



# Thermodynamic properties of 1-phenylnaphthalene and 2-phenylnaphthalene



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## ABSTRACT

Measurements leading to the calculation of thermodynamic properties in the ideal-gas state for 1-phenylnaphthalene (Chemical Abstracts registry number [605-02-7]) and 2-phenylnaphthalene (Chemical Abstracts registry number [612-94-2]) are reported. Experimental methods for 1-phenylnaphthalene were adiabatic heat-capacity calorimetry, differential scanning calorimetry, inclined-piston manometry, comparative ebulliometry, vibrating-tube densitometry, and combustion calorimetry. For 2-phenylnaphthalene, the experimental methods were adiabatic heat-capacity calorimetry, differential scanning calorimetry, and comparative ebulliometry. Critical properties were estimated for both compounds. Molar thermodynamic functions (enthalpies, entropies, and Gibbs free energies) for the condensed and ideal-gas states were derived from the experimental studies at selected temperatures. Statistical calculations were performed based on molecular geometry optimization and vibrational frequencies calculated at the B3LYP/6-31+G(d,p) and B3LYP/cc-pVTZ levels of theory. Ideal-gas entropies derived with two the independent methods are shown to be in good accord for 1-phenylnaphthalene, but significant differences are apparent for 2-phenylnaphthalene. These differences are likely due to a disorder of unknown type in the crystals of 2-phenylnaphthalene at low temperatures, as evidenced by the presence of a glass-like transition in the measured heat capacities for the solid state. All experimental results are compared with property values reported in the literature.

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## 1. Introduction

Phenylnaphthalenes are of interest in a variety of research areas, including modeling of solubilities for polycyclic aromatic hydrocarbons in water [1], development of high-temperature heat transfer fluids [2], as well as in fundamental studies of aromatic conjugation [3]. This work is a continuation of our investigations (cf., [4–7]) into the quantification of uncertainties for thermodynamic properties derived with computational chemistry with particular focus on entropies for the ideal-gas state. Entropies for the ideal-gas state can be calculated with structural information and the methods of computational chemistry, as well as through appropriate combination of experimentally determined thermodynamic properties. These two methods are completely independent and their study provides the means for their mutual validation through analysis of observed consistencies and deviations. Reliable ideal-gas properties have key roles in property predictions, thermodynamic-consistency analyses, constrained property

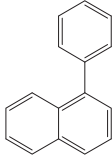
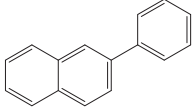
extrapolations, and they form the basis of important equation-of-state formulations, which are expressed as deviations from the ideal-gas state [8,9]. As noted previously [5], the ability to derive ideal-gas properties solely from computational methods with reliable uncertainties would provide key values that are difficult or impossible to obtain experimentally for numerous materials, such as those of high expense, high toxicity, or low stability.

This article describes thermodynamic property measurements for 1-phenylnaphthalene (Chemical Abstracts registry number [605-02-7]) and 2-phenylnaphthalene [612-94-2]. A summary of the new experimental property measurements reported here is provided in table 1. Entropies for the ideal-gas state are derived from the thermophysical property measurements for both compounds, and these are compared with independently derived values calculated with the methods of computational chemistry. It will be shown that very good accord is achieved for 1-phenylnaphthalene, while significant deviations are seen for 2-phenylnaphthalene. The deviations likely arise from a “frozen-in” disorder in the crystals of 2-phenylnaphthalene, as evidenced by the presence of a glass-like transition in the solid-state.

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**TABLE 1**  
Summary of experimental results reported here for 1-phenylnaphthalene and 2-phenylnaphthalene.

Property	Method	Temperature range/K
1-phenylnaphthalene		
		
Heat capacity	Adiabatic calorimetry	5 to 442
Triple-point temperature		
Enthalpy of fusion		
Heat capacity	Differential scanning calorimetry	400 to 650
Vapor pressure	Inclined-piston manometry	375 to 480
	Comparative ebulliometry	466 to 630
Density	Vibrating-tube densimetry	323 to 523
Enthalpy of combustion	Oxygen-bomb calorimetry	298.15
Mole fraction purity (this study) = 0.9993		
2-phenylnaphthalene		
		
Heat capacity	Adiabatic calorimetry	5 to 442
Triple-point temperature		
Enthalpy of fusion		
Heat capacity	Differential scanning calorimetry	400 to 650
Vapor pressure	Comparative ebulliometry	483 to 604
Mole fraction purity (this study) = 0.9998 <sub>5</sub>		

## 2. Experimental

### 2.1. Materials

The research group of Professor E.J. “Pete” Eisenbraun (retired) of Oklahoma State University synthesized and purified the samples of 1-phenylnaphthalene (1-PhN) and 2-phenylnaphthalene (2-PhN). Final purification was by high-performance liquid chromatography for 1-PhN and by fractional sublimation for 2-PhN. Sample purities were established in fractional-melting studies determined as part of the adiabatic heat-capacity calorimetric results reported here. The mole-fraction purities  $x$  were  $x = 0.9993$  for 1-PhN and  $x = 0.9998_5$  for 2-PhN. The purified samples were transferred under nitrogen or helium or by vacuum distillation prior to the property measurements. Purification of the water and decane used as reference materials in the ebulliometric vapor-pressure measurements reported here has been described [10].

### 2.2. Physical constants and standards

Property values are reported in terms of molar mass  $M = 204.256$  [11] based on the formula  $C_{16}H_{12}$  for the compounds and the gas constant  $R = 8.3144621 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$  adopted in 2010 by CODATA [12]. Platinum resistance thermometers used in these studies were calibrated by comparison with standard thermometers whose constants were determined at the National Bureau of Standards (NBS), now the National Institute of Standards and Technology (NIST). All temperatures were measured in terms of IPTS-68 [13] and were converted to ITS-90 with published temperature increments [14]. The platinum resistance thermometer used in the adiabatic heat-capacity study was calibrated below  $T/K = 13.81$  with the method of McCrackin and Chang [15]. Mass, time, electrical resistance, and potential difference were measured in terms of standards traceable to calibrations at NIST.

### 2.3. Apparatus and procedures

New experimental measurements reported here, including temperature ranges and methods used, are summarized in table 1. All derived properties are based on these measurements with the addition of the enthalpy of combustion for 2-PhN reported by Lima *et al.* [3] and unpublished vapor pressures for 1-PhN measured with the vapor-saturation method for the temperature range ( $313 < T/K < 371$ ) by Verevkin [16]. The enthalpy of combustion for 2-PhN was not measured in this research, but is necessary to calculate the Gibbs free energies of formation, and the vapor pressure measurements by Verevkin complement those measured here for the temperature range ( $375 < T/K < 630$ ).

Heat-capacities and enthalpy increments for 1-PhN and 2-PhN were measured with an adiabatic calorimetric system that has been described [17]. The calorimeter characteristics and sealing conditions are given in table 2. Energies were measured with a repeatability of 0.01%, and temperatures were measured with a repeatability of 0.0001 K. The energy increments to the filled platinum calorimeter were corrected for enthalpy changes in the empty calorimeter, for the helium exchange gas, and for vaporization of the sample into the free space of the sealed vessel. The maximum sizes of these corrections are indicated in table 2.

Densities for the liquid phase along the liquid–gas saturation line  $\rho_{\text{sat}}$  were measured with a vibrating-tube densimeter in this research for 1-PhN. The instrument and its operation have been described [18], as have test measurements on the density of benzene for the temperature range ( $310 < T/K < 523$ ) [19]. Results for benzene agree within  $5 \cdot 10^{-4} \rho_{\text{sat}}$  with the critical evaluation in the NIST REFPROP Database [20].

Heat capacities at vapor-saturation pressure  $C_{\text{sat,m}}$  for the liquid phase over the temperature range ( $400 < T/K < 650$ ) were determined with a differential scanning calorimeter (dsc) for both compounds. An intermittent heating method, as first described by Mraw and Naas [21], was used with sequential measurements

involving the sample, pure sapphire calibrant, and the empty sample pan. Heat capacities of sapphire used in calibration of the dsc were those critically evaluated by Archer [22]. A power-compensation dsc was used (Perkin Elmer DSC II), and the complete experimental method has been described [23,24].

Vapor pressures were measured with comparative ebulliometry and the procedures have been described [25,26]. Ebulliometers were used to reflux the compounds under study with standards of known vapor pressure (decane and water) under a common atmosphere of He(g). Boiling and condensation temperatures of the sample and standard were determined, and the vapor pressures of the phenyl naphthalenes were derived from the condensation temperatures of the standards. In the pressure range ( $25 < p/\text{kPa} < 270$ ), water was used as the standard, and the pressures were derived from the international equation of state for pure water [27]. In the pressure range ( $2 < p/\text{kPa} < 25$ ), decane was used as the standard, and pressures were calculated with equation (1) of reference [10].

The standard uncertainty  $u$  for the temperature measurements in the vapor-pressure studies by comparative ebulliometry was 0.002 K. Standard uncertainties in the pressures are described by:

$$u(p) = (0.002 \text{ K}) \{ (dp_{\text{ref}}/dT)^2 + (dp_x/dT)^2 \}^{1/2}, \quad (1)$$

where  $p_{\text{ref}}$  is the vapor pressure of the reference substance and  $p_x$  is the vapor pressure of the sample under study. The repeatability of the temperature measurements was near  $5 \cdot 10^{-4}$  K.

The enthalpy of combustion for 1-PhN has not been reported previously, so it was measured in this research. The experimental procedures, used in the combustion calorimetry of organic C, H, O, N containing compounds, have been described [28,29]. A rotating-bomb calorimeter (laboratory designation BMR II) [30] and platinum-lined bomb (laboratory designation Pt-3b) [31] with an internal volume of 0.3934 dm<sup>3</sup> were used without rotation. The calorimetric sample of 1-PhN was confined in flexible borosilicate-glass ampoules [29,32]. For each experiment, a volume of 0.0010 dm<sup>3</sup> of water was added to the bomb, and the bomb was charged to a pressure of 3.04 MPa with pure oxygen with flushing. Choice of sample and auxiliary masses allowed the temperature rise in the combustion series and its corresponding calibration series to be the same within 0.1%. All experiments were completed within 0.01 K of  $T = 298.15$  K. Due to the compound containing just carbon and hydrogen, and the oxygen used containing, at most, a few parts per million of nitrogen, no nitric or nitrous acids were produced in the experiments. Temperatures were measured by quartz-crystal thermometry [33,34]. The quartz-crystal thermometer was calibrated by comparison with a platinum resistance

thermometer. Counts of the crystal oscillation were taken over periods of 100 s throughout the experiments. Integration of the time-against-temperature curve is inherent in the quartz-crystal thermometer readings [35].

