K}$ using eq 5. ^b 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 eqs at a mean temperature of $T = 298.15\text{ K}$.

tography, 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 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 on a 0.25 mm, 30 m DB5MS 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. Helium was used as the carrier gas. Methane or the solvent was used as a nonretained reference. At the higher temperatures, the retention time of the cyclopentane or methanol, used as solvents, 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 by 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, at $T = 5\text{ K}$ intervals over a $T = 30\text{ K}$ range. Column temperatures were controlled by the gas chromatograph and were monitored independently by using a Fluke digital thermometer. The 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 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 fusion enthalpy of 1-benzylimidazole (99%) was measured on a Perkin-Elmer DSC 7 instrument. The instrument was calibrated using indium metal as a standard. The results of triplicate measurements are reported in Table 1.

Adjustments of the enthalpies reported in Tables 2 and 5 with temperature were achieved by using eqs 2–5. Equation 2 was used to adjust sublimation enthalpies, eq 3 was used to adjust the fusion enthalpies in Table 5, and eq 4 was used to adjust vaporization enthalpies to the temperature of interest. An assumed uncertainty equal to 30% of the total temperature adjustment was associated with temperature adjustments using eqs 2 and 3 and an uncertainty of $16\text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ was associated with the temperature independent term of eq 4.⁶ Equation 5 is the thermodynamic equality used to calculate vaporization enthalpies from sublimation and fusion enthalpies at $T = 298.15\text{ K}$. Equations 2–4 have been used previously and shown to provide reasonable adjustments for temperature.^{1–4} The heat capacity terms required for these temperature adjustments, $C_p(\text{cr})$ and $C_p(\text{l})$, are reported in Tables 2 and 5 and were evaluated by group additivity.^{6,7}

$$\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}(298.15\text{ K})/(\text{kJ}\cdot\text{mol}^{-1}) = \Delta_{\text{l}}^{\text{g}}H_{\text{m}}(T_{\text{m}}) + [0.75 + 0.15C_p(\text{cr})/(\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})][T_{\text{m}}/K - 298.15\text{ K}]/1000 \quad (2)$$

TABLE 3

A. Parameters of the Cox Equation Used for Reference ^a							
	A_0	A_1/T^{-1}	$10^7 A_2/T^{-2}$	T_b (K)	range (K)		
quinoline ⁸	2.85461	-0.00130236	9.3118	510.298	298–559		
acridine ⁹	2.89594	-0.00111538	6.486	618.059	383–637		
7,8-benzoquinoline ⁹	2.88454	-0.00111802	6.6824	14.49	373–672		
B. Parameters of the Wagner Equation ^a							
	A_w	B_w	C_w	D_w	T_c (K)	p_c (kPa)	range (K)
2,6-dimethylquinoline ¹⁰	-8.993312	3.594873	-4.63173	-2.907492	786	3480	337–592
C. Parameters of the Third-Order Polynomial, Eq 8							
	A (K ³)	B (K ²)	C (K)	D	range (K)		
2-phenylpyridine ⁴	82334650	-1199538.9	-2988.7	8.899	298– T_b		
4,7-phenanthroline ⁴	123705710	-1579329.8	-3296.6	8.741	298– T_b		
4-phenylpyrimidine ⁴	82739965	-1191247.0	-3078.93	8.993	298– T_b		
2,4,6-trimethylpyridine ^b	-160703781	870547.8	-6636.067	12.401	287–423		
2,5-dimethylpyrazine ^b	141666180.2	-1638517.3	524.965	5.924	302–411		

^a $T_r = T/T_c$. ^b Experimental data from ref 11 fit to eq 8.

$$\Delta_{\text{cr}}^1 H_m(298.15 \text{ K})/(\text{kJ}\cdot\text{mol}^{-1}) = \Delta_{\text{cr}}^1 H_m(T_{\text{fus}}) + [(0.15C_p(\text{cr}) - 0.26C_p(\text{l}))]/(\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}) - 9.83] \times [T_{\text{fus}}/\text{K} - 298.15 \text{ K}]/1000 \quad (3)$$

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

$$\Delta_{\text{l}}^{\text{g}} H_m(298.15 \text{ K}) = \Delta_{\text{cr}}^{\text{g}} H_m(298.15 \text{ K}) - \Delta_{\text{cr}}^1 H_m(298.15 \text{ K}) \quad (5)$$

Vaporization Enthalpies and Vapor Pressures of the Standards

Available vaporization enthalpy values of the compounds in this study from the literature are reported in Table 2. Liquid vapor pressures for quinoline, reported from $T = 298$ to 559 K,⁸ acridine,⁹ reported from $T = 383$ to 637 K, and 7,8-benzoquinoline,⁹ reported from $T = 373$ to 672 K, are available in the form of the Cox equation, eq 6. Liquid vapor pressures for 2,6-dimethylquinoline,¹⁰ reported from $T = 337$ to 592 K are available in the form of the Wagner equation, eq 7. The parameters for these equations are reported in Table 3A,B. Since both the Cox and Wagner equations are known to extrapolate reasonably well over a limited temperature range, vapor pressures for all three compounds were first extrapolated and then fit to the Clausius–Clapeyron equation over the temperature range $T = 283$ –313 K to provide vaporization enthalpies at the mean temperature, $T = 298.15$ K. The resulting vaporization enthalpies, reported in the last column of Table 2, were used for all subsequent correlations. For comparison, the vaporization enthalpies of acridine and 7,8-benzoquinoline were also adjusted to $T = 298.15$ K using eq 4. These values, which are in good mutual agreement, are reported in column 5 of Table 2. The vapor pressures of acridine, 7,8-benzoquinoline, and 2,6-dimethylquinoline used below were the values calculated from the Cox and Wagner equations. Vaporization enthalpies at $T = 298.15$ K and vapor pressures for 2-phenylpyridine and 4,7-phenanthroline from $T = 298.15$ K to the boiling temperature (T_b), have been evaluated previously by correlation-gas chromatography.⁴ The vaporization enthalpies are reported in Table 2 and constants for the calculation of liquid vapor pressure using

