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Dmitry Lipkind
University of Missouri-St. Louis

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Study of the Vaporization Enthalpies by Correlation-Gas Chromatography

Dmitry Lipkind

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Approved by the Following Members

of the Dissertation Advisory Committee

Professor James S. Chickos (chairman)

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Abstract

The focus of this thesis is on the measurement and collection of thermodynamic and physical property data, including vaporization, fusion, and sublimation enthalpies and vapor pressures of large n-alkanes, nitrogen heterocycles and related compounds by a technique developed in our laboratory referred to as correlation-gas chromatography (C-GC).

These thermodynamic data are of importance to several disciplines that include chemical engineering, as well as the pharmaceutical and the petrochemical industries. Vapor pressures of large hydrocarbons are fundamental data required in the petroleum industry to develop thermodynamic models for dealing with crude oil. Environmental chemists and engineers use vapor pressures and vaporization enthalpies to model the dispersal of spills in the environment, such as the BP Gulf of Mexico oil spill, and to design chemical reactors.

Alkanes are important components of petroleum. In the present work we have evaluated the vaporization enthalpies and vapor pressures of large n-alkanes with carbon chains up to 92 carbons by C-GC. These are the largest hydrocarbons ever evaluated with vaporization enthalpies that exceed the carbon-carbon bond strength and are good models for crude oil.

Polyaromatic hydrocarbons (PAHs) are an important group of environmental contaminants that are produced by a variety of incomplete combustion processes. Polyaromatic nitrogen heterocycles (PANH's) are their heterocyclic relatives that are also found environmentally in heavy petroleum. This study has also focused on the evaluation

of the vaporization enthalpies and vapor pressures of PANH’s, most of which have not been previously reported.

Finally, a study of aromatic diazines and diazoles (six- and five-membered heterocycles containing two nitrogen atoms, respectively), and related compounds has uncovered an interesting intermolecular interaction previously suspected but never measured. Our work has been able to assign a numerical value to this interaction. Since many biological molecules have similar structures, these interactions may be responsible for molecular association and signaling that occurs in such systems. The combination of planarity, polarity and extensive conjugation are common to all systems that appear to exhibit a higher degree of self-association.

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Introduction

Vaporization enthalpies and vapor pressures are fundamental thermodynamic properties of the condensed phase that are of great importance to several disciplines that include chemical engineering, as well asthe pharmaceutical and petrochemical industries. Vaporization enthalpies are necessaryfor adjusting enthalpies of formation of liquids to the standard state and in evaluating environmental transport properties. To the chemical engineer, these properties need to be taken into consideration in designing equipment for chemical processing and synthesis, in particular, for continuous gas flow reactions.[1] Environmental chemists and engineers use vapor pressure and vaporization enthalpies to model the dispersal of spills in the environment. The magnitude of these properties when viewed in perspective, provide valuable insight into the nature of both intra- and intermolecular interactions and thus are of interest to both experimentalists and theoreticians. While generally weaker than chemical bonds, the interactions responsible for these enthalpies are similar to those responsible for the self-assembly that occurs in everything from liquid crystals to biological systems.[2]

Measurement of phase change enthalpies and vapor pressures often go hand in hand, i.e. evaluation of vaporization and sublimation enthalpies are frequently based on vapor pressure measurements. Heats of vaporization have been measured for over a hundred years by a large variety of experimental methods. One way to classify these techniques is by construction of the experimental set-up used for a specific method[3]. Some of the widely used methods for investigation of vapor pressures and vaporization enthalpies are:

1. Static methods. In these methods, the sample is placed in a closed vessel, and then the vessel is evacuated and the temperature is held constant within a time interval to reach the equilibrium between the condensed and vapor phases. Pressure at equilibrium is determined with the aid of any measuring instrument, such as pressure gauges, high-precision manometers, etc.
2. Ebulliometry (Boiling point method). The method relies on the use of an ebulliometer, an apparatus in principle similar to an ordinary open boiler operating at atmospheric pressure. Saturated vapor pressure is measured at the temperature of boiling.
3. Knudsen effusion (mass effusion) methods. These methods are based on measurements of rate of vaporization through a small orifice from the cell saturated with vapor at constant temperature. The rate of mass effusion of the gas from the cell is then related to the value of vapor pressure using an equation derived initially by Knudsen.
4. Langmuir effusion methods. The process of vaporization occurs from free surface, and the relation between the rate of mass loss and the value of vapor pressure (Langmuir equation) is applied in this method.
5. Transpiration method (gas saturation method). The main part of the measurement system in this technique is the saturator, where the investigated substance is held under controlled temperature. Through the saturator either inert or reactive gas is passed ata sufficiently low rate to allow the equilibrium pressure of the substance to be maintained. Then the carrier gas is cooled, the vaporized substance is

collected, and its mass is determined. Applying Dalton's law and the ideal gas law, the relation between the mass collected and vapor pressure is used.

6. Chromatographic methods. The experimental set-up is the same as for classic gas chromatographic analysis. The correlation-gas chromatographic technique will be discussed in details further in text.
7. Thermogravimetric analysis (TGA). The technique measures the rate of mass loss and the enthalpy of vaporization can be derived directly from the activation energy which is measured from rate data obtained at different temperatures.
8. Calorimetric methods. This group of methods allows to measure the enthalpy of vaporization directly. The calorimeters used include: adiabatic calorimeters, drop calorimeters, and differential scanning calorimeters (DSC).

In this thesis, a technique called correlation-gas chromatography (c-gc), promoted by our group, has been used to measure the vaporization enthalpies and vapour pressures of large alkanes, and a variety of nitrogen heterocycles. Despite the large number of methods employed to measure vapour pressure and vaporization enthalpy, correlation-gas chromatography is a technique that is capable of evaluating these properties in cases where no other method is currently applicable. In this study it has also been used to single out those heterocycles that exhibit an unusual, enhanced intermolecular interaction not present in corresponding isomers and to measure the magnitude of this interaction. In addition, c-gc has been utilized to measure useful hypothetical thermodynamic properties such as vaporization enthalpies of crystalline materials at T = 298.15 K.

The use of gas chromatography to measure thermodynamic properties of solutions has been frequently reported, and a number of investigators have measured vaporization enthalpies of pure materials indirectly by this technique. Charcoal and other solid absorbents in columns had long been used in industry for cleaning gas streams and for solvent recovery before Martin and Synge (1941) suggested the use of gas-liquid partition chromatograms for analytical purposes.[4] Martin and James (1952) first described the application of the gas-liquid partition chromatography to the separation of volatile substances.[5] Littlewood et al. (1955) improved on the aforementioned gas chromatographic technique and recorded a large number of thermochemical data presented as plots of corrected retention volumes against the inverse of the column temperature.[6] Peacock and Fuchs (1977) reported a simple method for the measurement of heats of vaporization by using gas chromatography to measure enthalpies of transfer from solution to vapor and combining these results with solution calorimetry to correct for the heat of solution of the solute in the stationary phase of the column.[7] This combined calorimetric–gas chromatographic technique was modified by Chickos et al (1995) by eliminating the need for the calorimetric measurements and generally simplifying the experimental aspects of the experiment.[8]

Correlation gas chromatography (c-gc) is a fast and reliable method of evaluating vaporization enthalpies and vapor pressuresprovided appropriate standards are used with reliable vaporization enthalpies and liquid vapor pressures. It has proven to be successful in providing vaporization enthalpies of both liquids and solids.[9] C-gc involves the following experimental procedure. A small amount of sample is added to ~ 1ml of a volatile solvent such as carbon tetrachloride, methylene chloride or methanol. Several standards generally of similar functionality to that of the target and whose vaporization enthalpies bracket the compound of interest are chosen. If the solvent is retained at the temperature to be studied, a small amount of an unretained compound is added; e.g. methane, butane, etc., is bubbled into the solution. The standards are injected simultaneously with the target substances along with an unretained analyte in the gas chromatograph as a single mixture. Several unknowns can be determined in the same mixture providing that the compounds can be separated by chromatography. The method is thus a very fast means of making determinations when several compounds of the same family and similar volatility are to be measured.

Correlation-gas chromatographic technique relies on the linear correlation observed between enthalpies of transfer from solution to the vapor, $\Delta_{\mathrm{sln}}{}^{\mathrm{g}}H_{\mathrm{m}}$, as measured by gas chromatography and the vaporization enthalpy ($\Delta_{\mathrm{l}}{}^{\mathrm{g}}H_{\mathrm{m}}$) of a series of standards. The linear correlation that is observed between $\Delta_{\mathrm{sln}}{}^{\mathrm{g}}H_{\mathrm{m}}$ and $\Delta_{\mathrm{l}}{}^{\mathrm{g}}H_{\mathrm{m}}$ is empirical and needs independent confirmation. An advantage of using correlation gas chromatography to evaluate thermochemical data is that the choice of reference temperature is arbitrary. As long as proper standards are chosen for the correlation analysis, and their vaporization enthalpies and vapor pressures are known at the temperatures of interest, then reliable vaporization enthalpies vapor pressures of the target molecules can be determined.

Enthalpies of transfer from the condensed to the gas phase are determined by correlation gas chromatography by measuring the retention times of a mixture of standards and solutes as a function of temperature. The retention times are adjusted for the dead volume of the column by measuring the retention time of an unretained solute, usually the solvent. The adjusted retention time (t_a) measures the amount of time the solute spends on the stationary phase and is equal tothe retention time of the solute (t) minus the retention time of the unretained reference (t_{nr}).

$$t_a = t - t_{nr} \text{(I-1)}$$

This adjusted retention time, t_a, is inversely proportional to the compound's vapor pressure above the condensed phase. A plot of $\ln(t_o/t_a)$ versus $1/T$ (K^1) results in a linear plot with a slope equal to $-\Delta^g_{sln}H_m(T_m)/R7$, where t_o refers to the reference time, 1 min. The term $\Delta^g_{sln}H_m(T_m)$ can be equated in a thermodynamic cycle to the sum of the vaporization enthalpy measured at $T = T_m$ and the enthalpy of solution ($\Delta_{sln}H_m$) of each solute on the stationary phase of the column. Since the solute presumably dissolves or is adsorbed on the stationary phase, the same thermodynamic cycle applies to both solids and liquids.[10]

$$\Delta^g_{sln}H_m(T_m) = \Delta^g_l H_m(T_m) + \Delta_{sln}H_m(T_m) \qquad \text{(I-2)}$$

In correlation gas chromatography, $\Delta^g_{sln}H_m(T_m)$ values are correlated with the vaporization enthalpies of the standards at the temperature of interest. A linear correlation is observed between $\Delta^g_{sln}H_m(T_m)$ and $\Delta^g_l H_m(T_m)$ and the correlation equation derived from the known vaporization enthalpies is used to evaluate the vaporization enthalpies of the solutes of interest.[8]

In addition, $\ln(t_o/t_a)$ of each analyte has also been found to correlate linearly with the vapor pressure of the pure liquid phase of each analyte at a given temperature.Thus the same series of experiments can be used to evaluate vapor pressures if the mixture contains components with known vapor pressures.[11]

Correlation-gas chromatography has a number of advantages compare to other methods:

1. Purification generally is not needed. Since all compounds are analyzed as mixtures 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.
2. Small quantities of samples are needed (mg amounts).
3. Experiments are relatively quick (several hours).
4. Hypothetical thermodynamic properties can be measured. Since each analyte is dilutely adsorbed on the condensed phase and is not crystalline, the vapor pressure that it exhibits behaves as an excellent model for the subcooled liquid phase vapor pressure. Therefore, for crystalline solids, c-gc can be used to measure subcooled vaporization enthalpies. Combined with fusion enthalpies they provide reasonable values for sublimation enthalpies which often cannot be measured directly due to decomposition of compound.

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Part 1. Investigation of unusual interactions in heterocyclic systems

Heterocyclic molecules account for over half of all known organic compounds. A large portion of these heterocyclic compounds contain nitrogen. Many classes of important natural products, majority of synthetic drugs, dyes, etc. are based on nitrogen heterocycles.[1]

Trivial names are commonly used for N-heterocycles. A given semiotic syllable (usually a suffix) may indicate more than one structural feature in a heterocyclic system. The ending –ole, for example, indicates both a five-membered ring and maximum non-cumulative unsaturation, as in the case of ‘pyrrole’. The typical way of classifying heterocycles is by using their aromatic forms, when possible, for instance, azines and azoles.[2] Trivial names for some of the monocyclic heterocycles are listed in Figure 1-1.

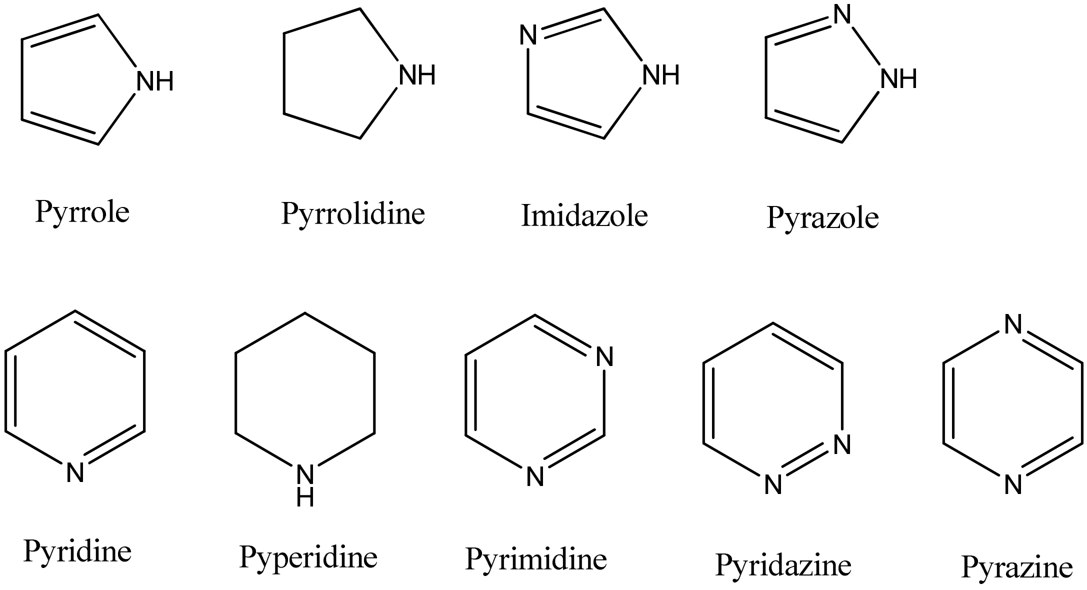

Figure 1-1. Trivial/Traditional names for monocyclic heterocycles sanctioned by IUPAC

Nitrogen heterocycles play an important role in environmental, biochemical and petrochemical processes. The availability of reliable thermochemical properties data for a large number of nitrogen heterocycles is of great importance for many fields.

Heterocyclic nitrogen-containingfunctional groups are prominent in organic fuels such as coal and biomass; these fuels can contain significant amounts of nitrogen, and in most coals this nitrogen is predominantly present in the pyrrolic form.[3] N-heterocyclic compounds are also formed from gasification of biomass, coal and their blends.[4]

Ionic liquids (ILs) are low melting organic-based salts that have been developed as a class of alternative solvents for a variety of applications. Many ILs have been synthesized using nitrogen-containing heterocycles, including imidazole, 1,2,4-triazole, and tetrazole, and, as such, are a natural framework for energetic materials, as they have inherently high nitrogen contents.[5] Knowledge of physical properties of such heterocycles is important in investigating thermochemical characteristics of these energetic salts.

Polyaromatic nitrogen heterocycles (PANHs) are an important group of environmental contaminants resulting from the incomplete combustion of organic material containing nitrogen. PANH have been found in automobile exhaust, the urban atmosphere, cigarette smoke condensate, and coal-tar isolates, shale oil, and in synthetic coal fuels.[6] PANHs exist mainly absorbed to aerosol particulates. Vapor pressure data can help describe behavior of polyaromatic nitrogen heterocycles in the atmosphere. The high-temperature reactions of five- and six-memberednitrogen-containing heterocycles are also of interest in atmospheric and combustion chemistry, due to the role of these compounds in the production of the pollutants NO and NO_2 during combustion processes.[7]

There is significant interest in the high-energy-density five-membered nitrogen-containing heterocycles, due to their possible applications as propellants and explosives. There is particularinterest in the triazoles (cyclo-$C_2N_3H_3$) and tetrazoles (cyclo-CN_4H_2), however, the one and two nitrogen atom heterocycles pyrrole (cyclo-C_4NH_4) and pyrazole and imidazole (cyclo-$C_3N_2H_3$) are also important, as they aid in the understanding of their morenitrogen-rich analogues.[8]

A significant amount of quality data have been reported on the thermodynamic properties of pyridine and its derivatives as a consequence of the increased demand for fuel, the subsequent use of heavier feedstocks, and the need to hydrodenitrogenate these feedstocks to meet current environmental requirements.[9]Thermochemical properties of the higher nitrogen content six- and five-membered heterocycles, however, are less well-studied which prompted us to investigate vaporization enthalpies and vapor pressures of azines and azoles, heterocyclic compounds with more than one nitrogen.

This study also focuses on the evaluation of the vaporization enthalpies and vapor pressures of series of more complex nitrogen heterocycles, most of which have not been previously reported. Some of the studied aromatic heterocycles are crystalline solids at T = 298.15 K. Vaporization enthalpies of crystalline materials are quite useful hypothetical properties. Combined with fusion enthalpies, they can provide sublimation enthalpies forcompounds that may be too non-volatileto be measured by conventional methods provided they survive the journey through a gas chromatograph.[10]

Correlation-gas chromatographic technique works very well when reference compounds with known literature vaporization enthalpies and compounds with the values of vaporization enthalpy in question have same functional groups. It can also be applied for substances with different functionalities, however, it is necessary to prove the validity of obtained thermodynamic values by comparing them against available literature data. This study demonstrates cases when pyridine derivatives act as suitable vaporization enthalpy and vapor pressure standards for systems containing more than one nitrogen atomon the aromatic ring, as well as instances when they do not. The later examples were used to identify compounds with enhanced intermolecular interactions based on vaporization enthalpy discrepancies. As a result, we have established 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 other heterocycles with more than one nitrogen.

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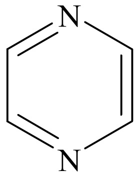
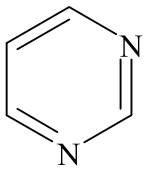
Chapter 1. Vaporization Enthalpies and Vapor Pressures of Pyrazine, Pyrimidine, Pyridazine and 1,3,5-Triazine

1.1. Introduction

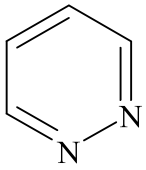
Pyrazine, pyrimidine, pyridazine and 1,3,5-triazine are the parent compounds of a diverse series of heterocycles, members of which are important components of many natural products and biological systems. Yet despite their structural and electronic similarity to benzene and pyridine, relatively few thermodynamic studies of these parent materials and their derivatives have been reported.[1]



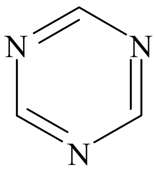
pyrazine



pyrimidine



pyridazine



1,3,5-triazine

In an effort to demonstrate the applicability of correlation–gas chromatography to obtain reliable vaporization enthalpies and vapor pressures of diazine and triazine derivatives, we decided to focus on the vaporization enthalpies and vapor pressures of the parent heterocyclic compounds. Previous work on the phenylpyridine isomers demonstrated that if necessary, the vaporization enthalpies of hydrocarbons could be used as standards to determine the vaporization enthalpies of tertiary amines using gas chromatography.[2]The lack of sufficient vapor pressure data on diazines and triazines, prompted a study of the vaporization enthalpies of the parent heterocycles. Unlike diazines and triazines, a substantial amount of quality data is available for pyridine and its derivatives, many of which are found environmentally in heavy petroleum.[3]

For organic compounds containing functional groups, it has been necessary to demonstrate independently that the vaporization enthalpy of the standards correlate with the enthalpies of transfer. Hence the need for standards with similar functionality. Thermochemical data for pyridine, 2,6-dimethylpyridine, 3-methylpyridine, 2,4,6-trimethylpyridine, pyrazine, 2-methylpyrazine, 2,5-dimethylpyrazine are available and these materials were used as standards.1,3,5-Triazine, pyrimidine, 4-methylpyrimidine, pyridazine and 3-methylpyridazine were treated as unknowns. This study is intended to validate the use of pyridine and its derivatives so they can be used as standards for future correlations of diazines, triazines and other materials containing multiple tertiary nitrogen atoms.

1.2. Experiment

All chemicals were obtained from various commercial sources and used as is. All were analyzed by gas chromatography and most found to have purities of >99%. Pentane and cyclopentane were used as solvents. Correlation gas chromatography experiments were performed on an HP 5890 Gas Chromatographs equipped with split/splitless capillary injection ports and flame ionization detectors at a split ratio of approximately 50/1. The compounds were run isothermally on a 30 m SPB 5 column. Temperature was controlled to ± 0.1 K. Helium was used as the carrier gas.Methane was used as a non-retained reference. The retention time of the non-reference was used to determine the dead volume of the column. At the higher temperatures, the retention time of the cyclopentane and pentane, 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 on the column.

Adjusted retention times, t_a, were calculated by subtracting the measured retention time of the non-retained reference from the retention time of each analyte as a function of temperature, over a 30 K range at 5 K intervals. 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 $\ln(t_o/t_a)$, vs $1/T$ and the gas constant, R. All plots of $\ln(t_o/t_a)$, vs $1/T$, where $t_o = 1$ min, were characterized with correlation coefficients, r^2, >0.99. Unless noted otherwise, $p_o = 101.325$ kPa.The uncertainties ($\pm\sigma$) reported for vaporization enthalpies 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.

1.3. Vaporization enthalpies and Vapor Pressures of the Standards

The vaporization enthalpies of the compounds used as reference materials and for comparison are provided in Table 1-1. The vaporization enthalpies for pyrazine, 2-methyl and 2,4-dimethylpyrazine and 2,4,6-trimethylpyridine were calculated from the available vapor pressure data[4]. The vaporization enthalpy used for pyrazine was an average of the value obtained from two references.[4,5] The value for 2,4,6-trimethylpyridine[6] was calculated from the Antoine constants reported for the global fit using eq. (1-1). Heat capacities at T = 298.15 K were estimated by a group additivity procedure[7] and vaporization enthalpies were adjusted to T = 298.15 K using eq. (1-2).[8]

$$\Delta_{vap}H_{\mathrm{m}}(T_{\mathrm{m}}) = \mathrm{RB}[T_{\mathrm{m}} /(T_{\mathrm{m}} -\mathrm{C})]2 \qquad \text{where } T_{\mathrm{m}} =371\ \mathrm{K} \tag{1-1}$$

$$\Delta_{vap}H_{\mathrm{m}}(298.15\ \mathrm{K})= \Delta_{vap}H_{\mathrm{m}}(T_{\mathrm{m}}/\mathrm{K}) + [[10.58 + 0.26C_p(\mathrm{l})]/\mathrm{J\ mol^{-1}\ K^{-1}}][(T_{\mathrm{m}}/\mathrm{K}-298.15]/1000 \tag{1-2}$$

Vaporization enthalpy values for 1,3,5-triazine and pyrazine were calculated using a thermochemical cycle, eq. (1-3) and the data provided in Table 1-2. Sublimation and fusion enthalpies were adjusted to T = 298.15 K using eq. (1-4) and (1-5), respectively. These values are included for reference only.

$$\Delta_{vap}H_{\mathrm{m}}(298.15\ \mathrm{K}) = + \Delta_{sub}H_{\mathrm{m}}(298.15\ \mathrm{K}) - \Delta_{fus}H_{\mathrm{m}}(298.15\ \mathrm{K}) \tag{1-3}$$

$$\Delta_{\mathrm{sub}}H_{\mathrm{m}}(298.15\ \mathrm{K})= \Delta_{\mathrm{sub}}H_{\mathrm{m}}(T_{\mathrm{m}}/\mathrm{K}) + [[0.75 + 0.15C_p(\mathrm{cr})]/\mathrm{J\ mol^{-1}\ K^{-1}}][(T/\mathrm{K}-298.15]/1000 \tag{1-4}$$

$$\Delta_{fus}H_{\mathrm{m}}(298.15\ \mathrm{K})=\Delta_{fus}H_{\mathrm{m}}(T_{fus}) + [[0.15\ C_p(\mathrm{cr})-0.26\ C_p(\mathrm{l})/\mathrm{J}-9.83)]/\mathrm{J\ mol^{-1}\ K^{-1}}][(T_{\mathrm{fus}}/\mathrm{K}-298.15]/1000 \tag{1-5}$$

Table 1-1. The vaporization enthalpies (kJ mol^{-}1) used as standards or for reference

	$\Delta_{\mathrm{vap}}H(T_{\mathrm{m}})$ kJ mol^{-1}	T_{m}/K	C_{pl}(298.15 K) J mol K-1	$\Delta_{\mathrm{vap}}H$ (298.15 K)	Ref
pyridine				40.21±0.1	9
pyrazine [a]				41.03±0.13	5
pyrazine [a]	37.77	352	128.6	40.16±0.24	4
pyrazine				41.5±0.85 [b]	4, 14
pyrimidine				50.00±0.25	14
pyridazine				53.47±0.42	14
1,3,5-triazine				41.8±0.5[b]	15, 16
2-methylpyrazine	42.0	340	157	44.1±2.0	4
2,5-dimethylpyrazine	43.59	357	185.4	47.04±1.9	4
3-picoline				44.47±0.16	10
2,6-lutadine				45.31±0.16	11
2,4,6-trimethylpyridine	47.17	356	214.9	51.0±1.0	4
2,4,6-trimethylpyridine	46.24	371	214.9	51.06	6

[a] The mean value, 40.58 kJ mol^{-1}, from references 4 and 5 was used in the correlations;
[b] Average value from Table 1-2 using eq. (1-3).

Vapor pressure values used for pyrazine[5], pyridine[9], 3-picoline[10], and 2,6-lutidine[11] have been calculated from the parameters reported for the Wagner equation (eq. (1-6)). Vapor pressures for 2-methylpyrazine[4], 2,5-dimethylpyrazine[4] and 2,4,6-trimethyl-pyridine[4] were obtained from the original article and fit to a third order polynomial, eq. (1-7), known to provide reasonably vapor pressure values upon extrapolation.[12,13]

The constants needed to calculate ln(p/p_{o}) for the Wagnerequation: p_{c} , T_{r} , A_{W}, B_{W},C_{W}, D_{W} Φ; Θ, and the third order polynomial: A, B. C. D are provided in Tables 1-3 and 1-4.

$$\ln(p/p_{\mathrm{c}}) = (1/T_{\mathrm{r}})[A_{\mathrm{W}}(1\text{-}T_{\mathrm{r}}) + B_{\mathrm{W}}(1\text{-}T_{\mathrm{r}})^{1.5} + C_{\mathrm{W}}((1\text{-}T_{\mathrm{r}})^{\Phi} + D_{\mathrm{W}}(1\text{-}T_{\mathrm{r}})^{\Theta}] \quad (1\text{-}6)$$

$$\ln(p/p_{\mathrm{o}}) = A\,(T/\mathrm{K})^{-3} + B(T/\mathrm{K})^{-2} + C(T/\mathrm{K})^{-1} + D \quad (1\text{-}7)$$

Table 1-2. Vaporization enthalpies calculated from sublimation enthalpies

	$\Delta_{sub}H(T_m)$ kJ.mol^{-1}	T_m/K	$\Delta_{sub}H$ (298 K) kJ.mol^{-1}	$\Delta_{fus}H$ (T_{fus}) kJ.mol^{-1}	T_{fus}/K	Cp(298.15 K) (cr) J mol-1 K^{-1}	(l)	$\Delta_{fus}H_m$ (298 K) kJ.mol^{-1}	Ref
pyrazine	56.3±0.5	298	56.3±0.5	15.6±0.32[a]	326	97.8	128.6	14.82±0.41	5, 14
pyrazine	56.2±1.0	303	56.3±1.0	15.6±0.32[a]	326	97.8	128.6	14.82±0.41	4, 5
1,3,5-triazine	54.8	313	55.0±0.12	14.56±0.01	353	94.2	127.5	12.97±0.53	15, 16

[a] Includes a phase transition of 0.9 kJ mol-1 at T = 300.5

Table 1-3. Parameters of the Wagner equation (eq. (1-6))

	A_W	B_W	C_W	D_W	T_c/K[a]	p_c/kPa	Φ	Θ	Ref
pyrazine	-7.97194	3.11079	-3.23885	-2.76341	627	6700	2.5	5.0	5
pyridine	-6.82447	0.47569	0.02974	-4.19797	620	5650	2.0	4.0	9
3-picoline	-8.216177	4.684186	-4.363634	-3.415866	644.5	4680	2	4.8	10
2,6-lutidine	-8.09336	2.51161	-3.40513	-3.23131	624	3850	2.5	5.0	11

[a]$T_r = T/T_c$

Table 1-4. Parameters of the third order polynomial, (eq. (1-7)) used as standards [a]

	$\frac{A}{T^3}$	$\frac{B}{T^2}$	$\frac{C}{T}$	D	Reference
2-methylpyrazine	-1729170077	15000207	-48064.622	53.233	4
2,5-dimethypyrazine	-1686812742	14141074	-44477.036	48.362	4
2,4,6-trimethylpyridine	-78931184.8	128347	-4404.98	10.181	4

[a] Constants derived from vapor pressure measurement reported in reference 4.

1.4. Results and Discussion

The retention times measured for the six mixtures (run 1-6) studied are reported in the Appendix A-1. The correlations between enthalpies of transfer measured for each mixture and available vaporization enthalpy values are reported in Table 1-5. The equation characterizing the correlation is given below each run. Uncertainties were calculated from the uncertainty associated with the slope and intercept of each equation. The results of the six runs are summarized in Table 1-6. The uncertainties listed in this table are averages of the uncertainties reported for each compound in Table 1-5.

A comparison of the values obtained for each of the compounds whose vaporization enthalpy was treated as an unknown shows that they are reproducible. This include 1,3,5-triazine, pyrimidine, 4-methylpyrimidine, pyridazine, and 3-methyl-pyridazine. The correlation coefficients, r^2, of Table 1-5 also suggest that the enthalpies of transfer and vaporization enthalpies of pyrazines and pyridines used as standards correlate linearly with each other. Comparison of the value in Table 1-1 calculated for 1,3,5-triazine from the sublimation and fusion enthalpies to the value in Table 1-6, suggests that pyridines and pyrazines can also be used as reasonable standards for 1,3,5-triazines. What is not clear is whether this correlation also applies to pyrimidines and pyridazines. Comparison of the average calculated vaporization enthalpy values of Table 1-6 to the literature values reported in the last column of this table for pyrimidine and pyridazine suggest that the correlation may not be applicable. Since to our knowledge there are no other vaporization enthalpies reported for pyrimidines and pyridazines in the literature for comparison, it was decided to attempt to predict the vapor pressures of these compounds in an effort to verify the applicability of the slopes and intercepts reported in Table 1-5 for measuring vaporization enthalpies.

Table 1-5: Vaporization enthalpies calculated by correlation of $\Delta_{sln}{}^{g}H_{\mathrm{m}}$(357 K) with $\Delta_{vap}H_{\mathrm{m}}$(298.15 K) for runs 1-6

Run 1	slope	intercept	$\Delta_{sln}{}^{g}H_{\mathrm{m}}$(357 K)	$\Delta_{vap}H_{\mathrm{m}}$(298.15 K)/ kJ·mol^{-1}	
	K		kJ·mol^{-1}	lit^{a}	calc
pyrazine	-3457	9.692	28.74	40.58	40.4±1.2
pyridine	-3452.7	9.599	28.70	40.16	40.4±1.2
2-methylpyrazine	-3896	10.291	32.39	44.08	43.8±1.3
3-picoline	-4003.4	10.866	33.28	44.47	44.6±1.3
2,5-dimethylpyrazine	-4336.3	10.266	36.05	47.04	47.1±1.5
pyridazine	-4230.2	10.539	35.17		46.3±1.4

$\Delta_{\mathrm{l}}{}^{\mathrm{g}}H_{\mathrm{m}}$ (298.15 K)/kJ·mol^{-1} = (0.914±0.040) $\Delta_{sln}{}^{g}H_{\mathrm{m}}$(357 K) - (14.17±0.25), (r^2 = 0.9942)

Run 2	slope	intercept	$\Delta_{sln}{}^{g}H_{\mathrm{m}}$(357 K)	$\Delta_{\mathrm{l}}{}^{\mathrm{g}}H_{\mathrm{m}}$(298.15 K)/ kJ·mol^{-1}	
	K		kJ·mol^{-1}	lit^{a}	calc
pyrazine	-3477.9	9.754	28.91	40.58	40.6±1.2
pyrimidine	-3548.9	10.316	29.5		41.2±1.2
2-methylpyrazine	-3914.2	10.337	32.54	44.08	43.8±1.3
3-picoline	-4020.2	10.91	33.42	44.47	44.6±1.3
2,5-dimethylpyrazine	-4353.2	9.831	36.19	47.04	47.1±1.4

$\Delta_{\mathrm{l}}{}^{\mathrm{g}}H_{\mathrm{m}}$ (298.15 K)/kJ·mol^{-1} = (0.883±0.039) $\Delta_{sln}{}^{g}H_{\mathrm{m}}$(357 K) - (15.1±0.20), ($r^2$ = 0.9960)

Run 3	slope	intercept	$\Delta_{sln}{}^{g}H_{\mathrm{m}}$(353 K)	$\Delta_{\mathrm{l}}{}^{\mathrm{g}}H_{\mathrm{m}}$(298.15 K)/ kJ·mol^{-1}	
	K		kJ·mol^{-1}	lit^{a}	calc
1,3,5-triazine	-3271.3	9.613	27.2		39.1±2.0
pyrazine	-3496.5	9.776	29.07	40.58	40.7±2.1
pyrimidine	-3566.4	9.852	29.65		41.2±2.2
2-methylpyrazine	-3935.8	10.349	32.72	44.08	43.7±2.4
3-picoline	-4053.3	10.402	33.7	44.47	44.5±2.5
2,6-lutidine	-4242.7	10.806	35.27	45.31	45.8±2.6
2,5-dimethylpyrazine	-4378.3	10.953	36.4	47.04	46.8±2.7
pyridazine	-4280.2	10.65	35.58		46.1±2.6

$\Delta_{\mathrm{l}}{}^{\mathrm{g}}H_{\mathrm{m}}$ (298.15 K)/kJ·mol^{-1} = (0.883±0.039) $\Delta_{sln}{}^{g}H_{\mathrm{m}}$(353 K) - (15.1±0.20), ($r^2$ = 0.9960)

Run 4	$\frac{\text{slope}}{\text{K}}$	intercept	$\frac{\Delta_{sln}{}^{g}H_{\text{m}}(358\text{ K})}{\text{kJ·mol}^{-1}}$	$\Delta_{\text{l}}{}^{\text{g}}H_{\text{m}}$(298.15 K)/ kJ·mol^{-1}	
				lit^{a}	calc
1,3,5-triazine	-3235.2	9.48	26.9		39.1±1.6
pyrazine	-3463.1	9.651	28.79	40.58	40.6±1.7
pyridine	-3460.8	9.564	28.77	40.16	40.6±1.7
2-methylpyrazine	-3895.5	10.207	32.39	44.08	43.5±1.9
3-picoline	-4002.1	10.23	33.27	44.47	44.2±1.9
2,6-lutadiene	-4201.3	10.66	34.93	45.31	45.5±2.0
2,5-dimethylpyrazine	-4464	11.17	37.11	47.04	47.3±2.1
pyridazine	-4371.3	10.877	36.34		46.7±2.1

$\Delta_{\text{l}}{}^{\text{g}}H_{\text{m}}$ (298.15 K)/kJ·mol^{-1} = (0.806±0.056) $\Delta_{sln}{}^{g}H_{\text{m}}$(358 K) - (17.38±0.42), (r^2 = 0.9807)

Run 5	$\frac{\text{slope}}{\text{K}}$	intercept	$\frac{\Delta_{sln}{}^{g}H_{\text{m}}(358\text{ K})}{\text{kJ·mol}^{-1}}$	$\Delta_{\text{l}}{}^{\text{g}}H_{\text{m}}$(298.15 K)/ kJ·mol^{-1}	
				lit^{a}	calc
s-triazine	-3220.5	9.476	26.77		38.5±2.0
pyrazine	-3453.4	9.65	28.71	40.58	40.3±2.0
pyrimidine	-3520.0	9.711	29.26		40.8±2.1
2-methylpyrazine	-3896	10.231	32.39	44.1	43.7±2.3
4-methylpyrimidine	-3949.6	10.293	32.84		44.1±2.3
3-picoline	-4008.7	10.268	33.33	44.47	44.6±2.4
2,6-lutidine	-4210.9	10.708	35.01	45.31	46.2±2.5
2,5-dimethylpyrazine	-4354.2	10.878	36.2	47.04	47.3±2.6
pyridazine	-4264.7	10.598	35.46		46.6±2.5
2,4,6-trimethylpyridine	-4758.8	11.467	39.56	51	50.4±2.8
3-methylpyridazine	-4665.1	11.156	38.78		49.7±2.8

$\Delta_{\text{l}}{}^{\text{g}}H_{\text{m}}$ (298.15 K)/kJ·mol^{-1} = (0.930±0.071) $\Delta_{sln}{}^{g}H_{\text{m}}$(358 K) - (13.61±0.59), (r^2 = 0.9771)

Run 6	slope	intercept	$\Delta_{sln}{}^{g}H_{m}$(358 K)	$\Delta_{l}{}^{g}H_{m}$(298.15 K)/ kJ·mol^{-1}	
	K		kJ·mol^{-1}	lit^{a}	calc
s-triazine	-3262.3	9.589	27.12		38.6±2.1
pyrazine	-3480.5	9.727	28.94	40.58	40.3±2.1
pyrimidine	-3545	9.785	29.47		40.8±2.2
2-methylpyrazine	-3924.5	10.307	32.63	44.08	43.8±2.4
4-methylpyrimidine	-3980.5	10.376	33.09		44.2±2.4
3-picoline	-4028.9	10.322	33.5	44.47	44.6±2.4
2,6-lutidine	-4232.5	10.765	35.19	45.31	46.2±2.6
2,5-dimethylpyrazine	-4376.4	10.935	36.38	47.04	47.3±2.7
pyridazine	-4294.1	10.675	35.7		46.7±2.6
2,4,6-trimethylpyridine	-4770.2	11.496	39.66	51	50.4±2.9
3-methylpyridazine	-4688.1	11.216	38.98		49.7±2.8

$\Delta_{l}{}^{g}H_{m}$ (298.15 K)/kJ·mol^{-1} = (0.941±0.07) $\Delta_{sln}{}^{g}H_{m}$(358 K) - (13.1±0.59), ($r^2 = 0.9765$)

[a] See Table 1-1

Table 1-6. A summary of the vaporization enthalpies of runs 1-6 and comparison with literature values

	$\Delta_{l}{}^{g}H_{m}$(298.15 K)/ kJ·mol^{-1}							
	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Average	Lit
1,3,5-triazine			39.1	39.1	38.5	38.6	38.8±1.9	41.8±0.5
pyridine	40.4			40.6			40.5±1.5	40.2±0.1
pyrazine	40.4	40.6	40.7	40.6	40.3	40.3	40.5±1.7	41.5±0.2
pyrimidine		41.2	41.2		40.8	40.8	41.0±1.9	50.0±0.3
2-methylpyrazine	43.8	43.8	43.7	43.5	43.7	43.8	43.7±1.9	44.1±2.0
4-methylpyrimidine					44.1	44.2	44.2±2.4	
3-picoline	44.6	44.6	44.5	44.2	44.6	44.6	44.5±2.0	44.5±0.2
2,6-lutidine			45.8	45.5	46.2	46.2	45.9±2.4	45.3±0.1
2,5-dimethylpyrazine	47.1	47.2	46.8	47.3	47.3	47.3	47.2±2.2	47.0±0.2
pyridazine	46.3		46.1	46.7	46.6	46.7	46.5±2.2	53.5±0.4
2,4,6-trimethylpyridine					50.4	50.4	50.4±2.9	51.0±1.0
3-methylpyridazine					49.7	49.7	49.7±2.8	

As it was shown in the Introduction to this thesis, the equations governing the temperature dependence of retention time along with some experimental vapor pressures can be used to predict the vapor pressures of compounds whose values are unknown in cases where enthalpies of transfer and vaporization enthalpies correlate. In this instance, the vapor pressures of pyridine and pyridazine are not known; however their boiling temperatures are known and a comparison of predicted boiling temperatures with experimental values would be a good indicator of whether the results of these equations can be trusted.

Table 1-7 illustrates the correlation between $\ln(t_o/t_a)$ and $\ln(p/p_o)$ at $T = 298.15$ K. Values of $\ln(t_o/t_a)$ were calculated using the slope and intercept of each compound appearing in Table 1-5 in runs 1-6. Values of (t_o/t_a) were averaged and the natural logarithm of (t_o/t_a), $\ln(t_o/t_a)_{av}$ (column 2, Table 1-7) was correlated with $\ln(p/p_o)$ calculated from eqs. (1-6) and (1-7) and the constants reported in Tables 1-3 and 1-4. The resulting correlation equation, eq. (1-8), was used to calculate $\ln(p/p_o)$ for each material. By repeating this process over a range of temperatures from $T = 298.15$ to $T = 400$ K at 10 K intervals, it was possible to obtain a profile of how the vapor pressure of each standard and unknown varies with temperature. The correlation coefficient is typical of the values obtained over this temperature range. The resulting $\ln(p/p_o)$ values for each entry was then plotted against $1/T$ and fit to eq. (1-7). The A, B, C and D constants resulting from this fit are given in Table 2-8. In eq. (1-7), p_o refers to 1 atmosphere, 101 kPa. By extrapolating the vapor pressures calculated by eq. (1-7), it was possible to predict the temperature at which the vapor pressure equals 1 atmosphere, the normal BTs.

