Consistent Thermodynamic Properties for Alicyclic Components of Jet Fuels: Experimental Data, Estimation Methods, and Homologous Series Trends

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Abstract

Alkylcycloalkanes represent a significant fraction of jet fuel components. An evaluation of their thermodynamic properties, enthalpies of formation in liquid and gas phases and enthalpies of vaporization, was conducted. A combination of available experimental data, up-to-date group-contribution methods, high-level quantum-chemical calculations, and homologous series trends was used to identify outliers and to recommend the most reliable values. The group-contribution approach was found to work well for the enthalpies of vaporization. Its performance for the enthalpies of formation in the liquid and gas phases was found to be substantially less effective, especially considering notable differences in this property among stereoisomers. Computationally affordable high-level *ab initio* results and homologous series trend analysis appeared more reliable. The recommended property values for 212 individual compounds and their isomeric mixtures were provided.

1. Introduction

Current efforts toward sustainable transportation include the conversion of renewable feedstocks, such as biomass, to jet-fuel-range molecules. Product molecules from combinations of feedstocks and their conversion processes can be assessed for jet fuel compatibility, either as blendstocks or standalone fuels. Currently, nine alternative fuel pathways are ASTM-approved in the U.S. for blending into the existing jet fuel [1]. The variety of alternative feedstocks and conversion processes will continue to grow, resulting in both very narrow and more diverse ranges of molecular product species [2,3]. Advancements in analytical methods such as GCxGC [4] enable rapid speciation and quantification of hundreds of compounds in fuels and blendstocks, allowing the prediction of fuel properties from those of the molecular species. Understanding the properties and behavior of individual molecular species and their impacts on overall fuel properties is essential to developing an integrated strategy toward sustainable fuels and blending approaches. Reliable property values or predictive procedures for individual constituent molecules and their families can provide a solid foundation for the overall fuel property predictions.

Previously [5,6], we analyzed the performance of composition-based methods for the properties of aviation fuels included in their specifications. The considered properties included net heat of combustion (NHC), density, freeze point, distillation characteristics, and flash point. NHC of hydrocarbons were found from either their experimental liquid-phase enthalpies of formation $\Delta_f H^\circ_m$ or the predicted gas-phase $\Delta_f H^\circ_m$ and corresponding enthalpies of vaporization. The present work was initiated upon realizing that current estimation methods may have systematic errors when predicting enthalpies of formation of alkylcycloalkanes. The latter represent a significant portion of jet fuels. Besides their presence in conventional petroleum-derived fuels [7], they can be found in even more significant amounts in fuels from alternative processes such as biomass-derived jet-fuel-range molecules via the catalytic fast pyrolysis process [5]. Further, future renewable fuels development may target process chemistries to produce some of these molecules for better fuel blendstock properties [8] since alicyclic (naphthenic) species like monocyclic alkanes have desirable characteristics for jet fuel and often exceed requirements for density, flash point, specific energy, and freeze point [3].

Initially [5], the list of compounds contained the hydrocarbons identified in the samples of the jet fuel cut of biomass-derived fuel obtained at the National Renewable Energy Laboratory. The scope of the project was subsequently expanded to conventional jet fuels and their blends with biofuels [6]. Multiple compounds identified in the works considered in this paper were added to the list, which included 190 hydrocarbons. The number of carbon atoms in molecules was limited to 20 in alkanes and 19 in cyclic compounds. Many of these compounds had at least one cyclohexane or cyclopentane ring. These cyclopentane and cyclohexane hydrocarbons are the subject of this work. The list was further augmented by the compounds exhibiting similar structural patterns. For some of these additional compounds, the experimentally determined thermochemical properties were available. This augmentation allowed us to assess property changes with the molecular structure and gain a better understanding of the performance of the used predictive methods.

We analyzed available data and prediction methods to produce recommendations for enthalpies of formation and vaporization for a range of cyclic compounds. *Ab initio* methods were used to support and supplement the recommendations because, in some cases, the experimental values were either lacking or unreliable. These thermodynamic properties are important and required to predict the enthalpies (heats) of combustion and are necessary for other basic calculations. Hence, this information will be helpful toward the development of future aviation fuels and used in other studies involving these molecules.

To experimentally determine enthalpies of formation and vaporization, a sample of a reasonable purity and a corresponding instrument (calorimeter, ebulliometer, etc.) should be available. For example, the enthalpies of formation of hydrocarbons are typically derived from their accurate energies of combustion. A purity close to 99.9 wt % is needed to obtain the combustion energies suitable for chemical thermodynamic calculations. The purity can sometimes be lower if an isomeric impurity is present. A significant number of high-purity hydrocarbons were synthesized or purified as part of the American Petroleum Institute (API) Research Projects (particularly Projects 45, 58A, and 58B). However, they still represent a relatively small portion of the cyclic compounds found in jet biofuels. Accurate measurements of thermodynamic properties are time-consuming and require significant expertise. National laboratories such as the National Bureau of Standards/National Institute of Standards and Technology (NBS/NIST) and the National Institute for Petroleum and Energy Research (NIPER) made significant experimental contributions to the field. These results formed a framework for the thermodynamics and thermochemistry of hydrocarbons as well as for the development of predictive methods.

Due to the above-mentioned experimental limitations, thermodynamic properties for many compounds considered in this work have not been studied experimentally and must be estimated. The property estimation faces several challenges. First, a significant number of these compounds participate in homologous series, and property consistency along these series should be taken into account. The importance of this factor has been demonstrated, for example, for the vapor pressure of *n*-alkanes [9]. Second, many of these compounds have several aliphatic cycles. The group-type transferability in those cases is questionable, and the performance of the group-contribution methods is degraded as compared to non-cyclic compounds. Finally, the predictions for polysubstituted alicyclic compounds are complicated by the presence of different relative stereo positions of the substituents. *Cis*- and *trans*-isomers can exist for two substituents in a monocylic compound. The situation is more complex for the number of substituents exceeding two or in polycyclic compounds. Each of these challenges is discussed in detail in the following sections.

In this work, we demonstrate that combining experimental results with empirical estimation procedures can facilitate the predictions of the enthalpy of vaporization and enthalpy of formation of alicyclic hydrocarbons found in jet fuels and structurally similar compounds. Significant progress in the *ab initio* methods [10] has made it possible to predict the gas-phase enthalpies of formation for these compounds accurately and include these results in the evaluation.

2. Methods

The values of the enthalpy of formation $\Delta_f H^\circ_m$ and enthalpy of vaporization $\Delta_{vap} H^\circ_m$ were obtained using three approaches. The primary source of this information is experimental data. It was preferred in most cases where these results were available. Group-contribution methods could be used to predict both properties of interest for most of the considered compounds. Finally, the *ab initio* protocol developed earlier [10] allowed us to reliably predict gas-phase enthalpies of formation for multiple compounds. More details are provided in the sections below.

2.1. Experimental data

Enthalpies of vaporization of hydrocarbons can be obtained from direct calorimetric measurements. Alternatively, they can be derived from the temperature-dependent vapor pressure data. Enthalpies of formation of these compounds are typically found using the experimental energies of combustion in a bomb calorimeter. Temperature-dependent chemical equilibrium constants or enthalpies of the other reactions (for example, hydrogenation) are useful to determine $\Delta_f H^\circ_m$ for some groups of compounds.

However, they did not significantly improve the data quality for alicyclic hydrocarbons and, therefore, were not used here.

The original publications were the primary source of experimental data. For some hydrocarbons, the experimental enthalpies of vaporization were evaluated by Majer et al. [11], and these recommendations were adopted in this work. Forziati et al. [12] measured vapor pressure for 60 hydrocarbons using an ebulliometer. If these were the only results that could be used to derive $\Delta_{\mathrm{vap}}H^{\circ}_{\mathrm{m}}$, the following procedure was applied. The critical temperature T_c and pressure p_c were estimated using the Nannoolal-Rarey-Ramjugernath-Cordes (NRRC) method [13,14] implemented in the NIST ThermoData Engine (TDE) v.10.4.6 software [15]. The reported vapor pressures were then fitted with the Wagner equation [16] in the form:

$$\ln(p/p_c) = (1/T_r)(A(1-T_r) + B(1-T_r)^{3/2} + C(1-T_r)^{5/2} + D(1-T_r)^5, \quad (1)$$

where $T_r = T/T_c$. The enthalpies of vaporization were obtained as $RT^2(d\ln p/dT)$ thus assuming the ideal gas phase and neglecting the liquid volume. By comparison of the ebulliometric values with the recommendations [11], the expanded uncertainty (0.95 level of confidence) of these values was estimated to be 0.2 kJ·mol^{-1}.

If multiple publications were available for the enthalpy of vaporization and related properties (vapor pressure, enthalpy of vaporization, liquid heat capacity, etc.) of a compound, the available data were evaluated using TDE.

The experimental enthalpies of formation were derived from the corresponding energies of combustion. If the energies of combustion were available in several sources, these values were weight-averaged using the reported uncertainties. Following Cox and Pilcher [17], some pre-1970 values were corrected with respect to the revised value of the combustion energy of benzoic acid.

All uncertainties reported in this work are expanded uncertainties for 0.95 level of confidence (k = 2).

2.2. *Empirical estimation procedures*

Two empirical approaches were used in this work: the NIST-modified Benson method (MBM) [18] and the incremental method based on a core structure. The former was used to calculate enthalpies of vaporization and formation. In the original publication [18], only acyclic compounds and benzene derivatives were considered. The version implemented in TDE v.10.4.6 and used in this work has additional corrections for the cyclohexane ring at T = 298.15 K equal to 19.0, 17.0, and 5.0 kJ·mol^{-1} for $\Delta_f H^\circ_m$(g), $\Delta_f H^\circ_m$(l), and $\Delta_{vap} H^\circ_m$, respectively. Similar corrections for the cyclopentane ring are 42.0, 40.0, and 6.0 kJ·mol^{-1}, respectively. Additionally, from $\Delta_{vap} H^\circ_m$ = (38.5 ± 0.3) kJ·mol^{-1} of cycloheptane evaluated by TDE [15], we estimated the cycloheptane ring correction for vaporization enthalpy to be 6.5 kJ·mol^{-1}. The corresponding ring corrections were used in the MBM predictions for $\Delta_{vap} H^\circ_m$ for bi- and tricyclic compounds.

An alternative approach is based on multiple incremental changes of a core structure leading to the structure of interest. The required property increments, as well as the property value for the core structure, are determined using available experimental data. This approach was originally outlined by Huffman et al. [19], while the first practical application for multiple compounds that we are aware of was reported in 1987 [20]. An example of this approach is shown in Figure 1. The property P of 1-butyl-4-methylbenzene can be found as

$$P(\text{1-butyl-4-methylbenzene}) = P(\text{PhEt}) + 2\Delta P(\text{H(in CH}_3) \rightarrow \text{CH}_3) + \Delta P(\text{H(aromatic)} \rightarrow \text{CH}_3\text{(aromatic)}) \quad (2)$$

where ΔP are property increments and P(PhEt) is the property of ethylbenzene. In some cases, these increments are mathematically equivalent to those in Benson-like approaches. For example, ΔP(H(in CH_3)→CH_3) is generally equal to ΔP(CH_2–2C).

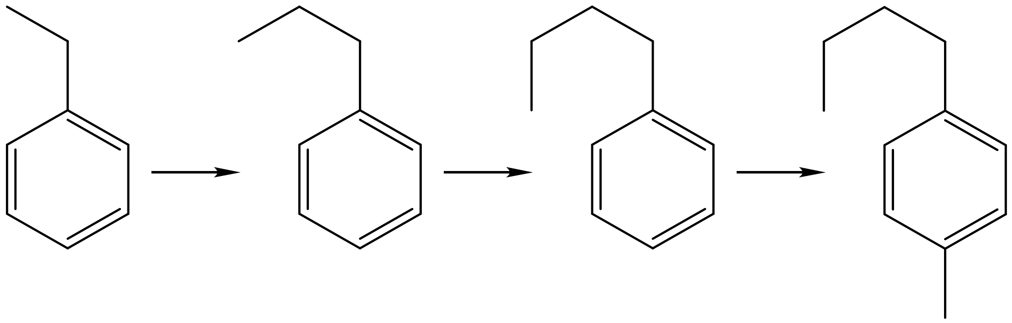

Figure 1. Schematic of a 1-butyl-4-methylbenzene property prediction sequence using ethylbenzene as a core structure.

2.3. *Computations*

The *ab initio* gas-phase enthalpies of formations were obtained using the aLL5 protocol described by Paulechka and Kazakov [10]. The vibrational frequencies were calculated at the B3LYP-D3(BJ)/def2-TZVP theory level. For zero-point vibrational energies (ZPVE), the frequencies were scaled by 0.99. For the thermal part of enthalpy, the scaling factors were 0.960 for hydrogen stretches and 0.985 for all other frequencies. The geometries for the coupled-cluster calculations were optimized at the density-fitted (DF) MP2/aug-cc-pVQZ level of theory. The single-point energy calculations were performed with the 2016 version of local CCSD(T) of Kállay et al. [21,22] and the same basis set. DFT, DF-MP2, and local CCSD(T) calculations were performed with the Gaussian 16 [23], Psi4 [24,25], and MRCC [26,27] software, respectively. Sample input file listings for each step are provided in the Supplementary Information.

For the compounds containing fused or bridged alicyclic rings, the Complete Basis Set (CBS) version of the aLL5 protocol [28] was also used. The extrapolation was based on the local CCSD(T) energies obtained with aug-cc-pVQZ and aug-cc-pV5Z basis sets.

For the molecules exhibiting multiple conformations, the conformational search was performed using the conformer ensemble generation procedure described in detail elsewhere [29]. Briefly, the procedure includes several steps for generating conformer candidates using different generators, validating them, and removing duplicates. The final pool of candidates is obtained using the B3LYP-D3(BJ)/def2-TZVP geometry optimization followed by full vibrational analysis and duplicate removal. The standard enthalpy of formation and entropy were found for each conformer using the rigid rotor/harmonic oscillator model. The enthalpy of formation of a compound was computed as the Gibbs-energy average over the conformer population.

The expanded uncertainty (0.95 level of confidence) of the *ab initio* results was estimated as

$$U(\Delta_f H^\circ_m) = s(1 + \mathbf{nAn}^T)^{1/2} , \tag{3}$$

where s is 2.5 kJ·mol^{-1} and 2.4 kJ·mol^{-1} for aug-cc-pVQZ and CBS versions, respectively, **n** is the row-vector of the atomic type counts in a molecule, and **A** is the scaled covariance matrix [10]. The coefficients of the latter were reported in Supporting Information of Ref. [10]. The atomic types include (C_{sat} + C_{arom}) and H for the considered group of compounds. The uncertainty contributions beyond the original model were discussed in a recent work [29].

3. Results and discussion

To facilitate reporting of the results, the compounds are split into four groups: monocyclic cyclohexanes, monocyclic cyclopentanes, polycyclic compounds, and tetralins and decalins. The numerical values of the enthalpies of vaporization and formation are reported in Tables 1-24. In each table, the experimental and predicted values are followed by the selected (recommended) ones.

The enthalpies of vaporization, experimental or predicted, are available for all liquids. If the experimental liquid-phase $\Delta_f H^\circ_m$ was available, the selected gas-phase value was found as $\Delta_f H^\circ_m(g) = \Delta_f H^\circ_m(l) + \Delta_{vap} H^\circ_m$. If the experimental value was not available, had an uncertainty greater than 3 kJ·mol^{-1}, or had been found to be problematic, the predicted gas-phase $\Delta_f H^\circ_m$ was used to find the selected value of $\Delta_f H^\circ_m(l) = \Delta_f H^\circ_m(g) - \Delta_{vap} H^\circ_m$.

The effective properties for some mixtures of stereoisomers are provided because, in some cases, the routine analytical techniques only provide the total content of all the isomers. To make an estimate, the average value over the specified isomers was found. The largest uncertainty of the individual values was added to the absolute maximum deviation of the individual values from this average to obtain a conservative uncertainty estimate.

3.1. Cyclohexanes

3.1.1. Monoalkylcyclohexanes

Among all compounds considered in this work, monosubstituted *n*-alkylcyclohexanes $C_6H_{11}C_nH_{2n+1}$ are the most studied. Their enthalpies of vaporization are collected in Table 1. For the short-chain homologs, the available high-quality data are used. The predicted values are in excellent agreement with them (Figure 2). At $n = 12$, the experimental value has a large uncertainty, and the MBM estimate is more credible. The expanded uncertainties (0.95 level of confidence) for the predictions are estimated to be 1.5 kJ·mol^{-1}, similar to the experimental uncertainty for n = (6 to 10). Additionally, the enthalpy of vaporization of dodecylcyclohexane ($n = 12$) determined by Fuchs and Peacock [30] using a combination of gas chromatography and calorimetry is consistent with the predicted values and expected linear dependence of the enthalpies of vaporization on the alkyl chain length.

The experimental enthalpies of formation in the liquid phase are available for eight *n*-alkylcyclohexanes (Table 2). They were converted to the gas-phase values (Table 3) using the selected enthalpies of vaporization from Table 1. The *ab initio* values (Table 3) are in excellent agreement with the experimental results (Figure 3); the deviations do not exceed ± 1 kJ·mol^{-1}. The experimental results for ethyl, propyl, butyl, decyl, and dodecylcyclohexanes were fitted by the unweighted least squares method with the equation:

$$\Delta_f H^\circ_m(C_6H_{11}C_nH_{2n+1}(g)) / (\text{kJ·mol}^{-1}) = -130.42 - 20.76n \qquad (4)$$

This equation was used to fill the missing values in Table 3. The reported uncertainties include both the uncertainty of the model and the data scatter. The experimental value for heptylcyclohexane has a large deviation from this prediction and should be discarded. For the compounds with no liquid-phase thermochemical data, $\Delta_f H^\circ_m(l)$ was found by subtracting the selected values in Table 1 from those in Table 3.

The increment per CH_2 group in eq. 4, -20.76 kJ·mol^{-1}, is close to the one for MBM (-20.58 kJ·mol^{-1}), i.e., the MBM alkyl-chain dependence is consistent with the experimental data. However, the MBM values are more negative by (3 to 5) kJ·mol^{-1} except for cyclohexane and methylcyclohexane (Figure 3). A similar problem is observed for the liquid-phase values in Table 2. Therefore, MBM should not be directly used for the enthalpies of formation of *n*-alkylcyclohexanes. However, if one uses ethylcyclohexane as a core structure, the enthalpies of formation can be adequately estimated using the increment $\Delta\Delta_f H(CH_2) = \Delta\Delta_f H(\text{H(in CH}_3) \rightarrow \text{CH}_3)$.

The experimental enthalpies of vaporization are available for three out of five considered isoalkylcyclohexanes. The MBM estimates are within ±1.1 kJ·mol^{-1} of the experimental values (Table 1). Thus, the MBM predictions were used for the remaining (methylbutyl)cyclohexanes. The selected gas-phase enthalpies of formation are taken from the *ab initio* calculations (Table 3). The MBM values of $\Delta_f H^\circ_m$(g) have deviations exceeding 10 kJ·mol^{-1} for some of these compounds. The liquid-phase $\Delta_f H^\circ_m$ were derived from the gas-phase values and enthalpies of vaporization.