eq 8 are provided in Table 3C. Unless noted otherwise, p_0 refers to 101.325 kPa, T_r refers to the reduced temperature, T/T_c , and p_c and T_c refer to the critical pressure and temperature, respectively. The experimental vapor pressures of 2,4,6-trimethylpyridine¹¹ and 2,5-dimethylpyrazole¹¹ were also fit to eq 8.

$$\ln(p/p_0) = (1 - T_b/T) \exp(A_0 + A_1(T/K) + A_2(T/K)^2) \quad (6)$$

$$\ln(p/p_c) = (1/T_r)[A_w(1 - T_r) + B_w(1 - T_r)^{1.5} + C_w((1 - T_r)^{2.5} + D_w(1 - T_r)^5)] \quad (7)$$

$$\ln(p/p_0) = A(T/K)^{-3} + B(T/K)^{-2} + C(T/K)^{-1} + D \quad (8)$$

Vaporization Enthalpy Results

The results of six correlations between *trans*-azobenzene, and various 1-substituted imidazoles and pyrazoles using other heterocycles as standards are reported in Table 4 as runs 1–6. Correlation eqs 9–14, located below each run, summarize the relationship observed between the enthalpy of transfer and vaporization enthalpies of the standards. The uncertainty associated with each vaporization enthalpy reported in the last column of the table represents the uncertainties in both the slope and intercept associated with these correlations. Since both *trans*-azobenzene and 1-benzylimidazole are solids at $T = 298.15$ K, Table 5 summarizes the necessary thermochemical properties needed to evaluate the vaporization enthalpy of these two compounds using eq 5.^{12–17}

The results for *trans*-azobenzene are summarized in run 1 of Table 4. The value $74.9 \pm 0.6 \text{ kJ}\cdot\text{mol}^{-1}$ compares quite favorably with $74.7 \pm 1.6 \text{ kJ}\cdot\text{mol}^{-1}$ calculated from the difference between the sublimation and fusion enthalpies reported in Table 5 and summarized as the first entry in Table 6. As discussed below, since the vaporization enthalpy of *trans*-azobenzene is reproduced using azines and other diazines, this result suggests that the anomalous behavior observed in aromatic 1,2-diazines requires a *cis* arrangement of the two adjacent

TABLE 4: Results of the Correlations of Runs 1–6

run 1	slope/T (K)	intercept	$\Delta_{\text{sin}}^{\text{g}}H_{\text{m}}(498 \text{ K})$ (kJ·mol ⁻¹)	$\Delta_{\text{f}}^{\text{g}}H_{\text{m}}(298 \text{ K})$ (kJ·mol ⁻¹) [lit.]	$\Delta_{\text{f}}^{\text{g}}H_{\text{m}}(298 \text{ K})$ (kJ·mol ⁻¹) [calc]
2,6-dimethylquinoline	-5268.9	10.614	43.8	67.07	67.1 ± 0.6
2-phenylpyridine	-5401.3	10.731	44.9	68.4	68.5 ± 0.7
<i>trans</i> -azobenzene	-5957.5	11.313	49.53		74.9 ± 0.7
acridine	-6288.3	11.318	52.28	78.63	78.7 ± 0.7
4,7-phenanthroline	-6469.8	11.492	53.79	80.8	80.8 ± 0.7
$\Delta_{\text{f}}^{\text{g}}H_{\text{m}}(298 \text{ K})$ (kJ·mol ⁻¹) = (1.37 ± 0.01) $\Delta_{\text{sin}}^{\text{g}}H_{\text{m}}(498 \text{ K})$ + (6.99 ± 0.47) $r^2 = 0.9999$ (9)					

run 2	slope/T (K)	intercept	$\Delta_{\text{sin}}^{\text{g}}H_{\text{m}}(473 \text{ K})$ (kJ·mol ⁻¹)	$\Delta_{\text{f}}^{\text{g}}H_{\text{m}}(298 \text{ K})$ (kJ·mol ⁻¹) [lit.]	$\Delta_{\text{f}}^{\text{g}}H_{\text{m}}(298 \text{ K})$ (kJ·mol ⁻¹) [calc]
quinoline	-4763.0	10.177	39.60	59.31	59.3 ± 1.2
1-phenylpyrazole	-5150.3	10.800	42.82		63.5 ± 1.2
1-phenylimidazole	-5542.0	11.163	46.07		67.7 ± 1.3
2-phenylpyridine	-5643.0	11.228	46.91	68.4	68.8 ± 1.3
acridine	-6549.8	11.854	54.45	78.63	78.6 ± 1.4
4,7-phenanthroline	-6761.2	12.090	56.21	80.8	80.8 ± 1.4
$\Delta_{\text{f}}^{\text{g}}H_{\text{m}}(298 \text{ K})$ (kJ·mol ⁻¹) = (1.30 ± 0.019) $\Delta_{\text{sin}}^{\text{g}}H_{\text{m}}(473 \text{ K})$ + (7.61 ± 0.92) $r^2 = 0.9995$ (10)					