Table 1-7. Results Obtained By Correlating $\ln(t_o/t_a)$ with $\ln(p/p_o)$ at $T = 298.15$ K

	$\ln(t_o/t_a)_{av}$	$\ln(p/p_o)$	$\ln(p/p_o)$
1,3,5-triazine	-1.352		-3.03
pyridine	-2.012	-3.593	-3.67
pyrazine	-1.934	-3.704	-3.60
pyrimidine	-2.095		-3.75
2-methylpyrazine	-2.836	-4.476	-4.47
4-methylpyrimidine	-2.964		-4.60
3-picoline	-3.173	-4.822	-4.8
2,6-lutadiene	-3.425	-4.891	-5.04
2,5-dimethylpyrazine	-3.728	-5.38	-5.34
pyridazine	-3.714		-5.32
2,4,6-trimethylpyridine	-4.499	-6.128	-6.08
3-methylpyridazine	-4.5		-6.08

$$\ln(p/p_o) = (0.97\pm0.04)\ \ln(t_o/t_a)_{av} - (1.72\pm0.095) \qquad r^2 = 0.9906 \qquad (1\text{-}8)$$

Table 1-8. Parameters for eq. (1-7) and predicted BTs obtained by correlating $\ln(t_o/t_a)$ with $\ln(p/p_o)$ from $T = 298.15$ K to $T = 400$ K

	$\frac{A}{T^3}$	$\frac{B}{T^2}$	$\frac{C}{T}$	D	BP/K calc	BP/K lit[a]
1,3,5-triazine	-257351030.9	2117317.87	-10228.618	17.168	372.8	385.2
pyridine	-322093844.2	2565357.61	-11299.75	17.523	390.4	388.2
pyrazine	-324948325	2615598.11	-11549.026	17.976	387.2	388.2
pyrimidine	-346777640	2784315.59	-12027.135	18.35	390.9	395
2-methylpyrazine	-454046742.1	3627796.62	-14472.256	20.391	407	408.2
4-methylpyrimidine	-470354160.6	3751479.12	-14813.823	20.636	410.1	413
3-picoline	-487718452.4	3862725.41	-15041.819	20.602	416.3	417.2
2,6-lutadiene	-545016214.7	4354009.32	-16618.099	22.279	418.6	416.2
2,5-dimethylpyrazine	-590317407.4	4713687.79	-17672.686	23.186	424.6	428.2
pyridazine	-566482741.6	4483588.67	-16846.004	22.116	427.7	481
2,4,6-trimethylpyridine	-703998173.6	5610818.05	-20286.539	25.402	439.5	443.8
3-methylpyridazine	-680672239	5381295.73	-19448.99	24.294	443.6	487.2

[a] Literature boiling temperatures from SciFinder Scholar under Experimental Properties provided by each parent name

The last two columns in Table 1-8 compare the calculated normal boiling temperatures and literature values. With the exception of pyridazine and 3-methylpyridazine, the boiling temperatures of the remaining compounds are reproduced with a standard deviation of ± 4.2 K. 1,3,5-Triazine has the largest error in boiling temperature of the remaining compounds. However its vaporization enthalpy is within experimental error of the literature value as noted in Table 1-6. This material has the shortest retention time measured and it is likely to have the largest uncertainty in the slope and intercept of all the compounds studied. If the boiling temperature of 1,3,5-triazine is omitted, the standard deviation is reduced to ±2.5 K. Several literature values are reported for the boiling temperature of pyrimidine. Values range from 395.2 to 397.2 K, in reasonable agreement with the value calculated by eq. (1-7). This suggests that the vapor pressures obtained for pyrimidine as a function of temperature are reasonable, which in turn confirms the magnitude of the vaporization enthalpy measured. This result raises a red flag regarding the vaporization enthalpy of this material reported previously in the literature.[14]

Unlike pyrimidine, the boiling temperatures calculated for pyridazine and 3-methylpyridazine are more than 40 K lower than literature values. This suggests that pyridines and pyrazines are not suitable standards to use for aromatic 1,2-diazines and that the vaporization enthalpies reported in Table 1-6 for these materials are not to be trusted.

1.5. Summary

While this study does validate the assumption that pyridines can be used as suitable vaporization enthalpy and vapor pressure standards, it also reveals a specific instance where this presumption is probably invalid. This study demonstrates that gas chromatographic retention time measurements of pyridine derivatives can be used in obtaining vaporization enthalpies and vapor pressures of six membered ring aromatic nitrogen heterocycles, provided the nitrogen atoms are separated from each other by one or more carbon atoms. The vaporization enthalpy and vapor pressure measurements obtained for pyridazine and its derivatives by correlation gas chromatography could not be validated. This study also brings into question the accuracy of previous calorimetric measurement of the vaporization enthalpy of pyrimidine.

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Chapter 2. Vaporization Enthalpies and Vapor Pressures of Polyaromatic Nitrogen Heterocycles

2.1. Introduction

Polyaromatic hydrocarbons (PAHs) are an important group of environmental contaminants that are produced by a variety of incomplete combustion processes. Their heterocyclic nitrogen relatives, PANHs, are also found environmentally in heavy petroleum. A significant amount of quality data has been reported on the thermodynamic properties of pyridine and its derivatives as a consequence of the increased demand for fuel, the subsequent use of heavier feedstocks, and the need to hydrodenitrogenate these feedstocks to meet current environmental requirements.[1] PANHs have been found in automobile exhaust, the urban atmosphere, cigarette smoke condensate, and coal-tar isolates, shale oil, and in synthetic coal fuels.[2] PANHs exist mainly absorbed to aerosol particulates. Vapor pressure data can help describe behavior of polyaromatic nitrogen heterocycles in the atmosphere.

In Chapter 1, it was demonstrated that pyridine derivatives can serve as suitable standards for aromatic heterocyclic compounds containing more than one nitrogen provided nitrogen atoms are not adjacent in the ring. Therefore, we intend to use pyridine derivatives as standards to investigate vapor pressures and vaporization enthalpies of a series of aromatic nitrogen heterocycles, most of which have not been previously reported. These include: tri-n-butylamine, 2-phenylpyridine, 3-phenylpyridine, quinazoline, (-)-nicotine, 4-phenylpyrimidine, 2,2-dipyridine, 2,4-dipyridine, 4,4-dipyridine, 1,7-phenanthroline, 4,7-phenanthroline, 2-benzylpyridine, and 9-

methylcarbazole. The structures of both the compounds used as standards and those evaluated are illustrated in Figure 2-1.

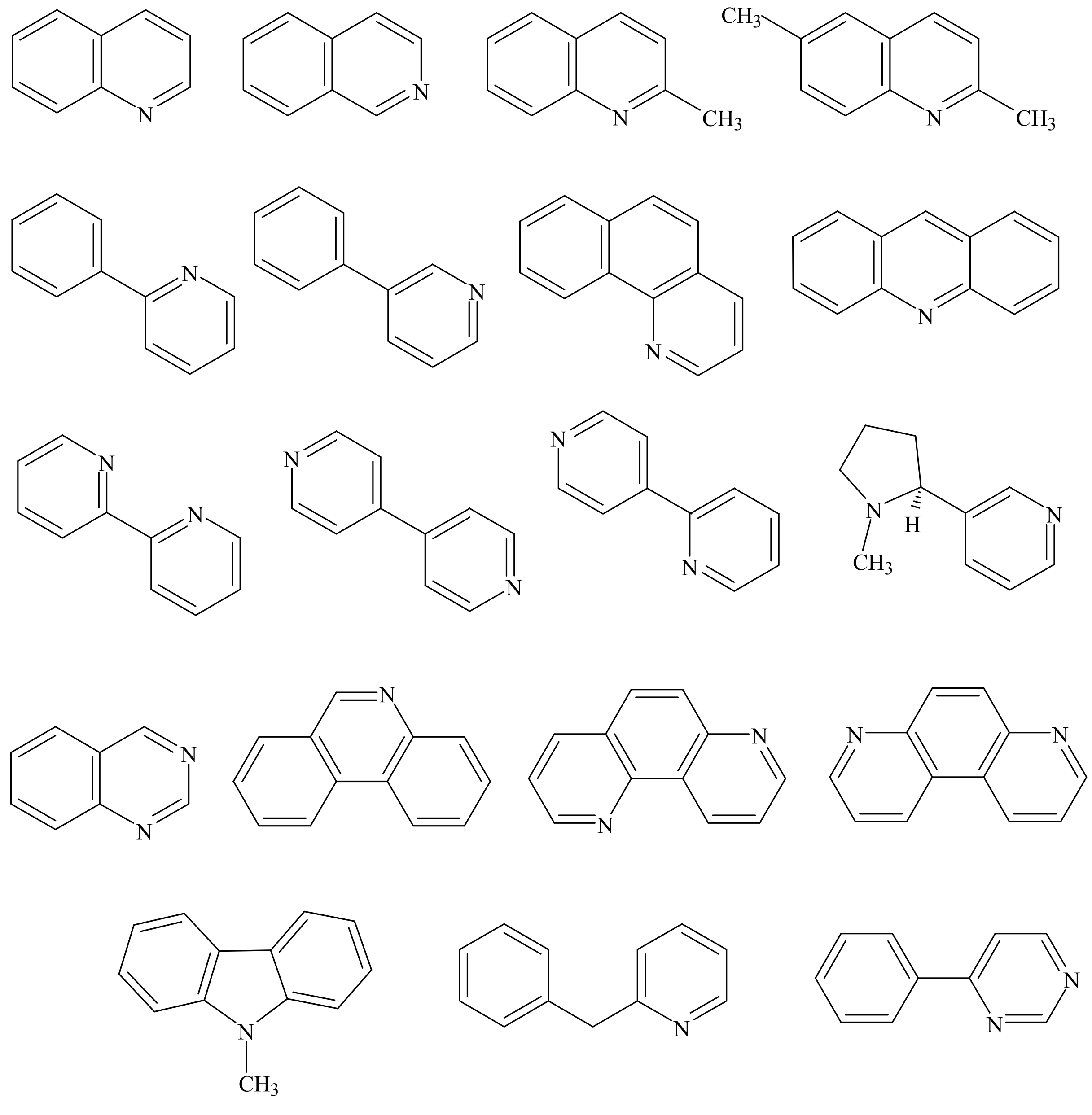

Figure 2-1. Structures of the standards and compounds investigated. From left to right, top to bottom; quinoline, isoquinoline, quinaldine, 2,6-dimethylquinoline, 2-phenylpyridine, 3-phenylpyridine, 7,8-benzoquinoline, acridine, 2,2-bipyridine, 4,4-bipyridine, 2,4-bipyridine, (-) nicotine, quinazoline,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

Ribeiro da Silva and Chickos demonstrated in their work on the phenylpyridine isomers that hydrocarbons can be used as standards for tertiary amines.[3]In that work, however, the vapor pressures of the phenylpyridines were not evaluated. In the current study we measure both vaporization enthalpies and liquid vapor pressures for 2- and 3-phenylpyridines using heterocyclic amines as standards. (-)-Nicotine and 9-methyl-carbazole both contain an aliphatic tertiary nitrogen atom. As a test of how well pyridine derivatives can serve as standards for aliphatic tertiary amines, the vaporization enthalpy and vapor pressure of tri-n-butylamine was also evaluated and the results compared with literature values.

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

Gas chromatography has been used in various ways to obtain vaporization enthalpies and vapor pressures of the sub-cooled liquid. Our group has been promoting correlation-gas chromatography as a simple and reliable manner in which vapor pressures and vaporization enthalpies of the sub-cooled liquid can be derived.[4,5]For compounds containing functional groups, it is generally necessary to include as standards, compounds with similar functionality. Hydrocarbons have previously been demonstrated to act as suitable standards for tertiary amines.[3] However best results are usually obtained when the standards are structurally more closely related to the compounds under evaluation.

2.2. Experiment

All compounds used in the vaporization enthalpy study were obtained from various commercial sources and used as purchased. All were analyzed by gas chromatography and most found to have purities of 98 % or better. Correlation gas chromatography experiments were performed on two different HP 5890 Gas Chromatographs equipped with split/splitless capillary injection ports and flame ionization detectors at a split ratio of approximately 100/1. The compounds were run isothermally on 30 m SPB 5 columns. While enthalpies of transfer do depend on the nature of the column used, the results 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, cyclopentane or cyclohexane were used as a non-retained reference. The remaining experimental details are same as described previously in Chapter 1.

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

dipyridine·xH_2O, 98%; 4,4-dipyridine (anhydrous), 98 %; 4-phenylpyrimidine, 96%; 4,7-phenanthroline, 98%; 1,7-phenanthroline, 99%. Anhydrous 2,4-dipyridine, 97% was purchased from Alpha Aesar. Analysis by gas chromatography (FID detection) confirmed the analyses of the commercial samples as minimum purities. Excluding water, analysis of the volatile components in all the samples, including 4-phenylpyrimidine, resulted in purities of 98.8%. No transitions other than melting were observed for all materials examined over the temperature range T = 305 K to T_{fus} except for 4,4-dipyridine and its hydrate. The results for 4,4-dipyridine and 4,4-dipridine·H_2O are discussed further in the text. The crystal structure of dipyridine·2H_2O has been reported but apparently it decomposes rather quickly at room temperature to an amorphous powder according to X-ray powder diffraction.[6] The water content in the 4,4-dipyridine·xH_2O sample was determined by integration of the ^{1}H NMR spectrum on a Bruker 300 MHz instrument in deuteriochloroform. Both DSC and NMR detected a small amount of water in the anhydrous form. The ratio of water to 4,4-dipyridine in the hydrated form was approximately 1.7/1.

2.3. Vaporization enthalpies and Vapor Pressures of the Standards

Vaporization enthalpies of all the standards and compounds used for comparison at T = 298.15 K are reported in Table 2-1. Vaporization enthalpies for tri-n-butylamine were calculated from three sets of vapor pressure data reported in the literature, all of which were calculated from the Antoine constantsat the mean temperature of measurement using eq. (2-1).[7,8] Temperature adjustments to T = 298.15 K were performed using eq. (2-2).[9] The C_{pl} term ineq. (2-2) refers to the heat capacity at T = 298.15 K and was estimated by group additivity.[10]

Table 2-1. Vaporization Enthalpies in the Literature

Compound [lit]	$\Delta_l^g H_m(T_m\ K)$ /kJ·mol^{-1}	T_m /K	C_{pl} /J·mol^{-1}·K^{-1}	$\Delta_l^g H_m$(298.15 K) /kJ·mol^{-1}		Ref
				calc	^{a}lit	
	62.75	318	413.8	65.0		7
tri-n-butylamine	48.14	410	413.8	61.4		7
	49.3	447	413.8	66.9		8
quinoline					59.31±0.2	11
isoquinoline					60.26±0.12	11
quinaldine					62.64±0.13	12
(*dl*)-nicotine[b]	50.5	463	285	64.5		7
nicotine[b]	53.1±0.4	446	285	65.7±2.7		13
nicotine[b]					67.4±0.3[c,d]	14, 15
2,6-dimethylquinoline					67.07±0.16	16
7,8-benzoquinoline	72.99±0.3	360	278.1	78.11±1.0	77.23[d]	17
phenanthridine	74.31±0.2	380	278.1	81.09±1.3	80.14[d]	17
acridine	72.94±0.1	380	278.1	79.72±1.3	78.63[d]	17
2-phenylpyridine					68.7±4.6	3
3-phenylpyridine					67.4±4.5	3
9-methylcarbazole					81.1±0.3[d]	18

[a] Literature data adjusted to T = 298.15 K using eq. (2-2);

[b] Chirality not specified;

[c] Calculated from the parameters of the Cox equation using data from reference 15 as reported by Basarova et al.[15]

[d] Calculated from the slope of the line by plotting ln(p) vs 1/T using extrapolating vapor pressures calculate from either the Cox or Wagner equations at a mean temperature of T = 298.15 K using the parameters of Table 2-2 as described in the text.

Table 2-2. Parameters of the Cox, Wagner, and Antoine Equations

Cox Equation[a]	A_o	A_1 T^{-1}	A_2*10^7 T^{-2}	T_b /K	Range /K
quinoline[11]	2.85461	-0.00130236	9.3118	510.298	298 to 559
isoquinoline[11]	2.85183	-0.00126768	8.8569	516.391	313 to 566
Acridine[17]	2.89594	-0.00111538	6.486	618.059	383 to 637
Phenanthridine[17]	2.90928	-0.00113569	6.7834	623	383 to 473
7,8-benzoquinoline[17]	2.88454	-0.00111802	6.6824	614.49	373 to 662
9-methylcarbazole[18,b]	2.94053	-0.73537	2679200	616.966	362 to 890

Wagner Equation [c]	A_W	B_W	C_W	D_W	T_c /K	p_c /kPa	Range /K
quinaldine[12]	-8.370206	2.914441	-3.761685	-3.195981	778	4030	320-570
2,6-dimethylquinoline[16]	-8.993312	3.594873	-4.63173	-2.907492	786	3480	337-592
nicotine[15,d]	-8.83376	3.40331	-5.13787	-6.91787	756.3	3059	300-520

Antoine Equation	A	B	C	Range/ K
tri-n-butylamine [7,e]	4.96696	1088.83	-134.511	298 to 337
tri-n-butylamine [7,e]	7.169	2515	0	333 to 487
tri-n-butylamine [8,f]	16.2878	3865.58	-86.15	362 to 531
(*dl*)-nicotine [7,e]	5.91387	1650.347	-96.779	406 to 520

[a] $p_o = 101.325$ kPa;

[b] Calculated from the Cox eq. in the form:
$\ln(p/p_o) = [1- 1/(T/T_b)]\exp[A_o + A_1(T/T_b) + A_2(T/T_b)^2]$

[c] $T_r = T/T_c$;

[d] Stereochemistry not specified;[13]

[e] $\log(p) = A - B/(T+C)$, p = kPa;

[f] $\ln(p) = A - B/(T+C)$, p = mm Hg.

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

$$\Delta^{g}{}_{l}H_{m}(T_{m}) = 2.303RB[T_{m}/(T_{m}+C)]^{2} \qquad (2\text{-}1)$$

$$\Delta^{g}{}_{l}H_{m}(298.15\ K)/\ kJ\cdot mol^{-1} = \Delta^{g}{}_{l}H_{m}(T_{m}) + [(10.58 + 0.26{*}C_{p}(l))(T_{m} - 298.15\ K)]/100 \qquad (2\text{-}2)$$

$$\ln(p/p_{o}) = (1-T_{b}/T)\exp(A_{o} + A_{1}(T/K) + A_{2}(T/K)^{2}) \qquad (2\text{-}3)$$

$$\ln(p/p_{c}) = (1/T_{r})[A_{W}(1-T_{r}) + B_{W}(1-T_{r})^{1.5} + C_{W}((1-T_{r})^{2.5} + D_{W}(1-T_{r})^{5}] \qquad (2\text{-}4)$$

2.4. Results and Discussion

The retention times measured for the fourteen mixtures (runs 1-14) studied are reported in the Appendix B-1. The correlations between enthalpies of transfer measured for each mixture and available vaporization enthalpy values are reported in Appendix B-2. The equation characterizing the correlation is given below each run.

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

This concern over the proper choice of standards arose when it was observed (in Chapter 1) that pyridine and its derivatives, appropriate and successful standards for the evaluation of pyrazines, pyrimidines and 1,3,5-triazines, appeared to be unsuccessful in the evaluation of these properties in pyridazine and its derivatives.Since 2- and 3-phenylpyridine have similar retention times, duplicate runs of two separate mixtures were evaluated. The results of four runs are reported in Appendix B-2 with the correlation equations between enthalpies of transfer and vaporization enthalpies provided below each run. The results of the four experiments are summarized in Table 2-3. The vaporization enthalpies for tri-n-butylamine fall in between the three literature values. Given the large temperature adjustment necessary for two of the three measurements reported in Table 2-1, agreement between the different sets of measurements in Table 2-3 can be considered reasonably satisfactory. Similarly, the vaporization enthalpies measured for 2- and 3-phenylpyridine are within the experimental uncertainties reported previously. In subsequent correlations that use 2-phenylpyridine and/or tri-n-butylamine as standards, the values evaluated from runs 1-4 were used. The mean value of the vaporization enthalpies derived for the compounds used as standards in these correlations are also reported in this instance for comparison of reproducibility and congruence with literature values. These values are reported in italics in Table 2-3.

Table 2-3. A Summary of the vaporization enthalpies of runs 1 to 4

			$\Delta_l^g H_m$(298.15 K) /kJ·mol^{-1}			$\Delta_l^g H_m$(298.15 K)
						Lit
	Run 1	Run 2	Run 3	Run 4	Average[a]	/kJ·mol^{-1}
tri-n-butylamine	62.7	62.6	62.6	62.7	62.7±1.3	65.0; 61.4, 66.9
quinoline	59.5	59.4	59.5	59.4	*59.5±1.3*	59.31±0.2
isoquinoline	60.1	60.0	60.1	60.1	*60.1±1.3*	60.26±0.12
quinaldine	62.7	62.8	62.7	62.8	*62.8±1.3*	62.64±0.13
2,6-dimethylquinoline	67.1	67.0	67.0	67.0	*67.0±1.5*	67.07±0.16
7,8-benzoquinoline			77.7	77.7	*77.7±1.3*	78.11±1.0; 77.23
acridine			78.2	78.2	*78.2±1.3*	79.72±1.3; 78.63
2-phenylpyridine	68.4	68.4			68.4±1.9	68.7±4.6
3-phenylpyridine			68.3	68.5	68.4±1.6	67.4±4.5

[a] The uncertainty is the average uncertainty associated with each run as reported in Appendix B-2.

As a test of how well the slopes and intercepts obtained from the gas chromatographic retention times are capable of reproducing experimental vapor pressures, values of ln(t_o/t_a) calculated from the slopes and intercepts of Appendix B-2 were correlated with ln(p/p_o) values calculated from the Cox and Wagner equations. Vapor pressures near ambient temperatures were extrapolated values in some cases. The correlation obtained at T = 298.15 K is illustrated in Table 2-4 for runs 1 to 4.

Table 2-4. Correlation between ln(t_o/t_a) and ln(p/p_o) at T = 298.25 K for Runs 1 to 4

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

$$\ln(p/p_o) = (1.326\pm0.034)\ \ln(t_o/t_a) - (1.80\pm0.148) \qquad r^2 = 0.9973 \qquad (2\text{-}5)$$

The correlation is characterized by eq. (2-5) reported below the table. This process was repeated for each compound over the temperature range T = 298.15 K to T = 500 K at 10 K intervals (not shown). The resulting $\ln(p/p_o)$ values were then fit to eq. (2-6), resulting in the parameters reported in Table 2-5.

$$\ln(p/p_o) = A(T/K)^{-3} + B(T/K)^{-2} + C(T/K)^{-1} + D; \qquad (2\text{-}6)$$

Table 2-5. The Constants of Equation (2-6) and Corresponding Estimated and Experimental Boiling Temperatures Derived from Runs 1 to 4

	A/K^3	B/K^2	C/K	D	$\mathrm{BT_{calc}}$[a] /K	$\mathrm{BT_{lit}}$[b] /K
tri-n-butylamine	30767110.1	-712464.53	-3836.038	10.769	481.3	486.2
quinoline	70264429.1	-1071875.28	-2317.095	8.142	509.6	510.3[c]
isoquinoline	73060204.0	-1098099.34	-2313.099	8.095	515	516.4[c]
quinaldine	70559084.1	-1076785.25	-2717.977	8.676	521.3	521.2
2,6-dimethylquinoline	77271221.9	-1140593.21	-3053.545	9.029	542.1	540.2
7,8-benzoquinoline	117024769.3	-1520001.94	-3074.300	8.498	615.8	614.5[c]
acridine	117215491.1	-1521846.26	-3126.912	8.566	617	618.1[c]
2-phenylpyridine	82334650.2	-1199538.89	-2988.675	8.899	550.2[d]	543.2[d]
3-phenylpyridine	78066389. 6	-1137160.48	-3293.956	9.322	547.4 [e]	543.2[e]

[a] Calculated boiling temperature using eq. (2-6); [b] Literature boiling temperature from ref [7] unless noted otherwise; [c] See Table 2-2; [d] 2007-8 Aldrich Catalog; [e] Boiling temperature at 99.8 kPa, 2007-8 Aldrich Catalog.

As noted above, three sets of vapor pressure values are available for tri-n-butylamine in the form of the Antoine equation over the following range of temperatures: from T = (298 to 337) K,[7] a second from T = (333 to 487) K[7] and a third from T = (362 to 531) K.[8] Vapor pressures reproduced from these equations are reported as solid circles, circles and squares at 10 K increments in Figure 2-2. The circles and squares represent vapor pressures calculated from the Antoine equation at temperatures offset by T = 5 K.

The line represents the results from this study over the same temperature interval calculated using eq. (2-6) and the constants from Table 2-5. The correlation observed between this work and the literature values improves with increasing temperature.

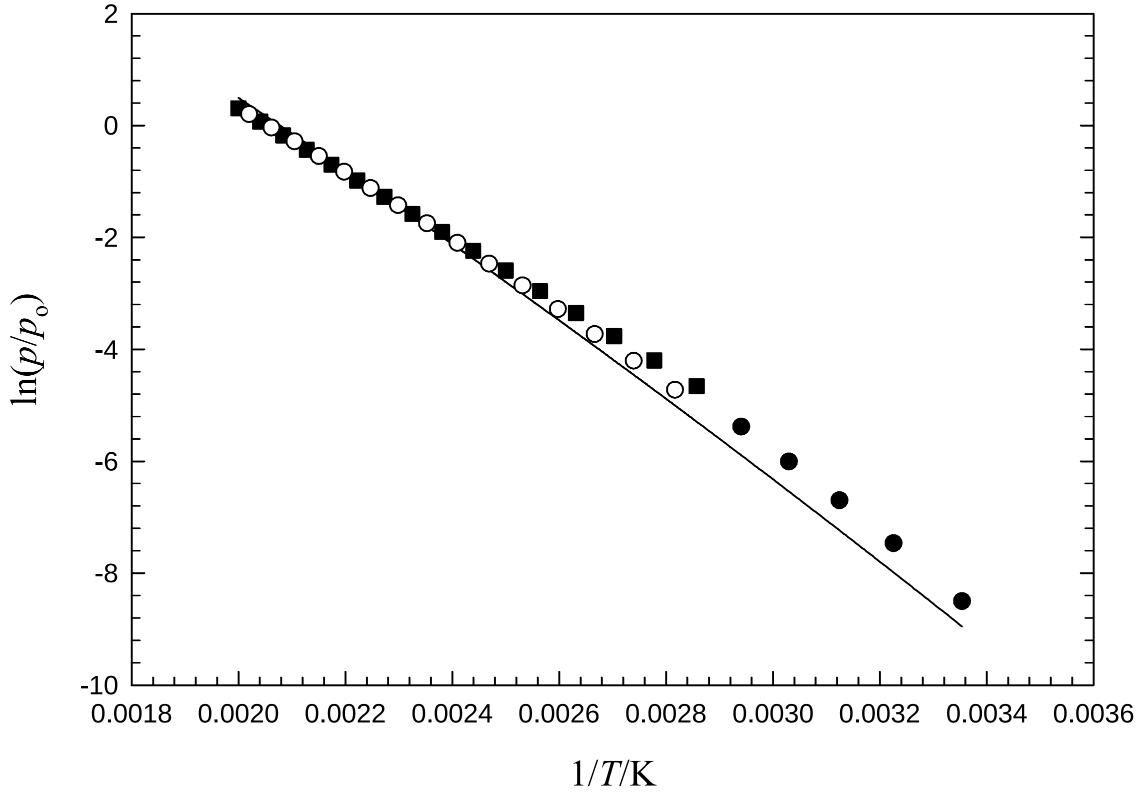

Figure 2-2. A comparison of ln(*p*/*po*) values for tri-n-butylamine (p_o =101.325 kPa) obtained in this work, eq. (2-6), with literature values;—— , this work; ●, ref 7; ■: ref 7; ○, ref 8. The ○ and ■ values are calculated at 10 K intervals offset by 5 K.

As a further test of how well vapor pressures calculated by eq. (2-6) are capable of reproducing experimental values, the normal boiling temperatures of all of the compounds involved in the correlation were estimated by extrapolation. The results are compared to experimental values in the last two columns of Table (2-5). The average absolute deviation is 3.2 K with the largest difference of 7 K measured for 2-phenylpyridine.

The success in using aromatic heterocyclic compounds for reproducing the vaporization enthalpy and vapor pressure of tri-n-butylamine encouraged us to evaluate the vaporization enthalpies of a series of other aromatic nitrogen heterocyclic compounds including (-)-nicotine, and 9-methylcarbazole, both of which contain a tertiary aliphatic nitrogen atom using the compounds just discussed as standards. With the exception of (-)-nicotine and benzylpyridine which are liquids at ambient temperatures, quinazoline, 2,2-dipyridine, 4,4-dipyridine·xH_2O, 9-methylcarbazole, 1,7- and 4,7-phenanthroline are solids at T = 298.15 K. The vaporization enthalpies of these materials at T = 298.15 K would correspond to the sub-cooled liquid and as such are hypothetical thermodynamic properties. While the vaporization enthalpy for 9-methylcarbazole at T = 298.15 K has not been reported, critically evaluated vapor pressure data for the liquid form are available at elevated temperatures in the form of the Cox eq.[18] Extrapolation of the vapor pressures calculated from the Cox equation to a mean temperature of T = 298.15 K as described above for acridine and 7,8-benzoquinoline resulted in the vaporization enthalpy reported in the last column of Table 2-1. As a test of how well the standards chosen were capable of reproducing both vapor pressure and vaporization enthalpy, 9-methylcarbazole was treated as an unknown in these experiments. Additionally, the sample of 4,4-dipyridine in the form of a hydrate was initially examined. Since water does not produce a signal in the FID detector, it was expected that the presence of water in the crystal would not interfere with the retention time of 4,4-dipyridine. As is described below, this was found to be the case. All runs that included 2-phenylpyridine and tri-n-butylamine as standards evaluated in this work also included a number of other vaporization enthalpies from the literature.

The results of six additional experiments are reported in Appendix B-2 as runs 5 to 10. The compounds evaluated include, quinazoline, (-)-nicotine, 2,2-dipyridine, 4,4-dipyridine·1.7H_2O, 1,7-and 4,7-phenanthroline, 2-benzylpyridine and 9-methylcarbazole. Equations below each run in Appendix B-2 describe the correlation measured between enthalpies of transfer of the standards and their corresponding vaporization enthalpies at T = 298.15 K. The resulting vaporization enthalpies obtained for duplicate runs are summarized in Table 2-6. The results are reproducible, and for two of the compounds, (-)-nicotine and 9-methylcarbazole, the results are in good agreement with literature values.

Table 2-6. A Summary of the Vaporization Enthalpies of Runs 5 to10

	$\Delta_l^g H_m$(298.15 K)/ kJ·mol^{-1}							$\Delta_l^g H_m$[Lit] (298.15 K)
	Run 5	Run 6	Run 7	Run 8	Run 9	Run 10	Average[a]	/ kJ·mol^{-1}
quinazoline	59.3	58.5					58.9±2.0	
(-)-nicotine	64.1	63.7					63.9±2.1	65.7±2.7;[b] 64.5[c] 67.4±0.3 [b]
2,2-dipyridine	67.1	66.9					67.0±2.3	
4,4-dipyridine·1.7H_2O	70.8	70.6					70.7±2.4	
1,7-phenanthroline			79.4	79.4			79.4±4.7	
4,7-phenanthroline			80.8	80.8			80.8±4.8	
2-benzylpyridine					70.0	69.5	69.8±2.8	
9-methylcarbazole					79.5	79.3	79.4±3.2	81.1±0.3

[a] The uncertainty is the average uncertainty associated with each run in Appendix B-2; [b]Stereochemistry not specified[13,15]; [c] Racemic form

Vapor pressures were similarly obtained by correlating ln(t_o/t_a) with ln(p/p_o) of the standards. For runs 5 through 10, with the exceptions of tri-n-butylamine, and 2-phenylpyridine, the compounds used as standards were literature values using the parameters given in Tables 2-2. Vapor pressures for tri-n-butylamine and 2-phenylpyridine were values calculated using eq. (2-6) evaluated in runs 1 to 4 and vapor pressures calculated for 4,7-phenanthroline in runs 7 and 8 were used as standards in runs 9 and 10. The protocol followed was the same as described above and illustrated in Table 2-4. Correlations were performed from T = (298.15 to 500 K) at 10 K intervals. The constants of eq. (2-6) calculated for quinazoline, (-)-nicotine, 2,2-dipyridine, 4,4-dipyridine, phenanthridine, 1,7- and 4,7-phenanthroline, 2-benzylpyridine and 9-methylcarbazole are summarized in Table 2-7. Vapor pressures for 9-methylcarbazole calculated from the Cox equation were not used in the correlations. Constants for eq. (2-6) obtained for the compounds used as standards are not included in Table 2-7. As a means of evaluating the quality of the vapor pressures obtained by these correlations, the boiling temperatures calculated using the constants of eq. (2-6) are included in column 6 of the table for both standards and unknowns. A normal boiling temperature for 4,7-phenanthroline could not be located.

Figure 2-3 provides a qualitative means of judging the reproducibility and quality of the vapor pressures obtained from these correlations. The top curve compares the vapor pressures of (-)-nicotine from this work (line) with literature values for *(dl)*-nicotine (triangles[7]), and for nicotine of unspecified stereochemistry (squares[14,15] and circles[13]). The middle two curves compare the vapor pressures of 2,2-dipyridine and 4,4-dipyridine calculated by averaging runs 5 and 6 (triangle and solid circles, respectively) to those obtained by averaging runs 7 and 8 (lines) using somewhat different standards. The lower curve compares vapor pressures calculated for 9-methylcarbazole from this work (line) with values calculated with the Cox eq. (solid squares) using the parameters given in Table 2-2. The comparisons for the most part are quite good suggesting that both the vapor pressure equations and vaporization enthalpies generated for those compounds are reasonably accurate.

Table 2-7. The Constants of Equation (2-6) and Corresponding Estimated and Experimental Normal Boiling Temperatures Derived from Runs 5 to 10

Runs 5 and 6	A/K^3	B/K^2	C/K	D	BT$_{calc}$[a] / K	BT$_{lit}$[b] / K
tri-n-butylamine					479.8	486.2
quinazoline	62950221.9	-1019157.75	-2388.439	8.073	512.4	516.2
(-)-nicotine	69850065.0	-1084705.54	-2782.671	8.667	528.8	520.2[c]
2,6-dimethylquinoline					543.6	540.2
2,2-dipyridine	81725945.6	-1192649.71	-2825.351	8.6	549.4	546.2
2-phenylpyridine					551	543.2
4,4-dipyridine·1.7H_2O	89520224.1	-1264611.03	-3050.209	8.891	563.7	578.2
7,8-benzoquinoline					614.6 [d]	611.2[d]
acridine					615.9	618.1
Runs 7 and 8						
tri-n-butylamine					480.6	486.2
2,2-dipyridine	82980265.7	-1197572.80	-2914.488	8.767	549.6	546.2
2-phenylpyridine					551.6	543.2
4,4-dipyridine·1.7H_2O	88090511.1	-1246867.02	-3194.165	9.087	564.2	578.2
7,8-benzoquinoline					617.9 [d]	614.5 [d]
phenanthridine					618.7 [d]	623 [d]
1,7-phenanthrolene	121578810.4	-1558844.12	-3192.849	8.625	623.7	633.2
4,7-phenanthrolene	123705709.5	-1579329.77	-3296.579	8.741	628.7	na
Runs 9 and 10						
tri-n-butylamine					481.3	486.2
7,8-benzoquinoline					618.1 [d]	614.5 [d]
acridine					619.4	618.1
4,7-phenanthrolene					620.7	na
2-benzylpyridine	79549255.1	-1163591.12	-3291.65	9.325	551.2	549.2
9-methylcarbazole	119137844.7	-1531860.0	-3317.94	8.855	619 [d]	617 [d]

[a] Calculated BT using eq. (2-6); [b] literature boiling temperature from ref 7 unless noted otherwise; [c] reported to decompose; [d] See Table 2-2

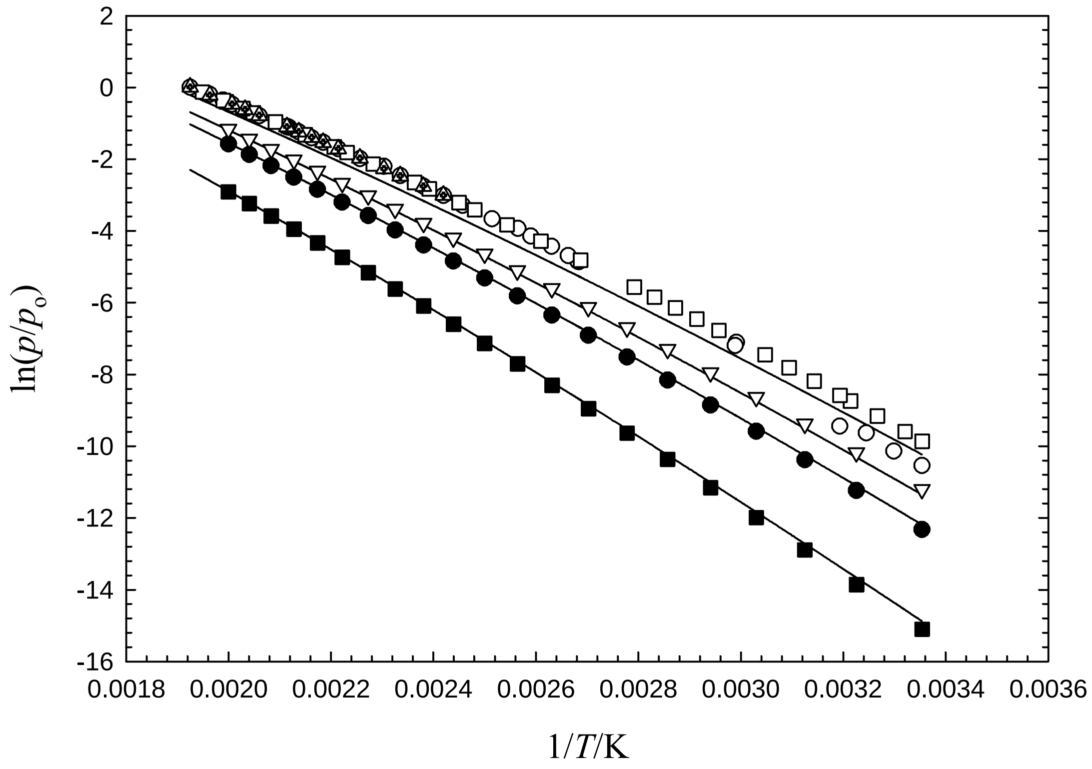

Figure 2-3. From top to bottom: A comparison of $\ln(p/p_o)$ of (-)-nicotine obtained by correlation (line) from T = (298.15 to 500 K) with literature values for nicotine (○, ref 13 □, ref 15 and ∆, ref 7, over the temperature range T = (298.15 to 520 K). Upper middle, a comparison of $\ln(p/p_o)$ for 2,2-dipyridine from duplicate runs 5 and 6 (▽) to the corresponding values obtained in duplicate runs 7 and 8 (line) from T = (298.15 to 500 K). Lower middle, a similar comparison for 4,4-dipyridine for duplicate runs 5 and 6 (●) to runs 7 and 9 (——). Bottom, calculated vapor pressures for 9-methylcarbazole from the Cox eq.[18] (■)with the results from this work, duplicate runs 9 and 10 ( ).——

As noted above, despite their hypothetical nature, vaporization enthalpies of solids combined with fusion enthalpies at $T = 298.15$ K can provide reliable sublimation enthalpy values. A number of the compounds used in this study have had their sublimation enthalpies reported in the literature. The fusion enthalpies of a few of these materials have also been reported. Table 2-8 lists fusion enthalpies reported in the literature along with some of the values measured in this work. Since fusion enthalpies are measured at temperatures other than $T = 298.15$ K, it is necessary to adjust these values for temperature. Eq. (2-7) has been used for these purposes.[19] Additionally, eq. (2-8) is the thermodynamic equality that relates sublimation, vaporization and fusion enthalpies.

$$\Delta_{cr}{}^{l}H_m(298.15\text{ K}) = \Delta_{cr}{}^{l}H_m(T_{fus}) + [[0.15\ C_p(\text{cr})-0.26\ C_p(\text{l})/\text{J}-9.83)]/\text{J mol}^{-1}\text{ K}^{-1}][(T_{fus}/\text{K}-298.15]/1000 \quad (2\text{-}7)$$

$$\Delta_{l}{}^{g}H_m(298.15\text{ K}) = \Delta_{cr}{}^{g}H_m(298.15\text{ K}) - \Delta_{cr}{}^{l}H_m(298.15\text{ K}) \quad (2\text{-}8)$$

Table 2-8. Fusion Enthalpies of the Compounds Studied

	$\Delta_{cr}{}^{l}H_m(T_{fus})$ /kJ·mol^{-1}	T_{fus}/K^a	C_p(l) /J·mol^{-1}·K^{-1}	C_p(cr) /J·mol^{-1}·K^{-1}	$\Delta_{cr}{}^{l}H_m$(298K) /kJ·mol^{-1}	Ref
quinazoline	16.95	320.8	202.8	149.8	16.0	20
2,2-dipyridine	20.4	345.2	246.4	184.8	18.3±0.7	21
9-methylcarbazole	17.15	362.5	299.1	211.7	13.56	22
4,7-phenanthroline	21.8±0.5	445.5	277	202	14.3±2.3	this work
1,7-phenanthroline	18.2±0.3	350.3	277	202	15.5±0.8	this work
4,4-dipyridine·1.7H_2O	35.5±0.5	341.3	≈374.4^b	≈247^b	≈31.4±1.6	this work

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

The temperature adjustments of fusion enthalpies to T = 298.15 K are summarized in Table 2-8. Adjustment of the fusion enthalpy of the hydrated form of 4,4-dipyridine to T = 298.15 K, however, is problematic. Eq. (2-7) was derived for pure materials and there is no guarantee that it can be applied to hydrates or amorphous materials. However since the fusion temperature is close to T = 298.15 K, this insures a small temperature adjustment. Using adjusted heat capacities derived as noted in footnote b of Table 2-8 and as is discussed below, a fusion enthalpy at T = 298.15 K of 31.4 kJ·mol^{-1} is estimated for 4,4-dipyridine hydrate. Accepting this value for the moment, the vaporization enthalpies measured in this work can be compared to the literature values calculated using eq. (2-8). This comparison is documented in Table 2-9. Most vaporization enthalpy comparisons are within experimental error of each other.