NIST Standard Reference Material benzoic acid (sample 39i) was used for calibration of the combustion calorimeter; its energy of combustion is  $-(26434.0 \pm 3.0) \text{ J} \cdot \text{g}^{-1}$  under certificate conditions. Conversion to standard states [36] gives  $-(26413.7 \pm 3.0) \text{ J} \cdot \text{g}^{-1}$  for  $\Delta_c U^0/M$ , the massic energy of the idealized combustion reaction. Calibration experiments were interspersed with measurements for 1-PhN. Due to the high purity of the oxygen used and preliminary bomb flushing, nitrogen oxides were not formed in the calibration experiments. The energy equivalent  $\epsilon(\text{calor})$  of the calorimeter was determined to be  $(16776.9 \pm 1.0) \text{ J} \cdot \text{K}^{-1}$  (mean and standard deviation of the mean for five combustions). The auxiliary oil (laboratory designation TKL66) had the empirical formula  $\text{CH}_{1.913}$ . For this material,  $\Delta_c U^0/M$  was  $-(46042.5 \pm 1.8) \text{ J} \cdot \text{g}^{-1}$ . For the cotton fuse, the empirical formula  $\text{CH}_{1.774}\text{O}_{0.887}$ ,  $\Delta_c U^0/M$  is  $-16,945 \text{ J} \cdot \text{g}^{-1}$ .

Auxiliary information, necessary for reducing apparent mass to mass, converting the energy of the actual bomb process to that of the isothermal process, and reducing to standard states [36], included a density at  $T = 298.15$  K of  $1100 \text{ kg} \cdot \text{m}^{-3}$  for liquid 1-PhN and a value of  $1.02 \cdot 10^{-7} \text{ m}^3 \cdot \text{K}^{-1}$  for  $(\partial V_m/\partial T)_p$ . These values were estimated by extrapolation of the density values given later in this article. The molar heat capacity at  $T = 298.15$  K used in the corrections to standard states is reported later in this article.

Carbon dioxide was recovered from the combustion products of each experiment. Anhydrous lithium hydroxide was used as adsorbent for the  $\text{CO}_2$  recoveries [37]. The combustion products were checked for unburned carbon and other products of incomplete combustion, but none were detected. The carbon dioxide recovery percentage was  $(100.012 \pm 0.004)$  mean and standard deviation of the mean for the calibrations with benzoic acid. The corresponding value for the combustions of 1-PhN was  $(100.003 \pm 0.009)$ .

### 3. Experimental results

#### 3.1. Heat capacities and properties of phase transitions measured with adiabatic calorimetry

Measurements of enthalpy increments and derived heat capacities for 1-PhN and 2-PhN were made with adiabatic calorimetry between the temperatures (5 and 442) K and included determination of the crystal–liquid–gas triple-point temperature  $T_{\text{tp}}$  and the molar enthalpy of fusion  $\Delta_{\text{cr}}^{\text{L}} H_m$ . The density of the liquid samples at saturation pressure {for 1-PhN,  $\rho_{\text{sat}} = (1100 \pm 10) \text{ kg} \cdot \text{m}^{-3}$  at  $T = 297$  K; for 2-PhN,  $\rho_{\text{sat}} = (1000 \pm 10) \text{ kg} \cdot \text{m}^{-3}$  at  $T = 423$  K} were determined with a pycnometric method during sample handling before these measurements.

The sample of 1-PhN did not crystallize on cooling. Crystallization in the calorimeter was initiated by cooling the sample to approximately  $T = 150$  K. On reheating, a glass transition was observed near  $T = 220$  K and the sample began to crystallize in the temperature range ( $260 < T/\text{K} < 270$ ), as evidenced by spontaneous warming of the calorimeter vessel to near the triple-point temperature ( $T_{\text{tp}} = 297.47_3$  K). This behavior allowed measurement of heat capacities in the supercooled liquid phase for the temperature range ( $225 < T/\text{K} < 253$ ). Complete crystallization was achieved by maintaining the sample under adiabatic conditions in the partially melted state (10% to 20% liquid) until ordering of the crystals was complete, as evidenced by the absence of spontaneous warming. Upon initial partial re-melting, the sample warmed for approximately 24 h. The sample was then cooled at an effective rate of  $1.6 \text{ mK} \cdot \text{s}^{-1}$  to crystallize the remaining liquid. Finally, the sample was thermally cycled from approximately 100 K to within 3 K of

**TABLE 2**  
Calorimeter and sample characteristics for adiabatic calorimetric studies.<sup>a</sup>

	1-Phenyl naphthalene	2-Phenyl naphthalene
$m/\text{g}$	45.671	35.013
$V_i$ (298.15 K)/cm <sup>3</sup>	59.06	61.00
$T_{\text{cal}}/\text{K}$	296.7	296.0
$p_{\text{cal}}/\text{kPa}$	6.76	10.4
$r(T_{\text{max}})$	3.1	2.6
$r_{\text{min}}$	1.7	1.5
$10^2 \cdot (\delta C/C)_{\text{max}}$	0.005	0.006
$x_{\text{pre}}$	0.00070	0.00012

<sup>a</sup>  $m$  is the sample mass;  $V_i$  is the internal volume of the calorimeter vessel;  $T_{\text{cal}}$  is the temperature of the calorimeter when sealed;  $p_{\text{cal}}$  is the pressure of the helium and sample when sealed;  $r(T_{\text{max}})$  is the ratio of the heat capacity of the full calorimeter to that of the empty at the highest temperature  $T_{\text{max}} \approx 442$  K of these measurements;  $r_{\text{min}}$  is the minimum value of  $r$  observed in this study;  $(\delta C/C)_{\text{max}}$  is the vaporization correction at the highest temperature measured (i.e.,  $T_{\text{max}} \approx 442$  K); and  $x_{\text{pre}}$  is the mole-fraction impurity used for pre-melting corrections.

**TABLE 3**  
Melting-study summaries.<sup>a</sup>

<i>F</i>	<i>T</i> ( <i>F</i> )/K	<i>F</i>	<i>T</i> ( <i>F</i> )/K
<i>1-Phenyl</i> naphthalene		<i>2-Phenyl</i> naphthalene	
0.1566	297.275	0.1997	374.762
0.2568	297.350	0.3327	374.763 <sub>5</sub>
0.4071	297.396	0.5490	374.765
0.6075	297.423	0.7486	374.766
$T_{\text{tp}} = (297.47_3 \pm 0.01) \text{ K}^b$		$T_{\text{tp}} = (374.76_7 \pm 0.01) \text{ K}^b$	
$x = 0.9993$		$x = 0.9998_5$	
$K = 0$		$K = 0.23^c$	

<sup>a</sup> *F* is the fraction melted at observed temperature *T*(*F*), *T*<sub>tp</sub> is the triple-point temperature, and *x* is the derived mole-fraction purity of the sample.

<sup>b</sup> The uncertainty is the expanded uncertainty with 0.95 level of confidence.

<sup>c</sup> *K* is the distribution coefficient for distribution of the impurity between the solid and liquid phase as defined by Mastrangelo and Dornte [39].

the triple-point temperature, where it was held for approximately 48 h to provide further tempering. All reported measurement results for the solid-phase were performed on crystals pre-treated with this method. Good repeatability (within  $0.0006 \cdot \Delta_{\text{cr}}^1 H_m$ ) was observed for two determinations of  $\Delta_{\text{cr}}^1 H_m$ , which is further indication of complete crystalline.

The sample of 2-PhN crystallized readily on cooling  $\sim 5$  K below the triple-point temperature ( $T_{\text{tp}} = 374.76_7$  K). Complete

crystallization was achieved with the annealing procedure described above for 1-PhN. No spontaneous warming of the sample was noticed near the melting temperature after initial crystallization. Here, excellent repeatability (within  $0.0001 \cdot \Delta_{\text{cr}}^1 H_m$ ) was observed for three determinations of  $\Delta_{\text{cr}}^1 H_m$ .

The triple-point temperature *T*<sub>tp</sub> and the mole fraction purity *x* for 1-PhN and 2-PhN were determined by measurement of the equilibrium melting temperatures *T*(*F*) as a function of fraction *F* of the sample in the liquid state [38]. The presence of the helium exchange gas in the calorimeters has a negligible effect on these results. The sample of 2-PhN showed evidence for the presence of solid-soluble impurities and the method of Mastrangelo and Dornte [39] was used to evaluate the purity. Equilibrium temperatures in the partially-melted state were determined by measuring temperatures at intervals of approximately 240 s for (1 to 1.5) h after an energy input and extrapolating to infinite time by assuming an exponential decay toward the equilibrium value. The observed temperatures at the end of the equilibration period were within 1 mK of the calculated equilibrium temperatures for *F* values listed in table 3 and used in the determination of purity and *T*<sub>tp</sub>.

Results of measurements of molar enthalpy for 1-PhN and 2-PhN are listed in table 4. The table includes measurement results used in the determination of the enthalpy of fusion  $\Delta_{\text{cr}}^1 H_m$  and measurements in single-phase regions, which serve as consistency checks against the integrated molar heat-capacity values.

**TABLE 4**  
Measurements of molar energy increment  $\Delta_{\text{tot}} U_m$  and derived results.

<i>N</i> <sup>a</sup>	<i>h</i> <sup>b</sup>	<i>T</i> <sub>i</sub> K	<i>T</i> <sub>f</sub> K	<i>T</i> <sub>trs</sub> K	$\Delta_{\text{tot}} H_m^c$ kJ · mol <sup>-1</sup>	$\Delta_{\text{trs}} H_m^d$ kJ · mol <sup>-1</sup>
<i>1-Phenyl</i> naphthalene						
<i>Single-phase measurements in the crystal phase</i>						
2	1	207.316	292.370		17.215	0.011
6	1	68.543	107.943		3.277	0.000
6	1	107.945	211.254		13.562	0.003
6	1	211.297	291.805		16.404	0.004
<i>Crystal-to-liquid phase transition</i>						
1	6	291.029	300.621	297.473	18.075	15.543
6	2	291.759	301.241		18.769	15.553
					Average	15.548
<i>Single-phase measurements in the liquid phase</i>						
7	2	260.133	300.363		12.110	0.001
10	1	305.058	409.331		36.018	-0.003
<i>2-Phenyl</i> naphthalene						
<i>Single-phase measurements in the glassy-crystal phase</i>						
7	1	52.741	101.906	-	3.574	0.001
7	1	102.473	161.28		6.486	-0.001
7	1	161.406	242.755		13.277	-0.003
7	1	242.766	307.488		14.621	-0.010
<i>Glassy-crystal to crystal conversion</i>						
1	1	330.048	340.562	331.4	2.994	-0.110
2	1	328.174	337.996		2.792	-0.071
3	1	327.171	337.444		2.930	-0.050
9	2	325.880	336.789		3.148	0.000 <sup>e</sup>
<i>Crystal-to-liquid phase transition</i>						
1	2	370.531	377.185	374.76 <sub>7</sub>	25.008	22.620
9	5	369.905	377.687		25.406	22.617
12	2	370.776	376.801		24.779	22.617
					Average	22.618
<i>Single-phase measurements in the liquid phase</i>						
11	1	384.052	416.382		12.114	-0.001
11	1	416.367	442.445		10.194	-0.001

<sup>a</sup> Adiabatic series number.