run 3	slope/T (K)	intercept	$\Delta_{\text{sin}}^{\text{g}}H_{\text{m}}(473 \text{ K})$ (kJ·mol ⁻¹)	$\Delta_{\text{f}}^{\text{g}}H_{\text{m}}(298 \text{ K})$ (kJ·mol ⁻¹) [lit.]	$\Delta_{\text{f}}^{\text{g}}H_{\text{m}}(298 \text{ K})$ (kJ·mol ⁻¹) [calc]
quinoline	-4711.3	10.047	39.17	59.31	59.2 ± 0.5
1-phenylpyrazole	-5086.4	10.645	42.29		63.3 ± 0.5
1-phenylimidazole	-5477.3	11.006	45.54		67.5 ± 0.5
2-phenylpyridine	-5568.3	11.05	46.29	68.4	68.5 ± 0.5
acridine	-6502.1	11.732	54.06	78.63	78.6 ± 0.5
4,7-phenanthroline	-6701.5	11.942	55.71	80.8	80.8 ± 0.5
$\Delta_{\text{f}}^{\text{g}}H_{\text{m}}(298 \text{ K})$ (kJ·mol ⁻¹) = (1.301 ± 0.007) $\Delta_{\text{sin}}^{\text{g}}H_{\text{m}}(473 \text{ K})$ + (8.30 ± 0.40) $r^2 = 0.9999$ (11)					

run 4	slope/T (K)	intercept	$\Delta_{\text{sin}}^{\text{g}}H_{\text{m}}(473 \text{ K})$ (kJ·mol ⁻¹)	$\Delta_{\text{f}}^{\text{g}}H_{\text{m}}(298 \text{ K})$ (kJ·mol ⁻¹) [lit.]	$\Delta_{\text{f}}^{\text{g}}H_{\text{m}}(298 \text{ K})$ (kJ·mol ⁻¹) [calc]
quinoline	-4722.0	10.072	39.26	59.31	59.4 ± 4.7
1-phenylpyrazole	-5103.4	10.678	42.43		63.5 ± 4.9
1-phenylimidazole	-5494.7	11.04	45.68		67.7 ± 5.0
4-phenylpyrimidine	-5576.2	11.045	46.36	68.8	68.6 ± 5.1
1-benzylimidazole	-5906	11.456	49.1		72.2 ± 5.2
7,8-benzoquinoline	-6466.8	11.695	53.76	77.23	78.2 ± 5.5
phenanthridine	-6564.8	11.782	54.58	80.14	79.3 ± 5.5
$\Delta_{\text{f}}^{\text{g}}H_{\text{m}}(298 \text{ K})$ (kJ·mol ⁻¹) = (1.300 ± 0.076) $\Delta_{\text{sin}}^{\text{g}}H_{\text{m}}(473 \text{ K})$ + (8.31 ± 3.7) $r^2 = 0.9933$ (12)					

run 5	slope/T (K)	intercept	$\Delta_{\text{sin}}^{\text{g}}H_{\text{m}}(378 \text{ K})$ (kJ·mol ⁻¹)	$\Delta_{\text{f}}^{\text{g}}H_{\text{m}}(298 \text{ K})$ (kJ·mol ⁻¹) [lit.]	$\Delta_{\text{f}}^{\text{g}}H_{\text{m}}(298 \text{ K})$ (kJ·mol ⁻¹) [calc]
pyridine	-3289.4	9.213	27.35	40.21	40.0 ± 2.3
3-picoline	-3844.1	9.906	31.96	44.47	45.0 ± 2.4
2,5-dimethylpyrazine	-4165.6	10.446	34.63	48.00	47.9 ± 2.5
1-methylimidazole	-4199.9	10.448	34.92		48.2 ± 2.6
2,4,6-trimethylpyridine	-4556.7	10.995	37.88	51.50	51.2 ± 2.7
1-ethylimidazole	-4538.7	10.834	37.73		51.4 ± 2.7
$\Delta_{\text{f}}^{\text{g}}H_{\text{m}}(298 \text{ K})$ (kJ·mol ⁻¹) = (1.083 ± 0.053) $\Delta_{\text{sin}}^{\text{g}}H_{\text{m}}(378 \text{ K})$ + (10.37 ± 1.8) $r^2 = 0.9952$ (13)					

run 6	slope/T (K)	intercept	$\Delta_{\text{sin}}^{\text{g}}H_{\text{m}}(458 \text{ K})$ (kJ·mol ⁻¹)	$\Delta_{\text{f}}^{\text{g}}H_{\text{m}}(298 \text{ K})$ (kJ·mol ⁻¹) [lit.]	$\Delta_{\text{f}}^{\text{g}}H_{\text{m}}(298 \text{ K})$ (kJ·mol ⁻¹) [calc]
1-methylimidazole	-3888.5	9.900	32.33		49.4 ± 4.3
1-ethylimidazole	-4138.4	10.039	34.4		52.0 ± 4.4
quinoline	-4827.0	10.292	40.13	59.31	59.3 ± 4.6
1-phenylpyrazole	-5217.1	10.919	43.37		63.5 ± 4.8
1-phenylimidazole	-5623.7	11.312	46.75		67.8 ± 4.9
4-phenylpyrimidine	-5705.9	11.317	47.44	68.8	68.7 ± 5.0
1-benzylimidazole	-6056.2	11.771	50.35		72.4 ± 5.1
7,8-benzoquinoline	-6606.7	11.989	54.93	77.23	78.2 ± 5.4
phenanthridine	-6710.2	12.086	55.79	80.14	79.3 ± 5.4
$\Delta_{\text{f}}^{\text{g}}H_{\text{m}}(298 \text{ K})$ (kJ·mol ⁻¹) = (1.275 ± 0.072) $\Delta_{\text{sin}}^{\text{g}}H_{\text{m}}(458 \text{ K})$ + (8.18 ± 3.6) $\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}(298 \text{ K})$ $r^2 = 0.9936$ (14)					