Table 2-9. A Comparison of Vaporization Enthalpies Using Eq. (2-8) With This Work

A	$\Delta_{cr}^{g}H_m$(298 K) /kJ·mol^{-1}	$\Delta_{cr}^{l}H_m$(298K) /kJ·mol^{-1}	$\Delta_{l}^{g}H_m$(298 K) /kJ·mol^{-1}	
			calc [a]	this work
quinazoline	77.6[b], 76.6±1.4[c]	16.0	61.6, 60.6	58.9±2.0
9-methylcarbazole	95.5±4.0[d]	13.56[e]	81.94; 81.1[f]	79.4±3.2
2,2-dipyridine	81.8±2.3[g]	18.3±0.7[h]	63.5±3.2	67.0±2.3
4,4-dipyridine·1.7H_2O	106.3±2.8[g]	≈31.4±1.6	≈74.9±3.4	70.7±2.4

[a] Calculated using eq. (2-8); [b] Ref 20; [c] Ref 23; [d] Reference 18 and 24; [e]Ref 22; [f] See Table 1; [g] Ref 25; [h] Ref 21.

As noted in Table 2-9, the vaporization enthalpy value calculated for 4,4-dipyridine hydrate is remarkably close to the value previously reported for the anhydrous material.[26] Since the sublimation enthalpy of 4,4-dipyridine was subsequently used in calculating the gas phase enthalpy of formation of 4,4-dipyridine,[26] a concern immediately arose concerning the possibility that either the sublimation enthalpy reported in the literature was for a hydrated form of 4,4-dipyridine or that the hydrated form used in our measurements somehow affected the retention times of 4,4-dipyridine. Consequently both the vaporization and fusion enthalpies of the anhydrous form of 4,4-dipyridine were also measured. As an added precaution, the vaporization and fusion enthalpies of a related compound, 2,4-bipyridine, for which an experimental sublimation enthalpy and condensed phase enthalpy of formation value is available,[26] were also measured. An additional compound that became available to us, 4-phenylpyrimidine, was also included in the mixture. Due to the similarity in retention times of the two dipyridines, two sets of duplicate mixtures were used. The retention times of the gas chromatographic experiments for runs 11-14 are available in the Appendix B-1 and the resulting correlations are reported in Appendix B-2. Table 2-10 summarizes the vaporization enthalpy results obtained using the protocol described above. The parameters of eq. (2-6) generated for 4-phenylpyrimidine, 4,4-dipyridine and 2,4-dipyridine in the liquid state along with the predicted boiling temperatures for each of the compound in the mixture are provided in Table 2-11. Although the extrapolated boiling temperatures of both the anhydrous and hydrated form differ from the literature value by approximately 15 K, the two differ from each other by less than 1 K in temperature. Similarly, the extrapolated value for 2,4-dipyridine differs by approximately 10 K from the experimental value while its vaporization enthalpy is consistent with experimental sublimation and fusion enthalpy results.

Table 2-10. A Summary of the Vaporization Enthalpies of Runs 11 to14

	$\Delta_l^gH_m$(298.15 K)/ kJ·mol^{-1}				$\Delta_l^gH_m$(298.15 K)	
	Run 11	Run 12	Run 13	Run 14	Average[a]	[Lit]/kJ·mol^{-1}
4-phenylpyrimidine	68.8	68.7			68.8±2.5	
4,4-dipyridine (anhyd)	71.1	71.1			71.1±2.6	
2,4-bipyridine			70.9	70.9	70.9±1.6	72.1±1.8[b]

[a] The uncertainty is the average uncertainty associated with each run in Appendix B-2;
[b] Calculated using eq. (2-8)

Table 2-11. Constants of Eq. (2-6) and Corresponding Estimated and Experimental Normal Boiling Temperatures Derived from Runs 11 to 14

Runs 11 and 12	A/K^3	B/K^2	C/K	D	BT$_{calc}$[a] /K	BT$_{lit}$[b] /K
tri-n-butylamine					481.0	486.2
4-phenylpyrimidine	82739965.41	-1191247.386	-3078.925	8.993	392.0	390.2 [c]
4,4-dipyridine (anhyd)	87876825.41	-1240023.916	-3205.124	9.104	563.4	578.2 [d]
7,8-benzoquinoline					615.4	614.5 [e]
acridine					616.7	618.1 [e]
4,7-phenanthrolene					623.5	na
Runs 13 and 14						
tri-n-butylamine					482.4	486.2
2-benzylpyridine					549.8	549.2
2,4-bipyridine	89785140.71	-1256837.408	-3110.722	8.95	564.7	554.2 [f]
7,8-benzoquinoline					614.1	614.5 [e]
acridine					615.4	619.5
9-methylcarbazole					615.2	617 [e]
4,7-phenanthrolene					624.5	na

[a] Calculated boiling temperature using eq 10; [b] Literature boiling temperature from ref 7 unless noted otherwise; [c] Boiling temperature at 0.53 kPa, experimental data: SciFinder Scholar; [d] Boiling temperature at 0.53 kPa, experimental data: SciFinder Scholar;
[e] See Table 2-2; [f] Experimental data, SciFinder Scholar

The heat flow diagrams obtained for the solid to liquid transition of both the hydrated and anhydrous forms of crystalline 4,4-dipyridine are compared in Figure 2-4. The anhydrous form melted at T = 377.5 K (onset temperature) with a fusion enthalpy of (102.4±3.0 J·g^{-1}). It also exhibited a smaller peak at T = 337 K (1.5±0.3 J·g^{-1}). Unlike the hydrated form, fusion of the anhydrous form appears to be characterized by several overlapping transitions. The hydrated form melted sharply at T = 341.3 K with a fusion enthalpy of (187.2±2.2) J·g^{-1}. The figure also shows two, and in one case (not shown) three weak peaks in repeated runs, two of which were not clearly resolved, at T = (382 and 386) K with transition enthalpies of (2.85±1.5) and (2.7±0.2) J·g^{-1}, respectively. It should be also noted that the hydrated form also shows a very weak peak at approximately T = 327 K which is too weak to be observed in Figure 4. The simplest explanation of the multiple peaks observed in both forms is that the hydrated form contains a small amount of the anhydrous material and the anhydrous material contains a small amount of water. The enthalpy ratio of the hydrated to anhydrous form on a mass basis is approximately 1.82/1. Using this ratio to correct for the heat flow of the hydrated form, suggests an anhydrous composition of 0.993 (top curve). Adjusting the experimental enthalpies per gram of the anhydrous form of 4,4-dipyridine for this composition results in a fusion enthalpy of (16.1±1.0) kJ·mol^{-1} as reported as the last entry in Table 2-12. Similarly, a composition of 0.984 is calculated for the hydrated form which adjusts to a value of 190.4 J·g^{-1} for the pure hydrated form, 4,4-dipyridine·xH_2O. Converting the value for the hydrated form from a mass basis to a molar basis is problematic. An ^{1}H NMR analysis in $CDCl_3$ of the hydrated form suggested a ratio of water/4,4-dipyridine of approximately 1.7/1.Assuming a molecular weight on this basis, 186.8 g·mol^{-1}, results in a fusion enthalpy of 35.5 kJ·mol^{-1}, reported in column 2, Table 2-8, as the last entry. As noted above, adjusting this value to T = 298.15 K using eq. (2-7) is equally problematic. However, since the fusion temperature is close to T = 298.15 K, this insures a small temperature adjustment. Using adjusted heat capacities derived as noted in footnote b of Table 2-8, a fusion enthalpy of approximately 31.4 kJ·mol^{-1} is estimated.

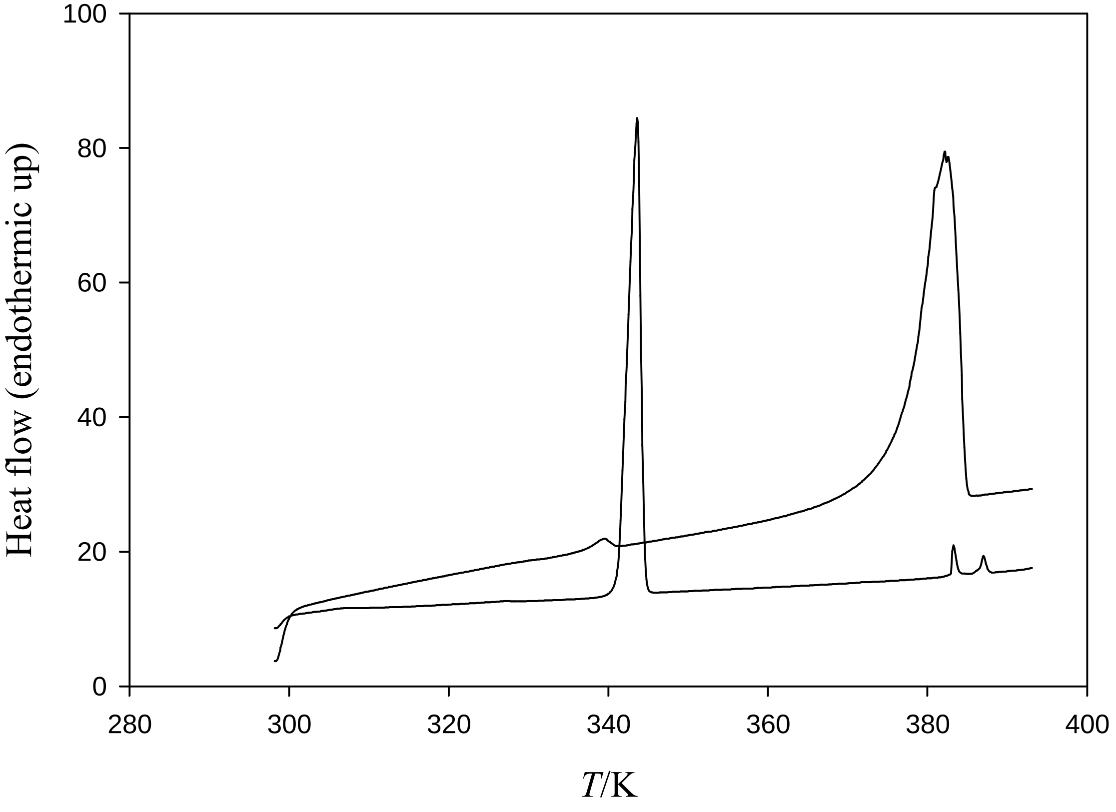

Figure 2-4. DSC trace of dipyridine·1.7H_2O (lower) and anhydrous dipyridine (upper). There is some evidence of a very weak transition at T = 327 K in dipyridine·1.7H_2O not evident on this scale. The weak peaks at approximately T = 386 K in dipyridine·1.7H_2O varied in relative intensity from run to run and a third peak was also observed in one run between the two.

Table 2-12. Fusion Enthalpies of 4-Phenylpyrimidine and the Dipyridines

	$\Delta_{cr}^{l}H_m(T_{fus})$ /kJ·mol^{-1}	T_{fus}/K^a	C_p(l) /J·mol^{-1}·K^{-1}	C_p(cr)	$\Delta_{cr}^{l}H_m$(298K) /kJ·mol^{-1}	Ref
4-phenylpyrimidine	18.8±0.3	334.1	246.4	184.8	17.1±0.6	this work
2,2-dipyridine	20.4	345.2	246.4	184.8	18.3±0.7	21
2,4-dipyridine	17.4±0.4	332.8	264.4	184.8	15.8±0.6	this work
4,4-dipyridine (anhyd)	16.1±1.0	377.5	264.4	184.8	12.3±1.5	this work

[a] Onset temperature.

[b] Estimated by adding the estimated molar heat capacity of the anhydrous form to the heat capacity of 1.7mols of water (75.3 and 36.6) J·mol^{-1}·K^{-1} for liquid and solid water, respectively).

Table 2-13. Comparison of Vaporization Enthalpies Using Eq (2-8) With This Work

	$\Delta_{cr}^{g}H_m$(298 K) /kJ·mol^{-1}	$\Delta_{cr}^{l}H_m$(298K) /kJ·mol^{-1}	$\Delta_{l}^{g}H_m$(298 K) /kJ·mol^{-1}	
			calc [a]	this work
4-phenylpyrimidine	85.9±2.6[b]	17.1±0.6		68.8±2.5
2,2-dipyridine	81.8±2.3[c]	18.3±0.7	63.5±3.2	67.0±2.3
2,4-dipyridine	87.9±1.7[c]	15.8±0.6	72.1±1.8	70.9±1.6
4,4-dipyridine (anhyd)	106.3±2.8[c]	12.4±1.4	93.9	71.1±2.6
4,4-dipyridine·1.7H_2O	106.3±2.8 [c]	≈31.4±1.6	≈74.9±3.4	70.7±2.4

[a] Calculated using eq. (2-8);

[b] Sum of the fusion and vaporization enthalpies;

[c] From ref 26.

The vaporization enthalpy results measured and calculated for all the dipyridines and the sublimation enthalpy obtained from the sum of the vaporization and fusion enthalpy of 4-phenylpyrimidine are summarized in Table 2-13. The similarity in vaporization enthalpy obtained for both the hydrate and anhydrous forms of 4,4-dipyridine, the last column in this table, implies that the sublimation enthalpy reported for 4,4-dipyridine in the literature is likely for a hydrated form.[26] If this conclusion is correct, several additional comments apply. The sublimation enthalpies of 2,2-, 2,4- and 4,4-dipyridine were all measured by drop calorimetry.[26] Since the enthalpy measured by this apparatus includes the enthalpy associated with heating the sample from T = 298.15 K to the temperature of the calorimeter, $T = 368$ K, a sizable heat capacity adjustment must be applied. In this case it was estimated to be 12.8 kJ·mol^{-1} for all the dipyridine isomers.[26] The vaporization enthalpies for 2,2- and 2,4-dipyridine calculated from the sublimation enthalpies reported [26] and the values measured in this work are within experimental error of each other as noted in Table 2-13. If the sublimation enthalpy of the sample of 4,4-dipyridine was in fact accidentally measured on a hydrated form, as these results suggest, the heat capacity correction for the hydrated form should probably be somewhat larger than 12.8 kJ·mol^{-1}, resulting in a somewhat larger temperature adjustment. This could bring the vaporization enthalpy calculated, (≈74.9±3.4) kJ·mol^{-1}, even closer in line with the value measured in this work, (70.7±2.4) kJ·mol^{-1}.

Accepting for the moment that the sublimation enthalpy measured by drop calorimetry was in fact for a hydrated form of 4,4-dipyridine, the gas phase enthalpy of formation of 4,4-dipyridine would need to be revised. Ribeiro da Silva *et al.*[26] point out that 4,4-dipyridine was repeatedly sublimed before the samples were burned and that good carbon dioxide recoveries were obtained. Whether similar precautions were followed prior to the sublimation enthalpy measurements is not clear. What is also of some concern is that combustion of the samples was performed in a bomb calorimeter in the presence of 1 mL of water. If anhydrous 4,4-dipyridine absorbs water on standing, given the fact that that the fusion enthalpy of the hydrate is greater than that of the anhydrous material, this could also have had some impact on the resulting enthalpy of combustion, resulting in a combustion enthalpy somewhat lower than for the truly anhydrous form.

Table 2-14 lists the condensed and gas phase enthalpies of formation of the dipyridines reported by Ribeiro da Silva *et al.*[26] and those calculated using the sublimation enthalpies calculated in this work using eq. (2-8). The sublimation enthalpies of 2,2- and 2,4-dipyridine measured in this work (column 4) are well with experimental error of each other and with the results reported by Ribeiro da Silva *et al.*[26] (column 5). Our results also suggest that the sublimation enthalpy of 4,4-dipyridine is also within experimental error of the 2,2- and 2,4-isomers. The condensed phase enthalpy of formation of the 2,4-isomer is some 10 kJ·mol^{-1} larger than the value measured for 2,2- and 4,4-isomers.[26] This makes the 2,4-isomer the least stable of the three isomers. Also included in Table 2-14 are the results of theoretical calculations previously performed on the three isomers.[26] If 4,4-bipyridine is kinetically very hygroscopic, partial formation of a hydrate in the combustion calorimeter prior to combustion would result in a smaller condensed phase enthalpy of formation. The *ab initio* calculations would appear to most closely parallel the experimental results in this case. Otherwise the PM3 results appear most consistent with the enthalpy of formation for at least two of the three isomers.

Table 2-14. Comparison of Enthalpies of Formation of 2,2-, 2,4- and 4,4-Dipyridine in kJ·mol^{-1}at $T = 298.15$ K

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

[a] Ref 26; [b] Sum of $\Delta_{cr}{}^{l}H_m+\Delta_l{}^{g}H_m$; this work; [c] Average of runs 11, and 12.

2.5. Summary

The vaporization and fusion enthalpies and constants of eq. (2-6) for all the compounds evaluated in this study are summarized in Table 2-15. The vaporization enthalpy results for the most part appear in good agreement with literature values. The only discrepancy encountered is with 4,4-dipyridine. Our results suggest that the sublimation enthalpy in the literature is most consistent with the hydrated form of 4,4-dipyridine.

Table 2-15. A Summary of The Vaporization and Fusion Enthalpies and Constants of Equation (2-6) Evaluated in the Study

	$\Delta_l^g H_m$ (298 K) /kJ·mol^{-1}	$\Delta_{cr}^l H_m$ (T_{fus}) /kJ·mol^{-1}	A/K^3	B/K^2	C/K	D
tri-n-butylamine	62.7±1.3		30767110.1	-712464.53	-3836.038	10.769
2-phenylpyridine	68.4±1.9		82334650.2	-1199538.89	-2988.675	8.899
3-phenylpyridine	68.4±1.6		78066389. 6	-1137160.48	-3293.956	9.322
quinazoline	58.9±2.0		62950221.9	-1019157.75	-2388.439	8.073
(-)-nicotine	63.9±2.1		69850065.0	-1084705.54	-2782.671	8.667
4-phenylpyrimidine	68.8±2.5	18.8±0.3	82739965.4	-1191247.39	-3078.925	8.993
4,4-dipyridine (anh)	71.1±2.6	16.1±1.0	87876825.4	-1240023.92	-3205.124	9.104
4,4-dipyridine·1.7H_2O	70.7±2.4	35.5±0.5	88090511.1	-1246867.02	-3194.165	9.087
2-benzylpyridine	69.8±2.8		79549255.1	-1163591.12	-3291.65	9.325
2,4-bipyridine	70.9±1.6	17.4±0.4	89785140.7	-1256837.41	-3110.722	8.950
2,2-dipyridine	67.0±2.3		81725945.6	-1192649.71	-2825.351	8.600
9-methylcarbazole	79.4±3.2		119137844.7	-1531860.00	-3317.940	8.855
1,7-phenanthrolene	79.4±4.7	18.2±0.3	121578810.4	-1558844.12	-3192.849	8.625
4,7-phenanthrolene	80.8±4.8	21.8±0.5	123705709.5	-1579329.77	-3296.579	8.741

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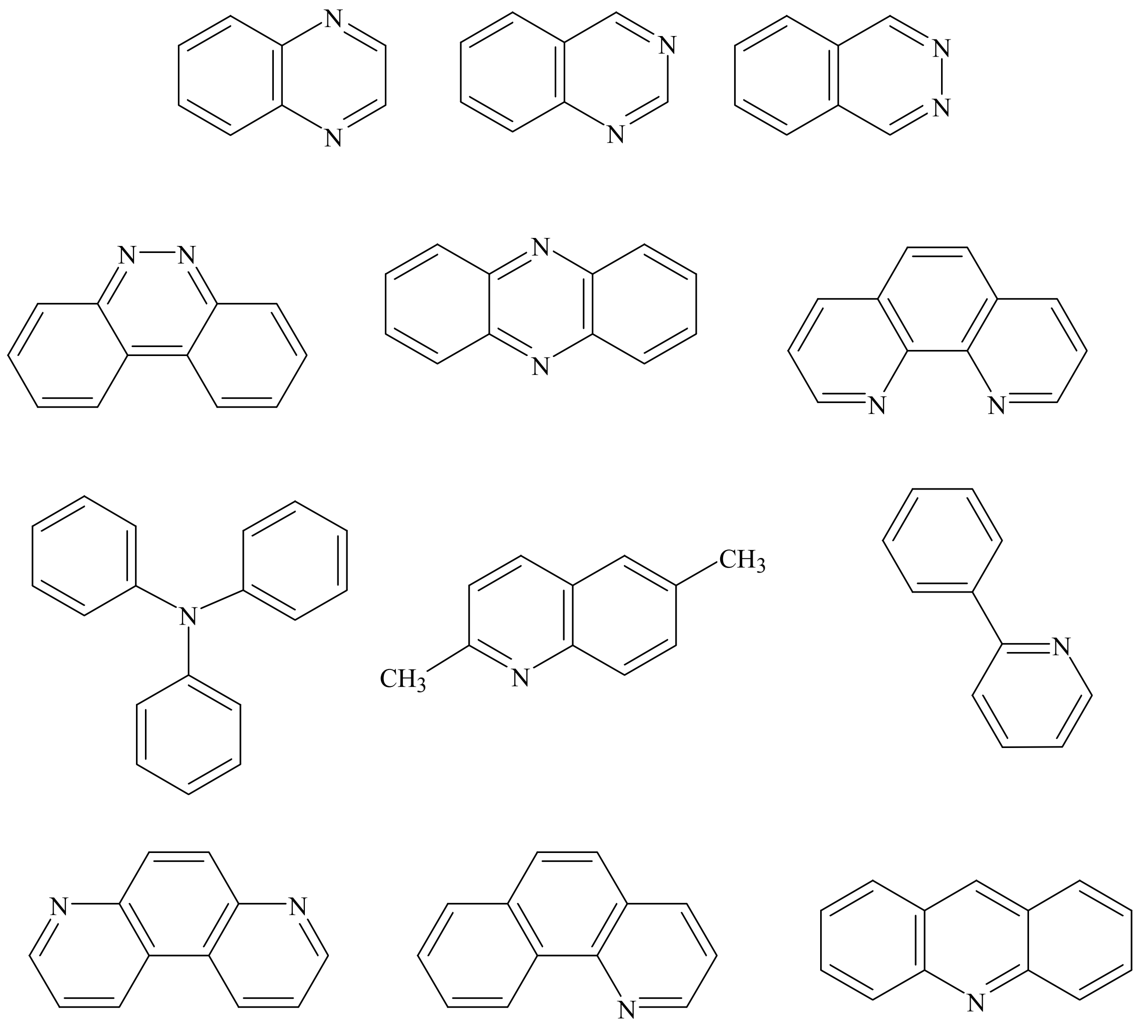
Chapter 3. Thermochemical Behavior of 1,2-Diazines

3.1. Introduction

Derivatives of pyrazine, pyrimidine and pyridazine comprise a set of diverse compounds, many of which are found in natural products and biological systems. In Chapter 2 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.This study is 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 both the compounds studied and those used as standards are illustrated in Figure 3-1. 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,[1] vaporization,[2] and fusion[3] enthalpies of triphenylamine have previously been reported. Our initial inclination was to use triphenylamine as one ofthe 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.



$[CH_3CH_2CH_2CH_2]_3N$

Figure 3-1. 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.

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 (Chapter 2). 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 condensed phase of aromatic 1,2-diazines. Pyridazine is the only liquid aromatic 1,2-diazine whose vaporization enthalpy has been measured.[4] However, the sublimation and fusion enthalpy of several isomeric crystalline aromatic heterocyclic 1,2-diazines have been measured. A summary of these results is reported in Table 3-1.

The second column of Table 3-1 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 Tables 3-1A and 3-1B to $T = 298.15$ K were achieved using equations (3-1) to (3-4). Eq. (3-1) was used to adjust sublimation enthalpies, eq. (3-2) was used to adjust fusion enthalpies and eq. (3-3) is the thermodynamic equality used to calculate vaporization enthalpies. Eq. (3-4) was used to adjust the vaporization enthalpy of triphenylamine reported in Table 3-1B to $T =$ 298.15 K. Equations (3-1), (3-2), and (3-4) have been used previously (Chapters 1 and 2) and have been shown to provide reasonable adjustments for temperature. The heat capacity terms required for these temperature adjustments are reported in Tables 3-1A and 3-1B and were evaluated by group additivity.[5,6]

Table 3-1. A 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	277/210.7	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	277/210.7	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 7; [b] Ref 8; [c] Ref 9, na in column three: not available; [d] Ref 10; [e] Ref 11; [f] Ref 12; [g] Ref 13; [h] Ref 14; [i] Ref 15; [j] Ref 1; [k] Ref 3; [l] Ref 2; [m] Ref 16.

$$\Delta_{cr}{}^{g}H_m(298.15\ \text{K})/\text{kJ·mol}^{-1} = \Delta_{cr}{}^{g}H_m(T_m) + [0.75 + 0.15\ C_p(\text{cr})/\ \text{J·mol}^{-1}\text{·K}^{-1}][\ T_m/\text{K} - 298.15\ \text{K}]/1000 \quad (3\text{-}1)$$

$$\Delta_{cr}{}^{l}H_m(298.15\ \text{K})/\text{kJ·mol}^{-1} = \Delta_{cr}{}^{l}H_m(T_{fus}) + [(0.15\ C_p(\text{cr}) - 0.26\ C_p(\text{l}))/\text{J·mol}^{-1}\text{·K}^{-1} - 9.83)]\ [(T_{fus}/\text{K} - 298.15]/1000 \quad (3\text{-}2)$$

$$\Delta_{l}{}^{g}H_m(298.15\ \text{K}) = \Delta_{cr}{}^{g}H_m(298.15\ \text{K}\ T_m) - \Delta_{cr}{}^{l}H_m(298.15\ \text{K}) \quad (3\text{-}3)$$

$$\Delta_{l}{}^{g}H_m(298.15\ \text{K})/\text{kJ·mol}^{-1} = \Delta_{l}{}^{g}H_m(T_m) + [(10.58 + 0.26 {*} C_p(\text{l})/\text{J·mol}^{-1}\text{·K}^{-1})(\ T_m/\text{K} - 298.15\ \text{K})]/1000 \quad (3\text{-}4)$$

Values in italics in Table 3-1 are considered to be unreliable. All of these data were obtained from the dissertation of G. D. Mills9 who measured a series of other compound 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. (3-3) in Table 3-1A differs by some 19 kJ·mol^{-1} from the value measured directly and adjusted to T = 298.15 K (Table 3-1B). Therefore, 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 3-1A, suggests that phthalazine does have a substantially larger vaporization enthalpy. Similarly, benzo[c]cinnoline also appears to have a larger value than either of its two 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 (Chapter 2).

3.2. Experiment

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 % 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 an HP 5890 Gas Chromatographs equipped with a split capillary injection port and 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. Helium was used as the carrier gas, cyclopentane used as solvent. Other experimental details are same as described in Chapters 1 and 2.

3.3. 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 3-2 and 3-3. 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. (3-5). Vapor pressures for 2,6-dimethylquinoline from T = (337 to 592) K are available in the form of the Wagner equation, eq. (3-6). The parameters for these equations are defined in Tables 3-2A and 3-2B. 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 3-3. For comparison, the vaporization enthalpies of acridine and 7,8-benzoquinoline were also adjusted to T = 298.15 K using eq. (3-4). These values, which are in good mutual agreement, are reported in column 5 of Table 3-3. 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 3-3, 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 (BT), eq. (3-7), have been evaluated previously by correlation-gas chromatography (Chapter 2). The parameters for this equation are defined in Table 3-2C.

$$\ln(p/p_o) = (1-T_b/T)\exp(A_o + A_1(T/K) + A_2(T/K)^2) \qquad (3\text{-}5)$$

$$\ln(p/p_c) = (1/T_r)[A_W(1-T_r) + B_W(1-T_r)^{1.5} + C_W((1-T_r)^{2.5} + D_W(1-T_r)^5] \qquad (3\text{-}6)$$

$$\ln(p/p_o) = A(T/K)^{-3} + B(T/K)^{-2} + C(T/K)^{-1} + D \qquad (3\text{-}7)$$

Table 3-2. Parameters of (A) the Cox Equation Used for Reference, (B) Wagner Equation, and (C) the Third-Order Polynomial

(A)

Cox Equation	A_o	A_1 T^{-1}	A_2*10^7 T^{-2}	T_b K	Range K
Acridine[17]	2.89594	-0.00111538	6.486	618.059	383 to 637
7,8-benzoquinoline[18]	2.88454	-0.00111802	6.6824	614.49	373 to 662

(B)

Wagner Equation [a]	A_W	B_W	C_W	D_W	T_c K	p_c kPa	Range K
2,6-dimethylquinoline[18]	-8.993312	3.594873	-4.63173	-2.907492	786	3480	337 to 592

(C)

	A/K^3	B/K^2	C/K	D	Range K
tri-n-butylamine	30767110	-712464.53	-3836	10.769	298 - BT
2-phenylpyridine	82334650	-1199538.89	-2988.7	8.899	298 - BT
4,7-phenanthrolene	123705710	-1579329.77	-3296.6	8.741	298 - BT

[a] $T_r = T/T_c$

Table 3-3. Vaporization Enthalpies in the Literature

Compound	$\Delta_l^g H_m(T_m\ K)$ $kJ \cdot mol^{-1}$	T_m K	C_{pl} $J \cdot mol^{-1} \cdot K^{-1}$	$\Delta_l^g H_m(298.15\ K)$		Ref
				$kJ \cdot mol^{-1}$ calc [a]	$kJ \cdot mol^{-1}$ lit.	
tri-n-butylamine					62.7±1.3	16
2,6-dimethylquinoline					67.07±0.16	19
2-phenylpyridine					68.4±1.9	16
7,8-benzoquinoline	72.99±0.3	360	278.1	78.11±1.0	77.23[b]	18
acridine	72.94±0.1	380	278.1	79.72±1.3	78.63[b]	18
4,7-phenanthrolene					80.8±4.8	16

[a] Literature data adjusted to $T = 298.15$ K using eq. (3-4);

[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.

3.4. Results and Discussion

The results of three sets of duplicate correlations are reported in Appendices C-1 and C-2 as runs 1-6. Equations below each run in Appendix C-2 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 slope and intercept associated with these correlations. Table 3-4 compares the results of the compounds used as unknowns to the values calculated in Table 3-1. 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 equation (3-3) 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 $\text{kJ}\cdot\text{mol}^{-1}$. Additionally, the value for triphenylamine (90.1 ± 0.4 $\text{kJ}\cdot\text{mol}^{-1}$) is in good agreement with the direct measurement of vaporization enthalpy by Forward *et al.* [2] (92.8 $\text{kJ}\cdot\text{mol}^{-1}$), but in much poorer agreement with the value of (73.7 ± 2.7) $\text{kJ}\cdot\text{mol}^{-1}$ calculated from the sublimation enthalpy reported by Steele.[1]

Table 3-4. A Summary of the Vaporization Enthalpies Evaluated in This Work

	$\Delta_l^gH_m$(298 K)[a]/ kJ·mol^{-1}				$\Delta\Delta_l^gH_m$(298 K)
	runs 1/3	runs 2/4	average[a]	lit(avg)[b]	kJ·mol^{-1}
phthalazine	*67.3±2.7*	*67.3±0.5*	*67.3±1.6*	71±1.9	3.7±2.5
quinoxaline	58.6±2.3	58.8±0.4	58.7±1.4	56.5±2.0	-2.2±2.4
quinazoline	59.5±2.3	59.7±0.4	59.6±1.4	61.1±1.1	1.5±1.8
phenazine	76.6±1.0	76.7±0.3	76.7±0.7	78.8±2.2 [c]	2.1±2.3
			76.7±0.7	80.7±2.2 [c]	4.0±2.3
benzo[c]cinnoline	*81.9±1.1*	*81.9±0.4*	*81.9±0.8*	89.2±2.3	7.3±2.4
triphenylamine	90.2±1.2	90.1±0.4	90.2±0.8	92.8±3.6	2.6±3.7
1,10-phenanthroline	86.2±1.1	86.1±0.4	86.1±0.8	*91.6* [d]	*5.5*
pyridazine			*46.4±2.0* [e]	53.5±0.4[f]	7.1±2.0

[a] Values in italics are considered unreliable; [b] The uncertainty reported is an average of the deviations reported in Table 3-1 except where noted otherwise; [c] The uncertainty represents the standard deviation of four runs associated with each fusion enthalpy reported in Table 3-1; [d] Ref 9; [e] Ref 19; [f] Ref 4.

As a further check on the reliability of these measurements, the vapor pressures and boiling temperatures of the compounds listed in Table 3-5 were evaluated using the vapor pressures of the compounds listed in Tables 3-2A to 3-2C as standards. Values of ln(t_o/t_a) were calculated using the slopes and intercepts reported in Appendix C-2 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 used in the run. A typical calculation is illustrated in Table 3-5 for runs 3 and 4 at T = 298.15 K. The correlation equation generated at this temperature is reported as eq. (3-8) 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. (3-7). The constants for this equation for each compound evaluated are listed in Table 3-6. 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 (Chapter 1).No conclusions can be inferred from the results obtained for benzo[c]cinnoline.

Table 3-5. The Correlation of $\ln(t_o/t_a)$ with $\ln(p/p_o)$ for Runs 3 and 4 at T = 298.15 K

	$\ln(t_o/t_a)_{avg}$	$\ln(p/p_o)_{lit}$	$\ln(p/p_o)_{calc}$
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

$$\ln(p/p_o)_{calc} = (1.413 \pm 0.016)\ln(t_o/t_a)_{avg} - (1.014 \pm 0.046) \qquad r^2 = 0.9997 \qquad (3\text{-}8)$$

Table 3-6. Constants of Equation (3-7) and Predicted Boiling Temperatures Evaluated [a]

	A/K^3	B/K^2	C/K	D	BT_{calc} [b] K	BT_{lit} [c] K
quinoxaline	61954207.1	-1012863	-2367.266	8.211	503.5	493.2-496.2
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. (3-7) 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 from SciFinder Scholar; [f] Ref 2.

With the exception of triphenylamine and pyridazine, the compounds listed in Table 3-4 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.*[2] who measured the vapor pressures of triphenylamine over the temperature range T =(473 to 573) K. Figure 3-2 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. (3-7). The comparison is remarkably good.

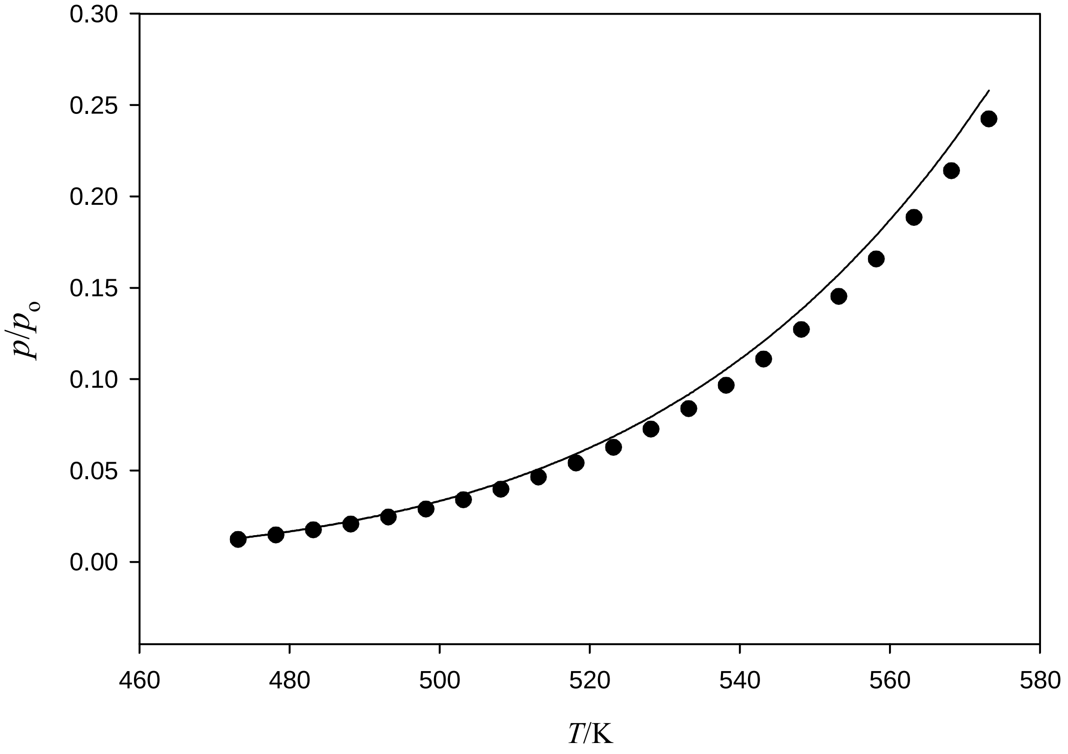


Figure 3-2. A comparison of the of vapor pressure of liquid triphenylamine reported previously by Forward *et al.* (●) with the values calculated by correlation (—); p_o = 101.325 kPa

While pyridines and other diazines cannot be used as vaporization enthalpy standards, 1,2-diazines should be appropriate vaporization enthalpy standards for other aromatic 1,2-diazines. For example, a mixture of 1,2-diazines, with pyridazine, phthalazine, and benzo[c]cinnoline used as standards, was examined by correlation-gas chromatography to estimate vaporization enthalpy of 3-methylpyridazine for which no literature data are available. The results are summarized in Appendix C-2, runs 5 and 6, by corresponding correlation equations below each run. The average vaporization enthalpy value calculated for 3-methylpyridazine is (56.0±4.4) kJ·mol^{-1}.The larger uncertainty in these correlations is probably related to the larger uncertainty associated with calculating vaporization enthalpies using eq. (3-3).

3.5. Summary

The vaporization enthalpies, evaluated from the difference in sublimation and fusion and by correlation-gas chromatography, clearly indicate an enhanced intermolecular interaction in aromatic1,2-diazines of approximately 6 kJ·mol^{-1} not present in other diazine isomers. Whether an interaction of similar magnitude is observed in analogous five-membered systems, or in acyclic 1,2-diazines, and what role if any stereochemistry plays in the acyclic analogs is discussed in the following chapter.

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Chapter 4. Vaporization Enthalpies and Vapor Pressures of 1-Substituted Imidazoles and Pyrazoles and related compounds

4.1. Introduction

The study of systems that self-assemble and the interactions responsible for self-assembly 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 but considerably less is known experimentally, about the magnitude of weaker interactions at T = 298.15 K, particularly in molecules found in biological systems. While the magnitude of the vaporization enthalpy can provide useful information regarding these interactions, 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. The presence of solvent obviously complicates any evaluation of the thermodynamics of self-association in solution

In Chapters 2 and 3 we examined the vaporization enthalpies of a series of aromatic diazines by correlation–gas chromatography and observed that compounds with adjacent nitrogens have anomalously larger vaporization enthalpies than other aromatic diazines. The 1,2-diazines examined included pyridazine and 3-methylpyridazine, both liquids, and phthalazine and benzo[c]cinnoline, two crystalline materials. While the literature 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 literature vaporization enthalpies of the aromatic 1,2-diazines consistently exceeded the values calculated by C-GC by approximately 6 kJ·mol^{-1}. The results suggested that aromatic 1,2-diazines have substantially larger intermolecular interactions than other isomeric diazines. 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 magnitude of interaction between the systems of interest and those of the reference compounds chosen as standards.

