Thermodynamic properties of 2-methylindole: experimental and computational results for gas-phase entropy and enthalpy of formation

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Abstract

Measurements leading to the calculation of thermodynamic properties in the ideal-gas state for 2-methylindole (Chemical Abstracts registry number [95-20-5]) are reported. Experimental methods were adiabatic heat-capacity calorimetry, differential scanning calorimetry (d.s.c.), comparative ebulliometry, inclined-piston manometry, and oxygen bomb calorimetry. The critical temperature of 2-methylindole was determined experimentally with d.s.c. Molar thermodynamic functions for the condensed and ideal-gas states were derived from the experimental results. Statistical calculations were performed based on molecular geometry optimization and vibrational frequencies using B3LYP hybrid density functional theory with the def2-TZVPPD basis set. Excellent accord between computed and experimentally-derived ideal-gas entropies is shown. The enthalpy of formation for 2-methylindole in the gas phase was computed with an atomization-based protocol described recently, and excellent agreement with the experimental values is seen. The experimental literature for enthalpies of formation in the gas phase for 1- and 2-ring pyrrollic compounds is reviewed, and comparisons with computed values further support the findings here. All experimental results are compared with property values reported in the literature, where possible.

Keywords: computational chemistry; critical temperature, enthalpy of formation; entropy; heat capacity; ideal-gas properties; 2-methylindole; vapor pressure

1. Introduction

This work is part of our continuing research [1-10] into quantification of uncertainties for thermodynamic properties derived with computational methods. In previous studies, the focus has been on entropies for the ideal-gas state. In the present work, comparison of experimental and computed enthalpies of formation for the ideal-gas state is also considered.

Entropies and enthalpies of formation for the ideal-gas state can be derived with structural information and computational methods, as well as through appropriate combination of experimentally determined properties. These methods are independent, and their study allows for mutual validation through analysis of observed differences. 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 [11]. As noted previously [3], the ability to derive ideal-gas properties solely from computational methods with reliable uncertainties would provide key values that are essentially unobtainable experimentally for many materials due to reasons such as high expense, high toxicity, or low stability.

This article describes thermodynamic property measurements for 2-methylindole (Chemical Abstracts registry number [95-20-5]). A summary of the experiments is provided in Table 1. Entropies for a wide range of temperatures ($298.15 \leq T/\mathrm{K} \leq 700$) and the enthalpy of formation at $T/\mathrm{K} = 298.15$ for the ideal-gas state are derived from the thermophysical property measurements. These are compared with values calculated independently with the methods of computational chemistry. This article follows our

recent work on a series of methyl-substituted pyrroles [10], where excellent accord between experimental and computed ideal-gas entropies was obtained. The present work provides a further test of the efficacy of computations for molecules containing a pyrrolic ring with the addition of the fused phenyl ring in 2-methylindole. This work also serves as a precursor to research on 3-ring carbazole systems.

2. Experimental

2.1 Materials

The sample of 2-methylindole used in this research was obtained by purification of a commercial product (Aldrich). Purification was carried out by the research group of Professor E. J. "Pete" Eisenbraun (retired) of Oklahoma State University. Commercial 2-methylindole (184 g) was passed through a column of basic alumina (3 cm wide by 5 cm long) contained in a Soxhlet apparatus using hexane as solvent under an argon atmosphere to yield a nearly colorless material. A deep red picrate was prepared by reaction of the nearly colorless 2-methylindole with 400 g picric acid in 2.9 l of hot methanol. The reaction mixture was cooled and filtered to yield 494 g of dark brown crystals. Four recrystallizations (2.0 l of hot methanol) gave 341 g of picrate with melting temperature T_m = (412 ± 2) K (0.95 level of confidence), determined visually. The picrate was cleaved in a Soxhlet extractor using basic and neutral alumina and diethylether. The product (65 g) was dried and sealed under vacuum.

The mole-fraction purity of the sample $x = 0.9995_4$ was determined in a fractional-melting study as part of the adiabatic calorimetric results reported here. Purification of the water and decane used as reference materials in the ebulliometric vapor-pressure

measurements has been described [12]. All transfers of samples were completed under nitrogen or helium or by vacuum distillation.

2.2. Physical constants and standards

The molar mass used for 2-methylindole was M = 131.178 g·mol^{-1} [13] based on the formula C_9H_9N and the gas constant R = 8.3144598 J·K^{-1}·mol^{-1} adopted by CODATA [14]. Platinum resistance thermometers 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). Temperatures were measured in terms of IPTS-68 [15] and were converted to ITS-90 with published temperature increments [16]. The thermometer used in the adiabatic heat-capacity study was calibrated below T/K = 13.81 with the method of McCrackin and Chang [17]. Mass, time, electrical resistance, and potential difference were measured in terms of standards traceable to calibrations at NIST.

2.3. Adiabatic calorimetry

Heat-capacities and enthalpy increments for the condensed phases of 2-methylindole were measured in the temperature range (11 < T/K < 437) with an adiabatic calorimetric system that has been described [18]. The enthalpy of melting and the triple point temperature T_{tp} were determined in these measurements. No solid-to-solid phase transitions were detected. Characteristics of the sample, the platinum sample container, and sealing conditions are given in Table 2. Energy increments to the filled 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 container. The

maximum sizes of these corrections are given in Table 2. The density ρ of 2-methylindole in the liquid state near atmospheric pressure at temperature T/K = (342 ± 1) (standard uncertainty) was determined with a standard uncertainty of ~1 percent as part of the sample loading process, based on the volume and mass of sample {ρ = (1020 ± 20) kg·m^{-3}; 0.95 level of confidence}.

2.4. Differential scanning calorimetry

Heat capacities at vapor-saturation pressure $C_{sat,m}$ for the liquid phase in the temperature range (355 < T/K < 735) were determined with a differential scanning calorimeter (d.s.c.). An intermittent heating method, first described by Mraw and Naas [19], was used with sequential measurements involving the sample, pure sapphire calibrant (high-purity reference material provided by Perkin Elmer), and the empty sample pan. Heat capacities of sapphire used for calibration were those critically evaluated by Archer [20]. A power-compensated d.s.c. was used (Perkin Elmer DSC II), and the method has been fully described [21,22].

The critical temperature of 2-methylindole was determined experimentally with the same d.s.c. The critical temperature T_c is determined as the maximum temperature of conversion from the two-phase (liquid + gas) to the one-phase (fluid) region for a series of filling densities of the hermetically sealed d.s.c. cells, where the phase change is indicated by a sudden decrease in heat capacity during heating. The method for determination of T_c has been described [21,22].

2.5. Comparative ebulliometry

The method for determination of vapor pressures with comparative ebulliometry has been described [23,24]. A sample of 2-methylindole was refluxed with standards of known vapor pressure (decane for $2 < p/\text{kPa} < 25$ and water $25 < p/\text{kPa} < 270$) under a common atmosphere of helium gas. Boiling and condensation temperatures of the sample and standard were determined, and the vapor pressure of 2-methylindole was derived from the condensation temperature of the standard. Vapor pressures for water were derived from the international equation of state for pure water [25], while the those for decane were calculated with equation 1 of reference 26. The standard uncertainty u for the temperature measurements in the ebulliometric studies was 0.002 K. Standard uncertainties in the pressures are described by:

$$u(p) = (0.002\ \text{K})\{(\mathrm{d}p_{\text{ref}}/\mathrm{d}T)^2 + (\mathrm{d}p_{\text{x}}/\mathrm{d}T)^2\}^{1/2}, \qquad (1)$$

where p_{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 $5 \cdot 10^{-4}$ K.

2.6. Inclined-piston manometry

Vapor pressures for 2-methylindole were measured with an inclined-piston apparatus described initially by Douslin and McCullough [27] and Douslin and Osborn [28]. Subsequent changes to the equipment and procedures were reported [12]. Standard uncertainties for the measured vapor pressures $u(p)$, based on estimated uncertainties in measuring the mass, area, and angle of inclination of the piston, are described by the expression:

$$u(p) = (1.5 \cdot 10^{-4}\, p + 0.2)\ \text{Pa}. \quad (2)$$

The standard uncertainties for the temperatures $u(T)$ are 0.002 K. Contributions of the temperature uncertainties to $u(p)$ are not significant.

2.7. Combustion Calorimetry

The experimental procedures used in the combustion calorimetry of organic nitrogen-containing compounds have been described [29,30]. A rotating-bomb calorimeter (laboratory designation BMR II) [31] and platinum-lined bomb (laboratory designation Pt-3b) [32] with an internal volume of 0.393_4 dm^3 were used without rotation. As the compound appeared to be hygroscopic, the calorimetric samples of 2-methylindole were compressed into pellets and heat-sealed in polyester bags in an argon atmosphere [32]. A volume of 1 cm^3 of water was added to the bomb in each experiment, and the bomb was charged to a pressure of 3.04 MPa with pure oxygen with flushing [29,30]. Sample and auxiliary masses were chosen to yield temperature rises in the combustion series and calibration series that agreed within 0.1 percent. Temperatures were measured by quartz-crystal thermometry [33,34], and all experiments were completed within 0.01 K of T = 298.15 K. The quartz-crystal thermometer was calibrated by comparison with a platinum resistance thermometer with a calibration traceable to NIST.

NIST Standard Reference Material benzoic acid (sample 39i) was used to calibrate the combustion calorimeter; its massic energy of combustion is -(26434.0 ± 3.0) $J \cdot g^{-1}$ under certificate conditions (0.95 level of confidence). Conversion to standard states [35] gives -(26413.7 ± 3.0) $J \cdot g^{-1}$ for $\Delta_c U^o/M$, the massic energy of the idealized combustion reaction. Calibration experiments with benzoic acid were interspersed with

the measurements on 2-methylindole. 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 of the calorimeter ε(calor), obtained with the calibration series, was (16769.2 ± 0.6) $J \cdot K^{-1}$ (mean and standard deviation of the mean). For the cotton fuse, empirical formula $CH_{1.774}O_{0.887}$, $\Delta_c U°/M$ was -16945 $J \cdot g^{-1}$. The value of $\Delta_c U°/M$ obtained for the polyester film (empirical formula $C_{10}H_8O_4$) was a function of the relative humidity (RH; expressed as a percentage) in the room during weighings [36].

$$\{(\Delta_c U°/M) / J \cdot g^{-1}\} = -22912.0 - 1.0560\ (RH) \qquad (3)$$

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 [35] included the density at T = 298.15 K of 1070 $kg \cdot m^{-3}$ for solid 2-methylindole and an estimated value of $1.05 \cdot 10^{-7}$ $m^3 \cdot K^{-1}$ for $(\partial V_m/\partial T)_p$. The crystal density was determined approximately {standard uncertainty ≈ 2 percent, including $u(T/K) \approx 1$} from the sample mass and dimensions of a freshly pressed pellet. The molar heat capacity at T = 298.15 K for 2-methylindole(cr) used in the corrections to standard states is that given later in this paper as part of the results of heat capacity measurements with adiabatic calorimetry.

Nitric acid formed during combustions of 2-methylindole was determined by titration with standardized sodium hydroxide [29,30]. Carbon dioxide was also recovered from the combustion products of each experiment, with anhydrous lithium hydroxide as the adsorbent for the CO_2 recoveries [37]. No products of incomplete combustion were detected. The carbon dioxide recovery percentage was

{(100.002 ± 0.005); mean and standard deviation of the mean} for the benzoic acid calibrations and (99.995 ± 0.004) for the combustions of 2-methylindole.

