

# Enthalpy of Formation and Strain of Norbornane from Thermochemical Measurements and from ab Initio Calculations

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The standard molar enthalpy of formation  $\Delta_f H_m^\circ(\text{cr}) = -91.6 \pm 1.2 \text{ kJ mol}^{-1}$  at  $T = 298.15 \text{ K}$  was determined by using combustion calorimetry for norbornane. The standard molar enthalpy of sublimation  $\Delta_{\text{cr}}^g H_m^\circ(298.15 \text{ K}) = 40.11 \pm 0.43 \text{ kJ mol}^{-1}$  of norbornane was obtained from the temperature dependence of the vapor pressure measured in a flow system. Its molar enthalpy of fusion  $\Delta_{\text{cr}}^l H_m^\circ = 4.35 \pm 0.21 \text{ kJ mol}^{-1}$  at  $T = 360.8 \text{ K}$  was measured by DSC. Thermochemical investigations of norbornane available in the literature were collected and combined with own experimental results to obtain a reliable standard molar enthalpy of formation of norbornane  $\Delta_f H_m^\circ(\text{g}) = -53.6 \pm 1.2 \text{ kJ mol}^{-1}$  at  $T = 298.15 \text{ K}$  in the gaseous state. Ab initio calculation of norbornane have been performed using the G3(MP2) basis set, and results from the bond separation method  $\Delta_f H_m^\circ(\text{g}) = -53.2 \text{ kJ mol}^{-1}$  are in close agreement with experiment. A strain enthalpy of  $71.8 \text{ kJ mol}^{-1}$  of norbornane has been assessed using a group-additive procedure.

## Introduction

Norbornane is a key compound in structural chemistry, and knowledge of its geometry<sup>1</sup> and energetics reveals how structural parameters respond to the presence of substantial strain.<sup>2,3</sup> Disappointingly, the data for enthalpy of formation of norbornane in the crystalline state are in disarray. Although  $\Delta_f H_m^\circ(\text{cr})$  has been reported for norbornane by several authors, the agreement between these values is poor. The reported results from combustion calorimetry<sup>4–6</sup> differ by  $10 \text{ kJ mol}^{-1}$  despite the acknowledged experience of the research groups involved. In contrast, the experimental results for the enthalpy of sublimation  $\Delta_{\text{cr}}^g H_m^\circ(298.15 \text{ K})$  measured in numerous studies are in excellent agreement (see Table 3).

In 1986, Pedley et al.<sup>13</sup> reconciled thermochemical results from combustion calorimetry<sup>4,5</sup> with the result from reaction calorimetry<sup>7,12</sup> and recommended the standard molar enthalpy of formation of norbornane  $\Delta_f H_m^\circ(\text{g}) = -54.7 \pm 4.7 \text{ kJ mol}^{-1}$  at  $T = 298.15 \text{ K}$ . This selected value was confirmed 1 year later by An et al.<sup>6</sup> They obtained, by means of combustion and vaporization calorimetry, the value  $\Delta_f H_m^\circ(\text{g}) = -54.9 \pm 1.1 \text{ kJ mol}^{-1}$ . Thus, it seems that experimental work of An et al.<sup>6</sup> resolved the inherent contradictions in the thermochemistry of norbornane. However, it is worth mentioning that their combustion results are in agreement within the experimental uncertainties of the earliest value reported by Bedford et al.,<sup>4</sup> but again differ by about  $10 \text{ kJ mol}^{-1}$  from those of Steele.<sup>5</sup> Taking into account that the experimental work of Steele<sup>5</sup> is the best documented experimental investigation of norbornane, we tried to understand the aforementioned disagreement. Careful reading of the paper from An et al.<sup>6</sup> shows that they performed only five combustion experiments, and in two of them traces of soot were observed. Since the value  $\Delta_f H_m^\circ(\text{cr})$  from An et al.<sup>6</sup> is based only on three successful combustion experiments, this fact decreases the reliability of their result. Moreover, another

fact increases our doubts concerning the reliability of the recommended<sup>13</sup> enthalpy of formation of norbornane. Recent results from ab initio calculation at the different modifications of G2 and G3 levels<sup>14,15</sup> provide values of  $\Delta_f H_m^\circ(\text{g})$  in the range of  $-57$  to  $-60 \text{ kJ mol}^{-1}$ , which are in rather close agreement with the result<sup>5</sup> of Steele ( $\Delta_f H_m^\circ(\text{g}) = -61.6 \pm 3.4 \text{ kJ mol}^{-1}$ ). Thus, additional experiments and calculations on norbornane seemed desirable in order to validate available experimental data as well as to reconcile experiment and theory. Having this in mind, we have measured  $\Delta_f H_m^\circ(\text{cr})$  of norbornane using oxygen bomb combustion calorimetry and have accompanied these measurements with additional vapor pressure measurement by transpiration. The resulting  $\Delta_f H_m^\circ(\text{g})$  was then compared to value calculated by high-level G3(MP2) ab initio calculations.