This study examines a series of model compounds, derivatives of which are commonly found in biological systems. The structures of the compounds used either as standards or as the subject of this study are provided in Figure 4-1.The compounds of this study include some 1-substituted imidazoles and pyrazoles, and 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-methyl- and 1-phenylpyrazole, and *trans*-azobenzene. The 1-substituded imidazoles were chosen because some physical properties available for these materials, also suggest the presence of strong intermolecular interactions. For example, the boiling temperature of 1-methyl and 1-ethylimidazole ($C_4H_6N_2$ and $C_5H_8N_2$), T_b = 478 and 481 K, respectively, are very similar to the boiling

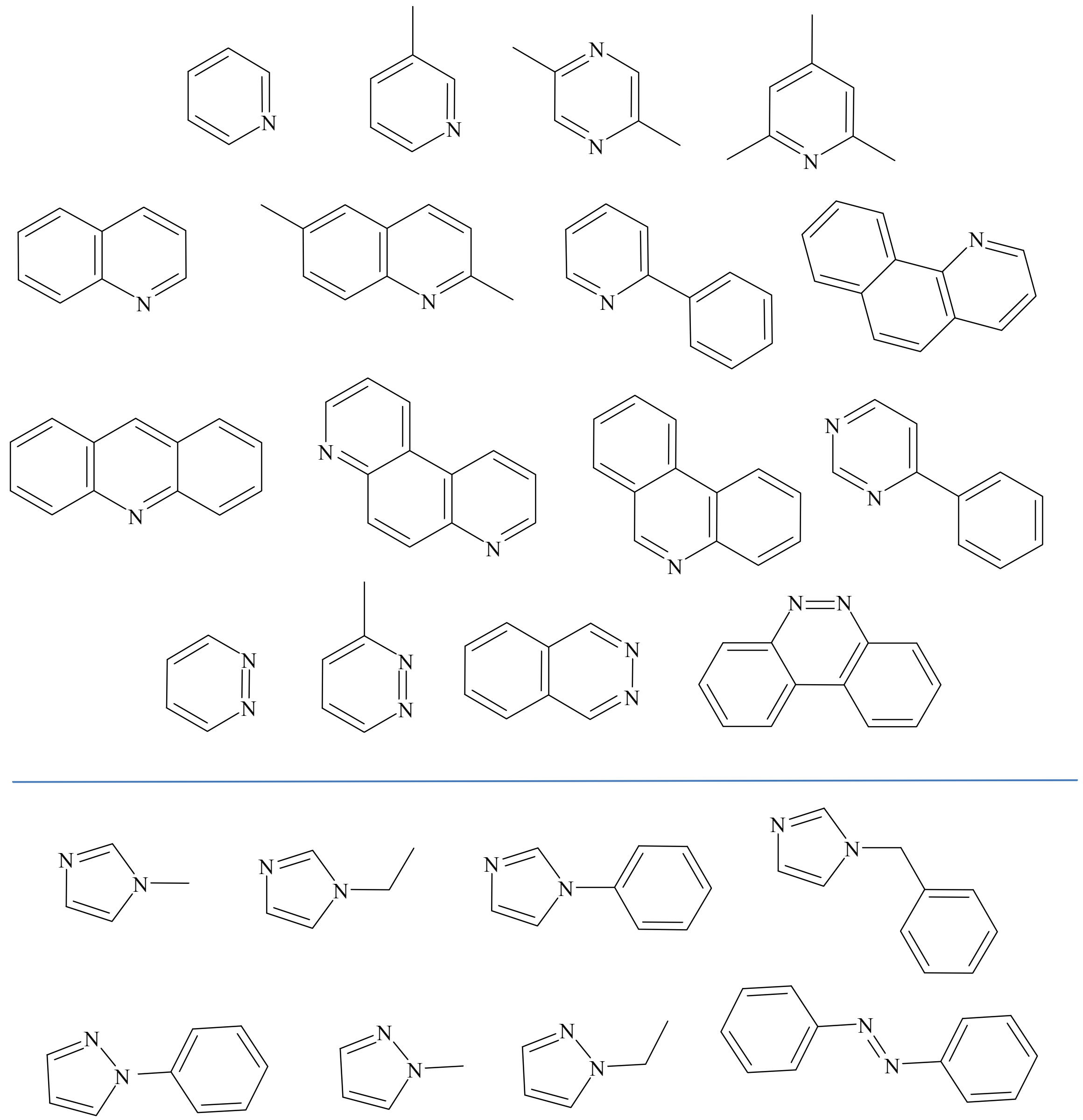

Figure 4-1. From left to right, top to bottom:

Compounds used as standards (top): pyridine, 3-picoline, 2,5-dimethylpyrazine, 2,4,6-trimethylpyridine, quinoline, 2,6-dimethylquinoline, 2-phenylpyridine, 7,8-benzoquinoline, acridine, 4,7-phenanthroline, phenanthridine, 2-phenylpyrimidine, pyridazine, 3-methylpyridazine, phthalazine, and benzo[c]cinnoline.

Compounds evaluated in this study (bottom): 1-methylimidazole, 1-ethylimidazole, 1-phenylimidazole, 1-benzylimidazole, 1-phenylpyrazole, 1-methylpyrazole, 1-ethyl-pyrazole, and *trans*-azobenzene.

temperatures of two compounds previously found to behave anomalously (Chapter 3), pyridazine ($C_4H_4N_2$, T_b = 481 K) and 3-methylpyridazine ($C_5H_6N_2$, T_b = 487 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 (Chapter 3) to determine what role if any stereochemistry and/or cyclization has on the vaporization enthalpy.

4.2. Experiment

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. 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 DB5 MS column. Helium was used as the carrier gas, cyclopentane and methanol were used as solvents. Other correlation-gas chromatographic experimental details are same as described in Chapter 1.

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 4-1.

Table 4-1. Fusion Enthalpies Measured by DSC

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

[a] Onset temperature

4.3. Vaporization Enthalpies and Vapor Pressures of the Standards

Adjustments of the enthalpies reported in Table 4-2to $T = 298.15$ K were achieved using equations (4-1) to (4-4). Eq. (4-1) was used to adjust sublimation enthalpies, eq. (4-2) was used to adjust fusion enthalpies, and eq. (4-3)was used to adjust vaporization enthalpies from the mean temperature of measurement to $T = 298.15$ K. Eq. (4-4) is the thermodynamic equality used to calculate vaporization enthalpies from sublimation and fusion enthalpies. Equations (4-1), (4-2), and (4-3) have been used in previous chapters and shown to provide reasonable adjustments for temperature.The heat capacity terms required for these temperature adjustments, C_p(cr) and C_p(l), are reported in Table 4-2 and were evaluated by group additivity.[1,2]

$$\Delta_{cr}{}^{g}H_m(298.15\text{ K})/(kJ \cdot mol^{-1}) = \Delta_{cr}{}^{g}H_m(T_m) + [0.75 + 0.15\, C_p(cr)/(J \cdot mol^{-1} \cdot K^{-1})][\, T_m/K - 298.15\text{ K}]/1000 \qquad (4\text{-}1)$$

$$\Delta_{cr}{}^{1}H_m(298.15\text{ K})/(kJ \cdot mol^{-1}) = \Delta_{cr}{}^{1}H_m(T_{fus}) + [(0.15\, C_p(cr) - 0.26\, C_p(l))/(J \cdot mol^{-1} \cdot K^{-1}) - 9.83)]\,[T_{fus}/K - 298.15]/1000 \qquad (4\text{-}2)$$

$$\Delta_{l}{}^{g}H_m(298.15\text{ K})/(kJ \cdot mol^{-1}) = \Delta_{l}{}^{g}H_m(T_m) + [(10.58 + 0.26 * C_p(l)/(J \cdot mol^{-1} \cdot K^{-1}))(\, T_m/K - 298.15\text{ K})]/1000 \qquad (4\text{-}3)$$

$$\Delta_{l}{}^{g}H_m(298.15\text{ K}) = \Delta_{cr}{}^{g}H_m(298.15\text{ K}) - \Delta_{cr}{}^{1}H_m(298.15\text{ K}) \qquad (4\text{-}4)$$

Available literature vaporization enthalpy values of the compounds in this study are reported in Table 4-2. Liquid vapor pressures forquinoline, reported from$T$ = 298 to 559 K,[3] acridine,[4] reported from T = (383 to 637) K and 7,8-benzoquinoline,4 reported from T = (373 to 672) K, are available in the form of the Cox equation, eq. (4-5).Liquid vapor pressures for 2,6-dimethylquinoline,[5] reported from T = (337 to 592) K are available in the form of the Wagner equation, eq. (4-6). The parameters for these equations are defined in Table 4-3A and 4-3B.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, reported in the last column of Table 4-2, 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. (4-3). These values, which are in good mutual agreement, are reported in column 5 of Table 4-2. The vapor pressures of acridine, 7,8-benzoquinoline and 2,6-dimethylquinoline used below were 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 (Chapter 2). The vaporization enthalpies are reported in Table 4-2 and constants for the calculation of liquid vapor pressure using eq. (4-7) are provided in Table 4-3C. Unless noted otherwise, p_o refers to 101.325 kPa, T_r refers to the reduced temperature, and p_c and T_c refers to the critical pressure and temperature, respectively. The experimental vapor pressures of 2,4,6-trimethylpyridine[6] and 2,5-dimethylpyrazole6 were also fit to equation (4-7).

$$\ln(p/p_o) = (1\text{-}T_b/T)\exp(A_o + A_1(T/K) + A_2(T/K)^2) \qquad (4\text{-}5)$$

$$\ln(p/p_c) = (1/T_r)[A_W(1\text{-}T_r) + B_W(1\text{-}T_r)^{1.5} + C_W((1\text{-}T_r)^{2.5} + D_W(1\text{-}T_r)^5] \qquad (4\text{-}6)$$

$$\ln(p/p_o) = A(T/K)^{-3} + B(T/K)^{-2} + C(T/K)^{-1} + D \qquad (4\text{-}7)$$

Table 4-2. Literature Vaporization Enthalpies

Compound	$\Delta_l^g H_m(T_m/K)$ (kJ·mol^{-1})	T_m /K	$C_{p(l)}$ (J·mol^{-1}·K^{-1})	$\Delta_l^g H_m$(298 K) (kJ·mol^{-1}) calc [a]	$\Delta_l^g H_m$(298 K) (kJ·mol^{-1}) lit	ref
pyridine					40.21±0.1	7
3-picoline					44.47±0.07	8
2,5-dimethylpyrazine	43.6	357	185.4	47.04±1.9		6
2,4,6-trimethylpyridine	47.2	356	214.9	51.0±1.0		6
quinoline					59.31±0.21	3
2,6-dimethylquinoline					67.07±0.16	9
2-phenylpyridine					68.4±1.9	10
7,8-benzoquinoline	73.0±0.3	360	278.1	78.11±1.0	77.23[b]	4
acridine					78.63[b]	4
4,7-phenanthroline					80.8±4.8	10
phenanthridine					80.14	4
4-phenylpyrimidine					68.8±2.5	10
pyridazine					53.5±0.4	11
3-methylpyridazine					56.1±4.4	12
phthalazine					72.8±5.6	12
benzo[c]cinnoline					89.2±2.3	12
1-methylpyrrolidine						13
1-methylpyrrole	37.7±0.05	353	150.7	40.4±0.8		14
1-methylpyrrole	38.8±0.1	339	150.7	40.8±0.7		15
1-methylindole					62.2±1.6	16

[a] Literature data adjusted to $T = 298.15$ K using equation (4-3);

[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 $T = 298.15$ K.

Table 4-3. Parameters of the (A) Cox Equation Used for Reference [a], (B)Wagner Equation [a], and (C) Third-Order Polynomial, eq. (4-7)

A	A_o	A_1/T^{1}	A_2*10^7/T^{-2}	T_b/K	Range/K
Quinolone 3	2.85461	-0.00130236	9.3118	510.298	298 - 559
acridine 4	2.89594	-0.00111538	6.486	618.059	383 - 637
7,8-benzoquinoline 4	2.88454	-0.00111802	6.6824	14.49	373 - 672

B	A_W	B_W	C_W	D_W	T_c/K	p_c/kPa	Range/K
2,6-dimethylquinoline 9	-8.99331	3.59487	-4.63173	-2.90749	786	3480	337 - 592

C	A/K^3	B/K^2	C/K	D	Range/K
2-phenylpyridine [10]	82334650	-1199538.89	-2988.7	8.899	298 - T_b
4,7-phenanthroline [10]	123705710	-1579329.77	-3296.6	8.741	298 - T_b
4-phenylpyrimidine [10]	82739965	-1191247	-3078.93	8.993	298 - T_b
2,4,6-trimethylpyridine[b]	-16070378	870548	-6636.067	12.401	287 -423
2,5-dimethylpyrazine[b]	141666180	-1638517	524.965	5.924	302 -411

[a] $T_r = T/T_c$.

[b] Experimental data from ref 6 fit to equation (4-7)

4.4. Results and Discussion

4.4.1. Vaporization Enthalpies

The retention times measured for all analytes are reported in the Appendix D-1. The correlations between enthalpies of transfer measured for each mixture and available vaporization enthalpy values are reported in Appendix D-2. The equation characterizing the correlation is given below each run. The uncertainties (±σ) reported for the estimated vaporization enthalpies 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. Since both *trans*-azobenzene and 1-benzylimidazole are solids at $T = 298.15$ K, Table 4-4 summarizes the necessary thermochemical properties needed to calculate the vaporization enthalpy of these two compounds using eq. (4-4).[17- 23]

The results for *trans*-azobenzene are summarized Table 4-5. The value of 74.9±0.7 kJ·mol^{-1} compares quite favorably with 74.7±1.6 kJ·mol^{-1} calculated from the difference between the sublimation and fusion enthalpies reported in Table 4-4. The results suggest that the anomalous behavior observed in 1,2-diazines requires a *cis*-arrangement of the two adjacent nitrogens. It is not presently possible to evaluate what role aromaticity and ring constraints have on the enhanced effect observed.

Table 4-4. A Summary of the Sublimation, Vaporization and Fusion Enthalpies of *trans*-Azobenzene and 1-Benzylimidazole

	$\Delta_{cr}^{g}H_m$(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})
trans-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 (298.15K),[17] 93.6 (298.15 K),[18] 94.9 kJ·mol^{-1} (323 K)[19]adjusted to T = 298.15 K using eq.(4-1); the uncertainty represents two standard deviations of the mean. [b] The mean of 22.65 (341.8 K),[19] 22.52 (341.0 K),[20] 22.53 kJ·mol^{-1}(341.1K).[21] [c] Literature value.23 [d] This work, see Table 4-1.

Table 4-5. A Summary of the Vaporization Enthalpies Evaluated in Runs 1-7 at 298 K

	$\Delta_l^g H_m$ (kJ·mol^{-1})				$\Delta_l^g H_m$ (kJ·mol^{-1})	$\Delta\Delta_l^g H_m$ (kJ·mol^{-1})
	Runs 1/3	Runs 2/5	Runs 4/6	Average[a]	[lit]	
trans-azobenzene	74.9±0.7			74.9±0.7	74.7±1.6 [b]	-1.2±1.7
1-phenylpyrazole	63.3 ±0.5	63.5±1.2	63.5±4.9 63.5±4.8	63.5±2.9	*70.2±3.4*[22]	*6.7±4.5*
1-methylimidazole		48.2±2.6	49.4±4.3	48.8±3.5	*64.7±1.3,* [23] 55.6±0.6 [24] 54.9±0.5 [26]	*15.9±3.7* 6.8±3.6 6.1±3.6
1-ethylimidazole		51.4±2.7	52.0±4.4	51.7±3.6	*66.0±3.9* [25]	*14.6±5.3*
1-phenylimidazole	67.5±0.3	67.7±1.3	67.7±5.0 67.8±4.9	67.7±2.9	*84.6±3.7* [22]	*16.9±4.7*
1-benzylimidazole			72.2±5.2 72.4±5.1	72.3±5.2	83.0±1.0 [23]	10.7±5.3
1-methylpyrazole				41.6±2.9 [c]	42±0.17 [d]	0.4±2.9

[a] The uncertainty reported is an average of the deviations reported in columns 2-4.
[b] See Table 4-4. [c] See run 7 in the Appendix D-1, D-2. [d] Estimated using the relationship existing between ΔH_{vap} and T_b in tertiary amines and N-methylazoles, ref 26.

Results on the 1-substituted imidazoles and pyrazoles measured in runs 2-7 as unknowns are summarized in Table 4-5 and compared to literature values. Significant discrepancies are observed between the literature values for the 1-substituted imidazoles and 1-phenylpyrazole. The standards used in this work do not appear to be appropriate for the five-membered ring heterocycles of this study (or at least for N-alkylimidazoles), but they do provide a measure of the enhanced intermolecular interaction that must be present in those molecules.

The comparison of the C-GC and literature results listed in Table 4-5 can be interpreted differently depending on the literature source. On the one hand, if we use experimental values measured by Da Silva et al. (values in italics),[22,23,25]then the last column in Table 4-5 suggests that the enhanced intermolecular interaction is worth approximately 7 $kJ\cdot mol^{-1}$for 1-phenylpyrazole and about 14 $kJ\cdot mol^{-1}$ for the imidazoles, with the latter being considerably larger than the 6 $kJ\cdot mol^{-1}$ reported previously for the aromatic 1,2-diazines. However, there is a big discrepancy between experimental vaporization enthalpy for 1-methylimidazole reported by Da Silva[23](64.7 ± 1.3 $kJ\cdot mol^{-1}$)and two other values cited by two different sources. The vaporization enthalpy of 55.6 ± 0.6 $kJ\cdot mol^{-1}$, measured by transpiration,has just been published by Verevkin *et al.* in 2011, [24] and it is in a very good agreement with the value of 54.9 ± 0.5 $kJ\cdot mol^{-1}$measured previously by use of an adiabatic calorimeter by Catalan et al.[26] These two values differ from the one estimated by correlation by 6-7 $kJ\cdot mol^{-1}$ which is same as the difference reported previously for 1,2-diazines. It is also possible that the other enthalpy values for 1-alkylimidazoles measured by DaSilva et al.[22,23,25]are overestimated. However, there is no other experimental data available at the moment for comparison.

For 1-methylimidazole, vaporization enthalpy was also estimated by Benoit et al.[27] from the extrapolated linear relation between ΔH_{vap} and normal boiling points, T_b, given by Wadso[28] for tertiary amines, since they found that relation to also hold for the cyclic compounds, including pyrrole and 1,2-diazine. The estimated value is 54 $kJ\cdot mol^{-}$

[1]and it's in perfect agreement with enthalpies measured by Catalan[26] and by Verevkin. [24] Catalan et al. also used the linear relationship observed between ΔH_{vap} and T_b in tertiary amines and N-methylazoles to estimate the enthalpy of vaporization of 1-methylpyrazole.[26] Their estimated vaporization enthalpy of 42±0.17 kJ·mol^{-1} matches remarkably well the value calculated by C-GC in run 7 (last row of Table 4-5), which suggests that 1-methylpyrazole does not show an enhanced interaction and may behave normally.

An examination of the vaporization enthalpies reported by Da Silva et al. (values in italics in Table 4-5) reveals that all imidazoles with the exception of 1-benzylimidazole were evaluated using drop calorimetry.[22,23,25] 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 and capillary tube from *T* = 298 K to the temperature of the calorimeter. For 1-phenylimidazole and 1-phenylpyrazole, for example, the heat capacity corrections which were estimated, amounted to approximately 12 kJ·mol^{-1}.[22] The uncertainty reported by these authors [22] represents the precision of the calorimetric results and does not include any uncertainty associated with the heat capacity adjustments.

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-methylpyrrole, and 1-methylindole were evaluated using several six-membered ring heterocycles as standards. The retention time data are reported in the Appendix D-1 (run 8). Information and the results are summarized in the last column of Table 4-6. 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 position 3 of the ring seems to be the source of the discrepancies in vaporization enthalpy observed in Table 4-5. Ring size does not appear to play a significant role.

Table 4-6. Vaporization Enthalpies of Some Five-Membered Ring Heterocycles

Run 8	slope T/K	intercept	$\Delta_{sln}{}^{g}H_m$ (473K) kJ·mol^{-1}	$\Delta_{l}{}^{g}H_m$(298 K) kJ·mol^{-1} [lit][a]	$\Delta_{l}{}^{g}H_m$(298 K) kJ·mol^{-1} [calc]/[lit][a]
N-methylpyrrolidine	-2939.3	8.848	24.44		36.6±2.4/34.2±0.7
N-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	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
N-methylindole	-5267.8	11.125	43.79		61.1±3.1/62.2±1.6

[a] See Table 4-2.

4.4.2. Vapor Pressures

A test used previously to corroborate the appropriateness of the compounds used as standards, was to correlate the temperature dependence of retention time with experimental vapor pressures when available. In cases where the selection of standards has been appropriate, the vapor pressures obtained by correlation when fit to eq. (4-7), provided parameters that gave upon extrapolation, frequently to p = 101.325 kPa, good agreement with reported boiling temperatures. In the case of aromatic 1,2-diazines where the standards chosen were not appropriate, the vapor pressures obtained by correlation, fit to the third order polynomial, eq. (4-7), consistently predicted much lower boiling temperatures. The predicted boiling temperatures in this case were observed to be more than T = 40 K lower than the experimental values. Since the vaporization enthalpy of *trans*-azobenzene obtained in run 1 is in good agreement with the literature value, according to what has previously been observed, a boiling temperature in reasonably good agreement with experiment would be expected. In the case of imidazoles (and possibly pyrazoles), runs 2-6, substantial differences between predicted and experimental values would be expected.

Since different standards have been used in runs 2-6 to evaluate the vaporization enthalpies of the pyrazoles and imidazoles studied, several independent correlations using experimental data were performed as a function of temperature. The quality of the correlations obtained between $\ln(p/p_o)$ and $\ln(t_o/t_a)$, as judged by the correlation coefficients (r^2) at T = 298.15 K, is typical of the results obtained at elevated temperatures. For runs 1, and 4, the correlation was performed over 30 K intervals from T = 298.15 K to T= (540 and 510) K, respectively and for runs 2, 3 and 6, over a T = 20 K interval from T =(298.15 to 500) K. The resulting values of $\ln(p/p_o)_{calc}$ calculated for each imidazole and pyrazole as a function of temperature were then fit to the third order polynomial, eq. (4-7). The constants for this equation for each compound evaluated are listed in columns 2-5 of Table 4-6. This equation was then used to predict each respective boiling temperature at the pressures indicated.

The vapor pressures of *trans*-azobenzene evaluated by the constants of correlation equation (4-7) from run 1 are in good agreement with the literature as is the boiling temperature predicted by eq. (4-7). The comparison, shown in Figure 4-2 compares the liquid vapor pressure obtained by correlation-gas chromatography to direct experimental measurements using an inclined piston apparatus over the temperature range T = (436 to

522*)* K. The experimental boiling temperature predicted by extrapolating the vapor pressures using eq. (4-7) is T = 577.5 K and can be compared to a value of 566.3 K reported in the Aldrich Catalog and a value of 573.1 K reported by Steele *et al*[17] (Table 4-6).

Liquid vapor pressures for the imidazoles and pyrazoles studied are not available. However boiling temperatures at various pressures are reported in SciFinder for each compound under experimental properties.Boiling temperatures reported at reduced pressures are often not as reliable as those reported at p = 101.325 kPa, presumably because of uncertainties in the control and measurement of pressure. Analogously to *trans*-azobenzene, the vapor pressure results for these compounds obtained from the correlation were fit to eq. (4-7) resulting in the constants reported in Table 4-6. Eq. (4-7) was then used to predict boiling temperatures. The boiling temperatures predicted for 1-methylimidazole, 1-ethylimidazole and 1-benzylimidazole are considerably lower than those measured experimentally, similar to what has been previously observed for the 1,2-diazines.The boiling temperatures predicted for 1-phenylpyrazole are in good agreement with the literature values. This suggests that the vapor pressures obtained for 1-phenylpyrazole as a function of temperature are reasonable, which in turn confirms the magnitude of the vaporization enthalpy measured by correlation–gas chromatography and suggests that the literature value may be in error.

Table 4-6. Constants of Equation (4-7) and Predicted/Experimental Boiling Temperatures at Various Pressures

Compound/Run	A/K^3	B/K^2	C/K	D	$T_{\mathrm{b\,calc}}/K$[a]	$T_{\mathrm{b\,lit}}/K$	p/kPa	ΔT_b
trans-azobenzene/1	97537878	-1348892.8	-3256.73	9.171	577.5	566.2[b]	101.3	11.3
					577.5	573.1[c]	101.3	4.4
1-methylimidazole/6	10705718	-484433.8	-3080.04	9.836	423.3	471.2	101.3	47.9
1-ethylimidazole/6	23783823	-609685.8	-2994.39	9.559	444.2	481	101.3	36.8
1-phenylpyrazole/2,3	64345662	-1009008.7	-3036.33	9.152	412.3	415.15[b]	4.0	2.85
					387	379.2[d]	1.3	7.8
					376	379.2[d]	0.8	3.2
1-phenylpyrazole/4	61510639	-980319.7	-3143.98	9.262	412.8	415.15[b]	4.0	2.35
					387.2	379.2[d]	1.3	8
					376.6	379.2	0.8	2.6
1-phenylimidazole/2,3	76046606	-1123368.6	-3169.50	9.191	542.1	549.15[d]	101.3	7.05
1-phenylimidazole/4	73397000	-1097203.8	-3265.66	9.294	542.2	549.15[d]	101.3	6.95
1-phenylimidazole/6	73824799	-1099641.6	-3271.63	9.314	542.1	549.15[d]	101.3	7.05
1-benzylimidazole/4	83592171	-1199161.4	-3457.17	9.440	564	583[b]	101.3	19
1-benzylimidazole/6	82920622	-1191985.3	-3507.75	9.520	563	583[b]	101.3	20

[a] Calculated boiling temperature using eq. (4-7) at the pressure indicated in the 8th column.
[b] Boiling temperatures from the 2009-10 Aldrich Catalog. [c] Reference 17. [d] Experimental properties from SciFinder Scholar.

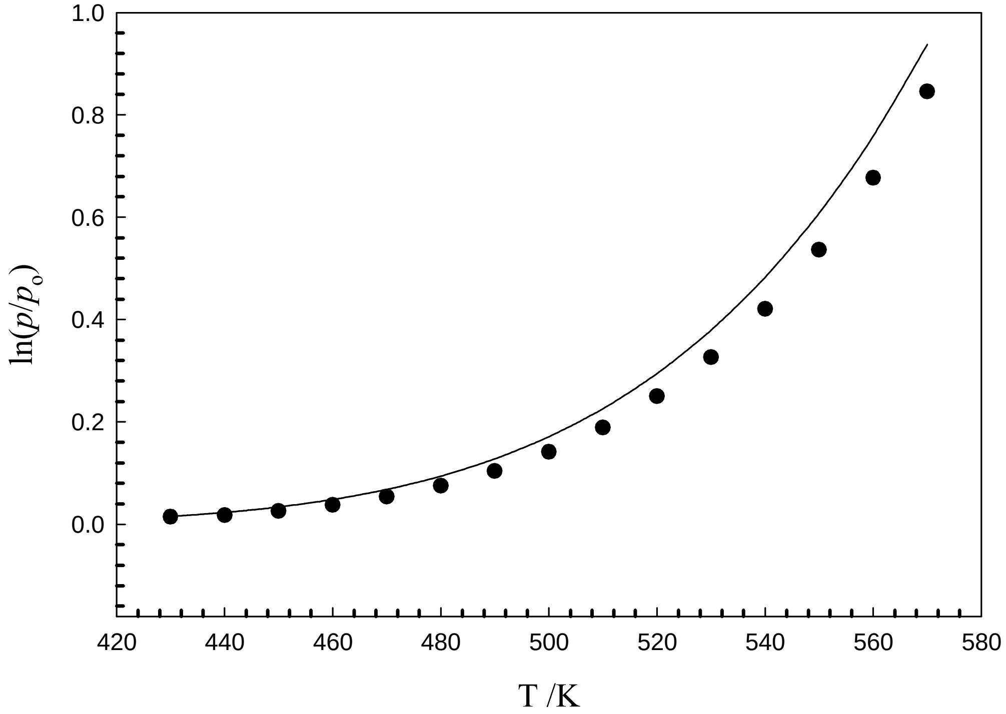

Figure 4-2. A comparison of the vapor pressure of liquid *trans*-azobenzene measured directly (●)[11]and by correlation (—).

The results obtained for 1-phenylimidazole are surprising. Boiling temperature difference is only 7 K. This result suggests that in some instances, prediction of boiling temperature may not always be a rigorously good criterion to use in corroborating the appropriateness of the compounds used as standards.

4.6. Summary

These results obtained for *trans*-azobenzene suggest that anomalous behavior observed in the aromatic 1,2-diazines must require a *cis*- configuration of the two nitrogens atoms. No conclusions are drawn on the importance of aromaticity since all heterocycles of this study can be considered as containing 6 π 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 that we observed with imidazoles. The magnitude of this enhanced effect in imidazoles, approximately 6-7 $kJ \cdot mol^{-1}$, seems to be consistent with the one observed previously in 1,2-diazines. Unlike imidazoles, pyrazoles are likely to behave normally.However, experimental vaporization enthalpies of 1-methylpyrazole and 1-phenylpyrazole need to be reevaluated in order to consolidate this conclusion.

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Chapter 5. Vaporization Enthalpies and Vapor Pressures 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

5.1. 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. In Chapters 1,2,3,4 we examined 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.[1-3] Pyridazine ($\Delta_l^g H_m(298\,\mathrm{K})$, 53.5 kJ·mol^{-1})[4] and 1-methylimidazole ($\Delta_l^g H_m(298\,\mathrm{K})$, 55.6 kJ·mol^{-1}),[5,6] for example have considerably larger vaporization enthalpies when compared to substances quite similar in size or structure such as pyrimidine ($\Delta_l^g H_m(298\,\mathrm{K})$ 41.0 kJ·mol^{-1})[1]. It has been demonstrated 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 (Chapter 3) whereas *trans*-azobenzene, an acyclic relative of benzocinnoline, does not (Chapter 4).

In this study we examine the vaporization enthalpy of six compounds with some structural features similar to *N*-alkylimidazoles. 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. Structures of these materials are provided in Figure 5-1. These materials have been evaluated by correlation-gas chromatography using the heterocycles provided in Figure 5-2 as standards. Figure 5-2 also provides structures for the other materials mentioned above.

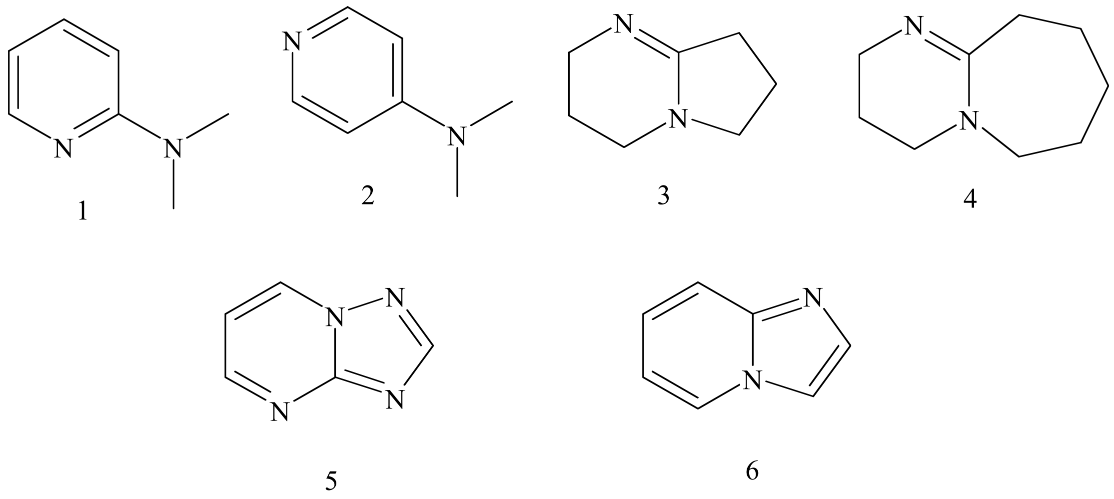

Figure 5-1. Compounds from left to right, top to bottom: 2-(*N*,*N*-dimethylamino)pyridine (1); 4-(*N*,*N*-dimethylamino)pyridine (2); 1,5-diazabicyclo[4.3.0]non-5-ene (3); 1,8-diaza-bicyclo-[5.4.0]undec-7-ene (4); 1,2,4-trazolo[1,5-a]pyrimidine (5), and imidazo[1,2-a]pyridine (6).

Vaporization enthalpies for five of the six 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.

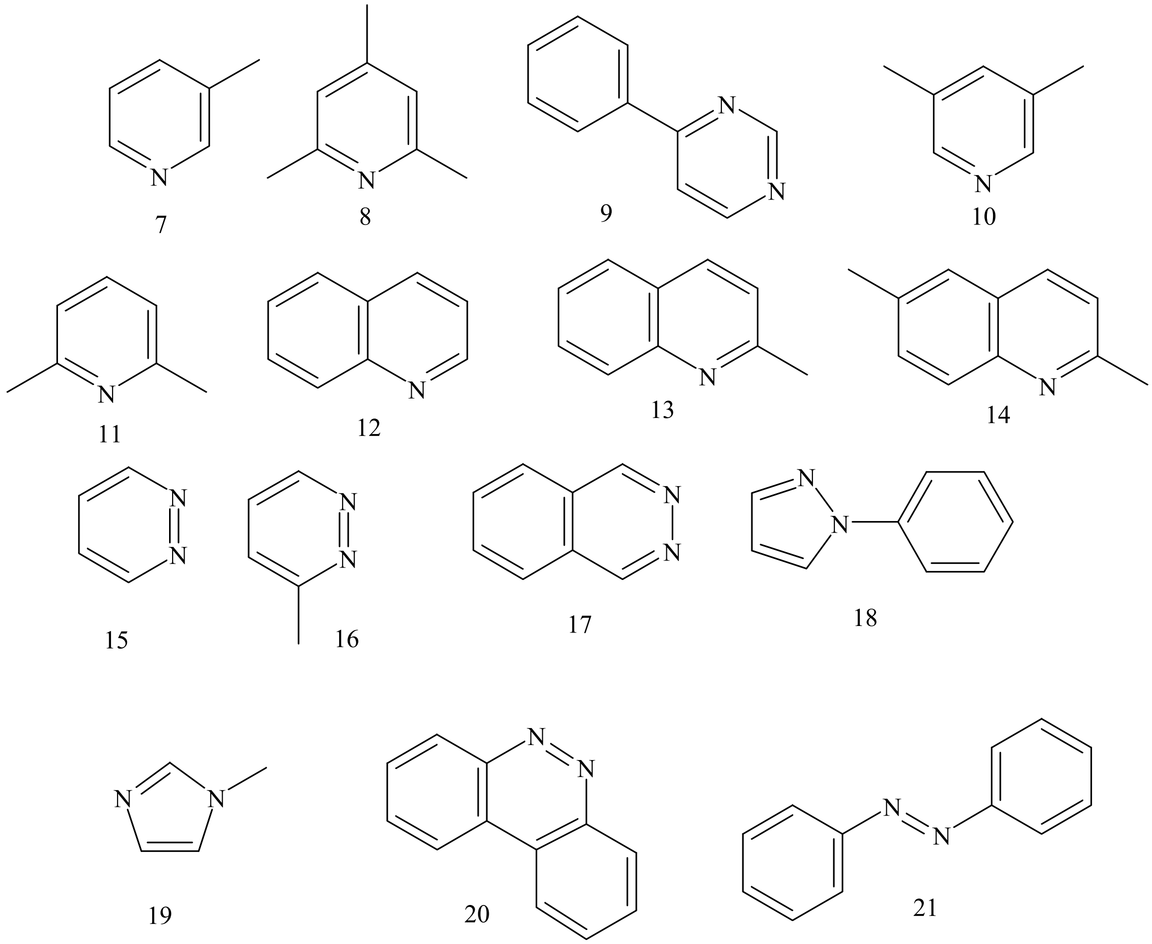

Figure 5-2. Compounds from left to right, top to bottom: 3-methylpyridine (7); 2,4,6-trimethyl-pyridine (8), 3-phenylpyrimidine (9); 3,5-dimethylpyridine (10); 2,6-dimethylpyridine (11); quinoline (12); 2-methylquinoline (13); 2,6-dimethylquinoline (14); pyridazine (15); 3-methyl-pyridazine (16); phthalazine (17); 1-phenylpyrazole (18); 1-methylimidazole (19); benzo-[c]cinnoline (20) and *trans*-azobenzene (21).

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 by our collaborators from University of Rostock, Vasiliy Pozdeev and Sergey Verevkin. The vaporization enthalpies of three of the five compounds measured by transpiration are consistent with the results obtained by C-GC using various pyridine heterocycles as standards. Transpiration results for the remaining three others reproduced results using derivatives of pyridazine and imidazoles as standards.

5.2. Experiment

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. C-GC 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 DB5 MS column or a Restek 0.5 mm, 30 m RTX-5 column. 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 retention time of the solvent, methanol, was used as a non-retained reference.

Vapor pressure and Vaporization Enthalpies by Transpiration. Transpiration measurements were performed by our collaborators form University of Rostock, Germany, Vasiliy Pozdeev and Sergey Verevkin. 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-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 equation (5-1) where $R = 8.314472\ J{\cdot}K^{-1}{\cdot}mol^{-1}$; 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.

$$p_i^{\mathrm{sat}} = m_{\mathrm{i}} \cdot R \cdot T_{\mathrm{a}} / V \cdot M_i \, ; \quad V = V_{N2} + V_i ; \, (V_{\mathrm{N2}} \gg V_{\mathrm{i}}) \tag{5-1}$$

$V_{N2}$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 equations (5-2) and (5-3), respectively, 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 $\Delta_{\mathrm{l}}^{\mathrm{g}} C_{\mathrm{p}}$ is the difference of the molar heat capacities of the gaseous and the liquid phase. Values of $\Delta_{\mathrm{l}}^{\mathrm{g}} C_{\mathrm{p}}$ were calculated using the group contribution method of Acree and Chickos.[11,12] Experimental results and parameters a and b are listed in Appendix E-3 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 to 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 $\ln(p_i^{\mathrm{sat}}) = f\,(\mathrm{T}^{-1})$ using the method of least squares. The uncertainty in the enthalpy of vaporization was assumed to be identical to the deviation of experimental $\ln(p_i^{\mathrm{sat}})$ values from this linear correlation.

$$\mathrm{R} \cdot \ln p_i^{\mathrm{sat}} = \mathrm{a} + \frac{\mathrm{b}}{\mathrm{T}} + \Delta_{\mathrm{l}}^{\mathrm{g}} C_{\mathrm{p}} \cdot \ln\left(\frac{T}{T_0}\right) \tag{5-2}$$

$$\Delta_{\mathrm{l}}^{\mathrm{g}} H_{\mathrm{m}}(T) = -\mathrm{b} + \Delta_{\mathrm{l}}^{\mathrm{g}} C_{\mathrm{p}} \cdot T \tag{5-3}$$

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. The X-ray diffraction studies were performed by Dr. Nigam Rath (UMSL Chemistry Department).

5.3. Vaporization Enthalpies and Vapor Pressures of the 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 studied for the 1,2-diazines (Chapter 3) and the 1,3-diazoles (Chapter 4), 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.

Available vaporization enthalpy values of the compound in this study from the literature are reported in Table 5-1. 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 equation. For comparison, vaporization enthalpies were also adjusted to this temperature using eq. (5-4).

$$\Delta_l^g H_m(298.15\ \mathrm{K})/(\mathrm{kJ{\cdot}mol^{-1}}) = \Delta_l^g H_m(T_\mathrm{m}) + [(10.58 + 0.26{*}C_p(\mathrm{l})/(\mathrm{J{\cdot}mol^{-1}{\cdot}K^{-1}}))(T_\mathrm{m}/\mathrm{K} - 298.15)]/1000 \quad (5\text{-}4)$$

The heat capacity terms required for these temperature adjustments, values of C_p(l), are reported in Table 5-1 and were evaluated by group additivity.[12] Agreement between the two $\Delta_l^g H_m$(298 K) values provided in the last two column of Table 5-1 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 equation and fit similarly.[13] Extrapolations of vapor pressures with temperature modeled by the Antoine equation are known to be more limited. We believe that the vaporization enthalpy calculated using eq. (5-4), which is still within the experimental uncertainty cited in the literature, is a more reasonably value.

Table 5-1. Literature Vaporization Enthalpies, $\Delta_l^g H_m$ (kJ·mol^{-1})

Compound	$\Delta_l^g H_m$ (T_m)	T_m /K	$\Delta_l^g H_m$ (440 K) [lit]	C_p(l) (J·mol^{-1}·K^{-1})	$\Delta_l^g H_m$ (298 K) [calc] [a]	$\Delta_l^g H_m$ (298 K) [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. (5-4).

To illustrate the applicability of eq. (5-4) in adjusting vaporization enthalpies over this temperature range, the vaporization enthalpies of some of the other standards in Table 5-1 were adjusted over this same temperature range using eq. (5-4) for comparison. Agreement between the two methods, columns 6 and 7 of Table 5-1 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. (5-5). Liquid vapor pressures for quinoline [18] are available in the form of the Cox equation, eq. (5-6). The parameters for these equations are reported in Table 5-2A and 5-2B. 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 C-GC and fit to the third order polynomial, eq. (5-7).[7] The constants for the calculation of liquid vapor pressure using eq. (5-7) are provided in Table 5-2C. Experimental vapor pressures for 2,4,6-trimethylpyridine[19] were also previously fit to eq. (5-7).[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 $p_o = 101.325$ kPa.

$$\ln(p/p_c) = (1/T_r)[A_W(1-T_r) + B_W(1-T_r)^{1.5} + C_W((1-T_r)^{\phi} + D_W(1-T_r)^{\theta}] \qquad (5\text{-}5)$$

$$\ln(p/p_o) = (1-T_b/T)\exp(A_o + A_1(T/K) + A_2(T/K)^2) \qquad (5\text{-}6)$$

$$\ln(p/p_o) = A(T/K)^{-3} + B(T/K)^{-2} + C(T/K)^{-1} + D \qquad (5\text{-}7)$$

Table 5-2A. 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]	-8.2162	4.68419	-4.3636	-3.4159	644.5	4680	2/4.8
2,6-dimethylpyridine[15]	-7.4687	1.1994	-1.03	-4.4899	624	3850	2/4
3,5-dimethylpyridine[15]	-8.318	3.38738	-2.5427	-4.0334	668	4050	2/4
2-methylquinoline [16]	-8.3702	2.91444	-3.7617	-3.196	778	4030	2.5/5
2,6-dimethylquinoline [17]	-8.9933	3.59487	-4.6317	-2.9075	786	3480	2.5/5

Table 5-2B. Parameters of the Cox Equation

Cox Equation[a]	A_o	A_1/T^{-1}	$A_2 * 10^7 / T^{-2}$	T_b/K[b]	Range/K
quinoline[18]	2.85461	-0.00130236	9.3118	510.298	298 to 559

Table 5-2C. Parameters of the Third Order Polynomial, Equation (5-7)

	A/K^3	B/K^2	C/K	D	Range/K
4-phenylpyrimidine [7]	82739965	-1191247.0	-3078.93	8.993	298- T_b
2,4,6-trimethylpyridine [c]	-160703781	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 reference 19 fit to eq. (5-7).

5.4. Results and Discussion

The retention times for all runs are reported in Appendix E-1. Results of six correlations are reported in Appendix E-2 and the equations describing the correlations between $\Delta_l^gH_m$(298.15 K) and $\Delta_{sln}^gH_m(T_m)$ are reported under each respective table. The resulting vaporization enthalpies of the substances targeted are summarized in Table 5-3. The vaporization enthalpy of triazolo[1,5-a]pyrimidine reported in Table 5-1 is the only 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

5-1 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 5-1 or calculated using eq. (5-4). On the basis of these results, triazolo[1,5-a]pyrimidine appears to have intermolecular interactions comparable to those found in pyridazines and imidazoles, approximately 7 kJ·mol^{-1} larger than found in pyridines, pyrimidines and derivatives.

Table 5-3. A Summary of the Vaporization Enthalpies Evaluated in Runs 1-6 [a]

	$\Delta_l^g H_m$(298 K) /kJ·mol^{-1}			
	Run 1	Run 2		Average (1&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.