TABLE 5: Summary of the Sublimation, Vaporization, and Fusion Enthalpies of *trans*-Azobenzene and 1-Benzylimidazole

	$\Delta_{\text{cr}}^{\text{l}}H_{\text{m}}(298 \text{ K})$ (kJ·mol ⁻¹)	$\Delta_{\text{cr}}^{\text{l}}H_{\text{m}}(T_{\text{fus}})$ (kJ·mol ⁻¹)	T_{fus} (K)	$C_p(1)/C_p(\text{cr})$ (J·mol ⁻¹ ·K)	$\Delta_{\text{cr}}^{\text{l}}H_{\text{m}}(298 \text{ K})$ (kJ·mol ⁻¹)	$\Delta_{\text{f}}^{\text{g}}H_{\text{m}}(298 \text{ K})$ (kJ·mol ⁻¹)
<i>trans</i> -azobenzene	94.5 ± 1.3 ^a	22.6 ± 0.04 ^b	341.4	337.4/213.4	19.8 ± 0.9	74.7 ± 1.6
1-benzylimidazole	102.1 ± 0.4 ^c	21.5 ± 0.5 ^d	343.9	270.9/185.7	19.1 ± 0.9	83.0 ± 1.0

^a The mean of 94.1 (298.15 K),¹² 93.6 (298.15 K),¹³ and 94.9 kJ·mol⁻¹ (323 K)¹⁴ adjusted to $T = 298.15 \text{ K}$ using eq 2; the uncertainty represents two standard deviations of the mean. ^b The mean of 22.65 (341.8 K),¹⁴ 22.52 (341.0 K),¹⁵ and 22.53 kJ·mol⁻¹(341.1 K).¹⁶
^c Literature value.¹⁷ ^d This work; see Table 1.

TABLE 6: Summary of the Vaporization Enthalpies Evaluated in Runs 1–6

	$\Delta_f^{\ddagger}H_m(298\text{ K})$ (kJ·mol ⁻¹)				$\Delta_f^{\ddagger}H_m(298\text{ K})$ (kJ·mol ⁻¹) [lit.]	$\Delta\Delta_f^{\ddagger}H_m(298\text{ K})$ (kJ·mol ⁻¹)
	runs 1/3	runs 2/5	runs 4/6	avg ^a		
<i>trans</i> -azobenzene	74.9 ± 0.7			74.9 ± 0.7	74.7 ± 1.6, ^b 72.8 ± 0.7 ¹²	-1.2 ± 1.7
1-phenylpyrazole		63.5 ± 1.2	63.5 ± 4.9		70.2 ± 3.4 ¹⁸	6.7 ± 4.5
	63.3 ± 0.5		63.5 ± 4.8	63.5 ± 2.9		
1-methylimidazole			49.4 ± 4.3	48.8 ± 3.5	64.7 ± 1.3 ¹⁷	15.9 ± 3.7
	48.2 ± 2.6					
1-ethylimidazole		51.4 ± 2.7	52.0 ± 4.4	51.7 ± 3.6	66.0 ± 3.9 ¹⁹	14.3 ± 5.3
1-phenylimidazole		67.7 ± 1.3	67.7 ± 5.0		84.6 ± 3.7 ¹⁸	16.9 ± 4.7
	67.5 ± 0.5	67.8 ± 4.9	67.7 ± 2.9			
1-benzylimidazole			72.2 ± 5.2		83.0 ± 1.0 ¹⁷	10.8 ± 5.3
			72.4 ± 5.1	72.3 ± 5.2		

^a The uncertainty reported is an average of the deviations reported in columns 2–4. ^b See Table 5.

TABLE 7: Vaporization Enthalpies of Some Five-Membered Ring Heterocycles

run 7	slope/ <i>T</i> (K)	intercept	$\Delta_{\text{sln}}^{\ddagger}H_m(428\text{ K})$ (kJ·mol ⁻¹)	$\Delta_f^{\ddagger}H_m(298\text{ K})$ (kJ·mol ⁻¹) [lit.]	$\Delta_f^{\ddagger}H_m(298\text{ K})$ (kJ·mol ⁻¹) [calc]/[lit.]
1-methylpyrrolidine	-2939.3	8.848	24.44		36.6 ± 2.4/34.2 ± 0.7
1-methylpyrrole	-3286.9	9.324	27.33		40.3 ± 2.5/40.6 ± 0.8
4-methylpyrimidine	-3625.2	9.543	30.14	44.2	43.8 ± 2.6
2,5-dimethylpyrazine	-3982.9	9.993	33.11	47.0	47.6 ± 2.7
2,4,6-trimethylpyridine	-4349.7	10.476	36.16	51.5	51.4 ± 2.8
quinoline	-5092.2	10.822	42.33	59.31	59.2 ± 3.0
1-methylindole	-5267.8	11.125	43.79		61.1 ± 3.1/62.2 ± 1.6

$$\Delta_f^{\ddagger}H_m(298.15\text{ K}) \text{ (kJ}\cdot\text{mol}^{-1}\text{)} = (1.263 \pm 0.055)\Delta_{\text{sln}}^{\ddagger}H_m(428\text{ K}) + (5.76 \pm 2.0) \quad r^2 = 0.9963 \quad (15)$$