3. Experimental Results

3.1 Heat capacities and properties of melting determined with adiabatic calorimetry

Crystals of 2-methylindole were prepared by slow cooling (~1 $mK \cdot s^{-1}$) the sample to ~3 K below T_{tp}, where the sample crystallized. Slow cooling was continued to ~20 K below T_{tp}. Complete crystallization was achieved by reheating and maintaining the sample under adiabatic conditions in the partially melted state (~20 percent liquid) until ordering of the crystals was complete, as evidenced by the absence of spontaneous warming. The sample of 2-methylindole warmed slowly for approximately 4 h, following the initial partial melt. The sample was, then, cooled at an effective rate of 1 $mK \cdot s^{-1}$ to crystallize the remaining liquid. As a final step, the sample was thermally cycled from temperatures near T = 100 K to within 3 K of T_{tp}, where it was held for ~24 h to provide further tempering. No further spontaneous warming was observed. All measurement results for the solid-phase were performed on crystals pre-treated with this method. Excellent repeatability (within 0.02·percent of the mean) was observed for three determinations of $\Delta_{cr}^{l}H_m$, which is further evidence of complete crystallization.

The triple-point temperature T_{tp} and the mole fraction purity x 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]. Equilibrium temperatures in the partially-melted state were determined with temperatures at intervals of ~240 s for 1 h 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 estimated equilibrium values for F values listed in Table 3 and used in the determination of purity and T_{tp}. The fractional-melting study indicated the presence of solid-soluble impurities, and the method of Mastrangelo and Dornte [39] was used to derive the sample purity. Results are summarized in Table 3.

Results of measurements of molar enthalpy increments for 2-methylindole are given in Table 4. The table includes measurement results for the enthalpy of fusion and measurements in single-phase regions, which serve as checks of consistency against the integrated molar heat-capacity values. Corrections for pre-melting caused by impurities were made. Results with the same series number N in Tables 4 and 5 were taken in sequence without interruption of adiabatic conditions.

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 30 K below T_{tp}. Equilibration times increased to approximately 6 h within 7 K of T_{tp}. The behavior is common for organic compounds near T_{tp} in the solid state.

Molar heat capacities under vapor saturation pressure $C_{sat,m}$ determined by adiabatic calorimetry for 2-methylindole are listed in Table 5 and shown in Fig. 1. Values in Table 5 were corrected for the effects of sample vaporization into the gas space of the calorimeter, although the size of this correction is very small (Table 2). Pre-melting corrections were also applied. Due to the purity of the sample, these corrections were also small, with a maximum correction of ~$0.008 \cdot C_{sat}$ near T/K = 320 and falling rapidly to less than ~$0.001 \cdot C_{sat}$ near 300 K (~30 K below T_{tp}). Corrections for nonlinear variation of $C_{sat,m}$ with temperature were not necessary due to the size of the temperature increments used. The average heat capacities for a given temperature increment are

listed in Table 5, and uncertainties are given in a footnote to the table. Extrapolation of the heat-capacity results to $T \rightarrow 0$ K was made with a least-squares fit of the Debye heat-capacity equation [40] to results for temperatures $T < 18$ K. The derived Debye characteristic temperature θ for 2-methylindole was $\theta = 104.3$ K with a multiplier of 4.11.

3.2. Critical temperature determination with d.s.c.

Temperatures of conversion from the two-phase (liquid + vapor) to one-phase (fluid) region as a function of filling density determined with d.s.c. are listed in Table 6 and shown in Fig. 2. The filling densities span the region near the critical density, and the value of T_c corresponds to the maximum in the plot. Values shown as unfilled circles in Fig. 2 were obtained as part of a series of intermittent heats used to determine heat capacities, and values represented with filled circles were obtained specifically to determine the temperature of phase change by continuous heating of the sample at the rate of 0.17 $K \cdot s^{-1}$ (*i.e*, 10 K per minute) to minimize decomposition. The dashed curve is provided as an aide to the eye.

3.3. Vapor pressures, estimated densities, and derived enthalpies of vaporization

Experimental vapor pressures for 2-methylindole are reported in Table 7. The Wagner equation [41] in the following form was used to represent the vapor pressures:

$$\ln(p/p_c) = (1/T_r)\{A(1-T_r) + B(1-T_r)^{1.5} + C(1-T_r)^{2.5} + D(1-T_r)^{3.0}\}, \quad (4)$$

where T_c and p_c are the critical temperature and critical pressure, and $T_r = T/T_c$. This form (abbreviated "1.5/2.5/3.0", where the numbers represent the equation exponents) was chosen over the more common 1.5/2.5/5.0 form to provide optimum extrapolation

to lower temperatures, as discussed later in Section 4.4. The quality of the fit was also improved relative to that obtained with the 1.5/2.5/5.0 form, particularly at the low-temperature extreme of the data. The value of T_c used in the fit was that determined experimentally in this research. The critical pressure was selected in accord with Waring's criterion [22,42], with a minimum at $T/T_c = 0.85$ for the function $-R \cdot d(\ln p)/d(1/T)$. The fitted parameters and estimated critical constants are listed in Table 8. The range of applicability for the equation is from ~290 K to T_c, and unconstrained extrapolation to lower temperatures is not advised.

Densities for the liquid phase of 2-methylindole have been reported in the literature for a few discrete temperatures only. Sources are Von Auwers and Susemihl [43] (T = 353.2 K; ρ = 1031 kg·m^{-3}) and Yokoyama et al. [44] (T = 333.2 K; ρ = 1046 kg·m^{-3}), in addition to the approximate value obtained in this research as part of vessel loading for adiabatic calorimetry (T = 342 K; ρ = 1020 kg·m^{-3}).

Densities for the saturated liquid of 2-methylindole for the temperature range $\{298.15 \leq (T/K) \leq 700\}$ were estimated with the values from the literature [43,44] and the extended corresponding-states equation of Riedel [45], as formulated by Hales and Townsend [46]:

$$\rho/\rho_c = 1.0 + 0.85(1 - T_r) + (1.6916 + 0.9846\omega)(1 - T_r)^{1/3}, \quad (5)$$

where T_r is the reduced temperature T/T_c. The acentric factor ω was obtained from the vapor-pressure fit, and the critical density ρ_c (317 kg·m^{-3}) was estimated with equation (5) by minimizing deviations between the calculated and literature values. The literature values [43,44] are both within 0.05 percent of the correlation, while the value obtained

in this research is 1.9 percent low, in accord with the relatively large uncertainty for this value (U_r = 0.02 with 0.95 level of confidence).

Molar enthalpies of vaporization $\Delta_l^g H_m$ were calculated with the Clapeyron equation:

$$(dp/dT) = \Delta_l^g H_m / (T \cdot \Delta_l^g V_m), \quad (6)$$

where $\Delta_l^g V_m$ is the increase in molar volume from the liquid to the vapor. The Wagner-equation fit was used to calculate dp/dT, and vapor-phase volumes were estimated with the virial equation of state truncated at the third virial coefficient. Second and third virial coefficients were computed with corresponding-states correlations [47,48]. The efficacy of this approach has been shown many times [1-10]. More recent correlations for the virial coefficients have been published [See reference 49]. Significant differences with the correlations we have used [47,48] occur at low reduced temperatures (below T_r = 0.7) and have insignificant effect on the results of our calculations. Due to uncertainties in the model parameters for 2-methylindole (i.e., the critical parameters), as well as uncertainties in the model itself when applied to a pyrrolic 2-ring compound, we conservatively estimated the relative standard uncertainties for the virial coefficients to be 10 percent. These are the dominant contributions to the uncertainties in the derived enthalpies of vaporization for p > 0.1 MPa. Derived molar enthalpies of vaporization are listed in Table 9.

3.4. Heat capacities measured with d.s.c.

Two-phase (liquid + gas) heat capacities $C_{x,m}^{II}$ for 2-methylindole were measured with d.s.c for four cell fillings in the temperature range (355 < T/K < 735) and are given

in Table 10. Calculation of $C_{sat,m}$ values from the measured $C_{x,m}^{II}$ values has been described [21,22]. Vapor pressures required for this conversion were calculated with the Wagner equation {equation (4)} and densities for the liquid phase were calculated with equation (5). Parameters for equations (4) and (5) are given in Table 8. A polynomial was fit to the liquid-phase heat capacities derived from the d.s.c. results together with values of $C_{sat,m}$ determined with adiabatic calorimetry in this research for the temperature range 380 < (T/K) < 437, which were weighted heavily to ensure a smooth junction between the values determined with the two methods.

All measured $C_{x,m}^{II}$ values (Table 10) are shown in Fig. 3 together with $C_{sat,m}$ values measured with adiabatic calorimetry (Table 5), plus the curve of $C_{sat,m}$ against temperature T derived with the method described above. The effect of vaporization of the sample into the free space of the d.s.c. cell is readily seen in the figure, with the largest effect seen for the smallest sample mass.

3.5. Thermodynamic functions for the condensed states

Molar entropies and molar enthalpies under vapor saturation pressure for the condensed phases of 2-methylindole relative to that of the crystals at $T \rightarrow 0$ K are listed in Table 11. These were derived by integration of the smoothed molar heat capacities corrected for pre-melting, plus the molar entropy and enthalpy of melting. Pre-melting corrections were made with published methods [38] for solid-insoluble impurities and the mole-fraction purity $x_{pre} = 0.9998$. This purity value was selected to provide heat capacities for the crystals that are nearly linear with temperature within 50 K of T_{tp}, resulting in a value that is slightly higher than that determined in the fractional melting study (Table 3), due to some of the impurity being solid soluble.

3.6. Enthalpy of combustion and derived enthalpy of formation for the crystalline state

Table 12 lists results of a typical combustion experiment for 2-methylindole. Measured values of $\Delta_c U°/M$ for all seven combustion experiments are reported in Table 13, where these refer to the reaction:

$$C_9H_9N(cr) + 11.25\ O_2(g) = 9\ CO_2(g) + 4.5\ H_2O(l) + 0.5\ N_2(g). \quad (7)$$

The derived standard energy of combustion $\Delta_c U^o_m$, standard enthalpy of combustion $\Delta_c H^o_m$, and the standard enthalpy of formation $\Delta_f H^o_m$ for the crystal phase are listed in Table 13. Values of $\Delta_c U^o_m$ and $\Delta_c H^o_m$ refer to reaction (7), and the value of $\Delta_f H^o_m$ refers to the reaction:

$$9\ C(cr, graphite) + 4.5\ H_2(g) + 0.5\ N_2(g) = C_9H_9N(cr). \quad (8)$$

Uncertainties given in Table 13 are expressed as the "uncertainty interval" defined in reference [50]. This representation is equivalent to the expanded uncertainty with 0.95 level of confidence. The standard enthalpies of formation of $CO_2(g)$, and $H_2O(l)$ were those assigned by CODATA [51] { -(393.51 ± 0.13) kJ·mol^{-1} and -(285.830 ± 0.042) kJ·mol^{-1}, respectively}.

