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Study of the Anomalous Thermochemical Behavior of 1,2-Diazines by Correlation−Gas Chromatography

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The vaporization enthalpies and liquid vapor pressures of quinoxaline, quinazoline, phthalazine, benzo[c]cinnoline, 1,10-phenanthroline, phenazine, and triphenylamine are measured by correlation−gas chromatography and compared to values calculated from available literature vaporization, sublimation, and fusion enthalpy data. Good agreement with the literature is observed for all compounds except the 1,2-diazines and the sublimation enthalpy of triphenylamine. The results suggest that liquid 1,2-diazines exhibit an additional intermolecular stabilizing interaction of approximately 6 kJ·mol^{-1} not present in other diazine isomers.

Introduction

Derivatives of pyrazine, pyrimidine, and pyridazine comprise a set of diverse compounds, many of which are found in natural products and biological systems. Recently we examined the vaporization enthalpies of the parent compounds by correlation−gas chromatography and observed that compounds that served as suitable standards for pyrazines, pyrimidines, and 1,3,5-triazines were unsuitable for use with pyridazines. Upon closer examination of their vaporization enthalpies, it was observed that intermolecular interactions occurring in pyridazines are considerably stronger than those in the corresponding pyrimidines and pyrazines. The origin of this enhanced intermolecular interaction was attributed to the presence of a 1,2-diazine.[1,2] This article reports the results of a study aimed at: (1) determining whether this enhanced intermolecular interaction is characteristic of all aromatic 1,2-diazines and (2) evaluating the magnitude of this interaction. The compounds evaluated in this study include quinoxaline, quinazoline, phthalazine, benzo[c]cinnoline, phenazine, and 1,10-phenanthroline. The structure of the compounds studied and those used as standards are illustrated in Figure 1. In the process of identifying additional standards that could be useful in correlation gas chromatography experiments, the vaporization enthalpy of triphenylamine was also investigated. The sublimation,[5] vaporization,[6] and fusion[7] enthalpies of triphenylamine have previously been reported. Our initial inclination was to use triphenylamine as one of the standards in this study, but upon closer inspection, one (or more) of these reported measurements appeared to be thermodynamically incompatible with the others. Correlation−gas chromatography experiments were performed to identify the discordant property.

Correlation−gas chromatography is a simple and reliable method for evaluating vaporization enthalpy and vapor pressure regardless of whether the target substance is a solid or liquid.[3,4] The method requires the use of standards with reliable vaporization enthalpies and liquid vapor pressures. The standards are injected simultaneously with the target substances. Since each analyte moves on the column according to its vapor pressure on the column, measurement of the temperature dependence of its retention time 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 retention time, a plot of $\ln(t_a/t_o)$ vs $1/T$, usually over a $T = 30$ K range, results in a linear relationship with a slope equal to the enthalpy of transfer of the analyte from the column to the gas phase, $\Delta_{sln}^g H_m(T)$, divided by the gas constant. The term t_o refers to a reference time, 1 min, and t_a is the time each analyte spends on the column. It is evaluated as the difference between the measured retention time of each analyte and that of a nonretained reference. The enthalpy of transfer can be related to the following thermodynamic relationship

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

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.[3] The quality of the correlation obtained is determined by both the quality of data available for the standards and selection of the appropriate standards.

The appropriateness of the standards used for the compounds studied in this work with the exception of the aromatic 1,2-diazines has previously been demonstrated.[1,4] The difference between the vaporization enthalpy value measured by correlation−gas chromatography and that obtained by other methods was chosen as a means of identifying and quantifying the magnitude of this additional stabilizing interaction found in the liquid phase of aromatic 1,2-diazines. Pyridazine is the only liquid aromatic 1,2-diazine whose vaporization enthalpy has been measured.[8] However, the sublimation and fusion enthalpy of several crystalline aromatic heterocyclic 1,2-diazines have been measured. A summary of these results is reported in Table 1.

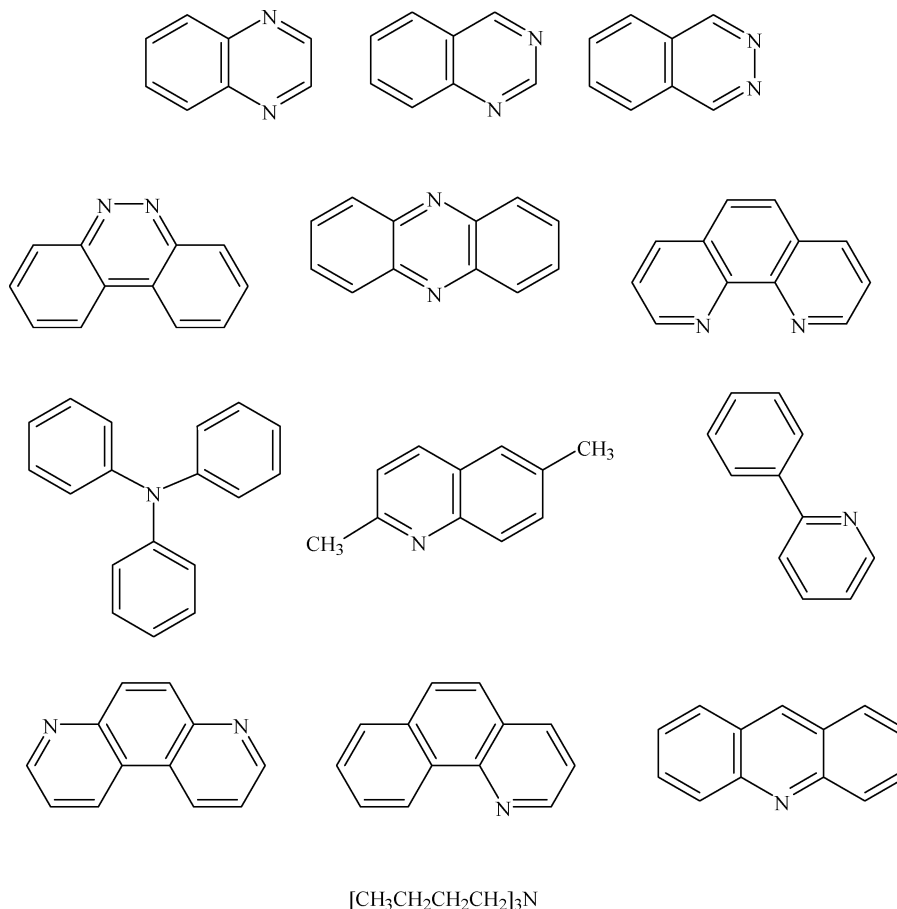* Corresponding author. E-mail: jsc@umsl.edu.