TABLE 8: Correlation of the Enthalpies of Transfer of 1-Substituted Imidazoles with Literature Vaporization Enthalpies

run 6	slope/ <i>T</i> (K)	intercept	$\Delta_{\text{sln}}^{\ddagger}H_m(458\text{ K})$ (kJ·mol ⁻¹)	$\Delta_f^{\ddagger}H_m(298\text{ K})$ (kJ·mol ⁻¹) [lit.]	$\Delta_f^{\ddagger}H_m(298\text{ K})$ (kJ·mol ⁻¹) [calc] ^a	$\Delta_f^{\ddagger}H_m(298\text{ K})$ (kJ·mol ⁻¹) [calc] ^b
1-methylimidazole	-3888.5	9.900	32.33	64.7 ± 1.3	64.5 ± 10.2	64.3 ± 2.2
1-ethylimidazole	-4138.4	10.039	34.40	66.0 ± 3.9	66.9 ± 10.4	66.5 ± 2.3
1-phenylpyrazole	-5217.1	10.919	43.37		77.4 ± 11.7	75.7 ± 2.5
1-phenylimidazole	-5623.7	11.312	46.75	84.6 ± 3.7	81.3 ± 12.1	79.2 ± 2.7
1-benzylimidazole	-6056.2	11.771	50.35	83.0 ± 1.0	85.5 ± 12.7	82.9 ± 2.8

$$\Delta_f^{\ddagger}H_m(298\text{ K}) \text{ (kJ}\cdot\text{mol}^{-1}\text{)} = (1.165 \pm 0.193)\Delta_{\text{sln}}^{\ddagger}H_m(458\text{ K}) + (26.87 \pm 8.1) \quad r^2 = 0.9476 \quad (16)$$

$$\Delta_f^{\ddagger}H_m(298\text{ K}) \text{ (kJ}\cdot\text{mol}^{-1}\text{)} = (1.034 \pm 0.043)\Delta_{\text{sln}}^{\ddagger}H_m(458\text{ K}) + (30.85 \pm 1.7) \quad r^2 = 0.9982 \quad (17)$$

^a Calculated using eq 16. ^b Calculated using eq 17, obtained by treating the vaporization enthalpies of both 1-phenylpyrazole and 1-phenylimidazole as unknown.

nitrogen atoms. It is not presently possible to evaluate what role aromaticity and ring constraints have on the enhanced effect observed.

Results on the 1-substituted imidazoles and pyrazoles measured in runs 2–6 as unknowns are also summarized in Table 6 and compared to literature values. Significant discrepancies are observed between the literature values for both 1-phenylpyrazole and the 1-substituted imidazoles. The literature values are significantly larger for both with the largest difference observed for the 1-substituted imidazoles. The standards used in this work do not appear to be appropriate for the five-membered ring heterocycles of this study, but they do provide a measure of the enhanced intermolecular interactions that must be present in both 1-phenylpyrazole and the 1-substituted imidazoles. The last column in Table 6 suggests that this additional interaction is worth approximately 6 kJ·mol⁻¹ for 1-phenylpyrazole and about 11–16 kJ·mol⁻¹ for the 1-substituted imidazoles. The differences observed for the imidazoles are considerably larger than the 6 kJ·mol⁻¹ reported previously for the aromatic 1,2-diazines.

All the compounds used as standards in runs 1–6 are six-membered ring heterocycles. To evaluate whether ring size plays any role in the vaporization enthalpies differences observed, the vaporization enthalpies of 1-methylpyrrolidine, 1-meth-

ylpyrrole, and 1-methylindole were evaluated using several six-membered ring heterocycles as standards. The retention time data are reported in the Supporting Information and the results are summarized in the last column of Table 7. The vaporization enthalpies of all the five-membered ring heterocycles are well reproduced using their six-membered ring counterparts as standards. Substitution of a second nitrogen for carbon in 1-methylpyrrole at either position 2 or 3 of the ring seems to be the source of the discrepancies in vaporization enthalpy observed in Table 6. Ring size does not appear to play a significant role.

While the standards used this study appear to be unsuitable as reference materials, the enthalpies of transfer measured for the imidazoles should correlate with their available vaporization enthalpies regardless of the standards chosen. The correlation that results when the enthalpies of transfer measured for the imidazoles are correlated with literature vaporization enthalpies is reported in Table 8 using the $\Delta_{\text{sln}}^{\ddagger}H_m(T_m)$ values measured in run 6. This correlation is also illustrated in Figure 3. With the exception of 1-phenylimidazole, the correlation is reasonably good. The error bars in the figure represent the uncertainty associated with each literature vaporization enthalpy value.

An examination of the vaporization enthalpies obtained from the literature reveals that all imidazoles with the exception of

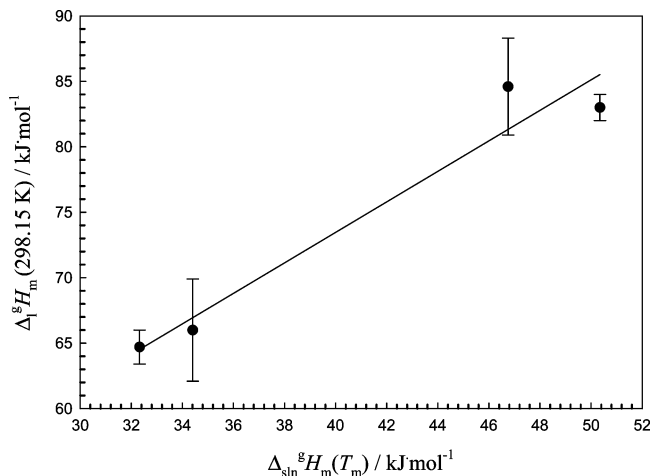


Figure 3. Correlation of literature vaporization enthalpies with the corresponding enthalpies of transfer enthalpies from run 6 of the four imidazoles: (from left to right) 1-methyl, 1-ethyl, 1-phenyl, and 1-benzylimidazole. The uncertainties are literature values.