In addition to vaporization enthalpies, the equations obtained from the C-GC results are capable of providing vapor pressures as well, provided vapor pressures of the standards are available over a broad temperature range. Table 5-4 illustrates a typical correlation between $\ln(p/p_o)_{lit}$ and $\ln(t_o/t_a)$ at $T = 298.15$ K for run 2.

Table 5-4. The 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	$\ln(t_o/t_a)$	$\ln(p/p_o)$ lit	$\ln(p/p_o)$ calc
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_o = 101.325 kPa; $\ln(p/p_o)_{calc} = (1.316\pm0.019)\ln(t_o/t_a) - (2.12\pm4.09)$; $r^2 = 0.9996$

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 $\ln(p/p_o)$ were calculated by correlations similar to the one illustrated in Table 5-4 and fit to eq. (5-7). The constants of eq. (5-7) are reported in Table 5-5 along with predicted boiling temperatures at various experimental pressures. The calculated boiling temperatures for the first three entries in Table 5-5 are in good agreement with the literature values. The boiling temperature for 4-(*N,N*-dimethylamino)pyridine 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 25 K at 3.6 kPa and 40 K at 0.133 kPa. This is similar to what was previously observed for various pyridazines and imidazoles using inappropriate standards. We conclude from the results of the first three entries that the vaporization enthalpies 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 2-*N,N*-dimethylaminopyridine is warranted.

Table 5-5. Constants of Equation (5-7)[a] and Experimental and Predicted BT

	A/K^3	B/K^2	C/K	D	*p*/kPa	*BT*/K[b]	
						lit	calc
		1,5-diazabicyclo[4.3.0]non-5-ene					
Run 1	32198211.83	-754501.37	-3352	9.262	1.47	370.2	379.2
Run 2	59025623.51	-963598.05	-2898.7	9.027	1.47	370.2	379.2
		1,8-diazabicyclo[5.4.0]undec-7-ene					
Run 1	61193659.29	-1025298.42	-3315.7	9.155	0.4	354.2	351.9
					0.08	370.2	380.4
Run 2	78641023.3	-1167533.73	-3000.7	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	-3277.6	9.164	101.3	469.2	476.1
					2	361.2	359
Run 2	45110792.05	-814218.84	-2620.4	8.72	101.3	469.2	474.3
					2	361.2	359.1
		4-*N,N*-(dimethylamino)pyridine					
Run 1	*37602851.35*	*-805105.12*	*-3245.3*	*9.064*	*6.67*	435.2	420
Run 2	*64357070.84*	*-1014884.62*	*-2745.3*	*8.73*	*6.67*	435.2	419.1
		imidazo [1,2-a] pyridine					
Run 3[b]	*69729011.12*	*-1073486.71*	*-2412.1*	*8.259*	0.133	376.2	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 from either the Aldrich Catalog or from SciFinder Scholar. Boiling temperatures are at the pressure noted in the column 6

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 vapor pressure results for these five compounds are reported in Appendix E-3 and the vaporization enthalpies calculated from these measurements are reported in Table 5-6 and Figure 5-3 which also compare the results obtained by the two methods. 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.

Table 5-6. A Comparison of Vaporization Enthalpies

	$\Delta_l^g H_m(298\ \mathrm{K})$ /kJ·mol^{-1}		
	transpiration	correlation-gc	$\Delta\Delta_l^g H_m(298\ \mathrm{K})$
		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 $\Delta_{\mathrm{cr}}^{\mathrm{g}} H_{\mathrm{m}}(298.15)$ and $\Delta_{\mathrm{cr}}^{\mathrm{l}} H_{\mathrm{m}}(298.15)$; [b] Measured by ebulliometry.[13]

The vapor pressures calculated by correlation eq. (5-7) using the constants for run 1 in Table 5-5 are compared with the values measured by transpiration in Figure 5-3. Comparisons appear best for 2-(*N*,*N*-dimethylamino)pyridine. Increasing divergence between the two methods is observed for 1,5-diazabicyclo[4.3.0]non-5-ene, and 1,8-diazabicyclo[5.4.0]undec-7-ene.

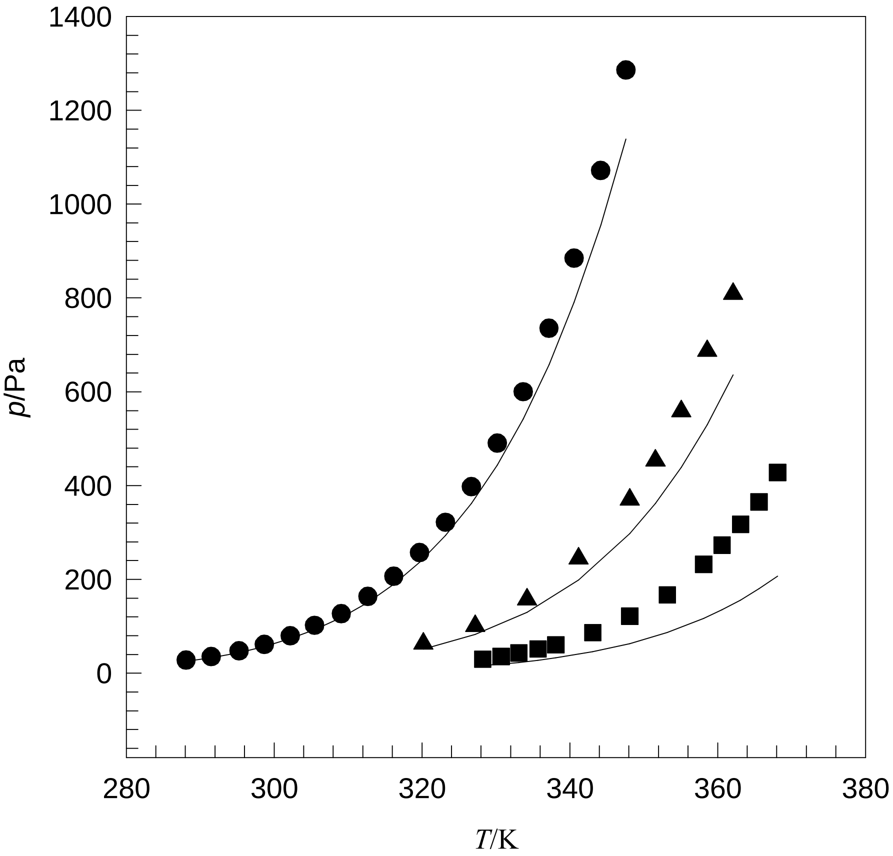

Figure 5-3. The vapor pressures measured by transpiration (symbols) and those calculated by correlation equation (5-7) (line) for 2-(*N*,*N*-dimethylamino)pyridine (circles), 1,5-diazabicyclo[4.3.0]non-5-ene (triangles), and 1,8-diazabicyclo[5.4.0]undec-7-ene (squares).

The vapor pressure comparison for 4-(*N*,*N*-dimethyl-amino)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})and the fusion enthalpy[20] (21.63 kJ·mol^{-1}).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.

5.5. Possible Factors Responsible for the Enhanced Intermolecular Interaction Observed in Some Heterocycles

In an effort to gain some understanding as to why the use of some standards in C-GC results in vaporization enthalpies that are smaller in magnitude than measured by other means, both structural and polar effects have been considered. 2-(*N*,*N*-Dimethyl-amino)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 C-GC using pyridines as standards whereas *N*-substituted imidazoles using similar standards were not (Chapter 4).[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 as evidenced by the results obtained for imidazo[1,2-a]pyridine and triazolo[1,5-a]pyrimidine.

In an effort to examine the role that polarity may play, Table 5-7 lists a series of compounds, many used as standards in various correlations, their literature vaporization enthalpies measured by various methods, their vaporization enthalpy obtained by C-GC, and their corresponding dipole moments if available, most measured in benzene. Only compounds whose dipole moments could be located are included in Table 5-7. Also included in column 6 of Table 5-7 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 5-7A 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 5-7B.

The enthalpy difference between the most of the literature values and those measured by correlation in Table 5-7B appears to be a constant 7 kJ·mol^{-1} larger. Only N-phenylimidazole shows a larger deviation.[3]Dipole moments of all these materials are greater than 2.5 D. 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 also observed in the crystal structure of 4-*N,N*-(dimethylamino)pyridine[23] although it is not clear whether the planarity is maintained in the liquid phase. The tertiary nitrogen adjacent to the methylene group in *N*-benzylimidazole, 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 another good test case to determine whether planarity is an important structural feature. Like 4-*N,N*-(dimethyl-amino)pyridine, 1,2,4-triazolo[1,5-a]pyrimidine is another material that formally contains an sp^3 hybridized bridgehead nitrogen.

Table 5-7. Experimental and C-GC Vaporization Enthalpies and Their Relation to Dipole Moments (μ)

Formula	Compound	$\Delta_l^g H_m$(298 K) (kJ·mol^{-1})			$\Delta\Delta_l^g H_m$(298 K) (kJ·mol^{-1})	μ (D)[b]
		Lit	CGC	Ref[a]		
			A			
C_5H_5N	pyridine	40.2±0.1	40.0±2.3	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	1,14	0 ±2.0	2.4 B
$C_7H_{10}N_2$	2-N,N-dimethylaminopyridine	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	1,19	-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
$C_4H_6N_2$	N-methylpyrazole	48.0±1.3	41.6±2.9	tw[e],6	6.4±3.2	2.29 B
$C_9H_8N_2$	N-phenylpyrazole	70.2±3.4	63.5±2.9	3,25	6.7±4.5	2.0 B
$C_{13}H_9N$	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	1,4	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
$C_7H_{10}N_2$	4-N,N-dimethylaminopyridine	68.4±0.9	61.3±2.5	tw	7.1±2.7	4.33 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 C-GC and literature values can be found; tw: this work.

[b] B: benzene; C: CCl_4. [21]

[c] Average of two or more runs.

[d] Ref 22.

[e] See run 7 in the Appendix E-1, E-2.

The crystal structure of 1,2,4-triazolo[1,5-a]pyrimidine is shown in Figure 5-4 and the packing in the crystal is provided in Figure 5-5. 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. 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.

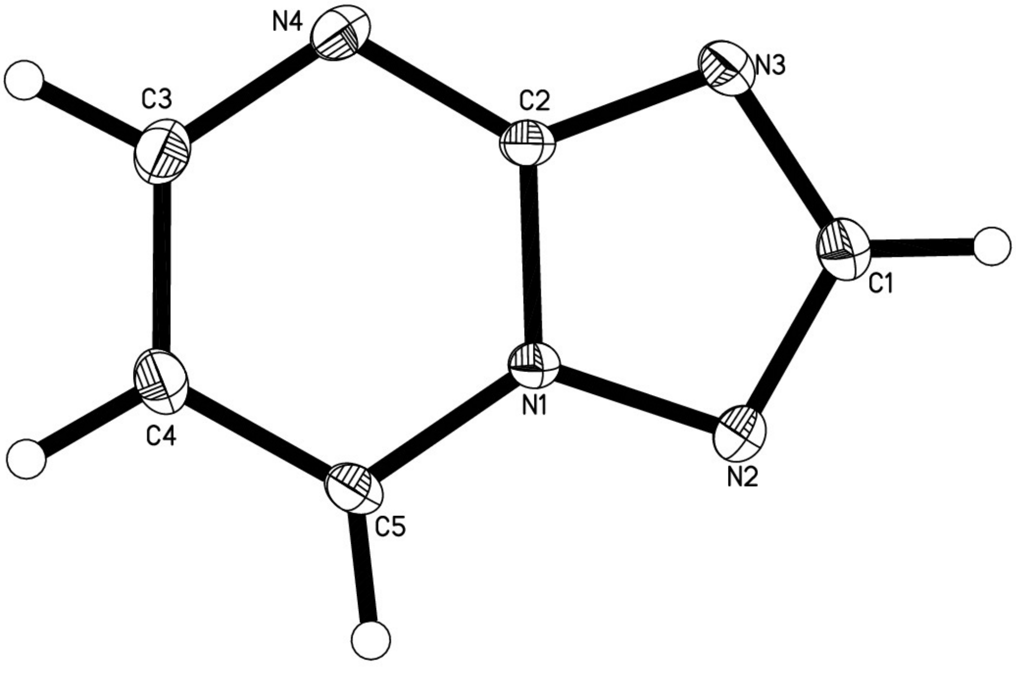

Figure 5-4. The crystal structure of 1,2,4-trazolo[1,5-a]pyrimidine. A projection view with 50% thermal ellipsoids.

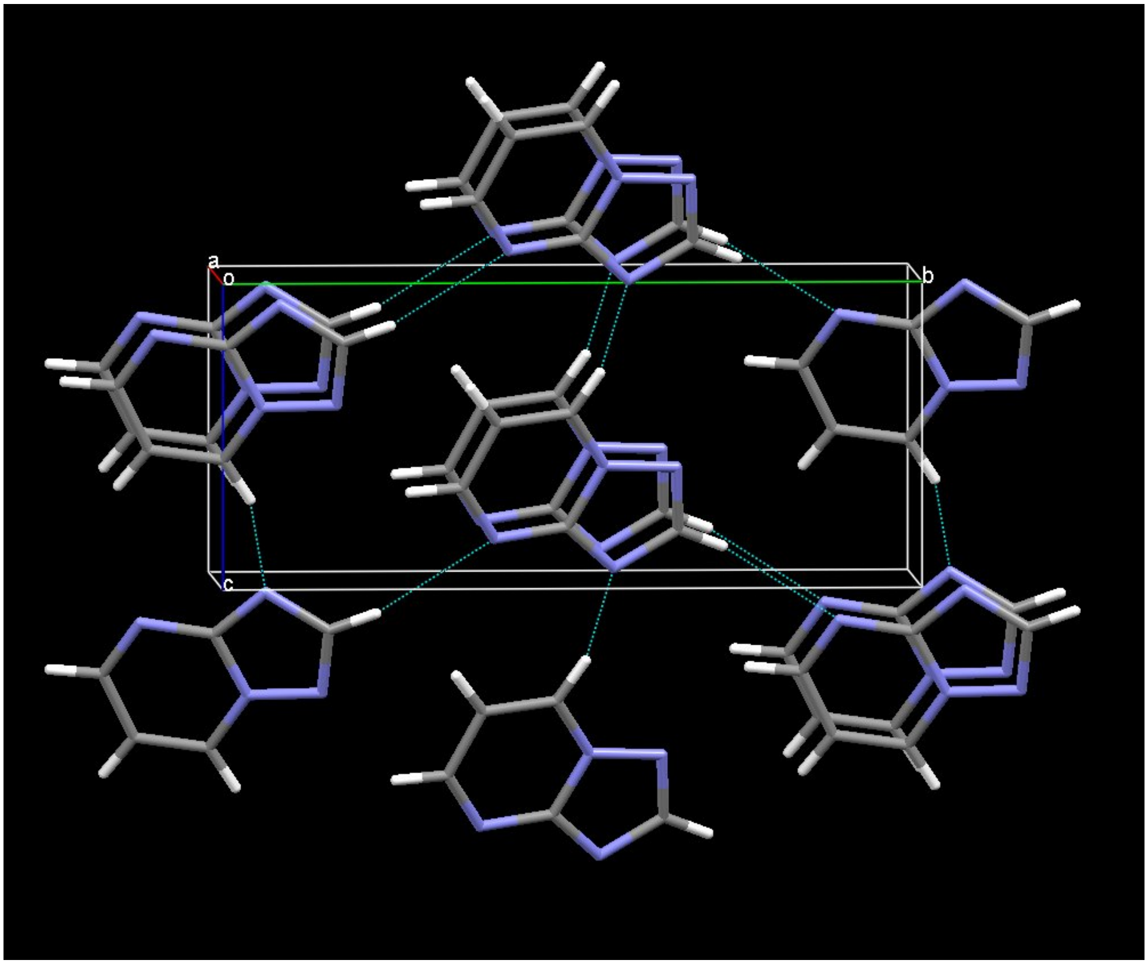

Figure 5-5. Molecular packing of 1,2,4-trazolo[1,5-a]pyrimidine down the a axis.

The combination of planarity, polarity and extensive conjugation are common to all the systems that appear to exhibit anomalously 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 $kJ \cdot mol^{-1}$ 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.

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Part 2. Miscellaneous Measurements

Chapter 6. Vaporization Enthalpies and Vapor Pressures of the Even n-Alkanes from C_{78} to C_{92}

6.1. Introduction

The n-alkanes serve as excellent standards for the measurement of vaporization enthalpies of hydrocarbons at T = 298.15 K, regardless of the physical state of the hydrocarbon.[1-4] An extensive study of thermochemical properties of even n-alkanes by correlation-gas chromatography has been previously done by Chickos et al.[1,2,5] Most recently, Chickos et al. have reported the vaporization enthalpies of the even hydrocarbons, tetracontane to hexaheptacontane (C_{40} to C_{76}), and described a protocol that could be used to evaluate the subcooled liquid vapor pressure values of these materials.[5] Equations were reported that were capable of reproducing the vapor pressures of the liquid state of these materials from T = (298.15 to 540) K. There are no experimental vapor pressures available for these large molecules for comparison. Experimental vaporization enthalpies and vapor pressures for molecules larger than eicosane are scarce; all the values cited in this study have been generated by extrapolation of recommended vaporization enthalpies and vapor pressure values[6] of the n-alkanes $<C_{21}$ using the technique of correlation-gas chromatography. In instances where the results obtained by this technique could be directly compared to experimental values, the comparisons have been very good.[1,2,5]

Interest in subcooled liquid vapor pressures of the larger n-alkanes is related to the fact that these compounds can serve as excellent standards in the evaluation of vaporization enthalpies and liquid vapor pressures of other hydrocarbons.[3,4,7,8]The vapor pressures are also of interest to the petroleum industry. This study expands vaporization enthalpy and vapor pressure data available for the even alkanes from octaheptacontane to dononacontane and summarizes the results obtained for heneicosane to dononacontane. It also examines indirectly if the magnitude of the vaporization enthalpy does approach a finite limit with size as suggested by the apparent convergence of the normal boiling and critical temperatures.[9]

The lack of experimental data for molecules of the size of this study has prompted us to compare our results to predictions based on a program, PERT2, developed by Morgan and Kobayashi[10,11]and on values calculated from the Antoine Constants predicted by Kudchadker and Zwolinski [13] and cited by Stephenson and Malanowski.[15] While the constants cited by Stephenson and Malanowski.[15] are numerically different from those reported by Kudchadker and Zwolinski,[13] identical vapor pressures are calculated. The temperature limits reported by Stephenson and Malanowski correspond to vapor pressures in the approximate range 0.1 to 101 kPa, and were adhered to in this work.

As observed previously[5], the values obtained by c-gc for both vapor pressure and vaporization enthalpy were in very good agreement with the predictions of PERT2 and the extrapolations of Kudchadker and Zwolinski up to about hexacontane. As the number of carbon atoms increased above sixty, the predictions of PERT2 and those of Kudchadker and Zwolinski began to increase less readily than the values obtained by correlation-gas chromatography, even though the results obtained by c-gc also began to show evidence of some curvature. This study expands the range of compounds studied and indicates that vaporization enthalpies do show continuing curvature with increasing carbon number, although somewhat less pronounced than predicted by earlier models.

6.2. Experiment

Pentacontane and hexacontane were purchased from Aldrich. All the remaining alkanes studied up to C_{92} were obtained as mixture present in Polywax 1000 purchased from Restek Corporation. Polywax 1000 is an oligomer of polyethylene with an average molecular weight of 1000 g mol^{-1}. The material consists of a series of even hydrocarbons, which in the C_{40} to C_{60} region, contained compounds with identical retention times as the n-alkanes purchased separately. A typical plot of Polywax 1000 spiked with C_{50} and C_{60} is shown in Figure 6-1.

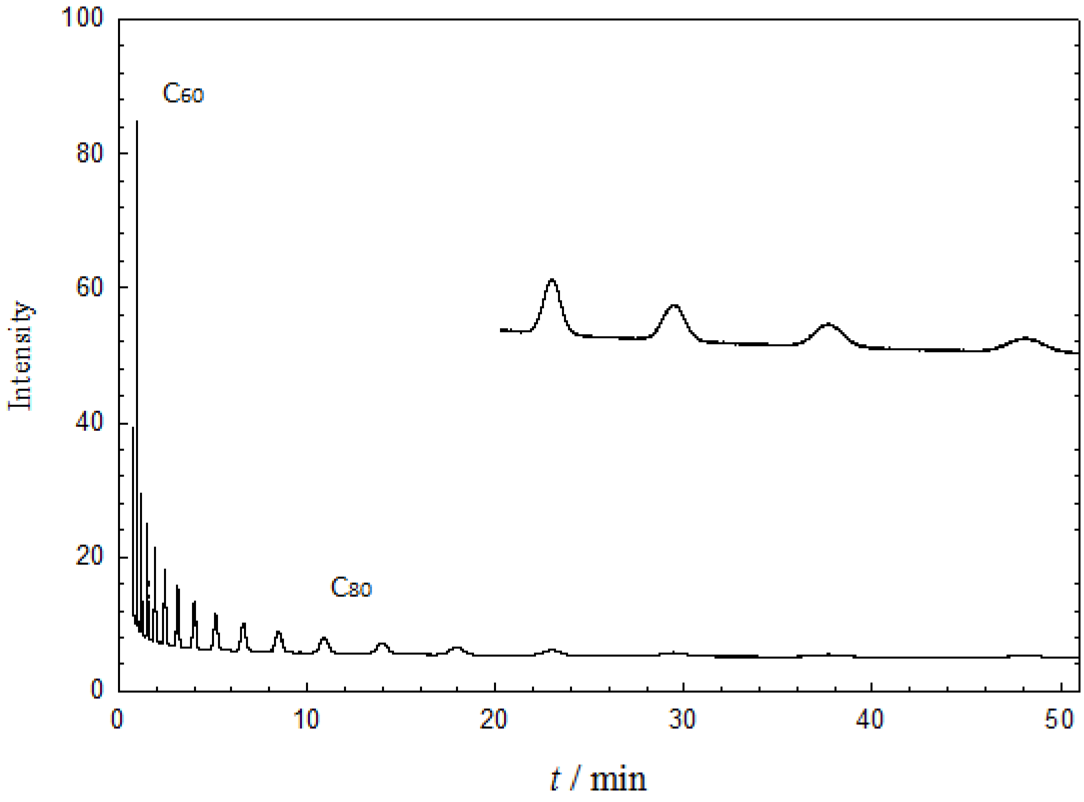

Figure 6-1. GC trace of Polywax1000 spiked with n-alkanes n-C_{50} and n-C_{60}at $T = 661$ K (Run 1). The solvent peak and C_{50} are not shown.

Correlation-gas chromatography experiments were performed on an HP 5890 Gas Chromatograph equipped with a split/splitless capillary injection port and a flame ionization detector run at a split ratio of approximately 50/1. Retention times were rounded to three significant figures following the decimal point using HP software interfaced to a computer. The instrument was run isothermally using two high temperature aluminum clad silica capillary column (0.25 mm ID, 0.01 μm methyl silicone film thickness, Quadex Corp., Catalog # 400 1HT-15-0.1F, 15 m; and a SGE Forte GC capillary column, 12 m x0.32 mm ID). Helium was used as the carrier gas. At the temperatures of the experiments, the retention time of the solvent used, octane or toluene, was used as the non-retained reference. The retention times of the solvent were used to determine the dead volume of the column. Adjusted retention times, t_a, were calculated by subtracting the measured retention time of the solvent from the retention time of each analyte as a function of temperature over a 30 K range. Column temperatures were controlled by the gas chromatograph and were monitored independently by using a Fluke digital thermometer. Temperature was maintained constant by the gas chromatograph to ± 0.5 K. All plots of $\ln(t_o/t_a)$, vs $1/T$, where t_o = 1 min, were characterized with correlation coefficients, r^2, >0.99. The retention times measured for all analytes are reported in Appendix F-1.

6.3. Results and Discussion

6.3.1. Vaporization Enthalpies

Experimental retention times are provided in Appendix F-1. A plot of ln(t_o/t_a)) versus 1/T resulted in linear plots whose slopes and intercepts are provided in Table 6-1 for runs 1, 2 and 3. Enthalpies of transfer from the stationary phase of the column to the gas phase at the mean temperature, $\Delta_{sln}{}^{g}H_m(T_m)$, were obtained by multiplying the slopes of the lines by the gas constant, R = 8.314 J mol^{-1}K^{-1}.

Table 6-1. Enthalpies of Transfer and Vaporization Enthalpies Obtained for the Even n-Alkanes From Pentacontane to Dononacontane

Run 1	slope (*T*/K)	intercept	$\Delta_{sln}{}^{g}H_m$(676 K) kJ mol^{-1}	$\Delta_l{}^{g}H_m$(298.15 K) /kJ mol^{-1} (lit)^5	(calcd)
pentacontane	-14177	23.047	117.862	252.5	254.6
dopentacontane	-14507	23.277	120.603	261.8	259.9
tetrapentacontane	-15180	24.022	126.204	271.0	270.8
hexapentacontane	-15851	24.763	131.779	279.7	281.6
octapentacontane	-16308	25.187	135.581	288.5	288.9
hexacontane	-16862	25.755	140.182	299.9	297.9
dohexacontane	-17397	26.299	144.628	306.8	306. 5
tetrahexacontane	-17919	26.824	148.970	315.4	314.9
hexahexacontane	-18449	27.364	153.381	324.0	323. 5
octahexacontane	-18968	27.887	157.695	331.9	331.8
heptacontane	-19487	28.411	162.006	340.3	340.2
doheptacontane	-20005	28.935	166.314	348.4	348.5
tetraheptacontane	-20501	29.429	170.439	356.2	356.5
hexaheptacontane	-21031	29.973	174.848	364.3	365.1
octaheptacontane	-21512	30.445	178.843		372.8±3.4
octacontane	-22009	30.942	182.971		380.8±3.5
dooctacontane	-22481	31.406	186.896		388.4±3.6
tetraoctacontane	-22935	31.842	190.671		395.8±3.6
hexaoctacontane	-23424	32.331	194.734		403.6±3.7
octaoctancontane	-23898	32.801	198.677		411.3±3.8
nonacontane	-24371	33.269	202.613		418.9±3.9
dononacontane	-24814	33.695	206.291		426.0±3.9

$$\Delta^{g}{}_{l}H_m(298.15\ \text{K})/\text{kJ mol}^{-1} = (1.939\pm0.018)\Delta_{sln}{}^{g}H_m(676\ \text{K}) - (26.07\pm1.20)\quad r^2 = 0.9990$$

Table 6-1. Continued

Run 2	slope (T/K)	intercept	$\Delta_{\mathrm{sln}}{}^{\mathrm{g}}H_{\mathrm{m}}$ (676 K) kJ mol^{-1}	$\Delta_{\mathrm{l}}{}^{\mathrm{g}}H_{\mathrm{m}}$ (298.15 K) kJ mol^{-1}(lit)^{5}	$\Delta_{\mathrm{l}}{}^{\mathrm{g}}H_{\mathrm{m}}$ (298.15 K) kJ mol^{-1}(calcd)
octapentacontane	-15979	24.825	132845	288.5	289.5
hexacontane	-16538	25.404	137.492	299.9	298.1
dohexacontane	-17131	26.037	142.420	306.8	307.2
tetrahexacontane	-17686	26.614	147.037	315.4	315.7
hexahexacontane	-18235	27.182	151.597	324.0	324.1
octahexacontane	-18763	27.722	155.990	331.9	332.2
heptacontane	-19287	28.256	160.345	340.3	340.2
doheptacontane	-19830	28.819	164.857	348.4	348.5
tetraheptacontane	-20338	29.334	169.085	356.2	356.3
hexaheptacontane	-20844	29.844	173.285	364.3	364.0
octaheptacontane	-21347	30.353	177.470		371.8±3.4
octacontane	-21828	30.829	181.467		379.1±3.5
dooctacontane	-22282	31.269	185.247		386.1±3.6
tetraoctacontane	-22783	31.775	189.407		393.8 ±3.6
hexaoctacontane	-23272	32.269	193.474		401.2±3.7
octaoctancontane	-23779	32.789	197.688		409.0±3.8
nonacontane	-24189	33.166	201.099		415.3±3.9
dononacontane	-24684	33.669	205.214		422.9±3.9

$\Delta^{\mathrm{g}}{}_{\mathrm{l}}H_{\mathrm{m}}$(298.15 K)/kJ mol^{-1} = (1.843±0.019)$\Delta_{\mathrm{sln}}{}^{\mathrm{g}}H_{\mathrm{m}}$(676 K) - (44.69±0.77) $r^2 = 0.9992$

Run 3	slope (T/K)	intercept	$\Delta_{\mathrm{sln}}{}^{\mathrm{g}}H_{\mathrm{m}}$(653 K) kJ mol^{-1}	$\Delta_{\mathrm{l}}{}^{\mathrm{g}}H_{\mathrm{m}}$ (298.15 K) kJ mol^{-1}(lit)^{5}	$\Delta_{\mathrm{l}}{}^{\mathrm{g}}H_{\mathrm{m}}$ (298.15 K) kJ mol^{-1}(calcd)
hexacontane	-17713	26.912	147.261	299.9	298.5
dohexacontane	-18308	27.559	152.202	306.8	307.2
tetrahexacontane	-18897	28.197	157.099	315.4	315.8
hexahexacontane	-19480	28.827	161.946	324.0	324.4
octahexacontane	-20037	29.42	166.580	331.9	332.5
heptacontane	-20622	30.054	171.440	340.3	341.1
doheptacontane	-21090	30.515	175.336	348.4	347.9
tetraheptacontane	-21639	31.097	179.902	356.2	356.0
hexaheptacontane	-22169	31.652	184.305	364.3	363.7
octaheptacontane	-22708	32.222	188.782		371.6±4.1
octacontane	-23197	32.717	192.850		378.7±4.1
dooctacontane	-23768	33.338	197.595		387.1±4.2
tetraoctacontane	-24146	33.666	200.742		392.6±4.3
hexaoctacontane	-24753	34.345	205.789		401.5±4.4
octaoctancontane	-25156	34.714	209.137		407.4±4.5
nonacontane	-25678	35.265	213.475		415.0±4.6

$\Delta^{\mathrm{g}}{}_{\mathrm{l}}H_{\mathrm{m}}$(298.15 K)/kJ mol^{-1} = (1.759±0.021)$\Delta_{\mathrm{sln}}{}^{\mathrm{g}}H_{\mathrm{m}}$(653 K) - (39.49±0.76) $r^2 = 0.9990$

Vaporization enthalpies reported previously for the even n-alkanes, pentacontane to hexaheptacontane[5]are reported in column 5 of Table 6-1.The last column reports the vaporization enthalpies calculated from the correlation equation listed below each run. The vaporization enthalpies and their mean values are summarized in Table 6-2. The uncertainties reported in Table 6-1 are standard errors calculated from the uncertainty associated with the slopes and intercepts of correlation equations. The uncertainties reported for the mean in Table 6-2 is an average of the uncertainties of each run.

Table 6-2. Summary of the Vaporization enthalpies (in kJ mol^{-1}) of the Even Alkanes from Octaheptacosane to Dononacosane

	Run 1	Run 2	Run 3	Average
octaheptacontane	372.8±3.4	371.8±3.6	371.6±4.1	372.1±3.7
octacontane	380.8±3.5	379.2±3.7	378.7±4.1	379.6±3.8
dooctacontane	388.5±3.6	386.1±3.7	387.1±4.2	387.2±3.8
tetraoctacontane	395.8±3.6	393.8±3.8	392.6±4.3	394.0±3.9
hexaoctacontane	403.7±3.7	401.3±3.9	401.5±4.4	402.1±4.0
octaoctancontane	411.3±3.8	409.1±4.0	407.4±4.5	409.2±4.1
nonacontane	418.9±3.9	415.4±4.0	415.0±4.6	416.4±4.3
dononacontane	426.1±3.9	423.0±4.1		424.5±4.0

The vaporization enthalpies of all n-alkanes in the literature[1,2,15] from pentane to eicosane along with the results of these sets of extrapolations are summarized in Table 6-3 and illustrated in Figure 6-2. This figure plots the vaporization enthalpies at $T = 298.15$ K of pentane on through to dononacontane as a function of the number of carbon atoms, N. Literature values for pentane through to eicosane ($N = 5 – 20$) as a function of the number of carbon atoms were used to establish the relationship between vaporization enthalpy and carbon number, N. The results are quite linear and are represented by the equation (6-1).

$$\Delta^{g}_{l}H_m(298.15\text{ K})/\text{kJ mol}^{-1} = (5.005\pm0.007)N + (1.487\pm0.137); \qquad r^2 = 0.9999 \qquad (6\text{-}1)$$

Table 6-3. The Vaporization Enthalpies of the n-Alkanes at T = 298.15 K as a Function of the Number of Carbon Atoms, N [a]

N	$\Delta_l^g H_m$ kJ mol^{-1}	N	$\Delta_l^g H_m$ kJ mol^{-1}	N	$\Delta_l^g H_m$ kJ mol^{-1}	N	$\Delta_l^g H_m$ kJ mol^{-1}
5	26.42	21	106.8±2.6	36	182.8±5.5	64	315.4±2.9
6	31.52	22	111.9±2.7	37	187.5±5.6	66	324.0±3.0
7	36.57	23	117.0±2.8	38	192.5±5.7 [b]	68	331.9±3.0
8	41.56	24	121.9±2.8	40	203.5±2.9	70	340.3±3.1
9	46.55	25	126.8±2.9	42	213.5±2.1	72	348.4±3.2
10	51.42	26	131.7±3.3	44	223.7±2.3	74	356.2±3.3
11	56.58	27	135.6±3.3	46	233.3±2.3	76	364.3±3.3
12	61.52	28	141.9±5.1	48	243.0±2.4	78	372.1±1.4
13	66.68	29	147.1±5.3	50	252.5±2.5	80	379.6±2.2
14	71.73	30	152.3±5.3	52	261.8±3.6	82	387.2±2.4
15	76.77	31	157.2±1.4	54	271.0±3.7	84	394.0±3.2
16	81.35	32	162.5±1.4	56	279.7±3.8	86	402.2±2.6
17	86.47	33	167.6±1.4	58	288.5±3.9	88	409.3±3.9
18	91.44	34	172.7±1.5	60	299.9±3.0	90	416.5±4.3
19	96.44	35	178.1±5.4	62	306.8±2.8	92	424.5±4.0
20	101.81						

[a] Values for N = 5 to N = 20 from ref 6;Uncertainties were calculated from the uncertainty associated with the slope and intercept and average over each run

The relationship (6-1) was used to generate the solid line in Figure 6-2. The values calculated using the program PERT2 are represented by the empty circles. These estimations fit the line generated by eq. (6-1) within experimental error up to about hexacontane. Larger alkanes begin to diverge from the line, and the PERT2 model predicts substantial curvature. This curvature is consistent with expectations which are based on the observance of convergence between critical and boiling temperature as a function of the number of carbon atoms. Results from correlation-gas chromatography are quantitatively consistent with the linear behavior predicted by eq. (6-1) up to about hexacontane and then also show the same divergence as predicted by PERT2.

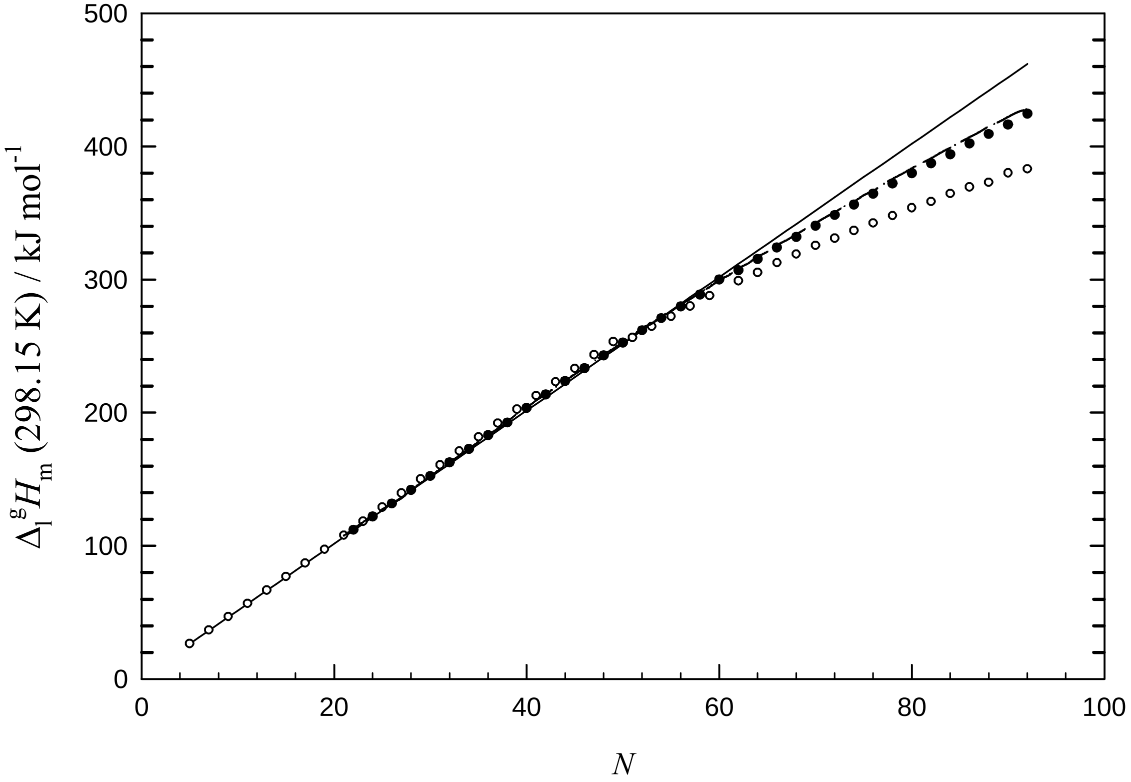

Figure 6-2. The vaporization enthalpies at T = 298.15 for pentane to dononacontane. N represents the number of carbon atoms. The solid line was derived using the recommended vaporization enthalpies of pentane to eicosane, eq. (6-1).[6] The empty circles are values calculated values using the program PERT2 for the odd alkanes from pentane to nonapentcontane and the even alkanes from dohexacontane to dononacontane.[11] The solid circles are values evaluated from correlations of $\Delta_{\text{sln}}{}^{g}H_m(T_m)$ with $\Delta_l{}^{g}H_m$(298.15K) in this study and previous works by Chickos et al.[1,2,5] The vaporization enthalpies indicated by the dashed line were calculated using the vapor pressures calculated from eq. (6-6) and the constants of Table 6-4.

It should be emphasized that the vaporization enthalpies of all the alkanes larger than eicosane have been measured by correlation-gas chromatography and all are based on extrapolations using the recommended values of pentane to eicosane as standards. It is quite possible that the curvature observed in $\Delta^g{}_l H_m$(298.15 K) is simply an artifact of the extrapolations. As a test of this possibility, the dependence of the enthalpy of transfer, measured by correlation-gas chromatography, as a function of the number of carbon atoms should be explored. Enthalpy of transfer values are experimental measurements that are not based on extrapolation. The enthalpy of transfer, $\Delta_{\mathrm{sln}}{}^{\mathrm{g}}H_{\mathrm{m}}(T_{\mathrm{m}})$, can be related to the vaporization enthalpy and the enthalpy of interaction of the analyte on the column, $\Delta_{\mathrm{sln}}H_{\mathrm{m}}(T_{\mathrm{m}})$, by the following thermodynamic relation:

$$\Delta_{\mathrm{sln}}{}^{\mathrm{g}}H_{\mathrm{m}}(T_{\mathrm{m}}) = \Delta_{\mathrm{l}}{}^{\mathrm{g}}H_{\mathrm{m}}(T_{\mathrm{m}}) + \Delta_{\mathrm{sln}}H_{\mathrm{m}}(T_{\mathrm{m}}) \qquad (6\text{-}2)$$

As the length of the hydrocarbon chain increases, the critical and boiling temperatures are observed to converge. Consequently, the vaporization enthalpy at the normal boiling temperature should reach some maximum value and then decrease to zero. At other temperatures, the vaporization enthalpy may not approach zero but is expected to show curvature.[5,9] A model consistent with the dependence of vaporization enthalpy with size is related to the type of interactions that may dominate in large molecules. As the size of the alkane increases, it can fold back on itself. With increasing size, the ratio of intermolecular interactions to intramolecular interaction decreases with chain length, *N,* and in the limit should approach zero.