## Experimental Section

The pure Aldrich product having a mass fraction purity of about 0.99 was purified by repeated sublimation in a vacuum. The degree of purity was determined by GLC and by DSC.<sup>16</sup> A purity greater than mass fraction 0.9998 was established by DSC studies of the melting process.<sup>16</sup> GLC analysis of the calorimetric samples on two different capillary columns (OV-17 and SE-30 of 50 m length) failed to show the presence of any impurities (greater than 0.01 mass %).

For measurements of the energies of combustion of norbornane, an isoperibolic rotating-bomb calorimeter and a platinum-lined bomb were used without rotation. Because of high vapor pressure, norbornane samples were placed in polyethylene capsules or in Mylar bags (under an inert atmosphere in a glovebox), which were burned in oxygen. The samples were ignited with help of cotton thread knotted to the sample container and platinum wire. The detailed procedure has been described previously.<sup>17</sup> Combustion products were examined for carbon monoxide (Dräger tube), but none was detected. The energy equivalent of the calorimeter  $\epsilon_{\text{calor}}$  was determined with a standard reference sample of benzoic acid (sample SRM 39i, NIST) from seven experiments. The conventional procedure was

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**TABLE 1: Results for a Typical Combustion Experiments on Norbornane in Mylar and Polyethene Bags at  $T = 298.15$  K ( $p^\circ = 0.1$  MPa)**

	in Mylar	in polyethene
$m$ (substance)/g <sup>b</sup>	0.316000	0.263372
$m'$ (cotton)/g <sup>b</sup>	0.000893	0.001423
$m''$ (mylar)/g <sup>b</sup>	0.031545	
$m'''$ (polyethene)/g <sup>b</sup>		0.196485
$\Delta T_c/\text{K}^c$	0.60106	0.86669
$(\epsilon_{\text{calor}})(-\Delta T_c)/\text{J}$	-15094.17	-21764.84
$(\epsilon_{\text{cont}})(-\Delta T_c)/\text{J}$	-7.67	-13.19
$\Delta U_{\text{corr}}/\text{J}$	5.30	6.37
$-m'\Delta_c u'/\text{J}^d$	15.13	24.11
$-m''\Delta_c u''/\text{J}^d$	720.99	
$-m'''\Delta_c u'''/\text{J}^d$		9109.23
$\Delta_c u^\circ(\text{sub})/(\text{J g}^{-1})$	-45439.7	-45452.6

<sup>a</sup> For the definition of the symbols see ref 18:  $T_h = 298.15$  K;  $V(\text{bomb}) = 0.2664$  dm<sup>3</sup>;  $p^\circ(\text{gas}) = 3.04$  MPa;  $m^i(\text{H}_2\text{O}) = 0.78$  g;  $\Delta U(\text{ign}) = 1.46$  J;  $m(\text{Pt}) = 12.18$  g. <sup>b</sup> Masses obtained from apparent masses. <sup>c</sup>  $\Delta T_c = T^- - T^+ + \Delta T_{\text{corr}}$ ;  $\epsilon_{\text{calor}} = 25112.6 \pm 1.9$  J K<sup>-1</sup>;  $(\epsilon_{\text{cont}})(-\Delta T_c) = (\epsilon_{\text{cont}}^i)(T^i - 298.15 \text{ K}) + (\epsilon_{\text{cont}}^f)(298.15 \text{ K} - T^f + \Delta T_{\text{corr}})$ . <sup>d</sup>  $\Delta U_{\text{corr}}$ , the correction to standard state, is the sum of items 81–85, 87–90, 93, and 94 in ref 18.

applied for converting the energy of the actual bomb process to that of the isothermal process and reducing to standard states.<sup>18</sup> Auxiliary quantities for the combustion experiments and information necessary for reducing apparent mass to mass are given as follows. The density  $\rho_{(293)} = 1.093$  g cm<sup>-3</sup> was determined by submerging tablet of the substance in water in a calibrated 10 cm<sup>3</sup> pycnometer. The massic heat capacity  $c_p = 1.59$  J K<sup>-1</sup> was measured with by DSC. The expansion coefficient was estimated to be  $(\partial v/\partial T)_p = 0.1 \times 10^{-6}$  dm<sup>3</sup> K<sup>-1</sup>. The energy of combustion of cotton thread  $\Delta_c u^\circ(\text{CH}_{1.774}\text{O}_{0.887}) = -16945.2 \pm 4.2$  J g<sup>-1</sup>, polyethene,  $\Delta_c u^\circ(\text{CH}_{1.930}) = -46361.0 \pm 3.1$  J g<sup>-1</sup>, and Mylar,  $\Delta_c u^\circ(\text{C}_{10}\text{H}_8\text{O}_4) = -22838.8 \pm 4.8$  J g<sup>-1</sup>, were measured in our laboratory earlier. Calculation of the mass of the dry Mylar film was made using the dependence of mass from humidity:  $m_{\text{dry}} = m_{\text{moist}}(1 - 4.64 \times 10^{-5} r_{\text{H}})$ , where  $r_{\text{H}}$  denotes the relative humidity. Experimental results for typical combustion experiments are presented in Table 1.

