Liquid Organic Hydrogen Carriers: Thermophysical and Thermochemical Studies of Carbazole Partly and Fully Hydrogenated Derivatives

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Ⓢ *Supporting Information*

ABSTRACT: Carbazole derivatives are promising liquid organic hydrogen carrier (LOHCs). They can take up and release hydrogen in catalytic hydrogenation/dehydrogenation reactions. The thermophysical properties (heat capacity, density, viscosity, surface tension, and refractive index) of carbazole and *N*-ethylcarbazole, as well as those of their hydrogenated derivatives, were measured. Furthermore, thermochemical properties (enthalpy of vaporization, sublimation, and fusion) were derived from experiments. Molar enthalpies of formation of the gaseous carbazole derivatives were calculated and validated with high-level quantum chemical calculations. Molar enthalpies of formation data in the liquid phase were derived by combining the high-level quantum chemistry values of the gas-phase enthalpies of formation with experimentally determined enthalpies of vaporization. Thermodynamic analysis of the hydrogenation/dehydrogenation reactions of the carbazole derivatives was performed. This analysis, among others, revealed a rather weak dependence of thermodynamic hydrogen release characteristics on the alkyl chain length. The thermophysical properties of the derivatives show a strong dependence on the degree of hydrogenation. Therefore, the state of hydrogenation should always be considered when dealing with substance properties of LOHCs. Using the data presented in this work, a more reliable process modeling is possible.

1. INTRODUCTION

The energy system is currently changing from nuclear and fossil energy sources to renewable energies, such as wind power or photovoltaics. Because of their intermittent character, energy storage technologies become more and more important to maintain a constant energy supply. In times of surplus energy, e.g., during very sunny or windy days, excess energy could be used to produce hydrogen from water by electrolysis. The production of hydrogen seems to be a promising approach to store huge amounts of energy. However, the volumetric energy storage density of hydrogen is rather poor under ambient conditions. Therefore, pressures up to 700 bar or very low temperatures (20 K) are necessary to enhance the volumetric storage density.[1] Chemical hydrogen storage by reversible catalytic (de)hydrogenation of liquid organic hydrogen carriers (LOHCs) appears to be a promising hydrogen storage technology.[2−4] The hydrogenation reaction of these usually aromatic compounds is favored by thermodynamics. In contrast, it is challenging to find aromatic compounds that release hydrogen at comparatively low temperatures, which is particularly desired for on-board vehicle systems. In 2004, Pez et al.[5] proposed *N*-ethylcarbazole as a potential substance for chemical hydrogen storage, because of its comparatively low dehydrogenation enthalpies (-50.5 kJ mol^{-1} H$_2$[18]). This allows the dehydrogenation reaction to be performed at relatively low temperatures (in the range of 473−523 K). In recent years, many works regarding the application of *N*-ethylcarbazole as an

LOHC have been published.[2−15] According to the literature,[8,16] intermediates with different degrees of hydrogenation are formed during the (de)hydrogenation of *N*-ethylcarbazole, turning the LOHC system into a complex mixture of intermediates (see Figure 1). Those intermediates are referred to as XH-NEC in the following, where X denotes the number of hydrogen atoms reversibly bound to the *N*-ethylcarbazole molecule (or just XH-C, if the basic form is carbazole). This mixture contains mostly *N*-ethyl-tetrahydro-carbazole (4H-NEC) and *N*-ethyl-octahydro-carbazole (8H-NEC). *N*-Ethyl-hexahydro-carbazole (6H-NEC) is present as stable intermediate to a far lesser extent. The presence of *N*-ethyl-dihydro-carbazole (2H-NEC) and *N*-ethyl-decahydro-carbazole (10H-NEC) is negligible and below detection limits. The concentration of the different intermediates in the reaction mixture is dependent on the extent of reaction and the properties of the catalyst used.[8−10] A similar distribution of the (de)hydrogenation intermediates was observed for carbazole as well.
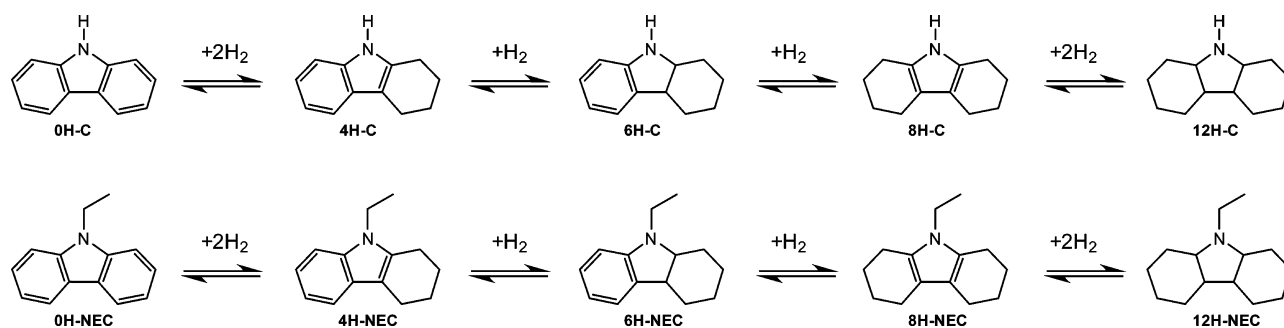
Eblagon et al.[8] noted that 16 different isomers of the fully hydrogenated product *N*-ethyl-dodecahydro-carbazole (12H-NEC) exist, which can be attributed to the four stereogenic

Figure 1. Major important intermediates formed during the consequent (de)hydrogenation of carbazole and N-ethylcarbazole[8] (arrows in this figure refer to the direction of the dehydrogenation or hydrogenation processes and do not indicate the equilibrium of these processes).

centers of the molecule (see Figure 2). These isomers can be divided into 10 enantiomers and 6 diastereomers.
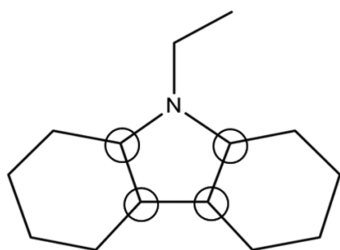
Figure 2. General notification of stereogenic centers in N-ethyl-dodecahydro-carbazole.

With increasing degree of hydrogenation, the properties of LOHC mixtures are significantly changing. For a detailed simulation and development of the LOHC process, property data of the different carbazole and N-ethylcarbazole derivatives are of particular importance. However, for the partly hydrogenated intermediates, property data are not published yet. Even for N-ethylcarbazole (0H-NEC) and its fully hydrogenated derivative N-ethyl-dodecahydro-carbazole, property data are scarcely available. This contribution complements and extends our previous work on the thermodynamics of the carbazole derivatives.[13−15] The objective of this study was the experimental and computational investigation of the most important intermediates of the carbazole and N-ethylcarbazole in the catalytic dehydrogenation and hydrogenation processes.

2. MATERIALS AND METHODS

2.1. Materials. Table 1 shows the samples studied in this work. Carbazole (0H-C, CAS:86-74-8) and N-ethylcarbazole (0H-NEC, CAS:86-28-2) were of commercial origin (Sigma−Aldrich), and they were further purified by recrystallization from acetone (carbazole) and cyclohexane (N-ethylcarbazole), respectively. Carbazole derivatives were synthesized at the Institute of Chemical Reaction Engineering (University of Erlangen-Nürnberg) via the catalytic hydrogenation of carbazole and N-ethylcarbazole. 4H-NEC, 8H-NEC, and 12H-NEC were separated by a batch distillation from a reaction mixture (see section 2.2). A diastereomeric mixture of 12H-Carbazole was recrystallized from a mixture of acetone and toluene (50/50 wt %). 4H-Carbazole was of commercial origin (Alfa Aesar) and was purified by recrystallization from acetone. Samples were kept cool and handled under inert gas stream (Ar, N₂) in a special glass device furnished with a septum for a sampling using a syringe.