[CH₃CH₂CH₂CH₂]₃N

Figure 1. Compounds evaluated in this study. From left to right, top to bottom: quinoxaline, quinazoline phthalazine, benzo[c]cinnoline, phenazine, 1,10-phenanthroline, and triphenylamine. Standards: 2,6-dimethylquinoline, 2-phenylpyridine, 4,7-phenanthroline, 7,8-benzoquinoline, acridine, and tributylamine.

Table 1. Summary of the (A) Sublimation, Vaporization, and Fusion Enthalpies Available in the Literature and (B) the Vaporization Enthalpy of Triphenylamine and Their Adjustment to $T = 298.15$ K

(A)	$\Delta_{cr}^{g}H_{m}(T_{m})$ (kJ·mol⁻¹)	T_{m} (K)	$\Delta_{cr}^{g}H_{m}(298\ K)$ (kJ·mol⁻¹)	$\Delta_{cr}^{l}H_{m}(T_{fus})$ (kJ·mol⁻¹)	T_{fus} (K)	$C_{p}(l)/C_{p}(cr)$ (J·mol⁻¹·K)	$\Delta_{cr}^{l}H_{m}(298\ K)$ (kJ·mol⁻¹)	$\Delta_{l}^{g}H_{m}(298\ K)$ (kJ·mol⁻¹)
phthalazine			81.1 ± 0.4[a]	13.3 ± 0.6[a]	364.5	202.8/149.8	10.7 ± 1.1	70.4 ± 1.2
			82.3 ± 2.3[b]				10.7 ± 1.1	71.6 ± 2.5
	96.7[c]	na	96.7				10.7 ± 1.1	*86.0*
quinoxaline			69.4 ± 0.6[a]	11.8 ± 0.1[a]	305.7	202.8/149.8	11.5 ± 0.1	57.9 ± 2.0
			66.6 ± 2.0[b]				11.5 ± 0.1	55.1 ± 2.0
quinazoline			77.6 ± 0.5[a]	17.0 ± 0.2[a]	320.9	202.8/149.8	16.0 ± 0.4	61.6 ± 0.6
			76.6 ± 1.4[b]				16.0 ± 0.4	60.6 ± 1.5
phenazine	92.7 ± 0.4[d]	354	95.1 ± 0.8	20.9 ± 0.7[g]	447.9	277/201.7	13.2 ± 2.6	81.9 ± 2.7
				18.9 ± 0.1[d]	447.9		11.2 ± 2.6	83.9 ± 2.7
	91.8 ± 2.1[e]	298	91.8 ± 2.1	20.9 ± 0.7[g]	447.9		13.2 ± 2.6	78.6 ± 3.4
				18.9 ± 0.1[d]	447.9		11.2 ± 2.6	80.6 ± 3.4
	90.4 ± 2.5[f]	298	90.4 ± 2.5	20.9 ± 0.7[g]	447.9		13.2 ± 2.6	77.2 ± 3.6
				18.9 ± 0.1[d]	447.9		11.2 ± 2.6	79.2 ± 3.6
	90.4 ± 1.7[g]	302	90.4 ± 1.7	20.9 ± 0.7[g]	447.9		13.2 ± 2.6	77.4 ± 3.1
				18.9 ± 0.1[d]	447.9		11.2 ± 2.6	79.2 ± 3.1
benzo[c]cinnoline	101.7 ± 0.2[h]	340	103.5 ± 0.6	20.9 ± 0.1[h]	430	277/201.7	14.1 ± 2.2	89.2 ± 2.3
	113.0[c]	na					14.1 ± 2.2	*98.9*
1,10-phenanthroline	*98.3[c]*	na		11.8 ± 0.1[i]	391.1	277/201.7	7.0 ± 1.6	*91.3*
4,7-phenanthroline								80.8 ± 4.8[m]
triphenylamine	87.9 ± 1.3[j]	348	90.9 ± 1.6	24.9 ± 0.4[k]	400.2	394.9/319.5	18.3 ± 2.2	73.7 ± 2.7

(B)	$\Delta_{l}^{g}H_{m}(T_{m})$ (kJ·mol⁻¹)	T_{m} (K)	$\Delta_{l}^{g}H_{m}(298\ K)$ (kJ·mol⁻¹)	$\Delta_{cr}^{l}H_{m}(T_{fus})$ (kJ·mol⁻¹)	T_{fus} (K)	$C_{p}(l)/C_{p}(cr)$ (J·mol⁻¹·K)	$\Delta_{cr}^{l}H_{m}(298\ K)$ (kJ·mol⁻¹)	$\Delta_{cr}^{g}H_{m}(298\ K)$ (kJ·mol⁻¹)
triphenylamine	67.4[l]	523	92.8 ± 6	24.9 ± 0.4[k]	400.2	394.9/319.5	18.3 ± 2.2	111.1 ± 3.6

[a] Ref 9. [b] Ref 10. [c] Ref 11. na in column three: not available. [d] Ref 12. [e] Ref 13. [f] Ref 14. [g] Ref 15. [h] Ref 16. [i] Ref 17. [j] Ref 5. [k] Ref 7. [l] Ref 6. [m] Ref 4.

The second column of Table 1 lists literature sublimation enthalpies evaluated at the mean temperature of measurement.