3.7. Thermodynamic functions in the ideal-gas state derived from experiment

Thermodynamic properties in the ideal-gas state ($p°$= 101.325 kPa) for 2-methylindole are listed in Table 14. Values were calculated with results given in Tables 9 and 11 and the enthalpy of formation at T = 298.15 K (Table 13). Enthalpies and entropies for $N_2(g)$ and equilibrium hydrogen were determined from the JANAF tables [52]. Values for graphite were determined with the polynomial [53] used to calculate the values from T = 298.15 K to T = 6000 K listed in the JANAF tables.

3.8. Computation of entropies for the ideal-gas state

Computational models used for generation of ideal-gas entropies were the same as used in our previous study involving pyrrole and methylpyrroles [10], so only a brief description is given here. Optimization of geometries and calculation of vibrational frequencies and methyl rotational potentials were performed using B3LYP hybrid density functional theory with the def2-TZVPPD basis set [54]. Methyl torsional barriers were evaluated at the DLPNO-CCSD(T)/def2-QZVP level of theory [55,56] using the B3LYP/def2-TZVPPD geometries. B3LYP/def2-TZVPPD calculations were made with the Gaussian 09 package [57]. DLPNO-CCSD(T) calculations for torsional barriers were carried out with Orca v3.0.3 [58]. The methyl torsion was treated as a three-fold one-dimensional hindered rotor, and the remaining vibrations were treated as harmonic oscillators with the frequencies scaled prior to entropy calculations using scaling factors optimized previously for pyrrole and methylpyrroles [10].

Computed molecular parameters are given in Table 15, where excellent agreement with the recent microwave measurements of Gurusinghe and Tubergen [59] is seen for rotational constants and the methyl barrier. Vibrational spectrum analysis for 2-methylindole was recently reported by Popoola [60] based on limited condensed-phase experimental data (above 550 cm^{-1}) and DFT (M06-L/6-311++G**) calculations. Our computational results are generally consistent with those reported by Popoola. A detailed comparison is not warranted.

The methyl torsional potential and corresponding reduced rotational constant are shown as a function of torsion angle in Fig. 4. The contribution of the methyl torsion

$\Delta_0^T S_m^o$(torsion) and the total computed ideal-gas entropy $\Delta_0^T S_m^o$(computed) are given in Table 16.

3.9. Computation of enthalpies of formation for the ideal-gas state

The enthalpies of formation were computed with an atomization-based protocol described recently by Paulechka and Kazakov [61]. The total energies were calculated at the DLPNO-CCSD(T)/def2-QZVP//RI-MP2/def-QZVP theory level using Orca 3.0.3 software [58], and the vibrational frequencies were computed at the B3LYP-D3(BJ)/def2-TZVP theory level and scaled by the factors of 0.96 for hydrogen stretches and 0.985 for all other modes, both for thermal correction and ZPVE. (This computational scheme is identified as "large" in reference 61.) In the enthalpy calculation, the torsional vibration of the methyl groups was treated as harmonic except for N-methylpyrrole, where free rotation was assumed.

4. Discussion

4.1. Comparisons with literature densities and properties of melting

As noted in section 3.3, only two values for the density of 2-methylindole in the liquid phase have been reported [43,44], and these were used in the present research with the Riedel equation {equation (5)} to estimate densities required to evaluate enthalpies of vaporization with the Clapeyron equation {equation (6)}. The values reported by von Auwers and Susemihl [43] and Yokoyama et al. [44] are in mutual accord, as noted earlier, and are consistent with with the approximate value determined in this research during loading of adiabatic calorimetric apparatus.

There are ~30 experimental melting temperatures T_m listed for 2-methylindole in SciFinder [62] with values ranging from T_m = 324 K to T_m = 334 K. These values were

determined primarily for compound identification and have uncertainties much larger than the uncertainty determined in the present work (T_{tp} = 331.966 ± 0.01 K). No previous determinations of the enthalpy of fusion were found in the literature.

4.2. Comparisons with literature vapor pressures

A sample of 2-methylindole was obtained from coal tar by Kruber [63], who determined the normal boiling temperature to be in the range 544.2 < (T/K) < 545.2, which is within ~2 K of the value measured in this research. Other determinations of vapor pressure for 2-methylindole reported in the literature are approximate values obtained at low pressures (*i.e.*, below ~2 kPa) as part of synthesis studies (cf. references 64-66). These values have large uncertainties and are, generally, within one order of magnitude of the vapor pressures evaluated here.

4.3. Comparison with literature enthalpy of combustion

The enthalpy of combustion for 2-methylindole in the crystalline state was determined previously by Ribeiro da Silva et al. [67]. Their value {$\Delta_c H^o_m$ = -(4865.7 ± 1.1) kJ·mol^{-1}} agrees well with that obtained here {$\Delta_c H^o_m$ = -(4864.8 ± 1.1) kJ·mol^{-1}}.

4.4 Comparison with literature enthalpies of sublimation

Ribeiro da Silva et al. [67] determined the enthalpy of sublimation at temperature *T* = 298.15 K for 2-methylindole {$\Delta^g_{cr} H_m$(298.15 K) = 88.7 ± 2.4 kJ·mol^{-1}} with a drop microcalorimetric technique, combined with an enthalpy for the gas phase $\Delta^{360.1\,K}_{298.15\,K} H^o_m(g)$ estimated with the group-contribution method of Stull et al. [68]. We recalculate their value to be (87.6 ± 2.4) kJ·mol^{-1} by including the enthalpy for the gas phase computed with the method described in section 3.8, rather than the very approximate group-contribution method. (The uncertainty of 2.4 kJ·mol^{-1} is that given

originally by Ribeiro da Silva et al. [67]. It is not clear if this value includes the contribution from the uncertainty in the estimated enthalpy for the gas.)

The enthalpy of sublimation is derived in the present work through the following relationship.

$$\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}(298.15\ \mathrm{K}) = \Delta_{298.15}^{331.966}H_{\mathrm{m}}(\mathrm{cr}) + \Delta_{\mathrm{cr}}^{\mathrm{l}}H_{\mathrm{m}}(T_{\mathrm{tp}}) + \Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}(T_{\mathrm{tp}}) + \Delta_{331.966}^{298.15}H_{\mathrm{m}}(\mathrm{g}) \qquad (9)$$

The enthalpy increment for the crystal (term 1 on the right-hand side of the equation) is given in Table 11, the enthalpy of fusion at temperature $T = T_{\mathrm{tp}}$ (term 2) is given in Table 4, the enthalpy of vaporization at $T = T_{\mathrm{tp}}$ (term 3) can be interpolated from values given in Table 9, and the computed enthalpy increment for the gas (term 4) can be interpolated from values in Table 16. The value of $\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}(298.15\ \mathrm{K})$ calculated with equation (9) is (86.0 ± 0.4) kJ·mol^{-1} (0.95 level of confidence), which is consistent with that recalculated here from the work of Ribeiro da Silva et al. [67] {(87.6 ± 2.4) kJ·mol^{-1}}.

4.5 Comparison of experimental and computed ideal-gas entropies

Entropies for the ideal-gas state of 2-methylindole obtained through combination of experimental results (described in section 3.7) $\Delta_0^T S_{\mathrm{m}}^{\mathrm{o}}(\mathrm{expt})$, are given in Table 14 (column 4), while values derived with computational chemistry (described in section 3.8) $\Delta_0^T S_{\mathrm{m}}^{\mathrm{o}}(\mathrm{computed})$ are given in Table 16 (column 3). Results of the two independent methods are in excellent agreement, as shown in Fig. 5 (see filled circles ●), with relative deviations well within 0.2 percent of $\Delta_0^T S_{\mathrm{m}}^{\mathrm{o}}(\mathrm{expt})$ over nearly the entire temperature range studied (298.15 < (T/K) < 700). Only near T = 700 K are deviations slightly greater, but still within the uncertainty for the experimental values.

A second curve in Fig. 5 {unfilled circles (○)} was calculated with values of $\Delta_0^T S_m^o$(expt) derived with enthalpies of vaporization based on a fit of the traditional 1.5/2.5/5.0 form of the Wagner equation {equation (4)} to the experimental vapor pressures (Table 7). Deviations represented by this curve exceed the experimental uncertainty at low temperatures. We ascribe this to the unconstrained extrapolation of the vapor-pressure fit for the 1.5/2.5/5.0 form. The dashed double-headed arrow in the Fig. 5 spans the temperature range of the measured vapor pressures. Extrapolation of the Wagner equation to low temperatures is sensitive to the value of the third exponent. In previous studies we have found cases where higher and lower values for the third exponent yield improved extrapolations over the traditional 1.5/2.5/5.0 form [5,8,69].

4.6 Comparison of experimental and computed ideal-gas enthalpies of formation

Enthalpies of formation in the ideal-gas state at the temperature T =298.15 K derived from experiment $\Delta_f H_m^o$(g, expt) are compared with values computed in this research $\Delta_f H_m^o$(g, computed) in Table 17. Values of $\Delta_f H_m^o$(g, expt) at T = 298.15 K were obtained through summation of the enthalpy of vaporization or sublimation $\Delta_{cr\ or\ l}^g H_m^o(298.15\ K)$, as appropriate, with the enthalpy of formation for the condensed phase $\Delta_f H_m^o$(cr or l) for each compound. Values and sources of experimental values leading to $\Delta_f H_m^o$(g, expt) are given in columns 2 and 3 of Table 17. In cases where multiple sources are available for $\Delta_f H_m^o$(cr or l) or $\Delta_{cr\ or\ l}^g H_m^o$, the weighted average was used in the sum to obtain a single value for the gas-phase enthalpy of formation $\Delta_f H_m^o$(g, expt) at T = 298.15 K.

As seen at the top of Table 17, agreement between experimental and computed values of $\Delta_f H_m^o$(g) for 2-methylindole are in excellent accord. In addition, the

experimental values of $\Delta_{cr}^{g}H_{m}^{o}(298.15\ K)$ and $\Delta_{f}H_{m}^{o}$(cr, 298.15 K) obtained in this research and by Ribeiro da Silva et al. [67] are also fully consistent. To provide additional support for the validity of these results, we assembled experimental literature for compounds containing pyrollic rings to derive additional values of $\Delta_{f}H_{m}^{o}$(g, expt) for comparison with values of $\Delta_{f}H_{m}^{o}$(g, computed). Computations were carried out as described in section 3.9. The following paragraph summarizes the origins of the experimental values.

Enthalpies of combustion were measured by Good [70] for indole, 2,3-dimethylindole, N-methylpyrrole, and 2,5-dimethylpyrrole, while Ribeiro da Silva et al. [67] reported values for N-methylindole and 3-methylindole, in addition to 2-methylindole, which was already discussed. Enthalpies of combustion for single compounds given in Table 17 were reported by Scott et al. [71] for pyrrole, Chirico and Kazakov [10] for 2,4-dimethylpyrrole, Santos and Ribeiro da Silva [72] for 1,2,5-trimethylpyrrole, and Verevkin et al. [73], who remeasured indole. Values of $\Delta_{cr\ or\ l}^{g}H_{m}^{o}(T = 298.15\ K)$ were derived from vapor-pressure or sublimation-pressure studies for pyrrole [71], N-methylpyrrole [74], 2,4-dimethylpyrrole [10], 2,5-dimethylpyrrole [10], indole [73,75], N-methylindole [73,76], and 2,3-dimethylindole [73]. Microcalorimetric methods were used for values reported for N-methylindole [67], 3-methylindole [67], and 1,2,5-trimethylpyrrole [72]. The microcalorimetric methods require knowledge of gas-phase enthalpies for adjustment of results to $T = 298.15$ K, and these values were computed here as described in section 3.8. The computed increments are ~10 percent larger than the values derived with a group-contribution scheme [68] in the original work.