The enthalpy of sublimation of norbornane was determined by the method of transpiration in a saturated N<sub>2</sub> stream.<sup>19,20</sup> The experimental procedure has been tested with measurements of vapor pressures and sublimation enthalpies of two reference materials—benzoic acid and naphthalene. To derive the standard molar enthalpy of sublimation at the mean temperature  $\langle T \rangle$  of the experimental temperature range,  $\Delta_{\text{cr}}^{\text{g}} H_{\text{m}}^\circ(T)$ , the integrated form of the linear Clausius–Clapeyron equation

$$\ln(p/\text{Pa}) = a - b(T/\text{K})^{-1} \quad (1)$$

where  $b = \Delta_{\text{cr}}^{\text{g}} H_{\text{m}}^\circ(T)R^{-1}$ , was used. Experimental vapor pressures and the observed enthalpy of sublimation  $\Delta_{\text{cr}}^{\text{g}} H_{\text{m}}^\circ(T_{\text{av}})$  obtained by this procedure are listed in Tables 2 and 3. Because the  $T_{\text{av}}$  ( $T_{\text{av}}$  is the average temperature of experimental range) of the vapor pressure measurements is slightly below  $T = 298.15$  K, the observed enthalpy of sublimation was adjusted to this reference temperature. The correction was estimated with help of eq 2 according to a procedure developed by Chickos.<sup>21,22</sup>

$$\{\Delta_{\text{cr}}^{\text{g}} H_{\text{m}}^\circ(\langle T \rangle) - \Delta_{\text{cr}}^{\text{g}} H_{\text{m}}^\circ(298.15 \text{ K})\}/(\text{kJ mol}^{-1}) = \Delta_{\text{cr}}^{\text{g}} C_p \{(\langle T \rangle/\text{K}) - 298.15\} \quad (2)$$

A value of  $\Delta_{\text{cr}}^{\text{g}} C_p$  has been derived from the experimental isobaric molar heat capacity of solid norbornane  $C_p^{\text{cr}} = 150.8$

**TABLE 2: Results from Measurements of the Vapor Pressure  $p$  of Norbornane Using the Transpiration Method<sup>a</sup>**

$T/\text{K}^a$	$m/\text{mg}$	$V(\text{N}_2)/\text{dm}^3$	$p/\text{Pa}$	$T/\text{K}$	$m/\text{mg}$	$V(\text{N}_2)/\text{dm}^3$	$p/\text{Pa}$
278.2	39.2	0.957	1152	293.2	36.3	0.335	2891
280.2	29.1	0.636	1273	295.2	36.3	0.302	3197
283.3	29.1	0.495	1608	298.1	29.1	0.208	3698
285.2	29.1	0.440	1798	303.2	31.4	0.175	4778
288.2	38.7	0.502	2085	308.2	30.1	0.127	6267

<sup>a</sup>  $\Delta_{\text{cr}}^{\text{g}} H_{\text{m}}^\circ(\langle T \rangle = 293.2 \text{ K}) = (40.27 \pm 0.43)$  kJ mol<sup>-1</sup>;  $\Delta_{\text{cr}}^{\text{g}} H_{\text{m}}^\circ(298.15 \text{ K}) = (40.12 \pm 0.43)$  kJ mol<sup>-1</sup>.  $\ln(p/\text{Pa}) = (24.46 \pm 0.18) - (4843 \pm 52)(T/\text{K})^{-1}$ .

**TABLE 3: Comparison with Earlier Values of Enthalpy of Sublimation  $\Delta_{\text{cr}}^{\text{g}} H_{\text{m}}^\circ/\text{kJ mol}^{-1}$  of Norbornane**

technique	$T_{\text{av}}/\text{K}$	obsd at $T_{\text{av}}$	extrapolated <sup>a</sup> to	
			$T = 298.15$ K	ref
Bourdon gauge	305.5	40.12 ± 0.84	40.36 ± 0.84	7
not available	331.9	39.32 ± 0.13	40.40 ± 0.13	8
transpiration	305.0	39.96 ± 0.80	40.18 ± 0.80	9
Bourdon gauge	300.0	40.40 ± 0.80	40.40 ± 0.80	5
calorimetry	298.2	40.26 ± 0.32	40.26 ± 0.32	10
inclined piston	232.5	40.94 ± 0.23	39.40 ± 0.23	11
calorimetry	298.2	40.04 ± 0.18	40.04 ± 0.18	6
transpiration	293.1	40.27 ± 0.43	40.12 ± 0.43	this work

av:<sup>b</sup> 40.12 ± 0.24<sup>c</sup>

<sup>a</sup> The observed value at  $T_{\text{av}}$  was extrapolated to 298.15 K using eq 3. <sup>b</sup> Average value (was calculated taking into consideration the uncertainty as a statistical weighting factor<sup>24</sup>) recommended for calculation of enthalpy of vaporization  $\Delta_{\text{f}}^{\text{g}} H_{\text{m}}^\circ = \Delta_{\text{cr}}^{\text{g}} H_{\text{m}}^\circ - \Delta_{\text{cr}}^{\text{l}} H_{\text{m}}^\circ = 40.12 - 1.82 = 38.30 \pm 0.34$  kJ mol<sup>-1</sup> and gaseous enthalpy of formation of norbornane (see Table 4). <sup>c</sup> Uncertainty is twice the SD of the mean.