Fusion enthalpies and fusion temperatures are reported in columns 5 and 6. Adjustments of the enthalpies reported in

Table 2. Parameters of (A) the Cox Equation Used for Reference, (B) the Wagner Equation, and (C) the Third-Order Polynomial

(A)		A_1	A_2*10^7	T_b	range	
Cox equation	A_o	T^{-1}	T^{-2}	K	K	
acridine[20]	2.89594	−0.00111538	6.486	618.059	383 to 637	
7,8-benzoquinoline[20]	2.88454	−0.00111802	6.6824	14.49	373 to 672	

(B)					T_c	p_c	range
Wagner equation[a]	A_W	B_W	C_W	D_W	K	kPa	K
2,6-dimethylquinoline[21]	−8.993312	3.594873	−4.63173	−2.907492	786	3480	337 to 592

	A	B	C		range
(C)	K^3	K^2	K	D	K
tri-*n*-butylamine[4]	30767110	−712464.53	−3836.0	10.769	298 to T_b
2-phenylpyridine[4]	82334650	−1199538.89	−2988.7	8.899	298 to T_b
4,7-phenanthroline[4]	123705710	−1579329.77	−3296.6	8.741	298 to T_b

[a] $T_r = T/T_c$.

Table 3. Vaporization Enthalpies in the Literature

compound	$\Delta_l^g H_m(T_m/K)$ (kJ·mol^{-1})	T_m K	C_{pl} (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
tri-*n*-butylamine					62.7 ± 1.3	4
2,6-dimethylquinoline					67.07 ± 0.16	21
2-phenylpyridine					68.4 ± 1.9	4
7,8-benzoquinoline	72.99 ± 0.3	360	278.1	78.11 ± 1.0	77.23[b]	20
acridine	72.94 ± 0.1	380	278.1	79.72 ± 1.3	78.63[b]	20
4,7-phenanthroline					80.8 ± 4.8	4

[a] Literature data adjusted to $T = 298.15$ 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 equations at a mean temperature of $T = 298.15$ K.

Tables 1A and 1B to $T = 298.15$ K were achieved using eqs 2 to 5. Equation 2 was used to adjust sublimation enthalpies; eq 3 was used to adjust fusion enthalpies; and eq 4 is the thermodynamic equality used to calculate vaporization enthalpies. Equation 5 was used to adjust the vaporization enthalpy of triphenylamine reported in Table 1B to $T = 298.15$ K. Equations 2, 3, and 5 have been used previously and shown to provide reasonable adjustments for temperature.[1−4] The heat capacity terms required for these temperature adjustments, $C_p(cr)$ and $C_p(l)$, are reported in Tables 1A and 1B and were evaluated by group additivity.[18,19]

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

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

$$\Delta_l^g H_m(298.15 \text{ K}) = \Delta_{cr}^g H_m(298.15 \text{ K}) - \Delta_{cr}^l H_m(298.15 \text{ K}) \quad (4)$$

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

Values in italics in Table 1A are considered to be unreliable. All of these data were obtained from the dissertation of G. D. Mills[11] who measured a series of other compounds in addition to those listed in this table. The measurements were performed by mass effusion at four temperatures over a 12 K range. The mean temperature of measurement is not reported in the thesis. All of the values reported in the thesis differ significantly from other literature values.

As noted above, the vaporization enthalpy calculated for triphenylamine using eq 4 in Table 1A differs by some 19 kJ·mol^{-1} from the value measured directly and adjusted to $T = 298.15$ K (Table 1B). As a result of this discrepancy, instead of using triphenylamine as a standard, it was also included as an unknown in the correlations described below.

Examining the calculated vaporization enthalpies of phthalazine, quinoxaline, and quinazoline, the last column of Table 1A suggests that phthalazine does have a substantially larger vaporization enthalpy. Similarly, benzo[c]cinnoline also appears to have a larger value than any of its three other isomers listed in the table. To confirm these observations and to establish a quantitative measure of the magnitude of this interaction, vaporization enthalpies were measured using structurally related standards and treating each of the diazines with the exception of 4,7-phenanthroline as unknowns. The vaporization enthalpy of 4,7-phenanthroline at $T = 298.15$ K has been measured previously.[4]

Experimental Section

All compounds used in this study were obtained from various commercial sources and used as purchased. All were analyzed by gas chromatography and most found to have purities of 98 % 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. Correlation−gas chromatography experiments were performed on HP 5890 Gas Chromatographs 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 DB5 MS column. While enthalpies of transfer do depend on the nature of the column used, the

Table 4. Vaporization Enthalpy Results of Runs 1 to 4

run 1	slope T/K	intercept	$\Delta_{sln}^g H_m(478\ K)$ (kJ·mol^{-1})	$\Delta_l^g H_m(298\ K)$ (kJ·mol^{-1}) lit.	$\Delta_l^g H_m(298\ K)$ (kJ·mol^{-1}) calcd
tributylamine	−4958.2	11.037	41.22	62.70	62.4 ± 2.4
quinoxaline	−4589.2	9.863	38.15		58.6 ± 2.3
quinazoline	−4675.3	9.909	38.87		59.5 ± 2.3
2,6-dimethylquinoline	−5385.9	10.776	44.78	67.07	66.9 ± 2.6
2-phenylpyridine	−5592.2	11.035	46.49	68.40	69.0 ± 2.7
phthalazine	−5423.7	10.564	45.09		67.3 ± 2.7
7,8-benzoquinoline	−6422.1	11.551	53.39	77.23	77.7 ± 3.1
acridine	−6448.0	11.572	53.61	78.63	78.0 ± 3.1

$$\Delta_l^g H_m(298.15\ K)/(kJ\cdot mol^{-1}) = (1.25 \pm 0.057)\Delta_{sln}^g H_m(478\ K) + (10.82 \pm 0.63) \quad r^2 = 0.9938 \quad (9)$$