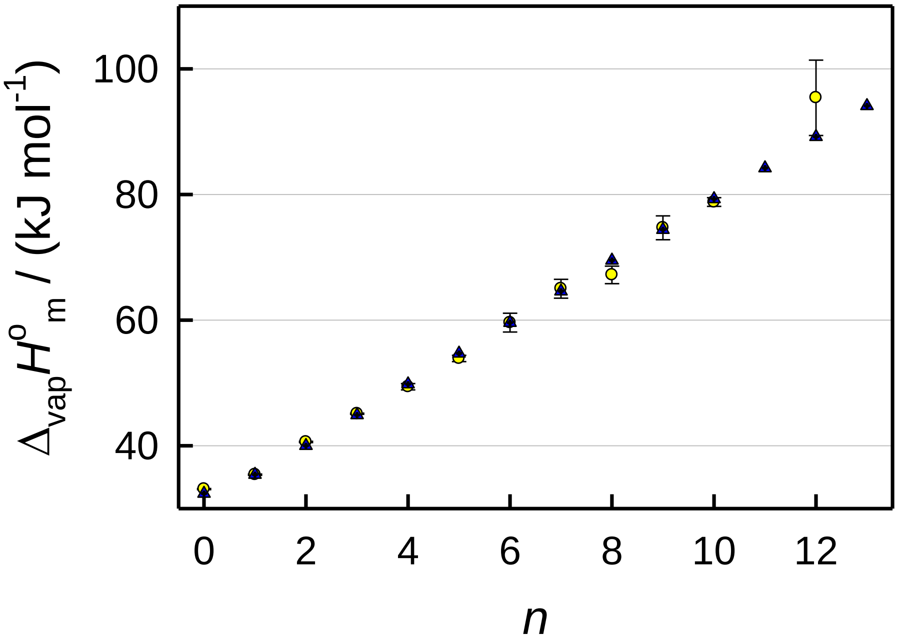

Figure 2. Standard molar enthalpies of vaporization of *n*-alkylcyclohexanes $C_6H_{11}C_nH_{2n+1}$: Comparison of experimental (yellow circles) and predicted by MBM (blue triangles) values

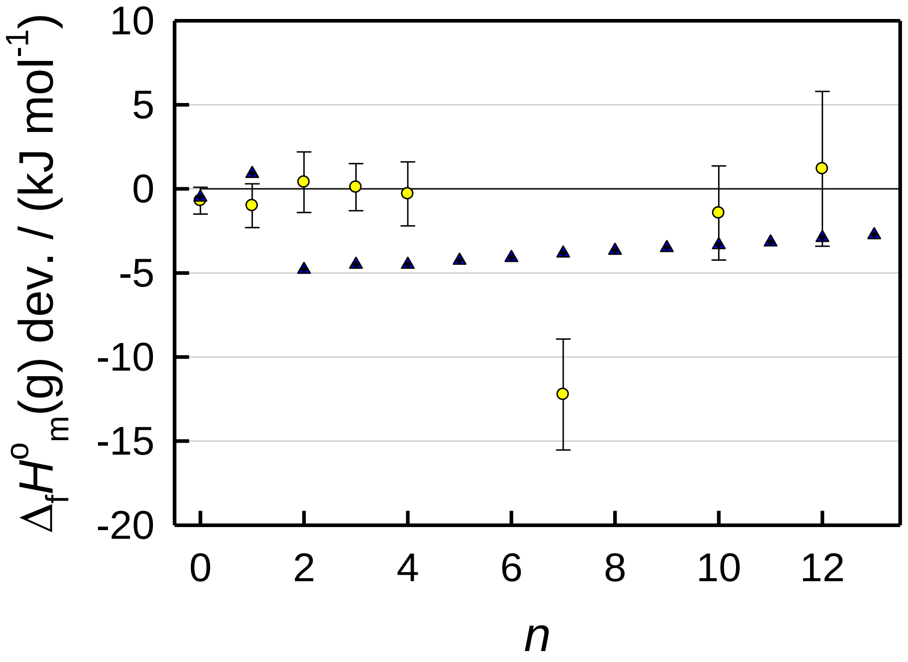

Figure 3. Deviation of standard molar enthalpies of formation of gaseous *n*-alkylcyclohexanes $C_6H_{11}C_nH_{2n+1}$ from the *ab initio* values for *n* = (0 to 4) and eq. 3 for *n* = (5 to 13): experimental (yellow circles) and predicted by MBM (blue triangles) values

Table 1. Standard enthalpies of vaporization $\Delta_{vap}H^{\circ}_{m}$ of monoalkylcyclohexanes at T = 298.15 K [a]

Compound	Alias	CASRN	$\Delta_{vap}H^{\circ}_{m}$ / (kJ·mol^{-1})			
			Experiment	Source	MBM	Selected
cyclohexane	**A.1**	110-82-7	33.1 ± 0.1	11	32.4	33.1 ± 0.1
methylcyclohexane	**A.2**	108-87-2	35.4 ± 0.1	11	35.4	35.4 ± 0.1
ethylcyclohexane	**A.3**	1678-91-7	40.6 ± 0.1	11	40.0	40.6 ± 0.1
propylcyclohexane	**A.4**	1678-92-8	45.1 ± 0.1	11	44.9	45.1 ± 0.1
butylcyclohexane	**A.5**	1678-93-9	49.4 ± 0.5	11	49.8	49.4 ± 0.5
pentylcyclohexane	**A.6**	4292-92-6	53.9 ± 0.5	11	54.7	53.9 ± 0.5
hexylcyclohexane	**A.7**	4292-75-5	59.6 ± 1.5	15	59.6	59.6 ± 1.5
heptylcyclohexane	**A.8**	5617-41-4	65.0 ± 1.5	15	64.6	65.0 ± 1.5
octylcyclohexane	**A.9**	1795-15-9	68.7 ± 1.3	15	69.5	68.7 ± 1.3
nonylcyclohexane	**A.10**	2883-02-5	74.3 ± 1.9	15	74.4	74.3 ± 1.9
decylcyclohexane	**A.11**	1795-16-0	78.8 ± 0.7	31	79.3	78.8 ± 0.7
undecylcyclohexane	**A.12**	54105-66-7			84.2	84.2 ± 1.5
dodecylcyclohexane	**A.13**	1795-17-1	94.3 ± 5.3 (88.9 ± 1.9)[b]	15	89.2	89.2 ± 1.5
tridecylcyclohexane	**A.14**	6006-33-3			94.1	94.1 ± 1.5

(1-methylethyl)cyclohexane	**A.15**	696-29-7	44.0 ± 0.4	11	42.9	44.0 ± 0.4
(1-methylpropyl)cyclohexane	**A.16**	7058-01-7	48.1 ± 0.7	15	48.2	48.1 ± 0.7
(2-methylpropyl)cyclohexane	**A.17**	1678-98-4	47.6 ± 0.5	11	48.2	47.6 ± 0.5
(2-methylbutyl)cyclohexane	**A.18**	54105-77-0			53.5	53.5 ± 1.5
(3-methylbutyl)cyclohexane	**A.19**	54105-76-9			53.1	53.1 ± 1.5

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[a] Expanded uncertainties for 0.95 level of confidence are reported following the ± signs

[b] Fuchs and Peacock [30]

Table 2. Standard enthalpies of formation $\Delta_f H^\circ_m$ of liquid monoalkylcyclohexanes at T = 298.15 K [a]

Compound	Alias	CASRN	$-\Delta_f H^\circ_m(\mathrm{l})$ / (kJ·mol^{-1})			
			Experiment	Source	MBM	Selected
cyclohexane	**A.1**	110-82-7	156.5 ± 0.8	15	156.1	156.5 ± 0.8
methylcyclohexane	**A.2**	108-87-2	190.3 ± 1.3	32,33,17	189.7	190.3 ± 1.3
ethylcyclohexane	**A.3**	1678-91-7	212.1 ± 1.8	33	218.5	212.1 ± 1.8
propylcyclohexane	**A.4**	1678-92-8	237.8 ± 1.4	33,34	244.4	237.8 ± 1.4
butylcyclohexane	**A.5**	1678-93-9	263.1 ± 1.8	33	270.3	263.1 ± 1.8
pentylcyclohexane	**A.6**	4292-92-6			296.2	288.1 ± 2.1
hexylcyclohexane	**A.7**	4292-75-5			322.1	314.6 ± 2.5
heptylcyclohexane	**A.8**	5617-41-4	*353.0 ± 2.9*[b]	32,17	348.0	340.7 ± 2.5
octylcyclohexane	**A.9**	1795-15-9			373.9	365.2 ± 2.5
nonylcyclohexane	**A.10**	2883-02-5			399.8	391.6 ± 3.6
decylcyclohexane	**A.11**	1795-16-0	418.3 ± 2.7	35,36	425.7	418.3 ± 2.7
undecylcyclohexane	**A.12**	54105-66-7			451.5	443.0 ± 2.7[c]
dodecylcyclohexane	**A.13**	1795-17-1	467.6 ± 4.3	32, 17	477.4	467.6 ± 4.3

tridecylcyclohexane	**A.14**	6006-33-3	503.3	494.5 ± 2.8[c]
(1-methylethyl)cyclohexane	**A.15**	696-29-7	252.1	238.9 ± 2.8
(1-methylpropyl)cyclohexane	**A.16**	7058-01-7	275.0	261.4 ± 3.0
(2-methylpropyl)cyclohexane	**A.17**	1678-98-4	275.0	268.8 ± 3.0
(2-methylbutyl)cyclohexane	**A.18**	54105-77-0	298.0	292.9 ± 3.4[c]
(3-methylbutyl)cyclohexane	**A.19**	54105-76-9	300.9	294.4 ± 3.4[c]

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[a] Expanded uncertainties for 0.95 level of confidence are reported following the ± signs

[b] This value is an outlier

[c] Enthalpies of vaporization are estimated using MBM

Table 3. Standard enthalpies of formation $\Delta_f H^\circ_m$ of gaseous monoalkylcyclohexanes at T = 298.15 K [a]

Compound	Alias	CASRN	$-\Delta_f H^\circ_m(g)$ / (kJ·mol^{-1})			
			Experiment	MBM	*ab initio*	Selected
cyclohexane	**A.1**	110-82-7	123.4 ± 0.8	123.2	122.7 ± 2.6	123.4 ± 0.8
methylcyclohexane	**A.2**	108-87-2	154.9 ± 1.3	153.0	153.9 ± 2.7	154.9 ± 1.3
ethylcyclohexane	**A.3**	1678-91-7	171.5 ± 1.8	176.7	171.9 ± 2.7	171.5 ± 1.8
propylcyclohexane	**A.4**	1678-92-8	192.7 ± 1.4	197.3	192.8 ±2.8	192.7 ± 1.4
butylcyclohexane	**A.5**	1678-93-9	213.7 ± 1.9	217.9	213.4 ±2.9	213.7 ± 1.9
pentylcyclohexane	**A.6**	4292-92-6		238.5		234.2 ± 2.0[d]
hexylcyclohexane	**A.7**	4292-75-5		259.1		255.0 ± 2.0[d]
heptylcyclohexane	**A.8**	5617-41-4	*288.0 ± 3.3* [b]	279.6		275.8 ± 2.0[d]
octylcyclohexane	**A.9**	1795-15-9		300.2		296.5 ± 2.0[d]
nonylcyclohexane	**A.10**	2883-02-5		320.8		317.3 ± 2.1[d]
decylcyclohexane	**A.11**	1795-16-0	339.5 ± 2.8	341.4		339.5 ± 2.8
undecylcyclohexane	**A.12**	54105-66-7		362.0		358.8 ± 2.2[d]
dodecylcyclohexane	**A.13**	1795-17-1	378.4 ± 4.6 [c]	382.5		378.4 ± 4.6

tridecylcyclohexane	**A.14**	6006-33-3	403.1		400.4 ± 2.4[d]
(1-methylethyl)cyclohexane	**A.15**	696-29-7	206.6	194.9 ± 2.8	194.9 ± 2.8
(1-methylpropyl)cyclohexane	**A.16**	7058-01-7	224.0	213.3 ± 2.9	213.3 ± 2.9
(2-methylpropyl)cyclohexane	**A.17**	1678-98-4	224.0	221.2 ± 3.0	221.2 ± 3.0
(2-methylbutyl)cyclohexane	**A.18**	54105-77-0	241.5	239.4 ± 3.1	239.4 ± 3.1
(3-methylbutyl)cyclohexane	**A.19**	54105-76-9	244.6	241.3 ± 3.0	241.3 ± 3.0

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[a] Expanded uncertainties for 0.95 level of confidence are reported following the ± signs

[b] This value is an outlier

[c] Enthalpies of vaporization are estimated using MBM

[d] These values were estimated using eq. 1.

3.1.2. Dialkylcyclohexanes

The dataset includes all dimethyl and ethylmethylcyclohexanes as well as 1,2-diethylcyclohexanes and 1-methyl-2-propylcyclohexanes. Two latter groups are used to analyze the property changes with the alkyl chain length. The number of C atoms in a molecule is limited to 11.

Reliable experimental enthalpies of vaporization are available for all dimethylcyclohexanes and cis-1-ethyl-3-methylcyclohexane (Table 4). The MBM values are within ± 1.1 kJ·mol^{-1} of the experimental counterparts. Therefore, the MBM predictions were used to fill the gaps in the selected values.

The reliable enthalpies of formation for these compounds in the liquid phase were reported by Johnson et al. [37] and Good [34] (Table 5). The *ab initio* values are in good agreement with the gas-phase values derived from the experimental data (Table 6), with the deviations not exceeding ± 1.6 kJ·mol^{-1}. The selected values are based either on the experimental data or *ab initio* values if the former were not available. The experimental liquid-phase $\Delta_f H^\circ_m$ of *p*-menthane [38] deviating from the *ab initio*-based value by over 20 kJ·mol^{-1} was rejected.

1,2-, 1,3-, and 1,4-dialkylcyclohexanes have two isomers, *cis* and *trans*, differing by the relative positions of the alkyls with respect to the cyclohexyl ring. MBM or any other method using only connectivity information does not distinguish between the two. The maximum difference between the enthalpies of vaporization of the isomers is 1.3 kJ·mol^{-1} (for 1,2-dimethylcyclohexanes). The prediction error of this magnitude is acceptable. The differences between $\Delta_f H^\circ_m(g)$ are more substantial and alternate with the alkyl positions. They are between (6 and 8) kJ·mol^{-1} for the dimethyl compounds and decrease with the alkyl chain length.

For dimethylcyclohexanes, MBM accurately predicts $\Delta_f H^\circ_m(g)$ for one of the isomers (within ± 3 kJ·mol^{-1}). However, the error is between –(5 to 11) kJ·mol^{-1} for the other isomer. The prediction error further increases for ethylmethylcyclohexanes except for the *cis*-1,3- and *trans*-1,4-isomers, where the error is still close to –3 kJ·mol^{-1}. This behavior is similar to the abovementioned trend for *n*-alkylcyclohexanes (Figure 3). One would expect that the predictions for the long-chain dialkylcyclohexanes work if a core structure with an ethyl substituent is used. This expectation is consistent with the fact that the deviations between MBM and selected values do not significantly change between 1-ethyl-2-methyl- and 1-methyl-2-propylcyclohexanes.

3.1.3. Trialkylcyclohexanes

The experimental $\Delta_{\text{vap}}H^{\circ}_{\text{m}}$ is only available for 1,1,3-trimethylcyclohexane. Considering the good performance of MBM for the vaporization enthalpies of mono- and dialkylcyclohexanes, the values from this method were accepted for all other compounds. We are not aware of any experimental enthalpies of formation for these compounds. The MBM gas-phase enthalpies of formation agree with the more reliable *ab initio* predictions for some isomeric trimethylcyclohexanes. However, the deviations up to ±13 kJ·mol^{-1} are also observed. The selected values are based on the *ab initio* gas-phase enthalpies of formation and the enthalpies of vaporization from MBM.

Table 4. Standard enthalpies of vaporization $\Delta_{vap}H^{\circ}_{m}$ of dialkylcyclohexanes at T = 298.15 K [a]

Compound	Alias	CASRN	$\Delta_{vap}H^{\circ}_{m}$ / (kJ·mol^{-1})			
			Experiment	Source	MBM	Selected
1,1-dimethylcyclohexane	**B.1**	590-66-9	38.0 ± 0.1	11	37.8	38.0 ± 0.1
cis-1,2-dimethylcyclohexane	**B.2**	2207-01-4	39.7 ± 0.1	11	38.3	39.7 ± 0.1
trans-1,2-dimethylcyclohexane	**B.3**	6876-23-9	38.4 ± 0.1	11	38.3	38.4 ± 0.1
1,2-dimethylcyclohexane[b]	**B.4**	583-57-3			38.3	39.1 ± 0.7
cis-1,3-dimethylcyclohexane	**B.5**	638-04-0	38.3 ± 0.1	11	38.3	38.3 ± 0.1
trans-1,3-dimethylcyclohexane	**B.6**	2207-03-6	39.2 ± 0.1	11	38.3	39.2 ± 0.1
1,3-dimethylcyclohexane[b]	**B.7**	591-21-9			38.3	38.8 ± 0.6
cis-1,4-dimethylcyclohexane	**B.8**	624-29-3	39.1 ± 0.1	11	38.3	39.1 ± 0.1
trans-1,4-dimethylcyclohexane	**B.9**	2207-04-7	38.0 ± 0.1	11	38.3	38.0 ± 0.1
1,4-dimethylcyclohexane[b]	**B.10**	589-90-2			38.3	38.6 ± 0.6

1-ethyl-1-methylcyclohexane	**B.11**	4926-90-3			42.4	42.4 ± 1.5
cis-1-ethyl-2-methylcyclohexane	**B.12**	4923-77-7			42.9	42.9 ± 1.5
trans-1-ethyl-2-methylcyclohexane	**B.13**	4923-78-8			42.9	42.9 ± 1.5
1-ethyl-2-methylcyclohexane[b]	**B.14**	3728-54-9			42.9	42.9 ± 1.5
cis-1-ethyl-3-methylcyclohexane	**B.15**	19489-10-2	43.1 ± 0.3	15	42.9	43.1 ± 0.3
trans-1-ethyl-3-methylcyclohexane	**B.16**	4926-76-5			42.9	42.9 ± 1.5
1-ethyl-3-methylcyclohexane[b]	**B.17**	3728-55-0			42.9	42.9 ± 1.5
cis-1-ethyl-4-methylcyclohexane	**B.18**	4926-78-7			42.9	42.9 ± 1.5
trans-1-ethyl-4-methylcyclohexane	**B.19**	6236-88-0			42.9	42.9 ± 1.5
1-ethyl-4-methylcyclohexane[b]	**B.20**	3728-56-1			42.9	42.9 ± 1.5
cis-1,2-diethylcyclohexane	**B.21**	824-43-1			47.5	47.5 ± 1.5
trans-1,2-diethylcyclohexane	**B.22**	13990-95-9			47.5	47.5 ± 1.5

1,2-diethylcyclohexane[b]	**B.23**	3642-13-5	47.5	47.5 ± 1.5
cis-1-methyl-2-propylcyclohexane	**B.24**	4926-71-0	47.8	47.8 ± 1.5
trans-1-methyl-2-propylcyclohexane	**B.25**	42806-77-9	47.8	47.8 ± 1.5
1-methyl-2-propylcyclohexane[b]	**B.26**	4291-79-6	47.8	47.8 ± 1.5
cis-1-methyl-4-isopropylcyclohexane (*cis*-*p*-menthane)	**B.27**	6069-98-3	45.9	45.9 ± 1.5
trans-1-methyl-4-isopropylcyclohexane (*trans*-*p*-menthane)	**B.28**	1678-82-6	45.9	45.9 ± 1.5
1-methyl-4-isopropylcyclohexane (*p*-menthane)[b]	**B.29**	99-82-1	45.9	45.9 ± 1.5

