

Liquid Organic Hydrogen Carriers: Thermophysical and Thermochemical Studies of Benzyl- and Dibenzyl-toluene Derivatives

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S Supporting Information

ABSTRACT: The heat transfer oils dibenzyltoluene and benzyltoluene are promising materials as a new class of liquid organic hydrogen carrier compounds (LOHC). Thermophysical properties (heat capacity, density, viscosity, and surface tension) of the commercially available thermofluids Marlothem LH (benzyltoluene) and Marlothem SH (dibenzyltoluene) and their completely hydrogenated derivatives were measured. Thermochemical properties (enthalpies of combustion and enthalpies of vaporization) were derived from experiments. Gas-phase molar enthalpies of formation were derived and validated with group-additivity and high-level quantum chemical calculations. Enthalpies of the hydrogenation/dehydrogenation reactions of the LOHC pairs under study were derived.

1. INTRODUCTION

Liquid organic hydrogen carriers (LOHCs) are an interesting option for the storage of hydrogen. The concept of LOHC is based on the reversible hydrogenation of an unsaturated, usually aromatic, compound. This reaction forms a saturated compound, which is the hydrogen-rich form of the carrier. In a dehydrogenation reaction, the hydrogenated (i.e., hydrogen rich) form releases the hydrogen for further utilization. The hydrogen uptake in the hydrogenation reaction requires elevated pressures of about 30 to 50 bar. The dehydrogenation on the other hand can be operated at ambient pressure but necessitates high temperatures of up to 300 °C. However, during storage time, ambient conditions can be applied to the carrier, without any negative influence on storage density or losses during storage time. This is one of the most important advantages compared to most other hydrogen storage technologies.^{1–3}

The design of a LOHC system is dependent on reliable data for substance properties. Important values are for example the enthalpies of the hydrogenated and dehydrogenated form, since the enthalpy of reaction, along with heat capacity, determines a major part of the energy demand of the process. Data concerning evaporation behavior can also be crucial, since evaporation during hydrogen release influences the energy balance. Furthermore, knowledge about the vapor pressure of the LOHC compounds is important for the removal of traces of LOHC from the hydrogen gas leaving the release unit.

Different materials have been under research as LOHCs, such as toluene⁴ and *N*-ethylcarbazole.⁵ Due to a favorable behavior in many aspects, benzyltoluene (often sold under the brand name Marlothem LH; abbreviation MLH) and

especially dibenzyltoluene (often sold under the brand name Marlothem SH; abbreviation MSH) have come into the focus of current research.⁶ Dibenzyltoluene has been used as a heat transfer fluid working in the temperature range from 343 to 653 K⁷ for many decades now (see Figure 1).

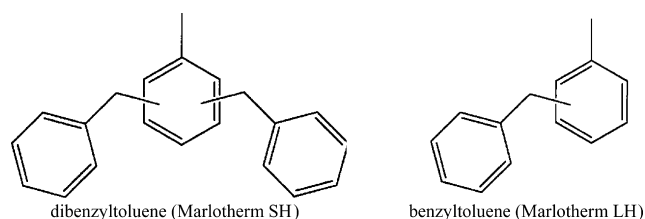


Figure 1. Benzyltoluenes studied in this work.

Nevertheless, availability of substance properties is still limited.⁸ Since hydrogenation of dibenzyltoluene is a rather new topic, substance data for the hydrogenated form are scarcely available so far. Both compounds are sold as isomeric mixtures consisting of different stereoisomers (see Figure S2). Due to the different possible isomers of dibenzyltoluene as starting material, the hydrogenation reaction leads to a mixture that is even more complex. Figure 2 shows an example for a simplified, potential reaction pathway. The catalytic hydrogenation of dibenzyltoluene works stepwise via the partly

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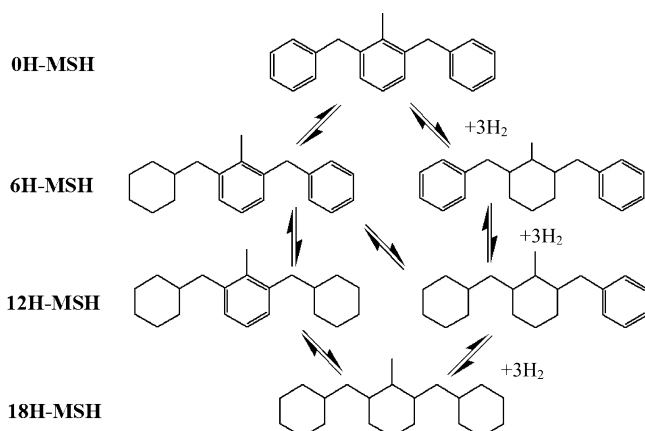


Figure 2. Reversible hydrogenation of ((5-methyl-1,3-phenylene)bis(methylene))dibenzene as one of the major compounds in the dibenzyltoluene isomeric mixture, sold under the brand name Marlotherm SH.

hydrogenated intermediates 6H-MSH and 12H-MSH to the fully hydrogenated form 18H-MSH which stores 9 mol of H_2 . The hydrogenated dibenzyltoluene is a mixture consisting of different stereoisomers and, owing to the chiral C atoms, also different diastereomers.

For a closer evaluation of benzyltoluene and dibenzyltoluene regarding its application as potential LOHCs, substance properties for the isomeric mixtures of both compounds in their hydrogenated and dehydrogenated form have been measured in this work. Data concerning heat capacity, enthalpy of formation, enthalpy of vaporization, vapor pressure, density, viscosity, and surface tension are reported. Gas-phase molar enthalpies of formation were compared with group-additivity and high-level quantum chemical calculations. The values were used to derive enthalpies of reactions of the reversible dehydrogenation and hydrogenation catalytic processes. This contribution complements and extends our previous work on thermodynamics of carbazole derivatives as LOHC.^{9–11}

2. MATERIALS AND METHODS

2.1. Materials. Benzyltoluene and dibenzyltoluene fluids were supplied by Sasol Germany GmbH and were not further purified. An isomeric mixture consisting of benzyltoluene is commercially available as Marlotherm LH (0H-MLH) with a benzyltoluene content of $\geq 98\%$. An isomeric mixture consisting of dibenzyltoluene is commercially available as Marlotherm SH (0H-MSH) with a dibenzyltoluene content of $\geq 98\%$. The purity of the mixtures was determined using GC-FID/MS (Agilent 7890 A5975C VL MSD). By catalytic hydrogenation of 0H-MLH and 0H-MSH at the Institute of Reaction Engineering in Erlangen (Prof. Wasserscheid), the perhydrogenated compounds 12H-MLH (perhydrogenated benzyltoluene) and 18H-MSH (perhydrogenated dibenzyltoluene) were formed.⁶ The degree of hydrogenation was determined to be $>99\%$ using a JEOL ECX 400 NMR. After hydrogenation, the hydrogenated compounds were filtered and centrifuged to separate solid catalyst particles from the liquid.