2.2. Separation and Purification of Reaction Intermediates. Since the reaction intermediates could not be obtained in high purity (>99%, required for the property measurements) by chemical reaction, they had to be separated from the reaction mixture. N-Ethylcarbazole (or carbazole) was partially hydrogenated to form a reaction mixture containing different reaction products. After that, the mixture was analyzed by GC-MS to determine its composition. The fully hydrogenated N-ethyl-dodecahydro-carbazole (12H-NEC) was obtained in at least 3 diastereomeric forms that could be separated by GC-MS analysis. In this reaction mixture, the intermediates 4H-NEC, 6H-NEC, and 8H-NEC also were found. As main impurities, N-methyl-dodecahydro-carbazole (12H-NMC) and dodecahydro-carbazole (12H-C), which also occurred in different diastereomeric forms, were identified. Their concentrations in the reaction mixture were <1%. It has been shown previously that it is possible to separate this reaction mixture by means of fractional batch distillation.[17] For a first proof of concept, a small volume of LOHC mixture was distilled using a micro spinning band column from Normag GmbH, which offers a high number of separation stages by still only requiring a small amount of liquid (≥10 mL). The distillation process was performed under vacuum conditions (p = 10 mbar) to reduce the boiling temperatures of the different components (bottom volume: 250 mL). During the distillation process, samples were withdrawn and analyzed using GC-MS.

Figure 4 shows the batch profile of the distillation process. First, the light boiling impurities that consist mainly of dodecahydro-carbazole isomers were separated. For simplification reasons, all isomers are summarized to 12H-C. Then, 12H-NEC-1 could be separated in high purity (>98%) from the reaction mixture. After a distillation time of 370 h, a mixture of the three diastereomers of 12H-NEC (12H-NEC-1, 12H-NEC2, 12H-NEC-3) was obtained. The remaining compounds reach the top of the distillation column in the following order: 6H-NEC, 8H-NEC, and 4H-NEC. The entire distillation experiment was very time-consuming (close to 1000 h) and only a few milliliters of each purified product fraction could be withdrawn.

In order to obtain a larger amount of the different fractions in a shorter period of time, a batch distillation column DN80 from Normag GmbH with 2m Sulzer gauze packing DXP was rigged up (bottom volume = 25 L).[16] Two different reaction mixtures from partial hydrogenation were distilled to obtain 12H-NEC, 8H-NEC, and 4H-NEC in high purity. For 12H-NEC and 8H-NEC, a reaction mixture with a high degree of hydrogenation (≈85%) was distilled (see Figure 5). A reaction mixture with a low degree of hydrogenation (∼27%) was used to obtain 4H-

Table 1. Carbazole and *N*-Ethylcarbazole Derivatives[a] with Different Degrees of Hydrogenation Studied in This Work

name	abbreviation	structure	purity/%
0-H-carbazole	0H-C		>99.8
4-H-carbazole	4H-C		>99.5
12-H-carbazole (diastereomeric mixture)	12H-C		>99.0
N-ethylcarbazole	0H-NEC		>99.9
N-ethyl-tetrahydro-carbazole	4H-NEC		>99.9
N-ethyl-octahydro-carbazole	8H-NEC		>99.8
N-ethyl-dodecahydro-carbazole	12H-NEC		>99.9

[a]According to NMR measurements (^{1}H, ^{13}C, and coupling measurements), it was assumed that the asymmetric diastereomer of *N*-ethyl-dodecahydro-carbazole (see Figure 3) was the one studied in this work. This diastereomer also was found to be the most stable in the publications by Eblagon et al.[8−10]
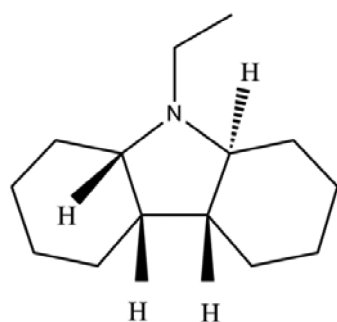
Figure 3. Structure of the diastereoisomer of *N*-ethyl-dodecahydro-carbazole investigated in this work.

Figure 4. Separation of a reaction mixture by spinning band batch distillation. [Conditions: pressure, p = 10 mbar; reflux ratio, ν = 4; rotary speed, n = 1000 rpm.]

NEC (see Figure 6). Only the first diastereomer of 12H-NEC was obtained in a purity of >99.9% (GC). Therefore, it was used for the property data measurements in this work. Because of the structural similarity of these diastereomers, it was assumed that their physical property data are rather similar. For 4H-NEC and 8H-NEC, no isomers could be found by GC analysis. Both substances were obtained in high purity (>99.8%). Because of the small amount of 6H-NEC in the
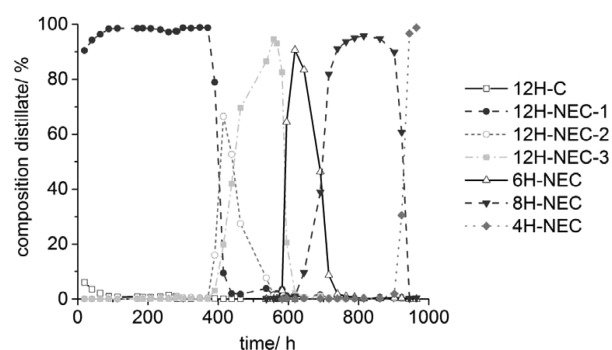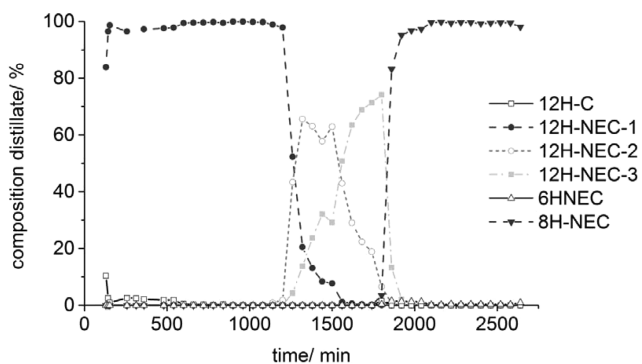
reaction mixtures, this compound could not be obtained in a sufficient amount and purity to perform property data measurements.

2.3. Thermophysical Properties. *2.3.1. Heat Capacity Measurements.* The specific heat capacity was measured using the differential scanning calorimeter (DSC) Maia 200 from Netzsch. The measurements according to DIN 51007 consisted

Figure 5. Separation of a reaction mixture with a high degree of hydrogenation (∼85%) by batch distillation using a Sulzer AG gauze packing DXP (DN80, 2 m); p = 10 mbar, ν = 4−8.
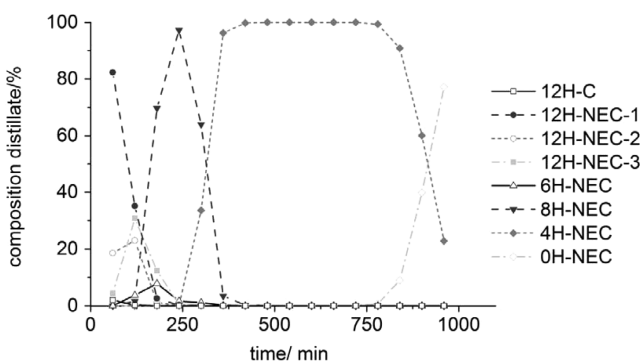
Figure 6. Separation of a reaction mixture with a low degree of hydrogenation (∼27%) by batch distillation using a Sulzer gauze packing DXP (DN80, 2 m); p = 2−5 mbar, ν = 8.

of three parts, baseline measurement, calibration measurement with sapphire and sample measurement. Each measurement consisted of three steps: an isothermal step for 20 min, a dynamic step with a heating rate of 10 K/min, and another isothermal step for 20 min.

2.3.2. Density. Density measurements were carried out using an oscillating U-tube densimeter (Model DMA 5000, Anton Paar Germany GmbH). The maximum error in water density was determined to be ±0.00005 g cm^{-3} after calibration with air and water at T = 293 K. Solid samples (0H-NEC, 8H-NEC) were melted and filled liquid into the measuring device. The standard deviation for the compounds 0H-NEC, 4H-NEC, and 12H-NEC was below ±0.00005 g cm^{-3}. The standard deviation for the compound 8H-NEC was comparatively higher (±0.0002 g cm^{-3}), because of the fact that the compound is less stable when it is exposed to atmospheric oxygen.

2.3.3. Viscosity. The dynamic viscosity was measured using the rotational rheometer (Model MCR 102, Anton Paar Germany GmbH). For 4H-NEC, 8H-NEC, and 12H-NEC, the Model C-DG26.7/T200 (double gap) measuring system was used. The dynamic viscosity of 0H-NEC was determined using the Model CP50-1 (cone−plate) measuring system, because of its high melting point (T = 342.4 K). The relative error for all substances was <5%.