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[a] Expanded uncertainties for 0.95 level of confidence are reported following the ± signs

[b] Mixture of stereoisomers

Table 5. Standard enthalpies of formation $\Delta_f H^\circ_m$ of liquid dialkylcyclohexanes at T = 298.15 K [a]

Compound	Alias	CASRN	$-\Delta_f H^\circ_m$(l) / (kJ·mol^{-1})			
			Experiment	Source	MBM	Selected
1,1-dimethylcyclohexane	**B.1**	590-66-9	218.7 ± 2.3	37	224.4	218.7 ± 2.3
cis-1,2-dimethylcyclohexane	**B.2**	2207-01-4	211.8 ± 2.2	37	221.2	211.8 ± 2.2
trans-1,2-dimethylcyclohexane	**B.3**	6876-23-9	218.2 ± 2.2	37	221.2	218.2 ± 2.2
1,2-dimethylcyclohexane[b]	**B.4**	583-57-3			221.2	215.0 ± 5.4
cis-1,3-dimethylcyclohexane	**B.5**	638-04-0	222.9 ± 2.1	37	221.2	222.9 ± 2.1
trans-1,3-dimethylcyclohexane	**B.6**	2207-03-6	215.7 ± 2.1	37	221.2	215.7 ± 2.1
1,3-dimethylcyclohexane[b]	**B.7**	591-21-9			221.2	219.3 ± 5.7
cis-1,4-dimethylcyclohexane	**B.8**	624-29-3	215.6 ± 2.1	37	221.2	215.6 ± 2.1
trans-1,4-dimethylcyclohexane	**B.9**	2207-04-7	222.4 ± 2.1	37	221.2	222.4 ± 2.1
1,4-dimethylcyclohexane[b]	**B.10**	589-90-2			221.2	219.0 ± 2.1

1-ethyl-1-methylcyclohexane	**B.11**	4926-90-3	240.2 ± 2.2	34	254.7	240.2 ± 2.2
cis-1-ethyl-2-methylcyclohexane	**B.12**	4923-77-7	236.2 ± 2.2	34	252.1	236.2 ± 2.2
trans-1-ethyl-2-methylcyclohexane	**B.13**	4923-78-8	240.2 ± 2.1	34	252.1	240.2 ± 2.1
1-ethyl-2-methylcyclohexane[b]	**B.14**	3728-54-9			252.1	238.2 ± 4.2
cis-1-ethyl-3-methylcyclohexane	**B.15**	19489-10-2	246.7 ± 2.5	34	252.1	246.7 ± 2.5
trans-1-ethyl-3-methylcyclohexane	**B.16**	4926-76-5			252.1	239.0 ± 3.2
1-ethyl-3-methylcyclohexane[b]	**B.17**	3728-55-0			252.1	242.9 ± 7.0
cis-1-ethyl-4-methylcyclohexane	**B.18**	4926-78-7	239.0 ± 2.3	34	252.1	239.0 ± 2.3
trans-1-ethyl-4-methylcyclohexane	**B.19**	6236-88-0	246.4 ± 2.1	34	252.1	246.4 ± 2.1
1-ethyl-4-methylcyclohexane[b]	**B.20**	3728-56-1			252.1	242.7 ± 6.0
cis-1,2-diethylcyclohexane	**B.21**	824-43-1			281.0	258.9 ± 3.3
trans-1,2-diethylcyclohexane	**B.22**	13990-95-9			281.0	261.3 ± 3.3

1,2-diethylcyclohexane[b]	**B.23**	3642-13-5			281.0	260.1 ± 4.5
cis-1-methyl-2-propylcyclohexane	**B.24**	4926-71-0			278.0	261.5 ± 3.3
trans-1-methyl-2-propylcyclohexane	**B.25**	42806-77-9			278.0	266.2 ± 3.3
1-methyl-2-propylcyclohexane[b]	**B.26**	4291-79-6			278.0	263.9 ± 5.6
cis-1-methyl-4-isopropylcyclohexane (*cis*-*p*-menthane)	**B.27**	6069-98-3			285.7	265.5 ± 3.3
trans-1-methyl-4-isopropylcyclohexane (*trans*-*p*-menthane)	**B.28**	1678-82-6			285.7	272.4 ± 3.3
1-methyl-4-isopropylcyclohexane (*p*-menthane)[b]	**B.29**	99-82-1	*293.8 ± 6.3* [c]	38	285.7	268.9 ± 6.6

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[a] Expanded uncertainties for 0.95 level of confidence are reported following the ± signs

[b] Mixture of stereoisomers

[c] This value is an outlier

Table 6. Standard enthalpies of formation $\Delta_f H^\circ_m$ of gaseous dialkylcyclohexanes at T = 298.15 K [a]

Compound	Alias	CASRN	$-\Delta_f H^\circ_m$(g) / (kJ·mol^{-1})			
			Experiment	MBM	*ab initio*	Selected
1,1-dimethylcyclohexane	**B.1**	590-66-9	180.7 ± 2.3	186.6	181.9 ± 2.7	180.7 ± 2.3
cis-1,2-dimethylcyclohexane	**B.2**	2207-01-4	172.1 ± 2.2	182.9	173.2 ± 2.7	172.1 ± 2.2
trans-1,2-dimethylcyclohexane	**B.3**	6876-23-9	179.8 ± 2.2	182.9	180.8 ± 2.7	179.8 ± 2.2
1,2-dimethylcyclohexane[b]	**B.4**	583-57-3		182.9		176.0 ± 6.1
cis-1,3-dimethylcyclohexane	**B.5**	638-04-0	183.5 ± 2.1	182.9	185.1 ± 2.7	183.5 ± 2.1
trans-1,3-dimethylcyclohexane	**B.6**	2207-03-6	177.5 ± 2.1	182.9	176.9 ± 2.7	177.5 ± 2.1
1,3-dimethylcyclohexane[b]	**B.7**	591-21-9		182.9		180.5 ± 5.1
cis-1,4-dimethylcyclohexane	**B.8**	624-29-3	176.6 ± 2.1	182.9	177.1 ± 2.7	176.6 ± 2.1
trans-1,4-dimethylcyclohexane	**B.9**	2207-04-7	184.6 ± 2.1	182.9	184.9 ± 2.7	184.6 ± 2.1
1,4-dimethylcyclohexane[b]	**B.10**	589-90-2		182.9		180.6 ± 6.1

1-ethyl-1-methylcyclohexane	**B.11**	4926-90-3	197.8 ± 2.7 [c]	210.3	197.3 ± 2.8	197.8 ± 2.7
cis-1-ethyl-2-methylcyclohexane	**B.12**	4923-77-7	193.3 ± 2.7 [c]	206.6	192.6 ± 2.8	193.3 ± 2.7
trans-1-ethyl-2-methylcyclohexane	**B.13**	4923-78-8	197.3 ± 2.6 [c]	206.6	197.3 ± 2.8	197.3 ± 2.6
1-ethyl-2-methylcyclohexane[b]	**B.14**	3728-54-9		206.6		195.3 ± 4.7
cis-1-ethyl-3-methylcyclohexane	**B.15**	19489-10-2	203.6 ± 2.5	206.6	203.5 ± 2.8	203.6 ± 2.5
trans-1-ethyl-3-methylcyclohexane	**B.16**	4926-76-5		206.6	196.1 ± 2.8	196.1 ± 2.8
1-ethyl-3-methylcyclohexane[b]	**B.17**	3728-55-0		206.6		199.8 ± 6.5
cis-1-ethyl-4-methylcyclohexane	**B.18**	4926-78-7	196.1 ± 2.7 [c]	206.6	196.1 ± 2.8	196.1 ± 2.7
trans-1-ethyl-4-methylcyclohexane	**B.19**	6236-88-0	203.5 ± 2.6 [c]	206.6	204.4 ± 2.8	203.5 ± 2.6
1-ethyl-4-methylcyclohexane[b]	**B.20**	3728-56-1		206.6		199.8 ± 6.4
cis-1,2-diethylcyclohexane	**B.21**	824-43-1		230.3	211.4 ± 2.9	211.4 ± 2.9
trans-1,2-diethylcyclohexane	**B.22**	13990-95-9		230.3	213.8 ± 2.9	213.8 ± 2.9

1,2-diethylcyclohexane[b]	**B.23**	3642-13-5		230.3		212.6 ± 4.1
cis-1-methyl-2-propylcyclohexane	**B.24**	4926-71-0		227.2	213.7 ± 2.9	213.7 ± 2.9
trans-1-methyl-2-propylcyclohexane	**B.25**	42806-77-9		227.2	218.4 ± 2.9	218.4 ± 2.9
1-methyl-2-propylcyclohexane[b]	**B.26**	4291-79-6		227.2		216.1 ± 5.2
cis-1-methyl-4-isopropylcyclohexane (*cis*-*p*-menthane)	**B.27**	6069-98-3		236.4	219.6 ± 2.9	219.6 ± 2.9
trans-1-methyl-4-isopropylcyclohexane (*trans*-*p*-menthane)	**B.28**	1678-82-6		236.4	226.5 ± 2.9	226.5 ± 2.9
1-methyl-4-isopropylcyclohexane (*p*-menthane)[b]	**B.29**	99-82-1	*247.9 ± 6.5* [c,d]	236.4		223.0 ± 6.4

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[a] Expanded uncertainties for 0.95 level of confidence are reported following the ± signs

[b] Mixture of stereoisomers

[c] Experimental liquid-phase enthalpy of formation is combined with the enthalpy of vaporization estimated by MBM

[d] This value is an outlier

315 Table 7. Standard enthalpies of vaporization $\Delta_{vap}H^{\circ}_{m}$ of trialkylcyclohexanes at T = 298.15 K [a]

Compound	Alias	CASRN	$\Delta_{vap}H^{\circ}_{m}$ / (kJ·mol^{-1})			
			Experiment	Source	MBM	Selected
1,1,2-trimethylcyclohexane	**C.1**	7094-26-0			40.8	40.8 ± 1.5
1,1,3-trimethylcyclohexane	**C.2**	3073-66-3	40.2 ± 0.2	12	40.0	40.2 ± 0.2
1,1,4-trimethylcyclohexane	**C.3**	7094-27-1			40.8	40.8 ± 1.5
(1α,2β,3α)-1,2,3-trimethylcyclohexane	**C.4**	1678-81-5			41.3	41.3 ± 1.5
(1α,2α,3β)-1,2,3-trimethylcyclohexane	**C.5**	7667-55-2			41.3	41.3 ± 1.5
(1α,2α,3α)-1,2,3-trimethylcyclohexane	**C.6**	1839-88-9			41.3	41.3 ± 1.5
1,2,3-trimethylcyclohexane[b]	**C.7**	1678-97-3			41.3	41.3 ± 1.5
(1α,2β,4β)-1,2,4-trimethylcyclohexane	**C.8**	7667-60-9			41.3	41.3 ± 1.5
(1α,2β,4α)-1,2,4-trimethylcyclohexane	**C.9**	7667-59-6			41.3	41.3 ± 1.5
(1α,2α,4α)-1,2,4-trimethylcyclohexane	**C.10**	1678-80-4			41.3	41.3 ± 1.5
(1α,2α,4β)-1,2,4-trimethylcyclohexane	**C.11**	7667-58-5			41.3	41.3 ± 1.5

1,2,4-trimethylcyclohexane[b]	**C.12**	2234-75-5	41.3	41.3 ± 1.5
(1α,3α,5α)-1,3,5-trimethylcyclohexane	**C.13**	1795-27-3	41.3	41.3 ± 1.5
(1α,3α,5β)-1,3,5-trimethylcyclohexane	**C.14**	1795-26-2	41.3	41.3 ± 1.5
1,3,5-trimethylcyclohexane[b]	**C.15**	1839-63-0	41.3	41.3 ± 1.5
cis-1-ethyl-1,3-dimethylcyclohexane	**C.16**	62238-31-7	44.5	44.5 ± 1.5
trans-1-ethyl-1,3-dimethylcyclohexane	**C.17**	62238-29-3	44.5	44.5 ± 1.5
1-ethyl-1,3-dimethylcyclohexane[b]	**C.18**	91351-88-1	44.5	44.5 ± 1.5
(1α,2α,3β)-2-ethyl-1,3-dimethylcyclohexane	**C.19**	80408-40-8	45.9	45.9 ± 1.5
(1α,2α,3α)-2-ethyl-1,3-dimethylcyclohexane	**C.20**	80408-39-5	45.9	45.9 ± 1.5
(1α,2β,3α)-2-ethyl-1,3-dimethylcyclohexane	**C.21**	80408-38-4	45.9	45.9 ± 1.5
2-ethyl-1,3-dimethylcyclohexane[b]	**C.22**	7045-67-2	45.9	45.9 ± 1.5

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[a] Expanded uncertainties for 0.95 level of confidence are reported following the ± signs

[b] mixture of stereoisomers

Table 8. Standard enthalpies of formation $\Delta_f H^\circ_m$ of liquid trialkylcyclohexanes at T = 298.15 K [a]

Compound	Alias	CASRN	$-\Delta_f H^\circ_m(\mathrm{l})$ / (kJ·mol^{-1})	
			MBM	Selected
1,1,2-trimethylcyclohexane	**C.1**	7094-26-0	259.4	245.5 ± 3.2
1,1,3-trimethylcyclohexane	**C.2**	3073-66-3	252.0	253.3 ± 2.8
1,1,4-trimethylcyclohexane	**C.3**	7094-27-1	259.4	253.6 ± 3.2
(1α,2β,3α)-1,2,3-trimethylcyclohexane	**C.4**	1678-81-5	256.8	246.9 ± 3.2
(1α,2α,3β)-1,2,3-trimethylcyclohexane	**C.5**	7667-55-2	256.8	241.1 ± 3.2
(1α,2α,3α)-1,2,3-trimethylcyclohexane	**C.6**	1839-88-9	256.8	241.4 ± 3.2
1,2,3-trimethylcyclohexane[b]	**C.7**	1678-97-3	256.8	243.1 ± 6.8
(1α,2β,4β)-1,2,4-trimethylcyclohexane	**C.8**	7667-60-9	256.8	253.4 ± 3.2
(1α,2β,4α)-1,2,4-trimethylcyclohexane	**C.9**	7667-59-6	256.8	245.1 ± 3.2
(1α,2α,4α)-1,2,4-trimethylcyclohexane	**C.10**	1678-80-4	256.8	246.1 ± 3.2
(1α,2α,4β)-1,2,4-trimethylcyclohexane	**C.11**	7667-58-5	256.8	245.6 ± 3.2

1,2,4-trimethylcyclohexane[b]	**C.12**	2234-75-5	256.8	247.6 ± 8.8
(1α,3α,5α)-1,3,5-trimethylcyclohexane	**C.13**	1795-27-3	256.8	257.4 ± 3.2
(1α,3α,5β)-1,3,5-trimethylcyclohexane	**C.14**	1795-26-2	256.8	249.4 ± 3.2
1,3,5-trimethylcyclohexane[b]	**C.15**	1839-63-0	256.8	253.4 ± 7.0
cis-1-ethyl-1,3-dimethylcyclohexane	**C.16**	62238-31-7	280.8	273.1 ± 3.3
trans-1-ethyl-1,3-dimethylcyclohexane	**C.17**	62238-29-3	280.8	273.6 ± 3.3
1-ethyl-1,3-dimethylcyclohexane[b]	**C.18**	91351-88-1	280.8	273.3 ± 3.5
(1α,2α,3β)-2-ethyl-1,3-dimethylcyclohexane	**C.19**	80408-40-8	285.7	263.2 ± 3.3
(1α,2α,3α)-2-ethyl-1,3-dimethylcyclohexane	**C.20**	80408-39-5	285.7	260.0 ± 3.3
(1α,2β,3α)-2-ethyl-1,3-dimethylcyclohexane	**C.21**	80408-38-4	285.7	268.8 ± 3.3
2-ethyl-1,3-dimethylcyclohexane[b]	**C.22**	7045-67-2	285.7	264.0 ± 7.8

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[a] Expanded uncertainties for 0.95 level of confidence are reported following the ± signs

[b] mixture of stereoisomers

Table 9. Standard enthalpies of formation $\Delta_f H^\circ_m$ of gaseous trialkylcyclohexanes at T = 298.15 K [a]

Compound	Alias	CASRN	$-\Delta_f H^\circ_m$(g) / (kJ·mol^{-1})		
			MBM	*ab initio*	Selected
1,1,2-trimethylcyclohexane	**C.1**	7094-26-0	216.5	204.7 ± 2.8	204.7 ± 2.8
1,1,3-trimethylcyclohexane	**C.2**	3073-66-3	210.1	213.1 ± 2.8	213.1 ± 2.8
1,1,4-trimethylcyclohexane	**C.3**	7094-27-1	216.5	212.8 ± 2.8	212.8 ± 2.8
(1α,2β,3α)-1,2,3-trimethylcyclohexane	**C.4**	1678-81-5	212.7	205.6 ± 2.8	205.6 ± 2.8
(1α,2α,3β)-1,2,3-trimethylcyclohexane	**C.5**	7667-55-2	212.7	199.8 ± 2.8	199.8 ± 2.8
(1α,2α,3α)-1,2,3-trimethylcyclohexane	**C.6**	1839-88-9	212.7	200.1 ± 2.8	200.1 ± 2.8
1,2,3-trimethylcyclohexane[b]	**C.7**	1678-97-3	212.7		201.8 ± 6.6
(1α,2β,4β)-1,2,4-trimethylcyclohexane	**C.8**	7667-60-9	212.7	212.1 ± 2.8	212.1 ± 2.8
(1α,2β,4α)-1,2,4-trimethylcyclohexane	**C.9**	7667-59-6	212.7	203.8 ± 2.8	203.8 ± 2.8
(1α,2α,4α)-1,2,4-trimethylcyclohexane	**C.10**	1678-80-4	212.7	204.8 ± 2.8	204.8 ± 2.8
(1α,2α,4β)-1,2,4-trimethylcyclohexane	**C.11**	7667-58-5	212.7	204.3 ± 2.8	204.3 ± 2.8

1,2,4-trimethylcyclohexane[b]	**C.12**	2234-75-5	212.7		206.3 ± 8.7
(1α,3α,5α)-1,3,5-trimethylcyclohexane	**C.13**	1795-27-3	212.7	216.1 ± 2.8	216.1 ± 2.8
(1α,3α,5β)-1,3,5-trimethylcyclohexane	**C.14**	1795-26-2	212.7	208.1 ± 2.8	208.1 ± 2.8
1,3,5-trimethylcyclohexane[b]	**C.15**	1839-63-0			212.1 ± 6.8
cis-1-ethyl-1,3-dimethylcyclohexane	**C.16**	62238-31-7	233.8	228.6 ± 2.9	228.6 ± 2.9
trans-1-ethyl-1,3-dimethylcyclohexane	**C.17**	62238-29-3	233.8	229.1 ± 2.9	229.1 ± 2.9
1-ethyl-1,3-dimethylcyclohexane[b]	**C.18**	91351-88-1	233.8		228.8 ± 3.2
(1α,2α,3β)-2-ethyl-1,3-dimethylcyclohexane	**C.19**	80408-40-8	236.4	217.3 ± 2.9	217.3 ± 2.9
(1α,2α,3α)-2-ethyl-1,3-dimethylcyclohexane	**C.20**	80408-39-5	236.4	214.1 ± 2.9	214.1 ± 2.9
(1α,2β,3α)-2-ethyl-1,3-dimethylcyclohexane	**C.21**	80408-38-4	236.4	222.9 ± 2.9	222.9 ± 2.9
2-ethyl-1,3-dimethylcyclohexane[b]	**C.22**	7045-67-2	236.4		218.1 ± 7.7

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[a] Expanded uncertainties for 0.95 level of confidence are reported following the ± signs

[b] mixture of stereoisomers

3.2. Cyclopentanes

3.2.1. Monoalkylcyclopentanes

The enthalpies of vaporization of monoalkylcyclopentanes are collected in Table 10. For the short-chain homologs, the predicted values are in excellent agreement with the high-quality experimental data. For decylcyclopentane, the ebulliometric data in the temperature range (455 to 552) K were reported by Camin et al. [39] and the smoothed vapor-pressure data in a range of (359 to 411) K were published in the API Research Project 42 report [40]. The ebulliometric results extrapolated using eq. 1 are higher than the low-temperature ones by about 12 %. As a result, the enthalpy of vaporization at T = 298.15 K, (71.9 ± 4.3) kJ·mol^{-1}, evaluated by TDE using these two sources has a relatively high uncertainty. A similar uncertainty can be expected if the vaporization enthalpy derived from the ebulliometric data is extrapolated to T = 298.15 K using estimated $\Delta_{\mathrm{vap}}C_p$ [41]. Therefore, the experimental $\Delta_{\mathrm{vap}}H_{\mathrm{m}}$ was rejected for this compound in favor of the MBM estimate.