The last column of Table 17 ("Δ") lists the differences between the experimental and computed enthalpies of formation for the ideal-gas phase. For the ten pyrrolic compounds considered, the standard deviation for the differences is 2.6 kJ·mol^{-1}, which drops to 1.2 kJ·mol^{-1} if the two largest outliers are not considered (3-methylindole, 5 kJ·mol^{-1}; 2,4-dimethylpyrrole, -5.5 kJ·mol^{-1}). If these inconsistencies were caused by problems in the computed results, the deviations would be expected to be of the same sign, and this is not observed. We speculate that the experimental uncertainties evaluated by the authors are too small, but it is not presently possible to identify as anomalous any of the contributions to $\Delta_f H_m^o$(g, expt) for either compound. Further analysis or experiment is needed to resolve the issue. The computations show only a slight bias relative to the experimental values, as the overall average deviation is -1.2 kJ·mol^{-1}. We conclude that the results are consistent with the uncertainty of 3 kJ·mol^{-1} (0.95 level of confidence) for $\Delta_f H_m^o$(g, computed), proposed by Paulechka and Kazakov [61].

5. Conclusions

In our work on a variety of aromatic ring systems [1-10], we have shown that calculations performed at the B3LYP/6-31+G (d,p) model chemistry with the scale factor (0.975 ± 0.005) can be applied for computation of entropies in the ideal-gas state with relative expanded uncertainties (0.95 level of confidence) near 0.2 percent. Most recently, we extended this type of analysis to a series of single-ring pyrrolic compounds (pyrrole, 1- methylpyrrole, 2,4-dimethylpyrrole, and 2,5-dimethylpyrrole) with excellent consistency shown between computations and experiment. In the present work, the two-ring pyrrolic compound 2-methylindole was studied, and excellent consistency between computation and experiment was obtained. Enthalpies of formation were also assessed,

with consistency between experiment and computation shown to be near the uncertainty limit of state-of-the-art experiments.

Future work will include extensions to larger pyrrolic molecules, such as carbazoles, as well as alkyl-substituted and partially saturated multi-ring hydrocarbons, where additional challenges related to low-frequency out-of-plane vibrational modes will need to be addressed. In this series [1-10], we use measurement results of high quality to aid in assessment of uncertainty quantification in computational thermodynamics. Practical application of these results in engineering software, such as the NIST ThermoData Engine (TDE) [11,77-84], can greatly improve upon group-contribution based prediction methods with poorly known uncertainties that remain in wide use today.

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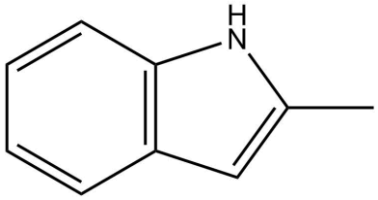
TABLE 1

Sample description and summary of experiments for 2-methylindole.[a]

Property	Method	Temperature Range/K
		
heat capacity triple point temperature (cr, l, g) enthalpy of melting (cr to l)	adiabatic calorimetry	11 to 437
heat capacity critical temperature	differential scanning calorimetry	355 to 735
vapor pressure	comparative ebulliometry inclined-piston manometry	427 to 595 340 to 430
density	pycnometric method	342
enthalpy of combustion	rotating-bomb calorimetry (without rotation)	298.15
sample purity [b]	fractional melting (mole fraction purity = 0.9995_4)	

[a] The sample of 2-methylindole used in all measurements was a commercial sample that was purified chemically through recrystallization of the picrate, following by cleaving in a Soxhlet extractor, as described in the text.

[b] Purity was determined by fractional melting, as described in the text.

TABLE 2

Calorimeter and sample characteristics for the adiabatic calorimetric measurements for 2-methylindole.[a]

m/g	53.306
V_i(298.15 K)/cm^3	62.47
T_{cal}/K	299.2
p_{cal}/kPa	6.16
$r(T_{max})$	3.8
r_{min}	2.0
$10^2 \cdot (\delta C/C)_{max}$	0.008
x_{pre}	0.0002

[a] m is the sample mass; V_i is the internal volume of the calorimeter vessel; T_{cal} is the temperature of the calorimeter when sealed; p_{cal} is the pressure of the helium and sample when sealed; $r(T_{max})$ is the ratio of the heat capacity of the full calorimeter to that of the empty at the highest temperature $T_{max} \approx 437$ K of these measurements; r_{min} is the minimum value of r observed in this study; $(\delta C/C)_{max}$ is the vaporization correction at the highest temperature measured (i.e., $T_{max} \approx 437$ K); and x_{pre} is the mole-fraction impurity used for pre-melting corrections, as described in section 3.5.

TABLE 3

Summary of fractional melt study for 2-methylindole.[a]

F	$T(F)$ / K
0.1395	331.833
0.2780	331.890
0.4628	331.917
0.6014	331.928
0.7400	331.935

$T_{tp} = (331.96_6 \pm 0.01)$ K [b]

$x = 0.9995_4$

$K = 0.045$ [c]

[a] F is the fraction melted at observed temperature T(F), T_{tp} is the triple-point temperature, and x is the derived purity expressed as mole fraction of the sample. The sample purity x is slightly less than that used in pre-melting corrections ($x_{pre} = 0.9998$), as described in section 3.5.

[b] The uncertainty is the expanded uncertainty with 0.95 level of confidence.

[c] K is the distribution coefficient for the impurity between solid and liquid phases, as defined in reference 39, where the mole fraction of impurity in the solid phase is in the numerator of the defining equation.

TABLE 4

Measurements of molar enthalpy increment $\Delta_{tot}H_m$ and derived results at vapor-saturation pressures for 2-methylindole.

N [a]	h [b]	T_i / K	T_f / K	T_{trs} / K	$\Delta_{tot}H_m$ [c] / kJ·mol^{-1}	$\Delta_{trs}H_m$ [d] / kJ·mol^{-1}
			single-phase measurements in phase cr			
6	1	54.852	151.998	---	6.760	0.002
6	1	152.139	245.453		11.144	0.000
6	1	245.401	305.732		9.791	0.003
6	1	305.666	325.572		3.713	0.000
			cr-to-liquid phase transition			
3	4	325.408	337.527	331.966	17.465	14.846
4	7	324.489	333.565		16.680	14.840
6	2	325.569	334.814		16.773	14.840
					average	14.842
			single-phase measurements in the liquid phase			
8	1	344.255	417.191	---	19.036	-0.002
8	1	417.149	437.284		5.637	-0.001

[a] Adiabatic series number.

[b] Number of heating increments.

[c] $\Delta_{tot}H_m$ is the molar enthalpy from the initial temperature T_i to the final temperature T_f. The relative expanded uncertainty (0.95 level of confidence) for $\Delta_{tot}H_m$ is 0.002, and the expanded uncertainty for all temperatures $U(T/\mathrm{K})$ is 0.01 K.

[d] $\Delta_{trs}H_m$ is the net molar enthalpy of transition at the transition temperature T_{trs} or the excess enthalpy for single-phase measurements relative to the heat-capacity curve described in the text and defined later in Table 11. The expanded uncertainty (0.95 level of confidence) for $\Delta_{trs}H_m$ for the cr-to-liquid phase transition (*i.e.*, the enthalpy of fusion) is 0.03 kJ·mol^{-1}.

TABLE 5

Molar heat capacities $C_{sat,m}$ at vapor-saturation pressure measured with adiabatic calorimetry for 2-methylindole (R = 8.3144598 J·K^{-1}·mol^{-1}).[a]

N [b]	<T>/K	ΔT/K	$C_{sat,m}/R$ [c]	N [b]	<T>/K	ΔT/K	$C_{sat,m}/R$ [c]
			cr				
5	11.266	1.127	0.388	1	134.713	10.038	10.331
5	12.408	1.130	0.500	1	144.774	10.080	10.946
5	13.641	1.329	0.636	1	154.903	10.141	11.569
5	15.084	1.545	0.808	1	165.052	10.114	12.203
5	16.682	1.644	1.006	1	175.190	10.158	12.834
5	18.459	1.898	1.234	1	185.364	10.187	13.477
5	20.492	2.159	1.489	1	195.556	10.197	14.131
5	22.773	2.392	1.782	1	205.761	10.216	14.789
5	25.304	2.662	2.098	1	215.961	10.192	15.454
5	27.770	2.262	2.399	1	226.137	10.173	16.130
5	30.588	3.383	2.723	1	236.278	10.164	16.803
5	34.095	3.647	3.117	1	246.379	10.182	17.482
5	37.854	3.872	3.517	1	256.593	10.271	18.180
5	41.965	4.350	3.923	1	266.918	10.408	18.885
5	46.597	4.908	4.362	2	276.466	10.627	19.548
5	51.651	5.200	4.802	1	277.407	10.607	19.610
1	53.690	5.215	4.977	2	287.091	10.584	20.334
5	57.120	5.736	5.252	1	288.080	10.788	20.393
1	59.066	5.492	5.412	2	297.661	10.561	21.079
1	64.851	6.044	5.856	1	298.876	10.859	21.179
1	71.317	6.855	6.327	3	302.772	8.985	21.462
1	78.489	7.471	6.825	4	304.062	7.962	21.544
1	86.426	8.312	7.351	2	308.051	10.318	21.842
1	95.280	9.239	7.916	1	309.629	10.709	21.968

1	104.887	9.752	8.512	3	311.788	8.995	22.143
1	114.731	9.910	9.114	4	312.143	8.024	22.172
1	124.690	9.997	9.718	4	320.336	8.223	22.801
			liquid				
4	337.631	8.150	29.128	7	374.856	12.734	31.110
6	338.881	8.147	29.199	7	387.502	12.564	31.765
3	341.574	8.111	29.348	7	399.884	12.410	32.372
3	349.893	8.547	29.788	7	412.602	13.078	32.997
7	350.315	10.473	29.815	7	425.577	12.925	33.601
7	362.025	12.916	30.445	7	436.983	9.978	34.124

---

[a] The relative expanded uncertainties (0.95 level of confidence) for the heat capacities are $U_r(C_{sat,m}) = (0.0140 - 0.0004 \cdot T)$ for the temperature range $\{10 \leq (T/\mathrm{K}) \leq 30\}$, and 0.002 for temperatures $T \geq 30$ K. The expanded uncertainty for all temperatures $U(T/\mathrm{K})$ is 0.01 K.

[b] Adiabatic series number.

[c] Average heat capacity for a temperature increment ΔT with mean temperature $<T>$.

TABLE 6

Measured temperatures T for densities ρ_{sat} determined with d.s.c. and used to define the two-phase (gas + liquid) coexistence curve near $T = T_c$ for 2-methylindole.

ρ_{sat} / (kg·m^{-3})	T / K
176.5	788.8 [b]
183.3	803.0
238.4	807.0 [b]
264.7	809.2
268.7	809.6 [b]
299.5	809.6
360.9	803.6 [b]
399.3	802.9
433.9	800.7
470.4	795.1

[a] Expanded uncertainties (0.95 level of confidence) are $U(\rho) = 0.05 \cdot \rho_{sat}$ and $U(T) = 2$ K.

[b] These values were obtained as part of a series of intermittent heats used to determine two-phase (liquid + gas) heat capacities (Table 10). All other values were determined in continuous temperature scans, as described in the text.