2.3.4. Surface Tension. The measurements of the surface tension of 4H-NEC, 8H-NEC, and 12H-NEC were carried out using a drop volume tensiometer (Model DVT50, Krüss GmbH Germany). Because of the high melting point of 0H-NEC (T = 342.4 K), measurements were only performed for

4H-NEC, 8H-NEC, and 12H-NEC. The relative error in surface tension was <1%.

2.3.5. Refractive Index. The refractive index was determined using a digital refractometer (Model DR6100-TF, A. Krüss Optronic GmbH); the prism was made from sapphire (LED 590 nm). The standard deviation of measurements was below ±0.0005 nD.

2.4. Thermochemical Properties. *2.4.1. Combustion Calorimetry.* The molar enthalpies of combustion of 12-H-carbazole, 4H-NEC, and 8H-NEC were measured with an isoperibolic calorimeter with a static bomb and a stirred water bath. The solid samples were pressed into pellets and weighed with a microbalance with a resolution of 10^{-6} g. We used small polyethylene pieces as an auxiliary material in order to reach a completeness of combustion. The liquid sample of 4H-NEC was burned in a polyethylene ampule (Fa. NeoLab, Heidelberg, Germany). The sample was transferred into the polyethylene bulb with a syringe under nitrogen stream in a glovebox. The sealed container was placed in the crucible and was burned in oxygen at a pressure of 3.04 MPa. The detailed procedure has been described previously.[18] The combustion products were examined for carbon monoxide (Dräger tube) and unburned carbon, but neither were detected. The energy equivalent of the calorimeter (ε_{calor}) was determined with a standard reference sample of benzoic acid (SRM 39j, National Institutes of Standards and Technology (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.[19] The relative atomic masses used for the elements—C = 12.010600, H = 1.007975, 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 2011[20] for each of these elements. Correction for nitric acid formation was based on titration with 0.1 mol dm^{-3} NaOH (aq). The sample masses were reduced to vacuum, taking into consideration their density values (see Table S1 in the Supporting Information). Results from combustion experiments are given in Tables S2 and S3 in the Supporting Information.

2.4.2. Vapor Pressure Measurements: Transpiration Method. Vapor pressures of 4-H-carbazole, 12-H-carbazole, 4H-NEC, and 8H-NEC were determined using the method of transpiration[21,22] in a saturated nitrogen stream. Approximately 0.5 g of the sample was mixed with small glass beads and placed in a thermostated U-shaped saturator. A well-defined nitrogen stream was passed through the saturator at a constant temperature (±0.1 K), and the transported material was collected in a cold trap. The amount of condensed sample of each compound was determined by GC analysis using an external standard n-C$_n$H$_{2n+2}$. The absolute vapor pressure p_i at each temperature T_i was calculated from the amount of the product collected within a definite period. Assuming validity of the Dalton's law applied to the nitrogen stream saturated with the substance i, values of p_i were calculated using the following equation:

$$p_i = \frac{m_i R T_a}{V M_i} \quad V = V_{N_2} + V_i \quad (V_{N_2} \gg V_i) \tag{1}$$

where R = 8.314462 J K^{-1} mol^{-1}, m_i is the mass of the transported compound, M_i is the molar mass of the compound, and V_i is its volume contribution to the gaseous phase. V_{N_2} is the volume of the carrier gas and T_a is the temperature of the

soap bubble meter used for measurement of the gas flow. The volume of the carrier gas V_{N_2} was determined from the flow rate and the time measurement. Uncertainties of absolute vapor pressures measured by the transpiration method were estimated according to the procedure described in detail in ref 22. They are governed mostly by the reproducibility of the GC analysis, as well as by the V_{N_2} volume determination. The standard uncertainties (u) of the measured vapor pressures have been calculated to be

$$u(p/\text{Pa}) = 0.025 + 0.025(p/\text{Pa}) \quad \text{for } p > 5 \text{ Pa to 1000 Pa}$$

$$u(p/\text{Pa}) = 0.005 + 0.025(p/\text{Pa}) \quad \text{for } p < 5 \text{ Pa}$$

To validate system operation, the vapor pressure of naphthalene and benzoic acid was determined at $p = 1-500$ Pa. Experimental vapor pressure of naphthalene and benzoic acid obtained using the transpiration agreed with the results reported in the literature[23,24] to within 0.5%−2.5%. For validation of our uncertainty estimations, we measured vapor pressures for series of n-alkanols[25] and aliphatic esters[21] where reliable data at $p = 0.1-1000$ Pa from different methods were available. It has turned out that vapor pressures of n-alkanols and esters derived from the transpiration method were comparable with the available high-precision data generally within 1%−3%.

2.4.3. GC Correlation Method. Temperature dependencies of retention times of the carbazole derivatives leading to enthalpies of transfer from solution (in the chromatographic phase) to the gas phase, $\Delta_{\text{sol}}^{\text{g}}H_m^{\circ}$, were measured by using gas−liquid chromatography (GC).[26,27] An Agilent 7890A gas chromatograph that was equipped with flame ionization detection (FID) and an autosampler was used. GC runs were done isothermally on an Agilent HP-5 capillary column with a length of 30 m and a diameter of 0.25 mm, packed with a film thickness of 0.25 μm. The volume flow of the helium carrier gas was pressure-controlled with an inlet pressure of 104 kPa. At each temperature, corrections of the retention times with the value for a nonretained component (dichloromethane) were made. The temperature was maintained constant within ±0.1 K. All compounds were dissolved in dichloromethane. Experiments on each compound were performed in the temperature range of 373−493 K in steps of 5 K. By using an autosampler, retention times were generally reproducible within 1−3 s.

2.5. Computations. Quantum chemical calculations of the carbazole derivatives were performed with the Gaussian 09 series software.[28] Energies of molecules were calculated using the G3MP2 method.[29] General computational details on this approach were reported elsewhere.[30] Enthalpies (H_{298}) of each compound were calculated according to standard thermodynamic procedures.[31]

3. RESULTS AND DISCUSSION

3.1. Thermophysical Properties. *3.1.1. Heat Capacity Measurements.* The experimental results for the heat capacities measured in this work are summarized in Table S4 in the Supporting Information. The solid−liquid transition for N-ethylcarbazole was observed at $T = 342.4$ K. The heat capacity measurements for this compound were performed below the melting temperature. The relative error of the measurements was <5%. The fully hydrogenated compound 12H-NEC was liquid throughout the entire temperature range under study.

Upon the hydrogenation, the specific heat capacity increases, so that the value for 12H-NEC is more than 20% higher than that for 0H-NEC at 388 K.

The temperature-dependent behavior of the molar heat capacities was described using eq 2:

$$C_{p,m}^0 = A + BT(K) \tag{2}$$

The regression parameters A and B are summarized in Table 2. The deviation of the experimental data and the calculated

Table 2. Heat Capacity ($C_{p,m}^{\circ}$, J K^{-1} mol^{-1}), as Determined Using the Regression Parameters for eq 2

parameter	0H-NEC		12H-NEC liquid
	<342.4 K, solid	>342.4 K, liquid	
A	−36.316	202.58	127.16
B	0.8654	0.3326	0.7543
standard deviation, s [J K^{-1} mol^{-1}]	1.0	0.4	0.6
relative error, δ [%]	0.4	0.1	0.1

$C_{p,m}^{\circ}$ values was estimated using the standard deviation (s) and the relative error (δ).

$$s = \sqrt{\frac{\sum_{i=1}^{n}\left(C_{p,m_{\text{exp}}}^{\circ} - C_{p,m_{\text{calc}}}^{\circ}\right)^2}{n-1}} \tag{3}$$

$$\delta = \frac{\sum_{i=1}^{n}\left|\dfrac{C_{p,m_{\text{exp}}}^{\circ} - C_{p,m_{\text{calc}}}^{\circ}}{C_{p,m_{\text{exp}}}^{\circ}}\right|}{n} \tag{4}$$

The only value of heat capacity available in the literature for N-ethyl carbazole ($C_{p,m}^{\circ} = 238.2$ J K^{-1} mol^{-1} at 298 K)[32] is in acceptable agreement with the result measured in this work ($C_{p,m}^{\circ} = 227.2$ J K^{-1} mol^{-1} at 298 K) (see Table S4).