The enthalpy of transfer from the column to the gas phase depends on two terms, the vaporization enthalpy and the interaction of the material on the column, $\Delta_{\mathrm{sln}}H_{\mathrm{m}}(T_{\mathrm{m}})$, both measured at the mean temperature of experiment (equation (6-2)). With increasing molecular size, both the vaporization enthalpy and the interaction of the material on the column should show the same dependence on size if the amount of folding of an alkane increases with increasing size.[5] Since enthalpies of transfer can be measured independent of any extrapolation, the behavior of $\Delta_{\mathrm{sln}}{}^{\mathrm{g}}H_{\mathrm{m}}(T_{\mathrm{m}})$ as a function of size should be a more reliable indicator of the validity of the model. Recently the correlation of the enthalpies of transfer as a function of the number of carbon atoms from dotetracontane to hexaheptacontane was reported.[5,9] While the relationship between N and $\Delta_{\mathrm{sln}}{}^{\mathrm{g}}H_{\mathrm{m}}(T_{\mathrm{m}})$ could be fit quite satisfactory by a linear function, a second order polynomial with a slope that decreases with increasing size provided a better fit consistent with the predictions of the model. This observation is similarly reproduced in plots of $\Delta_{\mathrm{sln}}{}^{\mathrm{g}}H_{\mathrm{m}}(T_{\mathrm{m}})$ versus N for larger alkanes as well. A corresponding plot of enthalpies of transfer versus N measured for pentacontane to dononacontane is illustrated in Figure 6-3. As quantified by the parabolic polynomials, equations (6-3) to (6-5), provided below the figure, curvature is indeed observed; a maximum $\Delta_{\mathrm{sln}}{}^{\mathrm{g}}H_{\mathrm{m}}(T_{\mathrm{m}})$ in the neighborhood of 225 carbons is suggested. The observed maximum would be expected to be dependent on temperature. [5]

6.3.2. Vapor Pressures

In addition to their usefulness in obtaining vaporization enthalpies, the slopes and intercepts provided in Table 6-1 can also be used to evaluate vapor pressures, p, when used in combination with experimental data. The equations associated with the slopes and intercepts of each compound relate the temperature dependence of the vapor pressure of the solute ($t_{\mathrm{o}}/t_{\mathrm{a}}$) above the stationary phase of the column over a narrow temperature range. Although these equations would not be expected to be accurate in predicting vapor pressures by themselves, when used in combination with a series of standards with known vapor pressures at the temperatures of interest, the results obtained by correlation have been shown to be satisfactory.[2]

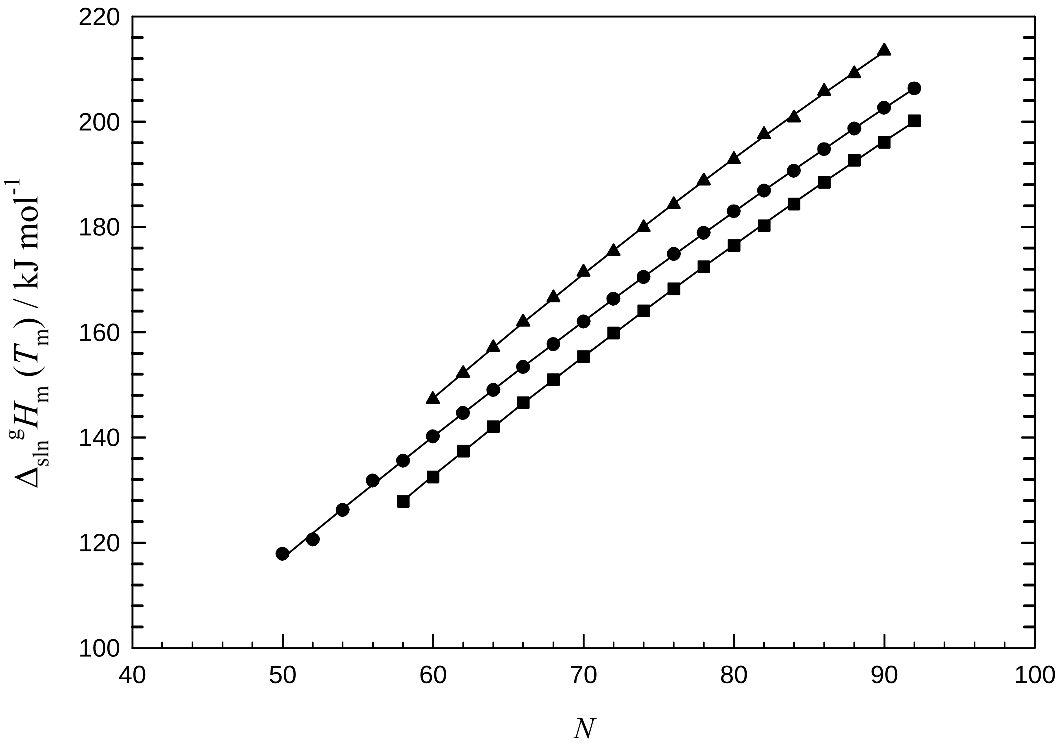

Figure 6-3. Enthalpies of transfer measured in this work as a function of the number of carbon atoms, *N*. The circles represent results of run 1 and the triangles represent the results of run 3. 5 kJ were arbitrarily subtracted from the results of run 2, squares, to separate these results from the results of run 1 for illustration in this figure. Fitting the experimental data to a second order polynomial result in the following equations:

$$\text{circles: } \Delta_{\mathrm{sln}}{}^{\mathrm{g}}H_{\mathrm{m}}(676\ \mathrm{K})/\mathrm{kJ\ mol^{-1}} = -(5.64\pm0.56)10^{-3}N^{2}+(2.93\pm0.08)N-(15.1\pm2.8);\quad r^{2} = 0.9998 \qquad (6\text{-}3)$$

$$\text{squares: } \Delta_{\mathrm{sln}}{}^{\mathrm{g}}H_{\mathrm{m}}(676\ \mathrm{K})/\mathrm{kJ\ mol^{-1}} = -(7.47\pm0.42)10^{-3}N^{2}+(3.24\pm0.06)N-(29.8\pm2.3);\quad r^{2} = 0.9999 \qquad (6\text{-}4)$$

$$\text{triangles: } \Delta_{\mathrm{sln}}{}^{\mathrm{g}}H_{\mathrm{m}}(653\ \mathrm{K})/\mathrm{kJ\ mol^{-1}} = -(8.37\pm0.96)10^{-3}N^{2}+(3.45\pm0.14)N-(29.6\pm5.3);\quad r^{2} = 0.9998 \qquad (6\text{-}5)$$

Vapor pressure equations for heneicosane to hexaheptacontane have previously been reported in the form of eq. (6-6).[1,2,5] The *A, B, C,* and *D* coefficients of this equation are reported in Table 6-4. *T* represents the temperature and p_o = 101325 Pa. Originally, Chickos and Hanshaw demonstrated the step-ladder approach to estimating vapor pressures of n-alkanes.[2] Literature vapor pressure data are available only for tetradecane to eicosane in the form of Cox equation. Therefore, they proceeded with a standard routine of correlating the extrapolated to T = 298.15 K $\ln(1/t_a)$ values (obtained from c-gc experiment) with experimental vapor pressures, $\ln(p/p_0)$ (calculated from the Cox equation), for n-C_{14} to C_{20}. The linearity observed between $\ln(p/p_0)$ and $\ln(1/t_a)$ for these seven alkanes suggested a mechanism by which vapor pressure data for the larger n-alkanes can be obtained. Using experimental $\ln(p/p_0)$ data for n-C_{17} to n-C_{20} and extrapolated $\ln(1/t_a)$ values for n-C_{17} to n-C_{23}, values of $\ln(p/p_0)$ for n-C_{21} to n-C_{23} can be obtained by correlation and subsequently treated as standard $\ln(p/p_0)$ values in further correlation. In this stepwise manner vapor pressure data was generated for n-alkanes up to hexaheptacontane.[1,2,5]

$$\ln(p/p_o) \;=\; A(T/\mathrm{K})^{-3} \;+\; B(T/\mathrm{K})^{-2} + C(T/\mathrm{K})^{-1} \;+ D \qquad (6\text{-}6)$$

The same step-ladder technique is used in this work. Values of $\ln(p/p_o)$ for the standards were calculated using eq. (6-6) at each temperature over the temperature range *T* = 298.15 to 540 K at 30 K intervals. In the first correlation, $\ln(p/p_o)$ values using eq. (6-6) and the appropriate constants of Table 6-4 were calculated for the n-alkane standards in Table 6-1 up to hexaheptacontane. The results were correlated with the corresponding

Table 6-4. *A, B, C,*and *D* Coefficients of Equation (6-6) for C_{20} to C_{92} [a] n-Alkanes

	$\frac{10^{-8}A}{T^3}$	$\frac{10^{-6}B}{T^2}$	$\frac{C}{T}$	D
heneicosane	1.9989	-2.9075	-98.135	6.6591
docosane	2.1713	-3.1176	110.72	6.5353
tricosane	2.3386	-3.322	310.77	6.4198
tetracosane	2.5072	-3.5286	530.15	6.282
pentacosane	2.6738	-3.7307	741.19	6.150
hexacosane	2.8244	-3.9193	910.53	6.070
heptacosane	3.0092	-4.1253	1198.8	5.811
octacosane	3.1389	-4.3120	1279.4	5.884
nonacosane	3.2871	-4.5043	1431.2	5.841
triacontane	3.4404	-4.6998	1601.6	5.770
hentriacontane	3.6037	-4.9002	1791.2	5.679
dotriacontane	3.7524	-5.0921	1947.2	5.630
tritriacontane	3.8983	-5.2809	2098.0	5.585
tetratriacontane	4.0435	-5.4679	2249.5	5.537
pentatriacontane	4.1746	-5.6480	2363.8	5.544
hexatriacontane	4.3320	-5.8432	2553.2	5.447
heptatriacontane	4.4890	-6.0370	2743.2	5.347
octatriacontane	4.6330	-6.2230	2891.9	5.304
tetracontane	4.9289	-6.6065	3183.3	5.270
dotetracontane	5.1471	-6.9224	3348.9	5.291
tetratetracontane	5.5011	-7.3467	3778.6	5.117
hexatetracontane	5.6451	-7.5992	3810.6	5.224
octatetracontane	5.8908	-7.9326	4039.6	5.187
pentacontane	6.1330	-8.2602	4268.3	5.143
dopentacontane	4.8707	-7.4087	1564.8	7.455
tetrapentacontane	5.0959	-7.7167	1772.4	7.410
hexapentacontane	5.3213	-8.0192	1997.2	7.326
octapentacontane	5.5446	-8.3203	2215.7	7.251
hexacontane	7.3061	-9.8448	5365.4	4.957
dohexacontane	6.1197	-9.0298	2863.7	7.000
tetrahexacontane	6.2051	-9.2215	2812.1	7.149
hexahexacontane	6.2905	-9.4126	2761.7	7.295
octahexacontane	6.3771	-9.5964	2731.5	7.398
heptacontane	6.4622	-9.7833	2688.6	7.527
doheptacontane	6.5473	-9.9677	2650.7	7.646
tetraheptacontane	6.6325	-10.1491	2619.6	7.750
hexaheptacontane	6.7165	-10.3320	2580.8	7.870
octaheptacontane	6.9185	-10.6352	2862.6	7.718
octacontane	7.0339	-10.8450	2927.0	7.731
dooctacontane	7.1142	-11.0100	2862.8	7.852
tetraoctacontane	7.2562	-11.2545	3066.0	7.726
hexaoctacontane	7.3278	-11.4184	2970.3	7.897
octaoctacontane	7.4656	-11.6595	3147.1	7.810
nonacontane	7.5587	-11.8287	3121.0	7.885
dononacontane	7.7815	-12.1830	4010.6	6.856

[a] *A, B, C,*and *D* coefficients for heneicosane to hexaheptacontane taken from refs 1, 2, 5.

$\ln(t_o/t_a)$ values calculated from the slopes and intercepts in Table 6-1 for both the standards and the alkanes whose values were being evaluated. For those alkanes being evaluated, t_o/t_a values for each run was first averaged and then $\ln(t_o/t_a)_{\text{average}}$ was correlated with $\ln(p/p_o)$. The results of this correlation is illustrated in Table 6-5 at T = 298.15 K by equation given at the bottom of the table. Similar correlations were repeated at 30 K intervals. From the linear correlations obtained, it was possible to calculate $\ln(p/p_o)$ values for all the target alkanes at each temperature over the temperature range T = 298.15 to 540 K. Values of $\ln(p/p_o)$ and $\ln(t_o/t_a)$ were always highly correlated. Once $\ln(p/p_o)$ values were evaluated at each temperature over this range, the values of $\ln(p/p_o)$ were plotted against $1/T$ and the results fit to eq. (6-6). The constants obtained for eq. (6-6) for octaheptacontane to dononacontane are also included in Table 6-4.

Table 6-5. Evaluation of the Vapor Pressures of the Even Alkanes from C_{78} to C_{92} at T=298.15 K

T = 298.15 K	slope (T/K)	intercept	$\ln(t_o/t_a)$	$\ln(t_o/t_a)_{avg}$[a]	$\ln(p/p_o)$ lit[1]	$\ln(p/p_o)$ calc
pentacontane	-14177	23.047		-24.50	-50.3	-50.7
dopentacontane	-14507	23.277		-25.38	-52.3	-52.0
tetrapentacontane	-15180	24.022		-26.89	-54.2	-54.2
hexapentacontane	-15851	24.763		-28.40	-56.1	-56.5
octapentacontane	-16308	25.187		-29.51	-58.0	-58.1
hexacontane	-16862	25.755	-30.8			
	-16538	25.404	-30.07			
	-17445	26.708	-31.8	-30.66	-60.2	-59.8
dohexacontane	-17397	26.299	-32.05			
	-17131	26.037	-31.42			
	-18030	27.347	-33.13	-31.98	-61.9	-61.8
tetrahexacontane	-17919	26.824	-33.28			
	-17686	26.614	-32.71			
	-18610	27.979	-34.44	-33.25	-63.7	-63.6
hexahexacontane	-18449	27.364	-34.52			
	-18235	27.182	-33.98			
	-19185	28.603	-35.74	-34.51	-65.6	-65.5

Table 6-5

T = 298.15 K	slope (T/K)	intercept	ln(t_o/t_a)	ln(t_o/t_a)$_{avg}$	ln(p/p_o) lit[1]	ln(p/p_o) calc
octahexacontane	-18968	27.887	-35.73			
	-18763	27.722	-35.21			
	-19734	29.189	-37	-35.74	-67.3	-67.3
heptacontane	-19487	28.411	-36.95			
	-19287	28.256	-36.43			
	-20309	29.816	-38.3	-36.97	-69.1	-69.1
doheptacontane	-20005	28.935	-38.16			
	-19830	28.819	-37.69			
	-20771	30.271	-39.39	-38.2	-70.9	-71.0
tetraheptacontane	-20501	29.429	-39.33			
	-20338	29.334	-38.88			
	-21312	30.847	-40.63	-39.39	-72.6	-72.7
hexaheptacontane	-21031	29.973	-40.57			
	-20844	29.844	-40.07			
	-21833	31.396	-41.83	-40.59	-74.4	-74.5
octaheptacontane	-21512	30.445	-41.71			
	-21347	30.353	-41.25			
	-22364	31.959	-43.05	-41.76		-76.2
octacontane	-22009	30.942	-42.87			
	-21828	30.829	-42.38			
	-22846	32.449	-44.18	-42.91		-77.9
dooctacontane	-22481	31.406	-43.99			
	-22282	31.269	-43.47			
	-23408	33.064	-45.45	-44.02		-79.6
tetraoctacontane	-22935	31.842	-45.08			
	-22783	31.775	-44.64			
	-23781	33.387	-46.37	-45.14		-81.2
hexaoctacontane	-23424	32.331	-46.23			
	-23272	32.269	-45.79			
	-24378	34.059	-47.71	-46.3		-82.9
octaoctancontane	-23898	32.801	-47.35			
	-23779	32.789	-46.97			
	-24775	34.423	-48.67	-47.44		-84.6
nonacontane	-24371	33.269	-48.47			
	-24189	33.166	-47.97			
	-25289	34.969	-49.85	-48.5		-86.2
dononacontane	-24814	33.695	-49.53			
	-24684	33.669	-49.12	-49.31		-87.4

$\ln(p/p_o)_{calc} = (1.480\pm0.012)\ln(t_o/t_a) - (14.43\pm0.22)$ $r^2 = 0.9992$

As noted above, there are no experimental values of vapor pressure and vaporization enthalpy available to our knowledge with which to compare our results. As a consequence of the lack of other experimental data, we have compared vapor pressures and vaporization enthalpies at T = 298.15 K with those predicted by PERT2 and vapor pressures at temperatures at which the Antoine Constants estimated by Kudchadker and Zwolinski and PERT2 were applicable. These comparisons are summarized in Table 6-6. As noted previously, both vapor pressures and vaporization enthalpies calculated at T = 298.15 K by PERT2 (columns 3 and 5, respectively) are in good agreement with the results of this work (columns 2 and 4) up to about C_{60}. Above hexacontane, the two results begin to diverge. Vaporization enthalpy values calculated by PERT2 above C_{60} increase more slowly and as a consequence, higher vapor pressures are predicted in comparison to the results by correlation-gas chromatography.

It should be noted that the vaporization enthalpies reported in column 4 of Table 6-6 at T = 298.15 K were obtained by direct correlation of $\Delta_{\mathrm{sln}}{}^{\mathrm{g}}H_{\mathrm{m}}(T_{\mathrm{m}})$ with $\Delta_{\mathrm{l}}{}^{\mathrm{g}}H_{\mathrm{m}}(298.15\mathrm{K})$ (Table 6-1). The vaporization enthalpies calculated at T_{m}, column 9 of Table 6-6, were calculated using eq. (6-6) and the constants of Table 6-4. Vaporization enthalpies using eq. (6-6) were calculated as the negative product of the slope of the line and gas constant generated from plots of $\ln(p/p_{\mathrm{o}})$ vs $1/T$ over a T = 30 K range. Use of eq. (6-6) to calculate vaporization enthalpies at T = 298.15 provided slightly different vaporization enthalpies than reported in the fourth column of this table. The standard deviation between vaporization enthalpies evaluated directly as in Table 6-1 and those evaluated using eq. (6-6) and the constants in Table 6-4 was (±1.57) kJ mol^{-1}.

Table 6-6.Comparison of Vaporization Enthalpies and Vapor Pressures of This Work (t.w.) with Estimated Values

	$\ln(p/p_o)$ $T = 298.15$ K		$\Delta_l^g H_m$(298 K) kJ mol^{-1}		T_m K	$\ln(p/p_o)$ (T_m/K)		$\Delta_l^g H_m$(T_m/K) kJ mol^{-1}		
	t.w.	PERT2	t.w.	PERT2		t.w.	ref 15	t.w.	ref 15	PERT2
henicosane	-18.8	-18.8	106.8	107.8	437	-6.4	-6.4	86.7	88.3	85.0
docosane	-20.0	-20.0	111.9	113.8	443	-6.6	-6.4	90.7	91.8	88.1
tricosane	-21.1	-21.1	117.0	118.4	455	-6.5	-6.5	91.3	93.9	90.3
tetracosane	-22.2	-22.2	121.9	123.7	463	-6.5	-6.5	93.2	94.6	93.1
pentacosane	-23.2	-23.3	126.8	128.9	472	-6.5	-6.5	96.4	99.1	95.5
hexacosane	-24.3	-24.4	131.7	134.2	481	-6.4	-6.5	97.5	101.4	97.8
heptacosane	-25.2	-25.6	135.6	139.5	488	-6.5	-6.5	99.1	104.1	100.4
octadocosane	-26.5	-26.7	141.9	144.7	496	-6.5	-6.5	102.2	106.4	102.7
nonacosane	-27.6	-27.8	147.1	150.1	503	-6.5	-6.5	104.7	108.9	104.0
triacontane	-28.7	-28.9	152.3	155.4	510	-6.6	-6.6	107.0	111.2	107.5
hentriacontane	-29.8	-30.0	157.3	160.6	518	-6.5	-6.5	109.7	113.7	109.6
dotriacontane	-31.0	-31.1	162.5	165.9	525	-6.5	-6.5	111.9	115.8	111.8
tritriacontane	-32.1	-32.2	167.6	171.2	532	-6.5	-6.5	113.3	117.9	114.0
tetratriacontane	-33.2	-33.3	172.7	176.4	538	-6.6	-6.5	115.5	120.2	116.2
pentatriacontane	-34.3	-34.4	178.0	181.7	544	-6.6	-6.6	117.9	122.2	118.4
hexatriacontane	-35.4	-35.4	182.8	186.9	550	-6.6	-6.6	119.8	124.3	120.5
heptatriacontane	-36.4	-36.5	187.5	192.1	556	-6.6	-6.6	121.6	126.2	122.5
octatriacontane	-37.5	-37.6	192.6	197.3	561	-6.7	-6.6	123.8	128.4	124.7
tetracontane	-39.8	-39.7	203.5	207.7	572	-6.7	-6.6	128.1	132.2	128.7
dotetracontane	-41.9	-41.9	213.5	218	582	-6.8	-6.6	132.1	136	132.7
tetratetracontane	-44.1	-43.9	223.7	228.1	592	-6.8	-6.6	135.9	139.3	136.4
hexatetacontane	-46.2	-46	233.3	238.2	601	-6.9	-6.6	139.7	142.8	140.2
octatetracontane	-48.3	-48.1	243	248.2	610	-6.9	-6.6	143.2	145.9	143.8
pentacontane	-50.3	-50.1	252.5	258.1	618	-7	-6.6	146.8	149	147.4
dopentacontane	-52.3	-50.8	261.8	260	626	-7	-6.6	152.8	152	147.5
tetrapentacontane	-54.2	-52.6	270.9	268.4	633	-7	-6.6	156.3	155	150.5
hexapentacontane	-56.1	-54.2	279.6	276.1	640	-7.1	-6.6	159.4	157.8	153.0
octapentacontane	-58	-55.8	288.3	283.9	647	-7.2	-6.6	162.4	160.3	155.5
hexacontane	-60.2	-57.3	299.9	290.8	653	-7.3	-6.6	163.4	163	157.8
dohexacontane	-61.9	-59	306.7	299	660	-7.3	-6.6	168.7	165.2	160.4
tetrahexacontane	-63.7	-60.3	315.3	305.2	665	-7.4	-6.7	172.3	168.3	162.4
hexahexacontane	-65.6	-61.8	323.9	312.5	671	-7.4	-6.6	175.5	170	164.7
octahexacontane	-67.3	-63.1	331.9	319	676	-7.5	-6.6	178.6	172.3	166.7
heptacontane	-69.1	-64.5	340.1	325.5	681	-7.6	-6.6	180.6	174.4	168.8
doheptacontane	-70.9	-65.7	348.2	331	686	-7.6	-6.6	184.9	176.4	170.3
tetraheptacontane	-72.6	-66.8	356.1	336.6	691	-7.7	-6.6	187.8	178.2	171.8
hexaheptacontane	-74.4	-68.0	364.2	342.3	695	-7.8	-6.6	192.2	180.4	173.6
octaheptacontane	-76.2	-69.2	372.1	348	700	-7.9	-6.6	193.7	181.6	175.2
octacontane	-77.9	-70.5	379.6	353.8	704	-8	-6.6	196.5	183.4	177.0
dooctacontane	-79.6	-71.4	387.2	358.5	708	-8.1	-6.6	199.4	185.1	178.3
tetraoctacontane	-81.2	-72.7	394.1	364.5	711	-8.2	-6.7	202.0	187.1	180.4
hexaoctacontane	-82.9	-73.7	402.2	369.4	715	-8.3	-6.6	205.2	188.4	181.7
octaoctacontane	-84.6	-74.5	409.3	373.0	718	-8.4	-6.7	207.8	190.2	182.6
nonacontane	-86.2	-75.5	416.5	380.0	722	-8.5	-6.6	210.4	191.4	183.9
dononacontane	-87.4	-76.6	425.5	383.0	725	-8.7	-6.6	209.2	192.8	185.5

All vaporization enthalpies calculated by using eq. (6-6) were slightly larger than those obtained by direct correlation of $\Delta_{\mathrm{sln}}{}^{\mathrm{g}}H_{\mathrm{m}}$ (T_{m}) with $\Delta_{\mathrm{l}}{}^{\mathrm{g}}H_{\mathrm{m}}$ (298.15K) except for two that were slightly smaller. The largest deviations were observed for the largest alkanes studied, those for which the extrapolations are the most extensive. The largest difference was 5.7 kJ mol^{-1} observed for octaoctacontane. The dashed line and the solid circles in Figure 6-2 illustrate this deviation. The two sets of results are probably still within experimental error of each other. The differences are probably a good indication of the magnitude of the absolute error in the values, and relative errors between homologs are probably less.

Since the vaporization enthalpies reported in column 9 of Table 6-6 were calculated at T_{m} using eq. (6-6), a question arises regarding the divergence in $\Delta_{\mathrm{l}}{}^{\mathrm{g}}H_{\mathrm{m}}$ (T_{m}) observed in Figure 6-2 between these results and those calculated using PERT2 both at T = 298.15 K and T_{m}. Is this divergence a consequence of the deviations just discussed and/or due to the extensive extrapolations associated with this work? To address this question the following correlations were performed. It has previously been demonstrated that vaporization enthalpies of hydrocarbons correlate linearly with enthalpies of transfer measured by gas chromatography.[1-5] This linear correlation has normally been demonstrated at T = 298.15 K, since this generally has been the temperature of interest. The choice in temperature, however, is arbitrary. Correlation between $\Delta_{\mathrm{sln}}{}^{\mathrm{g}}H_{\mathrm{m}}$ (T_{m}) and $\Delta_{\mathrm{l}}{}^{\mathrm{g}}H_{\mathrm{m}}$ (T) should be observed at any value of T, provided the vaporization enthalpies of the reference compounds are all available at the same reference temperature, T. To determine whether the divergence observed in Table 6 both at T = 298.15 K and T_{m} between the two sets of values is real, or simply an artifact of the extrapolations involved in this work, the experimental enthalpies of transfer measured at $T = 676$ K, run 1, were correlated with the vaporization enthalpies calculated by PERT2 at $T = 298.15$ K and 500 K. If the vaporization enthalpies calculated by PERT2 are indeed correct, then the experimental enthalpies of transfer of the larger alkanes, which have shown curvature with N (Figure 6-3), should correlate linearly with the results of PERT2; otherwise, some curvature should be observed.

Figure 6-4 illustrates the nature of the two correlations obtained. The results at both temperatures are fit quite satisfactorily by a linear correlation. However, some curvature is indeed observed by the quality of the fit, r^2, as described in the caption of the figure by the linear and parabolic functions, equations (6-7) – (6-10). Results with a similar curvature were also observed for runs 2 and 3 (not shown). These results suggest that the curvature observed using PERT2 (Figure 6-2) is somewhat exaggerated.

A similar trend is observed in $\ln(p/p_o)$ values calculated by correlation-gas chromatography and PERT2. Figure 6-5 illustrates the behavior of $\ln(p/p_o)$ versus N. As with vaporization enthalpies, these results suggest that the amount of curvature obtained in this study, equations (6-11), (6-12), as a function of the number of carbon atoms, N, is slightly less than predicted by PERT2.

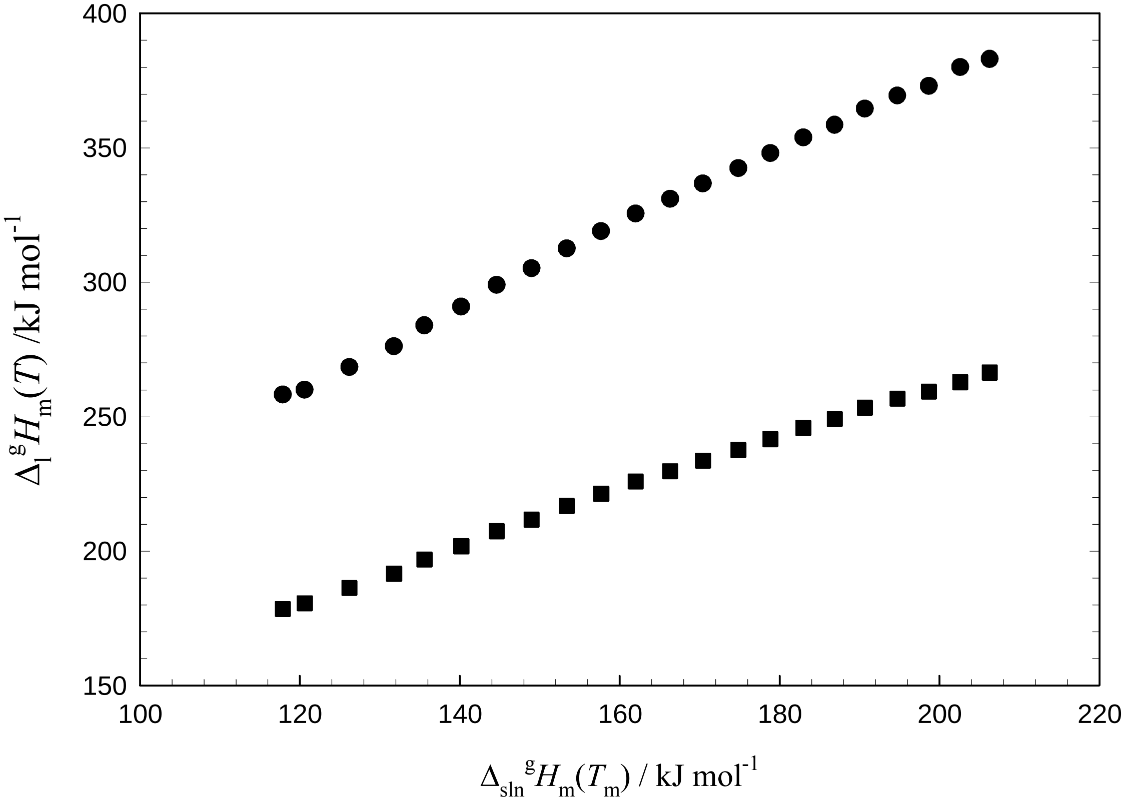

Figure 6-4. Plots of vaporization enthalpies calculated by PERT2 against enthalpies of transfer measured for run 1. Circles: T = 298.15 K; squares: T = 500 K. The lines calculated by linear regression and by using a second order polynomial are given by

circles: $\Delta_l{}^gH_m(298.15\ \text{K})/\text{kJ mol}^{-1} = (1.46 \pm 0.011)\Delta_{sln}{}^gH_m(676\ \text{K}) + (60.56 \pm 1.36)$;
$r^2 = 0.9977$ (6-7)

$\Delta_l{}^gH_m(298.15\ \text{K})/\text{kJ mol}^{-1} = -(2.58 \pm 0.33)10^{-3}\Delta_{sln}{}^gH_m(676\ \text{K}) + (2.28 \pm 0.11)\Delta_{sln}{}^gH_m(676\ \text{K})$
$+(22.3 \pm 8.59)$; $r^2 = 0.9994$ (6-8)

squares: $\Delta_l{}^gH_m(500\ \text{K})/\text{kJ mol}^{-1} = (1.008 \pm 0.011)\Delta_{sln}{}^gH_m(676\ \text{K}) + (60.56 \pm 1.36)$;
$r^2 = 0.9977$ (6-9)

$\Delta_l{}^gH_m(500\ \text{K})/\text{kJ mol}^{-1} = -(1.82 \pm 0.2)10^{-3}\Delta_{sln}{}^gH_m(676\ \text{K}) + (1.60 \pm 0.06)\Delta_{sln}{}^gH_m(676\ \text{K})$
$+(14.0 \pm 5.1)$; $r^2 = 0.9996$ (6-10)

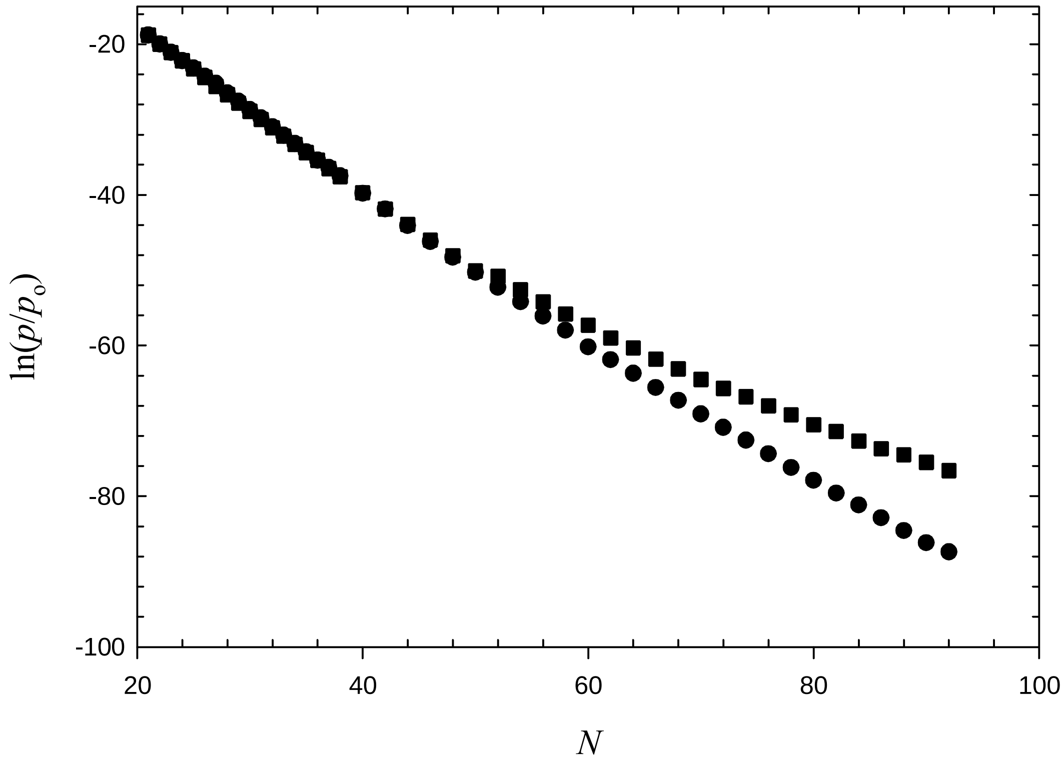

Figure 6-5. Plots of $\ln(p/p_o)$ against the number of carbon atoms, N, at $T = 298.15$ K. The circles are values calculated by correlation gas chromatography (eq. (6-6)), and the squares are values calculated by PERT2. Both results show varying amounts of curvature. The curves are fit by the following relationships

circles:

$$\ln(p/p_o) = (2.77\pm0.05)10^{-3}N^2 - (1.285\pm0.005)N + (7.21\pm0.1.4);\ r^2 = 0.9999; \qquad (6\text{-}11)$$

squares:

$$\ln(p/p_o) = (5.79\pm0.10)10^{-3}N^2 - (1.47\pm0.01)N + (9.69\pm0.27);\ r^2 = 0.9998; \qquad (6\text{-}12)$$

6.3.3. Thermodynamics of Correlation-Gas Chromatography as Applied to Large n-Alkanes

For larger n-alkanes from doheptacontane to dononacontane vaporization enthalpies measured by correlation-gas chromatography exceed in magnitude the strength of a single carbon-carbon bond (347 kJ/mol). Since vaporization enthalpy measures the strength of intermolecular forces in solution, the question arises: "How it is possible to evaluate vaporization enthalpies of materials whose magnitude significantly exceeds that of the weakest bonds in the molecule?"

As previously described, correlation-gas chromatographic technique relies on the linear correlation observed between enthalpies of transfer from solution to the vapor, $\Delta_{\mathrm{sln}}{}^{\mathrm{g}}H_{\mathrm{m}}(T_m)$, as measured by gas chromatography, and the vaporization enthalpy ($\Delta_{\mathrm{l}}{}^{\mathrm{g}}H_{\mathrm{m}}$) of a series of standards. The term $\Delta^{\mathrm{g}}{}_{\mathrm{sln}}H_{\mathrm{m}}(T_{\mathrm{m}})$ can be equated in a thermodynamic cycle, eq. (6-2), to the sum of the vaporization enthalpy measured at $T = T_{\mathrm{m}}$ and the enthalpy of solution ($\Delta_{\mathrm{sln}}H_{\mathrm{m}}$) of each solute on the stationary phase of the column.

The effect of temperature on the magnitude of $\Delta_{\mathrm{sln}}{}^{\mathrm{g}}H_{\mathrm{m}}(T_{\mathrm{m}})$ is illustrated in Table 6-7A to 6-7C for a series of n-alkanes. The retention times and the resulting values of $\Delta_{\mathrm{sln}}{}^{\mathrm{g}}H_{\mathrm{m}}(T_{\mathrm{m}})$ and $\Delta_{\mathrm{l}}{}^{\mathrm{g}}H_{\mathrm{m}}(298.15\ \mathrm{K})$ have been reported previously.[2] In this study, the vaporization enthalpies of tetradecane to eicosane have been adjusted to the mean temperature of the GC measurements, T = 449, 509 and 539 K, using the actual temperatures employed in the GC experiments for the calculations. An examination of the correlation equations and their corresponding coefficients associated with equations (6-13), (6-15), (6-17) of Tables 6-7A to 6-7C suggests good linear relationships between $\Delta_{\mathrm{sln}}{}^{\mathrm{g}}H_{\mathrm{m}}(T_{\mathrm{m}})$ and $\Delta_{\mathrm{l}}{}^{\mathrm{g}}H_{\mathrm{m}}(T_{\mathrm{m}})$ at these temperatures as well as with $\Delta_{\mathrm{l}}{}^{\mathrm{g}}H_{\mathrm{m}}(298.15\ \mathrm{K})$, equations (6-14), (6-16), and (6-18).[2] Uncertainties in $\Delta_{\mathrm{sln}}{}^{\mathrm{g}}H_{\mathrm{m}}(T_{\mathrm{m}})$ were calculated from the uncertainty associated with the slope of the $\ln(t_{\mathrm{o}}/t_{\mathrm{a}})$ vs $(1/T)$ plot and the uncertainties in $\Delta_{\mathrm{l}}{}^{\mathrm{g}}H_{\mathrm{m}}(T_{\mathrm{m}})$, from the uncertainties associated with the slopes and intercepts associated with the correlation equations, equations (6-13) to (6-18). Applying thermodynamic equality, eq. (6-2), to these results allows an evaluation of the magnitude of interaction of each solute, $\Delta_{\mathrm{sln}}H_{\mathrm{m}}(T_{\mathrm{m}})$, with the stationary phase of the column as a function of temperature. The resulting enthalpies of solution are summarized in Table 6-8. The results indicate that the enthalpy for the process of transferring the solute from the gas phase to the stationary phase of the column, $-\Delta_{\mathrm{sln}}{}^{\mathrm{g}}H_{\mathrm{m}}(T_{\mathrm{m}})$, is less exothermic than the process of condensing the vapor, $-\Delta_{\mathrm{l}}{}^{\mathrm{g}}H_{\mathrm{m}}(T_{\mathrm{m}})$. This implies that the enthalpy of interaction of the solute on the stationary phase of the column at the temperature of measurement is weaker than the interaction of the solute with itself, resulting in an endothermic enthalpy of solution. In turn, this reduces the enthalpy necessary to vaporize the solute off the column. In addition, this endothermic effect appears to be quite sensitive to temperature, increasing with increasing temperature. This is illustrated further in Figure 6-6 where $\Delta_{\mathrm{sln}}H_{\mathrm{m}}(T_{\mathrm{m}})$ from Table 6-8 is plotted against temperature for nonadecane and eicosane. Similar results are obtained for the other n-alkanes for which $\Delta_{\mathrm{sln}}H_{\mathrm{m}}(T_{\mathrm{m}})$ values are available at only two temperatures (not shown). The effect appears quite linear with temperature and though curvature might be observed with data at additional temperatures, the results suggest that $\Delta_{\mathrm{sln}}H_{\mathrm{m}}(T_{\mathrm{m}})$ will become thermoneutral at approximately 400 K and perhaps exothermic at lower temperatures if the trend continues.