J mol<sup>-1</sup> K<sup>-1</sup> (measured in this work by DSC; this value also is an agreement with those measured by Steele,<sup>5</sup>  $C_p^{\text{cr}} = 151.0$  J mol<sup>-1</sup> K<sup>-1</sup>). Doing so, the  $\Delta_{\text{cr}}^{\text{g}} H_{\text{m}}^\circ(298.15 \text{ K}) = 40.12 \pm 0.43$  kJ mol<sup>-1</sup> was calculated (see Tables 2 and 3).

The enthalpy of fusion was measured by a Perkin-Elmer DSC-2C. The temperature scale of the DSC was calibrated by measuring the melting temperatures of the recommended high-purity standards: benzoic acid, tin, and indium.<sup>16</sup> The power scale was calibrated using sapphire as a standard material. The experimental enthalpy of fusion,  $\Delta_{\text{cr}}^{\text{l}} H_{\text{m}}^\circ(T_{\text{fus}}) = 4.35 \pm 0.21$  kJ mol<sup>-1</sup>, was measured at a melting temperature 360.8 K. Because of the deviation from  $T = 298.15$  K, this observed value of the enthalpy of fusion of norbornane had to be adjusted to this reference temperature. The adjustment was calculated from the equation<sup>21,22</sup>

$$\{\Delta_{\text{cr}}^{\text{l}} H_{\text{m}}^\circ(T_{\text{fus}}/\text{K}) - \Delta_{\text{cr}}^{\text{l}} H_{\text{m}}^\circ(298.15 \text{ K})\}/(\text{J mol}^{-1}) = \{(0.75 + 0.15C_p^{\text{cr}})[(T_{\text{fus}}/\text{K}) - 298.15]\} - \{(10.58 + 0.26C_p^{\text{l}})[(T_{\text{fus}}/\text{K}) - 298.15]\} \quad (3)$$

where value of  $\Delta_{\text{cr}}^{\text{l}} C_p$  has been derived from the isobaric molar heat capacities of liquid norbornane,  $C_p^{\text{l}} = 204.3$  J mol<sup>-1</sup> K<sup>-1</sup>, calculated according to procedure developed by Chickos<sup>21,22</sup> and the isobaric molar heat capacities of solid norbornane measured in this work ( $C_p^{\text{cr}} = 150.8$  J mol<sup>-1</sup> K<sup>-1</sup>). With this adjustment (the uncertainty of the correlation was not taken into account), the standard enthalpy of fusion at  $T = 298.15$  K,  $\Delta_{\text{cr}}^{\text{l}} H_{\text{m}}^\circ(298.15 \text{ K}) = 1.82 \pm 0.21$  kJ mol<sup>-1</sup>, was calculated. The latter value was used to calculate enthalpy of vaporization of the liquid norbornane at the reference temperature 298.15 K (see Table

**TABLE 4: Experimental Results for Norbornane at 298.15 K in kJ mol<sup>-1</sup>**

	$\Delta_f H_m^\circ(\text{cr})$	$\Delta_f H_m^\circ(\text{liq})$	$\Delta_f H_m^\circ(\text{g})$	reference
combustion calorimetry	$-92.1 \pm 2.7$		$-52.0 \pm 2.7^a$	4
combustion calorimetry	$-102.0 \pm 3.3$		$-61.9 \pm 3.3^b$	5
combustion calorimetry	$-95.0 \pm 1.1$		$-54.9 \pm 1.1^a$	6
combustion calorimetry	$-91.6 \pm 1.2$		$-51.5 \pm 1.2^a$	this work
hydrogen calorimetry (1)		$-94.7 \pm 2.4$	$-56.4 \pm 2.4^c$	12
hydrogen calorimetry (1)		$-91.8 \pm 2.3$	$-53.5 \pm 2.3^c$	25
hydrogen calorimetry (1)			$-54.5 \pm 2.1$	26
hydrogen calorimetry (2)		$-90.9 \pm 2.1$	$-52.6 \pm 2.1^c$	12
hydrogen calorimetry (3)		$-92.9 \pm 3.0$	$-54.6 \pm 3.0^c$	12
			av.: <sup>d</sup> $-53.6 \pm 1.2^e$	

<sup>a</sup> Value calculated using combustion calorimetry data from column 2 and recommended enthalpy of sublimation from Table 3. <sup>b</sup> This result was disregarded by calculation of the average value of gaseous enthalpy of formation of norbornane. <sup>c</sup> Value calculated using hydrogenation calorimetry data from column 3 and recommended enthalpy of vaporization from Table 3. <sup>d</sup> Average value (was calculated taking into consideration the uncertainty as a statistical weighting factor<sup>24</sup>) recommended for calculation of strain of norbornane (see text). <sup>e</sup> Uncertainty is twice the SD of the mean.

3) with help of the averaged value of the sublimation enthalpy:  $\Delta_f^g H_m^\circ = \Delta_{\text{cr}}^g H_m^\circ - \Delta_{\text{cr}}^l H_m^\circ = 40.12 - 1.82 = 38.30 \pm 0.24$  kJ mol<sup>-1</sup>.