run 2	slope T/K	intercept	$\Delta_{sln}^g H_m(478\ K)$ (kJ·mol^{-1})	$\Delta_l^g H_m(298\ K)$ (kJ·mol^{-1}) lit.	$\Delta_l^g H_m(298\ K)$ (kJ·mol^{-1}) calcd
tributylamine	−5167.8	11.485	42.96	62.70	62.5 ± 1.6
quinoxaline	−4807.2	10.327	39.97		58.8 ± 1.5
quinazoline	−4893.7	10.373	40.68		59.7 ± 1.5
2,6-dimethylquinoline	−5599.7	11.229	46.55	67.07	67.1 ± 1.7
2-phenylpyridine	−5747.2	11.366	47.78	68.40	68.6 ± 1.8
phthalazine	−5615.7	10.97	46.69		67.2 ± 1.7
7,8-benzoquinoline	−6607.6	11.943	54.93	77.23	77.6 ± 2.0
acridine	−6657.5	12.016	55.35	78.63	78.2 ± 2.0

$$\Delta_l^g H_m(298.15\ K)/(kJ\cdot mol^{-1}) = (1.26 \pm 0.036)\Delta_{sln}^g H_m(478\ K) + (8.41 \pm 0.39) \quad r^2 = 0.9975 \quad (10)$$

run 3	slope T/K	intercept	$\Delta_{sln}^g H_m(508\ K)$ (kJ·mol^{-1})	$\Delta_l^g H_m(298\ K)$ (kJ·mol^{-1}) lit.	$\Delta_l^g H_m(298\ K)$ (kJ·mol^{-1}) calcd
2,6-dimethylquinoline	−5132.1	10.271	42.67	67.07	66.9 ± 0.9
2-phenylpyridine	−5273.5	10.405	43.84	68.40	68.6 ± 0.9
phenazine	−5957	10.799	49.52		76.6 ± 1.0
acridine	−6127.9	10.929	50.95	78.63	78.6 ± 1.1
4,7-phenanthroline	−6307.1	11.099	52.43	80.80	80.8 ± 1.1
benzo[c]cinnoline	−6402.8	11.124	53.23		81.9 ± 1.1
triphenylamine	−7108.7	12.312	59.1		90.2 ± 1.2
1,10-phenanthroline	−6768.4	11.551	56.27		86.2 ± 1.1

$$\Delta_l^g H_m(298.15\ K)/(kJ\cdot mol^{-1}) = (1.418 \pm 0.02)\Delta_{sln}^g H_m(508\ K) + (6.41 \pm 0.17) \quad r^2 = 0.9996 \quad (11)$$

run 4	slope T/K	intercept	$\Delta_{sln}^g H_m(508\ K)$ (kJ·mol^{-1})	$\Delta_l^g H_m(298\ K)$ (kJ·mol^{-1}) lit.	$\Delta_l^g H_m(298\ K)$ (kJ·mol^{-1}) calcd
2,6-dimethylquinoline	−5323.2	10.662	44.26	67.07	66.9 ± 1.0
2-phenylpyridine	−5465.3	10.797	45.44	68.40	68.6 ± 0.9
acridine	−6324.6	11.33	52.58	78.63	78.7 ± 1.1
phenazine	−6152.8	11.199	51.15		76.6 ± 1.1
4,7-phenanthroline	−6502.3	11.497	54.06	80.80	80.7 ± 1.1
benzo[c]cinnoline	−6598.9	11.523	54.86		81.9 ± 1.1
triphenylamine	−7311.1	12.724	60.78		90.2 ± 1.2
1,10-phenanthroline	−6958.8	11.939	57.85		86.1 ± 1.2

$$\Delta_l^g H_m(298.15\ K)/(kJ\cdot mol^{-1}) = (1.412 \pm 0.020)\Delta_{sln}^g H_m(508\ K) + (4.42 \pm 0.17) \quad r^2 = 0.9996 \quad (12)$$

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. At the temperatures of the experiments, the retention time of the cyclopentane used as solvent generally increased with increasing temperature. This is a consequence of the increase in viscosity of the carrier gas with temperature; it is the criterion that has been used to confirm that the reference was not being retained on the column. The retention time of the cyclopentane was used to determine the dead volume of the column. Adjusted retention times, t_a, were calculated by subtracting the measured retention time of the nonretained reference from the retention time of each analyte as a function of temperature, at $T = 5$ K intervals over a 30 K range. Column

temperatures were controlled by the gas chromatograph and were monitored independently by using a Fluke digital thermometer. Temperature maintained by the gas chromatograph was constant to ± 0.1 K. Enthalpies of transfer were calculated as the product of the slope of the line obtained by plotting $\ln(t_a/t_o)$ vs $1/T$ and the gas constant, R. All plots of $\ln(t_a/t_o)$, vs $1/T$, where $t_o = 1$ min, were characterized by correlation coefficients, r^2, >0.99. Unless noted otherwise, $p_o = 101.325$ kPa. The retention times measured for all analytes are reported in the Supporting Information. The uncertainties (± σ) reported in the last column of Tables 4 and 8 were calculated from the uncertainty in the slope and intercept of the equations listed at the bottom of each

Table 5. Summary of the Vaporization Enthalpies Evaluated in This Work

	$\Delta_l^g H_m(298\text{ K})^a/(\text{kJ}\cdot\text{mol}^{-1})$				$\Delta\Delta_l^g H_m(298\text{ K})$
	runs 1/3	runs 2/4	average^a	lit. (avg)^b	(kJ·mol^{-1})
phthalazine	*67.3 ± 2.7*	*67.2 ± 1.7*	67.3 ± 2.2	71 ± 1.9	3.7 ± 2.9
quinoxaline	58.6 ± 2.3	58.8 ± 1.5	58.7 ± 1.9	56.5 ± 2.0	−2.2 ± 2.8
quinazoline	59.5 ± 2.3	59.7 ± 1.5	59.6 ± 1.9	61.1 ± 1.1	1.5 ± 2.2
phenazine	76.6 ± 1.0	76.6 ± 1.1	76.6 ± 1.1	78.8 ± 2.2^c	2.1 ± 2.5
			76.6 ± 1.1	80.7 ± 2.2^c	4.0 ± 2.5
benzo[c]cinnoline	*81.9 ± 1.1*	*81.9 ± 1.1*	*81.9 ± 1.1*	89.2 ± 2.3	7.3 ± 2.5
triphenylamine	90.2 ± 1.2	90.2 ± 1.2	90.2 ± 1.2	92.8 ± 6	2.6 ± 6.1
1,10-phenanthroline	86.2 ± 1.1	86.1 ± 1.2	86.2 ± 1.2	*91.3^d*	*4.9*
pyridazine			*46.5 ± 2.2^e*	53.5 ± 0.4^f	7.0 ± 2.2