2.2. Thermophysical Properties. **2.2.1. Heat Capacity Measurements with the TMDSC Method.** The specific heat capacities of the (di)benzyltoluene derivatives were measured using the PerkinElmer DSC Pyris 1 equipped with an intracooler. We used the temperature modulated differential scanning calorimetry (TMDSC) method.^{12,13} This method has

an advantage over the standard DSC procedure because the high and the low frequency noises, particular signal drifts, are excluded due to the frequency selective data treatment. Application of the temperature modulation mode allowed for increasing accuracy of heat capacity measurements to 1% even at elevated temperatures.¹² Preliminary measurements were performed with a standard scanning mode with the heating rate of $10 \text{ K}\cdot\text{min}^{-1}$. The temperature–time profiles of the TMDSC program included a sequence of temperature steps and isotherms. The temperature was increased by 5 K, and the isotherms had a 5 min duration. The measurements were performed in three steps: baseline measurement, calibration measurement with sapphire, and sample measurement. Nitrogen was used as a purge gas.

2.2.2. Density. Density measurements were carried out using an oscillating U-tube densimeter DMA 5000 from Anton Paar Germany GmbH. The apparatus was calibrated with air and water at $T = 20 \text{ }^\circ\text{C}$ and ambient pressure. The maximum error in water density was determined to be $\pm 0.00005 \text{ g}\cdot\text{cm}^{-3}$ after calibration. Approximately 1 mL of substance was filled in the U-tube and measured at least 3 times in series for each temperature. In order to check the reproducibility of the sample introduction, the measurement was repeated so that in total at least 6 measurements for each temperature were performed. The standard deviation of the two measured substances 12H-MLH and 18H-MSH was determined to be $\pm 0.00005 \text{ g}\cdot\text{cm}^{-3}$.

2.2.3. Viscosity. The dynamic viscosity of 12H-MLH and 18H-MSH was measured using the rotational rheometer MCR 102 from Anton Paar Germany GmbH with the measuring system CP50-1 (cone–plate). Approximately 0.6 mL of substance was placed in the middle of the measuring plate. A Newtonian behavior of the substances was found when varying the shear rate from 100 to 700 s^{-1} . Subsequently, the dynamic viscosity was measured at a continuous heating rate of $5 \text{ K}\cdot\text{min}^{-1}$ for a shear rate of 400 s^{-1} . After a constant period of 2 min, the dynamic viscosity was measured again at a constant cooling rate of $5 \text{ K}\cdot\text{min}^{-1}$ to check the influence of the temperature adjustment. The deviations were within the general measuring uncertainty. The measurement was performed at least three times. After each measurement, the measuring plate was cleaned and a new sample was introduced. The standard deviation for all substances was below 5%.

2.2.4. Surface Tension. The measurements of the surface tension of 0H-MLH and 0H-MSH and their hydrogenated derivatives were carried out using a Drop Volume Tensiometer DVT50 from Krüss GmbH Germany using a volume flow rate of $100\text{--}1500 \mu\text{L}\cdot\text{min}^{-1}$ and a syringe volume of $500 \mu\text{L}$. One drop was approximately $25 \mu\text{L}$ depending on the surface tension. The obtained surface tension constitutes the average of three measurements. The relative error in reproducibility in surface tension is below 1%.

2.3. Thermochemical Properties. **2.3.1. Combustion Calorimetry.** The molar enthalpies of combustion of (di)benzyltoluene fluids and their hydrogenated products were measured using an isoperibolic calorimeter with a static bomb and a stirred water bath. Liquid samples were burned in a polyethylene ampule of 1 mL volume (Fa. NeoLab, Heidelberg, Germany). The sealed ampule was placed in the crucible, and it was burned in oxygen at a pressure of 3.04 MPa. The detailed procedure has been described previously.¹³ The combustion products were examined for carbon monoxide (Dräger tube) and unburned carbon, but neither were detected. The energy equivalent of the calorimeter $\epsilon_{\text{calor}} = 14\,891.55 \pm 0.95 \text{ J}\cdot\text{K}^{-1}$ was

Table 1. TMDSC Results of the Heat Capacity Measurements^a

	polynomial	R ²	c _p (298.15 K) ^b J·K ⁻¹ ·g ⁻¹
0H-MLH	1.5697 - 0.0050·T + 2.319 × 10 ⁻⁵ ·T ² - 2.255 × 10 ⁻⁸ ·T ³	0.9973	1.54
12H-MLH	1.1133 + 0.0019·T + 3.358 × 10 ⁻⁶ ·T ² - 1.826 × 10 ⁻⁹ ·T ³	0.9981	1.93
0H-MSH	1.9160 - 0.0075·T + 2.979 × 10 ⁻⁵ ·T ² - 2.905 × 10 ⁻⁸ ·T ³	0.9979	1.56
18H-MSH	1.5069 - 0.0043·T + 1.996 × 10 ⁻⁵ ·T ² - 1.680 × 10 ⁻⁸ ·T ³	0.9980	1.55

^aCoefficients of polynomials $c_p = a + bt + ct^2 + dt^3$ where c_p is specific heat capacity (in J·K⁻¹·g⁻¹) and t is temperature (in K). ^bUncertainty of the heat capacity measurements was ±1.0%.

determined with a standard reference sample of benzoic acid (sample SRM 39j, NIST). For converting the energy of the actual bomb process to that of the isothermal process and reducing to standard states, the conventional procedure was applied.¹⁴ The relative atomic masses used for the elements, C = 12.010600, H = 1.007975, O = 15.999400, and N = 14.006855, were calculated as the mean of the bounds of the interval of the standard atomic weights recommended by the IUPAC commission in 2011¹⁵ for each of these elements. Correction for nitric acid formation was based on titration with 0.1 mol·dm⁻³ NaOH (aq). The energy correction for production of nitric acid is based on $\Delta U^\circ = -59.7$ kJ·mol⁻¹ for the formation of nitric acid according to reaction: $1/2$ N₂(g) + $5/4$ O₂(g) + $1/2$ H₂O(l) = HNO₃ (0.1 mol·dm⁻³).