3.1.2. Density. Table S5 in the Supporting Information shows that the density decreases upon hydrogenation in the following order: 0H-NEC > 4H-NEC > 8H-NEC > 12H-NEC. The temperature dependency of the density was described using a linear approach:

$$\rho(T) = A + BT(K) \tag{5}$$

The regression parameters of eq 5 are given in Table 3.

3.1.3. Viscosity. The dynamic viscosity decreases upon hydrogenation in the following order: 0H-NEC > 4H-NEC > 8H-NEC > 12H-NEC (see Table S6 in the Supporting Information). Except for 12H-NEC, the dynamic viscosity was quite high at low temperatures (e.g., at 283.15 K: almost 700 mPas for 4H-NEC). However, at 353.15 K, the viscosity was

Table 3. Density (ρ, g cm^{-3}) of the Carbazole Derivatives at Different Temperatures, as Determined Using the Regression Parameters for eq 5

	0H-NEC	4H-NEC	8H-NEC	12H-NEC
A	1.313467	1.2553362	1.210127	1.1482329
B	−0.0007238	−0.0006966	−0.0006907	−0.0007092
standard deviation, s [g cm^{-3}]	4.8×10^{-6}	2.7×10^{-5}	1.6×10^{-5}	1.3×10^{-5}
relative error, δ [%]	0.0003	0.0021	0.0013	0.0011

Table 4. Dynamic Viscosities (η, mPa s) for 0H-NEC, 4H-NEC, 8H-NEC, and 12H-NEC, as Determined Using the Regression Parameters of eq 6

| | 0H-NEC | 4H-NEC | | 8H-NEC | 12H-NEC |
		$T \leq 323.15$ K	$T > 323.15$ K		
A	−198.5107397	54.77739118	−8.474341421	−51.67196212	−121.3831627
B	14092.471	14646.3196	5607.607	5951.08459	8035.86187
C	27.4111475	−21.0444126	−1.46520555	6.23125641	16.8924989
D	6.94×10^{-13}	2.35×10^{-4}	2.42×10^{-5}	-6.10×10^{-8}	-3.65×10^{-9}
standard deviation, s [mPa s]	0.1	5.5	0.2	0.4	0.1
relative error, δ [%]	1.5	0.8	2.5	3.2	1.0

already acceptably low (<10 mPa s) for all investigated substances. The temperature dependency of the dynamic viscosity was described with the DIPPR 115 equation:[33]

$$\ln(\eta(T)) = A + \frac{B}{T} + C \ln(T) + DT^2 \tag{6}$$

The regression parameters of eq 6 are listed in Table 4.

3.1.4. Surface Tension. According to the experimental results given in Table S7 in the Supporting Information, we observed that, with the increasing degree of hydrogenation, the surface tension of the carbazole derivatives decreased in the following order: 4H-NEC > 8H-NEC > 12H-NEC (see Table S7). For example, the surface tension of 12H-NEC was by 20% lower than those for 0H-NEC at 298 K. The temperature dependence of the surface tension was described using eq 7:

$$\sigma_i(T) = A + BT(K) \tag{7}$$

The regression parameters of eq 7 are listed in Table 5.

Table 5. Surface Tension (σ, mN m^{-1}) of 4H-NEC, 8H-NEC and 12H-NEC, as Determined Using the Regresssion Parameters of eq 7

	4H-NEC	8H-NEC	12H-NEC
A	71.1760	63.1091	59.3586
B	−0.0996	−0.0850	−0.0881
standard deviation, s [mN m^{-1}]	0.25	0.01	0.03
relative error, δ [%]	0.49	0.03	0.08

3.1.5. Refractive Index. According to the experimental results given in Table S8 in the Supporting Information, we observed that, as the degree of hydrogenation increased, the refractive index (n_D) of the carbazole derivatives decreased. The difference of refractive indices between 0H-NEC and 12H-NEC was ∼10% at 353.15 K. The temperature dependence of the refractive index was described using eq 8:
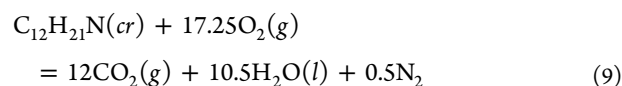
$$n_D(T) = A + BT(K) \tag{8}$$

Parameters of eq 8 with the uncertainties are given in Table 6.

Table 6. Refractive Indices (n_D) for 0H-NEC, 4H-NEC, 8H-NEC, and 12H-NEC, as Determined Using the Regression Parameters of eq 8
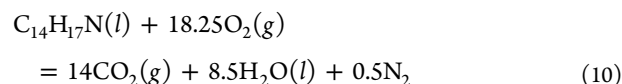
	0H-NEC	4H-NEC	8H-NEC	12H-NEC
A	1.831264	1.7269	1.656004	1.615182
B	−0.00056	−0.000439	−0.000391	−0.000405
standard deviation, s	0.0002	0.0002	0.0002	0.0002
relative error, δ [%]	0.008	0.009	0.009	0.012

3.2. Thermochemical Properties. *3.2.1. Standard Molar Enthalpy of Formation from Combustion Calorimetry.* Typical experiments on 12-H-carbazole, 4H-NEC and 8H-NEC, are given in Table S2. Values of the standard specific energies of combustion $\Delta_c u°$ (see Table S3) have been used to derive the standard molar enthalpies of combustion $\Delta_c H_m°$ and the standard molar enthalpies of formation in the liquid state $\Delta_f H_m°(\text{liq})$ or in the crystalline state $\Delta_f H_m°(\text{cr})$, which are given in Table 7. Values of $\Delta_c u°$ and $\Delta_c H_m°$ refer to reactions:
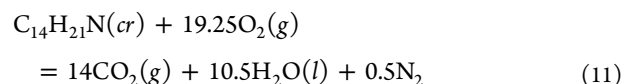
12H-Carbazole:

$$C_{12}H_{21}N(cr) + 17.25O_2(g)$$
$$= 12CO_2(g) + 10.5H_2O(l) + 0.5N_2 \tag{9}$$

4H-NEC:

$$C_{14}H_{17}N(l) + 18.25O_2(g)$$
$$= 14CO_2(g) + 8.5H_2O(l) + 0.5N_2 \tag{10}$$

8H-NEC:

$$C_{14}H_{21}N(cr) + 19.25O_2(g)$$
$$= 14CO_2(g) + 10.5H_2O(l) + 0.5N_2 \tag{11}$$

The enthalpies of formation, $\Delta_f H_m°(\text{liq or cr})$, of carbazole derivatives were calculated from the enthalpic balance according to eqs 9−11, using the standard molar enthalpies of formation of $H_2O(liq)$ and $CO_2(g)$ recommended by CODATA.[34] Uncertainties related to combustion experiments were calculated according to the guidelines presented by Olofsson[35] and by Hubbard et al.[19] 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 $\Delta_f H_m°(\text{liq or cr})$ is twice the overall standard deviation and includes the uncertainties from calibration, from the combustion energies of the auxiliary materials, and the uncertainties of the enthalpies of formation of the reaction products H_2O and CO_2. To the best of our knowledge, this is the first time that combustion energies of 12H-carbazole, 4H-NEC, and 8H-NEC have been measured.

3.2.2. Vapor Pressures of Carbazole Derivatives. Vapor pressures of carbazole derivatives are important for their practical application. To the best of our knowledge, this is the first time that the vapor pressures of 4H-carbazole, 12H-carbazole, 4H-NEC, and 8H-NEC have been measured (see Tables 8a and 8b). Temperature dependencies of the measured absolute vapor pressures p_i were fitted with the following equation:[25]

Table 7. Thermochemical Data at T = 298 K ($p°$ = 0.1 MPa) for Carbazole Derivatives[a]

compound		$\Delta_c H_m°$ (kJ mol^{-1})	$\Delta_f H_m°$(liq or cr) (kJ mol^{-1})	$\Delta_f^g H_m°$ (kJ mol^{-1})	$\Delta_{cr}^g H_m°$ (kJ mol^{-1})	$\Delta_f H_m°$(g) (kJ mol^{-1})
4-H-carbazole	cr				97.2 ± 0.9	
12-H-carbazole	cr	−7529.0 ± 2.1	−194.4 ± 2.3		84.0 ± 0.6	−110.4 ± 2.4
4-H-NEC	liq	−7913.4 ± 2.3	−25.3 ± 3.0	82.8 ± 0.4		57.5 ± 3.0
8-H-NEC	cr	−8360.0 ± 2.2	−150.3 ± 2.9	81.9 ± 0.5	99.3 ± 0.6[b]	−51.0 ± 3.0

[a]Uncertainties correspond to expanded uncertainties of the mean (95% confidence level). [b]Calculated as the sum of the measured by transpiration enthalpy of vaporization and the enthalpy of fusion from Table 9.