The experimental enthalpies of formation in the liquid phase have been reported for cyclopentane through propylcyclopentane and decylcyclopentane (Table 11). For these compounds, the available experimental data were used to derive the gas-phase enthalpies of formation (Table 12). As for alkylcyclohexanes, the *ab initio* values (Table 12) are within ±1 kJ·mol^{-1} of the experimental results (Figure 4). The experimental results for methyl-, ethyl-, propyl-, and decylcyclopentanes were fitted by the unweighted least squares method with the equation:

$$\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}(\mathrm{C_5H_9C}_n\mathrm{H}_{2n+1}(\mathrm{g}))\ /\ (\mathrm{kJ\cdot mol^{-1}}) = -86.03 - 20.56n \qquad (5)$$

which, in turn, was used to fill the missing values in Table 12. The expanded uncertainties derived from the regression of (1.0 to 1.5) kJ·mol^{-1} appear overly optimistic. They were replaced by the estimate of 3.0 kJ·mol^{-1}, which is close to the uncertainty of the *ab initio* values.

The MBM values for the gas phase are too positive by about 4 $kJ \cdot mol^{-1}$ except for cyclopentane and methylcyclopentane (Figure 4). For the compounds with no liquid-phase thermochemical data, $\Delta_f H^\circ_m(l)$ were found by subtracting the selected values in Table 10 from those in Table 12. The liquid-phase MBM values again systematically deviate from the experimental data or predictions based on eq. 5.

The enthalpy of vaporization of (1-methylethyl)cyclopentane is the only experimental result for isoalkylcyclopentanes. The *ab initio* gas-phase $\Delta_f H^\circ_m$ of isoalkylcyclopentanes (Table 12) were combined with the selected vaporization enthalpies (Table 10) to obtain the liquid-phase values (Table 11).

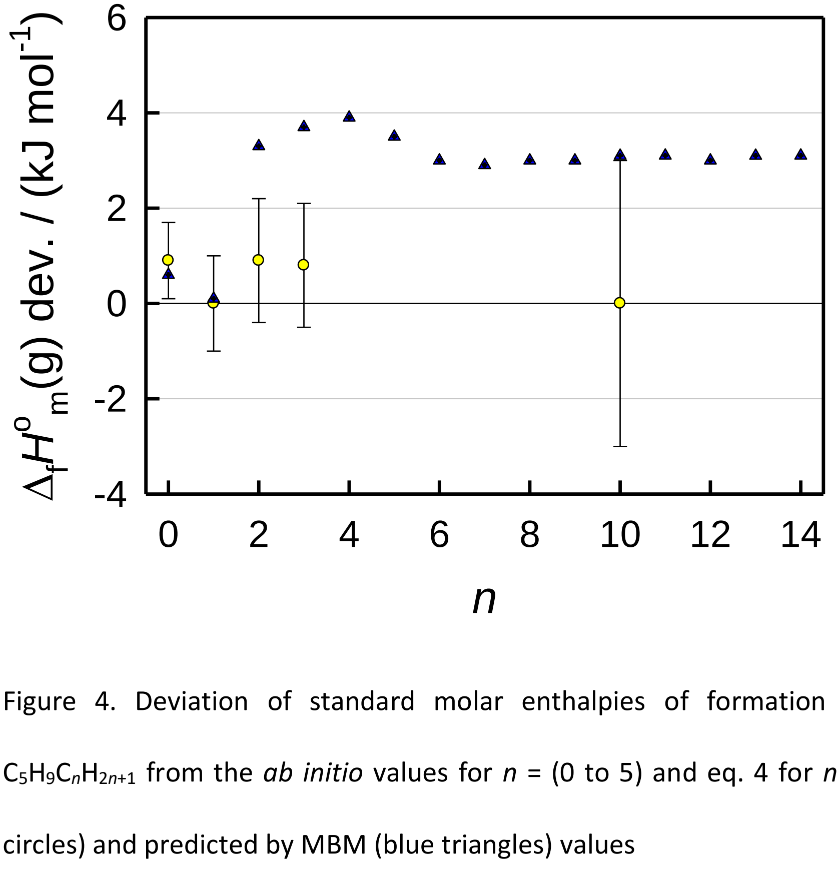

Figure 4. Deviation of standard molar enthalpies of formation of gaseous *n*-alkylcyclopentanes $C_5H_9C_nH_{2n+1}$ from the *ab initio* values for n = (0 to 5) and eq. 4 for n = (6 to 14): experimental (yellow circles) and predicted by MBM (blue triangles) values

3.3. 2. Dialkylcyclopentanes and trialkylcyclopentanes

Vapor pressures and enthalpies of formation for multiple dialkylcyclopentanes (Tables 13, 14) were published by Rossini et al. [12,48] and Good [46]. As for the other monocyclic hydrocarbons considered in this work, the MBM reliably predicted $\Delta_{vap}H^{\circ}{}_{m}$, and the *ab initio* demonstrated good performance for $\Delta_{f}H^{\circ}{}_{m}(g)$ (Table 15).

In 1955, Rossini and Li [47] concluded that the properties of *cis*- and *trans*-1,3-dimethylcyclopentanes were swapped in the tables of physical and thermodynamic data issued by API Research Project 44 due to misidentified samples. This problem should be taken into consideration when analyzing the measurements based on pre-1955 samples. In 1971, Good [46] reported the enthalpies of formation of *cis*- and *trans*-1-ethyl-3-methylcyclopentanes determined from combustion calorimetry measurements. The samples were provided by API Project 58B. The room-temperature density of both isomers was the only other reported property. The enthalpy of formation of the *trans*-isomer was found to be more negative (Table 14). However, the opposite order is observed for 1,3-dimethylcyclopentanes in the liquid phase and predicted by quantum chemical calculations for the gas phase. Because of this uncertainty, the liquid-phase enthalpies of formation of these isomers were derived from the *ab initio* values for the gas phase and predicted enthalpies of vaporization.

The enthalpies of vaporization of four trialkylcyclopentanes were determined from the ebulliometric results of Forziati et al. [12] (Table 16). For the other isomers, the MBM predictions were selected. The liquid-phase $\Delta_{f}H^{\circ}{}_{m}$ values (Table 17) were found using the *ab initio* results (Table 18) and the enthalpies of vaporization.

Table 10. Standard enthalpies of vaporization $\Delta_{vap}H°_m$ of monoalkylcyclopentanes at T = 298.15 K [a]

Compound	Alias	CASRN	$\Delta_{vap}H°_m$ / (kJ·mol^{-1})			
			Experiment	Source	MBM	Selected
cyclopentane	**D.1**	287-92-3	28.7 ± 0.1	11	28.9	28.7 ± 0.1
methylcyclopentane	**D.2**	96-37-7	31.8 ± 0.1	11	31.8	31.8 ± 0.1
ethylcyclopentane	**D.3**	1640-89-7	36.5 ± 0.2	11	36.4	36.5 ± 0.2
propylcyclopentane	**D.4**	2040-96-2	41.1 ± 0.1	11	41.3	41.1 ± 0.1
butylcyclopentane	**D.5**	2040-95-1	45.9 ± 0.5	11	46.2	45.9 ± 0.5
pentylcyclopentane	**D.6**	3741-00-2			51.1	51.1 ± 1.5
hexylcyclopentane	**D.7**	4457-00-5			56.1	56.1 ± 1.5
heptylcyclopentane	**D.8**	5617-42-5			61.0	61.0 ± 1.5
octylcyclopentane	**D.9**	1795-20-6			65.9	65.9 ± 1.5
nonylcyclopentane	**D.10**	2882-98-6			70.8	70.8 ± 1.5
decylcyclopentane	**D.11**	1795-21-7	71.9 ± 4.3	15	75.7	75.7 ± 1.5
undecylcyclopentane	**D.12**	6785-23-5			80.7	80.7 ± 1.5
dodecylcyclopentane	**D.13**	5634-30-0			85.6	85.6 ± 1.5
tridecylcyclopentane	**D.14**	6006-34-4			90.5	90.5 ± 1.5

tetradecylcyclopentane	**D.15**	1795-22-8			95.4	95.4 ± 1.5
(1-methylethyl)cyclopentane	**D.16**	3875-51-2	39.5 ± 0.1	11	39.3	39.5 ± 0.1
(1-methylpropyl)cyclopentane	**D.17**	4850-32-2			44.6	44.6 ± 1.5
(2-methylpropyl)cyclopentane	**D.18**	3788-32-7			44.6	44.6 ± 1.5
(2-methylbutyl)cyclopentane	**D.19**	53366-38-4			49.9	49.9 ± 1.5
(3-methylbutyl)cyclopentane	**D.20**	1005-68-1			49.5	49.5 ± 1.5

[a] Expanded uncertainties for 0.95 level of confidence are reported following the ± signs

Table 11. Standard enthalpies of formation $\Delta_f H^\circ_m$ of liquid monoalkylcyclocyclopentanes (kJ·mol^{-1}) at T = 298.15 K [a]

Compound	Alias	CASRN	$-\Delta_f H^\circ_m$(l) / (kJ·mol^{-1})			
			Experiment	Source	MBM	Selected
cyclopentane	**D.1**	287-92-3	105.5 ± 0.8	33,42,43	104.3	105.5 ± 0.8
methylcyclopentane	**D.2**	96-37-7	138.0 ± 0.9	33,44,45,32,17	137.8	138.0 ± 0.9
ethylcyclopentane	**D.3**	1640-89-7	164.1 ± 1.2	37,32,17	166.7	164.1 ± 1.2
propylcyclopentane	**D.4**	2040-96-2	188.8 ± 1.3	37,46	192.6	188.8 ± 1.3
butylcyclopentane	**D.5**	2040-95-1			218.5	213.2 ± 2.8
pentylcyclopentane	**D.6**	3741-00-2			244.4	239.4 ± 3.3
hexylcyclopentane	**D.7**	4457-00-5			270.2	265.5 ± 3.4
heptylcyclopentane	**D.8**	5617-42-5			296.1	291.0 ± 3.4
octylcyclopentane	**D.9**	1795-20-6			322.0	316.4 ± 3.4
nonylcyclopentane	**D.10**	2882-98-6			347.9	341.9 ± 3.4
decylcyclopentane	**D.11**	1795-21-7	367.3 ± 2.6	35,36	373.8	367.3 ± 2.6
undecylcyclopentane	**D.12**	6785-23-5			399.7	392.9 ± 3.4
dodecylcyclopentane	**D.13**	5634-30-0			425.6	418.4 ± 3.4

tridecylcyclopentane	**D.14**	6006-34-4	451.5	443.8 ± 3.4
tetradecylcyclopentane	**D.15**	1795-22-8	477.4	469.3 ± 3.4
(1-methylethyl)cyclopentane	**D.16**	3875-51-2	200.3	193.6 ± 2.9
(1-methylpropyl)cyclopentane	**D.17**	4850-32-2	223.2	216.0 ± 3.2
(2-methylpropyl)cyclopentane	**D.18**	3788-32-7	223.2	219.8 ± 3.2
(2-methylbutyl)cyclopentane	**D.19**	53366-38-4	246.1	242.7 ± 3.3
(3-methylbutyl)cyclopentane	**D.20**	1005-68-1	249.1	245.9 ± 3.3

[a] Expanded uncertainties for 0.95 level of confidence are reported following the ± signs

Table 12. Standard enthalpies of formation $\Delta_f H^\circ_m$ of gaseous monoalkylcyclopentanes (kJ·mol^{-1}) at T = 298.15 K [a]

Compound	Alias	CASRN	$-\Delta_f H^\circ_m$(g) / (kJ·mol^{-1})			
			Experiment	MBM	*ab initio*	Selected
cyclopentane	**D.1**	287-92-3	76.8 ± 0.8	76.5	75.9 ± 2.6[b]	76.8 ± 0.8
methylcyclopentane	**D.2**	96-37-7	106.2 ± 1.0	106.3	106.2 ± 2.6	106.2 ± 1.0
ethylcyclopentane	**D.3**	1640-89-7	127.6 ± 1.3	130.0	126.7 ± 2.7	127.6 ± 1.3
propylcyclopentane	**D.4**	2040-96-2	147.7 ± 1.3	150.6	146.9 ± 2.8	147.7 ± 1.3
butylcyclopentane	**D.5**	2040-95-1		171.2	167.3 ± 2.8	167.3 ± 2.8
pentylcyclopentane	**D.6**	3741-00-2		191.8	188.3 ± 2.9	188.3 ± 2.9
hexylcyclopentane	**D.7**	4457-00-5		212.4		209.4 ± 3.0[d]
heptylcyclopentane	**D.8**	5617-42-5		232.9		230.0 ± 3.0[d]
octylcyclopentane	**D.9**	1795-20-6		253.5		250.5 ± 3.0[d]
nonylcyclopentane	**D.10**	2882-98-6		274.1		271.1 ± 3.0[d]
decylcyclopentane	**D.11**	1795-21-7	291.6 ± 3.0[c]	294.7		291.6 ± 3.0
undecylcyclopentane	**D.12**	6785-23-5		315.3		312.2 ± 3.0[d]
dodecylcyclopentane	**D.13**	5634-30-0		335.8		332.8 ± 3.0[d]

tridecylcyclopentane	**D.14**	6006-34-4	356.4		353.3 ± 3.0[d]
tetradecylcyclopentane	**D.15**	1795-22-8	377.0		373.9 ± 3.0[d]
(1-methylethyl)cyclopentane	**D.16**	3875-51-2	159.9	154.1 ± 2.9	154.1 ± 2.9
(1-methylpropyl)cyclopentane	**D.17**	4850-32-2	177.3	171.4 ± 2.8	171.4 ± 2.8
(2-methylpropyl)cyclopentane	**D.18**	3788-32-7	177.3	175.2 ± 2.8	175.2 ± 2.8
(2-methylbutyl)cyclopentane	**D.19**	53366-38-4	194.8	192.8 ± 2.9	192.8 ± 2.9
(3-methylbutyl)cyclopentane	**D.20**	1005-68-1	197.9	196.4 ± 2.9	196.4 ± 2.9

[a] Expanded uncertainties for 0.95 level of confidence are reported following the ± signs

[b] The uncertainty can be higher because pseudorotation is considered as harmonic vibrations

[c] Experimental liquid-phase enthalpy of formation is combined with the enthalpy of vaporization estimated by MBM

[d] These values were estimated using eq. 4. The expanded uncertainties, including the contributions due to data scatter and the model itself, are (1.0 to 1.5) kJ·mol^{-1}

Table 13. Standard enthalpies of vaporization $\Delta_{vap}H^{\circ}_{m}$ of dialkylcyclopentanes at T = 298.15 K [a]

Compound	Alias	CASRN	$\Delta_{vap}H^{\circ}_{m}$ / (kJ·mol^{-1})			
			Experiment	Source	MBM	Selected
1,1-dimethylcyclopentane	**E.1**	1638-26-2	34.0 ± 0.2	12	34.2	34.0 ± 0.2
cis-1,2-dimethylcyclopentane	**E.2**	1192-18-3	35.9 ± 0.2	12	34.8	35.9 ± 0.2
trans-1,2-dimethylcyclopentane	**E.3**	822-50-4	34.8 ± 0.2	12	34.8	34.8 ± 0.2
1,2-dimethylcyclopentane[b]	**E.4**	2452-99-5			34.8	35.3 ± 0.8
cis-1,3-dimethylcyclopentane	**E.5**	2532-58-3	34.3 ± 0.2	11	34.8	34.3 ± 0.2
trans-1,3-dimethylcyclopentane	**E.6**	1759-58-6	34.7 ± 0.2	12,47	34.8	34.7 ± 0.2
1,3-dimethylcyclopentane[b]	**E.7**	2453-00-1			34.8	34.5 ± 0.4
1-ethyl-1-methylcyclopentane	**E.8**	16747-50-5	38.9 ± 0.2	11	38.8	38.9 ± 0.2
cis-1-ethyl-2-methylcyclopentane	**E.9**	930-89-2	40.1 ± 0.2	12	39.3	40.1 ± 0.2

trans-1-ethyl-2-methylcyclopentane	**E.10**	930-90-5	39.3	39.3 ± 1.5
1-ethyl-2-methylcyclopentane[b]	**E.11**	3726-46-3	39.3	39.3 ± 1.5
cis-1-ethyl-3-methylcyclopentane	**E.12**	2613-66-3	39.3	39.3 ± 1.5
trans-1-ethyl-3-methylcyclopentane	**E.13**	2613-65-2	39.3	39.3 ± 1.5
1-ethyl-3-methylcyclopentane[b]	**E.14**	3726-47-4	39.3	39.3 ± 1.5
cis-1,2-diethylcyclopentane	**E.15**	932-39-8	43.9	43.9 ± 1.5
trans-1,2-diethylcyclopentane	**E.16**	932-40-1	43.9	43.9 ± 1.5
1,2-diethylcyclopentane[b]	**E.17**	3728-68-5	43.9	43.9 ± 1.5
cis-1-methyl-2-propylcyclohexane	**E.18**	932-43-4	44.3	44.3 ± 1.5
trans-1-methyl-2-propylcyclopentane	**E.19**	932-44-5	44.3	44.3 ± 1.5
1-methyl-2-propylcyclopentane[b]	**E.20**	3728-57-2	44.3	44.3 ± 1.5
cis-1-methyl-3-(1-methylethyl)cyclopentane	**E.21**	61828-02-2	42.3	42.3 ± 1.5
trans-1-methyl-3-(1-methylethyl)cyclopentane	**E.22**	61828-03-3	42.3	42.3 ± 1.5