2.3.2. Vapor Pressure Measurements: Static Method. Vapor pressures of the degassed 18H-MSH were measured with the static method. We used a self-made experimental setup.¹⁶ The stainless steel cylindrical cell with the sample was kept at a constant temperature within ±0.02 K. The sample cell was connected to the high temperature capacitance manometers (MKS Baratron 631B13LBFP and MKS Baratron 631C13MBFP) covering the working range of (0.1 to 10⁵) Pa. Uncertainties of 0.5% for the pressure readings for both manometers were stated by the manufacturer. The temperature of tubing connections between the measuring cell and pressure gauges was kept higher by 30–50 K than those in the sample cell in order to avoid condensation of sample vapors in the tubing system. The uncertainty of absolute temperature determination was ±0.05 K over the working temperature interval of the system of (298–368) K. The detailed description of the experimental apparatus, procedure, and uncertainty analysis, is given in ref 16. The experimental setup and the measuring procedure were tested in our previous work with measurements on naphthalene, ferrocene, and benzophenone as reference compounds.

2.3.3. Computations. Conformational analysis of the molecules constituting the Marlotherm mixtures was performed by the molecular mechanics using the MM3(96) program.¹⁷ The geometric parameters of the molecules (dihedral angles) were modified randomly with preserving the cyclic system, and then, geometry was optimized. The stable conformers found this way were used as the initial structures for quantum-chemical calculations using the high-level method G3MP2¹⁸ included in the Gaussian 09 series software.¹⁹ General computational details within this approach were reported elsewhere.²⁰ Enthalpies of each compound were calculated according to standard thermodynamic procedures.²¹

3. RESULTS AND DISCUSSION

3.1. Thermophysical Properties. 3.1.1. Heat Capacity Measurements. The DSC is conventionally used to investigate phase transitions and heat capacities of materials. It is a well-established and easy to use technique. However, the DSC

technique is less precise in comparison to the classic adiabatic calorimetry, traditionally used for the precise heat capacity measurements. There are few reasons responsible for that. The main reason is that the measuring system is operated under nonadiabatic conditions and heat flows to the surrounding must be considered. Another reason for the less accurate DSC measurements is that studies of liquid samples in the standard pan (pan mass of ca. 24 mg) are not possible because the liquid leaks out from the standard light crucible. Thus, the larger hermetically sealed crucible is usually required in order to avoid the capillary effects, but the massive crucible deteriorates the experiment. One of the possible ways to improve accuracy of DSC heat capacity measurements is TMDSC. Here, we use a step-iso temperature profile.²¹ After each 5 K increase of the system temperature, an isothermal step for a definite time (sufficient to bring the system to thermal equilibrium) is required. The isotherm length depends on the size of the DSC-crucible, and it is usually established in the preliminary experiments; e.g., the crucible (with the mass of 375 mg) used in the current study needed approximately 5 min to reach thermal equilibrium. Test measurements with our equipment on methyl stearate (where reliable liquid heat capacity data are available²²) were employed to establish the following measurement procedure: a temperature step of 5 K at the heating rate of 30 K·min⁻¹ was followed by a 5 min isothermal period used for thermal equilibration of the sample (see Figure S2). Measurements were performed in the temperature range between 195 and 405 K with 5 K steps. The procedure includes the baseline measurement with two empty crucibles, i.e., empty sample and empty reference. The next run is performed with the substance in the sample crucible. The loaded data subtracted from the baseline are shown in Figure S3. To extract the heat capacity from the subtracted data, a Fourier transformation was applied.^{12,23} Results from the test measurements on methyl stearate are given on Figure S4. Experimental specific heat capacities for the (di)benzyltoluene derivatives measured in this work are given in Table S1. The data were fitted to a second order polynomial function. Coefficients of the polynomials are given in Table 1.

The benzyltoluene derivatives 0H-MLH and 12H-MLH remain as a liquid in the whole temperature range under study. The dibenzyltoluene derivatives 0H-MSH and 18H-MSH show solid–liquid phase transition at 225.5 K for the dehydrogenated form (dibenzyltoluene) 0H-MSH and at 215.5 K for the fully hydrogenated dibenzyltoluene derivative 18H-MSH.

Comparison of our precise TMDSC results with the technical Sasol data available for the dibenzyltoluene derivatives 0H-MLH and 0H-MSH are given in Figures 3 and 4. The agreement of our results with technical data for 0H-MLH is quite poor. In contrast, the results for 0H-MSH show an acceptable agreement at least within our experimental temperature range. In the absence of any experimental details on the heat capacity measurements performed at Sasol, we are reticent

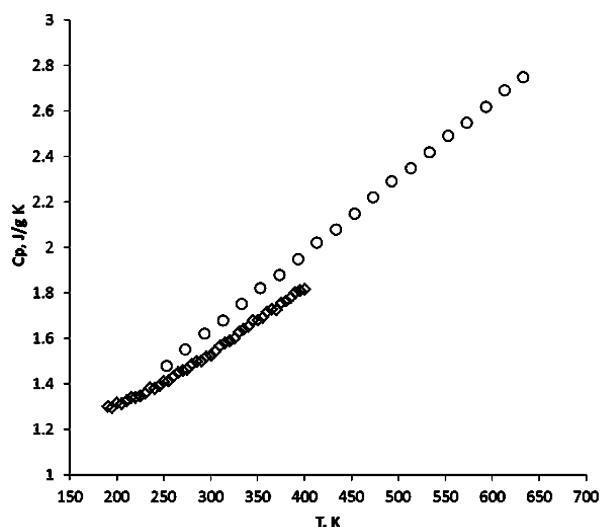


Figure 3. Comparison of experimental measurements of a heat capacity of 0H-MLH: \circ , Sasol; \diamond , this work.