**Computation.** Standard ab initio molecular orbital calculations were performed with the Gaussian 03 Rev.04 series of programs.<sup>35</sup> Energies were obtained at the G3MP2 level of theory. G3 theory is a procedure for calculating energies of molecules containing atoms of the first and second row of the periodic chart based on ab initio molecular orbital theory. G3 theory uses geometries from second-order perturbation theory and scaled zero-point energies from Hartree–Fock theory followed by a series of single-point energy calculations at the MP2, MP4, and QCISD(T) levels of theory (for details see ref 36). The enthalpy value of norbornane at  $T = 298$  K was evaluated according to standard thermodynamic procedures.<sup>37</sup> Thermal correction in G3 theory was made using scaled frequencies for the vibration in the harmonic approximation for vibrational energy, the classical approximation for translation, rotation, and PV term.<sup>38</sup>

## Results and Discussion

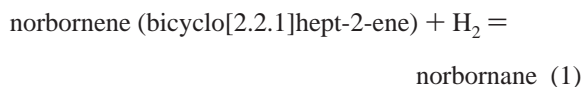
**Combustion Experiments.** In the course of our combustion experiments we were confronted with unusual incomplete burning of samples. In most of the 23 combustion experiments, massive soot residues were observed in the crucible as well as on the walls inside the bomb. We tested different variation of experimental conditions (mass of sample, pressure) without substantial success. We tested different kinds of encapsulation and enclosed sample of norbornane in Mylar or polythene bags. Nonetheless, six of the 23 experiments did result in complete combustion without traces of soot, and only these results were used to derive enthalpy of formation of norbornane. Typical successful combustion experiments of norbornane in Mylar and in a polyethene bag are given in Table 1. The results from both types of enclosures are practically indistinguishable. The individual values of the standard massic energy of combustion,  $\Delta_c u^\circ$ , are given as follows (in J g<sup>-1</sup>):  $-45\,439.7$ ,  $-45\,472.2$ ,  $45\,422.6$  (enclosed in Mylar) and  $-45\,452.6$ ,  $-45\,450.0$ ,  $-45\,429.8$  (enclosed in polyethene). The mean as well as its standard deviation is  $\Delta_c u^\circ = -45\,444.5 \pm 7.3$  J g<sup>-1</sup>. To derive  $\Delta_f H_m^\circ$  from  $\Delta_c H_m^\circ = -4378.00 \pm 0.79$  kJ mol<sup>-1</sup>, we used molar enthalpies of formation for H<sub>2</sub>O(l) and CO<sub>2</sub>(g) as recommended by CODATA.<sup>23</sup> The derived value of the standard molar enthalpy of formation is  $\Delta_f H_m^\circ(\text{cr}) = -91.6 \pm 1.2$  kJ mol<sup>-1</sup>. The assigned standard deviation of the mean include the uncertainties from calibration, from the combustion energies of the auxiliary materials, and reaction products H<sub>2</sub>O and CO<sub>2</sub>. The earlier result of Bedford,<sup>4</sup>  $\Delta_f H_m^\circ(\text{cr}) = -92.1 \pm 2.7$  kJ

mol<sup>-1</sup>, is in agreement with ours within experimental error; our result is in disagreement with the result of Steele<sup>5</sup> ( $\Delta_f H_m^\circ(\text{cr}) = -102.0 \pm 3.3$  kJ mol<sup>-1</sup>).

**DSC Study of Norbornane.** An enthalpy of fusion,  $\Delta_{\text{cr}}^l H_m^\circ = 4.35 \pm 0.21$  kJ mol<sup>-1</sup> at  $T = 360.8$  K, was measured by DSC. The sample was studied from 298 to 380 K at a rate of 5 K min<sup>-1</sup>. Steele<sup>5</sup> observed a phase transition at 305.9 K with an enthalpy of transition of 0.75 kJ mol<sup>-1</sup>, and his sample was claimed to have purity of 99.95 mol %. We did not observe the aforementioned phase transition. The melting temperature, measured by Steele,  $T = 360$  K, is slightly lower than in our measurement. This observation could imply that the specimens of norbornane used for combustion and DSC experiments by Steele had lower purities than claimed or that a different polymorph was used.

**Vapor Pressure Measurements.** Determinations of the enthalpy of sublimation of norbornane have been made by a number of groups in the past years (see Table 3). The observed values  $\Delta_{\text{cr}}^g H_m^\circ(T_{\text{av}})$  given in the literature were adjusted to the reference temperature,  $T = 298.15$  K, with the aid of eq 2. The values of  $\Delta_{\text{cr}}^g H_m^\circ$  measured by different techniques are very consistent, as can be seen by reference to Table 3. For estimation of the gaseous enthalpy of formation of norbornane, we used the average value  $\Delta_{\text{cr}}^g H_m^\circ = 40.12 \pm 0.24$  kJ mol<sup>-1</sup> calculated from data presented in Table 3. Hence, using this value and our result from combustion calorimetry, the standard molar enthalpy of formation  $\Delta_f H_m^\circ(\text{g}) = -51.5 \pm 1.2$  kJ mol<sup>-1</sup> of norbornane has been obtained (see Table 4).