1-benzylimidazole were evaluated using drop calorimetry.^{17–19} Calorimetric methods have proven to be quite reliable. Depending on molecular size, drop calorimetric methods, however, can require a large heat capacity correction to adjust heating the sample from $T = 298$ K to the temperature of the calorimeter. For 1-phenylimidazole and 1-phenylpyrazole, the heat capacity corrections, which were estimated, amounted to approximately $12 \text{ kJ}\cdot\text{mol}^{-1}$.¹⁸ The uncertainty reported by these authors¹⁸ represents the precision of the calorimetric results and does not include any uncertainty associated with the heat capacity adjustments. The larger uncertainties calculated by eq 16 in Table 8 may be a consequence of this fact. Treating 1-phenylimidazole as an unknown in run 6 of Table 8, results in correlation of eq 17 and the vaporization enthalpies provided in the last column of Table 8. While the correlation between $\Delta_{\text{sin}}^{\text{g}}H_{\text{m}}(T_{\text{m}})$ and $\Delta_{\text{f}}^{\text{g}}H_{\text{m}}(298.15 \text{ K})$ improves significantly, the calculated vaporization enthalpy of 1-phenylimidazole still remains within the combined experimental uncertainties of the literature value, (79.2 ± 2.7) versus (84.6 ± 3.7) $\text{kJ}\cdot\text{mol}^{-1}$.

1-Phenylpyrazole was treated as an unknown in both correlations of Table 8. While the value of $77.4 \pm 11.7 \text{ kJ}\cdot\text{mol}^{-1}$ obtained using correlation eq 16 is within experimental error of the literature value, $70.2 \pm 3.4 \text{ kJ}\cdot\text{mol}^{-1}$, the result obtained using eq 17, $75.7 \pm 2.5 \text{ kJ}\cdot\text{mol}^{-1}$, suggests that pyrazoles do not correlate well with imidazoles.

According to the single result reported in Table 6 for 1-phenylpyrazole, a difference of $6.7 \pm 4.5 \text{ kJ}\cdot\text{mol}^{-1}$ suggests that the aromatic 1,2-diazines may be more appropriate standards for these materials. To test this possibility, 1-methylpyrazole and 1-phenylpyrazole were correlated with several aromatic 1,2-diazines. The results obtained are reported in Table 9. The vaporization enthalpies of both pyrazoles calculated from the

correlation equation, eq 18, are within the experimental uncertainty of the literature results confirming this suggestion.

To confirm that the differences in vaporization enthalpy observed in Table 6 between literature values reported for the 1-substituted imidazoles and those obtained using the aromatic heterocyclic standards of runs 2–6 are real and larger than those obtained for the aromatic 1,2-diazines,³ a correlations using 1,2-diazines and 1-methylpyrazole as standards was also investigated. As suggested by the results in Table 10, runs 9–10, the vaporization enthalpies obtained for the imidazoles using these standards are still somewhat smaller than the literature values, confirming that the intermolecular interactions present in the 1-substituted imidazoles are larger than those observed in the aromatic 1,2-diazines and 1-substituted pyrazoles. Differences of 10.1 ± 2.3 , 8.6 ± 4.4 , 4.9 ± 3.7 , and $3.8 \pm 2.9 \text{ kJ}\cdot\text{mol}^{-1}$, are observed for 1-methyl, 1-ethyl, 1-phenyl, and 1-benzylimidazole, respectively. From the trend observed in both Tables 6 and 10, it appears that increasing the size of the hydrocarbon substituent on the imidazole ring at position 1 attenuates the magnitude of the effect.

Vapor Pressure Results

The vaporization enthalpies of *trans*-azobenzene, 1-methylpyrrolidine, 1-methylpyrrole, and 1-methylindole obtained in runs 1 and 7 are in good agreement with literature values. According to what has previously been observed,^{1–4,20,21} correlation of $\ln(p/p_0)$ with $\ln(t_0/t_a)$ of the standards as a function of temperature would be expected to provide reasonable predictions of vapor pressure as a function of temperature of those compounds treated as unknown. The prediction of the normal boiling temperature in reasonably good agreement with experiment is also possible. With the exception of 1-methylindole, experimental vapor pressures are available for these materials. This provides an opportunity to test how well the correlations work and to evaluate the vapor pressures of 1-methylindole. Values of $\ln(p/p_0)$ of the standards were correlated with their respective $\ln(t_0/t_a)$ terms. A typical correlation is provided in Table 11 and characterized by eq 20 for the results obtained in run 1 at $T = 298.15$ K. For run 1, additional correlations were performed over 30 K intervals from $T = 320$ to 540 K using the standards indicated, whereas for run 7, the correlations were conducted every 20 K intervals over the temperature range $T = 298.15$ to 400 K. The vapor pressures of all the standards used were calculated using the equations reported in Table 3A–C. The resulting values of $\ln(p/p_0)$ of *trans*-azobenzene, 1-methylpyrrolidine, 1-methylpyrrole, and 1-methylindole calculated as a function of temperature from the correlation equations were then fit to the third-order polynomial, eq 8, resulting in the coefficients reported in Table 12. Table 12 also compares the calculated boiling temperature of each compound calculated using eq 8 with the literature values. The results of these correlations over the entire temperature range cited above is also illustrated in Figure 4 for those compounds with available experimental vapor pressures.