TABLE 7

Measured vapor pressures for 2-methylindole.[a]

Method	T/K	p/kPa	Δp/kPa	$U(p)$/kPa
IP	339.988	0.0220	-0.0001	0.0004
IP	339.984	0.0220	-0.0001	0.0004
IP	349.983	0.0439	-0.0004	0.0004
IP	359.977	0.0849	-0.0002	0.0004
IP	369.978	0.1565	0.0000	0.0004
IP	369.978	0.1564	-0.0001	0.0004
IP	379.976	0.2769	-0.0001	0.0004
IP	389.975	0.4731	-0.0001	0.0006
IP	399.971	0.7822	0.0000	0.0006
IP	409.974	1.2551	-0.0002	0.0008
IP	419.965	1.9581	-0.0003	0.0010
IP	424.964	2.4229	-0.0002	0.0012
IP	424.968	2.4230	-0.0004	0.0012
decane	427.254	2.6660	0.0003	0.0006
IP	429.959	2.9790	0.0000	0.0014
decane	437.341	3.9999	0.0005	0.0010
decane	444.867	5.333	0.000	0.001
decane	456.037	7.999	0.000	0.002
decane	464.405	10.666	0.000	0.002
decane	471.162	13.332	0.000	0.003
decane	478.174	16.665	0.000	0.003
decane	483.994	19.933	0.000	0.004
decane	491.648	25.023	0.001	0.004
water	491.648	25.023	0.001	0.005
water	499.348	31.177	-0.003	0.006
water	507.085	38.565	-0.003	0.008
water	514.864	47.375	-0.003	0.009
water	522.684	57.817	-0.003	0.011
water	530.546	70.120	0.001	0.013
water	538.453	84.533	0.000	0.015
water	546.400	101.325	0.004	0.017
water	554.392	120.79	0.00	0.02
water	562.426	143.25	0.01	0.02
water	570.499	169.02	0.01	0.03
water	578.617	198.49	0.01	0.03
water	586.773	232.02	0.00	0.03
water	594.972	270.02	-0.03	0.04

[a] IP indicates results obtained with inclined-piston manometry. 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; Δp is the difference between the experimental vapor pressure and that calculated with equation (4) and the parameters listed in Table 8; $U(p)$ is the expanded uncertainty (0.95 level of confidence) calculated from equations (1) and (2). The expanded uncertainty for all temperatures $U(T/\mathrm{K})$ is 0.004 K (0.95 level of confidence).

TABLE 8

Parameters for the Wagner vapor-pressure equation {equation (4)}, Riedel density equation {equation (5)}, selected critical constants, and derived acentric factor ω.[a]

A	-8.097003	T_c/K = (810 ± 2)
B	0.356952	p_c/kPa = 4550
C	7.075935	ρ_c/kg·m^{-3} = 317
D	-12.336966	ω = 0.4609

[a] The critical temperature T_c was determined experimentally in this research with 0.95 level of confidence. The critical pressure p_c and critical density ρ_c were estimated, as described in the text. The estimated value of p_c is closely correlated with the value of T_c. The expanded uncertainty $U(T_c)$ = 2 K corresponds to $U(p_c) \approx 0.02\ p_c$ (0.95 level of confidence). The relative expanded uncertainty for ρ_c is $U_r(\rho_c) \approx 0.1$ (0.95 level of confidence).

TABLE 9

Derived enthalpies of vaporization $\Delta_l^g H_m$ for 2-methylindole.[a]

T/K	$\Delta_l^g H_m$/(kJ·mol^{-1})	T/K	$\Delta_l^g H_m$/(kJ·mol^{-1})	T/K	$\Delta_l^g H_m$/(kJ·mol^{-1})
298.15 [b]	72.72 ± 0.37	440.00	61.69 ± 0.22	600.00 [b]	48.71 ± 0.80
300.00 [b]	72.57 ± 0.35	460.00	60.16 ± 0.22	620.00 [b]	46.86 ± 0.96
320.00 [b]	71.01 ± 0.33	480.00	58.62 ± 0.22	640.00 [b]	44.91 ± 1.18
340.00	69.44 ± 0.30	500.00	57.06 ± 0.25	660.00 [b]	42.83 ± 1.41
360.00	67.88 ± 0.28	520.00	55.47 ± 0.32	680.00 [b]	40.58 ± 1.66
380.00	66.32 ± 0.27	540.00	53.86 ± 0.38	700.00 [b]	38.14 ± 1.95
400.00	64.77 ± 0.25	560.00	52.21 ± 0.50		
420.00	63.22 ± 0.23	580.00	50.49 ± 0.63		

[a] Uncertainties for $\Delta_l^g H_m$ are expanded uncertainties with 0.95 level of confidence.

[b] The value at this temperature was calculated with extrapolated vapor pressures.

TABLE 10

Measured two phase (liquid + vapor) heat capacities for 2-methylindole (R = 8.3144598 J.K^{-1}.mol^{-1}).[a]

T/K	$C^{\mathrm{II}}_{\mathrm{x,m}}/R$	$C^{\mathrm{II}}_{\mathrm{x,m}}/R$	$C^{\mathrm{II}}_{\mathrm{x,m}}/R$	$C^{\mathrm{II}}_{\mathrm{x,m}}/R$
m/g	0.009526	0.020098	0.014971	0.01269
V_{cell}/cm^3	0.0547	0.0547	0.0547	0.0547
355.00	30.03	30.01	29.98	30.09
375.00	31.20	31.15	30.96	30.84
395.00	32.17	32.10	32.00	32.00
415.00	33.14	33.18	33.11	33.12
435.00	34.45		34.01	34.21
455.00	35.36	34.98	34.46	35.25
475.00	36.38	35.82	35.91	36.24
495.00	37.77	36.89	37.19	36.96
515.00	38.92		38.12	38.00
535.00	40.01	38.56	39.17	39.24
555.00	41.18	39.88	40.22	40.38
575.00	42.63	40.55	40.98	41.68
595.00	43.64	41.84	42.33	42.52
615.00	45.52	42.40	43.06	43.63
635.00	47.12	43.14	44.47	45.20
655.00	48.62	44.33	45.83	46.51
675.00	50.49	44.84	47.24	47.51
695.00	52.04	45.71	48.02	48.78
715.00	54.98	46.77	48.82	50.76
735.00		47.83	50.57	51.99

[a] m is the mass of the sample, V_{cell} is the internal volume of the dsc cell at T = 298.15 K after sealing.

[b] The relative expanded uncertainty U_{r} for $C^{\mathrm{II}}_{\mathrm{x,m}}$ is 0.02 with 0.95 level of confidence. The expanded uncertainty for all temperatures $U(T/\mathrm{K})$ is 0.2 K.

TABLE 11

Molar thermodynamic functions at vapor-saturation pressure for 2-methylindole (R = 8.3144598 J·K^{-1}·mol^{-1}).[a]

T / K	$C_{sat,m}/R$	$\Delta_0^T S_m/R$	$\Delta_0^T H_m/RT$	T / K	$C_{sat,m}/R$	$\Delta_0^T S_m/R$	$\Delta_0^T H_m/RT$
			cr				
10.00 [b]	0.278	0.094	0.070	160.00	11.887	12.324	6.457
20.00	1.428	0.613	0.443	180.00	13.137	13.796	7.130
30.00	2.657	1.429	0.980	200.00	14.417	15.246	7.794
40.00	3.732	2.345	1.537	220.00	15.722	16.681	8.455
50.00	4.660	3.279	2.071	240.00	17.052	18.106	9.116
60.00	5.486	4.203	2.572	260.00	18.412	19.524	9.779
70.00	6.233	5.106	3.043	280.00	19.809	20.939	10.445
80.00	6.927	5.984	3.485	298.15	21.114	22.224	11.055
90.00	7.581	6.838	3.904	300.00	21.247	22.355	11.117
100.00	8.211	7.669	4.304	320.00	22.776	23.775	11.798
120.00	9.434	9.275	5.057	331.96$_6$ [b]	23.726	24.628	12.210
140.00	10.654	10.821	5.770				
			liquid				
298.15 [b]	27.010	27.008	16.416	500.00	36.926	43.432	22.787
300.00 [b]	27.110	27.175	16.481	520.00	37.758	44.897	23.347
320.00 [b]	28.187	28.959	17.179	540.00	38.566	46.337	23.895
331.96$_6$ [b]	28.829	30.006	17.588	560.00	39.348	47.754	24.433
340.00	29.263	30.700	17.858	580.00	40.106	49.148	24.961
360.00	30.335	32.403	18.522	600.00	40.839	50.520	25.478
380.00	31.379	34.071	19.171	620.00	41.548	51.871	25.985
400.00	32.380	35.706	19.807	640.00	42.242	53.201	26.482
420.00	33.344	37.310	20.429	660.00	42.930	54.511	26.970
440.00	34.267	38.882	21.037	680.00	43.632	55.803	27.450

460.00	35.186	40.426	21.632	700.00	44.382	57.078	27.923
480.00	36.069	41.942	22.215				

[a] Relative expanded uncertainties (0.95 level of confidence) U_r for all properties Θ for temperatures T/K < 450 are $U_r(\Theta) = (0.0140 - 0.0004 \cdot T)$ for the temperature range $\{10 \leq (T/\mathrm{K}) \leq 30\}$, and 0.002 for temperatures $T \geq 30$ K. The expanded uncertainty for all temperatures $U(T/\mathrm{K})$ is 0.01 K. For temperatures T/K > 450, U_r for the heat capacities increases approximately linearly from 0.002 to 0.02 at T/K = 700, while U_r for the integrated functions increases from 0.002 to 0.003.

[b] Values at this temperature were calculated with extrapolated heat capacities.

TABLE 12

Details of a typical combustion experiment at T = 298.15 K ($p°$ = 101.325 kPa) for 2-methylindole.[a]

m'(compound) / g	0.882620
m''(polyester) / g	0.066859
m'''(fuse) / g	0.002302
$n_i(H_2O)$ / mol	0.05535
m(Pt) / g	19.926
ΔT / K = ($T_i - T_f + \Delta T_{corr}$) / K	2.04585
ε(calor)(ΔT) / J	-34307.3
ε(cont)(ΔT) / J	-38.4
ΔU_{ign} / J	0.75
$\Delta U_{dec}(HNO_3)$ / J	56.9
ΔU(corrected to standard states)[b] / J	19.6
$-m''$ ($\Delta_c U^o_m/M$) (polyester) / J	1529.3
$-m'''$ ($\Delta_c U^o_m/M$) (fuse) / J	39.0
m'($\Delta_c U^o_m/M$) (compound) / J	-32700.1
($\Delta_c U^o_m/M$) (compound) / (J·g^{-1})	-37048.9

[a] m'(compound) is the mass of the studied compound adjusted to vacuum conditions; m''(polyester) and m'''(fuse) are the masses of the auxiliary compound (polyester film and cotton fuse, respectively) adjusted to vacuum conditions; $n_i(H_2O)$ is the amount of water added to the calorimetric bomb prior to the experiment; m(Pt) is the mass of the platinum crucible; ΔT is the corrected temperature rise in the experiment; T_i and T_f are the initial and final temperatures in the main period; ΔT_{corr} is the heat-exchange correction; ε_{calor} is the energy equivalent of the calorimeter; ε(cont)(ΔT) = ε_i(cont)(T_i - 298.15 K) + ε_f(cont)(298.15 K - T_f + ΔT_{corr}); ε_i(cont) and ε_f(cont) are the energy equivalent of the contents of the bomb in the initial and final states, respectively; ΔU_{ign} is the energy for igniting the sample; ΔU_{dec}(HNO3) is the energy required for decomposition of the HNO_3 solution formed; ΔU(corrected to standard states) is the energy correction to the standard state; $\Delta_c U^o_m/M$ is the specific combustion energy of a compound. Symbols and abbreviations in this table are in accord with those of reference 35.