**Thermochemical Calculations of Enthalpy of Formation of Norbornane.** In addition to the combustion calorimetry results, which led directly to the enthalpy of formation of norbornane in the crystalline state, there are an extended set of enthalpies hydrogenation of norbornane derivatives (norbornane, norbornadiene, and norbornene) measured calorimetrically.<sup>12,25,26</sup> The experimental technique of hydrogenation calorimetry is well established and provides reliable values of the enthalpies of reactions under study. We decided to utilize these reactions and to derive enthalpy of formation of norbornane independently. The first reaction examined is



(a) Combining the enthalpy of reaction 1 in the gaseous phase  $\Delta_f H_m^\circ(\text{g})_1 = -137.0 \pm 0.4$  kJ mol<sup>-1</sup> measured by Doering et al.<sup>26</sup> with  $\Delta_f H_m^\circ(\text{g})_{\text{norbornene}} = 82.6 \pm 2.1$  kJ mol<sup>-1</sup> recently measured by combustion calorimetry and inclined piston manometry by Steele et al.,<sup>27</sup> the enthalpy of formation of

norbornane can be derived:

$$\Delta_f H_m^\circ(\text{g})_{\text{norbornane}} = \Delta_f H_m^\circ(\text{g})_1 + \Delta_f H_m^\circ(\text{g})_{\text{H}_2} + \Delta_f H_m^\circ(\text{g})_{\text{norbornene}} = -54.5 \pm 2.1 \text{ kJ mol}^{-1}$$

(b) Combining the enthalpy of reaction 1 in the liquid phase  $\Delta_f H_m^\circ(\text{liq})_1 = -141.5 \pm 1.2 \text{ kJ mol}^{-1}$ , measured by Rogers et al.,<sup>12</sup> the enthalpy of formation of norbornane was derived:

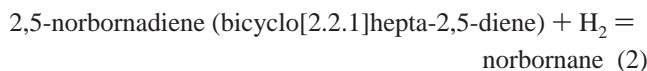
$$\Delta_f H_m^\circ(\text{liq})_{\text{norbornane}} = \Delta_f H_m^\circ(\text{liq})_1 + \Delta_f H_m^\circ(\text{liq})_{\text{H}_2} + \Delta_f H_m^\circ(\text{liq})_{\text{norbornene}} = -94.7 \pm 2.4 \text{ kJ mol}^{-1}$$

with  $\Delta_f H_m^\circ(\text{liq})_{\text{norbornene}} = 46.8 \pm 2.1 \text{ kJ mol}^{-1}$  obtained from  $\Delta_f H_m^\circ(\text{cr})_{\text{norbornene}} = 44.4 \pm 2.0 \text{ kJ mol}^{-1}$  measured by combustion calorimetry by Steele et al.<sup>27</sup> and the experimental enthalpy of fusion,  $\Delta_{\text{cr}}^1 H_m^\circ(T_{\text{fus}}) = 3.5 \pm 0.2 \text{ kJ mol}^{-1}$ , referred to the melting temperature 319.5 K.<sup>27</sup> Because of the deviation from  $T = 298.15 \text{ K}$ , this observed value of the enthalpy of fusion of norbornene had to be adjusted to the reference temperature in the same way as for norbornane. The adjusted value  $\Delta_{\text{cr}}^1 H_m^\circ(298.15 \text{ K}) = 2.4 \pm 0.2 \text{ kJ mol}^{-1}$  was calculated according to procedure developed by Chickos.<sup>21,22</sup> The latter value was used to calculate the enthalpy of formation of liquid norbornene.

(c) Combining the enthalpy of reaction 1 in the liquid phase  $\Delta_f H_m^\circ(\text{liq})_1 = -138.6 \pm 0.9 \text{ kJ mol}^{-1}$  measured by Turner et al.<sup>25</sup> with  $\Delta_f H_m^\circ(\text{liq})_{\text{norbornene}} = 46.8 \pm 2.1 \text{ kJ mol}^{-1}$  obtained from results by Steele et al.<sup>27</sup> as described above, the enthalpy of formation of norbornane was derived:

$$\Delta_f H_m^\circ(\text{liq})_{\text{norbornane}} = \Delta_f H_m^\circ(\text{liq})_1 + \Delta_f H_m^\circ(\text{liq})_{\text{H}_2} + \Delta_f H_m^\circ(\text{liq})_{\text{norbornene}} = -91.8 \pm 2.3 \text{ kJ mol}^{-1}$$

The second reaction examined is

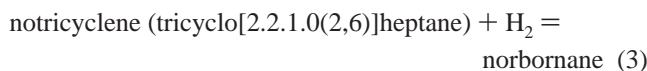


and using enthalpy of reaction 2 in the liquid phase  $\Delta_f H_m^\circ(\text{liq})_2 = -291.9 \pm 1.5 \text{ kJ mol}^{-1}$  measured by Rogers et al.,<sup>12</sup> the enthalpy of formation of liquid norbornane was derived:

$$\Delta_f H_m^\circ(\text{liq})_{\text{norbornane}} = \Delta_f H_m^\circ(\text{liq})_2 + \Delta_f H_m^\circ(\text{liq})_{\text{H}_2} + \Delta_f H_m^\circ(\text{liq})_{2,5\text{norbornadiene}} = -90.9 \pm 2.1 \text{ kJ mol}^{-1}$$

with  $\Delta_f H_m^\circ(\text{liq})_{2,5\text{norbornadiene}} = 201.0 \pm 1.5 \text{ kJ mol}^{-1}$  measured using combustion calorimetry by Skuratov et al.<sup>28</sup>