^{a} Values in italics are considered unreliable. ^{b} The uncertainty reported is an average of the deviations reported in Table 1 except where noted otherwise. ^{c} The uncertainty represents the standard deviation of four runs associated with each fusion enthalpy reported in Table 1. ^{d} Ref 11. ^{e} Ref 2. ^{f} Ref 8.

Table 6. Correlation of $\ln(t_o/t_a)$ with $\ln(p/p_o)$ for Runs 3 and 4 at T = 298.15 K

	$\ln(t_o/t_a)_{\text{avg}}$	$\ln(p/p_o)_{\text{lit}}$	$\ln(p/p_o)_{\text{calcd}}$
2,6-dimethylquinoline	−7.059	−10.957	−10.989
2-phenylpyridine	−7.4	−11.513	−11.471
acridine	−9.745	−14.754	−14.784
4,7-phenanthroline	−10.176	−15.415	−15.393
phenazine	−9.301		−14.157
benzo(c)cinnoline	−10.472		−15.812
triphenylamine	−11.656		−17.484
1,10-phenanthroline	−11.268		−16.936

$$\ln(p/p_o) = (1.413 \pm 0.016)\ln(t_o/t_a)_{\text{avg}} - (1.014 \pm 0.046)$$

$$r^2 = 0.9997 \quad (13)$$

respective table. These uncertainties reflect the potential error in the absolute value of the vaporization enthalpy.

Vaporization Enthalpies and Vapor Pressures of the Standards

Vapor pressures and vaporization enthalpies of all the compounds used as standards at T = 298.15 K are reported in Tables 2 and 3. Vapor pressures, reported from T = (383 to 637) K for acridine and from T = (373 to 672) K for 7,8-benzoquinoline, are available in the form of the Cox equation, eq 6. Vapor pressures for 2,6-dimethylquinoline from T = (337 to 592) K are available in the form of the Wagner equation, eq 7. The parameters for these equations are defined in Tables 2A and 2B. 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 to 313) K to provide vaporization enthalpies at the mean temperature, T = 298.15 K. The resulting vaporization

enthalpies are reported in the sixth column of Table 3. For comparison, the vaporization enthalpies of acridine and 7,8-benzoquinoline were also adjusted to T = 298.15 K using eq 5. These values, which are in good mutual agreement, are reported in column 5 of Table 3. The vapor pressures of acridine, 7,8-benzoquinoline, and 2,6-dimethylquinoline calculated from the Cox and Wagner equations were the values used in the vapor pressure correlations described below. Consequently, the vaporization enthalpy calculated from these two equations, reported in column 6, Table 3, were also the reference values used in all subsequent correlations. Vaporization enthalpies at T = 298.15 K and vapor pressures for tri-n-butylamine, 2-phenylpyridine, and 4,7-phenanthroline from T = 298.15 K to the boiling temperature (T_b), eq 8, have been evaluated previously by correlation−gas chromatography.[4] The constants for this equation are provided in Table 2C.

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

$$\ln(p/p_c) = (1/T_r)[A_W(1 - T_r) + B_W(1 - T_r)^{1.5} + C_W(1 - T_r)^{2.5} + D_W(1 - T_r)^5] \quad (7)$$

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

Results

The results of two sets of duplicate correlations are reported in Table 4 as runs 1 to 4. Equations 9 to 12 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

Table 7. Constants of Equation 8 and Predicted Boiling Temperatures Evaluated^a

	A	B	C		T_{bcalcd}	T_{blit}
	K^3	K^2	K	D	K^b	K^c
quinoxaline	61954207.1	−1012863	−2367.266	8.211	503.5	493.2 to 496.2
quinazoline	66404416.7	−1053219	−2352.612	8.134	511.2	516.2
phthalazine	*92448690.2*	*−1291445*	*−2548.666*	*8.114*	*440^d*	*462^d*
phenazine	114900829	−1498260	−3041.695	8.565	606.9	na
benzo[c]cinnoline	*132822266*	*−1653072*	*−3229.561*	8.605	638.3	>633, 612, 633^e
triphenylamine	134264982	−1668568	−4177.629	10.232	633.1	637.2^f
1,10-phenanthroline	141119405	−1725945	−3531.116	8.999	650.2	>573.2^e

^{a} Values in italics are considered unreliable. ^{b} Calculated normal boiling temperature using eq 8 unless noted otherwise. ^{c} Literature boiling temperatures from the 2009−10 Aldrich Catalog unless noted otherwise. ^{d} Boiling temperature at 3.9 kPa. ^{e} Boiling temperatures(s) from SciFinder Scholar. ^{f} Ref 6.
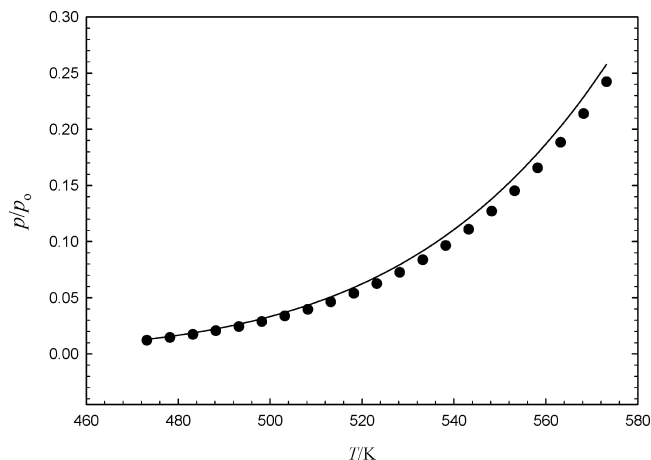
Figure 2. Comparison of the of vapor pressure of liquid triphenylamine: ●, ref 6; —, this work; $p_o = 101.325$ Pa.