[b] Items 81 to 85, 87 to 90, 93, and 94 of the computational form of reference 35.

TABLE 13

Summary of experimental energy of combustion results and molar thermodynamic functions at T = 298.15 K and $p°$ =101.325 kPa

$\{(\Delta_c U^\circ/M)$(2-methylindole, cr)$\}$ / (J·g^{-1})						
-37048.9	-37066.0	-37056.6	-37049.2	-37045.0	-37058.0	-37040.6

$<\{(\Delta_c U^o_m/M)$(2-methylindole, cr)$\}$ / (J·g^{-1})>	-37052.0 ± 3.3 [b]
$\Delta_c U^o_m$(2-methylindole, cr) / (kJ·mol^{-1})	-4860.41 ± 1.08 [b]
$\Delta_c H^o_m$ (2-methylindole, cr) / (kJ·mol^{-1})	-4864.75 ± 1.08 [b]
$\Delta_f H^o_m$ (2-methylindole, cr) / (kJ·mol^{-1})	36.93 ± 2.60 [c]

[a] Uncertainties for all molar values are the "uncertainty interval" as defined in reference 50. These values are equivalent to the combined expanded uncertainty with 95 percent level of confidence. The uncertainty listed for the specific energy of combustion is the standard deviation of the mean.

[b] Value for the idealized combustion reaction:

$$C_9H_9N(cr) + 11.25\ O_2(g) = 9\ CO_2(g) + 4.5\ H_2O(l) + 0.5\ N_2(g).$$

[c] Value for the formation reaction:

$$9\ C(cr, graphite) + 4.5\ H_2(g) + 0.5\ N_2(g) = C_9H_9N(cr).$$

TABLE 14

Molar thermodynamic properties of the ideal gas state at $p = p° = 101.325$ kPa for 2-methylindole. ($R = 8.3144598$ J·K^{-1}·mol^{-1}) [a]

T / K	$\Delta_0^T H_m^o / RT$	$\Delta_{imp} H_m$ [b] $/ RT$	$\Delta_0^T S_m^o / R$	$\Delta_{imp} S_m$ [c] $/ R$	$\Delta_f H_m^o / RT$	$\Delta_f S_m^o / R$	$\Delta_f G_m^o / RT$
298.15 [d]	45.75 ± 0.16	0.00	44.38 ± 0.16	0.00	49.59 ± 1.06	-44.02 ± 0.16	93.61 ± 1.06
300.00 [d]	45.57 ± 0.14	0.00	44.49 ± 0.16	0.00	49.23 ± 1.06	-44.08 ± 0.16	93.31 ± 1.04
320.00 [d]	43.87 ± 0.12	0.00	45.66 ± 0.14	0.00	45.61 ± 0.98	-44.64 ± 0.14	90.25 ± 0.98
340.00	42.42 ± 0.12	0.00	46.83 ± 0.12	0.00	42.42 ± 0.92	-45.16 ± 0.12	87.58 ± 0.92
360.00	41.20 ± 0.10	0.00	48.00 ± 0.12	0.00	39.61 ± 0.88	-45.63 ± 0.12	85.24 ± 0.88
380.00	40.16 ± 0.10	0.00	49.16 ± 0.10	0.00	37.11 ± 0.82	-46.05 ± 0.10	83.16 ± 0.82
400.00	39.29 ± 0.08	0.01	50.32 ± 0.10	0.00	34.89 ± 0.78	-46.43 ± 0.10	81.32 ± 0.78
420.00	38.54 ± 0.08	0.01	51.48 ± 0.10	0.01	32.89 ± 0.74	-46.77 ± 0.10	79.66 ± 0.74
440.00	37.92 ± 0.08	0.02	52.63 ± 0.10	0.01	31.10 ± 0.72	-47.08 ± 0.10	78.18 ± 0.72
460.00	37.39 ± 0.08	0.03	53.78 ± 0.10	0.02	29.48 ± 0.68	-47.35 ± 0.10	76.83 ± 0.68
480.00	36.95 ± 0.08	0.04	54.91 ± 0.10	0.03	28.01 ± 0.66	-47.60 ± 0.10	75.61 ± 0.66
500.00	36.58 ± 0.08	0.06	56.04 ± 0.10	0.05	26.67 ± 0.62	-47.82 ± 0.10	74.49 ± 0.64
520.00	36.27 ± 0.08	0.09	57.17 ± 0.12	0.07	25.45 ± 0.60	-48.02 ± 0.12	73.47 ± 0.60
540.00	36.02 ± 0.10	0.13	58.28 ± 0.12	0.09	24.33 ± 0.58	-48.20 ± 0.12	72.53 ± 0.58
560.00	35.82 ± 0.12	0.17	59.39 ± 0.14	0.13	23.30 ± 0.58	-48.36 ± 0.14	71.66 ± 0.56
580.00	35.66 ± 0.16	0.23	60.48 ± 0.18	0.17	22.36 ± 0.56	-48.50 ± 0.18	70.86 ± 0.56
600.00 [d]	35.53 ± 0.18	0.29	61.57 ± 0.20	0.21	21.49 ± 0.56	-48.62 ± 0.20	70.11 ± 0.54
620.00 [d]	35.44 ± 0.22	0.37	62.65 ± 0.24	0.27	20.68 ± 0.56	-48.73 ± 0.24	69.41 ± 0.54
640.00 [d]	35.38 ± 0.26	0.46	63.71 ± 0.28	0.34	19.94 ± 0.56	-48.83 ± 0.28	68.76 ± 0.54
660.00 [d]	35.33 ± 0.32	0.56	64.76 ± 0.32	0.42	19.24 ± 0.56	-48.91 ± 0.32	68.16 ± 0.54
680.00 [d]	35.30 ± 0.36	0.67	65.79 ± 0.36	0.50	18.59 ± 0.58	-48.99 ± 0.36	67.58 ± 0.54
700.00 [d]	35.28 ± 0.42	0.81	66.81 ± 0.42	0.60	17.97 ± 0.60	-49.07 ± 0.42	67.04 ± 0.54

[a] Uncertainties given in the table are expanded uncertainties at 0.95 level of confidence.

[b] Gas-imperfection correction that has been 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 $T \rightarrow 0$.

[c] Gas-imperfection correction that has been included in the listed molar entropy of the ideal gas. $\Delta_0^T S_m^o(\text{ideal gas}) = \Delta_0^T S_m^o(\text{real gas}) + \Delta_{imp} S_m$.

[d] Values at this temperature were calculated with extrapolated vapor pressures calculated from the fitted parameters (Table 8) of the Wagner equation {equation (4)}.

TABLE 15

Molecular properties of 2-methylindole.[a]

	rotational constants (GHz)	
	computed [b]	experimental [c]
A	3.821	3.791
B	0.993	0.990
C	0.792	0.789

methyl torsion barrier (kJ·mol^{-1})	
computed [b]	experimental [c]
4.28	4.48
4.52[d]	

computed (unscaled) vibrational frequencies (cm^{-1})[b,e]

119.9[f]	135.4	247.8	255.4	307.9	394.7	440.1	458.8	497.4
590.3	621.4	640.2	668.1	750.4	769.9	807.3	830.6	866.5
903.9	949.3	990.3	993.8	1013.5	1037.3	1065.4	1137.3	1165.6
1177.6	1231.5	1258.7	1303.0	1367.2	1373.2	1422.6	1435.1	1482.3
1483.3	1499.4	1526.2	1593.3	1627.0	1658.5	3017.5	3057.6	3120.7
3164.2	3170.0	3180.7	3192.5	3238.9	3665.7			

[a] All computed results were obtained at the B3LYP/def2-TZVPPD level, unless otherwise specified.

[b] This work.

[c] From the microwave study by Gurusinghe and Tubergen [59].

[d] Calculated at the DLPNO-CCSD(T)/def2-QZVP//B3LYP/def2-TZVPPD level.

[e] Scaling factors used in entropy calculations were 0.955 for hydrogen stretches and 0.9719 for all others [10].

[f] Methyl torsion, treated as a one-dimensional hindered rotor in the entropy calculations.

TABLE 16

Computed molar thermodynamic properties for 2-methylindole in the ideal gas state at $p = p^\circ = 101.325$ kPa ($R = 8.3144598$ J·K^{-1}·mol^{-1}).[a]

T/K	$\Delta_0^T S_\mathrm{m}^\mathrm{o}$(torsion)/$R$ [b]	$\Delta_0^T S_\mathrm{m}^\mathrm{o}$(total)/$R$ [c]	$\Delta_{298.15}^T H_\mathrm{m}^\mathrm{o}/RT$ [d]	$C_{p,\mathrm{m}}^\mathrm{o}/R$ [e]
298.15	1.621	44.362	0.000	17.571
300.00	1.626	44.471	0.109	17.678
320.00	1.675	45.648	1.243	18.825
340.00	1.720	46.824	2.310	19.957
360.00	1.761	47.996	3.322	21.065
380.00	1.798	49.164	4.284	22.145
400.00	1.834	50.326	5.203	23.192
420.00	1.866	51.483	6.084	24.206
440.00	1.897	52.631	6.930	25.182
460.00	1.926	53.772	7.744	26.122
480.00	1.953	54.903	8.529	27.025
500.00	1.978	56.023	9.286	27.891
520.00	2.002	57.134	10.018	28.722
540.00	2.026	58.233	10.726	29.518
560.00	2.047	59.320	11.410	30.280
580.00	2.068	60.395	12.074	31.011
600.00	2.089	61.459	12.717	31.712
620.00	2.108	62.510	13.341	32.384
640.00	2.126	63.548	13.946	33.029
660.00	2.144	64.574	14.534	33.648
680.00	2.161	65.587	15.105	34.243
700.00	2.178	66.588	15.660	34.814

[a] Based on comparisons with the calorimetric results in this work, as well as consideration of previous work [1-10], the relative expanded uncertainty (0.95 level of confidence) for all values Θ in this table is estimated to be $U_\mathrm{r}(\Theta) = 0.002$.

[b] $\Delta_0^T S_\mathrm{m}^\mathrm{o}$(torsion) is the contribution to the total entropy arising from the methyl torsion.

[c] $\Delta_0^T S_\mathrm{m}^\mathrm{o}$(total) is the total entropy in the ideal-gas state that includes $\Delta_0^T S_\mathrm{m}^\mathrm{o}$(torsion).

[d] $\Delta_{298.15}^T H_\mathrm{m}^\mathrm{o}$ is the enthalpy of the ideal gas at temperature T relative to that at $T = 298.15$ K.

[e] Heat capacity of the ideal gas.

TABLE 17

Experimental and computed enthalpies of formation (kJ·mol^{-1}) at the temperature T = 298.15 K in the condensed (cr or l) and ideal-gas states for indoles and pyrroles.