The third reaction examined is



using enthalpy of reaction 3 in the liquid phase  $\Delta_f H_m^\circ(\text{liq})_3 = -136.3 \pm 2.2 \text{ kJ mol}^{-1}$  measured by Rogers et al.,<sup>12</sup> the enthalpy of formation of liquid norbornane was derived:

$$\Delta_f H_m^\circ(\text{liq})_{\text{norbornane}} = \Delta_f H_m^\circ(\text{liq})_3 + \Delta_f H_m^\circ(\text{liq})_{\text{H}_2} + \Delta_f H_m^\circ(\text{liq})_{\text{notricyclene}} = -92.9 \pm 3.0 \text{ kJ mol}^{-1}$$

with  $\Delta_f H_m^\circ(\text{liq})_{\text{notricyclene}} = 43.4 \pm 2.0 \text{ kJ mol}^{-1}$  measured using combustion calorimetry by Steele.<sup>5</sup>

A summary of experimental enthalpies of formation of norbornane is presented in Table 4. As can be seen from this table, enthalpies of formation in the gaseous state derived from

**TABLE 5: Results of Calculation of the Standard Enthalpy of Formation for Norbornane in the Gaseous Phase at 298.15 K in kJ mol<sup>-1</sup>**

method	$\Delta_f H_m^\circ(\text{g})$	
	bond separation	atomization
G2	-59.0 <sup>14</sup> -70.3 <sup>15</sup>	-59.0 <sup>15</sup>
G2(MP2)	-56.9 <sup>14</sup> -56.1 <sup>15</sup>	-44.8 <sup>15</sup>
G2(MP2, SVP)	-61.5 <sup>14</sup>	
B3LYP/MP2 (full)	-13.4 <sup>14</sup>	
6-311+G(3df,2p)		
G3(MP2)	-57.7 (this work) <sup>a</sup> -53.2 (this work) <sup>b</sup>	-57.7 <sup>15</sup> -57.3 (this work)
experimental (recommended)		-53.6 ± 1.2

<sup>a</sup> Calculated using reaction 4; see text. <sup>b</sup> Calculated using reaction 5; see text.

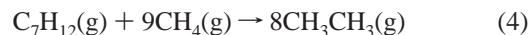
different sources are very consistent (except for result from ref 5) within the boundaries of experimental uncertainties. Therefore, the average of results presented in Table 4,  $\Delta_f H_m^\circ(\text{g}) = -53.6 \pm 1.2 \text{ kJ mol}^{-1}$ , of norbornane could be considered as a reliable experimental value, which could be recommended for further thermochemical calculations.

**Quantum Chemical Calculations for Norbornane.** Theoretical calculation of the enthalpy of formation of norbornane has been a popular endeavor during the past 30 years. Force-field calculation methods have been developed by Allinger and co-workers.<sup>29</sup> The earliest version, MM1, gave<sup>30</sup>  $\Delta_f H_m^\circ(\text{g}) = -56.4 \text{ kJ mol}^{-1}$  and then MM2 gave<sup>31</sup>  $\Delta_f H_m^\circ(\text{g}) = -53.7 \text{ kJ mol}^{-1}$ . We used version MM3 in this work, and our estimation gave the value  $\Delta_f H_m^\circ(\text{g}) = -50.3 \text{ kJ mol}^{-1}$ , which is surprisingly a poorer result than that obtained by MM2.

Wiberg<sup>32</sup> has applied ab initio quantum mechanical method for calculation of the enthalpy of formation of norbornane using a 3-21G, 4-31G, and 6-31G basis sets and estimated values of  $\Delta_f H_m^\circ(\text{g})$  as follows: -84.1, -72.3, and -55.2 kJ mol<sup>-1</sup> using group equivalents. Recently, Rogers et al.<sup>14</sup> carried out a systematic investigation of the feasibility and accuracy of the G2 family of computational methods in calculating the enthalpy of formation of C<sub>7</sub> cyclic hydrocarbons. They calculated the following results for  $\Delta_f H_m^\circ(\text{g})$  of norbornane with G2, G2(MP2), G3(MP2), and B3LYP/6-311+G(3df,2p) which are collected in Table 5. Results for the G2 family and B3LYP were calculated by the bond separation method. The G3(MP2) value was obtained by the atomization method. Castano et al.<sup>15</sup> also examined the ab initio molecular orbital method at the G2 and G2(MP2) levels of theory (see Table 5) for calculation of the enthalpy of formation of norbornane. As can be seen from this table, the literature results derived in 1999<sup>14,15</sup> from both atomization and bond separation methods are systematically 3–4 kJ mol<sup>-1</sup> higher (except for B3LYP) than the experimental value, and an average value of -58 kJ mol<sup>-1</sup> is fairly close to the experimental value of -53.6 ± 1.2 kJ mol<sup>-1</sup> derived and recommended in this work.