1-methyl-3-(1-methylethyl)cyclopentane[b]	**E.23**	53771-88-3	42.3	42.3 ± 1.5

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[a] Expanded uncertainties for 0.95 level of confidence are reported following the ± signs

[b] Mixture of stereoisomers

Table 14. Standard enthalpies of formation $\Delta_f H^\circ_m$ of liquid dialkylcyclopentanes (kJ·mol^{-1}) at T = 298.15 K [a]

Compound	Alias	CASRN	$-\Delta_f H^\circ_m(l)$ / (kJ·mol^{-1})			
			Experiment	Source	MBM	Selected
1,1-dimethylcyclopentane	**E.1**	1638-26-2	172.1 ± 1.4	48	174.0	172.1 ± 1.4
cis-1,2-dimethylcyclopentane	**E.2**	1192-18-3	165.3 ± 1.6	48	171.4	165.3 ± 1.6
trans-1,2-dimethylcyclopentane	**E.3**	822-50-4	171.2 ± 1.5	48	171.4	171.2 ± 1.5
1,2-dimethylcyclopentane[b]	**E.4**	2452-99-5			171.4	168.3 ± 4.6
cis-1,3-dimethylcyclopentane	**E.5**	2532-58-3	170.1 ± 1.4	48,47	171.4	170.1 ± 1.4
trans-1,3-dimethylcyclopentane	**E.6**	1759-58-6	168.1 ± 1.7	48,47	171.4	168.1 ± 1.7
1,3-dimethylcyclopentane[b]	**E.7**	2453-00-1			171.4	169.1 ± 2.7
1-ethyl-1-methylcyclopentane	**E.8**	16747-50-5	193.8 ± 1.4	46	202.8	193.8 ± 1.4
cis-1-ethyl-2-methylcyclopentane	**E.9**	930-89-2	190.8 ± 1.4	46	200.3	190.8 ± 1.4

trans-1-ethyl-2-methylcyclopentane	**E.10**	930-90-5	195.1 ± 1.4	46	200.3	195.1 ± 1.4
1-ethyl-2-methylcyclopentane[b]	**E.11**	3726-46-3			200.3	193.0 ± 3.6
cis-1-ethyl-3-methylcyclopentane	**E.12**	2613-66-3	*194.4 ± 1.4*[c]	46	200.3	195.6 ± 3.3
trans-1-ethyl-3-methylcyclopentane	**E.13**	2613-65-2	*196.0 ± 1.4*[c]	46	200.3	194.5 ± 3.3
1-ethyl-3-methylcyclopentane[b]	**E.14**	3726-47-4			200.3	195.1 ± 3.8
cis-1,2-diethylcyclopentane	**E.15**	932-39-8			229.1	214.3 ± 3.2
trans-1,2-diethylcyclopentane	**E.16**	932-40-1			229.1	220.7 ± 3.2
1,2-diethylcyclopentane[b]	**E.17**	3728-68-5			229.1	217.5 ± 6.2
cis-1-methyl-2-propylcyclohexane	**E.18**	932-43-4			226.2	216.3 ± 3.2
trans-1-methyl-2-propylcyclopentane	**E.19**	932-44-5			226.2	221.9 ± 3.2
1-methyl-2-propylcyclopentane[b]	**E.20**	3728-57-2			226.2	219.1 ± 5.8
cis-1-methyl-3-(1-methylethyl)cyclopentane	**E.21**	61828-02-2			233.8	226.6 ± 3.2
trans-1-methyl-3-(1-methylethyl)cyclopentane	**E.22**	61828-03-3			233.8	224.7 ± 3.2

1-methyl-3-(1-methylethyl)cyclopentane[b]	**E.23**	53771-88-3	233.8	225.7 ± 4.1

[a] Expanded uncertainties for 0.95 level of confidence are reported following the ± signs

[b] Mixture of stereoisomers

[c] Experimental data for these isomers are likely swapped. See text

Table 15. Standard enthalpies of formation $\Delta_f H^\circ_m$ of gaseous dialkylcyclopentanes (kJ·mol^{-1}) at T = 298.15 K [a]

Compound	Alias	CASRN	$-\Delta_f H^\circ_m$(g) / (kJ·mol^{-1})			
			Experiment	MBM	*ab initio*	Selected
1,1-dimethylcyclopentane	**E.1**	1638-26-2	138.1 ± 1.4	139.9	138.2 ± 2.7	138.1 ± 1.4
cis-1,2-dimethylcyclopentane	**E.2**	1192-18-3	129.4 ± 1.6	136.2	130.1 ± 2.7	129.4 ± 1.6
trans-1,2-dimethylcyclopentane	**E.3**	822-50-4	136.4 ± 1.5	136.2	137.3 ± 2.7	136.4 ± 1.5
1,2-dimethylcyclopentane[b]	**E.4**	2452-99-5		136.2		132.9 ± 5.1
cis-1,3-dimethylcyclopentane	**E.5**	2532-58-3	135.8 ± 1.4	136.2	135.7 ± 2.7	135.8 ± 1.4
trans-1,3-dimethylcyclopentane	**E.6**	1759-58-6	133.4 ± 1.7	136.2	134.5 ± 2.7	133.4 ± 1.7
1,3-dimethylcyclopentane[b]	**E.7**	2453-00-1		136.2		134.6 ± 2.9
1-ethyl-1-methylcyclopentane	**E.8**	16747-50-5	154.9 ± 1.4	163.6	154.8 ± 2.9	154.9 ± 1.4
cis-1-ethyl-2-methylcyclopentane	**E.9**	930-89-2	150.7 ± 1.4	159.9	150.6 ± 2.8	150.7 ± 1.4

trans-1-ethyl-2-methylcyclopentane	**E.10**	930-90-5	155.8 ± 2.1[c]	159.9	156.4 ± 2.9	155.8 ± 2.1
1-ethyl-2-methylcyclopentane[b]	**E.11**	3726-46-3		159.9		153.3 ± 4.7
cis-1-ethyl-3-methylcyclopentane	**E.12**	2613-66-3	*155.1 ± 2.1*[c,d]	159.9	156.3 ± 2.9	156.3 ± 2.9
trans-1-ethyl-3-methylcyclopentane	**E.13**	2613-65-2	*156.7 ± 2.0*[c,d]	159.9	155.2 ± 2.9	155.2 ± 2.9
1-ethyl-3-methylcyclopentane[b]	**E.14**	3726-47-4		159.9		155.8 ± 3.5
cis-1,2-diethylcyclopentane	**E.15**	932-39-8		183.6	170.4 ± 2.8	170.4 ± 2.8
trans-1,2-diethylcyclopentane	**E.16**	932-40-1		183.6	176.8 ± 2.8	176.8 ± 2.8
1,2-diethylcyclopentane[b]	**E.17**	3728-68-5		183.6		173.6 ± 6.0
cis-1-methyl-2-propylcyclohexane	**E.18**	932-43-4		180.5	172.0 ± 2.8	172.0 ± 2.8
trans-1-methyl-2-propylcyclopentane	**E.19**	932-44-5		180.5	177.6 ± 2.8	177.6 ± 2.8
1-methyl-2-propylcyclopentane[b]	**E.20**	3728-57-2		180.5		174.8 ± 5.6
cis-1-methyl-3-(1-methylethyl)cyclopentane	**E.21**	61828-02-2		189.7	184.3 ± 2.8	184.3 ± 2.8
trans-1-methyl-3-(1-methylethyl)cyclopentane	**E.22**	61828-03-3		189.7	182.4 ± 2.8	182.4 ± 2.8

1-methyl-3-(1-methylethyl)cyclopentane[b]	**E.23**	53771-88-3	189.7	183.4 ± 3.8

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[a] Expanded uncertainties for 0.95 level of confidence are reported following the ± signs

[b] Mixture of stereoisomers

[c] Experimental liquid-phase enthalpy of formation is combined with the enthalpy of vaporization estimated by MBM

[d] Experimental data for these isomers are likely swapped. See text

Table 16. Standard enthalpies of vaporization $\Delta_{vap}H^\circ_m$ of trialkylcyclopentanes at T = 298.15 K [a]

Compound	Alias	CASRN	$\Delta_{vap}H^\circ_m$ / (kJ·mol^{-1})			
			Experiment	Source	MBM	Selected
1,1,2-trimethylcyclopentane	**F.1**	4259-00-1	37.4 ± 0.2	12	37.2	37.4 ± 0.2
1,1,3-trimethylcyclopentane	**F.2**	4516-69-2	36.2 ± 0.2	12	36.4	36.2 ± 0.2
(1α,2β,3α)-1,2,3-trimethylcyclopentane	**F.3**	19374-46-0			37.7	37.7 ± 1.5
(1α,2α,3β)-1,2,3-trimethylcyclopentane	**F.4**	15890-40-1			37.7	37.7 ± 1.5
(1α,2α,3α)-1,2,3-trimethylcyclopentane	**F.5**	2613-69-6			37.7	37.7 ± 1.5
1,2,3-trimethylcyclopentane[b]	**F.6**	2815-57-8			37.7	37.7 ± 1.5
(1α,2β,4α)-1,2,4-trimethylcyclopentane	**F.7**	16883-48-0	37.0 ± 0.2	12	37.7	37.0 ± 0.2
(1α,2α,4α)-1,2,4- trimethylcyclopentane	**F.8**	2613-72-1			37.7	37.7 ± 1.5
(1α,2α,4β)-1,2,4- trimethylcyclopentane	**F.9**	4850-28-6	37.9 ± 0.2	12	37.7	37.9 ± 0.2
1,2,4- trimethylcyclopentane[b]	**F.10**	2815-58-9			37.7	37.7 ± 1.5

(1α,2β,3α)-2-ethyl-1,3-dimethylcyclopentane	**F.11**	19902-98-8	42.3	42.3 ± 1.5
(1α,2α,3β)-2-ethyl-1,3-dimethylcyclopentane	**F.12**	19902-99-9	42.3	42.3 ± 1.5
(1α,2α,3α)-2-ethyl-1,3-dimethylcyclopentane	**F.13**	19903-00-5	42.3	42.3 ± 1.5
2-ethyl-1,3-dimethylcyclopentane[b]	**F.14**	19714-68-2	42.3	42.3 ± 1.5
(1α,2β,3α)-2-(1-methylethyl)-1,3-dimethylcyclopentane	**F.15**		45.3	45.3 ± 1.5
(1α,2α,3β)-2-(1-methylethyl)-1,3-dimethylcyclopentane	**F.16**		45.3	45.3 ± 1.5
(1α,2α,3α)-2-(1-methylethyl)-1,3-dimethylcyclopentane	**F.17**		45.3	45.3 ± 1.5
2-(1-methylethyl)-1,3-dimethylcyclopentane[b]	**F.18**	32281-85-9	45.3	45.3 ± 1.5

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[a] Expanded uncertainties for 0.95 level of confidence are reported following the ± signs

[b] mixture of stereoisomers

Table 17. Standard enthalpies of formation $\Delta_f H^\circ_m$ of liquid trialkylcyclopentanes ($kJ \cdot mol^{-1}$) at T = 298.15 K [a]

Compound	Alias	CASRN	$-\Delta_f H^\circ_m(l)$ / ($kJ \cdot mol^{-1}$)	
			MBM	Selected
1,1,2-trimethylcyclopentane	**F.1**	4259-00-1	207.6	202.8 ± 2.9
1,1,3-trimethylcyclopentane	**F.2**	4516-69-2	200.1	203.1 ± 2.9
(1α,2β,3α)-1,2,3-trimethylcyclopentane	**F.3**	19374-46-0	205.0	204.9 ± 3.3
(1α,2α,3β)-1,2,3-trimethylcyclopentane	**F.4**	15890-40-1	205.0	196.8 ± 3.3
(1α,2α,3α)-1,2,3-trimethylcyclopentane	**F.5**	2613-69-6	205.0	194.8 ± 3.3
1,2,3-trimethylcyclopentane[b]	**F.6**	2815-57-8	205.0	198.8 ± 9.1
(1α,2β,4α)-1,2,4-trimethylcyclopentane	**F.7**	16883-48-0	205.0	202.1 ± 2.9
(1α,2α,4α)-1,2,4- trimethylcyclopentane	**F.8**	2613-72-1	205.0	196.0 ± 3.3
(1α,2α,4β)-1,2,4- trimethylcyclopentane	**F.9**	4850-28-6	205.0	196.7 ± 2.9
1,2,4- trimethylcyclopentane[b]	**F.10**	2815-58-9	205.0	198.4 ± 7.5

(1α,2β,3α)-2-ethyl-1,3-dimethylcyclopentane	**F.11**	19902-98-8	233.8	226.2 ± 3.2
(1α,2α,3β)-2-ethyl-1,3-dimethylcyclopentane	**F.12**	19902-99-9	233.8	223.1 ± 3.2
(1α,2α,3α)-2-ethyl-1,3-dimethylcyclopentane	**F.13**	19903-00-5	233.8	213.6 ± 3.2
2-ethyl-1,3-dimethylcyclopentane[b]	**F.14**	19714-68-2	233.8	221.0 ± 10.4
(1α,2β,3α)-2-(1-methylethyl)-1,3-dimethylcyclopentane	**F.15**		267.4	253.5 ± 3.3
(1α,2α,3β)-2-(1-methylethyl)-1,3-dimethylcyclopentane	**F.16**		267.4	248.6 ± 3.3
(1α,2α,3α)-2-(1-methylethyl)-1,3-dimethylcyclopentane	**F.17**		267.4	242.5 ± 3.3
2-(1-methylethyl)-1,3-dimethylcyclopentane[b]	**F.18**	32281-85-9	267.4	248.2 ± 8.7

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[a] Expanded uncertainties for 0.95 level of confidence are reported following the ± signs

[b] mixture of stereoisomers

Table 18. Standard enthalpies of formation $\Delta_f H^\circ_m$ of gaseous trialkylcyclopentanes (kJ·mol^{-1}) at T = 298.15 K [a]

Compound	Alias	CASRN	$-\Delta_f H^\circ_m$(g) / (kJ·mol^{-1})		
			MBM	*ab initio*	Selected
1,1,2-trimethylcyclopentane	**F.1**	4259-00-1	169.8	165.4 ± 2.9	165.4 ± 2.9
1,1,3-trimethylcyclopentane	**F.2**	4516-69-2	163.4	166.9 ± 2.9	166.9 ± 2.9
(1α,2β,3α)-1,2,3-trimethylcyclopentane	**F.3**	19374-46-0	166.0	167.2 ± 2.9	167.2 ± 2.9
(1α,2α,3β)-1,2,3-trimethylcyclopentane	**F.4**	15890-40-1	166.0	159.1 ± 2.9	159.1 ± 2.9
(1α,2α,3α)-1,2,3-trimethylcyclopentane	**F.5**	2613-69-6	166.0	157.1 ± 2.9	157.1 ± 2.9
1,2,3-trimethylcyclopentane[b]	**F.6**	2815-57-8	166.0		161.1 ± 9.0
(1α,2β,4α)-1,2,4-trimethylcyclopentane	**F.7**	16883-48-0	166.0	165.1 ± 2.9	165.1 ± 2.9
(1α,2α,4α)-1,2,4- trimethylcyclopentane	**F.8**	2613-72-1	166.0	158.3 ± 2.9	158.3 ± 2.9
(1α,2α,4β)-1,2,4- trimethylcyclopentane	**F.9**	4850-28-6	166.0	158.8 ± 2.9	158.8 ± 2.9
1,2,4- trimethylcyclopentane[b]	**F.10**	2815-58-9	166.0		160.7 ± 7.3

(1α,2β,3α)-2-ethyl-1,3-dimethylcyclopentane	**F.11**	19902-98-8	189.7	183.9 ± 2.8	183.9 ± 2.8
(1α,2α,3β)-2-ethyl-1,3-dimethylcyclopentane	**F.12**	19902-99-9	189.7	180.8 ± 2.8	180.8 ± 2.8
(1α,2α,3α)-2-ethyl-1,3-dimethylcyclopentane	**F.13**	19903-00-5	189.7	171.3 ± 2.8	171.3 ± 2.8
2-ethyl-1,3-dimethylcyclopentane[b]	**F.14**	19714-68-2	189.7		178.7 ± 10.3
(1α,2β,3α)-2-(1-methylethyl)-1,3-dimethylcyclopentane	**F.15**		219.6	208.2 ± 2.9	208.2 ± 2.9
(1α,2α,3β)-2-(1-methylethyl)-1,3-dimethylcyclopentane	**F.16**		219.6	203.3 ± 2.9	203.3 ± 2.9
(1α,2α,3α)-2-(1-methylethyl)-1,3-dimethylcyclopentane	**F.17**		219.6	197.2 ± 2.9	197.2 ± 2.9
2-(1-methylethyl)-1,3-dimethylcyclopentane[b]	**F.18**	32281-85-9	219.6		202.9 ± 8.6

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[a] Expanded uncertainties for 0.95 level of confidence are reported following the ± signs

[b] mixture of isomers

3.3. Bi- and tricyclic compounds

This group includes bi- and tricyclic compounds containing at least one cyclopentane or cyclohexane ring. The results are reported in Tables 19-21. Decalins and tetralins are discussed in Section 3.4. For the compounds with fused and bridged rings as well as spiro compounds, the CBS *ab initio* enthalpies of formation are used in the discussion. The quadruple-zeta and CBS results are compared in Section 3.5.

The experimental enthalpies of vaporization are available for three out of five bicyclic compounds with separated rings (Table 19). For cyclopentylcyclohexane, the enthalpy of vaporization can be estimated as a half-sum of the values for 1,1’-bicyclopentyl and 1,1’-bicyclohexyl. The good performance of MBM toward the enthalpies of vaporization of these compounds is expected based on the discussion in the previous sections. Therefore, the MBM value was used for (cyclopentylmethyl)cyclohexane. In the case of 1,1'-(1,2-ethanediyl)biscyclohexane, the predicted value was preferred over the experimental one. The latter deviates from the expected trend by 3 kJ·mol^{-1}.

The reliable experimental enthalpies of formation have been published only for 1,1’-bicyclopentyl and 1,1’-bicyclohexyl (Table 20), and their expanded uncertainty is 1.6 kJ·mol^{-1}. For the other three compounds, the liquid-phase values were obtained from the *ab initio* gas-phase enthalpies of formation and enthalpies of vaporization. The $\Delta_f H^\circ_m$ values predicted with MBM both for the liquid and gas phases are systematically too negative, with deviations up to 13 kJ·mol^{-1} (Tables 20 and 21). This performance is consistent with the results obtained above for monocyclic compounds.

Evaluation of repeatability-based uncertainty is an important part of combustion calorimetry experiments [49]. It characterizes the lower limit of uncertainty for these measurements. Typically, at least six experiments are conducted to obtain a reasonable statistical sample. $\Delta_f H^\circ_m$ of cyclopentylcyclohexane [65] (Table 20) was obtained from two combustion experiments; therefore, its uncertainty could not be estimated.

The experimental properties, including condensed-phase enthalpies of formation and vaporization/sublimation, have been reported for 13 compounds with bridged or fused rings (Tables 19, 20). Four of these compounds are solid at $T = 298.15$ K, and their liquid-phase properties were estimated using the gas-phase enthalpy of formation and predicted $\Delta_{\mathrm{vap}}H^{\circ}_{\mathrm{m}}$. Also, the liquid-phase $\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}$ is available for two individual compounds and two isomeric mixtures and $\Delta_{\mathrm{vap}}H^{\circ}_{\mathrm{m}}$ has been reported for two pinane isomers.