Table 8a. Absolute Vapor Pressures (p) and Standard ($p°$ = 0.1 MPa) Molar Sublimation or Vaporization Enthalpies, Obtained Using the Transpiration Method: 4H-Carbazole and 12H-Carbazole

T [K][a]	m [mg][b]	$V(N_2)$[c] [dm^3]	flow [dm^3 h^{-1}]	p [Pa][d]	$u(p)$ [Pa][e]	$\Delta_{cr}^g H_m°/\Delta_l^g H_m°$ [kJ mol^{-1}]

4H-carbazole; $\Delta_{cr}^g H_m°$(298 K) = 97.2 ± 0.9 kJ mol^{-1}

$$\ln(p(\text{Pa})) = \frac{316.19}{R} - \frac{107241.57}{RT(\text{K})} - \frac{33.6}{R}\ln\left(\frac{T(\text{K})}{298.15}\right)$$

335.6	1.78	61.57	4.95	0.42	0.02	95.97
341.5	0.53	10.07	4.95	0.76	0.02	95.77
346.4	0.27	3.27	3.64	1.19	0.03	95.60
348.3	1.14	11.47	4.95	1.43	0.04	95.54
351.5	1.21	9.24	4.95	1.88	0.05	95.43
354.6	0.90	5.15	3.64	2.53	0.07	95.33
357.2	1.33	5.86	4.95	3.27	0.09	95.24
360.4	1.91	6.18	3.64	4.45	0.12	95.13
363.2	1.06	2.72	4.95	5.59	0.16	95.04
366.3	1.01	2.00	3.64	7.30	0.21	94.94

12H-carbazole: $\Delta_{cr}^g H_m°$(298 K) = 84.0 ± 0.6 kJ mol^{-1}

$$\ln(p(\text{Pa})) = \frac{320.29}{R} - \frac{96150.89}{RT(\text{K})} - \frac{40.9}{R}\ln\left(\frac{T(\text{K})}{298.15}\right)$$

305.7	0.86	6.75	4.31	1.76	0.05	83.65
308.9	1.06	5.89	4.31	2.46	0.07	83.52
312.1	0.85	3.30	4.31	3.52	0.09	83.39
315.8	1.06	2.87	4.31	5.05	0.13	83.24
321.8	0.88	1.36	4.31	8.87	0.25	82.99
327.5	1.16	1.01	4.31	15.79	0.42	82.76
333.3	0.99	0.514	2.06	26.45	0.69	82.52
339.0	1.61	0.514	2.06	43.03	1.10	82.29
342.9	1.83	0.411	2.06	61.10	1.55	82.13

[a]Saturation temperature ($u(T)$ = 0.1 K). [b]Mass of transferred sample condensed at T = 243 K. [c]Volume of nitrogen ($u(V)$ = 0.005 dm^3) used to transfer m ($u(m)$ = 0.0001 g) of the sample. [d]Vapor pressure at temperature T, obtained from the value of m and the residual vapor pressure at T = 243 K, calculated by an iteration. [e]Uncertainties of experimental vapor pressures were calculated according to the following equations: $u(p/\text{Pa}) = 0.005 + 0.025(p/\text{Pa})$ for $p < 5$ Pa and $u(p/\text{Pa}) = 0.025 + 0.025(p/\text{Pa})$ for $p > 5$ Pa.

$$R\ln p_i = a + \frac{b}{T} + \Delta_l^g C_{p,m}°\ln\left(\frac{T}{T_0}\right) \quad (12)$$

where a and b are adjustable parameters and $\Delta_l^g C_{p,m}°$ (or $\Delta_{cr}^g C_{p,m}$) is the difference of the molar heat capacities of the gaseous and the condensed phase, respectively. The T_0 term that appears in eq 12 is an arbitrarily chosen reference temperature (which has been chosen to be equal to T = 298.15 K) and R is the molar gas constant. Values of $\Delta_l^g C_{p,m}°$ or $\Delta_{cr}^g C_{p,m}$ in eq 12 were calculated (see Table S9 in the Supporting Information), according to the procedure developed by Chickos and Acree,[36] based on the isobaric molar heat capacity $C_{p,m}°$(l or cr, 298 K). The latter values were estimated by the group-additivity procedure[37] or taken from the results of this work.

According to Tables 8a and 8b, the vapor pressure of the investigated carbazole derivatives decreased as the degree of hydrogenation decreased, in the following order: 12H-NEC > 8H-NEC > 4H-NEC > 0H-NEC. For example, the vapor pressure of 12H-NEC was almost 30 times higher than that for 0H-NEC at 353 K.

3.2.3. Vaporization and Sublimation Enthalpies of Carbazole Derivatives. In this work, the vaporization enthalpies of 4H-NEC and 8H-NEC and sublimation enthalpies of 4-H-carbazole and 12H-carbazole at temperatures T were indirectly derived from the temperature dependencies of vapor pressures measured by the transpiration using eq 13, where b is the adjustable parameter from eq 12:

$$\Delta_l^g H_m°(T) = -b + \Delta_l^g C_{p,m}° T \quad (13)$$

Experimental absolute vapor pressures for carbazole derivatives from the transpiration method and coefficients a and b of eq 12 are given in Tables 8a and 8b. The procedure for calculation of the combined uncertainties of the vaporization or sublimation enthalpy was described elsewhere.[22] They include uncertainties from the transpiration experimental conditions, uncertainties of vapor pressure, and uncertainties from temperature adjustment to T = 298 K.

3.2.4. Enthalpy of Fusion. It has turned out that the volatility of 8H-NEC in the temperature range below the melting point of 316.0 K was too low to perform transpiration measurements in an extended temperature range with reasonable accuracy. In such cases, we used to perform transpiration experiments above the melting point. The enthalpy of vaporization derived from vapor pressures temperature dependencies, according to eqs 12 and 13, combined with the DSC-measured enthalpy of fusion, $\Delta_{cr}^l H_m°$, provides the desired enthalpy of sublimation for the compound of interest. Experimental enthalpies of fusion for the carbazole derivatives of interest for this work were measured by the DSC just recently[37] (see Table 9). Values of the fusion enthalpies measured by DSC are referenced to the melting temperature (T_{fus}). Because of the differences in the reference temperatures, the experimental enthalpies of fusion must be adjusted to T = 298 K. The adjustment was calculated by the equation[36]

$$\{\Delta_{cr}^l H_m°(T_{fus}(\text{K})) - \Delta_{cr}^l H_m°(298\,\text{K})\}\,(\text{J mol}^{-1})$$
$$= \{(0.75 + 0.15 C_{p,m}°(cr))[(T_{fus}(\text{K})) - 298\,\text{K}]\}$$
$$- \{(10.58 + 0.26 C_{p,m}°(liq))[(T_{fus}(\text{K})) - 298\,\text{K}]\} \quad (14)$$

where $C_{p,m}°(cr)$ and $C_{p,m}°(liq)$ are the isobaric molar heat capacities of the solid and the liquid carbazole derivatives,

Table 8b. Absolute Vapor Pressures (p) and Standard ($p° = 0.1$ MPa) Molar Sublimation or Vaporization Enthalpies, Obtained Using the Transpiration Method: 4H-NEC and 8H-NEC

T [K][a]	m [mg][b]	$V(N_2)$[c] [dm³]	flow [dm³ h⁻¹]	p [Pa][d]	$u(p)$ [Pa][e]	$\Delta_{cr}^g H_m°/\Delta_l^g H_m°$ [kJ mol⁻¹]
						4H-NEC: $\Delta_l^g H_m°$(298 K) = 82.8 ± 0.4 kJ mol⁻¹

$$\ln(p(\text{Pa})) = \frac{354.31}{R} - \frac{113845.09}{RT(\text{K})} - \frac{104.1}{R}\ln\left(\frac{T(\text{K})}{298.15}\right)$$