Our own updated calculations using G3(MP2) are also presented in Tables 5 and 6. Similar to work performed in refs 14 and 15, we derived an enthalpy of formation of norbornane with help from both atomization and bond separation methods,<sup>39</sup> and our results are essentially indistinguishable with those reported earlier by Rogers et al. using the G3(MP2) basis set.

In refs 14 and 15 the following bond separation reaction for norbornane was applied:

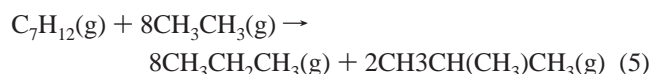


**TABLE 6: G3(MP2) Total Energies at 0 K, Thermal Correction, and Enthalpies at 298.15 K of the Studied Compounds and Molecules Used in This Work**

compound	G3MP2				
	$E_0$	ZPVE <sup>a</sup>	trans + rot + PV term	TCH	$H_{298}$
norbornane	-273.437 597	0.003 005	0.003 776	0.006 782	-273.430 815
methane	-40.422 100	0.000 039	0.003 776	0.003 815	-40.418 285
ethane	-79.651 199	0.000 708	0.003 776	0.004 484	-79.646 715
propane	-118.885 057	0.001 803	0.003 776	0.005 579	-118.879 478
2-methylpropane	-158.122 289	0.003 030	0.003 776	0.006 806	-158.115 483

<sup>a</sup> Values TCH were calculated using scaled HF/6-31G(d) frequencies for the vibration in the harmonic approximation for vibrational energy, classical approximation for translation, rotation, and additional PV term.

to derive enthalpy of formation of norbornane with help of the known enthalpies of formation of the reference molecules, methane and ethane. As the first step we also used reaction 4 and enthalpies of formation  $\Delta_f H_m^\circ(\text{g}) = -74.4 \pm 0.4 \text{ kJ mol}^{-1}$  for methane<sup>13</sup> and  $\Delta_f H_m^\circ(\text{g}) = -83.8 \pm 0.4 \text{ kJ mol}^{-1}$  for ethane.<sup>13</sup> We obtained  $\Delta_f H_m^\circ(\text{g}) = -57.7 \text{ kJ mol}^{-1}$  for norbornane, which is in close agreement with earlier calculations<sup>14,15</sup> but still in disagreement with the experiment. We then decided to apply another bond separation reaction:



In our opinion, this reaction seems to be more suitable because propane and 2-methylpropane in the right side of reaction 5 mimic the branched structural pattern of norbornane more properly. Using the bond separation reaction 5 and enthalpy of formation  $\Delta_f H_m^\circ(\text{g}) = -103.55 \pm 0.67 \text{ kJ mol}^{-1}$  for propane,<sup>33,34</sup> we obtained  $\Delta_f H_m^\circ(\text{g}) = -53.3 \text{ kJ mol}^{-1}$  of norbornane, which now is in excellent agreement with the experiment value.

**Strain of Norbornane.** We define the strain of a molecule as the difference between the experimental standard molar enthalpy of formation  $\Delta_f H_m^\circ(\text{g})$  and the calculated sum of strain-free increments<sup>40</sup> of the Benson type<sup>41</sup> for the molecule. The system of strain-free increments is based on the standard enthalpies of formation  $\Delta_f H_m^\circ(\text{g})$  of simple homologous ("strain-less") molecules. Strain-free group-additivity increments for hydrocarbons are well-defined.<sup>40</sup> Their advantage with respect to the classic Benson increments<sup>41</sup> is the possibility of determining strain enthalpies. Increments necessary to assess the strain in hydrocarbons are as follows:<sup>40</sup>  $\text{CH}_3[\text{C}] = -42.05 \text{ kJ mol}^{-1}$ ;  $\text{CH}_2[2\text{C}] = -21.46 \text{ kJ mol}^{-1}$ ;  $\text{CH}[3\text{C}] = -9.04 \text{ kJ mol}^{-1}$ ;  $\text{C}[4\text{C}] = -1.26 \text{ kJ mol}^{-1}$ . By using these group-additivity parameters and the experimental value of  $\Delta_f H_m^\circ(\text{g}) = -53.6 \pm 1.2 \text{ kJ mol}^{-1}$  derived in this research, the value of strain enthalpy  $H_s = \{\Delta_f H_m^\circ(\text{g}) - \Sigma \text{increments}\} = 71.8 \text{ kJ mol}^{-1}$  of norbornane has been estimated. This strain can be applied in thermochemical calculation for organic compounds containing the norbornane moiety.

## Conclusions

This investigation was undertaken to establish a consistent set of experimental thermochemical quantities for norbornane. Together with our own results, we collected from the literature a large number of the primary experimental results. These values have been used to derive a reliable value for the enthalpy of formation of norbornane at the reference temperature 298.15 K. This collection together with the own results helps to resolve the contradictions in the experimental thermochemistry of norbornane.

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