<sup>b</sup> Number of heating increments.

<sup>c</sup>  $\Delta_{\text{tot}} U_m$  is the molar energy input from the initial temperature *T*<sub>i</sub> to the final temperature *T*<sub>f</sub>. The relative expanded uncertainty (0.95 level of confidence) for  $\Delta_{\text{tot}} U_m$  is 0.001.

<sup>d</sup>  $\Delta_{\text{trs}} H_m$  is the net molar enthalpy of transition at the transition temperature *T*<sub>trs</sub> or the excess enthalpy for single-phase measurements relative to the heat-capacity curve described in the text and defined in table 7.

<sup>e</sup> The longest annealing time was applied to the sample prior to this measurement, as described in the text.

TABLE 5

Molar heat capacities  $C_{\text{sat,m}}$  at vapor-saturation pressure measured with adiabatic calorimetry ( $R = 8.3144621 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ ).<sup>a</sup>

$N^b$	$\langle T \rangle / \text{K}$	$\Delta T / \text{K}$	$C_{\text{sat,m}} / R^c$	$N^b$	$\langle T \rangle / \text{K}$	$\Delta T / \text{K}$	$C_{\text{sat,m}} / R^c$
<i>1-Phenylnaphthalene</i>							
<i>Crystal</i>							
3	4.666	0.894	0.052	2	70.040	6.665	8.539
3	5.509	0.914	0.083	4	71.832	4.991	8.686
3	6.425	0.907	0.136	4	76.823	4.995	9.100
3	7.372	0.953	0.201	2	77.081	7.424	9.130
3	8.352	0.974	0.285	4	81.769	4.977	9.521
3	9.357	0.995	0.390	2	84.847	8.195	9.750
3	10.418	1.077	0.523	4	86.699	4.981	9.899
3	11.583	1.223	0.663	2	93.503	9.122	10.426
3	12.870	1.335	0.858	2	102.858	9.594	11.141
3	14.300	1.511	1.073	2	112.568	9.834	11.890
3	15.895	1.674	1.346	2	122.362	9.765	12.647
3	17.675	1.886	1.655	2	132.221	9.959	13.424
3	19.661	2.084	2.008	2	142.616	10.837	14.262
3	21.860	2.315	2.407	2	153.972	11.881	15.197
3	24.295	2.554	2.852	2	165.781	11.815	16.239
3	26.974	2.806	3.330	2	177.525	11.806	17.261
3	29.935	3.116	3.834	1	183.802	11.432	17.831
3	33.231	3.477	4.367	2	189.343	11.901	18.340
3	36.922	3.906	4.924	1	195.078	11.072	18.888
3	41.048	4.348	5.488	2	201.236	11.970	19.455
3	45.648	4.852	6.089	1	206.162	11.007	19.932
3	50.772	5.399	6.675	1	217.015	10.690	21.016
3	56.481	6.019	7.287	1	227.569	10.407	22.055
4	57.014	4.925	7.311	1	238.353	11.145	23.146
2	57.982	5.357	7.433	1	249.845	11.827	24.322
4	61.923	4.900	7.827	1	261.656	11.782	25.573
2	63.685	6.055	7.960	1	273.406	11.660	26.830
4	66.855	4.969	8.249	1	285.162	11.888	28.511
<i>Liquid</i>							
7	224.638	5.207	33.031	6	306.217	9.949	37.929
7	230.273	6.069	33.306	1	314.201	9.249	38.487
10	233.283	9.350	33.446	9	321.376	15.945	38.990
7	239.398	12.290	33.771	9	337.190	15.678	40.110
10	242.590	9.261	33.939	9	352.740	15.423	41.226
10	252.376	10.312	34.480	9	368.542	16.190	42.355
7	252.838	14.601	34.518	9	384.764	15.932	43.519
8	284.544	6.113	36.462	9	400.586	15.692	44.643
8	293.304	11.573	37.049	9	415.692	14.506	45.710
8	304.209	10.396	37.788	9	428.683	11.474	46.595
1	305.106	8.939	37.846	9	439.150	9.475	47.315
9	305.830	15.136	37.902				
<i>Glass</i>							
7	92.699	9.442	10.460	7	172.315	14.152	16.957
7	102.164	9.479	11.189	7	184.398	10.014	18.057
7	111.984	10.155	11.947	7	193.620	8.430	18.899
7	122.484	10.841	12.768	10	198.882	12.720	19.459
7	133.239	10.659	13.624	7	201.339	7.007	19.536
7	144.863	12.585	14.582	10	212.825	14.974	21.761
7	158.225	14.027	15.716				
<i>2-Phenylnaphthalene</i>							
<i>Glassy crystal</i>							
6	5.559	0.941	0.088	4	100.110	9.458	10.669
6	6.480	0.891	0.141	4	109.666	9.649	11.434
6	7.437	0.939	0.219	4	119.509	9.783	12.228
6	8.415	1.009	0.303	4	129.293	9.777	13.030
6	9.445	1.054	0.419	4	139.127	9.887	13.849
6	10.547	1.149	0.558	4	149.037	9.927	14.700
6	11.764	1.286	0.711	4	159.052	10.096	15.569
6	13.121	1.396	0.907	4	169.135	10.068	16.482
6	14.583	1.503	1.119	4	179.218	10.053	17.402
6	16.160	1.651	1.374	4	189.277	10.049	18.348
6	17.893	1.816	1.640	4	199.329	10.048	19.313
6	19.784	1.964	1.940	4	210.426	12.093	20.402
6	21.836	2.142	2.268	4	222.542	12.135	21.609
6	24.080	2.348	2.621	4	234.704	12.180	22.866
6	26.553	2.596	3.012	4	246.897	12.198	24.113
6	29.304	2.905	3.432	4	260.129	14.259	25.511
6	32.360	3.207	3.889	4	274.337	14.154	27.039
6	35.767	3.607	4.372	8	281.755	7.836	27.857
6	39.574	4.008	4.885	2	287.175	12.241	28.489
6	43.812	4.469	5.432	4	288.455	14.050	28.625

(continued on next page)

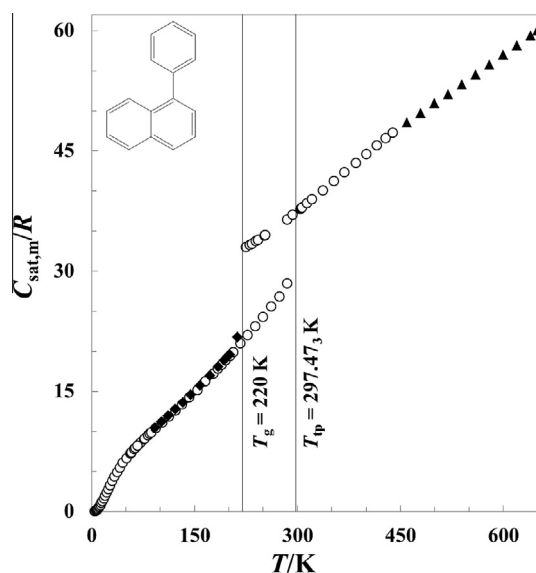
TABLE 5 (continued)

$N^b$	$\langle T \rangle / K$	$\Delta T / K$	$C_{\text{sat,m}} / R^c$	$N^b$	$\langle T \rangle / K$	$\Delta T / K$	$C_{\text{sat,m}} / R^c$
6	48.554	5.014	5.983	9	288.880	15.195	28.659
6	53.865	5.606	6.580	8	289.672	8.083	28.783
5	54.566	5.065	6.644	3	290.857	10.067	28.958
6	59.817	6.296	7.190	8	297.621	8.226	29.738
5	59.833	5.459	7.195	2	302.221	17.732	30.286
5	65.643	6.149	7.748	3	303.659	15.387	30.484
6	66.409	6.884	7.817	9	304.260	15.381	30.527
5	72.140	6.836	8.342	8	305.951	8.302	30.757
5	79.329	7.532	8.963	9	316.274	8.373	31.961
4	84.658	6.061	9.412	3	319.322	15.578	32.362
5	87.375	8.552	9.624	2	319.626	17.048	32.405
4	91.534	7.687	9.970	9	323.177	5.343	32.896
5	96.286	9.263	10.366	9	328.640	5.519	33.875
Crystal							
9	334.104	5.370	35.535	12	355.252	10.185	38.909
9	339.547	5.317	36.118	1	356.408	10.152	39.210
3	340.548	6.072	36.302	3	360.854	9.710	40.256
9	345.849	7.143	37.123	9	364.778	10.266	41.280
3	346.701	6.147	37.330	12	365.472	10.240	41.442
3	352.895	6.210	38.485	1	365.991	8.988	41.765
9	354.521	10.181	38.945	3	368.758	6.110	42.477
Liquid							
1	381.146	7.920	43.786	1	390.223	10.236	44.396
12	381.641	10.099	43.801	10	405.186	16.794	45.404
9	382.947	10.522	43.907	10	422.042	16.854	46.529
10	388.394	16.739	44.266	10	436.242	11.425	47.474

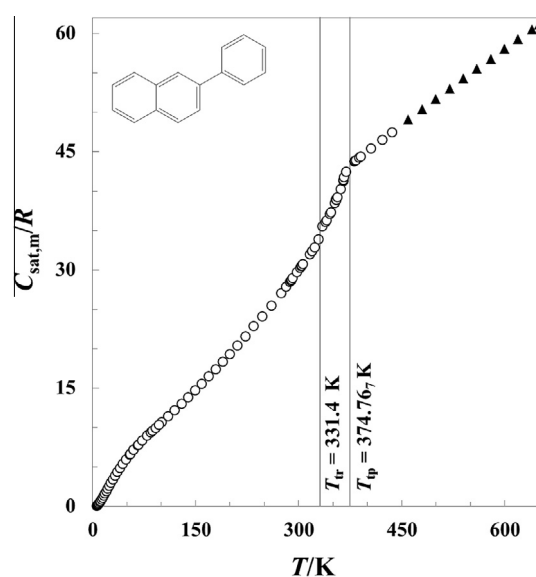
<sup>a</sup> The relative expanded uncertainty (0.95 level of confidence) for the heat capacities  $U_r(C_{\text{sat,m}})$  are 0.03 at  $T/K = 5$ , 0.005 at  $T/K = 10$ , and 0.001 for temperatures  $T \geq 30$  K.