TABLE 9: Correlations of Aromatic 1,2-Diazines with 1-Substituted Pyrazoles

run 8	slope/ T (K)	intercept	$\Delta_{\text{sin}}^{\text{g}}H_{\text{m}}(408 \text{ K})$ ($\text{kJ}\cdot\text{mol}^{-1}$)	$\Delta_{\text{f}}^{\text{g}}H_{\text{m}}(298 \text{ K})$ ($\text{kJ}\cdot\text{mol}^{-1}$) [lit.]	$\Delta_{\text{f}}^{\text{g}}H_{\text{m}}(298 \text{ K})$ ($\text{kJ}\cdot\text{mol}^{-1}$) [calc]	$\Delta_{\text{f}}^{\text{g}}H_{\text{m}}(298 \text{ K})$ ($\text{kJ}\cdot\text{mol}^{-1}$) [lit.]	
1-methylpyrazole	−3272.3	9.263	27.20		48.0 ± 2.3	48.0 ± 1.3^{16}	
pyridazine	−3814.7	9.524	31.71	53.5	53.1 ± 2.4		
3-methylpyridazine	−4183.3	9.990	34.78	56.1	56.6 ± 2.5		
1-phenylpyrazole	−5462.6	11.417	45.41		68.6 ± 2.9	70.2 ± 3.4	
phthalazine	−5898.9	11.621	49.04	72.8	72.7 ± 3.0		
$\Delta_{\text{f}}^{\text{g}}H_{\text{m}}(298 \text{ K}) (\text{kJ}\cdot\text{mol}^{-1}) = (1.132 \pm 0.048)\Delta_{\text{sin}}^{\text{g}}H_{\text{m}}(408 \text{ K}) + (17.22 \pm 1.87)$						$r^2 = 0.9982$	(18)

TABLE 10: Correlations of Aromatic 1,2-Diazines with 1-Substituted Imidazoles

run 9	slope/ <i>T</i> (K)	intercept	$\Delta_{\text{sin}}^{\text{g}}H_{\text{m}}(363 \text{ K})$ (kJ·mol ⁻¹)	$\Delta_{\text{f}}^{\text{g}}H_{\text{m}}(298 \text{ K})$ (kJ·mol ⁻¹) [lit.]	$\Delta_{\text{f}}^{\text{g}}H_{\text{m}}(298 \text{ K})$ (kJ·mol ⁻¹) [calc]	$\Delta_{\text{f}}^{\text{g}}H_{\text{m}}(298 \text{ K})$ (kJ·mol ⁻¹) [lit.]
1-methylpyrazole	-3536.6	10.00	29.40	48.0	48.1 ± 1.7	
pyridazine	-4197.4	10.611	34.90	53.5	53.3 ± 1.9	
1-methylimidazole	-4564.0	11.085	37.94		54.6 ± 1.9	64.7 ± 1.3
3-methylpyridazine	-4354.9	11.013	36.21	56.1	56.2 ± 1.9	
1-ethylimidazole	-4708.8	11.452	39.15		57.4 ± 2.0	66.0 ± 3.9
$\Delta_{\text{f}}^{\text{g}}H_{\text{m}}(298 \text{ K})$ (kJ·mol ⁻¹) = (0.955 ± 0.0038) $\Delta_{\text{sin}}^{\text{g}}H_{\text{m}}(363 \text{ K})$ + (20.00 ± 1.3)					$r^2 = 0.9984$	(19)
run 10	slope/ <i>T</i> (K)	intercept	$\Delta_{\text{sin}}^{\text{g}}H_{\text{m}}(448 \text{ K})$ (kJ·mol ⁻¹)	$\Delta_{\text{f}}^{\text{g}}H_{\text{m}}(298 \text{ K})$ (kJ·mol ⁻¹) [lit.]	$\Delta_{\text{f}}^{\text{g}}H_{\text{m}}(298 \text{ K})$ (kJ·mol ⁻¹) [calc]	$\Delta_{\text{f}}^{\text{g}}H_{\text{m}}(298 \text{ K})$ (kJ·mol ⁻¹) [lit.]
pyridazine	-3600.4	9.053	29.39	53.5	52.8 ± 2.1	
3-methylpyridazine	-3950.7	9.479	32.84	56.1	56.4 ± 2.2	
phthalazine	-5622.8	11.012	46.75	72.8	73.7 ± 2.6	
1-phenylimidazole	-5682.4	11.409	47.24		74.3 ± 2.6	84.6 ± 3.7 79.2 ± 2.7 ^a 83.0 ± 1.0
1-benzylimidazole	-6149.2	11.947	51.12		79.2 ± 2.7	
benzo[<i>c</i>]cinnoline	-7066.7	12.521	58.75	89.2	88.6 ± 3.0	
$\Delta_{\text{f}}^{\text{g}}H_{\text{m}}(298.15 \text{ K})$ (kJ·mol ⁻¹) = (1.24 ± 0.04) $\Delta_{\text{sin}}^{\text{g}}H_{\text{m}}(448 \text{ K})$ + (15.62 ± 1.8)					$r^2 = 0.9979$	(19)

^a This work, result from Table 8, run 6.