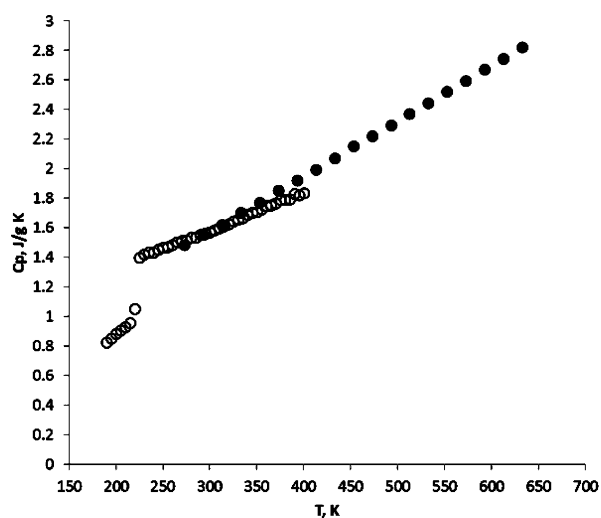


Figure 4. Comparison of experimental measurements of a heat capacity of 0H-MSH: \bullet , Sasol; \circ , this work.

to explain the differences observed. However, our result for 0H-MLH $C_{p,m}^{\circ}$ (298.15 K) = $281 \pm 3 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ was in acceptable agreement with the value $C_{p,m}^{\circ}$ (298.15 K) = $296.6 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ reported for 1-methyl-4-(phenylmethyl)-benzene,²⁴ which is one of the three isomers contained in 0H-MLH.

Experimental heat capacity measurements of the (di)-benzyltoluene derivatives are important for technical purposes. Moreover, we need the standard molar heat capacities, $C_{p,m}^{\circ}$ (298.15 K), in order to adjust vaporization enthalpies measured by static measurements to the reference temperature $T = 298.15 \text{ K}$ (see Table 2), as well as for the adjustment of the combustion calorimetry results to the standard conditions (see Table S2). These values were derived from the TMDSC results and given in Table 2.

3.1.2. Density. Table S3 shows the densities measured in this work and those from the literature. The density of benzyltoluene (0H-MLH) and dibenzyltoluene (0H-MSH) is more than 10% higher than the density of the hydrogenated compounds 12H-MLH and 18H-MSH. On a molecular basis, this might be due to the planar nature of the aromatic rings in

Table 2. Compilation of Data on Liquid Phase Molar Heat Capacities (in $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$) at 298.15 K

	$C_{p,m}^{\circ}$ ^a	$-\Delta_f^{\circ}C_{p,m}^{\circ}$ ^b
0H-MLH	281 ± 3^c	83.6 ± 13
12H-MLH	375 ± 3	108.1 ± 17
0H-MSH	425 ± 4	121.1 ± 19
18H-MSH	450 ± 4	127.6 ± 20

^aMeasured by the TMDSC method in this work. ^bCalculated according to the procedure developed by Chickos and Acree.²⁵ Uncertainties were calculated using an assumption that a standard deviation of $\pm 16 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ of the liquid phase heat capacity, C_p° , can be ascribed for a broad range of small organic molecules.²⁵ ^cFor comparison $C_{p,m}^{\circ}$ (298.15 K) = $296.6 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ was reported for 4-methyl-diphenylmethane.³³

0H-MLH and 0H-MSH. In the hydrogenated ring systems, the rings are not planar anymore and thus occupy more space.

The temperature dependency of the density was fitted with a linear equation:

$$\rho(T) = A + B \cdot T/K \quad (1)$$

The parameters for this equation are given in Table 3.

Table 3. Density of the (Di)benzyltoluene Derivatives at Different Temperatures^a

ρ , $\text{g}\cdot\text{cm}^{-3}$	0H-MSH	18H-MSH	0H-MLH	12H-MLH
A	1.2537113	1.1005251	1.2201083	1.0800347
B	-0.0007150	-0.0006384	-0.0007645	-0.0006954
s, $\text{g}\cdot\text{cm}^{-3}$	3.2×10^{-04}	4×10^{-05}	1.20×10^{-03}	2×10^{-05}
δ , %	0.027	0.003	0.101	0.002

^aParameters for eq 1.

3.1.3. Viscosity. The experimental dynamic viscosities are given in Table S4. The dynamic viscosity of hydrogenated benzyltoluene (12H-MLH) is only slightly higher than for 0H-MLH. Both compounds show dynamic viscosities $< 10 \text{ mPa}\cdot\text{s}$ at $T = 293.15 \text{ K}$. The data sheets^{26,27} from Sasol show that the dynamic viscosity of 0H-MSH at $T = 293.15 \text{ K}$ is more than 10 times greater than 0H-MLH. The dynamic viscosity of the perhydrogenated dibenzyltoluene (18H-MSH) is even higher. It reaches $425 \text{ mPa}\cdot\text{s}$ at $T = 293.15 \text{ K}$.

The parameters have been fitted for the description of temperature dependence of the dynamic viscosity. Due to the large viscosity range of the compounds, the determination of the standard deviation was not performed in this case.

$$\ln(\eta(T)) = A + \frac{B}{T} + C \cdot \ln(T) \quad (2)$$

The parameters for this equation are listed in Table 4.

3.1.4. Surface Tension. Table S5 shows the experimental values of surface tension of 0H-MSH, 0H-MLH, and their hydrogenated derivatives. The surface tension of 0H-MSH is slightly higher than for 0H-MLH at $T = 298.15 \text{ K}$. The hydrogenated derivatives show a lower surface tension than the dehydrogenated ones. The temperature dependence of the surface tension can be described using a linear approach:

$$\sigma_i(T) = A + B \cdot T/K \quad (3)$$

The parameters for this equation are listed in Table 5.

3.2. Thermochemical Properties. **3.2.1. Standard Molar Enthalpy of Formation from Combustion Calorimetry.**

Table 4. Dynamic Viscosities for the (Di)benzyltoluene Derivatives^a

η , mPa·s	0H-MSH (>293.15 K)	18H-MSH (<313 K)	18H-MSH (>313 K)	0H-MLH	12H-MLH
A	-124.51101	-26.7272214	-231.7406117	-39.3966559	-94.6172747
B	9262.53778	9620.10641	15784.3287	3655.68111	6569.32652
C	17.0230528	0	32.2896344	4.99820468	13.0445002
δ , %	5.8	3.8	3.0	2.1	2.2

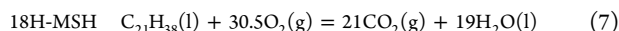
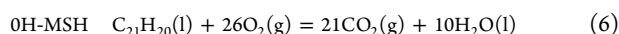
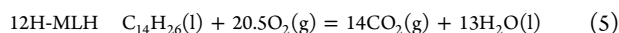
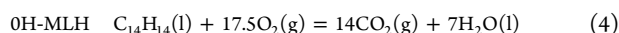
^aParameters of eq 2.Table 5. Surface Tension of the (Di)benzyltoluene Derivatives^a

σ , mN·m ⁻¹	0H-MSH	0H-MLH	18H-MSH	12H-MLH
A	77.263	64.138	67.332	58.137
B	-0.1195	-0.0904	-0.1085	-0.0892
S	0.1	0.1	0.2	0.1
δ , %	0.3	0.1	0.4	0.1

^aParameters of eq 3.