For the fused-ring compounds, the MBM-predicted $\Delta_{\mathrm{vap}}H^{\circ}_{\mathrm{m}}$ agree with the experimental data within ± 1.5 kJ·mol^{-1}, similar to the monocyclic compounds. The experimental $\Delta_{\mathrm{vap}}H^{\circ}_{\mathrm{m}}$ are available for four bridged compounds, including three methyl-substituted bicyclo[2.2.1]heptanes and JP-10, and the predicted values are greater by (1.7 to 3.8) kJ·mol^{-1}. Therefore, the estimated uncertainty for the predicted enthalpies of vaporization of bridged compounds was increased to 4 kJ·mol^{-1}. Pinanes contain a cyclobutane ring, and the corresponding ring correction is unknown. Therefore, the MBM predictions for these compounds could not be generated.

The vaporization enthalpies of 1,4-dimethylbicyclo[2.2.1]heptane and *trans*-2,3-dimethylbicyclo[2.2.1]heptane were measured in a calorimeter in the same work [58]. The reported difference of -3.2 kJ·mol^{-1} appears excessive. The difference close to -1 kJ·mol^{-1}, also predicted by the MBM, is expected for this pair of compounds. Additional experimental data are required to resolve this inconsistency.

The experimental gas-phase enthalpies of formation are compared with their *ab initio* counterparts in Table 21. For most compounds with bridged or fused rings, the CBS *ab initio* values agree with the experimental ones within their combined uncertainties. For 7,7-dimethylbicyclo[2.2.1]heptane, the difference is larger but still within a sum of the experimental and computational uncertainties. The experimental values for *trans*-bicyclo[3.3.0]octane and the isomeric mixtures of 2-

ethylbicyclo[2.2.1]heptane and pinane have large deviations (-6, 9, and -37 $kJ \cdot mol^{-1}$, respectively) from the calculated values. Considering the very good performance of the *ab initio* protocol, these experimental results were rejected.

The enthalpies of vaporization of all three spiro compounds considered in this work can be derived from the vapor-pressure [50] and calorimetric [51] measurements for the same samples (Table 19). The difference between the calorimetric $\Delta_{vap}H^{\circ}_{m}$ for spiro[4.5]decane and spiro[5.5]undecane is only 1.2 $kJ \cdot mol^{-1}$. Also, for spiro[4.5]decane, the value is higher than the tensimetric and MBM values by 6 and 5 $kJ \cdot mol^{-1}$, respectively. Therefore, the vaporization enthalpies derived from the temperature-dependent vapor pressures were selected for all three compounds despite their higher repeatability-based uncertainty.

The liquid-phase enthalpies of formation (Table 20) were derived from two consistent studies by combustion calorimetry [52,53]. The gas-phase values (Table 21) were obtained using these results, and the vaporization enthalpies were selected as described above. The *ab initio* $\Delta_{f}H^{\circ}_{m}$ values are within ±2.7 $kJ \cdot mol^{-1}$ of the corresponding experimental data.

Table 19. Standard enthalpies of vaporization $\Delta_{\mathrm{vap}}H^{\circ}_{\mathrm{m}}$ of bi- and tricyclic compounds at T = 298.15 K [a]

Compound	Alias	CASRN	$\Delta_{\mathrm{vap}}H^{\circ}_{\mathrm{m}}$ / (kJ·mol^{-1})			
			Experiment	Source	MBM	Selected
1,1′-bicyclopentyl	**G.1**	1636-39-1	50.4 ± 0.2	54	51.6	50.4 ± 0.2
cyclopentylcyclohexane	**G.2**	1606-08-2	54.6 ± 0.5[b]		55.2	54.6 ± 0.5
1,1'-bicyclohexyl	**G.3**	92-51-3	58.8 ± 0.4	55	58.7	58.8 ± 0.4
(cyclopentylmethyl)cyclohexane	**G.4**	4431-89-4			59.7	59.7 ± 1.5
1,1'-(1,2-ethanediyl)biscyclohexane	**G.5**	3321-50-4	*71.0 ± 1.5*[c]	56	68.2	68.2 ± 1.5
bicyclo[2.2.1]heptane (norbornane)	**G.6**	279-23-2	40.2 ± 0.7 (subl)[d]	15	37.9	37.9 ± 4.0
1-methylbicyclo[2.2.1]heptane	**G.7**	10052-18-3	38.1 ± 0.2	57	40.3	38.1 ± 0.2
rel-(1S,2R,4S)-2-methylbicyclo[2.2.1]heptane	**G.8**	765-90-2			40.8	40.8 ± 4.0
rel-(1R,2R,4R)-2-methylbicyclo[2.2.1]heptane	**G.9**	872-78-6			40.8	40.8 ± 4.0
1,4-dimethylbicyclo[2.2.1]heptane	**G.10**	20454-81-3	38.9 ± 0.2	58,11	42.7	38.9 ± 0.2
trans-2,3-dimethylbicyclo[2.2.1]heptane	**G.11**	20558-16-1	42.1 ± 0.1	58	43.8	42.1 ± 0.1
7,7-dimethylbicyclo[2.2.1]heptane	**G.12**	2034-53-9	47.0 ± 1.0 (subl)[d]	57	43.3	43.3 ± 4.0

rel-(1S,2R,4S)-2-ethylbicyclo[2.2.1]heptane	**G.13**	19901-79-2			45.4	45.4 ± 4.0
rel-(1R,2R,4R)-2-ethylbicyclo[2.2.1]heptane	**G.14**	19901-80-5			45.4	45.4 ± 4.0
2-ethylbicyclo[2.2.1]heptane[e]	**G.15**	2146-41-0			45.4	45.4 ± 4.0
(1*S*,2*R*,5*S*)-2,6,6-trimethylbicyclo[3.1.1]heptane ((-)-*cis*-pinane)	**G.16**	4755-33-3	46.0 ± 0.8	15		46.0 ± 0.8
(1*S*,2*S*,5*S*)-2,6,6-trimethylbicyclo[3.1.1]heptane ((+)-*trans*-pinane)	**G.17**	10281-53-5	46.1 ± 0.3	59		46.1 ± 0.3
2,6,6-trimethylbicyclo[3.1.1]heptane (pinane)[e]	**G.18**	473-55-2				46.1 ± 0.8
cis-bicyclo[3.3.0]octane (*cis*-octahydropentalene)	**G.19**	1755-05-1	43.1 ± 0.8	60	42.4	43.1 ± 0.8
trans-bicyclo[3.3.0]octane (*trans*-octahydropentalene)	**G.20**	5597-89-7	42.7 ± 0.8	60	42.4	42.7 ± 0.8
(1R,3r,5S)-3-methylbicyclo[3.3.0]octane	**G.21**	1551-79-7			45.4	45.4 ± 1.5
(1R,3s,5S)-3-methylbicyclo[3.3.0]octane	**G.22**	1551-78-6			45.4	45.4 ± 1.5
3-methyl-*cis*-bicyclo[3.3.0]octane[e]	**G.23**	3868-64-2			45.4	45.4 ± 1.5

bicyclo[3.3.1]nonane	**G.24**	280-65-9	50.6 ± 2.1 (subl)[d]	61	45.0	45.0 ± 4.0
1-methylbicyclo[3.3.1]nonane	**G.25**	25107-02-2			47.4	47.4 ± 4.0
9-methylbicyclo[3.3.1]nonane	**G.26**	25107-01-1			48.0	48.0 ± 4.0
cis-bicyclo[4.3.0]nonane (*cis*-octahydroindene)	**G.27**	4551-51-3	46.3 ± 0.3	15	46.0	46.3 ± 0.3
trans-bicyclo[4.3.0]nonane (*trans*-octahydroindene)	**G.28**	3296-50-2	45.0 ± 0.3	15	46.0	45.0 ± 0.3
cis-1-methylbicyclo[4.3.0]nonane	**G.29**	824-16-8			48.4	48.4 ± 1.5
trans-1-methylbicyclo[4.3.0]nonane	**G.30**	42608-34-4			48.4	48.4 ± 1.5
cis-bicyclo[5.3.0]decane	**G.31**	16189-46-1	53.6 ± 1.3	60	52.1	53.6 ± 1.3
trans-bicyclo[5.3.0]decane	**G.32**	16189-47-2			52.1	52.1 ± 1.5
endo-tricyclo[5.2.1.$0^{2,6}$]decane	**G.33**	2825-83-4	51.5 ± 5.4 (subl)[d]	15	51.5	51.5 ± 4.0
exo-tricyclo[5.2.1.$0^{2,6}$]decane (JP-10)	**G.34**	2825-82-3	49.0 ± 0.2	62	51.5	49.0 ± 0.2
rel-(3a*R*,3b*R*,6a*R*,7a*R*)-decahydro-1H-cyclopenta[a]pentalene	**G.35**	64839-76-5			56.0	56.0 ± 1.5

rel-(3a*R*,3b*S*,6a*S*,7a*R*)-decahydro-1H-cyclopenta[a]pentalene	**G.36**	58116-67-9			56.0	56.0 ± 1.5
decahydro-1H-cyclopenta[a]pentalene[e]	**G.37**	6053-75-4			56.0	56.0 ± 1.5
(3aα,6aα,9aα,9bβ)-perhydrophenalene	**G.38**	40250-64-4			58.6	58.6 ± 4.0
(3aα,6aα,9aβ,9bα)-perhydrophenalene	**G.39**	86118-18-5			58.6	58.6 ± 4.0
spiro[4.5]decane	**G.40**	176-63-6	49.0 ± 1.5[f] (*54.9 ± 0.1*)[g]	50	50.0	49.0 ± 1.5
spiro[5.5]undecane	**G.41**	180-43-8	55.0 ± 2.2[f] (*56.1 ± 0.1*)[g]	50	53.6	55.0 ± 2.2
spiro[5.6]dodecane	**G.42**	181-15-7	60.5 ± 3.1[f]	50	59.7	60.5 ± 3.1

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[a] Expanded uncertainties for 0.95 level of confidence are reported following the ± signs

[b] Average of 1,1’-bicyclopentyl and 1,1’-bicyclohexyl

[c] Estimated using $\Delta_{\mathrm{vap}}C_p$ = -(97 ± 18) J·K^{-1}·mol^{-1} based on the experimental data from Ref. [63] and ideal-gas calculations in this work, the real uncertainty of this value is close to 3 kJ·mol^{-1}

[d] Enthalpy of sublimation

[e] Mixture of stereoisomers

[f] Estimated using $\Delta_{\mathrm{vap}}C_p = -14.30 - 0.35C_p(\mathrm{g})$ [41] and the ideal-gas heat capacities at T = 298.15 K calculated in this work

[g] These values [51] appear to be too high, and the repeatability-based uncertainty is not credible

481 Table 20. Standard enthalpies of formation $\Delta_f H^\circ_m$ of liquid bi- and tricyclic compounds at T = 298.15 K [a]

Compound	Alias	CASRN	$-\Delta_f H^\circ_m(l)$ / (kJ·mol^{-1})			
			Experiment[b]	Source	MBM	Selected
1,1′-bicyclopentyl	**G.1**	1636-39-1	179.0 ± 1.6	64,65	183.7	179.0 ± 1.6
cyclopentylcyclohexane	**G.2**	1606-08-2	230.2 [c]	65	235.6	228.5 ± 2.9[d]
1,1'-bicyclohexyl	**G.3**	92-51-3	274.1 ± 1.6	64,66	287.4	274.1 ± 1.6
(cyclopentylmethyl)cyclohexane	**G.4**	4431-89-4			264.4	255.1 ± 3.4[d]
1,1'-(1,2-ethanediyl)biscyclohexane	**G.5**	3321-50-4			342.1	329.8 ± 3.4[d]
bicyclo[2.2.1]heptane (norbornane)	**G.6**	279-23-2	93.9 ± 1.7 (cr)	67,68,69		90.7 ± 3.5[d]
1-methylbicyclo[2.2.1]heptane	**G.7**	10052-18-3	130.9 ± 1.4	70		130.9 ± 1.4
rel-(1S,2R,4S)-2-methylbicyclo[2.2.1]heptane	**G.8**	765-90-2	122.1 ± 1.5	70		122.1 ± 1.5
rel-(1R,2R,4R)-2-methylbicyclo[2.2.1]heptane	**G.9**	872-78-6	122.4 ± 1.4	70		122.4 ± 1.4
1,4-dimethylbicyclo[2.2.1]heptane	**G.10**	20454-81-3	167.4 ± 2.8	71		169.1 ± 2.7
trans-2,3-dimethylbicyclo[2.2.1]heptane	**G.11**	20558-16-1	150.2 ± 4.3	71		153.6 ± 2.7
7,7-dimethylbicyclo[2.2.1]heptane	**G.12**	2034-53-9	148.2 ± 1.7 (cr)	72		144.6 ± 4.5[d]

rel-(1S,2R,4S)-2-ethylbicyclo[2.2.1]heptane	**G.13**	19901-79-2			148.2 ± 4.8[d]
rel-(1R,2R,4R)-2-ethylbicyclo[2.2.1]heptane	**G.14**	19901-80-5			150.9 ± 4.8[d]
2-ethylbicyclo[2.2.1]heptane[e]	**G.15**	2146-41-0	*140.2 ± 2.0*	72	149.6 ± 6.1
(1*S*,2*R*,5*S*)-2,6,6-trimethylbicyclo[3.1.1]heptane ((-)-*cis*-pinane)	**G.16**	4755-33-3			103.8 ± 2.7[d]
(1*S*,2*S*,5*S*)-2,6,6-trimethylbicyclo[3.1.1]heptane ((+)-*trans*-pinane)	**G.17**	10281-53-5			115.3 ± 2.6[d]
2,6,6-trimethylbicyclo[3.1.1]heptane (pinane)[e]	**G.18**	473-55-2	*147.4 ± 6.2*	38	109.6 ± 8.5
cis-bicyclo[3.3.0]octane (*cis*-octahydropentalene)	**G.19**	1755-05-1	136.0 ± 2.6	60	136.0 ± 2.6
trans-bicyclo[3.3.0]octane (*trans*-octahydropentalene)	**G.20**	5597-89-7	*109.3 ± 2.8*	60	103.0 ± 2.6[d]
(1R,3r,5S)-3-methylbicyclo[3.3.0]octane	**G.21**	1551-79-7			170.8 ± 3.0[d]
(1R,3s,5S)-3-methylbicyclo[3.3.0]octane	**G.22**	1551-78-6			169.3 ± 3.0[d]
3-methyl-*cis*-bicyclo[3.3.0]octane[e]	**G.23**	3868-64-2			170.1 ± 3.8

bicyclo[3.3.1]nonane	**G.24**	280-65-9	178.0 ± 1.5 (cr)	61	172.4 ± 4.7[d]
1-methylbicyclo[3.3.1]nonane	**G.25**	25107-02-2			211.0 ± 4.8[d]
9-methylbicyclo[3.3.1]nonane	**G.26**	25107-01-1			198.9 ± 4.8[d]
cis-bicyclo[4.3.0]nonane (*cis*-octahydroindene)	**G.27**	4551-51-3	173.1 ± 2.0	73	173.1 ± 2.0
trans-bicyclo[4.3.0]nonane (*trans*-octahydroindene)	**G.28**	3296-50-2	176.2 ± 2.2	73	176.2 ± 2.2
cis-1-methylbicyclo[4.3.0]nonane	**G.29**	824-16-8			207.1 ± 3.0[d]
trans-1-methylbicyclo[4.3.0]nonane	**G.30**	42608-34-4			200.8 ± 3.0[d]
cis-bicyclo[5.3.0]decane	**G.31**	16189-46-1	183.9 ± 4.2	60	188.1 ± 2.9[d]
trans-bicyclo[5.3.0]decane	**G.32**	16189-47-2			183.5 ± 3.0[d]
endo-tricyclo[5.2.1.0(2,6)]decane	**G.33**	2825-83-4	112.3 ± 2.8 (cr)	74	114.2 ± 4.8[d]
exo-tricyclo[5.2.1.0(2,6)]decane (JP-10)	**G.34**	2825-82-3	122.8 ± 1.9 [f]	75	122.8 ± 1.9
rel-(3a*R*,3b*R*,6a*R*,7a*R*)-decahydro-1H-cyclopenta[a]pentalene	**G.35**	64839-76-5			158.4 ± 3.0[d]

rel-(3a*R*,3b*S*,6a*S*,7a*R*)-decahydro-1H-cyclopenta[a]pentalene	**G.36**	58116-67-9			152.9 ± 3.0[d]
decahydro-1H-cyclopenta[a]pentalene[e]	**G.37**	6053-75-4			155.7 ± 5.8
(3aα,6aα,9aα,9bβ)-perhydrophenalene	**G.38**	40250-64-4			279.3 ± 4.9[d]
(3aα,6aα,9aβ,9bα)-perhydrophenalene	**G.39**	86118-18-5			263.6 ± 4.9[d]
spiro[4.5]decane	**G.40**	176-63-6	200.3 ± 2.0	52,53	200.3 ± 2.0
spiro[5.5]undecane	**G.41**	180-43-8	247.0 ± 2.1	52,53	247.0 ± 2.1
spiro[5.6]dodecane	**G.42**	181-15-7	253.0 ± 1.6	52,53	253.0 ± 1.6

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[a] Expanded uncertainties for 0.95 level of confidence are reported following the ± signs

[b] The outlier values are in italics

[c] Based on two combustion experiments

[d] Obtained by subtracting the selected $\Delta_{vap}H^{\circ}_{m}$ value (Table 19) from the ideal-gas $\Delta_{f}H^{\circ}_{m}$ (Table 21)

[e] Mixture of stereoisomers

[f] The value from Ref. [38] was not considered due to its large uncertainty

Table 21. Standard enthalpies of formation $\Delta_f H^\circ_m$ of gaseous bi- and tricyclic compounds at T = 298.15 K [a]