Table 6-7A. Values of at $\Delta_{sln}{}^{g}H_{m}$(449 K) and $\Delta_{l}{}^{g}H_{m}$(449 K) on an SPB-5 Column

T_m = 449 K	-slope (T/K)	intercept	$\Delta_{sln}{}^{g}H_{m}$ (449 K) kJ·mol^{-1}	$\Delta_{l}{}^{g}H_{m}$(449 K) kJ·mol^{-1}		$\Delta_{l}{}^{g}H_{m}$(298 K) kJ·mol^{-1}	
				(lit) [6]	calc	(lit) [6]	(calc) [2]
tetradecane	6393.8±95	14.161±0.01	53.2±0.8	56.92	57.0±0.8	71.7	71.8±1.0
pentadecane	6787.9±73	14.597±0.01	56.4±0.6	60.71	60.6±0.8	76.8	76.5±1.0
hexadecane	7251.5±62	15.190±0.01	60.3±0.5	64.50	64.8±0.9	81.4	82.0±1.1
heptadecane	7612.6±65	15.587±0.01	63.3±0.5	68.19	68.1±0.9	86.5	86.3±1.2
octadecane	8014.8±71	16.070±0.01	66.6±0.6	72.11	71.8±1.0	91.4	91.1±1.3
nonadecane	8457.4±74	16.640±0.01	70.3±0.6	76.01	75.8±1.0	96.4	96.4±1.4
eicosane	8919.6±85	17.257±0.01	74.2±0.7	79.81	80.1±1.1	101.8	101.9±1.4

$\Delta^{g}{}_{l}H_{m}$(449 K)/kJ·mol^{-1} = (1.098±0.013) $\Delta_{sln}{}^{g}H_{m}$(449 K) - (1.39±0.25) $r^2 = 0.9993$ (6-13)

$\Delta^{g}{}_{l}H_{m}$(298 K)/kJ·mol^{-1} = (1.436±0.019) $\Delta_{sln}{}^{g}H_{m}$(449 K) + (4.54±0.35) $r^2 = 0.9991$ (6-14)

Table 6-7B. Values of at $\Delta_{sln}{}^{g}H_{m}$(509K) and $\Delta_{l}{}^{g}H_{m}$(509 K) on an SPB-5 Column

	-slope (T/K)	intercept	$\Delta_{sln}{}^{g}H_{m}$ (509 K) kJ·mol^{-1}	$\Delta_{l}{}^{g}H_{m}$(509 K) kJ·mol^{-1}		$\Delta_{l}{}^{g}H_{m}$(298 K) kJ·mol^{-1}	
				(lit)	calc	(lit)[6]	(calc)[2]
heptadecane	6108.2±78	12.148±0.008	50.8±0.7	62.83[6]	62.9±0.3	86.5	86.4±2.0
octadecane	6489.9±63	12.584±0.006	54.0±0.5	66.34[6]	66.2±0.3	91.4	91.4±2.2
nonadecane	6901.0±58	13.077±0.006	57.4±0.5	69.74[6]	69.8±0.3	96.4	96.7±2.3
eicosane	7270.0±60	13.496±0.006	60.4±0.5	73.07[6]	73.1±0.3	101.8	101.6±2.4
heneicosane	7670.9±65	13.974±0.006	63.8±0.5	76.66[2]	76.6±0.3		106.8±2.5
docosane	8064.5±71	14.439±0.007	67.1±0.6	80.13[2]	80.1±0.4		111.9±2.7
tricosane	8451.1±73	14.897±0.008	70.3±0.7	83.54[2]	83.5±0.4		117.0±2.8

$\Delta^{g}{}_{l}H_{m}$(509 K)/kJ·mol^{-1} = (1.062±0.004) $\Delta_{sln}{}^{g}H_{m}$(509 K) + (8.94±0.07) $r^2 = 0.9999$ (6-15)

${}^{g}{}_{l}H_{m}$(298 K)/kJ·mol^{-1} = (1.57±0.04) $\Delta_{sln}{}^{g}H_{m}$(509 K) + (6.66±0.30)[9] $r^2 = 0.9985$ (6-16)

Table 6-7C. Values of at $\Delta_{sln}{}^{g}H_{m}$(539 K) and $\Delta_{l}{}^{g}H_{m}$(539 K) on an SPB-5 Column

	-slope (T/K)	intercept	$\Delta_{sln}{}^{g}H_{m}$ (539 K) kJ·mol^{-1}	$\Delta_{l}{}^{g}H_{m}$(539 K) kJ·mol^{-1}		$\Delta_{l}{}^{g}H_{m}$(298 K) kJ·mol^{-1}	
				(lit)	calcd	(lit)	(calc) [2]
nonadecane	6165.3±125	11.692±0.01	51.3±1.1	67.08[6]	67.2±0.5	96.4[6]	96.8±2.2
eicosane	6483.0±128	12.013±0.01	53.9±1.1	70.15[6]	70.0±0.5	101.8[6]	101.8±2.3
heneicosane	6888.5±128	12.487±0.01	57.3±1.1	73.41[2]	73.5±0.5	106.8 [2]	106.8±2.5
docosane	7256.5±121	12.906±0.01	60.3±1.0	76.68[2]	76.7±0.5	111.9 [2]	112.0±2.5
tricosane	7619.9±116	13.318±0.01	63.4±1.0	79.89[2]	79.9±0.5	117.0 [2]	117.0±2.7
tetracosane	7972.5±113	13.713±0.01	66.3±0.9	83.0[2]	83.0±0.6		121.9±2.8
pentacosane	8320.7±112	14.105±0.01	69.2±0.9	86.05[2]	86.0±0.6		126.8±2.9

$\Delta^{g}{}_{l}H_{m}$(539 K)/kJ·mol^{-1} = (1.053±0.007) $\Delta_{sln}{}^{g}H_{m}$(539 K) + (13.20±0.106) $r^2 = 0.9998$ (6-17)

$\Delta^{g}{}_{l}H_{m}$(298 K)/kJ·mol^{-1} = (1.67±0.042) $\Delta_{sln}{}^{g}H_{m}$(539 K) + (11.04±0.41) [9] $r^2 = 0.9985$ (6-18)

Table 6-8. Values of $-\Delta_{\mathrm{sln}}{}^{\mathrm{g}}H_{\mathrm{m}}(T)$, $-\Delta_{\mathrm{l}}{}^{\mathrm{g}}H_{\mathrm{m}}(T)$ and $\Delta_{\mathrm{sln}}H_{\mathrm{m}}(T)$ as a Function of Temperature[a]

	$-\Delta_{\mathrm{sln}}{}^{\mathrm{g}}H_{\mathrm{m}}$(449 K) kJ·mol^{-1}	$-\Delta_{\mathrm{l}}{}^{\mathrm{g}}H_{\mathrm{m}}$(449 K) kJ·mol^{-1}(lit)	$\Delta_{\mathrm{sln}}H_{\mathrm{m}}$(449 K) kJ·mol^{-1}
tetradecane	-53.2±0.8	-56.92	3.7±0.8
pentadecane	-56.4±0.6	-60.71	4.3±0.6
hexadecane	-60.3±0.5	-64.5	4.2±0.5
heptadecane	-63.3±0.5	-68.19	4.9±0.5
octadecane	-66.6±0.6	-72.11	5.5±0.6
nonadecane	-70.3±0.6	-76.01	5.7±0.6
eicosane	-74.2±0.7	-79.81	5.6±0.7
	$-\Delta_{\mathrm{sln}}{}^{\mathrm{g}}H_{\mathrm{m}}$(509 K) kJ·mol^{-1}	$-\Delta_{\mathrm{l}}{}^{\mathrm{g}}H_{\mathrm{m}}$(509 K) kJ·mol^{-1}(lit)	$\Delta_{\mathrm{sln}}H_{\mathrm{m}}$(509 K) kJ·mol^{-1}
heptadecane	-50.8±0.7	-62.83	12.0±0.7
octadecane	-54.0±0.5	-66.34	12.3±0.5
nonadecane	-57.4±0.5	-69.82	12.4±0.5
eicosane	-60.4±0.5	-73.07	12.7±0.5
heneicosane	-63.8±0.5	-76.66	12.9±0.5
docosane	-67.1±0.6	-80.13	13.0±0.6
tricosane	-70.3±0.7	-83.54	13.2±0.7
	$-\Delta_{\mathrm{sln}}{}^{\mathrm{g}}H_{\mathrm{m}}$(539 K) kJ·mol^{-1}	$-\Delta_{\mathrm{l}}{}^{\mathrm{g}}H_{\mathrm{m}}$(539 K) kJ·mol^{-1}(lit)	$\Delta_{\mathrm{sln}}H_{\mathrm{m}}$(539 K) kJ·mol^{-1}
nonadecane	-51.3±1.1	-67.17	15.9±1.1
eicosane	-53.9±1.1	-70.15	16.3±1.1
heneicosane	-57.3±1.1	-73.41	16.1±1.1
docosane	-60.3±1.0	-76.68	16.4±1.0
tricosane	-63.4±1.0	-79.89	16.5±1.0
tetracosane	-66.3±0.9	-83.00	16.7±0.9
pentacosane	-69.2±0.9	-86.05	16.9±0.9

[a] Measured on a 30 m Supelco SPB-5 capillary column.[2]

The enthalpy of interaction of the solute with the stationary phase of the column appears both endothermic and also highly sensitive to temperature. This endothermicity does not preclude attractive interactions between the analyte and the stationary phase. The endothermicity is simply a reflection of the fact that the interaction of the analyte with the column is weaker than analyte-analyte interactions. The process of condensation of the vapor still remains highly exothermic. The sensitivity of $\Delta_{\mathrm{sln}}H_{\mathrm{m}}(T_{\mathrm{m}})$ to increasing temperature may be due to a decrease in the accessible surface area of both the stationary phase and analyte with increasing temperature. An increase in temperature should increase the amplitudes and populations of excited low lying vibrational frequencies which may contribute to a decrease in the accessible surface area of both the analyte and the stationary phase. This could result in a decrease in stabilizing interactions. The endothermic nature of $\Delta_{\mathrm{sln}}H_{\mathrm{m}}(T_{\mathrm{m}})$ and its sensitivity to temperature provides an explanation as to why it has been possible to evaluate the vaporization enthalpies of larger hydrocarbons whose vaporization enthalpies exceed the magnitude of the C-C bond strength.

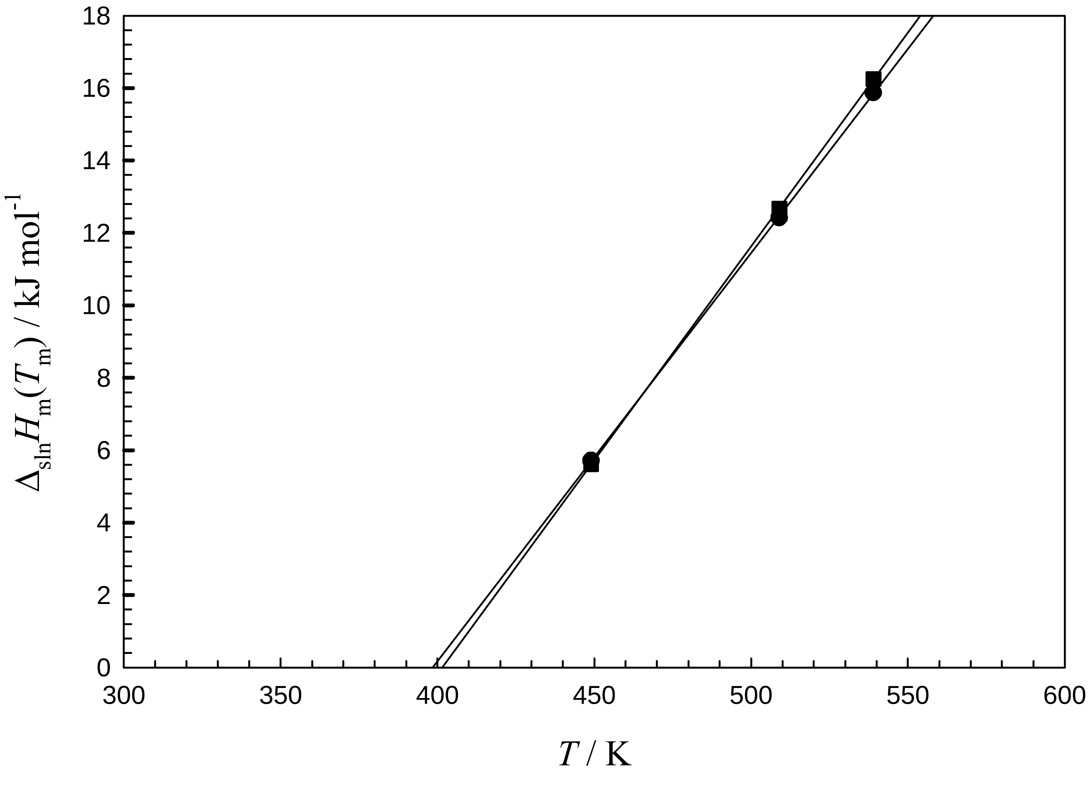

Figure 6-6. The effect of temperature on the magnitude of $\Delta_{\mathrm{sln}}H_{\mathrm{m}}(T/\mathrm{K})$. ■, eicosane; ●, nonadecane.

6.4. Summary

The vaporization enthalpies and vapor pressures of the even n-alkanes from eicosane to dononacontane have been evaluated through a process of extrapolation by correlation-gas chromatography. The vaporization enthalpies of all these hydrocarbons are measurements of the sub-cooled liquid and as such are hypothetical properties. The results are compared to two sets of estimated values. The results are generally in good agreement up to approximately hexacontane. Above hexacontane, the estimated and measured values begin to diverge. However, both experimental and estimation methods are in agreement with the prediction that vaporization enthalpies of linear molecules will show some curvature with increasing size at temperatures below boiling.

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Appendix A

Appendix A-1: Retention times (t/min) for runs 1-6 as a function of temperature (T/K)

Run 1	342.3	347.4	352.3	357.5	362.5	367.5	372.6
				t/min			
methane	2.716	2.709	2.731	2.782	2.817	2.847	2.883
pentane	2.922	2.893	2.898	2.928	2.951	2.967	2.994
pyrazine	4.225	4.008	3.856	3.757	3.672	3.599	3.548
pyridine	4.351	4.117	3.951	3.84	3.745	3.663	3.604
2-methylpyrazine	5.784	5.301	4.932	4.66	4.435	4.246	4.1
3-picoline	6.809	6.151	5.644	5.257	4.938	4.674	4.467
2,5-dimethylpyrazine	8.813	7.764	6.944	6.317	5.809	5.392	5.062
pyridazine	8.91	7.886	7.047	6.418	5.921	5.497	5.15

Run 2	342.3	347.4	352.3	357.5	362.5	367.5	372.6
				t/min			
methane	2.709	2.721	2.758	2.795	2.826	2.821	2.89
pentane	2.912	2.899	2.922	2.937	2.958	2.942	2.993
pyrazine	4.217	4.018	3.88	3.77	3.68	3.572	3.548
pyrimidine	4.426	4.195	4.028	3.897	3.787	3.664	3.627
2-methylpyrazine	5.782	5.32	4.964	4.683	4.446	4.222	4.102
3-picoline	6.809	6.174	5.677	5.284	4.95	4.65	4.468
2,5-dimethylpyrazine	8.821	7.798	6.99	6.359	5.825	5.37	5.065

Run 3	337.9	342.9	348	353	358.1	363.2	368.2
				t/min			
methane	2.676	2.712	2.73	2.79	2.811	2.844	2.873
cyclopentane	3.119	3.103	3.074	3.099	3.088	3.089	3.099
1,3,5-triazine	3.754	3.642	3.537	3.496	3.43	3.389	3.359
pyrazine	4.46	4.235	4.039	3.925	3.798	3.706	3.634
pyrimidine	4.71	4.443	4.214	4.072	3.923	3.813	3.726
2-methylpyrazine	6.367	5.804	5.34	5.01	4.708	4.474	4.287
3-picoline	7.639	6.843	6.198	5.727	5.31	4.982	4.719
2,6-lutidine	8.473	7.504	6.726	6.143	5.642	5.249	4.933
2,5-dimethylpyrazine	10.146	8.855	7.826	7.039	6.379	5.86	5.441
pyridazine	10.231	8.957	7.959	7.148	6.486	5.964	5.535

Run 4	342.9	348	353.1	358.1	363.2	368.3	373.3
				t/min			
methane	2.819	2.584	2.866	2.877	2.918	2.918	2.983
pentane	3.029	2.774	3.034	3.033	3.057	3.049	3.1
1,3,5-triazine	3.778	3.418	3.593	3.516	3.48	3.418	3.428
pyrazine	4.39	3.937	4.034	3.895	3.806	3.7	3.674
pyridine	4.52	4.051	4.132	3.981	3.88	3.766	3.732
2-methylpyrazine	6.004	5.274	5.15	4.83	4.594	4.371	4.246
3-picoline	7.067	6.154	5.885	5.445	5.114	4.814	4.626
2,6-lutadiene	7.757	6.701	6.316	5.791	5.39	5.036	4.805
2,5-dimethylpyrazine	9.15	7.828	7.239	6.549	6.017	5.56	5.137
pyridazine	9.336	7.941	7.373	6.655	6.124	5.672	5.245

Run 5	372.8	367.7	362.6	357.5	352.5	347.5	342.5
				t/min			
methane	3.044	2.982	2.958	2.934	2.922	2.904	2.87
s-triazine	3.482	3.472	3.508	3.559	3.619	3.705	3.827
pyrazine	3.73	3.756	3.838	3.944	4.069	4.229	4.439
pyrimidine	3.815	3.855	3.953	4.078	4.225	4.415	4.662
2-methylpyrazine	4.304	4.423	4.623	4.874	5.183	5.564	6.055
4-methylpyrimidine	4.412	4.548	4.772	5.051	5.396	5.822	6.369
3-picoline	4.689	4.868	5.147	5.497	5.923	6.453	7.134
2,6-lutidine	4.868	5.087	5.419	5.837	6.356	6.998	7.824
2,5-dimethylpyrazine	5.304	5.605	6.039	6.585	7.28	8.125	9.215
pyridazine	5.397	5.701	6.142	6.69	7.395	8.244	9.334
2,4,6-trimethylpyridine	6.761	7.352	8.171	9.206	10.561	12.195	14.328
3-methylpyridazine	6.989	7.606	8.453	9.513	10.911	12.594	14.763

Run 6	372.7	367.8	362.7	357.7	352.6	347.5	342.5
				t/min			
methane	3.025	3.013	2.981	2.952	2.918	2.897	2.863
s-triazine	3.466	3.495	3.528	3.576	3.637	3.713	3.808
pyrazine	3.711	3.777	3.853	3.953	4.077	4.229	4.419
pyrimidine	3.794	3.873	3.965	4.084	4.231	4.411	4.635
2-methylpyrazine	4.285	4.449	4.645	4.892	5.198	5.574	6.048
4-methylpyrimidine	4.392	4.575	4.794	5.07	5.412	5.833	6.367
3-picoline	4.666	4.895	5.169	5.513	5.938	6.461	7.12
2,6-lutidine	4.845	5.117	5.445	5.858	6.371	7.009	7.819
2,5-dimethylpyrazine	5.283	5.638	6.071	6.616	7.295	8.143	9.228
pyridazine	5.376	5.734	6.172	6.726	7.41	8.266	9.362
2,4,6-trimethylpyridine	6.73	7.391	8.208	9.244	10.55	12.202	14.34
3-methylpyridazine	6.963	7.643	8.492	9.572	10.913	12.617	14.818

Appendix B

Appendix B-1: Retention times (t/min) for runs 1-14 as a function of temperature (T/K)

Run 1

T/K	424.6	429.5	434.4	439.3	444.2	449.1	454
				t/min			
cyclopentane	2.043	2.044	2.063	2.08	2.105	2.125	2.161
tri-n-butylamine	3.508	3.31	3.165	3.046	2.958	2.88	2.836
quinoline	4.195	3.92	3.711	3.536	3.4	3.28	3.202
isoquinoline	4.435	4.127	3.89	3.691	3.535	3.4	3.308
quinaldine	4.99	4.591	4.281	4.024	3.819	3.643	3.519
2,6-dimethylquinoline	6.965	6.247	5.68	5.217	4.841	4.525	4.285
2-phenylpyridine	7.895	7.029	6.342	5.777	5.315	4.931	4.64

Run 2

T/K	424.7	429.6	434.5	439.4	444.2	449.2	454.1
				t/min			
cyclopentane	2.06	2.061	2.07	2.075	2.092	2.101	2.115
tri-n-butylamine	3.533	3.33	3.17	3.035	2.935	2.843	2.771
quinoline	4.225	3.941	3.715	3.521	3.372	3.236	3.127
isoquinoline	4.468	4.149	3.893	3.675	3.506	3.354	3.23
quinaldine	5.029	4.615	4.285	4.005	3.787	3.592	3.434
2,6-dimethylquinoline	7.012	6.275	5.682	5.189	4.798	4.457	4.179
3-phenylpyridine	7.961	7.058	6.338	5.743	5.269	4.857	4.521

Run 3

T/K	425.4	430.3	435.3	440.3	445.25	450.25	454.4
				t/min			
cyclopentane	1.835	1.85	1.86	1.883	1.917	1.945	1.962
tri-n-butylamine	3.154	2.991	2.853	2.757	2.691	2.635	2.575
quinoline	3.775	3.543	3.345	3.202	3.095	3	2.909
isoquinoline	3.991	3.729	3.505	3.342	3.217	3.109	3.005
quinaldine	4.49	4.147	3.858	3.642	3.475	3.33	3.195
2,6-dimethylquinoline	6.262	5.636	5.117	4.719	4.402	4.134	3.89
2-phenylpyridine	7.11	6.346	5.714	5.223	4.835	4.509	4.214
7,8-benzoquinoline	24.128	20.37	17.335	14.982	13.076	11.544	10.219
acridine	25.195	21.229	18.029	15.551	13.55	11.936	10.554

Run 4

T/K	425.4	430.35	435.35	440.3	445.2	450.1	455.1
				t/min			
cyclopentane	1.829	1.843	1.86	1.883	1.921	1.954	1.978
tributylamine	3.145	2.983	2.852	2.756	2.7	2.646	2.595
quinoline	3.761	3.532	3.343	3.2	3.103	3.015	2.93
isoquinoline	3.977	3.718	3.503	3.34	3.226	3.124	3.026
quinaldine	4.479	4.139	3.856	3.64	3.485	3.347	3.219
2,6-dimethylquinoline	6.246	5.625	5.114	4.716	4.417	4.153	3.919
3-phenylpyridine	7.097	6.337	5.708	5.222	4.851	4.529	4.243
7,8-benzoquinoline	24.028	20.292	17.305	14.955	13.128	11.6	10.28
acridine	25.079	21.141	17.998	15.525	13.602	12.005	10.612

Run 5

T/K	449.6	454.5	459.5	464.5	469.5	474.4	479.5
				t/min			
cyclohexane	3.418	3.444	3.453	3.466	3.477	3.519	3.512
tri-n-butylamine	4.456	4.359	4.256	4.175	4.107	4.085	4.013
quinazoline	5.171	5	4.832	4.693	4.575	4.511	4.398
(-)-nicotine	6.057	5.761	5.479	5.25	5.058	4.937	4.765
2,6-dimethylquinoline	7.09	6.647	6.244	5.909	5.629	5.433	5.196
2,2-bipyridine	7.489	6.993	6.542	6.169	5.855	5.635	5.372
2-phenylpyridine	7.802	7.26	6.748	6.342	6.003	5.775	5.481
4,4-bipyridine·xH2O	9.297	8.522	7.841	7.276	6.802	6.45	6.073
7,8-benzoquinoline	20.681	18.122	15.933	14.144	12.66	11.509	10.384
acridine	21.461	18.764	16.49	14.599	13.038	11.815	10.653

Run 6

T/K	449.5	454.4	459.4	464.3	469.3	474.3	479.3
				t/min			
cyclohexane	3.454	3.465	3.481	3.499	3.51	3.537	3.547
tri-n-butylamine	4.499	4.385	4.289	4.214	4.144	4.101	4.051
quinazoline	5.222	5.029	4.869	4.736	4.615	4.53	4.439
(-)-nicotine	6.11	5.797	5.521	5.298	5.103	4.951	4.807
2,6-dimethylquinoline	7.156	6.685	6.29	5.962	5.676	5.452	5.242
2,2-bipyridine	7.557	7.034	6.591	6.223	5.905	5.653	5.419
2-phenylpyridine	7.858	7.319	6.801	6.403	6.061	5.777	5.529
4,4-bipyridine·xH2O	9.384	8.569	7.898	7.336	6.858	6.477	6.125
7,8-benzoquinoline	20.849	18.232	16.045	14.249	12.759	11.534	10.466
acridine	21.675	18.858	16.6	14.719	13.138	11.875	10.733

Run 7

T/K	449.3	454.4	459.3	464.3	469.2	474.2	479.2
				t/min			
cyclopentane	3.452	3.463	3.484	3.501	3.519	3.56	3.592
tributylamine	4.569	4.443	4.349	4.268	4.201	4.174	4.143
2,2-bipyridine	7.676	7.125	6.681	6.302	5.985	5.752	5.539
2-phenylpyridine	7.977	7.379	6.894	6.479	6.137	5.883	5.651
4,4-bipyridine·xH2O	9.524	8.68	8.001	7.428	6.947	6.584	6.258
7,8-benzoquinoline	21.221	18.496	16.287	14.442	12.934	11.746	10.703
phenanthridine	21.961	19.084	16.784	14.858	13.274	12.029	10.942
1,7-phenathrolene	23.755	20.587	18.047	15.906	14.164	12.799	11.599
4,7-phenanthrolene	26.875	23.138	20.166	17.688	15.651	14.043	12.652

Run 8

T/K	449.4	454.4	459.2	464.1	469.3	474.2	479.2
				t/min			
cyclopentane	3.404	3.463	3.44	3.455	3.474	3.504	3.534
tri-n-butylamine	4.504	4.443	4.294	4.213	4.148	4.107	4.075
2,2-bipyridine	7.569	7.125	6.598	6.226	5.912	5.661	5.449
2-phenylpyridine	7.87	7.379	6.812	6.407	6.066	5.789	5.559
4,4-bipyridine·xH2O	9.393	8.68	7.902	7.337	6.863	6.483	6.158
7,8-benzoquinoline	20.921	18.496	16.08	14.286	12.807	11.551	10.529
phenanthridine	21.64	19.084	16.569	14.686	13.135	11.842	10.765
1,7-phenanthrolene	23.408	20.587	17.806	15.733	14.035	12.584	11.41
4,7-phenanthrolene	26.516	23.138	19.912	17.481	15.479	13.846	12.456

Run 9

T/K	474	479.1	484	489	494	498.9	503.9
				t/min			
cyclopentane	3.228	3.247	3.261	3.281	3.297	3.315	3.336
tributylamine	3.787	3.752	3.714	3.687	3.665	3.648	3.637
2-benzylpyridine	5.408	5.172	4.965	4.791	4.644	4.517	4.413
7,8-benzoquinoline	10.668	9.71	8.888	8.191	7.609	7.106	6.682
acridine	10.943	9.945	9.088	8.364	7.754	7.233	6.793
9-methylcarbazole	11.299	10.233	9.326	8.557	7.914	7.367	6.901
4,7-phenanthrolene	12.751	11.481	10.394	9.477	8.712	8.051	7.499

Run 10

T/K	472.9	478	483	487.8	492.8	497.7	502.6
				t/min			
cyclopentane	3.27	3.282	3.288	3.304	3.312	3.326	3.348
tributylamine	3.834	3.784	3.738	3.709	3.677	3.655	3.647
2-benzylpyridine	5.458	5.203	4.982	4.81	4.652	4.521	4.42
7,8-benzoquinoline	10.774	9.767	8.918	8.221	7.62	7.113	6.694
acridine	11.076	10.017	9.134	8.402	7.771	7.243	6.806
9-methylcarbazole	11.421	10.299	9.362	8.592	7.928	7.371	6.914
4,7-phenanthrolene	12.903	11.563	10.445	9.521	8.725	8.064	7.514

Run 11

T/K	478.8	483.9	488.9	493.7	498.7	503.7	508.7
				t/min			
cyclopentane	3.366	3.355	3.373	3.391	3.407	3.425	3.447
tributylamine	3.888	3.822	3.792	3.771	3.752	3.739	3.733
4-phenylpyrimidine	5.354	5.108	4.934	4.786	4.656	4.548	4.461
4,4-bipyridyl(anhyd)	5.88	5.561	5.328	5.13	4.957	4.813	4.694
7,8-benzoquinoline	10.054	9.144	8.427	7.826	7.311	6.875	6.506
acridine	10.299	9.35	8.605	7.977	7.442	6.986	6.603
4,7-phenanthrolene	11.884	10.686	9.751	8.957	8.282	7.715	7.235

Run 12

T/K	473.8	478.7	483.7	488.7	493.7	498.8	503.7
				t/min			
cyclopentane	3.347	3.387	3.364	3.38	3.392	3.415	3.423
tributylamine	3.927	3.91	3.831	3.8	3.772	3.757	3.736
4-phenylpyrimidine	5.591	5.384	5.122	4.943	4.788	4.662	4.546
4,4-bipyridyl(anhyd)	6.199	5.913	5.578	5.337	5.133	4.962	4.812
7,8-benzoquinoline	11.044	10.101	9.171	8.443	7.832	7.311	6.876
acridine	11.34	10.349	9.378	8.623	7.981	7.444	6.985
4,7-phenanthrolene	13.216	11.945	10.722	9.764	8.962	8.291	7.713

Run 13

T/K	474.7	479.7	484.7	489.7	494.7	499.7	504.8
				t/min			
cyclopentane	3.252	3.266	3.279	3.297	3.311	3.325	3.346
tri-n-butylamine	3.81	3.765	3.727	3.7	3.676	3.656	3.646
2-benzylpyridine	5.418	5.175	4.968	4.797	4.648	4.52	4.418
2,4-bipyridine	6.09	5.76	5.482	5.248	5.047	4.872	4.73
7,8-benzoquinoline	10.701	9.718	8.893	8.205	7.617	7.11	6.688
acridine	10.999	9.966	9.106	8.384	7.769	7.242	6.802
9-methylcarbazole	11.342	10.248	9.338	8.573	7.925	7.37	6.91
4,7-phenanthrolene	12.817	11.505	10.415	9.499	8.723	8.063	7.511

Run 14

T/K	474.8	479.6	484.6	489.7	494.7	499.7	504.7
t/min							
cyclopentane	3.279	3.29	3.297	3.297	3.317	3.331	3.351
tributylamine	3.843	3.791	3.747	3.701	3.682	3.662	3.651
2-benzylpyridine	5.468	5.209	4.995	4.801	4.658	4.528	4.424
2,4-bipyridine	6.145	5.796	5.509	5.25	5.055	4.88	4.736
7,8-benzoquinoline	10.797	9.773	8.935	8.21	7.627	7.12	6.699
acridine	11.095	10.022	9.145	8.388	7.778	7.253	6.808
9-Methylcarbazole	11.44	10.306	9.379	8.581	7.937	7.384	6.918
4,7-phenanthrolene	12.924	11.567	10.459	9.501	8.733	8.073	7.52

Appendix B-2: Vaporization enthalpies results of runs 1 to 14

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

$\Delta^{g}{}_{l}H_m(298.15\text{ K})/\text{kJmol}^{-1} = (1.225\pm0.038)\Delta_{sln}{}^{g}H_m(439\text{ K}) + (10.96\pm0.18)$ $r^2 = 0.9981$

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

$\Delta^{g}{}_{l}H_m(298.15\text{ K})/\text{kJmol}^{-1} = (1.213\pm0.041)\Delta_{sln}{}^{g}H_m(439\text{ K}) + (9.17\pm0.20)$ $r^2 = 0.9977$

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

$\Delta^{g}{}_{l}H_m(298.15\text{ K})/\text{kJmol}^{-1} = (1.202\pm0.022)\Delta_{sln}{}^{g}H_m(440\text{ K}) + (12.43\pm0.36)$ $r^2 = 0.9986$

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

$\Delta^{\mathrm{g}}{}_{\mathrm{l}}H_{\mathrm{m}}$(298.15 K)/kJmol^{-1} = (1.22±0.023$\Delta_{\mathrm{sln}}{}^{\mathrm{g}}H_{\mathrm{m}}$(440 K) + (12.75±0.36) $r^2 = 0.9985$

Run 5	slope T/K	intercept	$\Delta_{\mathrm{sln}}{}^{\mathrm{g}}H_{\mathrm{m}}$(465 K) /kJ·mol^{-1}	$\Delta_{\mathrm{l}}{}^{\mathrm{g}}H_{\mathrm{m}}$(298.15 K) /kJ·mol^{-1} (lit)	$\Delta_{\mathrm{l}}{}^{\mathrm{g}}H_{\mathrm{m}}$(298.15 K) /kJ·mol^{-1} (calcd)
tri-n-butylamine	-5238.3	11.618	43.549	62.70	62.9±1.7
quinazoline	-4904.9	10.352	40.778		59.3±1.6
(-)-nicotine	-5355.1	10.945	44.520		64.1±1.7
2,6-dimethylquinoline	-5608.4	11.178	46.626	67.07	66.9±1.8
2,2-dipyridine	-5634.4	11.133	46.842		67.1±1.8
2-phenylpyridine	-5746.5	11.309	47.774	68.40	68.3±1.9
4,4-dipyridine·1.7H_2O	-5980.4	11.535	49.719		70.8±1.9
7,8-benzoquinoline	-6624.8	11.892	55.076	77.23	77.7±2.1
acridine	-6672.3	11.953	55.471	78.63	78.2±2.2

$\Delta^{\mathrm{g}}{}_{\mathrm{l}}H_{\mathrm{m}}$(298.15 K)/kJmol^{-1} = (1.287±0.038)$\Delta_{\mathrm{sln}}{}^{\mathrm{g}}H_{\mathrm{m}}$(465 K) + (6.85±0.41) $r^2 = 0.9974$

Run 6	slope T/K	intercept	$\Delta_{\mathrm{sln}}{}^{\mathrm{g}}H_{\mathrm{m}}$(464 K) /kJ·mol^{-1}	$\Delta_{\mathrm{l}}{}^{\mathrm{g}}H_{\mathrm{m}}$(298.15 K) /kJ·mol^{-1} (lit)	$\Delta_{\mathrm{l}}{}^{\mathrm{g}}H_{\mathrm{m}}$(298.15 K) /kJ·mol^{-1} (calcd)
tri-n-butylamine	-5272.4	11.686	43833	62.70	63.2±2.5
quinazoline	-4830.0	10.178	40154		58.5±2.3
(-)-nicotine	-5315.7	10.850	44192		63.7±2.5
2,6-dimethylquinoline	-5578.9	11.105	46380	67.07	66.5±2.7
2,2-dipyridine	-5612.1	11.076	46657		66.9±2.7
2-phenylpyridine	-5741.6	11.290	47733	68.40	68.3±2.7
4,4-bipyridine·1.7H_2O	-5961.6	11.486	49562		70.6±2.8
7,8-benzoquinoline	-6631.0	11.898	55128	77.23	77.8±3.1
acridine	-6675.0	11.951	55493	78.63	78.3±3.2

$\Delta^{\mathrm{g}}{}_{\mathrm{l}}H_{\mathrm{m}}$(298.15 K)/kJmol^{-1} = (1.29±0.056)$\Delta_{\mathrm{sln}}{}^{\mathrm{g}}H_{\mathrm{m}}$(464 K) + (6.69.01±0.59) $r^2 = 0.9944$

Run 7	slope T/K	intercept	$\Delta_{\mathrm{sln}}{}^{\mathrm{g}}H_{\mathrm{m}}$(464 K) /kJ·mol^{-1}	$\Delta_{\mathrm{l}}{}^{\mathrm{g}}H_{\mathrm{m}}$(298.15 K) /kJ·mol^{-1} (lit)	$\Delta_{\mathrm{l}}{}^{\mathrm{g}}H_{\mathrm{m}}$(298.15 K) /kJ·mol^{-1} (calcd)
tri-n-butylamine	-5092.5	11.23	42.337	62.70	62.2±3.6
2,2-dipyridine	-5585.7	10.997	46.437	67.00	67.4±3.9
2-phenylpyridine	-5681.0	11.14	47.229	68.40	68.4±3.9
4,4-dipyridine·1.7H_2O	-5935.8	11.414	49.348	70.70	71.1±4.1
7,8-benzoquinoline	-6606.7	11.833	54.925	77.23	78.2±4.5
phenanthridine	-6660.6	11.913	55.374	80.14	78.8±4.6
1,7-phenanthroline	-6712.8	11.936	55.808		79.4±4.6
4,7-phenanthroline	-6849.6	12.098	56.945		80.8±4.7

$\Delta^{\mathrm{g}}{}_{\mathrm{l}}H_{\mathrm{m}}$(298.15 K)/kJmol^{-1} = (1.276±0.081)$\Delta_{\mathrm{sln}}{}^{\mathrm{g}}H_{\mathrm{m}}$(464 K) + (8.18±0.92) $r^2 = 0.9841$

Run 8	slope T/K	intercept	$\Delta_{\mathrm{sln}}{}^{\mathrm{g}}H_{\mathrm{m}}$(464 K) /kJ·mol^{-1}	$\Delta_{\mathrm{l}}{}^{\mathrm{g}}H_{\mathrm{m}}$(298.15 K) /kJ·mol^{-1} (lit)	$\Delta_{\mathrm{l}}{}^{\mathrm{g}}H_{\mathrm{m}}$(298.15 K) /kJ·mol^{-1} (calcd)
tri-n-butylamine	-5163.9	11.397	42930	62.70	62.2±3.7
2,2-dipyridine	-5649.2	11.146	46965	67.0	67.4±4.0
2-phenylpyridine	-5750.6	11.302	47809	68.4	68.5±4.1
4,4-dipyridine·1.7H_2O	-5995.1	11.553	49841	70.7	71.1±4.2
7,8-benzoquinoline	-6668.9	11.979	55443	77.23	78.3±4.7
phenanthridine	-6715.6	12.043	55831	80.14	78.8±4.7
1,7-phenanthroline	-6770.3	12.072	56285		79.4±4.8
4,7-phenanthroline	-6902.7	12.223	57386		80.8±4.9

$\Delta^{\mathrm{g}}{}_{\mathrm{l}}H_{\mathrm{m}}$(298.15 K)/kJmol^{-1} = (1.286±0.083)$\Delta_{\mathrm{sln}}{}^{\mathrm{g}}H_{\mathrm{m}}$(464 K) + (7.00±0.94) $r^2 = 0.9834$

Run 9	slope T/K	intercept	$\Delta_{\mathrm{sln}}{}^{\mathrm{g}}H_{\mathrm{m}}$(489 K) /kJ·mol^{-1}	$\Delta_{\mathrm{l}}{}^{\mathrm{g}}H_{\mathrm{m}}$(298.15 K) /kJ·mol^{-1} (lit)	$\Delta_{\mathrm{l}}{}^{\mathrm{g}}H_{\mathrm{m}}$(298.15 K) /kJ·mol^{-1} (calcd)
tri-n-butylamine	-4949.8	11.022	41.150	62.70	62.6±2.4
2-benzylpyridine	-5645.5	11.132	46.935		70.0±2.7
7,8-benzoquinoline	-6396.3	11.488	53.176	77.23	78.0±3.0
acridine	-6429.5	11.522	53.452	78.63	78.3±3.0
9-methylcarbazole	-6539.1	11.709	54.364		79.5±3.1
4,7-phenanthrolene	-6625.9	11.726	55.085	80.80	80.4±3.1

$\Delta^{\mathrm{g}}{}_{\mathrm{l}}H_{\mathrm{m}}$(298.15 K)/kJmol^{-1} = (1.276±0.056)$\Delta_{\mathrm{sln}}{}^{\mathrm{g}}H_{\mathrm{m}}$(489 K) + (10.12±0.063) $r^2 = 0.9960$

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

$\Delta^{g}{}_{l}H_m$(298.15 K)/kJmol^{-1} = (1.292±0.06)$\Delta_{sln}{}^{g}H_m$(488 K) + (8.09±0.58) $r^2 = 0.9978$

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

$\Delta^{g}{}_{l}H_m$(298.15 K)/kJmol^{-1} = (1.246±0.055)$\Delta_{sln}{}^{g}H_m$(489 K) + (11.9±0.64) $r^2 = 0.9960$

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

$\Delta^{g}{}_{l}H_m$(298.15 K)/kJmol^{-1} = (1.264±0.05)$\Delta_{sln}{}^{g}H_m$(489 K) + (10.46±0.57) $r^2 = 0.9968$

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

$\Delta^{\mathrm{g}}{}_{\mathrm{l}}H_{\mathrm{m}}$(298.15 K)/kJmol^{-1} = (1.272±0.033)$\Delta_{\mathrm{sln}}{}^{\mathrm{g}}H_{\mathrm{m}}$(490 K) + (10.28±0.40) $r^2 = 0.9974$

Run 14	slope T/K	intercept	$\Delta_{\mathrm{sln}}{}^{\mathrm{g}}H_{\mathrm{m}}$(490 K) /kJ·mol^{-1}	$\Delta_{\mathrm{l}}{}^{\mathrm{g}}H_{\mathrm{m}}$(298.15 K) /kJ·mol^{-1} (lit)	$\Delta_{\mathrm{l}}{}^{\mathrm{g}}H_{\mathrm{m}}$(298.15 K) /kJ·mol^{-1} (calcd)
tri-n-butylamine	-5030.2	11.177	41.819	62.7	62.7±1.4
2-benzylpyridine	-6452.6	11.583	47.243	69.8	69.7±1.6
2,4-bipyridine	-5682.7	11.194	48.165		70.9±1.6
7,8-benzoquinoline	-6503.1	11.65	53.644	77.2	77.9±1.8
acridine	-6599.6	11.81	54.064	78.6	78.4±1.8
9-methylcarbazole	-6693	11.84	54.867	79.4	79.4±1.8
4,7-phenanthrolene	-5793.5	11.159	55.643	80.8	80.5±1.8

$\Delta^{\mathrm{g}}{}_{\mathrm{l}}H_{\mathrm{m}}$(298.15 K)/kJmol^{-1} = (1.285±0.032)$\Delta_{\mathrm{sln}}{}^{\mathrm{g}}H_{\mathrm{m}}$(490 K) + (8.96±0.39) $r^2 = 0.9976$

Appendix C

Appendix C-1. Retention times (t/min) for runs 1-6 as a function of temperature (T/K)

Run 1

T/K	462.9	467.9	472.9	477.9	482.8	487.7	492.8
				t/min			
cyclopentane	3.214	3.218	3.241	3.267	3.287	3.306	3.324
tributylamine	3.937	3.864	3.815	3.784	3.751	3.724	3.703
quinoxaline	4.269	4.167	4.091	4.039	3.986	3.941	3.903
quinazoline	4.428	4.307	4.216	4.15	4.086	4.03	3.982
2,6-dimethylquinoline	5.584	5.308	5.084	4.909	4.75	4.612	4.495
2-phenylpyridine	6.062	5.731	5.437	5.22	5.02	4.841	4.697
phthalazine	6.392	6.021	5.704	5.463	5.244	5.048	4.888
7,8-benzoquinoline	13.458	12.037	10.841	9.881	9.057	8.341	7.743
acridine	13.821	12.329	11.098	10.098	9.238	8.504	7.881

Run 2

T/K	463.1	467.9	473	477.9	482.8	487.7	492.8
				t/min			
cyclopentane	3.248	3.257	3.214	3.234	3.248	3.257	3.279
tributylamine	3.977	3.903	3.783	3.741	3.704	3.672	3.65
quinoxaline	4.314	4.209	4.057	3.993	3.936	3.886	3.848
quinazoline	4.473	4.35	4.181	4.103	4.034	3.974	3.926
2,6-dimethylquinoline	5.64	5.356	5.043	4.853	4.69	4.551	4.432
2-phenylpyridine	6.115	5.764	5.398	5.156	4.956	4.788	4.631
phthalazine	6.461	6.067	5.664	5.399	5.178	4.992	4.82
7,8-benzoquinoline	13.568	12.113	10.761	9.767	8.944	8.259	7.638
acridine	13.941	12.423	11.012	9.979	9.121	8.402	7.772

Run 3

T/K	492.8	497.7	502.6	507.7	512.8	517.8	522.9
				t/min			
cyclopentane	3.32	3.349	3.367	3.382	3.402	3.413	3.441
2,6-dimethylquinoline	4.48	4.392	4.306	4.231	4.171	4.111	4.078
2-phenylpyridine	4.672	4.561	4.455	4.363	4.288	4.216	4.171
phenazine	6.972	6.574	6.222	5.922	5.667	5.439	5.26
acridine	7.857	7.342	6.89	6.506	6.178	5.889	5.656
4,7-phenanthroline	8.831	8.178	7.613	7.134	6.726	6.366	6.074
benzo[c]cinnoline	9.849	9.057	8.377	7.8	7.308	6.878	6.526
triphenylamine	11.663	10.538	9.584	8.789	8.119	7.542	7.071
1,10-phenanthroline	12.264	11.11	10.13	9.303	8.599	7.991	7.491