<sup>b</sup> Adiabatic series number.

<sup>c</sup> Average heat capacity for a temperature increment  $\Delta T$  with mean temperature  $\langle T \rangle$ .



**FIGURE 1.** Plot of molar heat capacities against temperature at saturation pressure  $C_{\text{sat,m}}$  for 1-phenylnaphthalene measured in this research. The vertical line indicates the triple-point temperature  $T_{\text{tp}}$  and the glass transition temperature  $T_g$ . Experimental values determined in this research;  $\circ$ , crystal and liquid phase with adiabatic calorimetry;  $\blacklozenge$ , glass phase with adiabatic calorimetry;  $\blacktriangle$ , liquid phase with DSC.



**FIGURE 2.** Plot of molar heat capacities against temperature at saturation pressure  $C_{\text{sat,m}}$  for 2-phenylnaphthalene measured in this research. The vertical line indicates the triple-point temperature  $T_{\text{tp}}$  and glassy crystal-to-crystal transition temperature  $T_{\text{tr}}$ . Experimental values determined in this research;  $\circ$ , crystal and liquid phase with adiabatic calorimetry;  $\blacktriangle$ , liquid phase with DSC.

Corrections for pre-melting caused by impurities were made. Results with the same series number  $N$  in tables 4 and 5 were taken without interruption of adiabatic conditions.

Results in table 4 for 2-PhN include measurements spanning a region of conversion from a glassy-crystal to the high-temperature crystal phase. Presence of the glassy-crystal was first evidenced by

spontaneous warming of the sample near the temperature 315 K. This warming occurred subsequent to annealing of the high-temperature phase near the melting temperature, as described earlier. Results for series 9 were obtained for the glassy crystals that had been most extensively annealed (several weeks), so the “transition temperature” was adjusted to yield zero excess enthalpy for this series. Earlier series that had been annealed to a lesser extent

showed excess enthalpies that are consistent with a higher conversion temperature. This behavior is common for glass-like systems, as shown previously in studies on quinoline [17] and phenanthridine [6,40].

For both 1-PhN and 2-PhN, equilibrium was reached in less than 1 h for all measurements in the liquid phase, as well as in the solid phase for measurements more than 50 K below the respective triple-point temperatures. As the triple-point temperature was approached in the solid phase, equilibration times increased gradually to approximately 24 h within 10 K of  $T_{tp}$ . Such variation in equilibration times is common for organic compounds in the solid state near  $T_{tp}$ . For 2-PhN, measurements were complicated in the region of the glassy-crystal to crystal conversion ( $328 < T/K < 334$ ) due to simultaneous slow equilibration and sample annealing. It was not possible to determine if the sample had reached equilibrium in this region at any temperature, so detailed measurements with small temperature increments were not made.

The experimental molar heat capacities under vapor saturation pressure  $C_{sat,m}$  determined by adiabatic calorimetry for 1-PhN and 2-PhN are listed in table 5 and shown in figures 1 and 2. Values in table 5 were corrected for effects of sample vaporization into the gas space of the calorimeter, although the size of this correction is small, as indicated in table 2. The values listed in table 5 were not corrected for premelting, but an independent calculation can be made with the temperature increments provided. The temperature increments were small enough to eliminate the need for corrections for nonlinear variation of  $C_{sat,m}$  with temperature. Expanded relative uncertainties (0.95 level of confidence) for the heat-capacity measurements ranged from approximately 3% at  $T = 5$  K, to 0.5% at 10 K, and improved gradually to better than 0.1 percent for temperatures  $T \geq 30$  K. Extrapolation of the heat-capacity results to  $T \rightarrow 0$  K was made with a plot of  $C_{sat,m}/T$  against  $T^2$  for temperatures below 10 K.

**TABLE 6**  
Measured two phase (liquid + vapor) heat capacities ( $R = 8.3144621 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ ).<sup>a</sup>

	$T/\text{K}$	$C_{x,m}^{\text{ll}}/R$	$C_{x,m}^{\text{ll}}/R$	$C_{x,m}^{\text{ll}}/R$
<i>1-Phenylnaphthalene</i>				
m/g		0.00853	0.01534	0.02378
$V_{\text{cell}}/\text{cm}^3$		0.0520	0.0545	0.0520
	410.0	45.05	44.73	44.63
	430.0	46.36	46.20	46.01
	450.0	48.36	47.52	47.37
	470.0	48.97	48.50	48.69
	490.0	50.40	49.49	50.05
	510.0	51.61	51.26	51.52
	530.0	52.76	52.33	52.81
	550.0	53.77	53.48	54.10
	570.0	55.38	54.46	55.40
	590.0	56.66	56.08	56.42
	610.0	57.83	57.31	57.64
<i>2-Phenylnaphthalene</i>				
m/g		0.01341	0.02088	
$V_{\text{cell}}/\text{cm}^3$		0.0527	0.0551	
	410.1	45.74	46.02	
	430.0	47.03	47.46	
	450.0	48.29	48.78	
	470.1	49.73	49.45	
	490.0	50.93	51.08	
	510.0	51.40	52.31	
	530.1	53.43	53.74	
	550.1	54.84	54.99	
	570.1	56.20	56.32	
	590.1	57.26	57.48	
	610.1	58.27	58.23	

<sup>a</sup>  $m$  is the mass of the sample,  $V_{\text{cell}}$  is the internal volume of the dsc cell at  $T = 298.15$  K after sealing. The relative expanded uncertainty  $U_r$  for  $C_{x,m}^{\text{ll}}$  is 0.01 with 0.95 level of confidence.

### 3.2. Heat capacities measured with dsc

Table 6 lists two-phase heat capacities  $C_{x,m}^{\text{ll}}$  for 1-PhN and 2-PhN in the liquid phase measured with dsc for several cell fillings for the temperature range ( $410 < T/\text{K} < 610$ ). These measurements did not exceed the normal boiling temperature for either compound, and results for the various cell fillings were assumed equivalent to  $C_{sat,m}$ . Decomposition of the samples precluded reliable measurements at higher temperatures.

### 3.3. Thermodynamic functions for the condensed states

Molar entropies and molar enthalpies for the condensed phases relative to that of the crystals at  $T \rightarrow 0$  K for the solid and liquid phases under vapor saturation pressure for 1-PhN and 2-PhN are listed in table 7. These were derived by integration of the smoothed molar heat capacities (tables 5 and 6) corrected for pre-melting, together with the molar entropy and molar enthalpy of fusion. Pre-melting corrections were made using published methods [38] for solid-insoluble impurities and the mole-fraction purities  $x_{\text{pre}}$  values shown in table 2. For 2-PhN, this is value is slightly less than the sample impurity given in table 3, due to distribution of the impurity between the solid and liquid phases, as noted earlier.

### 3.4. Vapor pressures, densities, and derived enthalpies of vaporization

Experimental vapor pressures for 1-PhN and 2-PhN are reported in table 8. The Wagner equation [41] in the form shown here was used to represent the vapor pressures:

$$\ln(p/p_c) = (1/T_r)\{A(1 - T_r) + B(1 - T_r)^{1.5} + C(1 - T_r)^{2.5} + D(1 - T_r)^{5.0}\}, \quad (2)$$

where  $T_r = T/T_c$  and  $T_c$  is the critical temperature. The unpublished vapor pressures provided by Verevkin [16] for 1-PhN for the temperature range ( $313 < T/\text{K} < 371$ ) were included in the fit for that compound. The average deviation from the fitted curve for these values was 0.03  $\cdot p$ , which is within the expected uncertainty for values determined by the vapor-saturation method. The critical temperature for 1-PhN and 2-PhN were estimated initially with the method of Joback [42]. For 1-PhN, it was found necessary to adjust the estimated  $T_c$  lower by 30 K to allow good representation of measured densities with the Riedel equation (below). The same adjustment was applied to the estimated  $T_c$  for 2-PhN. The critical pressures were evaluated with Waring's criterion for  $T/T_c = 0.85$  [24,43]. The fitted parameters and estimated critical constants are listed in table 9.

Molar enthalpies of vaporization  $\Delta_1^{\text{g}}H_m$  were calculated with the Clapeyron equation:

$$dp/dT = \Delta_1^{\text{g}}H_m / (T \cdot \Delta_1^{\text{g}}V_m), \quad (3)$$

where  $\Delta_1^{\text{g}}V_m$  is the increase in molar volume from the liquid to the vapor. The Wagner-equation fit was employed to calculate  $dp/dT$ . Molar volumes for the liquid phase were estimated with the extended corresponding states equation of Riedel [44], as formulated by Hales and Townsend [45]:

$$\rho/\rho_c = 1.0 + 0.85(1 - T_r) + (1.6916 + 0.9846\omega)(1 - T_r)^{1/3}, \quad (4)$$

where  $T_r$  is the reduced temperature  $T/T_c$  and  $T_c$  was that estimated for the vapor pressure fit. The acentric factor  $\omega$  was obtained from the vapor-pressure fit, and the critical density  $\rho_c$  was estimated with equation (4) and the densities measured in this research for 1-PhN (table 10) and with the single density measured during sample loading into the calorimeter vessel for studies with adiabatic calorimetry for 2-PhN, as described earlier. Vapor-phase volumes

were calculated with the virial equation of state truncated at the third virial coefficient. Second and third virial coefficients were estimated with the corresponding-states correlations of Pitzer and Curl [46] and Orbey and Vera [47], respectively. This approach has been applied successfully in many studies reported by this research group, including most recently for a series of three-ring aza-aromatics [5,6] and 9-fluorenone [4]. Third virial coefficients are required for calculation of the volume of gas for pressures greater than 0.1 MPa [19]. Relative expanded uncertainties for the virial coefficients were estimated to be 10%, and these are the dominant contributions to the uncertainties in the derived enthalpies of vaporization for  $p > 0.1$  MPa. The derived enthalpies of vaporization are reported in table 11.