Compound	Alias	CASRN	$-\Delta_f H^\circ_m$(g) / (kJ·mol^{-1})				
			Experiment[b]	MBM	*ab initio* QZ	*ab initio* CBS	Selected
1,1′-bicyclopentyl	**G.1**	1636-39-1	128.6 ± 1.6	130.1	129.9 ± 2.9		128.6 ± 1.6
cyclopentylcyclohexane	**G.2**	1606-08-2	175.6	176.8	173.9 ± 2.9		173.9 ± 2.9
1,1'-bicyclohexyl	**G.3**	92-51-3	215.3 ± 1.6	223.5	214.1 ± 2.9		215.3 ± 1.6
(cyclopentylmethyl)cyclohexane	**G.4**	4431-89-4		200.5	195.4 ± 3.1		195.4 ± 3.1
1,1'-(1,2-ethanediyl)biscyclohexane	**G.5**	3321-50-4		267.7	261.6 ± 3.1		261.6 ± 3.1
bicyclo[2.2.1]heptane (norbornane)	**G.6**	279-23-2	53.7 ± 1.8		56.3 ± 2.6	56.6 ± 2.5	53.7 ± 1.8
1-methylbicyclo[2.2.1]heptane	**G.7**	10052-18-3	92.8 ± 1.4		93.2 ± 2.7	92.2 ± 2.5	92.8 ± 1.4
rel-(1*S*,2*R*,4*S*)-2-methylbicyclo[2.2.1]heptane	**G.8**	765-90-2	81.3 ± 4.3[c]		81.5 ± 2.7	80.9 ± 2.5	80.9 ± 2.5
rel-(1*R*,2*R*,4*R*)-2-methylbicyclo[2.2.1]heptane	**G.9**	872-78-6	81.6 ± 4.3[c]		85.2 ± 2.7	84.5 ± 2.5	84.5 ± 2.5
1,4-dimethylbicyclo[2.2.1]heptane	**G.10**	20454-81-3	128.5 ± 2.8		130.2 ± 2.7	128.4 ± 2.6	128.5 ± 2.8
trans-2,3-dimethylbicyclo[2.2.1]heptane	**G.11**	20558-16-1	108.1 ± 4.3		111.5 ± 2.7	109.9 ± 2.6	109.9 ± 2.6
7,7-dimethylbicyclo[2.2.1]heptane	**G.12**	2034-53-9	101.2 ± 2.0		107.7 ± 2.7	105.5 ± 2.6	101.2 ± 2.0

rel-(1*S*,2*R*,4*S*)-2-ethylbicyclo[2.2.1]heptane	**G.13**	19901-79-2		103.9 ± 2.7	102.8 ± 2.6	102.8 ± 2.6
rel-(1*R*,2*R*,4*R*)-2-ethylbicyclo[2.2.1]heptane	**G.14**	19901-80-5		106.5 ± 2.7	105.5 ± 2.6	105.5 ± 2.6
2-ethylbicyclo[2.2.1]heptane[d]	**G.15**	2146-41-0	*94.8 ± 4.5*[c]			104.2 ± 4.0
(1*S*,2*R*,5*S*)-2,6,6-trimethylbicyclo[3.1.1]heptane ((-)-*cis*-pinane)	**G.16**	4755-33-3		60.7 ± 2.8	57.8 ± 2.6	57.8 ± 2.6
(1*S*,2*S*,5*S*)-2,6,6-trimethylbicyclo[3.1.1]heptane ((+)-*trans*-pinane)	**G.17**	10281-53-5		72.0 ± 2.8	69.2 ± 2.6	69.2 ± 2.6
2,6,6-trimethylbicyclo[3.1.1]heptane (pinane)[e]	**G.18**	473-55-2	*101.3 ± 6.2*			63.5 ± 8.3
cis-bicyclo[3.3.0]octane (*cis*-octahydropentalene)	**G.19**	1755-05-1	92.9 ± 2.7	95.7 ± 2.7	95.1 ± 2.5	92.9 ± 2.7
trans-bicyclo[3.3.0]octane (*trans*-octahydropentalene)	**G.20**	5597-89-7	*66.6 ±2.9*	61.7 ± 2.7	60.3 ± 2.5	60.3 ± 2.5
(1*R*,3*r*,5*S*)-3-methylbicyclo[3.3.0]octane	**G.21**	1551-79-7		126.7 ± 2.7	125.4 ± 2.6	125.4 ± 2.6
(1*R*,3*s*,5*S*)-3-methylbicyclo[3.3.0]octane	**G.22**	1551-78-6		125.2 ± 2.7	123.9 ± 2.6	123.9 ± 2.6
3-methyl-*cis*-bicyclo[3.3.0]octane[d]	**G.23**	3868-64-2				124.7 ± 3.4

bicyclo[3.3.1]nonane	**G.24**	280-65-9	127.4 ± 2.5	128.6 ± 2.7	127.2 ± 2.6	127.4 ± 2.5
1-methylbicyclo[3.3.1]nonane	**G.25**	25107-02-2		166.0 ± 2.8	163.6 ± 2.6	163.6 ± 2.6
9-methylbicyclo[3.3.1]nonane	**G.26**	25107-01-1		153.0 ± 2.8	150.9 ± 2.6	150.9 ± 2.6
cis-bicyclo[4.3.0]nonane (*cis*-octahydroindene)	**G.27**	4551-51-3	126.8 ± 2.0	127.6 ± 2.7	125.8 ± 2.6	126.8 ± 2.0
trans-bicyclo[4.3.0]nonane (*trans*-octahydroindene)	**G.28**	3296-50-2	131.2 ± 2.2	131.9 ± 2.7	130.4 ± 2.6	131.2 ± 2.2
cis-1-methylbicyclo[4.3.0]nonane	**G.29**	824-16-8		161.3 ± 2.8	158.7 ± 2.6	158.7 ± 2.6
trans-1-methylbicyclo[4.3.0]nonane	**G.30**	42608-34-4		154.9 ± 2.8	152.4 ± 2.6	152.4 ± 2.6
cis-bicyclo[5.3.0]decane	**G.31**	16189-46-1	130.3 ± 4.4	136.2 ± 2.8	134.5 ± 2.6	134.5 ± 2.6
trans-bicyclo[5.3.0]decane	**G.32**	16189-47-2		133.5 ± 2.8	131.4 ± 2.6	131.4 ± 2.6
endo-tricyclo[5.2.1.0(2,6)]decane	**G.33**	2825-83-4	60.8 ± 6.1	64.2 ± 2.7	62.7 ± 2.6	62.7 ± 2.6
exo-tricyclo[5.2.1.0(2,6)]decane (JP-10)	**G.34**	2825-82-3	73.8 ± 1.9	77.5 ± 2.8	76.2 ± 2.6	73.8 ± 1.9
rel-(3a*R*,3b*R*,6a*R*,7a*R*)-decahydro-1H-cyclopenta[a]pentalene	**G.35**	64839-76-5		104.5 ± 2.8	102.4 ± 2.6	102.4 ± 2.6

rel-(3a*R*,3b*S*,6a*S*,7a*R*)-decahydro-1H-cyclopenta[a]pentalene	**G.36**	58116-67-9		98.9 ± 2.8	96.9 ± 2.6	96.9 ± 2.6
decahydro-1H-cyclopenta[a]pentalene[d]	**G.37**	6053-75-4				99.7 ± 5.4
(3aα,6aα,9aα,9bβ)-perhydrophenalene	**G.38**	40250-64-4		224.2 ± 2.9	220.7 ± 2.8	220.7 ± 2.8
(3aα,6aα,9aβ,9bα)-perhydrophenalene	**G.39**	86118-18-5		208.8 ± 2.9	205.0 ± 2.8	205.0 ± 2.8
spiro[4.5]decane	**G.40**	176-63-6	151.3 ± 2.5	156.2 ± 2.8	154.0 ± 2.6	151.3 ± 2.5
spiro[5.5]undecane	**G.41**	180-43-8	192.0 ± 3.0	197.1 ± 2.9	194.5 ± 2.7	192.0 ± 3.0
spiro[5.6]dodecane	**G.42**	181-15-7	192.5 ± 3.5	193.2 ± 2.9	189.9 ± 2.8	192.5 ± 3.5

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[a] Expanded uncertainties for 0.95 level of confidence are reported following the ± signs

[b] The outlier values are in italics

[c] Experimental liquid-phase enthalpy of formation is combined with the enthalpy of vaporization estimated by MBM

[d] Mixture of stereoisomers

3.4. Tetralins and decalins

The available experimental data allow derivation of the enthalpy of vaporization for tetralin, *cis*-decalin, and *trans*-decalin. The value for tetralin in Table 22 is derived from the state-of-the-art vapor pressures [76], and the values for the decalins are evaluated by TDE using experimental results from multiple works. The MBM estimates agree with the experiment within ±1.5 $\mathrm{kJ{\cdot}mol^{-1}}$.

The liquid-phase thermochemical data are available for the same three compounds as well as *cis*- and *trans*-9-methyldecalins (Table 23). Their CBS *ab initio* gas-phase enthalpies of formation are in good agreement with the experimental values for tetralin, both decalins, and *trans*-9-methyldecalin. For *cis*-9-methyldecalin, the *ab initio* value is more negative by 4.7 $\mathrm{kJ{\cdot}mol^{-1}}$, which slightly exceeds the combined uncertainty of the experimental and computed values (3.9 $\mathrm{kJ{\cdot}mol^{-1}}$) but is still within a sum of the uncertainties (5.5 $\mathrm{kJ{\cdot}mol^{-1}}$).

There are no MBM parameters for the enthalpies of formation of tetralins and decalins; therefore, they could not be predicted directly. *Ab initio* calculations were carried out for 1-alkyltetralins up to the 1-butyl derivative. For the long-chain compounds, the values were derived with 1-butyltetralin as a base structure using the -20.6 $\mathrm{kJ{\cdot}mol^{-1}}$ increment per CH_2 group.

Monomethyldecalins have two or three stereo centers and, therefore, multiple stereoisomers. *Ab initio* calculations were conducted for all isomeric monomethyldecalins (Table 15). The computed gas-phase $\Delta_f H^\circ_m$ values vary from –(212.8 to 195.9) $\mathrm{kJ{\cdot}mol^{-1}}$. In Table 24, the values for isomeric mixtures are given as well. The enthalpies of formation for 1- and 2-alkyldecalins $C_{10}H_{17}C_nH_{2n+1}$ were estimated by adding -20.6(n – 1) $\mathrm{kJ{\cdot}mol^{-1}}$ to the value for the corresponding methyldecalin. This approximation is reasonable considering a large uncertainty of $\Delta_f H^\circ_m$ for the isomeric methyldecalin mixtures. For 2,6-dimethyldecalin, the following equation was used:

$\Delta_f H^\circ_m$(2,6-dimethyldecalin) = 2$\Delta_f H^\circ_m$(2-methyldecalin) – $\Delta_f H^\circ_m$(decalin) (6)

For all compounds, except tetralin, two decalins, and two 9-methyldecalins, the liquid-phase enthalpies of formation were estimated by subtracting the enthalpies of vaporization from the gas-phase enthalpies of formation.

3.5. *Evaluation of the accuracy of ab initio results*

In Figures 5, 6 and 7, the *ab initio* $\Delta_f H^\circ_m$ values are compared with their experimental counterparts. For some compounds, the predicted enthalpies of vaporization were used to convert the experimental liquid-phase values to the gas-phase ones. This does not affect the conclusions made in this section because of the relatively low uncertainty of the predicted $\Delta_{vap} H^\circ_m$. For monocyclic compounds, the observed deviations (Figure 5) lie within (-1.6 to 1.0) kJ·mol^{-1} indicating a very good performance of the original *ab initio* protocol.

The comparisons for bi- and tricyclic compounds except include 24 compounds (tetralin and *trans*-bicyclo[3.3.0]octane not included) for the original version of the *ab initio* protocol (Figure 6). The deviations are between (-7.9 and 1.7) kJ·mol^{-1}, and the average deviation is -2.6 kJ·mol^{-1}. The CBS version of the protocol demonstrates a significantly better agreement with the experiment (Figure 7). For 22 considered compounds (excluding those with isolated cycles), the deviations are between (-4.7 and 2.6) kJ·mol^{-1}, and the average deviation is -1.4 kJ·mol^{-1}. All results are consistent within a sum of the experimental and *ab initio* uncertainties.

The scatter is still more significant than in the case of monocyclic compounds. The molar masses for these hydrocarbons are greater than those of the monocyclic ones and, as a result, the experimental uncertainties of $\Delta_f H^\circ_m$ are also higher. Another potential factor contributing to the observed scatter is that the measurements were conducted in different laboratories. For example, the thermochemistry laboratory of the Moscow State University (Soviet Union) is the major contributor for the bridged compounds. Most results for the compounds with fused rings (including decalins and tetralin) came from NBS and the University of Utah. However, no noticeable, statistically significant deviations between different types of compounds are observed, thus supporting the consistency of the procedures used in different laboratories.

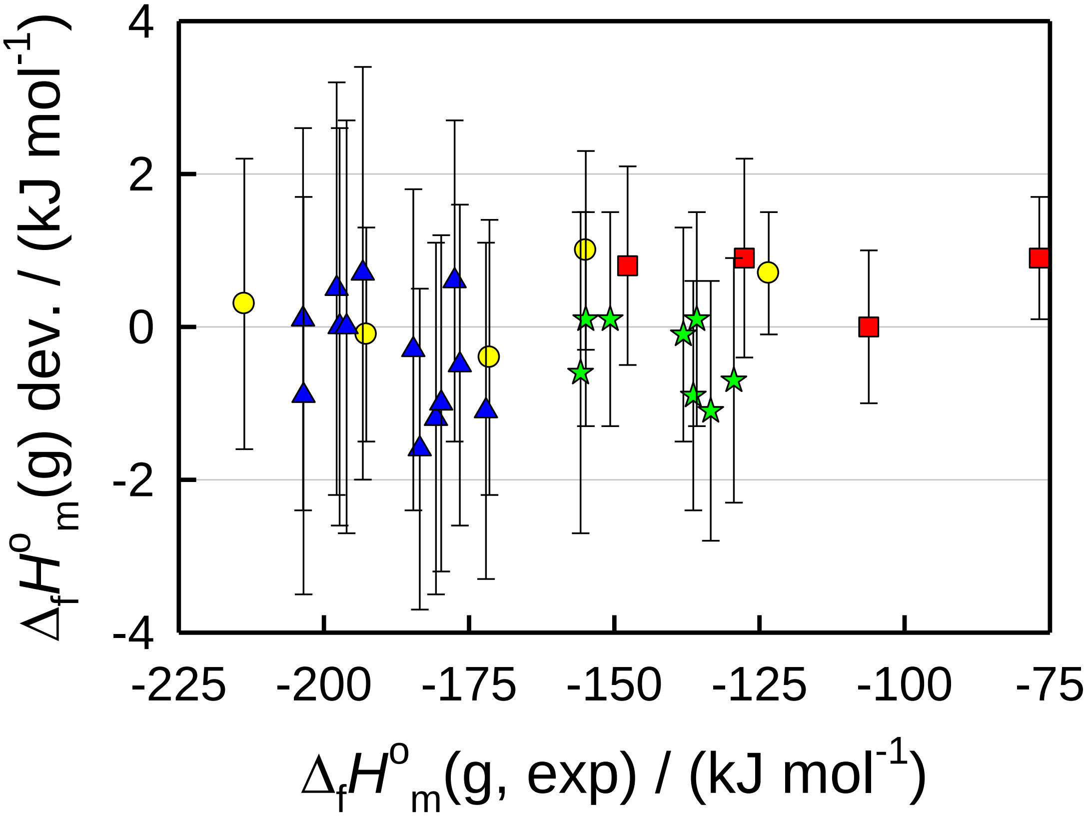

Figure 5. Deviation of the *ab initio* gas-phase standard molar enthalpies of formation of monocyclic compounds from the experimental values: monoalkylcyclohexanes (yellow circles), dialkylcyclohexanes (blue triangles), monoalkylcyclopentanes (red squares), and dialkylcyclopentanes (green stars). For some compounds, the enthalpies of vaporization estimated by MBM are used (see Tables 6, 12, and 15). The results for 1-ethyl-3-methylcyclopentanes are not shown due to potential ambiguity in the isomer identification (see text).

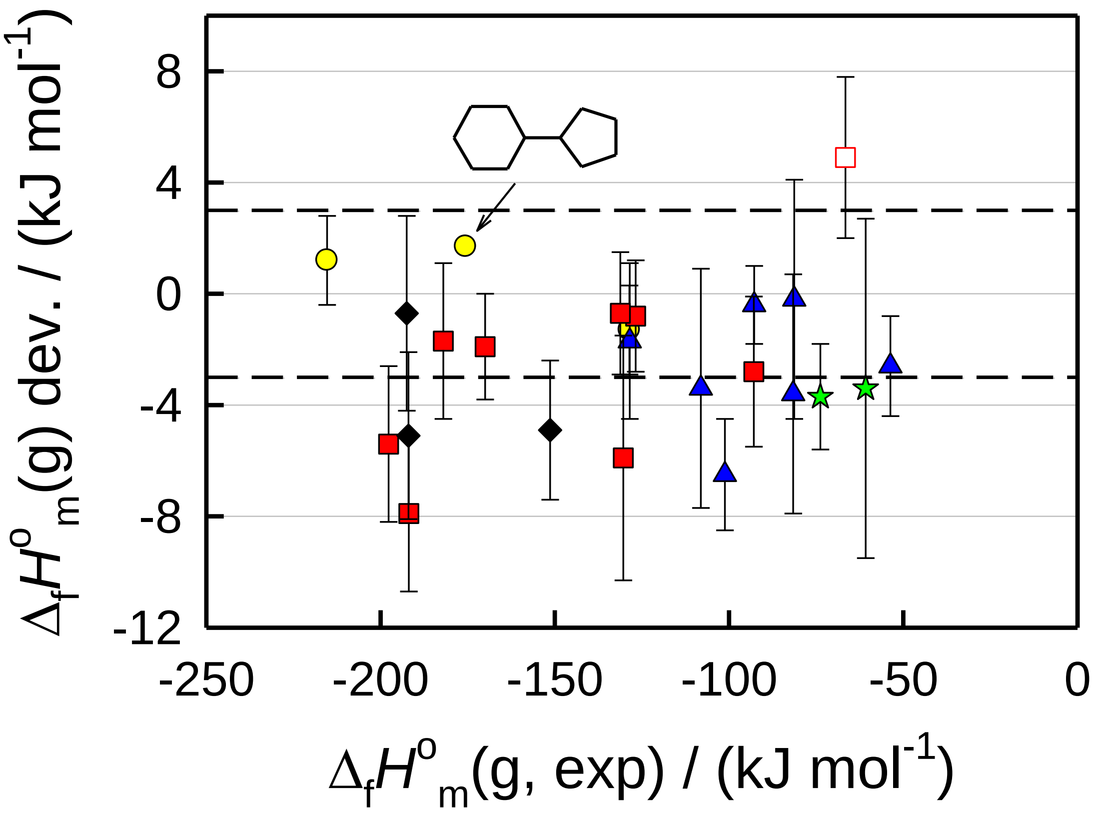

Figure 6. Deviation of the *ab initio* (quadruple-zeta version of the protocol) gas-phase standard molar enthalpies of formation of polycyclic compounds from the experimental values: bicyclic compounds with separated rings (yellow circles), bridged compounds (blue triangles), compounds with fused rings including decalins (red squares), tricyclic compounds (green stars), and spiro compounds (black diamonds). For some compounds, the enthalpies of vaporization estimated by MBM are used. See Tables 21 and 24 for more details. The outlier (*trans*-bicyclo[3.3.0]octane) is marked with an empty symbol. The experimental uncertainty for cyclopentylcyclohexane (marked by an arrow and a structure depiction) is unknown (see text). The dashed lines indicate the estimated uncertainty of the *ab initio* results (3 kJ·mol^{-1}).