Compound	$\Delta_f H^o_m$(cr or l)	$\Delta^g_{cr\ or\ l} H^o_m$	$\Delta_f H^o_m$(g, expt)	$\Delta_f H^o_m$(g, computed)	Δ [a]
		Indoles			
2-Methylindole (cr)	36.9 ± 2.6 [this work] 37.7 ± 2.7 [67]	86.0 ± 0.3 [this work] 87.6 ± 2.4 [67] [c]	123.3 ± 1.9	125.3 ± 3 [b]	-2.0
Indole (cr)	86.7 ± 0.8 [70] 86.5 ± 1.3 [73]	78.0 ± 4.0 [75] [d] 74.1 ± 2.1 [73] [d]	161.6 ± 2.0	163.8	-2.2
3-Methylindole (cr)	47.4 ± 2.3 [67]	89.6 ± 1.9 [67] [c]	137.0 ± 3.0	132.0	5.0
N-Methylindole (l)	93.6 ± 2.3 [67]	61.7 ± 1.6 [67][c] 63.6 ± 1.6 [73] [d] 61.6 ± 0.5 [76] [d]	155.4 ± 2.3	157.0	-1.6
2,3-Dimethylindole (cr)	4.2 ± 1.0 [70]	86.9 ± 1.4 [73] [d]	91.1 ± 1.7	94.2	-3.1
		Pyrroles			
Pyrrole (l)	63.1 ± 0.4 [71]	45.13 ± 0.15 [71,10] [e]	108.2 ± 0.4	107.7	0.5
N-Methylpyrrole (l)	62.4 ± 0.5 [70]	40.78 ± 0.13 [74,10] [e]	103.2 ± 0.5	103.7 [f]	-0.5
2,4-Dimethylpyrrole (l)	-15.1 ± 1.1 [10]	54.48 ± 0.23 [10]	39.4 ± 1.1	44.9	-5.5
2,5-Dimethylpyrrole (l)	-16.8 ± 0.8 [70]	56.31 ± 0.27 [10]	39.5 ± 0.9	39.7	-0.2
1,2,5-Trimethylpyrrole (l)	-16.1 ± 2.3 [72]	50.7 ± 1.3 [72]	34.6 ± 2.6	36.9	-2.3

[a] $\Delta = \Delta_f H^o_m$(g, expt) - $\Delta_f H^o_m$(g, computed) in units of kJ·mol^{-1}.

[b] Expanded uncertainty (0.95 level of confidence) U = 3 kJ·mol^{-1} for all computed values of $\Delta_f H^o_m$(g), as given in reference 61.

[c] Recalculated as described in section 4.5. In all cases the gas-phase enthalpy increment required to adjust the microcalorimetric results to T = 298.15 K was determined to be ~10 percent larger than that estimated by Ribeiro da Silva et al. [67] with the group-contribution method of Stull et al. [68].

[d] Expanded uncertainties was estimated in this research based on the uncertainty in slope of a $\ln(p/p^{o})$ against inverse temperature plot, where p is pressure and p^{o} = 1 Pa. Adjustment of enthalpies of vaporization/sublimation derived with the Clapeyron equation from the mid-temperature of the measurements to T = 298.15 K was made with $\Delta_{cr}^{g}C_{p,m}$ = -30 J·K^{-1}·mol^{-1}, as determined in the present research for 2-methylindole.

[e] Enthalpies of vaporization were derived in reference 10 through application of the Clapeyron equation. The reference listed first is the source of the vapor pressures used.

[f] Free rotation of the methyl group was assumed.

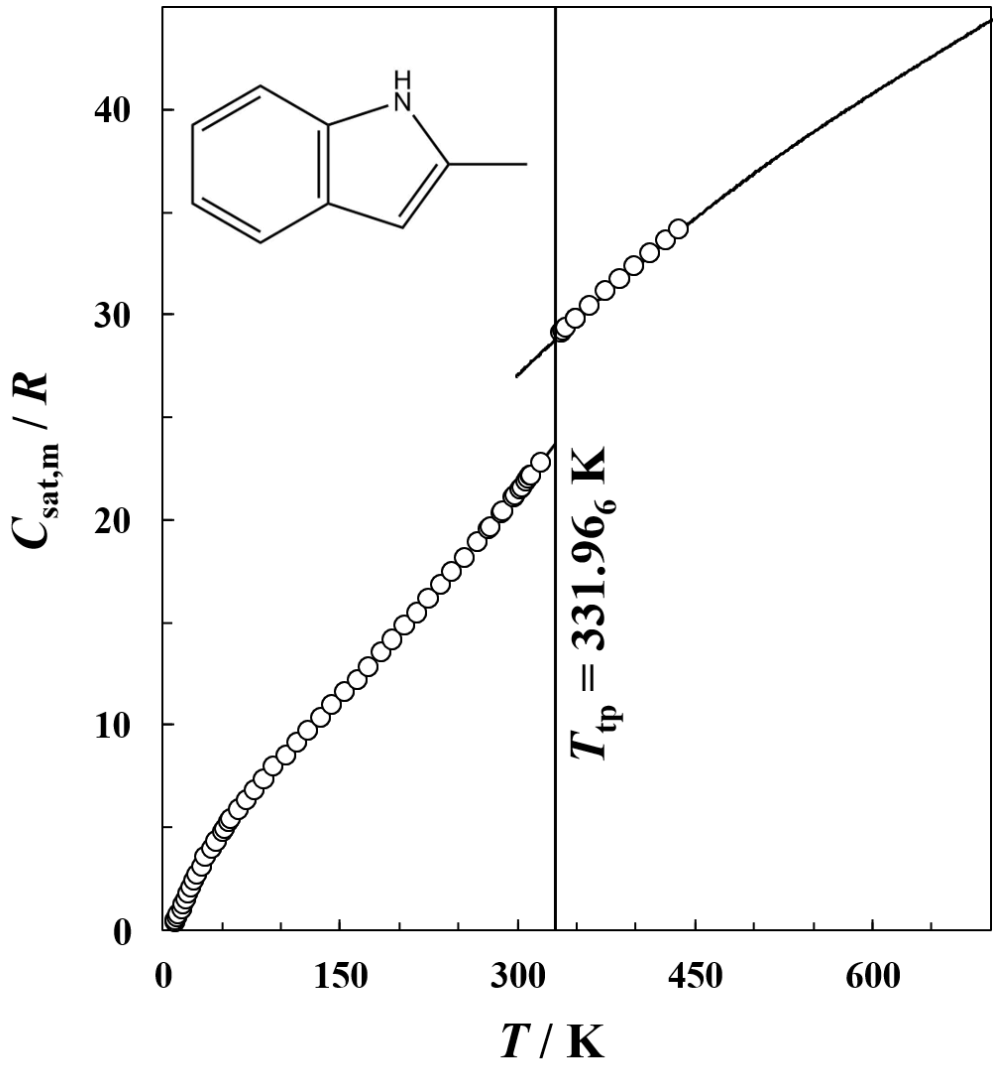


FIGURE 1. Plot of molar heat capacities at saturation pressure $C_{sat,m}$ against temperature for 2-methylindole. The vertical line indicates the triple-point T_{tp} temperature. The smooth curve for temperatures greater than 440 K represents results obtained with d.s.c. Heat capacities for the liquid for temperatures below T_{tp} were estimated by linear extrapolation of measured values for temperatures T < 400 K.

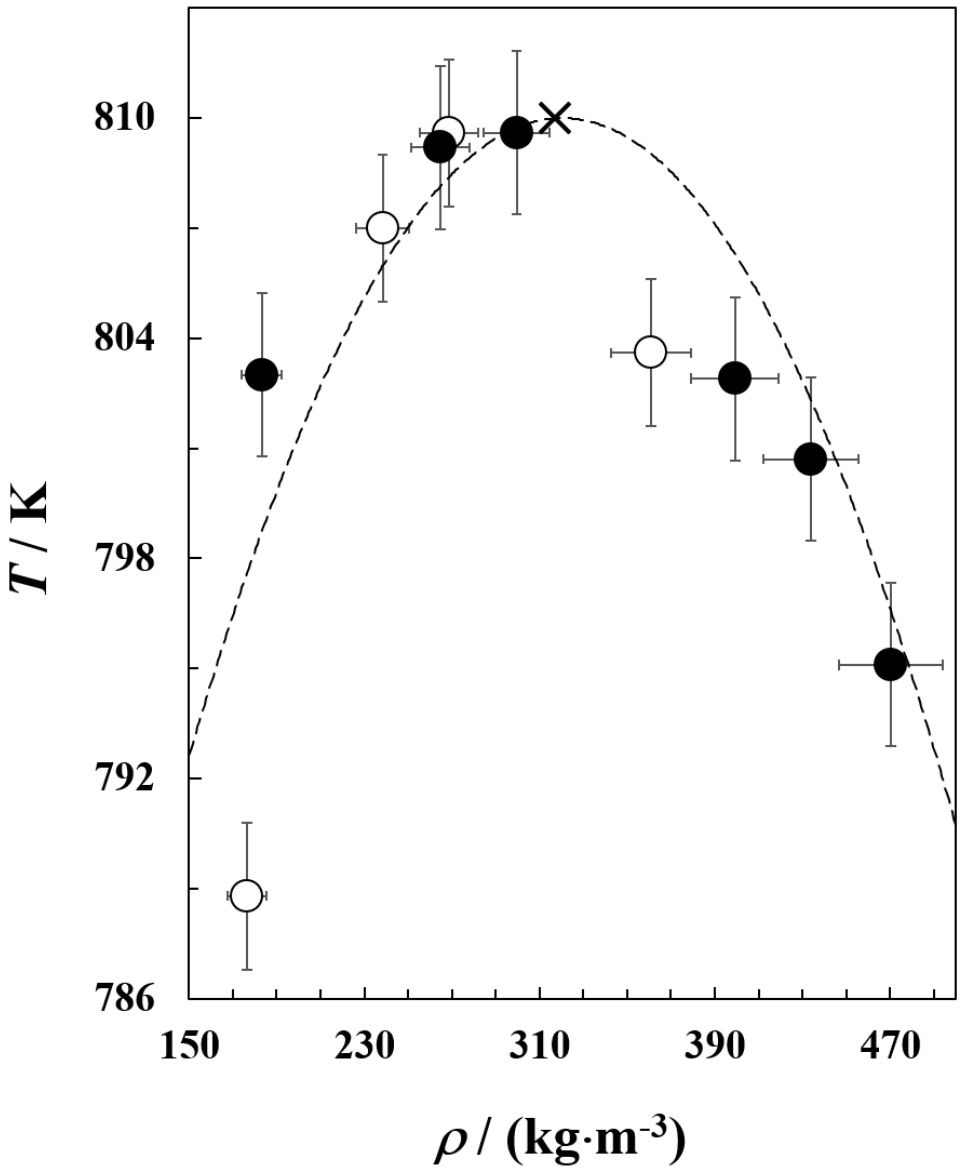


FIGURE 2. Plot of temperature against density ρ for the (gas + liquid) coexistence region for 2-methylindole. ●, experimental values obtained with single fast scans; ○, values obtained with the intermittent heating method, as described in the text. x, experimental critical temperature T_c and critical density ρ_c of this research estimated with the Riedel equation {equation (5)}, as described in the text. The curve is provided as an aide to the eye.