Detailed results from combustion experiments on the (di)-benzyltoluene derivatives are given in the Supporting Information (Tables S6–S9).

Values of the standard specific energies of combustion $\Delta_c u^\circ$ were used to derive the standard molar enthalpies of combustion $\Delta_c H_m^\circ$ and the standard molar enthalpies of formation in the liquid state $\Delta_f H_m^\circ$ (l) given in Table 6. Values of $\Delta_c u^\circ$ and $\Delta_c H_m^\circ$ refer to reactions:



Enthalpies of formation, $\Delta_f H_m^\circ$ (l), of the (di)benzyltoluene derivatives were calculated from the enthalpic balance according to eqs 4–7 using standard molar enthalpies of formation of H₂O(l) and CO₂(g) recommended by CODATA.²⁸ Uncertainties related to combustion experiments were calculated according to the guidelines presented by Olofsson²⁹ and by Hubbard et al.¹⁴ The uncertainties of the standard molar energy and enthalpy of combustion correspond to expanded uncertainties of the mean (0.95 confidence level) and include the contribution from the calibration with benzoic acid and from the values of the auxiliary quantities used. The uncertainty assigned to $\Delta_f H_m^\circ$ (l) is twice the overall standard deviation and includes the uncertainties from calibration, from the combustion energies of the auxiliary materials, and from the uncertainties of the enthalpies of formation of the reaction products H₂O(l) and CO₂(g).

The (di)benzyltoluene derivatives are not individual compounds. For 0H-MLH and 0H-MSH, they can be considered as mixtures of the *ortho*-, *meta*-, and *para*-benzyl-substituted toluenes. From our experiences on alkyl substituted

benzenes,^{30,31} the differences in energetics between such *ortho*-, *meta*-, and *para*-benzyl derivatives are expected to be within a few kJ·mol⁻¹. Thus, taking into account the experimental uncertainties of the liquid phase enthalpies of formation on the level of 5 kJ·mol⁻¹ (see Table 6), these values can be discussed as the average energetics of isomers contained in the dehydrogenated form. Differences in energetics between hydrogenated isomers in 12H-MLH and 18H-MSH are expected to be at the level of 5–10 kJ·mol⁻¹ and they also can be considered as indistinguishable within the experimental uncertainties of the $\Delta_f H_m^\circ$ (l).

Combustion enthalpies for the (di)benzyltoluene derivatives measured in this work can be compared (see Table 7) to those of parent compounds available in the literature.^{32,33} An extended calorimetric study of isomeric 1-methyl-4-(phenylmethyl)-benzene, 1-methyl-3-(phenylmethyl)-benzene, and 1-methyl-2-(phenylmethyl)-benzene as well as the combustion energies of their hydrogenated products was reported by Lamneck et al.³³ Authors of this extended study claimed that the hydrocarbons were prepared in a state of purity of 99 mol % and better. However, the focus of this working group was on the synthesis of aviation fuels, and the combustion experiments were disposed to the service analytical department. Thus, details on the experimental combustion procedure are totally absent. Nevertheless, we calculated enthalpies of formation of compounds reported in this work (see Table 7) for comparison with results on the 0H-MLH and the 12H-MLH. To our surprise, the disagreement between our results and those reported by Lamneck et al.³³ is beyond belief. However, good agreement of the high-precise enthalpy of formation for 1-methyl-4-(phenylmethyl)-benzene reported by Good and Lee³² and our result for the benzyltoluene allow one to disregard the data set reported by Lamneck et al.³³ as the only data of technical quality.

3.2.2. Vapor Pressures of 18H-MSH. Vapor pressures of the (di)benzyltoluene derivatives are important for their practical application. Vapor pressures of 18H-MSH have been measured with the static method (see Table S10). Temperature dependences of the measured absolute vapor pressures p_i were treated with the following equation:³¹

$$R \cdot \ln p_i = a + \frac{b}{T} + \Delta_f^\circ C_{p,m} \cdot \ln \left(\frac{T}{T_0} \right) \quad (8)$$

Table 6. Thermochemical Properties of the (Di)benzyltoluene Derivatives at $T = 298.15$ K and $p^\circ = 0.1$ MPa (in kJ·mol⁻¹)^a

	$\Delta_c H_m^\circ$ (l)	$\Delta_f H_m^\circ$ (l)	$\Delta_f^\circ H_m^{b}$	$\Delta_f H_m^\circ$ (g)
0H-MLH	-7564.4 ± 4.3	54.5 ± 4.7	69.9 ± 3.0	124.4 ± 5.6
12H-MLH	-8898.2 ± 3.8	-326.7 ± 4.2	65.1 ± 3.0	-261.6 ± 5.2
0H-MSH	-11234.9 ± 4.9	112.9 ± 5.6	112.8 ± 3.0	225.7 ± 6.4
18H-MSH	-13218.9 ± 7.1	-475.6 ± 7.6	88.2 ± 1.5	-387.4 ± 7.7

^aUncertainties correspond to expanded uncertainties of the mean (0.95 confidence level). ^bFrom Table 8.

Table 7. Comparison of Experimental Liquid Phase Enthalpies of Combustion and Formation for the Compounds Parent to the (Di)benzyltoluene Derivatives at $T = 298.15$ K and $p^\circ = 0.1$ MPa ($\text{kJ}\cdot\text{mol}^{-1}$)

compounds	$\Delta_c H_m^\circ$	$\Delta_f H_m^\circ$	ref.
1-methyl-4-(phenylmethyl)-benzene	-7301	-209	33
	-7571.5 ± 1.0	61.5 ± 1.2	32
1-methyl-2-(phenylmethyl)-benzene	-7259	-251	33
1-methyl-3-(phenylmethyl)-benzene	-7322	-188	33
0H-MLH	-7564.4 ± 4.3	54.5 ± 4.7	this work
cis-1-(cyclohexylmethyl)-2-methyl-cyclohexane	-8263	-962	33
trans-1-(cyclohexylmethyl)-2-methyl-cyclohexane	-8305	-920	33
cis-1-(cyclohexylmethyl)-3-methyl-cyclohexane	-8305	-920	33
trans-1-(cyclohexylmethyl)-3-methyl-cyclohexane	-8326	-899	33
cis-1-(cyclohexylmethyl)-4-methyl-cyclohexane	-8368	-857	
trans-1-(cyclohexylmethyl)-4-methyl-cyclohexane	-8326	-899	
12H-MLH	-8898.2 ± 3.8	-326.7 ± 4.2^a	