slope and intercept associated with these correlations. Table 5 compares the results of the compounds used as unknowns to the values calculated in Table 1. With the exception of the 1,2-diazines (phthalazine, benzo[c]cinnoline, and pyridazine) and 1,10-phenanthroline, a compound whose literature value is questionable, all remaining vaporization enthalpies are in good agreement with the values calculated from the sublimation and fusion enthalpies. If the enthalpy differences between vaporization enthalpies measured by correlation−gas chromatography and eq 4 for phthalazine, benzo[c]cinnoline, and pyridazine are averaged, this suggests a difference in the strength of intermolecular interactions between 1,2-diazines and their isomeric counterparts of the order of 6 kJ·mol^{-1}. Additionally, the value for triphenylamine [(90.1 ± 0.4) kJ·mol^{-1}] is in good agreement with the direct measurement of vaporization enthalpy by Forward et al.[6] (92.8 kJ·mol^{-1}) but in much poorer agreement with the value of (73.7 ± 2.7) kJ·mol^{-1} calculated from the sublimation enthalpy reported by Steele.[5]

As a further check on the reliability of these measurements, the vapor pressures and boiling temperatures of the compounds listed in Table 6 were evaluated using the vapor pressures of the compounds listed in Tables 2A to 2C as standards. Values of $\ln(t_o/t_a)$ were calculated using the slopes and intercepts reported in Table 4 to calculate t_o/t_a values for each run. These values were subsequently averaged, and the logarithm of $(t_o/t_a)_{avg}$ plotted against $\ln(p/p_o)$ of the standards was used in the run. A typical calculation is illustrated in Table 6 for runs 3 and 4 at $T = 298.15$ K. The correlation equation generated at this temperature is reported as eq 13 listed below the table. This process was repeated at $T = 10$ K intervals from $T = (298.15$ to $500)$ K for runs 1 and 2 and from $T = (298.15$ to $540)$ K for runs 3 and 4. The resulting values of $\ln(p/p_o)_{calc}$ calculated for each unknown as a function of temperature were then fit to the third-order polynomial, eq 8. The constants for this equation for each compound evaluated are listed in Table 7. This equation was then used to predict each respective boiling temperature. The boiling temperatures for quinoxaline, quinazoline, and triphenylamine are in good agreement with those reported. The value for phthalazine is considerably lower than the experimental value. For pyridazine, the predicted boiling temperature using this protocol was found to be 53 K lower than the experimental value.[2] No conclusions can be inferred from the results obtained for benzo[c]cinnoline.

With the exception of triphenylamine and pyridazine, the compounds listed in Table 5 are all solids at room temperature. Liquid vapor pressures are only available for triphenylamine. As noted above, the vaporization enthalpy measured for triphenylamine was most consistent with the value reported by Forward et al.[6] who measured the vapor pressures of triphenylamine over the temperature range $T = (473$ to $573)$ K. Figure 2 compares vapor pressure results reported by Forward et al. to those calculated by this study over the same temperature range. The solid circles refer to the values reported by Forward et al., and the line represents values calculated using eq 8. The comparison is remarkably good.

Vapor pressures for the crystalline compounds in Table 5 are only available for the solid form. Recently, we reported a protocol that was able to evaluate sublimation vapor pressures using fusion enthalpies and liquid vapor pressures evaluated using correlation−gas chromatography, eq 8, within a factor of 2 to 3.[22] The protocol involved combining the vaporization enthalpy, evaluated at the fusion temperature using eq 8, with the fusion enthalpy and adding a heat capacity term to adjust the resulting sublimation enthalpy for temperature, eq 14. The fusion temperature was used as an approximation of the triple point temperature, and the vapor pressure evaluated at the fusion temperature was used as the temperature and pressure common to both liquid and solid. The heat capacity term was evaluated using eq 2 and the values given in Table 1A.

$$\ln(p_2/p_{fus}) = -\Delta_{cr}^{g}H_m(T)/R[1/T_2 - 1/T_{fus}] \quad (14)$$

where

$$-\Delta_{cr}^{g}H_m(T) = \{\Delta_{l}^{g}H_m(T_{fus}) + \Delta_{cr}^{l}H_m(T_{fus}) + \Delta_{cr}^{g}C_p(T_{fus} - T_2)\}$$

Sublimation vapor pressures were calculated from $T = (T_{fus}$ to $298.15)$ K and the results fit to the second-order polynomial, eq 15. The results of applying this protocol to the solids of Table 5 are summarized in Table 8. The table lists the constants of eq 15 in columns 2 to 4, the temperature range to which they apply (column 5), and the temperature corresponding to the calculated and literature vapor pressure, columns 6 to 8. Agreement between literature values and those calculated using eq 14 are within a factor of 3 of the literature values except for the 1,2-diazines. The constants of eq 15 for phthalazine and benzo[c]cinnoline are reported in italics and are considered to be unreliable. The literature vapor pressure of solid triphenylamine is also considered suspect.

$$\ln(p/p_o) = A'(T/\text{K})^{-2} + B'(T/\text{K}) + C' \quad (15)$$

Both the solid and liquid vapor pressure results also support the conclusion that liquid 1,2-diazines interact more strongly intermolecularly than other diazines. This implies that while the use of pyridines and other diazines can not be used as vaporization enthalpy standards, 1,2-diazines should be appropriate vaporization enthalpy standards for other aromatic 1,2-diazines. As a test of this hypothesis, a mixture of pyridazine, 3-methylpyridazine, phthalazine, and benzo[c]cinnoline was examined by correlation−gas chromatography. The results are summarized in Table 9, runs 5 and 6, by eqs 16 and 17. The results suggest that such is the case. The larger uncertainty associated with these correlations is probably related to the larger uncertainty associated with vaporization enthalpies calculated using eq 4.