T [K]	m [mg]	$V(N_2)$ [dm³]	flow [dm³ h⁻¹]	p [Pa]	$u(p)$ [Pa]	$\Delta_{cr}^g H_m°/\Delta_l^g H_m°$
307.8	0.59	69.28	4.62	0.10	0.01	81.81
310.5	0.68	59.38	4.47	0.14	0.01	81.52
313.4	0.61	40.89	2.77	0.18	0.01	81.23
317.2	0.63	28.63	1.91	0.27	0.01	80.83
322.0	0.59	17.05	4.85	0.42	0.02	80.33
324.5	0.77	18.03	4.51	0.52	0.02	80.06
326.3	0.57	11.54	4.62	0.61	0.02	79.88
327.5	0.64	11.66	4.66	0.68	0.02	79.75
329.4	0.80	11.55	4.47	0.85	0.03	79.55
329.9	0.67	9.32	4.66	0.88	0.03	79.51
332.3	0.84	9.74	4.50	1.05	0.03	79.25
334.3	0.53	5.36	4.60	1.21	0.04	79.04
337.1	0.66	5.21	4.47	1.55	0.04	78.76
340.3	0.77	4.66	4.67	2.01	0.06	78.42
341.0	0.67	3.99	4.61	2.06	0.06	78.35
342.1	0.68	3.55	4.43	2.37	0.06	78.23
346.9	0.65	2.31	4.62	3.42	0.09	77.74
347.1	1.35	4.64	4.49	3.58	0.09	77.72
347.9	0.58	1.87	1.25	3.76	0.10	77.63
349.9	0.58	1.63	1.22	4.37	0.11	77.43
351.4	1.76	4.48	4.48	4.82	0.13	77.27
354.8	0.54	1.02	1.22	6.45	0.19	76.92
354.9	0.63	1.22	1.18	6.34	0.18	76.91
356.9	0.65	1.10	1.89	7.22	0.21	76.70
359.0	0.58	0.844	1.18	8.41	0.24	76.48
360.8	0.63	0.791	1.90	9.75	0.27	76.29
362.9	0.65	0.682	1.17	11.63	0.32	76.07
364.8	0.69	0.635	1.91	13.33	0.36	75.87
366.8	0.60	0.487	1.17	15.07	0.40	75.67
368.8	0.67	0.478	1.91	17.10	0.45	75.46
370.8	0.44	0.290	1.16	18.44	0.49	75.25
370.8	0.52	0.330	1.20	19.16	0.50	75.25

8H-NEC: $\Delta_l^g H_m°$(298 K) = 81.9 ± 0.5 kJ mol⁻¹

$$\ln(p(\text{Pa})) = \frac{364.27}{R} - \frac{115153.32}{RT(\text{K})} - \frac{111.4}{R}\ln\left(\frac{T(\text{K})}{298.15}\right)$$

T [K]	m [mg]	$V(N_2)$ [dm³]	flow [dm³ h⁻¹]	p [Pa]	$u(p)$ [Pa]	$\Delta_{cr}^g H_m°/\Delta_l^g H_m°$
324.3	1.59	19.08	4.64	1.01	0.03	79.03
327.8	0.63	5.79	4.64	1.31	0.04	78.64
331.8	1.35	8.84	4.38	1.85	0.05	78.20
333.7	1.91	10.29	4.75	2.26	0.06	77.98
337.8	0.82	3.29	4.38	3.02	0.08	77.53
338.8	2.01	7.10	4.68	3.43	0.09	77.42
343.1	0.58	1.50	4.50	4.66	0.12	76.94
343.6	0.87	2.09	1.68	5.01	0.13	76.88
346.6	1.91	3.72	4.65	6.23	0.18	76.55
347.9	0.64	1.12	4.50	6.86	0.20	76.40
348.6	1.93	3.11	4.78	7.53	0.21	76.32
351.5	1.88	2.53	4.75	9.01	0.25	75.99
353.6	1.10	1.26	1.67	10.58	0.29	75.76
353.6	1.80	2.06	4.76	10.57	0.29	75.76
355.1	1.66	1.78	4.64	11.27	0.31	75.60
356.6	1.76	1.64	4.10	12.96	0.35	75.43
358.6	1.51	1.19	1.71	15.25	0.41	75.21
360.9	1.58	1.08	4.64	17.65	0.47	74.95
361.5	1.61	1.03	4.10	18.93	0.50	74.88
363.7	2.11	1.17	4.70	21.66	0.57	74.64
365.6	2.03	1.00	4.64	24.48	0.64	74.43
366.5	1.47	0.679	1.77	26.05	0.68	74.33

[a]Saturation temperature ($u(T) = 0.1$ K). [b]Mass of transferred sample condensed at $T = 243$ K. [c]Volume of nitrogen ($u(V) = 0.005$ dm³) used to transfer m ($u(m) = 0.0001$ g) of the sample. [d]Vapor pressure at temperature T, obtained from the m and the residual vapor pressure at $T = 243$ K, calculated by an iteration. [e]Uncertainties of experimental vapor pressures were calculated according to the following equations: $u(p/\text{Pa}) = 0.005 + 0.025(p/\text{Pa})$ for $p < 5$ Pa and $u(p/\text{Pa}) = 0.025 + 0.025(p/\text{Pa})$ for $p > 5$ Pa.

Table 9. Compilation of Experimental Data on Enthalpies of Phase Transitions

compound	T_{fus} [K]	$\Delta_{cr}^l H_m°$ [kJ mol⁻¹]	$\Delta_{cr}^l H_m°$(298 K)[a] [kJ mol⁻¹]
0H-carbazole	513.2	27.1[b]	15.6 ± 3.4
N-methyl-carbazole	362.5	17.15[b]	13.6 ± 1.1
1,2,3,4-tetrahydro-N-methylcarbazole	323.7	14.7[c]	13.4 ± 0.4
N-ethyl-carbazole	343.1	15.1[b]	13.0 ± 0.8
4H-carbazole	391.3	17.9[d]	12.5 ± 1.6
12H-carbazole	349.5	22.9[d]	20.2 ± 0.8
8H-N-ethyl-carbazole	316.0	20.6[d]	19.4 ± 0.5

[a]Adjusted to the reference temperature according to ref 36. [b]Data taken from refs 38 and 41. [c]Data taken from ref 39. [d]Data taken from ref 42.

respectively (given in Table S9). With this adjustment, the molar enthalpies of fusion ($\Delta_{cr}^l H_m$(298 K)) were calculated (see Table 9). Uncertainties in the temperature adjustment of fusion enthalpies from T_{fus} to the reference temperature given in Table 9 were estimates and amounted to 30% of the total

adjustment.[40] Values of $\Delta_{cr}^l H_m°$ adjusted to 298 K were used to derive the required enthalpies of sublimation ($\Delta_{cr}^g H_m°$(298 K)) or enthalpies of vaporization ($\Delta_l^g H_m°$(298 K)) of the carbazole derivatives listed in Table 10.

3.2.5. Experimental Gas-Phase Standard Molar Enthalpies of Formation. Values of vaporization, sublimation, and solid phase transition enthalpies of carbazole derivatives (Tables 7–9) can now be used, together with the combustion calorimetry data, to yield the gas-phase standard enthalpies of formation ($\Delta_f H_m°$(g)) at 298 K. The resulting values are given in Tables 7 and 10. These values can now be compared to the results from the high-level quantum-chemical calculations.