^aFrom Table 9.**Table 8. Vaporization Enthalpies of the (Di)benzyltoluene Derivatives Derived From the Experiment and the Group-Additivity Method ($\text{kJ}\cdot\text{mol}^{-1}$)**

1	T range	$\Delta_f^{\ddagger} H_m^\circ / T_{av}$	at 298.15 K		exp-GA
			$\Delta_f^{\ddagger} H_m^\circ$ (exp)	$\Delta_f^{\ddagger} H_m^\circ$ (GA)	
2	3	4	5	6	
0H-MLH	293–333	68.7 ± 0.4	69.9 ± 0.5^a		
	373–633	58.0 ± 0.5	73.3 ± 3.0^b	72.0	1.3 ± 3.0
12H-MLH				65.1	
0H-MSH	413–633	87.3 ± 1.0	112.8 ± 3.0^a	106.0	6.8 ± 3.0
18H-MSH	343–371	80.4 ± 0.6	88.2 ± 1.5	94.7	-6.5 ± 1.5

^aData for (4-methylphenyl)-phenylmethane from ref 37 treated by using eqs 8 and 10. ^bData from Sasol^{26,27} treated by using eqs 8 and 10.

where a and b are adjustable parameters and $\Delta_f^{\ddagger} C_{p,m}^\circ$ is the difference of the molar heat capacities of the gaseous and the condensed phase, respectively. T_0 appearing in eq 8 is an arbitrarily chosen reference temperature (which has been chosen to be $T = 298.15$ K), and R is the molar gas constant. Values of $\Delta_f^{\ddagger} C_{p,m}^\circ$ in eq 8 were calculated (see Table 2) according to the procedure developed by Chickos and Acree²⁵ based on the isobaric molar heat capacity $C_{p,m}^\circ$ (l, 298.15 K) measured in this work. Experimental data given in Table S10 were fitted with equation:

$$\ln(p/\text{Pa}) = \frac{377.98}{R} - \frac{126201.14}{R \cdot (T/\text{K})} - \frac{127.6}{R} \ln\left(\frac{T/\text{K}}{298.15}\right) \quad (9)$$

3.2.3. Standard Molar Vaporization Enthalpies of the (Di)benzyltoluene Derivatives. Enthalpies of vaporization of the 18H-MSH in the temperature range of 343–373 K were derived (see Table S10) using eq 10 according to the procedure described earlier:³¹

$$\Delta_f^{\ddagger} H_m^\circ(T) = -b + \Delta_f^{\ddagger} C_{p,m}^\circ \cdot T \quad (10)$$

In addition, we also used vapor pressures available in the literature for 0H-MLH and 0H-MSH in order to derive their vaporization enthalpies using eq 10 and values of $\Delta_f^{\ddagger} C_{p,m}^\circ$ estimated from $C_{p,m}^\circ$ (l, 298.15 K) measured in this work (see Table 2). Vapor pressures available from Sasol and coefficients a and b of eq 8, as well as values of $\Delta_f^{\ddagger} H_m^\circ(T)$, are given in Table S11. Literature data³⁷ on vapor pressures of (4-methylphenyl)-phenylmethane (see Table S12), as one of the main components of the 0H-MLH, were also treated by using eqs 8 and 10 for the sake of comparison. Resulting vaporization

enthalpies of the (di)benzyltoluene derivatives are collected in Tables 6 and 8.

3.2.4. Validation of Vaporization Enthalpies Using the Group-Additivity Method. Vaporization enthalpies of 0H-MLH and 0H-MSH were derived from the vapor pressure temperature dependencies published by Sasol.⁷ Experimental details and reliability of these measurements are not available. That is why, any kind of validation for these $\Delta_f^{\ddagger} H_m^\circ$ values has to be performed, e.g., with empirical methods.

Group-additivity (GA) methods^{34,35} are an empirical tool to prove experimental results for consistency or estimate missing values with a reasonable accuracy. The Benson's methodology³⁶ was adjusted for prediction of vaporization enthalpies in our previous work.³⁴ The group-additivity values (GAVs) requiring one to calculate $\Delta_f^{\ddagger} H_m^\circ$ (298.15 K) of the (di)benzyltoluene derivatives are collected in Table S13. Comparison of the experimental and predicted enthalpies of vaporization is given in Table 8.

Agreement between experimental and calculated values for 0H-MLH is very good. Moreover, vaporization enthalpy $\Delta_f^{\ddagger} H_m^\circ$ (298.15 K) = 73.3 ± 3.0 $\text{kJ}\cdot\text{mol}^{-1}$, derived for 0H-MLH, is in agreement with the vaporization enthalpy $\Delta_f^{\ddagger} H_m^\circ$ (298.15 K) = 69.9 ± 0.5 $\text{kJ}\cdot\text{mol}^{-1}$ available for the individual isomer (4-methylphenyl)-phenylmethane.³⁷ The difference between experimental and calculated values for 0H-MSH is not small, but it is quite acceptable, taking into account that this value was derived from vapor pressures measured between 413 and 633 K. The calculated vaporization enthalpy of the 18H-MSH is somewhat larger than the experimental value (see Table 8). However, this difference is justified because of poor additivity of contributions arising from contributions of three cyclohexane rings presented in the 18H-MSH. Thus, the acceptable

agreement between the experimental and GA-estimated values can serve as evidence of the internal consistency of vaporization enthalpies collected in Table 8.

3.2.5. Gas-Phase Standard Molar Enthalpies of Formation. Consistent experimental vaporization enthalpies of (di)benzyltoluene derivatives evaluated in this work can now be used together with the results from combustion calorimetry (Table 9) for further calculation of the gaseous standard

Table 9. Comparison of Experimental, Estimated, and Theoretical Enthalpies of Formation $\Delta_f H_m^\circ$ (g) for the (Di)benzyltoluene Derivatives at $T = 298.15$ K ($\text{kJ}\cdot\text{mol}^{-1}$)

1	$\Delta_f H_m^\circ$ (g)/exp ^a	$\Delta_f H_m^\circ$ (g)/GA ^b	$\Delta_f H_m^\circ$ (g)/QC ^c	H_s ^d
0H-MLH	124.4 ± 5.6	132.5	126.6	-8.1 ± 6.4
12H-MLH	261.6 ± 5.2	-283.8	-274.0	22.2 ± 5.2
0H-MSH	225.7 ± 6.4	215.0	203.7	10.7 ± 5.6
18H-MSH	-387.4 ± 7.7	-409.2	-396.4	21.8 ± 7.7

^aFrom Table 6. ^bCalculated using GAVs from Table S13. ^cAverage value from three isomers given in Tables 10 and 11. ^dDifference between columns 2 and 3.

enthalpy of formation, $\Delta_f H_m^\circ$ (g) at 298.15 K. Resulting values are given in Table 9. Since the significant discrepancy between available experimental enthalpies of formation of the 0H-MLH and 12H-MLH has been discussed in Section 3.2.1, any additional arguments to assess the reliability of calculated $\Delta_f H_m^\circ$ (g, 298.15 K) are required. In this work, we used the GA procedure, as well as the quantum-chemical calculations for evaluation of the experimental results.