**TABLE 7**  
Molar thermodynamic functions at vapor-saturation pressure ( $R = 8.3144621 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ ).<sup>a</sup>

T K	$C_{\text{sat,m}}$ R	$\Delta_0^{\ddagger}S_{\text{m}}$ R	$\Delta_0^{\ddagger}H_{\text{m}}$ RT	T K	$C_{\text{sat,m}}$ R	$\Delta_0^{\ddagger}S_{\text{m}}$ R	$\Delta H_{\text{m}}$ RT
<i>1-Phenyl naphthalene</i>							
<i>Crystal</i>							
5.00	0.063	0.021	0.016	120.00	12.464	12.898	6.898
10.00	0.469	0.165	0.123	140.00	14.049	14.937	7.806
20.00	2.069	0.944	0.670	160.00	15.724	16.921	8.689
30.00	3.845	2.125	1.437	180.00	17.480	18.874	9.568
40.00	5.349	3.445	2.234	200.00	19.331	20.811	10.451
50.00	6.593	4.777	2.986	220.00	21.298	22.745	11.347
60.00	7.624	6.073	3.675	240.00	23.295	24.683	12.259
70.00	8.531	7.317	4.305	260.00	25.338	26.628	13.186
80.00	9.366	8.511	4.886	280.00	27.426	28.582	14.129
90.00	10.157	9.661	5.428	297.47 <sup>b</sup>	29.317	30.299	14.965
100.00	10.923	10.771	5.940				
<i>Liquid</i>							
297.47	37.328	36.587	21.253	480.00	49.577	57.251	29.784
298.15	37.374	36.672	21.290	500.00	50.805	59.300	30.600
300.00	37.501	36.903	21.389	520.00	52.033	61.316	31.401
320.00	38.893	39.368	22.439	540.00	53.261	63.303	32.188
340.00	40.312	41.768	23.449	560.00	54.484	65.262	32.962
360.00	41.745	44.113	24.426	580.00	55.712	67.196	33.725
380.00	43.178	46.408	25.375	600.00	56.94	69.105	34.479
400.00	44.603	48.659	26.301	620.00	58.168	70.992	35.223
420.00	46.005	50.870	27.206	640.00	59.394	72.858	35.959
440.00	47.344	53.041	28.091	650.00	60.005	73.784	36.324
460.00	48.344	55.168	28.950				
<i>2-Phenyl naphthalene</i>							
<i>Glassy crystal</i>							
5.00	0.066	0.022	0.017	160.00	15.655	16.303	8.453
10.00	0.488	0.172	0.128	180.00	17.475	18.251	9.354
20.00	1.974	0.945	0.665	200.00	19.378	20.190	10.260
30.00	3.537	2.044	1.364	220.00	21.354	22.130	11.179
40.00	4.942	3.259	2.087	240.00	23.406	24.075	12.112
50.00	6.150	4.496	2.783	260.00	25.496	26.031	13.061
60.00	7.211	5.713	3.435	280.00	27.648	27.999	14.025
70.00	8.150	6.896	4.042	298.15	29.808	29.801	14.919
80.00	9.018	8.042	4.611	300.00	30.032	29.986	15.011
90.00	9.843	9.151	5.146	320.00	32.458	32.000	16.025
100.00	10.661	10.231	5.657	330.05	34.181	33.028	16.549
120.00	12.268	12.317	6.624	331.40	34.504	33.168	16.621
140.00	13.924	14.331	7.548				
<i>Crystal</i>							
331.40	35.098	33.17	16.623	360.00	39.923	36.252	18.263
340.00	36.244	34.083	17.104	374.76 <sup>b</sup>	43.552	37.927	19.186
<i>Liquid</i>							
374.76 <sup>b</sup>	43.345	45.186	26.445	520.00	52.924	60.881	32.516
380.00 <sup>b</sup>	43.701	45.789	26.680	540.00	54.202	62.903	33.295
400.00	45.054	48.065	27.565	560.00	55.469	64.897	34.065
420.00	46.394	50.296	28.430	580.00	56.730	66.865	34.825
440.00	47.720	52.485	29.276	600.00	57.981	68.810	35.576
460.00	49.033	54.635	30.107	620.00	59.222	70.731	36.318
480.00	50.338	56.750	30.923	640.00	60.450	72.631	37.053
500.00	51.636	58.831	31.725	650.00	61.056	73.573	37.418

<sup>a</sup> Relative expanded uncertainties (0.95 level of confidence)  $U_r$  for all properties are 0.03 for temperatures  $T/K < 10$ , 0.005 for  $10 \leq T/K \leq 30$ , and 0.001 for  $T/K > 30$  K.

<sup>b</sup> Values at this temperature were calculated with graphically extrapolated heat capacities.

### 3.5. Enthalpy of formation for 1-phenyl naphthalene

Results of a typical combustion experiment for 1-PhN are given in table 12. Values of  $\Delta_c U_{\text{m}}^0/M$  for all combustions are reported in table 13. Values of  $\Delta_c U_{\text{m}}^0/M$  in table 13 refer to the reaction:

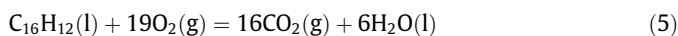


Table 13 also gives derived values of the standard molar energy of combustion, the standard molar enthalpy of combustion  $\Delta_c H_{\text{m}}^0$  and the standard molar enthalpy of formation  $\Delta_f H_{\text{m}}^0$  for  $\text{C}_{16}\text{H}_{12}$  (1-PhN). Values of  $\Delta_c U_{\text{m}}^0$  and  $\Delta_c H_{\text{m}}^0$  refer to reaction (5). Values of  $\Delta_f H_{\text{m}}^0$  refer to the reaction:

**TABLE 8**  
Vapor pressure results.<sup>a</sup>

Method	T/K	p/kPa	U(p)/kPa	Δp/kPa
<i>1-Phenylnaphthalene</i>				
IP	375.005	0.0218	0.0004	0.0002
IP	385.002	0.0404	0.0004	0.0001
IP	395.002	0.0732	0.0004	0.0007
IP	405.002	0.1265	0.0004	0.0006
IP	415.002	0.2126	0.0004	0.0008
IP	425.008	0.3464	0.0006	0.0007
IP	434.994	0.5490	0.0006	0.0004
IP	445.004	0.8490	0.0006	-0.0004
IP	455.000	1.2829	0.0008	-0.0007
IP	465.001	1.8964	0.0010	-0.0016
Decane	466.359	1.9995	0.0006	0.0012
IP	475.004	2.7467	0.0012	-0.0032
IP	479.998	3.2812	0.0014	-0.0041
Decane	485.686	4.0021	0.0010	0.0011
Decane	494.306	5.3360	0.0012	0.0002
Decane	507.127	8.0046	0.0016	-0.0006
Decane	516.730	10.670	0.002	0.000
Decane	524.516	13.340	0.002	-0.001
Decane	532.527	16.645	0.004	-0.002
Decane	539.267	19.926	0.004	-0.002
Water	548.097	25.014	0.006	-0.001
Decane	548.110	25.022	0.004	-0.002
Water	556.999	31.175	0.006	-0.001
Water	565.958	38.574	0.008	0.005
Water	574.939	47.359	0.008	0.006
Water	584.016	57.819	0.010	0.012
Water	593.130	70.114	0.012	0.016
Water	602.325	84.545	0.014	0.008
Water	611.559	101.34	0.02	0.00
Water	620.849	120.80	0.02	-0.01
Water	630.200	143.27	0.02	-0.03
<i>2-Phenylnaphthalene</i>				
Decane	482.850	1.9960	0.0006	-0.0001
Decane	502.827	3.9975	0.0010	0.0000
Decane	511.750	5.3352	0.0012	0.0004
Decane	524.935	7.9928	0.0016	0.0004
Decane	534.903	10.672	0.002	-0.001
Decane	542.892	13.331	0.002	0.000
Decane	551.198	16.656	0.004	0.000
Decane	558.161	19.949	0.004	0.000
Decane	567.231	25.028	0.004	0.001
Water	576.353	31.163	0.006	0.001
Water	585.573	38.564	0.008	0.002
Water	594.822	47.364	0.008	-0.001
Water	604.125	57.796	0.010	-0.002

<sup>a</sup> IP denotes inclined piston; water or decane refers to the material used as the standard in the reference ebulliometer; *T* is the condensation temperature of the sample; the pressure *p* for ebulliometric measurements was calculated from the condensation temperature of the reference substance; Δ*p* is the difference between the experimental vapor pressure and that calculated with equation (5) and the parameters listed in table 9; *U*(*p*) is the expanded uncertainty (0.95 level of confidence) calculated from equations (1) and (2).

**TABLE 9**  
Parameters for the Wagner vapor pressure equation, selected critical constants, and derived acentric factor.<sup>a</sup>

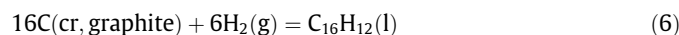
<i>1-Phenylnaphthalene</i>		
A	-10.401478	$T_c/K = 830^b$
B	5.334154	$p_c/kPa = 2200$
C	-6.959231	$\rho_c/kg \cdot m^{-3} = 312.2$
D	-2.535163	$\omega = 0.6089$
<i>2-Phenylnaphthalene</i>		
A	-10.340671	$T_c/K = 860^b$
B	4.979454	$p_c/kPa = 2300$
C	-6.478804	$\rho_c/kg \cdot m^{-3} = 306.0$
D	-2.716704	$\omega = 0.6193$

<sup>a</sup> All critical parameters were estimated, as described in the text.

<sup>b</sup> The standard uncertainty for the estimated  $T_c$  is ~10 K, and the values for  $T_c$  and  $p_c$  are closely correlated. Consequently, this uncertainty makes a negligible contribution to the uncertainties for the derived properties.

**TABLE 10**  
Measured liquid densities at temperature *T* and vapor-saturation pressure  $\rho_{sat}$  for 1-phenylnaphthalene.

T/K	$\rho_{sat}$	T/K	$\rho_{sat}$
323.136	1082.7	448.111	986.7
348.131	1064.6	473.111	967.0
373.124	1045.5	498.108	945.0
423.113	1006.3	523.110	921.4



Uncertainties given in table 13 are expressed as the “uncertainty interval” defined in reference [48]. This value is equivalent to the expanded uncertainty with a 0.95 level of confidence. The standard molar enthalpies of formation of CO<sub>2</sub>(g) and H<sub>2</sub>O(l) were taken to be  $-(393.51 \pm 0.13) \text{ kJ} \cdot \text{mol}^{-1}$  and  $-(285.830 \pm 0.042) \text{ kJ} \cdot \text{mol}^{-1}$ , respectively, as assigned by CODATA [49].