Run 4

T/K	492.9	497.9	502.8	507.8	512.8	517.8	522.9
				t/min			
cyclopentane	3.316	3.315	3.317	3.327	3.34	3.358	3.368
2,6-dimethylquinoline	4.471	4.346	4.242	4.161	4.094	4.041	3.989
2-phenylpyridine	4.664	4.514	4.389	4.29	4.209	4.143	4.081
phenazine	6.953	6.508	6.131	5.822	5.561	5.342	5.145
acridine	7.836	7.269	6.79	6.396	6.063	5.782	5.532
4,7-phenanthroline	8.805	8.099	7.503	7.014	6.6	6.25	5.943
benzo(c)cinnoline	9.816	8.971	8.256	7.669	7.173	6.752	6.383
triphenylamine	11.624	10.435	9.446	8.639	7.967	7.402	6.915
1,10-phenanthroline	12.223	11.003	9.984	9.147	8.442	7.846	7.329

Run 5

T/K	453.2	458	463	468	472.8	477.9	482.8
				t/min			
pyridazine	0.303	0.276	0.25	0.232	0.213	0.197	0.182
3-methylpyridazine	0.446	0.404	0.366	0.334	0.306	0.281	0.258
phthalazine	4.149	3.623	3.186	2.796	2.475	2.197	1.95
benzo[c]cinnoline	22.578	19.069	16.217	13.800	11.849	10.207	8.785

Run 6

T/K	453.2	458.1	463.1	468	473	478	483
				t/min			
cyclopentane	3.187	3.197	3.215	3.245	3.268	3.284	3.315
pyridazine	3.484	3.468	3.464	3.474	3.479	3.478	3.493
3-methylpyridazine	3.625	3.594	3.577	3.575	3.571	3.561	3.569
phthalazine	7.27	6.763	6.343	6.008	5.714	5.457	5.251
benzo[c]cinnoline	25.328	21.874	19.064	16.815	14.917	13.318	11.98

Appendix C-2. Vaporization enthalpy results of runs 1 to 6

Run 1	$\frac{\text{slope}}{T/\text{K}}$	intercept	$\frac{\Delta_{\text{sln}}^{\text{g}}H_{\text{m}}(478\text{ K})}{\text{kJ}\cdot\text{mol}^{-1}}$	$\frac{\Delta_{\text{l}}^{\text{g}}H_{\text{m}}(298\text{ K})}{\text{kJ}\cdot\text{mol}^{-1}}$ (lit)	$\frac{\Delta_{\text{l}}^{\text{g}}H_{\text{m}}(298\text{ K})}{\text{kJ}\cdot\text{mol}^{-1}}$ (calc)
tributylamine	-4958.2	11.037	41.22	62.64	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	67.0±2.6
2-phenylpyridine	-5592.2	11.035	46.49	68.40	69.2±2.7
phthalazine	-5423.7	10.564	45.09		67.3±2.7
7,8-benzoquinoline	-6422.1	11.551	53.39	77.81	77.9±3.1
acridine	-6448.0	11.572	53.61	78.48	78.2±3.2

$\Delta_{\text{l}}^{\text{g}}H_{\text{m}}(298.15\text{ K})/\text{kJ}\cdot\text{mol}^{-1} = (1.25\pm0.057)\Delta_{\text{sln}}^{\text{g}}H_{\text{m}}(478\text{ K}) + (10.82\pm0.63)$ $r^2 = 0.9938$

Run 2	$\frac{\text{slope}}{T/\text{K}}$	intercept	$\frac{\Delta_{\text{sln}}^{\text{g}}H_{\text{m}}(478\text{ K})}{\text{kJ}\cdot\text{mol}^{-1}}$	$\frac{\Delta_{\text{l}}^{\text{g}}H_{\text{m}}(298\text{ K})}{\text{kJ}\cdot\text{mol}^{-1}}$ (lit)	$\frac{\Delta_{\text{l}}^{\text{g}}H_{\text{m}}(298\text{ K})}{\text{kJ}\cdot\text{mol}^{-1}}$ (calc)
tributylamine	-5167.8	11.485	42.96	62.70	62.5±0.8
quinoxaline	-4807.2	10.327	39.97		58.7±0.8
quinazoline	-4893.7	10.373	40.68		59.6±0.8
2,6-dimethylquinoline	-5599.7	11.229	46.55	67.07	67.1±0.9
2-phenylpyridine	-5747.2	11.366	47.78	68.4	68.7±0.9
phthalazine	-5615.7	10.97	46.69		67.3±0.9
7,8-benzoquinoline	-6607.6	11.943	54.93	77.81	77.8±1.1
acridine	-6657.5	12.016	55.35	78.48	78.4±1.1

$\Delta_{\text{l}}^{\text{g}}H_{\text{m}}(298.15\text{ K})/\text{kJ}\cdot\text{mol}^{-1} = (1.279\pm0.019)\Delta_{\text{sln}}^{\text{g}}H_{\text{m}}(478\text{ K}) + (7.55\pm0.21)$ $r^2 = 0.9993$

Run 3	$\frac{\text{slope}}{T/\text{K}}$	intercept	$\frac{\Delta_{\text{sln}}^{\text{g}}H_{\text{m}}(478\text{ K})}{\text{kJ}\cdot\text{mol}^{-1}}$	$\frac{\Delta_{\text{l}}^{\text{g}}H_{\text{m}}(298\text{ K})}{\text{kJ}\cdot\text{mol}^{-1}}$ (lit)	$\frac{\Delta_{\text{l}}^{\text{g}}H_{\text{m}}(298\text{ K})}{\text{kJ}\cdot\text{mol}^{-1}}$ (calc)
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±1.0
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

$\Delta_{\text{l}}^{\text{g}}H_{\text{m}}(298.15\text{ K})/\text{kJ}\cdot\text{mol}^{-1} = (1.418\pm0.02)\Delta_{\text{sln}}^{\text{g}}H_{\text{m}}(508\text{ K}) + (6.41\pm0.17)$ $r^2 = 0.9996$

Run 4	slope T/K	intercept	$\Delta_{\mathrm{sln}}{}^{\mathrm{g}}H_{\mathrm{m}}$(478 K) kJ·mol^{-1}	$\Delta_{\mathrm{l}}{}^{\mathrm{g}}H_{\mathrm{m}}$(298 K) kJ·mol^{-1} (lit)	$\Delta_{\mathrm{l}}{}^{\mathrm{g}}H_{\mathrm{m}}$(298 K) kJ·mol^{-1} (calc)
2,6-dimethylquinoline	-5323.2	10.662	44.26	67.07	67.1±0.3
2-phenylpyridine	-5465.3	10.797	45.44	68.40	68.7±0.3
acridine	-6324.6	11.33	52.58	78.63	78.7±0.3
4,7-phenanthroline	-6502.3	11.497	54.06	80.8	80.8±0.3
phenazine	-6152.8	11.199	51.15		76.7±0.3
benzo[c]cinnoline	-6598.9	11.523	54.86		81.9±0.4
triphenylamine	-7311.1	12.724	60.78		90.1±0.4
1,10-phenanthroline	-6958.8	11.939	57.85		86.1±0.4

$\Delta_{\mathrm{l}}{}^{\mathrm{g}}H_{\mathrm{m}}$(298.15 K)/kJ·mol^{-1} = (1.397±0.006)$\Delta_{\mathrm{sln}}{}^{\mathrm{g}}H_{\mathrm{m}}$(508 K) +(5.23±0.054) $r^2 = 0.9999$

Run 5	slope T/K	intercept	$\Delta_{\mathrm{sln}}{}^{\mathrm{g}}H_{\mathrm{m}}$(478 K) kJ·mol^{-1}	$\Delta_{\mathrm{l}}{}^{\mathrm{g}}H_{\mathrm{m}}$(298 K) kJ·mol^{-1} (lit)	$\Delta_{\mathrm{l}}{}^{\mathrm{g}}H_{\mathrm{m}}$(298 K) kJ·mol^{-1} (calc)
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	72.9±6.2
benzo[c]cinnoline	-6949.3	12.224	57.77	89.2	88.1±7.5

$\Delta_{\mathrm{l}}{}^{\mathrm{g}}H_{\mathrm{m}}$(298.15 K)/kJ·mol^{-1} = (1.32±0.124)$\Delta_{\mathrm{sln}}{}^{\mathrm{g}}H_{\mathrm{m}}$(478 K) + (12.0±2.4) $r^2 = 0.9913$

Run 6	slope T/K	intercept	$\Delta_{\mathrm{sln}}{}^{\mathrm{g}}H_{\mathrm{m}}$(478 K) kJ·mol^{-1}	$\Delta_{\mathrm{l}}{}^{\mathrm{g}}H_{\mathrm{m}}$(298 K) kJ·mol^{-1} (lit)	$\Delta_{\mathrm{l}}{}^{\mathrm{g}}H_{\mathrm{m}}$(298 K) kJ·mol^{-1} (calc)
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	72.6±5.0
benzo(c)cinnoline	-6869.5	12.068	57.11	89.2	88.3±7.2

$\Delta_{\mathrm{l}}{}^{\mathrm{g}}H_{\mathrm{m}}$(298.15 K)/kJ·mol^{-1} = (1.25±0.057)$\Delta_{\mathrm{sln}}{}^{\mathrm{g}}H_{\mathrm{m}}$(478 K) + (10.82±0.63) $r^2 = 0.9938$

Appendix D

Appendix D-1. Retention times (t/min) for runs 1 - 8 as a function of temperature (T/K)

Run 1

T/K	482.8	487.8	492.8	497.9	502.8	507.8	512.8
				t/min			
cyclopentane	3.093	3.108	3.121	3.139	3.147	3.166	3.185
2,6-dimethylquinoline	4.446	4.316	4.202	4.108	4.019	3.955	3.9
2-phenylpyridine	4.676	4.518	4.381	4.264	4.156	4.077	4.009
trans-azobenzene	5.892	5.571	5.294	5.061	4.852	4.688	4.546
acridine	8.62	7.937	7.35	6.855	6.423	6.07	5.767
4,7-phenanthroline	9.863	8.999	8.258	7.639	7.098	6.657	6.279

Run 2

T/K	458	462.7	467.6	472.6	477.6	482.6	487.6
				t/min			
cyclopentane	3.042	3.043	3.066	3.082	3.098	3.124	3.143
quinoline	4.302	4.166	4.072	3.984	3.91	3.861	3.812
1-phenylpyrazole	4.617	4.435	4.301	4.18	4.078	4.006	3.938
1-phenylimidazole	5.619	5.3	5.05	4.831	4.646	4.505	4.378
2-phenylpyridine	6.051	5.677	5.375	5.113	4.891	4.719	4.566
acridine	14.732	13.011	11.643	10.472	9.498	8.71	8.033
4,7-phenanthroline	17.712	15.483	13.707	12.212	10.972	9.968	9.107

Run 3

T/K	457.8	462.7	467.8	472.8	477.7	482.7	487.7
				t/min			
cyclopentane	3.09	3.114	3.125	3.143	3.16	3.191	3.194
quinoline	4.371	4.259	4.15	4.064	3.989	3.943	3.875
1-phenylpyrazole	4.689	4.532	4.382	4.262	4.16	4.091	4.003
1-phenylimidazole	5.707	5.414	5.145	4.925	4.739	4.601	4.451
2-phenylpyridine	6.143	5.794	5.475	5.211	4.988	4.82	4.643
acridine	14.976	13.299	11.872	10.681	9.69	8.898	8.166
4,7-phenanthroline	17.987	15.826	13.983	12.463	11.196	10.19	9.262

Run 4

T/K	487.5	482.6	477.6	472.6	467.6	462.7	457.8
				t/min			
cyclopentane	3.211	3.184	3.181	3.175	3.134	3.112	3.097
quinoline	3.891	3.934	4.014	4.101	4.158	4.254	4.376
1-phenylpyrazole	4.022	4.086	4.191	4.307	4.396	4.533	4.702
1-phenylimidazole	4.473	4.598	4.777	4.979	5.162	5.417	5.727
4-phenylpyrimidine	4.695	4.851	5.062	5.307	5.538	5.847	6.223
1-benzylimidazole	5.146	5.372	5.667	6.014	6.357	6.809	7.358
7,8-benzoquinoline	8.028	8.697	9.52	10.501	11.564	12.9	14.527
phenanthridine	8.611	9.377	10.311	11.435	12.661	14.2	16.077

Run 5

T/K	362.7	367.7	373.2	378.1	383.1	388.1	393.2
				t/min			
CH4	2.668	2.698	2.753	2.759	2.78	2.801	2.812
cyclopentane	2.885	2.902	2.947	2.938	2.941	2.94	2.939
pyridine	3.531	3.46	3.437	3.362	3.311	3.278	3.242
3-picoline	4.649	4.422	4.262	4.07	3.916	3.794	3.689
2,5-dimethylpyrazine	5.464	5.114	4.834	4.554	4.318	4.124	3.968
1-methylimidazole	5.688	5.349	5.064	4.725	4.465	4.256	4.048
2,4,6-trimethylpyridine	7.892	7.232	6.641	6.036	5.561	5.166	4.801
1-ethylimidazole	7.412	6.741	6.174	5.677	5.252	4.89	4.616

Run 6

T/K	443.1	448	453	457.8	462.7	468	472.8
				t/min			
cyclopentane	3.045	3.064	3.082	3.1	3.121	3.161	3.171
1-methylimidazole	3.372	3.36	3.351	3.344	3.343	3.366	3.359
1-ethylimidazole	3.545	3.515	3.487	3.467	3.453	3.466	3.449
quinoline	4.881	4.689	4.519	4.38	4.264	4.192	4.095
1-phenylpyrazole	5.41	5.143	4.898	4.702	4.54	4.429	4.299
1-phenylimidazole	7.033	6.567	6.082	5.721	5.43	5.2	4.974
4-phenylpyrimidine	7.841	7.212	6.673	6.23	5.861	5.584	5.301
1-benzylimidazole	9.745	8.849	8.01	7.361	6.831	6.41	6.011
7,8-benzoquinoline	21.756	18.882	16.475	14.528	12.921	11.65	10.484
phenanthridine	24.491	21.132	18.347	16.095	14.236	12.76	11.428

Run 7

T/K	323.2	328.2	333.3	338.3	343.5	348.5	353.5
				t/min			
methane	2.277	2.33	2.348	2.387	2.424	2.437	2.445
methanol	2.364	2.408	2.418	2.45	2.48	2.491	2.494
N-methylpyrrole	4.986	4.599	4.267	4.013	3.811	3.623	3.47
N-methylpyrazole	5.318	4.856	4.468	4.172	3.94	3.727	3.554
2-methylpyrazine	8.106	7.113	6.313	5.683	5.188	4.758	4.417
4-methylpyrimidine	8.762	7.635	6.732	6.022	5.465	4.984	4.604
4-methylpyridine	10.375	8.917	7.766	6.864	6.16	5.556	5.08
2,5-dimethylpyrazine	14.888	12.448	10.554	9.07	7.921	6.964	6.22

Run 8

T/K	413.6	418.6	423.5	428.5	433.4	438.3	443.1
				t/min			
methanol	3.006	3.027	3.048	3.071	3.092	3.112	3.131
N-methylpyrrolidine	3.182	3.188	3.197	3.207	3.219	3.23	3.241
N-methylpyrrole	3.259	3.257	3.258	3.263	3.268	3.274	3.279
4-methylpyrimidine	3.467	3.441	3.422	3.41	3.4	3.393	3.388
2,5-dimethylpyrazine	3.704	3.648	3.604	3.569	3.541	3.518	3.498
2,4,6-trimethylpyridine	4.05	3.947	3.862	3.793	3.737	3.689	3.649
quinoline	7.456	6.866	6.373	5.964	5.623	5.335	5.09
N-methylindole	8.033	7.342	6.767	6.291	5.896	5.564	5.282

Appendix D-2. Vaporization Enthalpy Results of Runs 1 to 7

Run 1	$\frac{\text{slope}}{T/\text{K}}$	intercept	$\frac{\Delta_{\mathrm{sln}}{}^{\mathrm{g}}H_{\mathrm{m}}(498\ \mathrm{K})}{\mathrm{kJ\cdot mol^{-1}}}$	$\frac{\Delta_{\mathrm{l}}{}^{\mathrm{g}}H_{\mathrm{m}}(298\ \mathrm{K})}{\mathrm{kJ\cdot mol^{-1}}}$ (lit)	$\frac{\Delta_{\mathrm{l}}{}^{\mathrm{g}}H_{\mathrm{m}}(298\ \mathrm{K})}{\mathrm{kJ\cdot mol^{-1}}}$ (calc)
2,6-dimethylquinoline	-5268.9	10.614	43.8	67.07	67.0±0.5
2-phenylpyridine	-5401.3	10.731	44.9	68.4	68.5±0.5
trans azobenzene	-5957.5	11.313	49.53		74.9±0.6
acridine	-6288.3	11.318	52.28	78.63	78.7±0.6
4,7-phenanthroline	-6469.8	11.492	53.79	80.8	80.8±0.6

$\Delta_{\mathrm{l}}{}^{\mathrm{g}}H_{\mathrm{m}}$(298.15 K)/kJ·mol^{-1} = (1.38±0.01)$\Delta_{\mathrm{sln}}{}^{\mathrm{g}}H_{\mathrm{m}}$(498 K) +(6.54±0.10) $r^2 = 0.9998$

Run 2	$\frac{\text{slope}}{T/\text{K}}$	intercept	$\frac{\Delta_{\mathrm{sln}}{}^{\mathrm{g}}H_{\mathrm{m}}(473\ \mathrm{K})}{\mathrm{kJ\cdot mol^{-1}}}$	$\frac{\Delta_{\mathrm{l}}{}^{\mathrm{g}}H_{\mathrm{m}}(298\ \mathrm{K})}{\mathrm{kJ\cdot mol^{-1}}}$ (lit)	$\frac{\Delta_{\mathrm{l}}{}^{\mathrm{g}}H_{\mathrm{m}}(298\ \mathrm{K})}{\mathrm{kJ\cdot mol^{-1}}}$ (calc)
quinoline	-4763.0	10.177	39.60	59.31	59.3±0.8
1-phenylpyrazole	-5150.3	10.800	42.82		63.5±0.8
1-phenylimidazole	-5542.0	11.163	46.07		67.7±0.9
2-phenylpyridine	-5643.0	11.228	46.91	68.4	68.8±0.9
acridine	-6549.8	11.854	54.45	78.63	78.6±1.0
4,7-phenanthroline	-6761.2	12.090	56.21	80.8	80.8±1.1

$\Delta_{\mathrm{l}}{}^{\mathrm{g}}H_{\mathrm{m}}$(298.15 K)/kJ·mol^{-1} = (1.30±0.019)$\Delta_{\mathrm{sln}}{}^{\mathrm{g}}H_{\mathrm{m}}$(473 K) + (7.61±0.25) $r^2 = 0.9995$

Run 3	$\frac{\text{slope}}{T/\text{K}}$	intercept	$\frac{\Delta_{\mathrm{sln}}{}^{\mathrm{g}}H_{\mathrm{m}}(473\ \mathrm{K})}{\mathrm{kJ\cdot mol^{-1}}}$	$\frac{\Delta_{\mathrm{l}}{}^{\mathrm{g}}H_{\mathrm{m}}(298\ \mathrm{K})}{\mathrm{kJ\cdot mol^{-1}}}$ (lit)	$\frac{\Delta_{\mathrm{l}}{}^{\mathrm{g}}H_{\mathrm{m}}(298\ \mathrm{K})}{\mathrm{kJ\cdot mol^{-1}}}$ (calc)
quinoline	-4711.3	10.047	39.17	59.31	59.2±0.3
1-phenylpyrazole	-5086.4	10.645	42.29		63.3±0.3
1-phenylimidazole	-5477.3	11.006	45.54		67.5±0.3
2-phenylpyridine	-5568.3	11.05	46.29	68.4	68.5±0.4
acridine	-6502.1	11.732	54.06	78.63	78.6±0.4
4,7-phenanthroline	-6701.5	11.942	55.71	80.8	80.8±0.4

$\Delta_{\mathrm{l}}{}^{\mathrm{g}}H_{\mathrm{m}}$(298.15 K)/kJ·mol^{-1} = (1.301±0.007)$\Delta_{\mathrm{sln}}{}^{\mathrm{g}}H_{\mathrm{m}}$(473 K) + (8.30±0.10) $r^2 = 0.9999$

Run 4	$\frac{\text{slope}}{T/\text{K}}$	intercept	$\frac{\Delta_{\mathrm{sln}}{}^{\mathrm{g}}H_{\mathrm{m}}(473\mathrm{K})}{\mathrm{kJ\cdot mol^{-1}}}$	$\frac{\Delta_{\mathrm{l}}{}^{\mathrm{g}}H_{\mathrm{m}}(298\ \mathrm{K})}{\mathrm{kJ\cdot mol^{-1}}}$ (lit)	$\frac{\Delta_{\mathrm{l}}{}^{\mathrm{g}}H_{\mathrm{m}}(298\ \mathrm{K})}{\mathrm{kJ\cdot mol^{-1}}}$ (calc)
quinoline	-4722.0	10.072	39.26	59.31	59.4±3.1
1-phenylpyrazole	-5103.4	10.678	42.43		63.5±3.3
1-phenylimidazole	-5494.7	11.04	45.68		67.7±3.6
4-phenylpyrimidine	-5576.2	11.045	46.36	68.8	68.6±3.6
1-benzylimidazole	-5906	11.456	49.1		72.2±3.8
7,8-benzoquinoline	-6466.8	11.695	53.76	77.23	78.2±4.2
phenanthridine	-6564.8	11.782	54.58	80.14	79.3±4.2

$\Delta_{\mathrm{l}}{}^{\mathrm{g}}H_{\mathrm{m}}$(298.15 K)/kJ·mol^{-1} = (1.300±0.076)$\Delta_{\mathrm{sln}}{}^{\mathrm{g}}H_{\mathrm{m}}$(473 K) + (8.31±0.94) $r^2 = 0.9933$

Run 5	slope T/K	intercept	$\Delta_{\mathrm{sln}}^{\mathrm{g}}H_{\mathrm{m}}$(378 K) kJ·mol^{-1}	$\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}$(298 K) kJ·mol^{-1} (lit)	$\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}$(298 K) kJ·mol^{-1} (calc)
pyridine	-3289.4	9.213	27.35	40.21	40.0±1.4
3-picoline	-3844.1	9.906	31.96	44.47	44.7±1.7
2,5-dimethylpyrazine	-4165.6	10.446	34.63	47.04	47.4±1.8
1-methylimidazole	-4199.9	10.448	34.92		47.7±1.8
2,4,6-trimethylpyridine	-4556.7	10.995	37.88	51.00	50.5±2.0
1-ethylimidazole	-4538.7	10.834	37.73		50.7±2.0

$\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}$(298.15 K)/kJ·mol^{-1} = (1.014±0.051)$\Delta_{\mathrm{sln}}^{\mathrm{g}}H_{\mathrm{m}}$(378 K) +(12.26±0.39) $r^2 = 0.9950$

Run 6	slope T/K	intercept	$\Delta_{\mathrm{sln}}^{\mathrm{g}}H_{\mathrm{m}}$(458K) kJ·mol^{-1}	$\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}$(298 K) kJ·mol^{-1} (lit)	$\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}$(298 K) kJ·mol^{-1} (calc)
1-methylimidazole	-3888.5	9.900	32.33		49.4±2.5
1-ethylimidazole	-4138.4	10.039	34.4		52.0±2.6
quinoline	-4827.0	10.292	40.13	59.31	59.3±3.0
1-phenylpyrazole	-5217.1	10.919	43.37		63.5±3.3
1-phenylimidazole	-5623.7	11.312	46.75		67.8±3.5
4-phenylpyrimidine	-5705.9	11.317	47.44	68.8	68.7±3.5
1-benzylimidazole	-6056.2	11.771	50.35		72.4±3.7
7,8-benzoquinoline	-6606.7	11.989	54.93	77.23	78.2±4.1
phenanthridine	-6710.2	12.086	55.79	80.14	79.3±4.1

$\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}$(298.15 K)/kJ·mol^{-1} = (1.275±0.072)$\Delta_{\mathrm{sln}}^{\mathrm{g}}H_{\mathrm{m}}$(458 K) + (8.18±0.91) $r^2 = 0.9936$

Run 7	slope T/K	intercept	$\Delta_{\mathrm{sln}}^{\mathrm{g}}H_{\mathrm{m}}$ (431 K) kJ·mol^{-1}	$\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}$(298 K) kJ·mol^{-1}	
				(lit)	(calc)
N-methylpyrrole	-3661	10.335	30.44	40.6	40.5±2.8
N-methylpyrazole	-3796.7	10.641	31.56		41.6±2.9
2-methylpyrazine	-4079.4	10.864	33.91	44.08	43.9±3.0
4-methylpyrimidine	-4140.1	10.945	34.42	44.2	44.4±3.0
4-methylpyridine	-4222.7	10.98	35.11	44.73	45.1±3.0
2,5-dimethylpyrazine	-4538.9	11.515	37.73	48	47.7±3.1

$\Delta_{l}^{g}H_{m}$(298 K) /kJ·mol^{-1} = (0.996±0.06) $\Delta_{s\,\ln}^{g}H_{m}$(338 K) /kJ·mol^{-1} + (10.14±2.1); $r^2 = 0.9887$

Appendix E

Appendix E-1. Retention times (t/min) for runs 1 - 7 as a function of temperature (T/K)

Run 1

T/K	415.4	420.5	425.6	430.7	435.8	440.7	445.7
				t/min			
methanol	0.689	0.697	0.702	0.706	0.71	0.717	0.721
3-methylpyridine	0.943	0.924	0.905	0.893	0.88	0.873	0.864
2,4,6-trimethylpyridine	1.171	1.123	1.075	1.045	1.012	0.994	0.967
2-(N,N-dimethylamino)pyridine	1.596	1.492	1.395	1.326	1.258	1.212	1.16
1,5-diazabicyclo[4.3.0]non-5-ene	2.63	2.37	2.146	1.968	1.809	1.689	1.575
4-(N,N-dimethylamino)pyridine	2.871	2.58	2.32	2.121	1.942	1.804	1.675
1,8-diazabicyclo[5.4.0]undec-7-ene	5.374	4.665	4.069	3.592	3.185	2.862	2.579
4-phenylpyrimidine	6.278	5.417	4.689	4.113	3.621	3.231	2.891

Run 2

T/K	399.4	403.8	409.1	414.4	419.6	424.7	429.9
				t/min			
methanol	0.619	0.607	0.622	0.618	0.627	0.602	0.654
2,6-dimethylpyridine	0.993	0.937	0.914	0.879	0.861	0.816	0.846
3,5-dimethylpyridine	1.288	1.192	1.135	1.073	1.032	0.968	0.98
2-(N,N-dimethylamino)pyridine	1.984	1.782	1.637	1.503	1.405	1.292	1.261
1,5diazabicyclo[4.3.0]non-5-ene	3.727	3.246	2.875	2.547	2.276	2.033	1.899
4-(N,N-dimethylamino)pyridine	4.128	3.558	3.118	2.756	2.477	2.21	2.047
2-methylquinoline	4.893	4.202	3.66	3.213	2.862	2.537	2.328
1,8-diazabicyclo[5.4.0]undec-7-ene	8.59	7.226	6.158	5.267	4.545	3.941	3.507
4-phenylpyrimidine	10.258	8.546	7.193	6.127	5.291	4.567	4.025

Run 3

T/K	414.8	420	425	430	435	440	445
				t/min			
methanol	0.846	0.821	0.841	0.844	0.839	0.863	0.851
2,6-dimethylpyridine	1.181	1.122	1.111	1.089	1.065	1.064	1.035
quinoline	3.247	2.903	2.649	2.427	2.239	2.088	1.941
imidazo[1,2-a]pyridine	3.549	3.151	2.854	2.598	2.387	2.211	2.046
2-methylquinoline	4.183	3.686	3.306	2.981	2.712	2.49	2.285
triazolo[1,5-a]pyrimidine	4.526	3.962	3.529	3.162	2.88	2.625	2.404
2,6-dimethylquinoline	6.547	5.652	4.95	4.361	3.878	3.478	3.128

Run 4

T/K	414.6	419.8	424.7	429.8	434.6	439.9	444.8
				t/min			
methanol	0.887	0.893	0.897	0.904	0.904	0.92	0.925
pyridazine	1.319	1.281	1.253	1.221	1.191	1.183	1.166
3-methylpyridazine	1.542	1.474	1.422	1.369	1.321	1.299	1.269
imidazo[1,2-a]pyridine	3.592	3.228	2.929	2.664	2.438	2.281	2.125
triazolo[1,5-a]pyrimidine	4.548	4.03	3.605	3.231	2.918	2.695	2.479
phthalazine	8.307	7.187	6.268	5.474	4.819	4.338	3.886

Run 5

T/K	399.3	404.4	409.5	414.5	419.7	424.7	429.9
				t/min			
methanol	0.6	0.615	0.617	0.616	0.646	0.637	0.662
pyridazine	1.076	1.043	0.991	0.956	0.96	0.909	0.907
3-methylpyridazine	1.345	1.274	1.19	1.128	1.111	1.041	1.022
imidazo[1,2-a]pyridine	3.993	3.514	3.062	2.729	2.492	2.216	2.034
triazolo[1,5-a]pyrimidine	5.322	4.619	3.954	3.48	3.129	2.741	2.475
phthalazine	10.49	8.91	7.454	6.421	5.625	4.816	4.228
1-benzylimidazole	15.522	12.889	10.569	8.911	7.645	6.421	5.526

Run 6

T/K	414.3	419.2	424.2	429.2	434.1	439	443.9
				t/min			
methanol	2.695	2.726	2.811	2.838	2.866	2.742	2.852
pyridazine	3.394	3.35	3.378	3.346	3.325	3.155	3.227
3-methylpyridazine	3.763	3.671	3.659	3.592	3.54	3.344	3.393
4-N,N-dimethylaminopyridine	7.347	6.709	6.27	5.819	5.455	4.992	4.821
triazolo[1,5-a]pyrimidine	8.985	8.086	7.449	6.811	6.297	5.701	5.428
1-benzylimidazole	16.008	13.943	12.408	10.97	9.813	8.664	7.949

Run 7

T/K	323.2	328.2	333.3	338.3	343.5	348.5	353.5
				t/min			
methane	2.277	2.33	2.348	2.387	2.424	2.437	2.445
methanol	2.364	2.408	2.418	2.45	2.48	2.491	2.494
N-methylpyrrole	4.986	4.599	4.267	4.013	3.811	3.623	3.47
N-methylpyrazole	5.318	4.856	4.468	4.172	3.94	3.727	3.554
2-methylpyrazine	8.106	7.113	6.313	5.683	5.188	4.758	4.417
4-methylpyrimidine	8.762	7.635	6.732	6.022	5.465	4.984	4.604
4-methylpyridine	10.375	8.917	7.766	6.864	6.16	5.556	5.08
2,5-dimethylpyrazine	14.888	12.448	10.554	9.07	7.921	6.964	6.22

Appendix E-2. Results of the Correlations of Runs 1-7

Run 1	slope T/K	intercept	$\Delta_{\text{sln}}^{\text{g}}H_{\text{m}}$ (431 K) kJ·mol^{-1}	$\Delta_{\text{l}}^{\text{g}}H_{\text{m}}$(298 K) kJ·mol^{-1} (lit)	(calc)
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

$\Delta_{l}^{g}H_{m}(298\text{ K})\,/\text{kJ·mol}^{-1} = (1.25\pm0.05)\,\Delta_{s\ln}^{g}H_{m}(431\text{ K})\,/\text{kJ·mol}^{-1} + (8.792\pm2.0)$; $r^2 = 0.9982$

Run 2	slope T/K	intercept	$\Delta_{\text{sln}}^{\text{g}}H_{\text{m}}$ (431 K) kJ·mol^{-1}	$\Delta_{\text{l}}^{\text{g}}H_{\text{m}}$(298 K) kJ·mol^{-1} (lit)	(calc)
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

$\Delta_{l}^{g}H_{m}(298\text{ K})\,/\text{kJ·mol}^{-1} = (1.31\pm0.033)\ \Delta_{s\ln}^{g}H_{m}(415\text{ K})\,/\text{kJ·mol}^{-1} + (5.56\pm1.33)$; $r^2 = 0.9986$

Run 3	slope T/K	intercept	$\Delta_{\text{sln}}^{\text{g}}H_{\text{m}}$ (431 K) kJ·mol^{-1}	$\Delta_{\text{l}}^{\text{g}}H_{\text{m}}$(298 K) kJ·mol^{-1} (lit)	(calc)
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

$\Delta_{l}^{g}H_{m}(298\text{ K})\,/\text{kJ·mol}^{-1} = (1.348\pm0.045)\ \Delta_{s\ln}^{g}H_{m}(430\text{ K})\,/\text{kJ·mol}^{-1} + (4.51\pm1.84)$; $r^2=0.9977$

Run 4	slope T/K	intercept	$\Delta_{\mathrm{sln}}{}^{g}H_{\mathrm{m}}$ (431 K) kJ·mol^{-1}	$\Delta_{\mathrm{l}}{}^{g}H_{\mathrm{m}}$(298 K) kJ·mol^{-1} (lit)	(calc)
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

$\Delta_{l}^{g}H_{m}(298\text{ K})\,/\text{kJ·mol}^{-1} = (1.15\pm0.046)\ \Delta_{\mathrm{sln}}^{g}H_{m}(432\text{ K})\ /\text{kJ·mol}^{-1} + (18.7\pm1.7);\ r^2 = 0.9984$

Run 5	slope T/K	intercept	$\Delta_{\mathrm{sln}}{}^{g}H_{\mathrm{m}}$ (431 K) kJ·mol^{-1}	$\Delta_{\mathrm{l}}{}^{g}H_{\mathrm{m}}$(298 K) kJ·mol^{-1} (lit)	(calc)
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

$\Delta_{l}^{g}H_{m}(298\text{ K})\,/\text{kJ·mol}^{-1} = (1.33\pm0.11)\ \Delta_{\mathrm{sln}}^{g}H_{m}(415\text{ K})\,/\text{kJ·mol}^{-1} + (11.7\pm4.8);\ r^2 = 0.9854$

Run 6	slope T/K	intercept	$\Delta_{\mathrm{sln}}{}^{g}H_{\mathrm{m}}$ (431 K) kJ·mol^{-1}	$\Delta_{\mathrm{l}}{}^{g}H_{\mathrm{m}}$(298 K) kJ·mol^{-1} (lit)	(calc)
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

$\Delta_{l}^{g}H_{m}(298\text{ K})\,/\text{kJ·mol}^{-1} = (1.37\pm0.06)\ \Delta_{\mathrm{sln}}^{g}H_{m}(415\text{ K})\,/\text{kJ·mol}^{-1} + (8.95\pm2.6);\ r^2 = 0.9978$

Run 7	slope T/K	intercept	$\Delta_{\mathrm{sln}}{}^{g}H_{\mathrm{m}}$ (431 K) kJ·mol^{-1}	$\Delta_{\mathrm{l}}{}^{g}H_{\mathrm{m}}$(298 K) kJ·mol^{-1} (lit)	(calc)
N-methylpyrrole	-3661	10.335	30.44	40.6	40.5±2.8
N-methylpyrazole	-3796.7	10.641	31.56		41.6±2.9
2-methylpyrazine	-4079.4	10.864	33.91	44.08	43.9±3.0
4-methylpyrimidine	-4140.1	10.945	34.42	44.2	44.4±3.0
4-methylpyridine	-4222.7	10.98	35.11	44.73	45.1±3.0
2,5-dimethylpyrazine	-4538.9	11.515	37.73	48	47.7±3.1

$\Delta_{l}^{g}H_{m}(298\text{ K})\,/\text{kJ·mol}^{-1} = (0.996\pm0.06)\,\Delta_{\mathrm{sln}}^{g}H_{m}(338\text{ K})\,/\text{kJ·mol}^{-1} + (10.14\pm2.1);\ r^2 = 0.9887$

Appendix E-3.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·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±0.10)kJ·mol^{-1}						
$\ln(p/p_o) = \frac{285.36}{R} - \frac{74972.37}{(R \cdot T/K)} - \frac{66.5}{R}\ln\left(\frac{T/K}{298.15}\right)$						
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 (2); $\Delta_{cr}^g H_m$ (298.15 K) = (87.02±0.19)kJ·mol^{-1}						
$\ln(p/p_o) = \frac{313.49}{R} - \frac{95610.41}{(R \cdot T/K)} - \frac{28.8}{R}\ln\left(\frac{T/K}{298.15}\right)$						
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±0.21)kJ·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·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

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

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

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

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	$\Delta_l^g H_m$ / kJ·mol^{-1}
E. Imidazo[1,2-a]pyridine (6); $\Delta_l^g H_m$ (298.15 K) = (67.41±0.23)kJ·mol^{-1} $\ln(p/p_o) = \frac{292.77}{R} - \frac{85716.18}{(R \cdot T/K)} - \frac{61.4}{R}\ln\left(\frac{T/K}{298.15}\right)$						
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_o = 1 Pa.

Appendix F

Appendix F-1. Retention Times of Polywax 1000

T/K	660.9	665.6	670.9	676.1	681.1	686.1	691.1
Run 1				t/min			
octane	0.149	0.151	0.156	0.155	0.153	0.148	0.157
pentacontane	0.355	0.324	0.303	0.279	0.261	0.24	0.237
dopentacontane	0.42	0.377	0.346	0.316	0.292	0.266	0.26
tetrapentacontane	0.504	0.447	0.403	0.362	0.33	0.297	0.286
hexapentacontane	0.615	0.536	0.476	0.423	0.379	0.338	0.319
octapentacontane	0.758	0.651	0.57	0.499	0.442	0.391	0.362
hexacontane	0.947	0.802	0.691	0.597	0.523	0.457	0.416
dohexacontane	1.189	0.994	0.846	0.722	0.623	0.538	0.483
tetrahexacontane	1.504	1.243	1.045	0.88	0.751	0.642	0.567
hexahexacontane	1.913	1.564	1.299	1.083	0.913	0.773	0.672
octahexacontane	2.442	1.976	1.624	1.339	1.118	0.937	0.804
heptacontane	3.125	2.507	2.039	1.665	1.376	1.143	0.969
doheptacontane	4.008	3.189	2.569	2.08	1.703	1.402	1.174
tetraheptacontane	5.139	4.059	3.242	2.603	2.113	1.725	1.43
hexaheptacontane	6.613	5.181	4.102	3.268	2.632	2.131	1.748
octaheptacontane	8.494	6.599	5.188	4.107	3.282	2.64	2.145
octacontane	10.919	8.427	6.576	5.16	4.098	3.275	2.641
dooctacontane	13.977	10.733	8.311	6.495	5.123	4.064	3.245
tetraoctacontane	17.924	13.685	10.539	8.177	6.409	5.052	4.012
hexaoctacontane	22.946	17.456	13.37	10.29	8.028	6.285	4.943
octaoctancontane	29.461	22.156	16.849	12.936	10.015	7.816	6.102
nonacontane	37.65	28.233	21.381	16.292	12.508	9.693	7.557
dononacontane	48.045	35.895	26.844	20.404	15.678	12.068	9.303

T/K	661	666	671.1	676.2	681.2	686.1	691.2
Run 2				t/min			
octane	0.162	0.142	0.162	0.162	0.162	0.163	0.163
octapentacontane	0.691	0.581	0.522	0.461	0.417	0.378	0.348
hexacontane	0.853	0.71	0.626	0.544	0.487	0.435	0.395
dohexacontane	1.062	0.876	0.758	0.65	0.574	0.506	0.453
tetrahexacontane	1.333	1.09	0.928	0.786	0.685	0.596	0.527
hexahexacontane	1.683	1.364	1.145	0.958	0.826	0.709	0.618
octahexacontane	2.133	1.716	1.421	1.175	1.003	0.85	0.733
heptacontane	2.715	2.167	1.773	1.45	1.226	1.028	0.875
doheptacontane	3.467	2.746	2.221	1.799	1.506	1.249	1.052

tetraheptacontane	4.429	3.483	2.788	2.24	1.858	1.527	1.272
hexaheptacontane	5.666	4.421	3.51	2.796	2.3	1.873	1.546
octaheptacontane	7.249	5.617	4.425	3.495	2.854	2.303	1.885
octacontane	9.27	7.148	5.574	4.381	3.551	2.844	2.306
dooctacontane	11.829	9.08	7.032	5.483	4.416	3.514	2.829
tetraoctacontane	15.156	11.538	8.887	6.894	5.5	4.349	3.475
hexaoctacontane	19.342	14.648	11.238	8.598	6.851	5.378	4.268
octaoctancontane	24.635	18.648	14.23	10.778	8.529	6.649	5.245
nonacontane	31.51	23.555	17.868	13.577	10.644	8.27	6.464
dononacontane	40.21	29.75		17.042	13.251	10.2	7.971

T/K	638.2	643.2	648.2	653.2	658.2	663.2	668.2
Run 3				t/min			
hexacontane	1.9	1.514	1.224	0.993	0.81	0.668	0.557
dohexacontane	2.509	1.986	1.592	1.28	1.037	0.855	0.706
tetrahexacontane	3.312	2.604	2.071	1.653	1.329	1.092	0.895
hexahexacontane	4.374	3.41	2.688	2.132	1.702	1.395	1.133
octahexacontane	5.748	4.463	3.49	2.746	2.18	1.776	1.435
heptacontane	7.567	5.832	4.534	3.536	2.791	2.263	1.813
doheptacontane	9.896	7.58	5.854	4.567	3.557	2.883	2.294
tetraheptacontane	12.997	9.877	7.593	5.836	4.563	3.667	2.897
hexaheptacontane	16.973	12.878	9.764	7.531	5.812	4.649	3.651
octaheptacontane	22.213	16.663	12.654	9.652	7.407	5.889	4.599
octacontane	28.955	21.662	16.282	12.344	9.419	7.484	5.797
dooctacontane	37.718	28.096	20.941	15.783	12.024	9.457	7.243
tetraoctacontane	49.173	36.352	26.927	20.161	15.258	11.967	9.243
hexaoctacontane	63.868	46.846	34.654	25.868	19.334	15.067	11.478
octaoctancontane	82.593	60.438	44.148	33.073	24.605	19.062	14.403
nonacontane	107.494	77.785	56.622	41.823	31.086	24.013	18.069