TABLE 11: Correlation of ln(*p*/*p*₀) with (*t*₀/*t*_a) for Run 1 at *T* = 298.15 K

run 1	slope/ <i>T</i> (K)	intercept	ln(<i>t</i> ₀ / <i>t</i> _a)	ln(<i>p</i> / <i>p</i> ₀) _{lit}	ln(<i>p</i> / <i>p</i> ₀) _{calcd}
2,6-dimethylquinoline	-5268.9	10.614	-7.058	-10.957	-11.002
2-phenylpyridine	-5401.3	10.731	-7.385	-11.513	-11.458
acridine	-6288.3	11.318	-9.773	-14.754	-14.786
4,7-phenanthroline	-6469.8	11.492	-10.208	-15.415	-15.393
<i>trans</i> -azobenzene	-5957.5	11.313	-8.668		-13.246
2,6-dimethylquinoline	-5268.9	10.614	-7.058	-10.957	-11.002
$\ln(p/p_0)_{\text{calc}} = (1.448 \pm 0.021) \ln(t_0/t_{a,\text{avg}}) - (1.162 \pm 0.0179)r^2 = 0.9996$					(20)

TABLE 12: Constants of Equation 8 and Predicted/Experimental Boiling Temperatures at *p* = 101.325 kPa

compound	<i>A</i> /(K ³)	<i>B</i> /(K ²)	<i>C</i> /(K)	<i>D</i>	<i>T</i> _{b,calcd} (K) ^a	<i>T</i> _{b,lit} (K)
1-methylpyrrolidine	-392058339	3036856.7	-11751.36	17.582	361	354–355 ^b
1-methylpyrrole	-332022889	2504900.1	-10616.58	16.633	380.3	385.9 ^c
<i>trans</i> -azobenzene	97537878	-1348892.9	-3256.737	9.171	577.5	573.1 ^d
1-methylindole	129400821	-1596564.4	-953.29	6.900	516	510.2 ^e

^a Calculated boiling temperature using eq 8. ^b Boiling temperatures from the 2009-10 Aldrich Catalog. ^c Reference 29. ^d Reference 12. ^e From experimental properties of 1-methylindole, SciFinder Scholar.

The vapor pressures of *trans*-azobenzene and 1-methylpyrrole evaluated by the constants of correlation eq 8 from runs 1 and 7 are in reasonably good agreement with the literature. The liquid vapor pressures obtained by correlation for *trans*-azobenzene and 1-methylpyrrole (line) are compared to direct experimental measurements using an inclined piston apparatus over the temperature range *T* = 436 to 522 for the former and *T* = 322 to 386 K for the latter compound. The experimental boiling temperature predicted for *trans*-azobenzene using eq 8 is *T*_b = 577.5 K and can be compared to a value of *T*_b = 573.1 K reported by Steele et al.¹² Similarly for 1-methylpyrrole, a predicted boiling temperature of *T*_b = 380.3 K can be compared to an experimental value of *T*_b = 385.9 K.²³ Vapor pressures for 1-methylpyrrolidine are available at and below ambient temperatures.²² Extrapolating eq 8 from these temperatures to the boiling temperature provides the agreement illustrated in Figure 4. Agreement with the experimental boiling temperature is within 6 K. For 1-methylindole, the experimental boiling temperature is reported as *T*_b = 510.2. The value predicted by eq 8 is *T*_b = 516 K. Agreement with experiment is good, especially considering the predicted value was obtained by extrapolation of eq 8 of over *T* = 100 K. Provided reliable vapor pressures are available and the standards appropriately chosen, these results are typical of the agreement obtained previously.¹⁻⁴

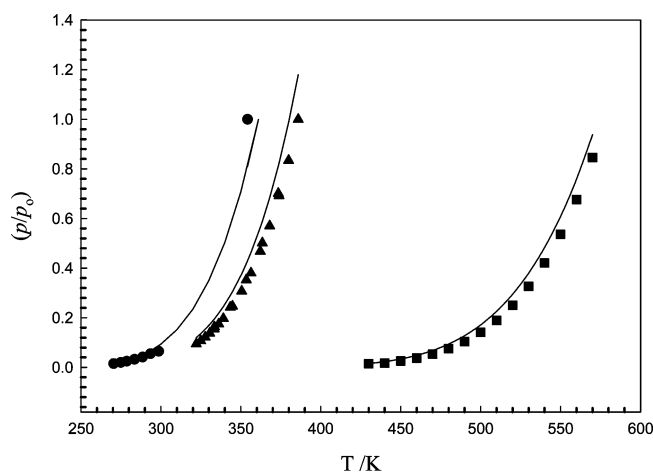


Figure 4. Comparison of experimental vapor pressures (*p*₀ = 101.325 Pa) of liquid 1-methylpyrrolidine (●),²² 1-methylpyrrole (▲),^{23,24} and *trans*-azobenzene (■)¹¹ with results obtained by correlation (—), eq 8.

Summary

The results obtained for *trans*-azobenzene suggest that anomalous behavior observed in the aromatic 1,2-diazines must require a *cis* configuration of the two nitrogen atoms. No

conclusions are drawn on the importance of aromaticity since all heterocycles of this study can be considered as containing 6π electrons. The fact that the vaporization enthalpies of N-substituted pyrroles behave normally suggests that ring size is not the factor responsible for the enhanced effect observed with imidazoles and pyrazoles. Of all the heterocyclic systems studied to date, N-substituted imidazoles clearly appear to have the largest enthalpies of association in the liquid state. The size of the hydrocarbon substituent at position 1 of the imidazole ring appears to have an attenuating effect. In instances where vaporization enthalpies are well reproduced, vapor pressures obtained by correlation are able to reproduce experimental values reasonably well.

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Supporting Information Available: Tables of enthalpies, experimental retention times, vapor pressures, and Γ values. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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