### 3.6. Thermodynamic function in the ideal-gas state

Molar thermodynamic properties in the ideal-gas state with  $p^\circ = 101.325 \text{ kPa}$  for 1-PhN and 2-PhN are given in table 14. These were calculated based on values from tables 7, 11 and 13. Enthalpies and entropies for equilibrium hydrogen were determined from the JANAF tables [50]. Values for graphite were determined with the polynomial [51] used to calculate the values from  $T = 298.15 \text{ K}$  to  $T = 6000 \text{ K}$  listed in the JANAF tables.

## 4. Discussion

### 4.1. Comparisons with literature melting temperatures

The range of normal melting temperatures  $T_m$  reported in the literature for 1-PhN is large and none agree with the value reported in the present research. Melting temperatures have been reported by Karami *et al.* [52] ( $T_m = 364$  to  $369 \text{ K}$ ), Nandurkar and Bhanage [53] ( $T_m = 319$  to  $320 \text{ K}$ ), Cologne *et al.* [54] ( $T_m = 318 \text{ K}$ ), Penso *et al.* [55] ( $T_m = 316 \text{ K}$ ), Zhang *et al.* ( $T_m = 314$  to  $316 \text{ K}$ ) [56], and Molander and Beaumard [57] ( $T_m = 313$  to  $314 \text{ K}$ ). All of these sources reported a melting temperature only, except for Cologne *et al.* [54], who also reported a single boiling temperature ( $T_b = 468$  to  $473 \text{ K}$  at pressure  $p = 1.9 \text{ kPa}$ ) that is 20% low relative to the values measured in this research.

In contrast to findings noted above, all researchers reporting more extensive studies of physical properties for 1-PhN [16,58,59] found the compound to be a liquid at room temperature, which is in accord with the triple-point temperature measured here ( $T_{tp} = 297.473 \text{ K}$ ). Also, single boiling temperatures at reduced pressures  $p$ , between  $p = 0.01 \text{ kPa}$  and  $p = 3.3 \text{ kPa}$ , have been reported as part of research into various organic syntheses [60–68] without mention of a solid phase at ambient temperature. Verevkin [16] measured vapor pressures for the temperature range ( $313 < T/K < 371$ ), Binns and Squire [58] measured densities for the liquid over the temperature range ( $298 < T/K < 378$ ), and Rocha *et al.* [59] measured the enthalpy of vaporization of the liquid at the temperature  $T = 298.15 \text{ K}$ . Rocha *et al.* [59] attempted to crystallize 1-PhN in a dsc, but found only a glass transition ( $T_g = 227 \text{ K}$ ) that is near the value observed in this research ( $T_g = 220 \text{ K}$ ). (Measurements at low temperatures are difficult with a dsc, plus the value of  $T_g$  for any particular compound is a function of the extent to which the glass was annealed, so the difference of 7 K in the  $T_g$  values is not significant.)

A common “rule of thumb” for organic compounds is  $T_g/T_m$  is  $\sim 2/3$  (cf., [69–71]). Based on this, the measured glass transition temperatures for 1-PhN ( $T_g = 220 \text{ K}$ , this research;  $T_g = 227 \text{ K}$  [59])

**TABLE 11**  
Enthalpies of vaporization  $\Delta_1^{\circ}H_m$  derived with the fitted vapor-pressure curves and the Clapeyron equation.<sup>a</sup>

T/K	$\Delta_1^{\circ}H_m/(\text{kJ} \cdot \text{mol}^{-1})$	T/K	$\Delta_1^{\circ}H_m/(\text{kJ} \cdot \text{mol}^{-1})$	T/K	$\Delta_1^{\circ}H_m/(\text{kJ} \cdot \text{mol}^{-1})$
<i>1-Phenylnaphthalene</i>					
298.15	82.11 ± 0.50	420.00	71.79 ± 0.30	560.00	60.52 ± 0.38
300.00	81.96 ± 0.50	440.00	70.17 ± 0.28	580.00	58.80 ± 0.48
320.00	80.21 ± 0.43	460.00	68.59 ± 0.27	600.00	57.01 ± 0.62
340.00	78.48 ± 0.40	480.00	67.01 ± 0.25	620.00	55.16 ± 0.78
360.00	76.77 ± 0.37	500.00	65.42 ± 0.25	640.00	53.22 ± 0.98
380.00	75.08 ± 0.33	520.00	63.82 ± 0.27	650.00	52.21 ± 1.08
400.00	73.42 ± 0.32	540.00	62.19 ± 0.32		
<i>2-Phenylnaphthalene</i>					
440.00	73.93 ± 0.30	520.00	67.76 ± 0.27	600.00	61.36 ± 0.50
460.00	72.37 ± 0.28	540.00	66.22 ± 0.28	620.00	59.62 ± 0.63
480.00	70.83 ± 0.27	560.00	64.64 ± 0.33	640.00	57.82 ± 0.78
500.00	69.30 ± 0.27	580.00	63.02 ± 0.40	650.00	56.88 ± 0.88

<sup>a</sup> Uncertainties are expanded uncertainties with 0.95 level of confidence.**TABLE 12**  
Typical details of a combustion experiment at  $T = 298.15$  K for 1-phenylnaphthalene ( $p^{\circ} = 101.325$  kPa).<sup>a</sup>

$m'$ (compound)/g	0.908725
$m''$ (oil)/g	0.049460
$m'''$ (fuse)/g	0.001510
$n_i(\text{H}_2\text{O})/\text{mol}$	0.055345
$m(\text{Pt})/\text{g}$	38.798
$\Delta T/\text{K} = (T_i - T_f + \Delta T_{\text{corr}})/\text{K}$	2.30176
$e(\text{calor})(\Delta T)/\text{J}$	-38616.3
$e(\text{cont})(\Delta T)/\text{J}^b$	-52.7
$\Delta U_{\text{ign}}/\text{J}$	0.8
$\Delta U(\text{correction to standard states})/\text{J}^c$	24.8
$-m'(\Delta_c U^{\circ}/M)(\text{oil})/\text{J}$	2277.3
$-m'''(\Delta_c U^{\circ}/M)(\text{fuse})/\text{J}$	25.6
$m'(\Delta_c U^{\circ}/M)(1\text{-phenylnaphthalene})/\text{J}$	-36340.6
$(\Delta_c U^{\circ}/M)(1\text{-phenylnaphthalene})/(\text{J} \cdot \text{g}^{-1})$	-39990.8

<sup>a</sup> The symbols and abbreviations of this table are those of reference [36], except as noted.<sup>b</sup>  $e_i(\text{cont})(T_i - 298.15 \text{ K}) + e_f(\text{cont})(298.15 \text{ K} - T_f + \Delta T_{\text{corr}})$ .<sup>c</sup> Items 81 to 85, 87 to 90, 93, and 94 of the computational form of reference [36].

imply a value of  $T_m$  in the region of 335 K, which is not observed. In summary, the literature concerning the normal melting temperature of 1-PhN is contradictory and appears to indicate that 1-PhN can exist in more than one crystal form. In our measurements, 1-PhN was maintained in the partially-melted state for extended periods of time (hours to days) and no evidence of conversion to a higher-melting form was observed.

There are numerous reports in the literature of the normal melting temperature of 2-PhN and these are in general accord with the value of  $T_{\text{tp}}$  determined here ( $T_{\text{tp}} = 374.76_7$  K).

#### 4.2. Comparisons with literature densities

For 1-PhN, single density values for the liquid phase at temperature  $T = 293.2$  K were reported by von Braun and Anton [60] and Kutz *et al.* [72]. Densities for the liquid phase of 1-PhN and for

**TABLE 13**  
Summary of experimental energy of combustion results and molar thermodynamic functions at  $T = 298.15$  K, and  $p^{\circ} = 101.325$  kPa for 1-phenylnaphthalene (1-PhN).<sup>a</sup>

-39990.8	-39997.5	$\{(\Delta_c U_m^{\circ}/M)(1\text{-phenylnaphthalene})\}/(\text{J} \cdot \text{g}^{-1})$	-39996.8	-39986.8	-39998.8	-39997.3
	$\{(\Delta_c U_m^{\circ}/M)(1\text{-PhN})\}/(\text{J} \cdot \text{g}^{-1})$			-39994.7 ± 3.1 <sup>a</sup>		
	$\Delta_c U_m^{\circ}(1\text{-PhN})/(\text{kJ} \cdot \text{mol}^{-1})$			-8169.79 ± 1.28 <sup>b</sup>		
	$\Delta_c H_m^{\circ}(1\text{-PhN})/(\text{kJ} \cdot \text{mol}^{-1})$			-8177.23 ± 1.28 <sup>b</sup>		
	$\Delta_f H_m^{\circ}(1\text{-PhN})/(\text{kJ} \cdot \text{mol}^{-1})$			166.09 ± 1.48 <sup>c</sup>		

<sup>a</sup> Uncertainties are expressed as the uncertainty interval, which is defined in reference [48]. This is equivalent to the expanded uncertainty with 0.95 level of confidence.<sup>b</sup> Value for reaction (5) (see text).<sup>c</sup> Value for reaction (6) (see text).

the solid and liquid phase of 2-PhN were determined with a dilatometer and reported in equation form by Binns and Squire [58]. The literature densities and those measured in this research for both compounds are shown in figure 3. Densities reported by Binns and Squire [58] for 1-PhN are 1% lower than those measured in this research, but the expansion coefficient is in good accord. The values of density and expansion coefficient for 1-PhN and 2-PhN are very similar, as seen in figure 3.

#### 4.3. Comparisons with literature vapor pressures and sublimation pressures

The vapor pressures reported as single values as part of synthesis studies [60–68] are in approximate agreement (within  $0.7 \cdot p$ , on average) with the values of this research (table 9). Similar qualitative agreement was seen for single boiling temperatures reported [66,73,74] for 2-PhN.

Sublimation pressures for 2-PhN were measured with the Knudsen-effusion method by Rocha *et al.* [59]. Sublimation pressures were calculated in this research through combination of vapor pressures extrapolated to below  $T_{\text{tp}}$  (parameters of table 9 with equation (2)), the thermodynamic functions for the crystals (table 5), and thermodynamic functions extrapolated linearly to temperature  $T = 330$  K for the liquid phase. The method has been described in detail previously [75]. Agreement between the measured [59] and calculated sublimation pressures is excellent, with deviations evenly distributed over  $\pm 0.04 \cdot p$ . This agreement may be partially fortuitous, as a long extrapolation of the vapor pressures for the liquid (table 8) are involved, as seen in figure 4.