Table 8. Constants of Equation 15 and Predicted Vapor Pressures[a]

	A'	B'	C'	range	T	$p(T)_{calcd}$	$p(T)_{lit}$	
				T/K	K	Pa	Pa	lit.
quinoxaline	−242021	−6846.8	16.784	306 to 298	298	$13.6 \cdot 10^{-5}$	$7.90 \cdot 10^{-5}$	9
quinazoline	−257680	−7428.0	18.234	321 to 298	298	$6.90 \cdot 10^{-5}$	$3.90 \cdot 10^{-5}$	9
phthalazine	*−273364*	*−7671.9*	*16.417*	365 to 298	333	*$11.3 \cdot 10^{-5}$*	1.30·10⁻⁵	9
phenazine	−401152	−8862.5	17.379	448 to 298	298	$4.80 \cdot 10^{-8}$	$3.90 \cdot 10^{-8}$	15
benzo[c]cinnoline	*−391281*	*−9563*	*18.187*	430 to 298	298	*$11.5 \cdot 10^{-9}$*	$4.50 \cdot 10^{-9}$	16
triphenylamine	−601806	−10089	20.442	400 to 298	348	$1.30 \cdot 10^{-6}$	*$7.80 \cdot 10^{-6}$*	5

[a] Values in italics are considered unreliable.

Table 9. Vaporization Enthalpy Results of the 1,2-Diazines, Runs 5 and 6

	slope		$\Delta_{sln}^g H_m$(468 K)	$\Delta_l^g H_m$(298 K)	$\Delta_l^g H_m$(298 K)
run 5	T/K	intercept	$(kJ \cdot mol^{-1})$	$(kJ \cdot mol^{-1})$ lit.	$(kJ \cdot mol^{-1})$ calcd
pyridazine	−3714.4	9.399	30.88	53.5	52.7 ± 4.5
3-methylpyridazine	−4029.4	9.705	33.50		56.1 ± 4.8
phthalazine	−5562.8	10.857	46.25	71.0	72.9 ± 6.2
benzo[c]cinnoline	−6949.3	12.224	57.77	89.2	88.1 ± 7.5

$$\Delta_l^g H_m(298.15\ K)/(kJ \cdot mol^{-1}) = (1.32 \pm 0.124)\Delta_{sln}^g H_m(468\ K) + (12.0 \pm 2.4) \quad r^2 = 0.9913 \tag{16}$$

	slope		$\Delta_{sln}^g H_m$(468 K)	$\Delta_l^g H_m$(298 K)	$\Delta_l^g H_m$(298 K)
run 6	T/K	intercept	$(kJ \cdot mol^{-1})$	$(kJ \cdot mol^{-1})$ lit.	$(kJ \cdot mol^{-1})$ calcd
pyridazine	−3705.5	9.392	30.81	53.5	52.8 ± 3.8
3-methylpyridazine	−3994.6	9.642	33.21		56.0 ± 4.0
phthalazine	−5467.8	10.665	45.46	71.0	72.6 ± 5.0
benzo(c)cinnoline	−6869.5	12.068	57.11	89.2	88.3 ± 7.2

$$\Delta_l^g H_m(298.15\ K)/(kJ \cdot mol^{-1}) = (1.25 \pm 0.057)\Delta_{sln}^g H_m(468\ K) + (10.82 \pm 0.63) \quad r^2 = 0.9938 \tag{17}$$

Table 10. Standard Enthalpies of Formation and Mean Ph−N Bond Dissociation Energies (<D>)[5] in kJ·mol⁻¹

	ΔH_f(g, 298 K)		ΔH_f(g, 298 K)		$<D>$(Ph−N)
Ph	325.2 ± 8.4	PhNH₂	87.1 ± 0.8	PhNH₂	405.8 ± 8.4
NH₂	167.8 ± 4.2	Ph₂NH	219.2 ± 2.9	Ph₂NH	384.9 ± 12.6
NH	337.7 ± 7.1	Ph₃N	326.8 ± 4.2	Ph₃N	373.7 ± 15^a
N	472.8 ± 0.4	Ph₃N	343.2 ± 4.1	Ph₃N	368.2 ± 15^b

[a] Literature value[5] using a sublimation enthalpy of 92.0 kJ·mol⁻¹. [b] This work using a sublimation enthalpy of 108.5 kJ·mol⁻¹.

Conclusions

The vaporization enthalpies, evaluated from the difference in sublimation and fusion and by correlation−gas chromatography, clearly indicate an enhanced intermolecular interaction in aromatic 1,2-diazines of approximately 6 kJ·mol⁻¹. Whether an interaction of similar magnitude is observed in acyclic 1,2-diazines and what role if any stereochemistry plays in the acyclic analogs remains to be determined.

A sublimation enthalpy of (108.5 ± 2.3) kJ·mol⁻¹ at $T =$ 298.15 K is calculated (90.2 + 18.3) for triphenylamine which differs considerably from (92.0 ± 2.5) kJ·mol⁻¹, the value measured previously. Using the data reported in Table 10, a bond dissociation energy of (373.7 ± 15) kJ·mol⁻¹ was calculated by Steele.[5] This compares to a new value of (368.2 ± 15) kJ·mol⁻¹ using a sublimation enthalpy of (108.5 ± 2.3) kJ·mol⁻¹. Despite the difference in sublimation enthalpy, the C−N bond dissociation energy in triphenylamine is calculated to be only a few kilojoules lower and well within the uncertainty reported.[5] This change of 16.4 kJ·mol⁻¹ in sublimation enthalpy largely ameliorates an earlier enunciated anomaly in phenylation enthalpies dis

cussed in a review of the thermochemistry of aniline and its derivatives.[23]

Supporting Information Available:

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

Literature Cited

(1) Lipkind, D.; Chickos, J. S. An Examination of the Vaporization Enthalpies and Vapor Pressures of Pyrazine, Pyrimidine, Pyrazine, and 1,3,5-Triazine. *Struct. Chem.* **2009**, *20*, 49–58.