3.2.6. Validation of the Gas Phase Enthalpies of Formation by Using GA: Strain Enthalpy H_s . The embarrassing disagreement of our results with the literature reported by Lamneck et al.³³ shown in Table 7 have prompted us to perform an independent validation of our data by using the GA procedure in a similar way to the validation of vaporization enthalpies in Section 3.2.3. Group-additivity values (GAVs) required to calculate $\Delta_f H_m^\circ$ (g, 298.15 K) are given in Table S13. Comparison of experimental and estimated gas phase enthalpies of formation is given in Table 9. Agreement between experimental and calculated values for the 0H-MLH is within the experimental uncertainties. Such an agreement supports our previous findings, that the parents to the 0H-MLH diphenylalkanes are about “strainless” and obey the group-additivity rules.³⁷

The strain, H_s , of a molecule is defined as the difference between the experimental standard enthalpy of formation $\Delta_f H_m^\circ$ (g) and the calculated sum of the increments given in Table S13. Strain enthalpy reflects a nonadditive component of the enthalpy of a molecule. In contrast to the Benson type³⁶ increments, we used the system of strain-free increments in this work (Schleyer et al.³⁸). This system is based on the standard molar enthalpies of formation $\Delta_f H_m^\circ$ (g) of simple homologous (“strainless”) molecules.

As can be seen in Table 9, the difference between experimental and calculated values for the 0H-MSH of 10.8 $\text{kJ}\cdot\text{mol}^{-1}$ exceeds the experimental uncertainties, but in comparison to the “strainless” diphenylalkanes and 0H-MLH, a reasonable amount of strain is observed in 0H-MSH, similar to

that also observed in different triphenyl-alkanes.³⁹ More profound manifestations of the strain, H_s , of about 22 $\text{kJ}\cdot\text{mol}^{-1}$ are logical for the 12H-MLH and 18H-MSH (see Table 9), where the cyclohexyl rings with their own inherent strain share the restricted space around the geminal CH_2 unity. Thus, the hydrogenated forms apparently do not obey the GA rules. However, the interplay of strains in the (di)benzyltoluene derivatives meet the logical expectations, as described above. This logic can serve as an evidence of the internal consistency of the gas-phase enthalpies of formation derived in this work. These values can now be compared to results from the high-level quantum-chemical calculations.

3.2.7. Validation of the Gas Phase Enthalpies of Formation by Using the QC Method. Another possibility to test consistency of the experimental data can be provided by high-level quantum chemistry (QC).^{40–42} We have used the composite method G3MP2 for calculation of the gaseous enthalpies of formation of isomers constituting the (di)-benzyltoluene derivatives for comparison with the experimental data.

The (di)benzyltoluene derivatives contain flexible molecules, and in the gas-phase, they exist as the equilibrium mixture of conformers. In general, a calculation of energetics for all possible conformers is important for the exact calculation of $\Delta_f H_m^\circ$ (g). However, as a rule, only the few most stable conformers contribute to the theoretical enthalpy of formation significantly, provided that their energies do not differ from other conformers by 1–3 $\text{kJ}\cdot\text{mol}^{-1}$. The conformers, in which energy differs from the most stable conformer by a difference of ≥ 10 $\text{kJ}\cdot\text{mol}^{-1}$, are practically not populated in the gas phase.⁴³ Such a simplification allows for estimation of enthalpies of formation of large flexible molecules with a sufficient accuracy. Analysis of the conformational space for the 0H-MLH and 0H-MSH and their hydrogenated derivatives has revealed that the most stable conformers for each isomer possess comparable energies and the differences do not exceed 1–5 $\text{kJ}\cdot\text{mol}^{-1}$ even for the most flexible isomers of the 12H-MLH. This observation has reduced the amount of computational work, and we calculated only the most stable conformers for each isomer by the high-level G3MP2 method. The optimized structures obtained for the most stable conformer are illustrated in Figures S6 and S7.

The enthalpies calculated for the isomers of the (di)-benzyltoluene derivatives were converted to enthalpies of formation $\Delta_f H_m^\circ$ (g, 298.15 K) using the atomization procedure.²⁰ As it has been already noticed in our previous studies,^{19,41,42} enthalpies of formation derived from the atomization procedure (AT) for the aromatic molecules deviate systematically from the experimental values. For example, the value $\Delta_f H_m^\circ$ (g, 298.15 K) = 77.9 $\text{kJ}\cdot\text{mol}^{-1}$ derived using the AT for benzene is less positive in comparison with the experimental value 82.9 ± 0.9 $\text{kJ}\cdot\text{mol}^{-1}$ recommended⁴⁴ for this molecule. However, agreement between the experiment and the AT calculated enthalpies of formation is good for the aliphatic cyclic molecules.¹¹ For example, for cyclopentane, $\Delta_f H_m^\circ$ (g, 298.15 K) = -74.3 $\text{kJ}\cdot\text{mol}^{-1}$ derived using the AT is in fair agreement with the experiment (-76.4 ± 0.7 $\text{kJ}\cdot\text{mol}^{-1}$),⁴⁵ or for cyclopentene, $\Delta_f H_m^\circ$ (g, 298.15 K) = -32.4 $\text{kJ}\cdot\text{mol}^{-1}$ derived from AT is in very good agreement with the experiment (-32.6 ± 0.7 $\text{kJ}\cdot\text{mol}^{-1}$).⁴⁶ A similar observation was valid for N-ethylcarbazole and its hydrogenated derivatives.¹¹