#### 4.4. Comparisons with literature phase-change enthalpies

The normal melting temperature,  $T_m = (373.5 \pm 0.2 \text{ K})$ , and molar enthalpy of fusion =  $(17.90 \pm 0.12 \text{ kJ} \cdot \text{mol}^{-1})$ , were measured with dsc for 2-phenylnaphthalene by Rocha *et al.* [59]. The melting temperature is in good agreement with the triple-point temperature ( $T_{\text{tp}} = 374.76_7 \text{ K}$ ) measured in this research, although the

claimed uncertainty is too small. In contrast, the reported enthalpy of fusion is  $\sim 20\%$  lower than the value reported here  $\Delta_{\text{cr}}^{\text{H}}H_{\text{m}} = (22.62 \pm 0.02) \text{ kJ} \cdot \text{mol}^{-1}$ . The origin of this large discrepancy is not known.

The molar enthalpy of vaporization of 1-PhN at the temperature  $T = 298.15 \text{ K}$ ,  $\Delta_{\text{l}}^{\text{H}}H_{\text{m}} = (81.0 \pm 1.8) \text{ kJ} \cdot \text{mol}^{-1}$  was measured with the Calvet microcalorimetric drop method by Rocha *et al.* [59]. This value is in excellent agreement with the value reported here (table 11) that was derived with the fitted vapor-pressure curve and the Clapeyron equation  $= (82.1 \pm 0.5) \text{ kJ} \cdot \text{mol}^{-1}$ .

#### 4.5. Comparison with literature enthalpies of formation

The enthalpy of formation  $\Delta_{\text{f}}H_{\text{m}}$  for 1-PhN based on experimental property measurements has not been reported previously. The enthalpy of formation for the ideal gas state  $\Delta_{\text{f}}H_{\text{m}}^{\circ}$  at the temperature  $T = 298.15 \text{ K}$  was estimated with a group-additive method by Lima *et al.* [3] using experimental data for structurally-related compounds. The value estimated by Lima *et al.* [3]  $\Delta_{\text{f}}H_{\text{m}}^{\circ} = (252.3 \pm 3.4) \text{ kJ} \cdot \text{mol}^{-1}$  is in good agreement with the value determined here  $\Delta_{\text{f}}H_{\text{m}}^{\circ} = (248.2 \pm 1.6) \text{ kJ} \cdot \text{mol}^{-1}$  (table 14).

#### 4.6. Mutual validation of experimental and computed ideal-gas entropies

Computations for 1-PhN and 2-PhN were performed with the hybrid Density Functional Theory (DFT) method B3LYP [76] using two basis sets, 6-31+g(d,p) and cc-pVTZ. The former was used in

our previous publications and was shown to provide good performance in conjunction with B3LYP for a variety of aromatic compounds (cf., [4–7] and references therein). The latter, B3LYP/cc-pVTZ was recommended for polycyclic aromatic compounds by Martin *et al.* [77] and was also used successfully to predict ideal-gas thermodynamic properties of biphenyl by Dorofeeva *et al.* [78]. All calculations were performed with Gaussian 09 [79]. The computed rotation constants and vibrational frequencies are included in the Supporting Information for this article.

The thermodynamic functions were calculated from the computed geometries and vibrational spectra following standard rigid rotor-harmonic oscillator approximations [80]. Treatment of hindered rotation for the phenyl group in 1-PhN and 2-PhN was based on numerical solution of the one-dimensional Schrödinger equation for the rotor with the rotational potential and reduced rotational constants represented with truncated Fourier series. Details of the software used are described by Li *et al.* [81]. The full angular dependencies of the rotational potentials and reduced rotational constants for 1-PhN and 2-PhN were computed at the B3LYP/6-31+g(d,p) level. Figures showing the angular dependencies for these quantities are given in the Supporting Information. The extrema (ground states and barriers) were also computed at the B3LYP/cc-pVTZ level and were used to rescale the full B3LYP/6-31+g(d,p) curves for thermodynamic property calculations based on B3LYP/cc-pVTZ. To test the quality of the predicted rotational barriers, the calculations were performed for the well-studied model compound, biphenyl. The barriers predicted for biphenyl using B3LYP/6-31+g(d,p) and B3LYP/cc-pVTZ were found to be

TABLE 14

Molar thermodynamic properties for in the ideal gas state at  $p = p^{\circ} = 101.325 \text{ kPa}$  ( $R = 8.3144621 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ ).<sup>a</sup>

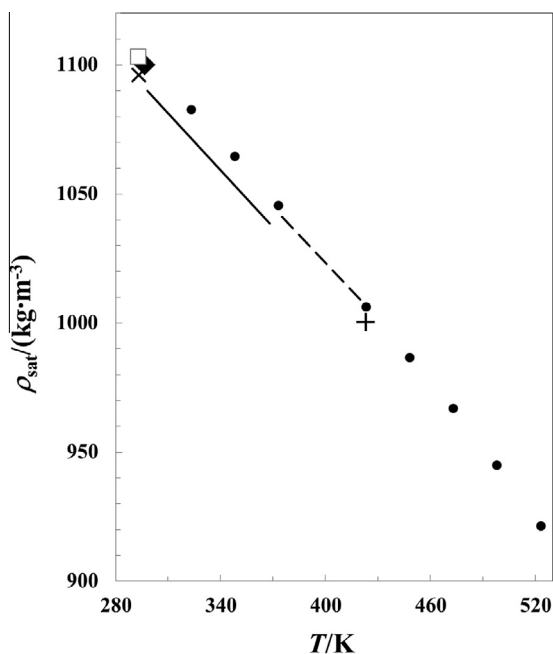
$T$ K	$\Delta_{\text{f}}^{\text{H}}H_{\text{m}}$ $RT$	$\Delta_{\text{imp}}H_{\text{m}}^{\text{b}}$ $RT$	$\Delta_{\text{f}}^{\text{S}}S_{\text{m}}^{\circ}$ $R$	$\Delta_{\text{imp}}S_{\text{m}}^{\text{c}}$ $R$	$\Delta_{\text{f}}H_{\text{m}}^{\circ}$ $RT$	$\Delta_{\text{f}}S_{\text{m}}^{\circ}$ $R$	$\Delta_{\text{f}}G_{\text{m}}^{\circ}$ $RT$
<i>1-Phenylnaphthalene</i>							
298.15 <sup>d</sup>	54.41 ± 0.20	0.00	54.81 ± 0.22	0.00	100.12 ± 0.64	-50.46 ± 0.22	150.59 ± 0.60
300.00 <sup>d</sup>	54.25 ± 0.20	0.00	54.97 ± 0.21	0.00	99.44 ± 0.62	-50.53 ± 0.22	149.97 ± 0.60
320.00	52.59 ± 0.16	0.00	56.76 ± 0.18	0.00	92.58 ± 0.58	-51.19 ± 0.18	143.78 ± 0.56
340.00	51.21 ± 0.14	0.00	58.53 ± 0.16	0.00	86.54 ± 0.54	-51.81 ± 0.16	138.35 ± 0.54
360.00	50.07 ± 0.14	0.00	60.29 ± 0.15	0.00	81.18 ± 0.50	-52.38 ± 0.14	133.56 ± 0.50
380.00	49.14 ± 0.12	0.00	62.03 ± 0.14	0.00	76.40 ± 0.48	-52.90 ± 0.14	129.30 ± 0.48
400.00	48.38 ± 0.10	0.00	63.77 ± 0.14	0.00	72.11 ± 0.46	-53.38 ± 0.14	125.49 ± 0.46
420.00	47.77 ± 0.10	0.00	65.51 ± 0.13	0.00	68.26 ± 0.44	-53.81 ± 0.14	122.07 ± 0.44
440.00	47.28 ± 0.10	0.01	67.23 ± 0.13	0.01	64.77 ± 0.42	-54.20 ± 0.14	118.97 ± 0.42
460.00	46.90 ± 0.10	0.01	68.94 ± 0.13	0.01	61.60 ± 0.40	-54.57 ± 0.12	116.16 ± 0.40
480.00	46.60 ± 0.08	0.02	70.63 ± 0.13	0.02	58.69 ± 0.38	-54.91 ± 0.14	113.61 ± 0.38
500.00	46.37 ± 0.08	0.04	72.30 ± 0.13	0.03	56.04 ± 0.36	-55.23 ± 0.14	111.27 ± 0.38
520.00	46.22 ± 0.10	0.05	73.96 ± 0.14	0.04	53.60 ± 0.36	-55.52 ± 0.14	109.12 ± 0.36
540.00	46.12 ± 0.12	0.08	75.61 ± 0.16	0.06	51.35 ± 0.34	-55.79 ± 0.16	107.14 ± 0.36
560.00	46.07 ± 0.16	0.11	77.24 ± 0.19	0.08	49.27 ± 0.34	-56.03 ± 0.18	105.30 ± 0.38
580.00	46.07 ± 0.18	0.15	78.85 ± 0.22	0.11	47.36 ± 0.36	-56.25 ± 0.22	103.61 ± 0.40
600.00	46.11 ± 0.22	0.20	80.46 ± 0.26	0.15	45.58 ± 0.38	-56.45 ± 0.26	102.03 ± 0.42
620.00	46.19 ± 0.26	0.27	82.05 ± 0.31	0.20	43.93 ± 0.40	-56.63 ± 0.30	100.56 ± 0.44
640.00 <sup>d</sup>	46.30 ± 0.32	0.34	83.63 ± 0.35	0.26	42.41 ± 0.42	-56.78 ± 0.36	99.19 ± 0.48
650.00 <sup>d</sup>	46.37 ± 0.34	0.38	84.42 ± 0.38	0.29	41.69 ± 0.44	-56.85 ± 0.38	98.54 ± 0.50
<i>2-Phenylnaphthalene</i>							
440.00 <sup>d</sup>	49.49 ± 0.10	0.00	67.01 ± 0.14	0.00	64.22 ± 0.82	-54.42 ± 0.14	118.64 ± 0.82
460.00 <sup>d</sup>	49.04 ± 0.10	0.01	68.75 ± 0.14	0.01	61.10 ± 0.78	-54.76 ± 0.14	115.86 ± 0.80
480.00 <sup>d</sup>	48.68 ± 0.10	0.01	70.48 ± 0.14	0.01	58.25 ± 0.76	-55.06 ± 0.14	113.32 ± 0.76
500.00	48.42 ± 0.10	0.02	72.19 ± 0.14	0.02	55.65 ± 0.72	-55.34 ± 0.14	110.99 ± 0.74
520.00	48.23 ± 0.10	0.04	73.89 ± 0.14	0.03	53.27 ± 0.70	-55.59 ± 0.14	108.86 ± 0.70
540.00	48.10 ± 0.12	0.05	75.58 ± 0.16	0.04	51.08 ± 0.68	-55.81 ± 0.16	106.89 ± 0.68
560.00	48.03 ± 0.14	0.08	77.26 ± 0.18	0.06	49.06 ± 0.66	-56.01 ± 0.18	105.07 ± 0.68
580.00	48.00 ± 0.18	0.11	78.92 ± 0.22	0.08	47.19 ± 0.64	-56.18 ± 0.22	103.38 ± 0.68
600.00	48.02 ± 0.22	0.15	80.57 ± 0.26	0.11	45.47 ± 0.64	-56.34 ± 0.26	101.81 ± 0.68
620.00 <sup>d</sup>	48.08 ± 0.26	0.20	82.21 ± 0.30	0.15	43.87 ± 0.64	-56.47 ± 0.30	100.34 ± 0.68
640.00 <sup>d</sup>	48.17 ± 0.30	0.25	83.83 ± 0.34	0.19	42.38 ± 0.64	-56.59 ± 0.34	98.97 ± 0.68
650.00 <sup>d</sup>	48.23 ± 0.32	0.29	84.64 ± 0.36	0.22	41.68 ± 0.64	-56.64 ± 0.36	98.32 ± 0.70

<sup>a</sup> Uncertainties are the combined expanded uncertainty at 0.95 level of confidence.