(2) Lipkind, D.; Chickos, J. S.; Liebman, J. F. Chemistry, Commentary and Community: Discussion of: An Examination of the Vaporization Enthalpies and Vapor Pressures of Pyrazine, Pyrimidine, Pyrazine, and 1,3,5-Triazine by Lipkind and Chickos. *Struct. Chem.* **2009**, *20*, 617–618.

(3) Lipkind, D.; Chickos, J. S. An Examination of Factors Influencing the Thermodynamics of Correlation-Gas Chromatography as Applied to Large Molecules and Chiral Separations. *J. Chem. Eng. Data* **2009**, *54*, DOI: 10.1021/je900422c.

(4) Lipkind, D.; Hanshaw, W.; Chickos, J. S. Hypothetical Thermodynamic Properties. Subcooled Vaporization Enthalpies and Vapor Pressures of Polyaromatic Heterocycles and Related Compounds. *J. Chem. Eng. Data* **2009**, *54*, 2930–2943.

(5) Steele, W. V. The Standard Enthalpies of Formation of the Triphenyl Compounds of the Group V Elements. 1. Triphenylamine and the Ph-N Bond Dissociation Energy. *J. Chem. Thermodyn.* **1978**, *10*, 441–444.

(6) Forward, M. V.; Bowden, S. T.; Jones, W. J. Physical Properties of Triphenyl Compounds of Group VB Elements. *J. Chem. Soc.* **1949**, S121–S126.

(7) Chickos, J. S.; Braton, C. M.; Hesse, D. G. Estimating Entropies and Enthalpies of Fusion of Organic Compounds. *J. Org. Chem.* **1991**, *56*, 927–38.

(8) Tjebbes, J. The Heats of Combustion and Formation of the Three Diazines and Their Resonance Energies. *Acta Chem. Scand.* **1962**, *16*, 916–921.

(9) Sabbah, R.; Pemenzi, O. Energetics of Intermolecular Bonds in the Three Diazines: Phthalazine, Quinazoline and Quinoxaline. *C. R. Acad. Sci. Paris Ser. II* **1993**, *317*, 575–83.

(10) Ribeiro da Silva, M. A. V.; Matos, M. A. Thermochemical and Theoretical Studies of Some Benzodiazines. *J. Chem. Soc. Faraday Trans* **1995**, *91*, 1907–1910.

(11) Mills, G. D. Diss. Abstr. Int B. Ph. D. Thesis, 1972; Vol. 33p 1485.

(12) Sabbah, R.; El Watik, L. Thermodynamic Study of Anthrone, Coumarin and Phenazine. *J. Therm. Anal.* **1992**, *38*, 803–809.

(13) Leitao, M. L. P.; Pilcher, G.; Acree, W. E., Jr.; Zvaigzne, A. I.; Tucker, S. A.; Ribeiro da Silva, M. D. M. C. Enthalpies of Combustion of Phenazine N-oxide, Phenazine, Benzofuroxan, and Benzofurazan: The Dissociation Enthalpies of the (N-O) Bonds. *J. Chem. Thermodyn.* **1990**, *22*, 923–928.

(14) DeKruif, C. G.; van Ginkel, V. J. *4th International Conference of Chemical Thermodynamics*, Montpellier r. 8/2, 11, 1975; cited in: Colomina, M.; Jimenez, P.; Turrion, C. *J. Chem. Thermodyn.* **1982**, *14*, 779–784.

(15) McEachern, D. M.; Sandoval, O.; Iniguez, J. C. The Vapor Pressures, Derived Enthalpies of Sublimation, Enthalpies of Fusion, and Resonance Energies of Acridine and Phenazine. *J. Chem. Thermodyn.* **1975**, *7*, 299–306.

(16) Schulze, F. W.; Petrick, H. J.; Cammenga, H. K.; Klinge, H. Thermodynamic Properties of the Structural Analogues Benzo[c]cinnoline, trans-Azobenzene, and cis- Azobenzene. *Z. Physik. Chem. Neue Folge (Wiesbaden)* **1977**, *107*, 1–19.

(17) Bonicelli, M. G.; Catalani, A.; Mariano, G.; Vecchio, S. Heat Capacity and Molar Enthalpies and Entropies of Fusion for Anhydrous 1,10-Phenanthroline and 2,9-Dimethyl-1,10-phenanthroline. *Thermochim. Acta* **2007**, *466*, 69–71.

(18) Chickos, J. S.; Hesse, D. G.; Liebman, J. F. Heat Capacity Corrections to a Standard State: A Comparison of New and Some Literature Methods for Organic Liquids and Solids. *Struct. Chem.* **1993**, *4*, 271–278.

(19) Chickos, J. S.; Hesse, D. G.; Liebman, J. F. A Group Additivity Approach for the Estimation of Heat Capacities of Organic Liquids and Solids at 298 K. *Struct. Chem.* **1993**, *4*, 261–269.

(20) Steele, W. V.; Chirico, R. D.; Hossenlopp, I. A.; Nguyen, A.; Smith, N. K.; Gammon, B. E. The Thermodynamic Properties of the Five Benzoquinolines. *J. Chem. Thermodyn.* **1989**, *21*, 81–107.

(21) Chirico, R. D.; Johnson, R. D., III; Steele, W. V. Thermodynamic Properties of Methylquinolines. Experimental Results for 2,6-Dimethylquinoline and Mutual Validation Between Experiments and Computational Methods for Methylquinolines. *J. Chem. Thermodyn* **2007**, *39*, 698–711.

(22) Chickos, J. S. Sublimation Vapor Pressures as Evaluated by Correlation−Gas Chromatography. *J. Chem. Eng. Data* **2009**, DOI: 10.1021/je900680f.

(23) Slayden, S. W.; Liebman, J. F. Thermochemistry of Anilines. In *The Chemistry of Anilines*; Rappoport, Z., Ed.; Wiley: Chichester, 2007; pp 259−292.