3.3. Validation and Prediction of Thermochemical Properties Carbazole Derivatives. Despite our significant efforts to separate reaction mixtures of hydrogenated derivatives of N-ethylcarbazole, we failed to obtain reasonable amounts of pure samples of 6H-NEC and 10H-NEC, as well as of 6H-carbazole, 8H-carbazole, and 10H-carbazole, for experimental studies. However, knowledge of thermodynamic properties of these intermediates is required for optimization of their practical applications. In this context study of structure–

Table 10. Compilation of Thermochemical Data for the Carbazole Derivatives at 298 K

compound	$\Delta_f H_m^\circ$(cr or liq)[a] [kJ mol^{-1}]	$\Delta_{cr}^g H_m^\circ$ [kJ mol^{-1}]	$\Delta_f^g H_m^\circ$ [kJ mol^{-1}]	$\Delta_f H_m^\circ(g)$ [kJ mol^{-1}] exp	G3MP2
0H-carbazole	101.7 ± 2.8 (cr)[a]	104.3 ± 0.5[a]	88.7 ± 3.4[d]	206.0 ± 2.9	207.1
N-methylcarbazole	103.7 ± 2.4 (cr)[a]	92.7 ± 1.9[a]	79.1 ± 1.2[d]	196.4 ± 3.1	196.0
1,2,3,4-tetrahydro-N-methylcarbazole	−1.0 ± 1.3 (cr)[b]	93.5 ± 1.4[b]	80.1 ± 1.3[d]	92.5 ± 1.9	93.4
N-ethylcarbazole	70.6 ± 2.6 (cr)[a]	97.1 ± 1.0[a]	84.1 ± 1.3[d]	167.7 ± 2.8	163.9
4H-carbazole	4.5 (cr)[d]	97.2 ± 0.9			101.7
	17.0 (liq)[e]		84.7 ± 1.8[d]		
6H-carbazole	−137.8 (liq)[e]		(79.2)		−58.6
8H-carbazole	−90.4 (liq)[e]		(80.7)		−9.7
10H-carbazole	−85.0 (liq)[e]		(80)		−5.0
12H-carbazole	−194.4 ± 2.3 (cr)	84.0 ± 0.6		−110.4 ± 2.4	−111.4
	−175.2 (liq)[e]		63.8 ± 1.0[d]		
4H-N-ethylcarbazole	−25.3 ± 3.0 (liq)		82.8 ± 0.4	57.5 ± 3.0	61.3
6H-N-ethylcarbazole	−62.5 (liq)[e]		(82.8)		20.3
8H-N-ethylcarbazole	−150.3 ± 2.9 (cr)	101.3 ± 0.6[f]		−49.0 ± 3.0	−48.6
	−130.5 (liq)[e]		81.9 ± 0.5		
10H-N-ethylcarbazole	−121.8 (liq)[e]		(82)		−39.8
12H-N-ethylcarbazole	−219.8 ± 4.2 (liq)[c]		68.4 ± 0.5[c]	−151.4 ± 4.4	−151.0

[a]Data taken from ref 41. [b]Data taken from ref 39. [c]Data taken from ref 18. Values in brackets were derived from the correlation GC method (see text). [d]Calculated as the difference $\Delta_{cr}^g H_m^\circ$ (from column 3 in this table) and $\Delta_{cr}^l H_m^\circ$ (from column 4 in Table 9). [e]Calculated as the difference of column 6 and column 4 in this table. [f]Calculated as the sum of $\Delta_f^g H_m^\circ$ (from column 4 in this table) and $\Delta_{cr}^l H_m^\circ$ (from column 4 in Table 9).

property relationships in the series of carbazole and N-ethylcarbazole families can help to reveal general rules that are useful for the validation of measured thermochemical properties as well as for the prediction of properties for hardly available intermediates.

3.3.1. Quantum Chemical Calculation of the Gas-Phase Enthalpies of Formation. The high-level quantum-chemical (QC) methods are able to predict enthalpies of formation, $\Delta_f H_m^\circ(g, 298\ K)$, of small to middle size molecules with a "chemical accuracy"[43,44] of 2–5 kJ mol^{-1}. Substituted carbazoles studied in this work seem to be on the boundary in size to fulfill this expectation. However, according to the results from our previous work, the composite G3MP2 was able to reproduce the experimental values for 0H-NEC and 12H-NEC within the experimental uncertainties of 3–4 kJ mol^{-1}. These results have encouraged further use of the high-level QC calculations as a valuable tool to test experimental and theoretical results for the mutual consistency. In this work, we continued to use the composite method G3MP2 for calculation of the gaseous enthalpies of formation of carbazole derivatives for comparison with the experimental data.

The optimized structures obtained for the most stable conformer of each compound are illustrated in Figure 7.

It is apparent that, in contrast to the flat and rigid structures of the starting molecules carbazole and N-ethylcarbazole, all partly hydrogenated intermediates gain more and more flexibility upon the degree of hydrogenation (see Figure 7). Generally, a proper calculation of energetics for all possible conformers is important for the exact calculation of $\Delta_f H_m^\circ(g)$. However, from our experiences, in many cases, only a few most stable conformers significantly contribute to the theoretical enthalpy of formation, provided that their energies do not differ from other conformers by 1–3 kJ mol^{-1}. As a rule, the conformers with an energy difference of ≥ 10 kJ mol^{-1} from the most stable conformer are practically not populated in the gas phase. Such a simplification is often used for large molecules with an abundant flexibility[45] and sufficient accuracy. Analysis of the conformational space for the hydrogenated derivatives of

carbazole and N-ethylcarbazole has revealed that the most stable conformers for each species possess comparable energies and the differences do not exceed 1–5 kJ mol^{-1}, even for the most flexible molecule, 12H-NEC.[18] This observation has reduced the amount of computational work, and, using the high-level G3MP2 method, we calculated only the most stable conformers for each carbazole derivative.

The enthalpies H_{298} calculated for the carbazole derivatives (see Table S10) were converted to enthalpies of formation $\Delta_f H_m^\circ(g, 298\ K)$, using the atomization procedure reinforced in our previous work for highly hydrogenated carbazole derivatives.[18] However, as it has been noticed in our previous studies,[30,41,46] the enthalpies of formation from the atomization procedure (AT) for the aromatic molecules deviate systematically from the experimental values. For example, the value of $\Delta_f H_m^\circ(g, 298\ K)$ derived using the AT for the benzene (77.9 kJ mol^{-1}) is less positive, in comparison with the experimental value that is recommended for this molecule (82.9 ± 0.9 kJ mol^{-1}).[47] Surprisingly, the agreement between the experiment and the AT calculated enthalpies of formation becomes better upon the consequent hydrogenation of the benzene ring to 1,3-cyclohexadiene,[48] cyclohexene,[49] and cyclohexane[50] (see Table S10). In our recent works,[30,41,46] we successfully used a linear correlation between the experimental and the calculated by atomization procedure enthalpies of formation 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 formation of carbazole, N-methylcarbazole, 1,2,3,4-tetrahydro-N-methylcarbazole, and N-ethylcarbazole (see column 5 in Table 10), in order to establish the linear equation:

$$\Delta_f H_m^\circ(g)(exp)\ (kJ\ mol^{-1}) = 1.00 \times \Delta_f H_m^\circ(g)(AT) + 10.7$$

(15)

which is valid for carbazole derivatives containing the benzene ring: 4H-carbazole, 6H-carbazole, 4H-NEC, and 6H-NEC. Using the correlation described by eq eq 15, the AT-"corrected" enthalpies of formation of the carbazole derivatives have been
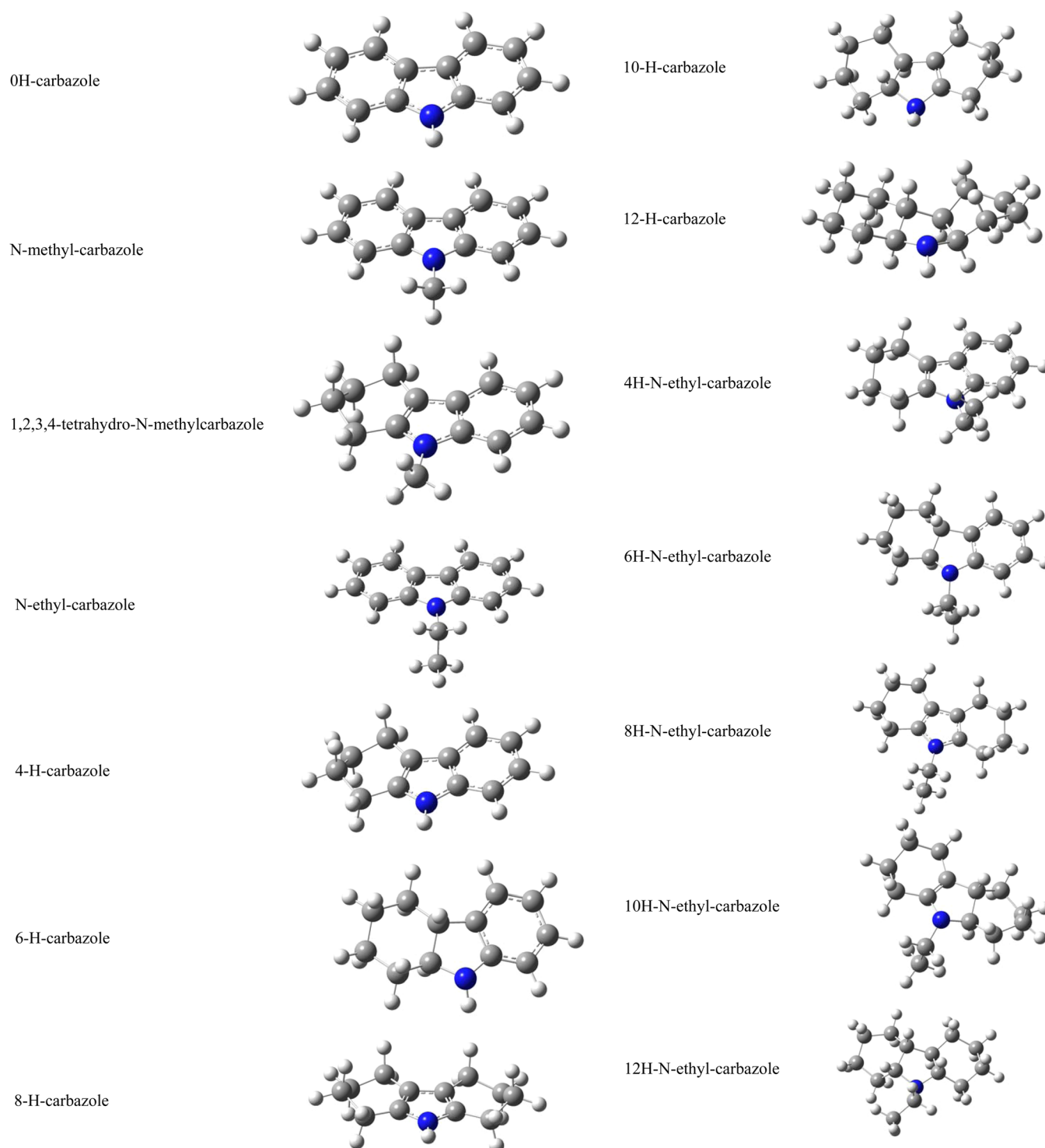
Figure 7. Optimized structures of carbazole derivatives obtained with the G3MP2 method.