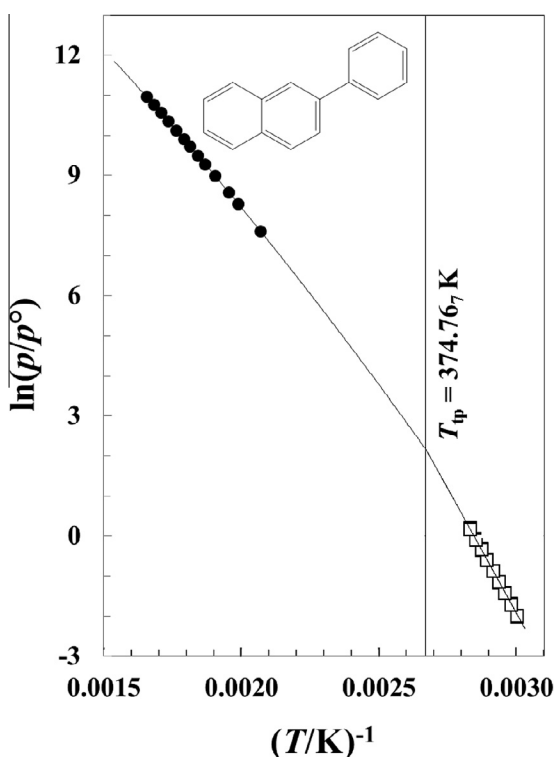
<sup>b</sup> Gas-imperfection correction included in the listed molar enthalpy for the ideal gas. The molar enthalpy of the gas is calculated relative to that of the crystals at  $T \rightarrow 0$ .

<sup>c</sup> Gas-imperfection correction included in the listed molar entropy of the ideal gas.

<sup>d</sup> Values at this temperature were calculated with extrapolated vapor pressures calculated from the fitted parameters (table 9) of the Wagner equation (equation (2)).



**FIGURE 3.** Experimental densities measured for the liquid phase of 1-phenylnaphthalene (1-PhN) and 2-phenylnaphthalene (2-PhN). 1-PhN: ●, this research (vibrating-tube densitometry); ◆, this research (filling of the calorimeter vessel); □, von Braun and Anton [60]; ×, Kutz *et al.* [72]; –, Binns and Squire [58]. 2-PhN: +, this research (filling of the calorimeter vessel); ---, Binns and Squire [58].



**FIGURE 4.** Plot of the natural logarithm of vapor or sublimation pressure  $\ln(p/p^o)$  against inverse temperature for 2-phenylnaphthalene, where  $p^o = 1$  Pa. ●, this research (table 8); □, Rocha *et al.* [59]. For  $T > T_{tp}$ , the curve represents the fitted equation of this research for (equation (2) and the parameters of table 9). The curve for sublimation pressures was calculated from the property measurements of this research, as described in the text.

within  $1 \text{ kJ} \cdot \text{mol}^{-1}$  of the highest-level *ab initio* calculations available in the literature to-date [82].

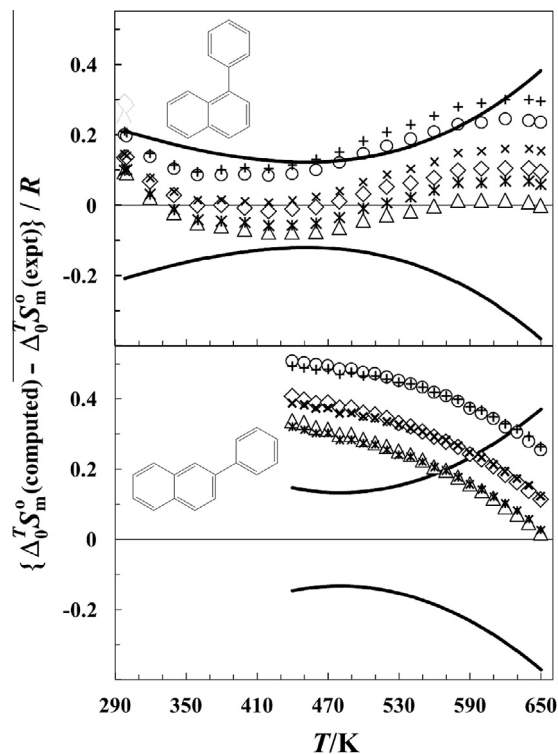
The calculated rotational potential for 2-PhN resembles closely that of biphenyl, as expected based on the structural similarities of the compounds. The potential curve has maxima in the planar and  $90^\circ$  configurations with the calculated barriers of  $(8.7$  ( $9.2$ ) and  $8.6$  ( $7.8$ ))  $\text{kJ} \cdot \text{mol}^{-1}$ , respectively. (The first value of the pair was calculated at the B3LYP/6-31+g(d,p) level, and the second, bracketed, value ( $9.2$  and  $7.8$ )  $\text{kJ} \cdot \text{mol}^{-1}$  at the B3LYP/cc-pVTZ level.) The equilibrium angle obtained is about  $40^\circ$  for both basis sets.

The nature of the phenyl rotation in 1-PhN is more complex. Like 2-PhN, it has a pronounced, but much lower, barrier at  $90^\circ$  of  $2.0$  ( $1.9$ )  $\text{kJ} \cdot \text{mol}^{-1}$ . However, the approach to the planar ( $0^\circ$ ) configuration cannot be rigorously treated as one-dimensional rotation, because strong steric interactions cause in-plane deformation, as shown previously with lower-level computational methods by Nori-Shargh *et al.* [83]. We calculated the transition state for this near-planar configuration to be  $\sim 50 \text{ kJ} \cdot \text{mol}^{-1}$  higher than those for the equilibrium structure, consistent with the results of Nori-Shargh *et al.* [83]. Because of such a high barrier at  $0^\circ$ , the property calculations for 1-PhN are not expected to be affected significantly by behavior near the planar configuration. The thermodynamic property calculations were performed with a one-dimensional hindered rotor model with the barrier and reduced rotational constant at  $0^\circ$  taken from the transition state configuration.

Differences between ideal gas entropies based on the scaled calculated frequencies  $\Delta_0^T S_m^o$  (computed) and those derived with the experimental measurements of this research  $\Delta_0^T S_m^o$  (expt) (table 14) are shown in figure 5. Comparisons were made with calculations at both the B3LYP/6-31+g(d,p) and cc-pVTZ levels. A range of scaling factors was used to demonstrate the sensitivity of the calculations to small changes in this factor. The B3LYP/6-31+g(d,p) level was used in our previous work on rigid nitrogen-containing aromatics [4–55], where a scaling factor of 0.975 was found to provide excellent agreement between  $\Delta_0^T S_m^o$  (computed) and  $\Delta_0^T S_m^o$  (expt) in all cases. Differences involving this particular combination of basis set and scaling factor are shown as open circles for both compounds in figure 5.

As seen in figure 5 (upper plot), agreement between  $\Delta_0^T S_m^o$  (expt) and  $\Delta_0^T S_m^o$  (computed) is excellent for 1-PhN for the various computed values. In contrast, the values of  $\Delta_0^T S_m^o$  (expt) for 2-PhN are seen to be significantly low relative to  $\Delta_0^T S_m^o$  (computed) (figure 5, lower plot), particularly for temperatures below  $T = 600$  K, where  $\Delta_0^T S_m^o$  (expt) should be most reliable. We conclude that some disorder is retained in the crystal of 2-PhN for temperatures below the crystal to glassy-crystal conversion near temperature  $T = 330$  K. A similar result was seen in our recent work on phenanthridine [6], which also exhibits a glass-like step in the heat-capacity curve for the solid phase. We plan to look at other compounds that show similar behavior in future work. The existence of disorder in the solid state of 2-PhN at room temperature may also account for the inability of Lima *et al.* [3] to obtain crystals suitable for X-ray diffraction.

In previous work [4–55,84], we established that for nitrogen-containing aromatic ring systems (pyridines, quinolines, benzoquinolines, *etc.*) the scale factor  $\{(0.975 \pm 0.005)$  with 0.95 level of confidence) in combination with calculations performed at the B3LYP/6-31+G(d,p) model chemistry can be applied for evaluation of derived thermodynamic properties with relative uncertainties near 0.1%. In the present work, we have extended this analysis to compounds involving phenyl-group rotations. The confidence that we have developed in the quality of the computed values of  $\Delta_0^T S_m^o$  for these systems has here allowed their application in interpretation of thermophysical property measurements for a glassy crystal. Application of these results for aromatic systems in engineering software, such as the NIST ThermoData Engine [8,9,85], can greatly improve upon prediction and correlation methods currently in place that are based on group-contributions.



**FIGURE 5.** Plots of differences between ideal-gas entropies  $\Delta_0^T S_m^0$  against temperature for 1-phenylnaphthalene (upper) and 2-phenylnaphthalene (lower) derived with computed vibrational frequencies and the methods described in the text  $\Delta_0^T S_m^0$  (computed) and those derived from the experimental thermodynamic property measurements  $\Delta_0^T S_m^0$  (expt).  $\Delta_0^T S_m^0$  (computed) was calculated with two different basis sets (with three scaling factors each) for both compounds.  $\circ$ ,  $\diamond$ ,  $\triangle$ , values computed with B3LYP/6-31+g(d,p) for scale factors 0.975, 0.978, and 0.980, respectively;  $+$ ,  $\times$ ,  $\star$ , values computed with B3LYP/cc-pVTZ for scale factors 0.970, 0.973, and 0.975, respectively. The continuous curved lines represent the expanded uncertainties for  $\Delta_0^T S_m^0$  (expt).

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jct.2014.01.006>.

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