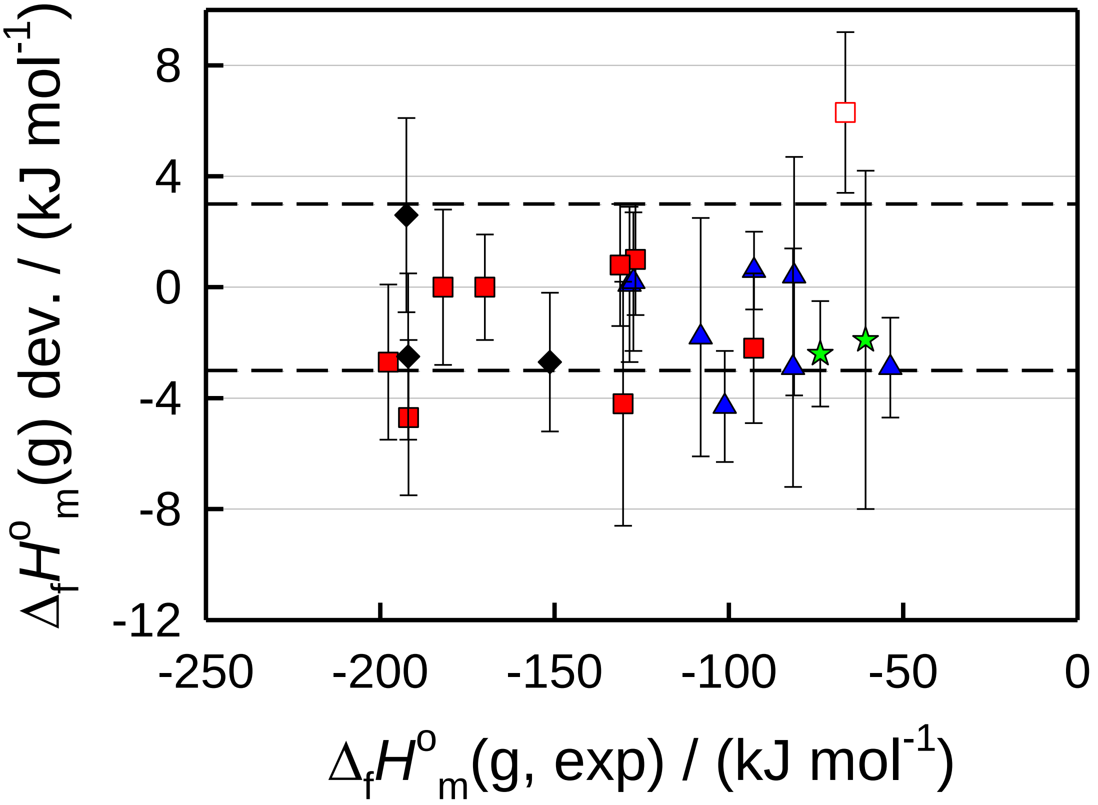

Figure 7. Deviation of the *ab initio* (CBS version of the protocol) gas-phase standard molar enthalpies of formation of polycyclic compounds from the experimental values: bridged compounds (blue triangles), compounds with fused rings including decalins (red squares), tricyclic compounds (green stars), and spiro compounds (black diamonds). For some compounds, the enthalpies of vaporization estimated by MBM are used. See Tables 21 and 24 for more details. The outlier (*trans*-bicyclo[3.3.0]octane) is marked with an empty symbol. The dashed lines indicate the estimated uncertainty of the *ab initio* results (3 kJ·mol^{-1}).

4. Conclusions

The recommended enthalpies of vaporization and formation in liquid and gas phases were produced for 212 aliphatic cyclic compounds and their alkyl derivatives. A thorough evaluation of available experimental data combined with group-contribution estimates, high-level *ab initio* results, and homologous trend analysis was conducted. It was found that the NIST-modified Benson method [18] generally performs well for the enthalpies of vaporization. For the enthalpies of formation in the gas phase, the approach based on local CCSD(T) methods [10] combined with structural series trend analysis for extrapolation toward longer side chains appears a much better alternative to the group-contribution methods. This is especially relevant for compounds with different stereo configurations for two or more side chains. Group-contribution methods typically do not distinguish these configurations, while the quantum chemical methods yield substantial differences. The distinction between stereoisomers is also frequently ignored in engineering applications. While recognizing the need for such a lumped representation in many practical situations, it should be emphasized that it substantially increases the corresponding uncertainties. In the course of the study, several likely-erroneous experimental values (outliers) were identified.

CRediT authorship contribution statement

Eugene Paulechka: Conceptualization, Methodology, Formal analysis, Investigation, Software, Data Curation, Writing – Original Draft.

Andrei Kazakov: Methodology, Investigation, Software, Writing – Review & Editing.

Suphat Watanasiri: Conceptualization, Review & Editing.

Abhijit Dutta: Project administration, Funding acquisition, Review & Editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgements

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The calculations, in part, were carried out using NIST high-performance computing facilities raritan and simba and Texas Advanced Computing Center cluster, stampede3.

Table 22. Standard enthalpies of vaporization $\Delta_{\mathrm{vap}}H^{\circ}_{\mathrm{m}}$ of tetralins and decalins at T = 298.15 K [a]

Compound	Alias	CASRN	$\Delta_{\mathrm{vap}}H^{\circ}_{\mathrm{m}}$ / (kJ·mol^{-1})			
			Experiment	Source	MBM	Selected
tetralin (1,2,3,4-tetrahydronaphthalene)	**H.1**	119-64-2	53.8 ± 0.2	76	53.4 ± 1.5	53.8 ± 0.2
5-methyltetralin	**H.2**	2809-64-5			59.1 ± 1.5	59.1 ± 1.5
6-methyltetralin	**H.3**	1680-51-9			58.6 ± 1.5	53.6 ± 1.5
1-methyltetralin	**H.4**	1559-81-5			56.3 ± 1.5	56.3 ± 1.5
2-methyltetralin	**H.5**	3877-19-8			56.3 ± 1.5	56.3 ± 1.5
1-ethyltetralin	**H.6**	13556-58-6			60.9 ± 1.5	60.9 ± 1.5
1-propyltetralin	**H.7**	66324-83-2			65.8 ± 1.5	65.8 ± 1.5
1-butyltetralin	**H.8**	38857-76-0			70.7 ± 1.5	70.7 ± 1.5
1-pentyltetralin	**H.9**	66359-06-6			75.6 ± 1.5	75.6 ± 1.5
1-hexyltetralin	**H.10**	66325-11-9			80.6 ± 1.5	80.6 ± 1.5
1-heptyltetralin	**H.11**	66563-99-3			85.5 ± 1.5	85.5 ± 1.5
1-octyltetralin	**H.12**	29138-91-8			90.4 ± 1.5	90.4 ± 1.5
1-nonyltetralin	**H.13**	33425-49-9			95.3 ± 1.5	95.3 ± 1.5

cis-decalin (*cis*-decahydronaphthalene)	**H.14**	493-01-6	50.5 ± 0.9	15	49.6 ± 1.5	50.5 ± 0.9
trans-decalin (*trans*-decahydronaphthalene)	**H.15**	493-02-7	48.1 ± 1.0	15	49.6 ± 1.5	48.1 ± 1.0
decalin (decahydronaphthalene)[b]	**H.16**	91-17-8			49.6 ± 1.5	48.8 ± 1.7
rel-(1*R*,4a*R*,8a*R*)-1-methyldecalin	**H.17**	4683-95-8			52.5 ± 1.5	52.5 ± 1.5
rel-(1*R*,4a*S*,8a*S*)-1-methyldecalin	**H.18**	14398-67-5			52.5 ± 1.5	52.5 ± 1.5
rel-(1*R*,4a*R*,8a*S*)-1-methyldecalin	**H.19**	14398-69-7			52.5 ± 1.5	52.5 ± 1.5
rel-(1*R*,4a*S*,8a*R*)-1-methyldecalin	**H.20**	14398-68-6			52.5 ± 1.5	52.5 ± 1.5
1-methyldecalin[b]	**H.21**	2958-75-0			52.5 ± 1.5	52.5 ± 1.5
rel-(2*R*,4a*R*,8a*R*)-2-methyldecalin	**H.22**	14398-71-1			52.5 ± 1.5	52.5 ± 1.5
rel-(2*R*,4a*S*,8a*S*)-2-methyldecalin	**H.23**	4683-94-7			52.5 ± 1.5	52.5 ± 1.5
rel-(2*R*,4a*R*,8a*S*)-2-methyldecalin	**H.24**	14398-72-2			52.5 ± 1.5	52.5 ± 1.5
rel-(2*S*,4a*R*,8a*S*)-2-methyldecalin	**H.25**	14386-57-3			52.5 ± 1.5	52.5 ± 1.5
2-methyldecalin[b]	**H.26**	2958-76-1			52.5 ± 1.5	52.5 ± 1.5

cis-9-methyldecalin	**H.27**	2547-26-4	52.0 ± 1.5	52.0 ± 1.5
trans-9-methyldecalin	**H.28**	2547-27-5	52.0 ± 1.5	52.0 ± 1.5
9-methyldecalin[b]	**H.29**	6596-97-0	52.0 ± 1.5	52.0 ± 1.5
1-ethyldecalin[b]	**H.30**	1008-17-9	57.1 ± 1.5	57.1 ± 1.5
2-ethyldecalin[b]	**H.31**	1618-23-1	57.1 ± 1.5	57.1 ± 1.5
2,6-dimethyldecalin[b]	**H.32**	1618-22-0	55.5 ± 1.5	55.5 ± 1.5
1-propyldecalin[b]	**H.33**	91972-45-1	62.0 ± 1.5	62.0 ± 1.5
1-butyldecalin[b]	**H.34**	92369-80-7	67.0 ± 1.5	67.0 ± 1.5
1-pentyldecalin[b]	**H.35**	1772625-95-2	71.9 ± 1.5	71.9 ± 1.5
1-hexyldecalin[b]	**H.36**	1772625-96-3	76.8 ± 1.5	76.8 ± 1.5
1-heptyldecalin[b]	**H.37**	1772625-97-4	81.7 ± 1.5	81.7 ± 1.5
1-octyldecalin[b]	**H.38**	95278-30-1	86.6 ± 1.5	86.6 ± 1.5
1-nonyldecalin[b]	**H.39**		91.6 ± 1.5	91.6 ± 1.5

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[a] Expanded uncertainties for 0.95 level of confidence are reported following the ± signs

[b] Mixture of stereoisomers

Table 23. Standard enthalpies of formation $\Delta_f H^\circ_m$ of liquid tetralins and decalins ($kJ \cdot mol^{-1}$) at T = 298.15 K [a]

Compound	Alias	CASRN	$-\Delta_f H^\circ_m(l)$ / ($kJ \cdot mol^{-1}$)		
			Experiment	Source	Selected
tetralin (1,2,3,4-tetrahydronaphthalene)	**H.1**	119-64-2	29.1 ± 1.5	74,64	29.1 ± 1.5
5-methyltetralin	**H.2**	2809-64-5			65.7 ± 3.2
6-methyltetralin	**H.3**	1680-51-9			65.0 ± 3.2
1-methyltetralin	**H.4**	1559-81-5			57.1 ± 3.2
2-methyltetralin	**H.5**	3877-19-8			62.5 ± 3.2
1-ethyltetralin	**H.6**	13556-58-6			80.7 ± 3.2
1-propyltetralin	**H.7**	66324-83-2			106.9 ± 3.3
1-butyltetralin	**H.8**	38857-76-0			132.7 ± 3.3
1-pentyltetralin	**H.9**	66359-06-6			158.2 ± 3.4
1-hexyltetralin	**H.10**	66325-11-9			183.8 ± 3.4
1-heptyltetralin	**H.11**	66563-99-3			209.3 ± 3.4
1-octyltetralin	**H.12**	29138-91-8			234.8 ± 3.4
1-nonyltetralin	**H.13**	33425-49-9			260.3 ± 3.4

cis-decalin (*cis*-decahydronaphthalene)	**H.14**	493-01-6	219.5 ± 1.6	77,78,17	219.5 ± 1.6
trans-decalin (*trans*-decahydronaphthalene)	**H.15**	493-02-7	230.2 ± 2.6	77,78,17	230.2 ± 2.6
decalin (decahydronaphthalene)[b]	**H.16**	91-17-8			224.9 ± 8.0
rel-(1*R*,4a*R*,8a*R*)-1-methyldecalin	**H.17**	4683-95-8			253.4 ± 3.1
rel-(1*R*,4a*S*,8a*S*)-1-methyldecalin	**H.18**	14398-67-5			260.1 ± 3.1
rel-(1*R*,4a*R*,8a*S*)-1-methyldecalin	**H.19**	14398-69-7			248.4 ± 3.1
rel-(1*R*,4a*S*,8a*R*)-1-methyldecalin	**H.20**	14398-68-6			249.0 ± 3.1
1-methyldecalin[b]	**H.21**	2958-75-0			253 ± 10
rel-(2*R*,4a*R*,8a*R*)-2-methyldecalin	**H.22**	14398-71-1			265.3 ± 3.1
rel-(2*R*,4a*S*,8a*S*)-2-methyldecalin	**H.23**	4683-94-7			257.6 ± 3.1
rel-(2*R*,4a*R*,8a*S*)-2-methyldecalin	**H.24**	14398-72-2			252.9 ± 3.1
rel-(2*S*,4a*R*,8a*S*)-2-methyldecalin	**H.25**	14386-57-3			253.6 ± 3.1
2-methyldecalin[b]	**H.26**	2958-76-1			257 ± 11

cis-9-methyldecalin	**H.27**	2547-26-4	243.9 ± 2.4	79	243.9 ± 2.4
trans-9-methyldecalin	**H.28**	2547-27-5	249.7 ± 2.4	79	249.7 ± 2.4
9-methyldecalin[b]	**H.29**	6596-97-0			246.8 ± 5.3
1-ethyldecalin[b]	**H.30**	1008-17-9			278 ± 10
2-ethyldecalin[b]	**H.31**	1618-23-1			283 ± 11
2,6-dimethyldecalin[b]	**H.32**	1618-22-0			290 ± 23
1-propyldecalin[b]	**H.33**	91972-45-1			303 ± 10
1-butyldecalin[b]	**H.34**	92369-80-7			329 ± 10
1-pentyldecalin[b]	**H.35**	1772625-95-2			355 ± 10
1-hexyldecalin[b]	**H.36**	1772625-96-3			380 ± 10
1-heptyldecalin[b]	**H.37**	1772625-97-4			406 ± 10
1-octyldecalin[b]	**H.38**	95278-30-1			431 ± 10
1-nonyldecalin[b]	**H.39**				457 ± 10

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[a] Expanded uncertainties for 0.95 level of confidence are reported following the ± signs

[b] Mixture of stereoisomers

Table 24. Standard enthalpies of formation $\Delta_f H^\circ_m$ of gaseous tetralins and decalins (kJ·mol^{-1}) at T = 298.15 K [a]

Compound	Alias	CASRN	$-\Delta_f H^\circ_m$(g) / (kJ·mol^{-1})			
			Experiment	*ab initio* QZ	*ab initio* CBS	Selected
tetralin (1,2,3,4-tetrahydronaphthalene)	**H.1**	119-64-2	-(24.4 ± 2.6)	-(25.0 ± 2.7)		-(24.4 ± 2.6)
5-methyltetralin	**H.2**	2809-64-5		6.6 ± 2.8		6.6 ± 2.8
6-methyltetralin	**H.3**	1680-51-9		6.4 ± 2.8		6.4 ± 2.8
1-methyltetralin	**H.4**	1559-81-5		0.8 ± 2.8		0.8 ± 2.8
2-methyltetralin	**H.5**	3877-19-8		6.2 ± 2.8		6.2 ± 2.8
1-ethyltetralin	**H.6**	13556-58-6		19.8 ± 2.8		19.8 ± 2.8
1-propyltetralin	**H.7**	66324-83-2		41.1 ± 2.9		41.1 ± 2.8
1-butyltetralin	**H.8**	38857-76-0		62.0 ± 2.9		62.0 ± 2.9
1-pentyltetralin	**H.9**	66359-06-6		82.6 ± 3.0 [b]		82.6 ± 3.0
1-hexyltetralin	**H.10**	66325-11-9		103.2 ± 3.0 [b]		103.2 ± 3.0
1-heptyltetralin	**H.11**	66563-99-3		123.8 ± 3.0 [b]		123.8 ± 3.0
1-octyltetralin	**H.12**	29138-91-8		144.4 ± 3.0 [b]		144.4 ± 3.0
1-nonyltetralin	**H.13**	33425-49-9		165.0 ± 3.0 [b]		165.0 ± 3.0

cis-decalin (*cis*-decahydronaphthalene)	**H.14**	493-01-6	170.0 ± 1.9	171.9 ± 2.8	170.0 ± 2.6	170.0 ± 1.9
trans-decalin (*trans*-decahydronaphthalene)	**H.15**	493-02-7	182.0 ± 2.8	183.7 ± 2.8	182.0 ± 2.6	182.0 ± 2.8
decalin (decahydronaphthalene)[c]	**H.16**	91-17-8				176.0 ± 8.8
rel-(1*R*,4a*R*,8a*R*)-1-methyldecalin	**H.17**	4683-95-8		203.4 ± 2.9	200.7 ± 2.7	200.7 ± 2.7
rel-(1*R*,4a*S*,8a*S*)-1-methyldecalin	**H.18**	14398-67-5		210.4 ± 2.9	207.6 ± 2.7	207.6 ± 2.7
rel-(1*R*,4a*R*,8a*S*)-1-methyldecalin	**H.19**	14398-69-7		198.9 ± 2.9	195.9 ± 2.7	195.9 ± 2.7
rel-(1*R*,4a*S*,8a*R*)-1-methyldecalin	**H.20**	14398-68-6		199.2 ± 2.9	196.5 ± 2.7	196.5 ± 2.7
1-methyldecalin[c]	**H.21**	2958-75-0				200.2 ± 10.1
rel-(2*R*,4a*R*,8a*R*)-2-methyldecalin	**H.22**	14398-71-1		215.1 ± 2.9	212.8 ± 2.7	212.8 ± 2.7
rel-(2*R*,4a*S*,8a*S*)-2-methyldecalin	**H.23**	4683-94-7		207.4 ± 2.9	205.1 ± 2.7	205.1 ± 2.7
rel-(2*R*,4a*R*,8a*S*)-2-methyldecalin	**H.24**	14398-72-2		203.1 ± 2.9	200.4 ± 2.7	200.4 ± 2.7
rel-(2*S*,4a*R*,8a*S*)-2-methyldecalin	**H.25**	14386-57-3		203.6 ± 2.9	201.1 ± 2.7	201.1 ± 2.7
2-methyldecalin[c]	**H.26**	2958-76-1				204.9 ± 10.7

cis-9-methyldecalin	**H.27**	2547-26-4	191.9 ± 2.8[d]	199.8 ± 2.9	196.6 ± 2.7	191.9 ± 2.8
trans-9-methyldecalin	**H.28**	2547-27-5	197.7 ± 2.8[d]	203.1 ± 2.9	200.4 ± 2.7	197.7 ± 2.8
9-methyldecalin[c]	**H.29**	6596-97-0				194.8 ± 5.7
1-ethyldecalin[c]	**H.30**	1008-17-9				221 ± 10
2-ethyldecalin[c]	**H.31**	1618-23-1				226 ± 11
2,6-dimethyldecalin[c]	**H.32**	1618-22-0				234 ± 23
1-propyldecalin[c]	**H.33**	91972-45-1				241 ± 10
1-butyldecalin[c]	**H.34**	92369-80-7				262 ± 10
1-pentyldecalin[c]	**H.35**	1772625-95-2				283 ± 10
1-hexyldecalin[c]	**H.36**	1772625-96-3				303 ± 10
1-heptyldecalin[c]	**H.37**	1772625-97-4				324 ± 10
1-octyldecalin[c]	**H.38**	95278-30-1				344 ± 10
1-nonyldecalin[c]	**H.39**					365 ± 10

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[a] Expanded uncertainties for 0.95 level of confidence are reported following the ± signs

[b] Calculated using the *ab initio* value for 1-butyltetralin and the CH_2 increment of -20.6 kJ·mol^{-1}

[c] Mixture of isomers

[d] Experimental liquid-phase enthalpy of formation is combined with the enthalpy of vaporization estimated by MBM

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