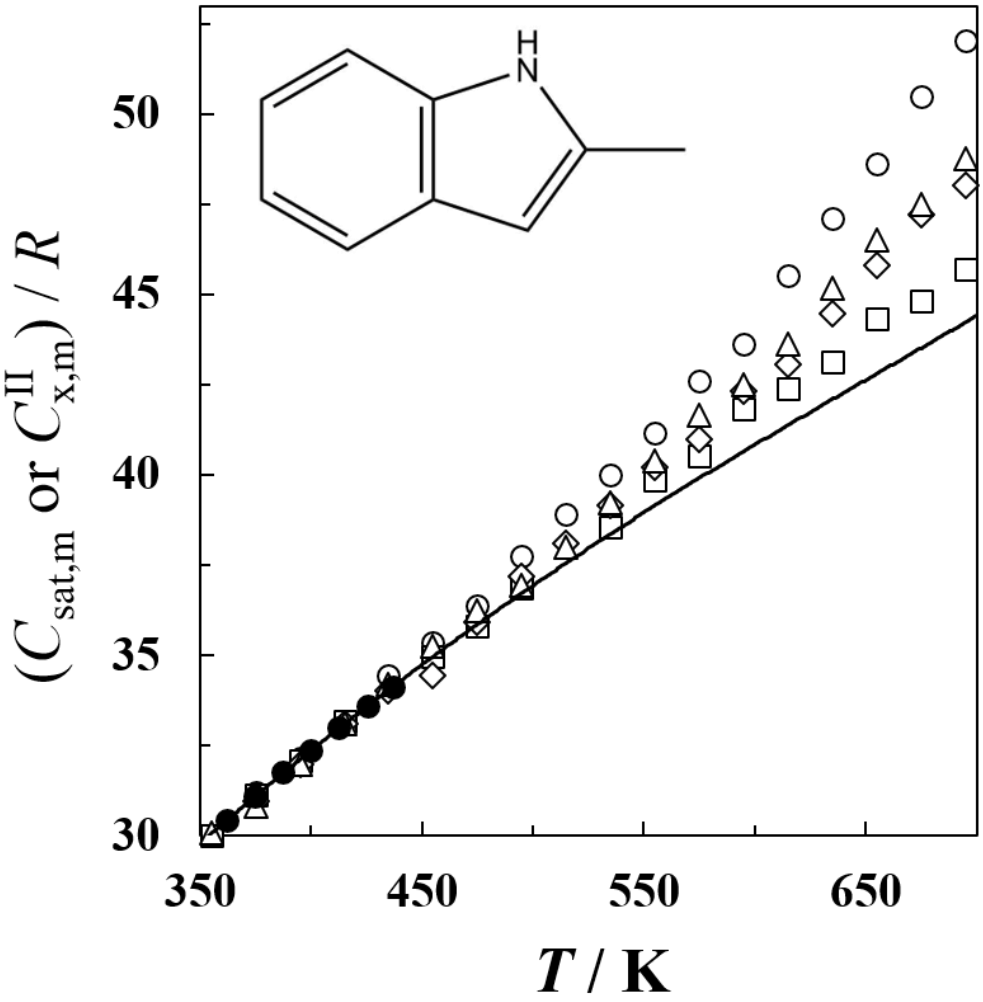


FIGURE 3. Plot of heat capacity $C_{sat,m}$ or $C^{II}_{x,m}$ against temperature T for 2-methylindole. $C^{II}_{x,m}$ values were measured in a cell of 0.0547 cm^3 internal volume at T = 298.15 K (see Table 8). ○, $C^{II}_{x,m}$ for 0.009526 g sample; △, 0.01269 g sample; ◊, 0.014971 g sample; □, 0.020098 g sample. ●, $C_{sat,m}$ determined with adiabatic calorimetry (Table 5); —, $C_{sat,m}$ derived in this research with the d.s.c. results, as described in the text.

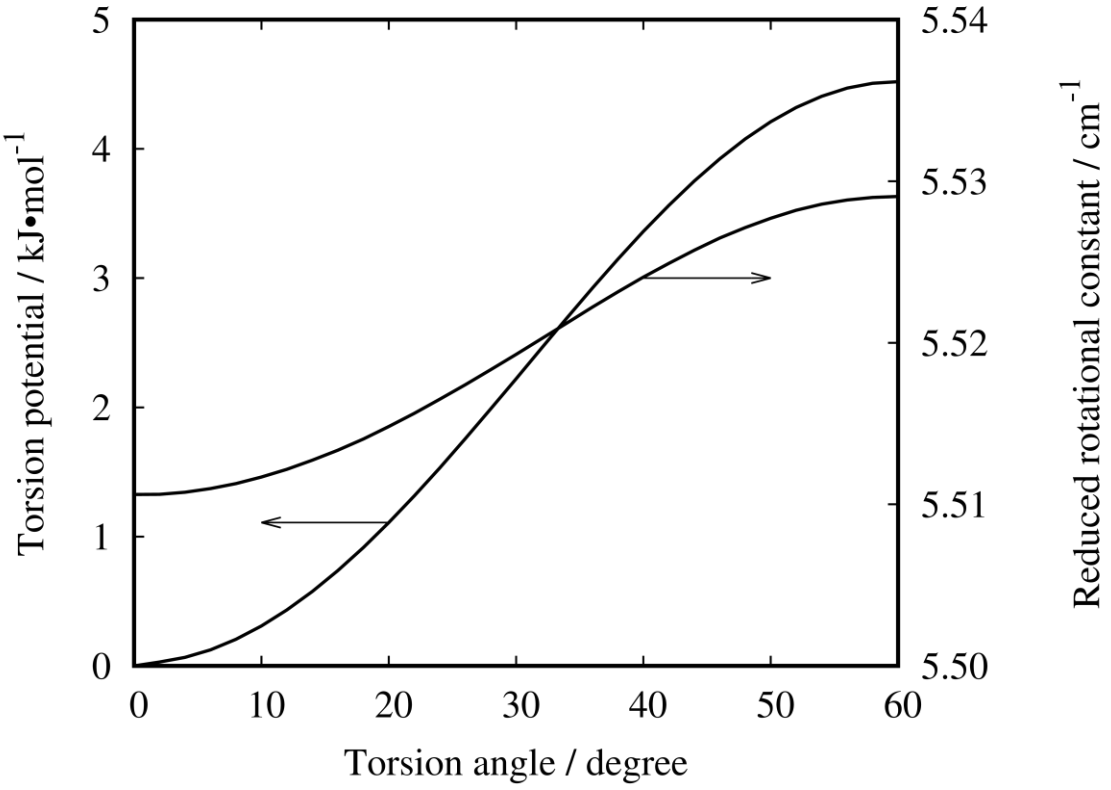


FIGURE 4. Torsion potential and reduced rotational constant for rotation of the methyl group used in the computation of ideal-gas entropies. The portion beyond the 60º torsion angle was omitted due to symmetry.

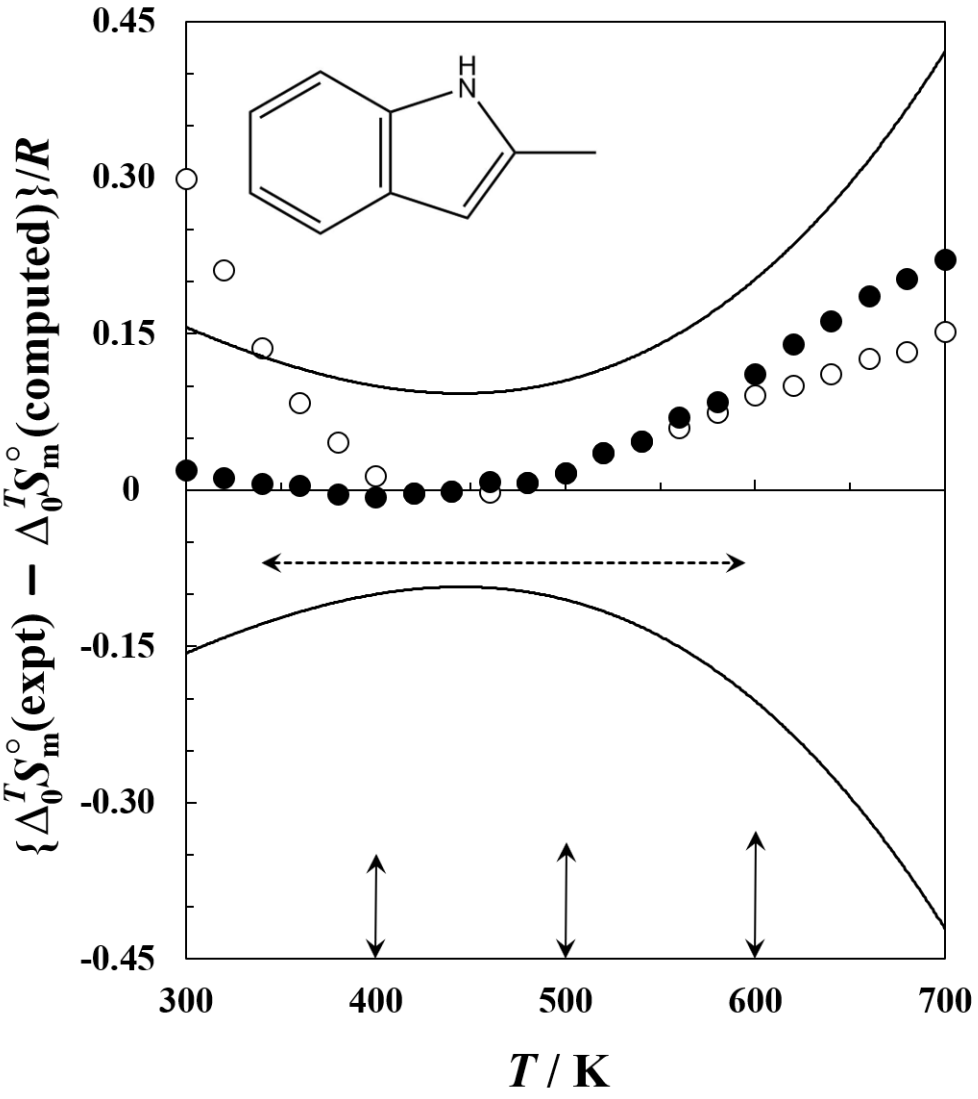


FIGURE 5. Deviation plot for ideal-gas entropies $\Delta_0^T S_{\mathrm{m}}^{\mathrm{o}}$ for 2-methylindole calculated with computed vibrational frequencies and the methods described in the text $\Delta_0^T S_{\mathrm{m}}^{\mathrm{o}}$ (computed) (Table 16) and those derived from the experimental property measurements $\Delta_0^T S_{\mathrm{m}}^{\mathrm{o}}$ (expt). $\Delta_0^T S_{\mathrm{m}}^{\mathrm{o}}$ (expt) was calculated, in part, with entropies of vaporization derived with; ●, the 1.5/2.5/3.0 form of the Wagner equation {equation (4)}; ○, the 1.5/2.5/5.0 form of the Wagner equation. The solid curves represent the expanded uncertainties (0.95 level of confidence) for $\Delta_0^T S_{\mathrm{m}}^{\mathrm{o}}$ (expt). The three vertical bars represent 0.2 percent of $\Delta_0^T S_{\mathrm{m}}^{\mathrm{o}}$ (expt) at the temperatures indicated. The dashed horizontal line indicates the range of vapor pressures measured in this work.