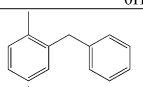
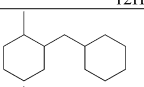
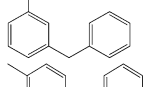
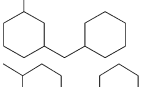
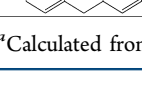
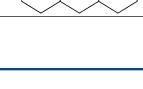
In our recent works,^{19,41,42} we already successfully used a linear correlation between the experimental and the calculated

enthalpies of formation by the atomization procedure in order to “correct” the AT result using the reliable experimental data on the similarly shaped aromatic compounds. In this work, we used the experimental gas-phase enthalpies of formation of a number of benzyl and phenyl-substituted benzenes (see Table S14) in order to establish the linear equation:

$$\Delta_f H_m^\circ(\text{g})(\text{exp})/\text{kJ}\cdot\text{mol}^{-1} = 1.10 \times \Delta_f H_m^\circ(\text{g})(\text{AT}) - 1.3 \quad (11)$$

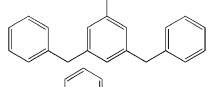
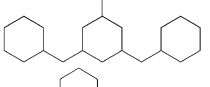
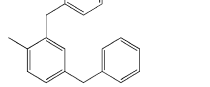
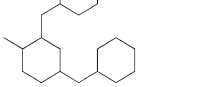
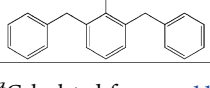
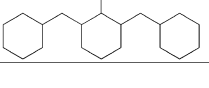
which is valid for (di)benzyltoluene derivatives LH and SH containing benzene rings. Using eq 11, the AT “corrected” enthalpies of formation of the isomers constituting the (di)benzyltoluene derivatives have been calculated (see Tables 10 and 11).

Table 10. Results of G3MP2 Calculation of the Standard Enthalpy of Formation $\Delta_f H_m^\circ(\text{g})$ for the 0H-MLH and 12H-MLH in the Gas Phase at 298.15 K, in $\text{kJ}\cdot\text{mol}^{-1}$

	$\Delta_f H_m^\circ$ AT		$\Delta_f H_m^\circ$ AT
0H-MLH		12H-MLH	
	(124.2) ^a 114.1		-273.0
	(127.4) ^a 117.0		-278.3
	(128.4) ^a 117.9		-270.8

^aCalculated from eq 11.

Table 11. Results of G3MP2 Calculation of the Standard Enthalpy of Formation $\Delta_f H_m^\circ(\text{g})$ for the 0H-MSH and 18H-MSH in the Gas Phase at 298.15 K, in $\text{kJ}\cdot\text{mol}^{-1}$

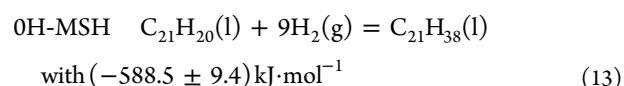
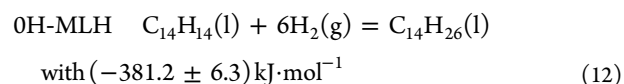
	$\Delta_f H_m^\circ$ AT		$\Delta_f H_m^\circ$ AT
0H-MSH		18H-MSH	
	(205.0) ^a 187.5		-404.6
	(202.2) ^a 185.0		-396.6
	(204.0) ^a 186.6		-388.1

^aCalculated from eq 11.

Comparison of the experimental and the G3MP2 calculated enthalpies of formation is given in Table 9. As it can be seen in Table 9, there is an overall good agreement between theoretical and experimental data (except for the 0H-MSH), particularly if the combined uncertainties of about 2–4 $\text{kJ}\cdot\text{mol}^{-1}$ associated with the G3MP2 gas-phase enthalpies of formation and the uncertainties of the combustion experiments are taken into account. Disagreement observed for 0H-MSH can be ascribed rather to the vaporization enthalpy for this fluid, which already was under suspicion in Section 3.2.4. The Sasol values of vapor pressures used to estimate the vaporization enthalpies might be correct; however, they were measured at very high temperatures, and their use for estimation of $\Delta_f H_m^\circ(298.15 \text{ K})$ apparently suffered from the long extrapolation to the reference temperature $T = 298.15 \text{ K}$. Nevertheless, the general acceptable agreement among empirical and theoretical methods reinforces

the reliability of the experimental and theoretical results presented in this work.

3.2.8. Calculation of the Hydrogenation/Dehydrogenation Enthalpy. The enthalpy of hydrogenation/dehydrogenation enthalpy is an important quantity for the hydrogen storage using the dibenzyltoluene fluids. We use their experimental liquid phase enthalpies from Table 9 to calculate the reaction enthalpies, $\Delta_r H_m^\circ$, at 298.15 K for the following reaction:



The values per mol hydrogen are very similar (-63.5 and $-65.4 \text{ kJ}\cdot\text{mol}^{-1}\text{-H}_2$, respectively). For comparison, enthalpy of hydrogenation for the LOHC *N*-ethylcarbazole is $-50.5 \pm 0.8 \text{ kJ}\cdot\text{mol}^{-1}\text{-H}_2$. As expected, the hydrogenation of the homocyclic toluene derivatives MLH and MSH is enthalpically favored over hydrogenation of *N*-ethylcarbazole. On the other hand, hydrogen release from *N*-ethylcarbazole will be more favorable compared to MLH and MSH.

4. CONCLUSIONS

In this work, we have obtained a consistent set of thermophysical and thermochemical properties of the potential LOHC materials benzyltoluene (Marlotherm LH) and dibenzyltoluene (Marlotherm SH) and their hydrogenated derivatives. These properties are important for the process design, modeling, and engineering of the reversible hydrogenation/dehydrogenation processes. From the results, it can for example be seen that due to its lower vapor pressure dibenzyltoluene is suited better than benzyltoluene. However, benzyltoluene has a lower viscosity which eases its application. The enthalpies of hydrogenation per mole of hydrogen for benzyltoluene and dibenzyltoluene are similar and within a reasonable range for their application as a LOHC.

■ ASSOCIATED CONTENT

§ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.iecr.5b01840.

Results of the heat capacity measurements for the Marlotherm Fluids (Table S1); auxiliary properties of the materials used in the present study (Table S2); densities of the (di)benzyltoluene derivatives at different temperatures (Table S3); dynamic viscosities of the (di)benzyltoluene derivatives at different temperatures (Table S4); surface tension of the (di)benzyltoluene derivatives at different temperatures (Table S5); results for combustion experiments (Tables S6–S9); experimental vapor pressures of 18H-MSH measured by the static method (Table S10); vapor pressures of Marlotherm fluids (Tables S11 and S12); group-additivity contributions (Table S13); data used for correction of the enthalpies of formation calculated with the G3MP2 (Table S14). (PDF)

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Notes

The authors declare no competing financial interest.

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