calculated (see column 6 in Table 10). It should be mentioned that the coefficients of eq 15 developed in this work are indistinguishable from the correlation established for the broad range of cyclic, aromatic, and heterocyclic structures in our previous work:[41]

$$\Delta_f H_m^\circ(g)(\exp) \ (kJ \ mol^{-1})$$
$$= 0.992 \times \Delta_f H_m^\circ(g)(AT) + 10.3 \qquad (16)$$

Thus, with this "modified atomization procedure", we could estimate the enthalpies of formation for the similarly shaped compounds using the G3MP2 method, combined with the atomization reaction and correlation, according to eq 16. As it can be seen in Table 10, there is an overall good agreement between theoretical and experimental data, particularly if the common uncertainties of ~2−4 kJ mol^{-1} associated with the G3MP2 gas-phase enthalpies of formation are taken into account. This good agreement further reinforces the reliability
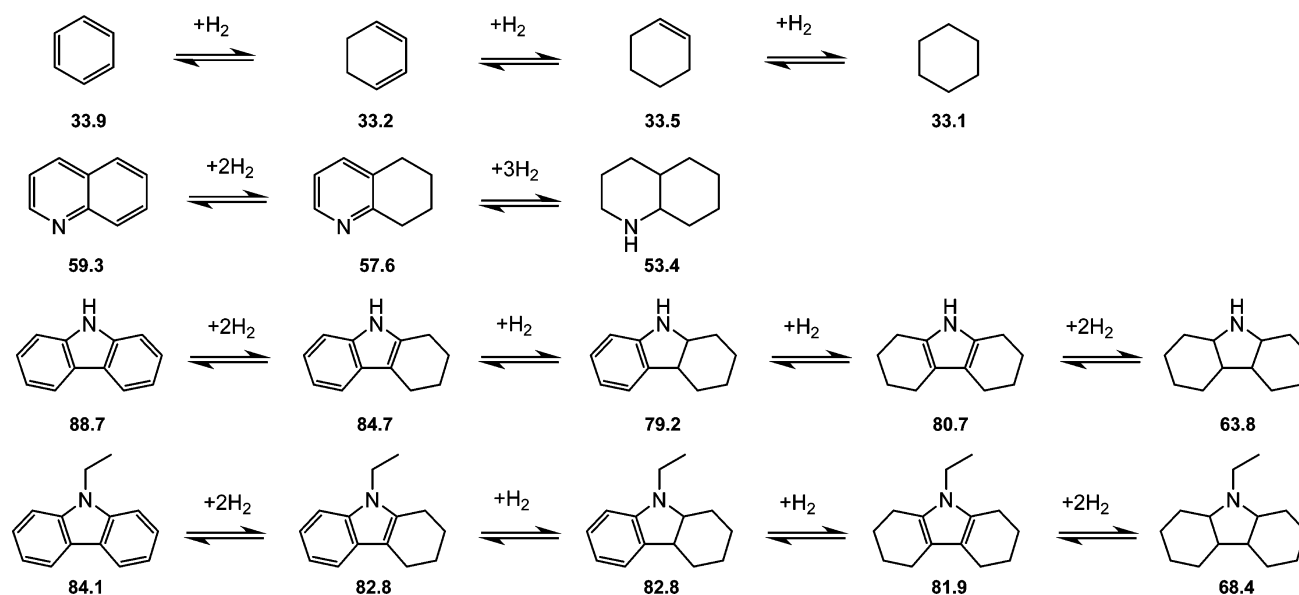
Figure 8. Structure−property relations for vaporization enthalpies $\Delta_l^g H_m^\circ(298\ K)$ of aromatic compounds (in kJ mol^{-1}). Data for the benzene family are taken from refs 44−47 Data for the quinoline family are taken from refs 51 and 52.

of the experimental and theoretical results presented in this work.

3.3.2. Missing Vaporization Enthalpies from the Structure–Property Pattern. In the frame of the current work, only enthalpies of vaporization of two representatives of the carbazole series (4H-carbazole and 12H-carbazole), as well as of the N-ethylcarbazole series (4H-NEC and 8H-NEC) were derived with the help of the transpiration method (see column 4 in Table 10). At first glance, the structures of family members in both series are quite different, in order to anticipate any similarities in their properties (e.g., in vaporization enthalpies). However, let us consider vaporization enthalpies of the benzene derivatives upon consequent hydrogenation of the ring from benzene itself to cyclohexane (see Figure 8). Surprisingly, for this series, the vaporization enthalpies $\Delta_l^g H_m^\circ(298\ K)$ remain without changes independent of the degree of hydrogenation. Moreover, the same pattern was observed for the quinolone series (see Figure 8), where the quinoline and the 5,6,7,8-tetrahydroquinoline exhibit very similar vaporization enthalpies, but the fully hydrogenated quinolone has already significantly smaller vaporization enthalpy. This observation also seems to be valid for the 0H-NEC family (see Figure 8), where N-ethylcarbazole and the partly hydrogenated species (4H-NEC and 8H-NEC) show almost-identical vaporization enthalpies, but for the complete hydrogenated 12H-NEC, the vaporization enthalpy is 14 kJ mol^{-1} lower. The similar pattern is apparent also for the carbazole family (see Figure 8). Such a simple structure−property relationship can be considered as evidence of the consistency of vaporization enthalpies measured in this work. Moreover, these trends are helpful to assess at least a level of the missing vaporization enthalpies of 6H-carbazole, 8H-carbazole, 10H-carbazole, 6H-NEC, and 10H-NEC.

3.3.3. Missing Vaporization Enthalpies from the Correlation GC Analysis. More-reliable assessment of the missing vaporization enthalpies was obtained from the correlation GC method (CGC).[26,27] This method correlates the gas chromatography behavior (retention time t_r) of a compound of interest with the net of the retention times of some parent compounds with the known enthalpies of vaporization. For

each compound, the retention times are utilized for calculation of enthalpies of transfer from solution to the gas phase ($\Delta_{sol}^g H_m^\circ$) by plotting $\ln(1/t_r)$ vs $1/T$ (see Table S11 in the Supporting Information). The slope of this linear correlation $\ln(1/t_r) = m + n/T$ when multiplied by the gas constant R affords $\Delta_{sol}^g H_m^\circ$. As a rule, the linear relationship between $\Delta_{sol}^g H_m^\circ$ and $\Delta_l^g H_m^\circ(298\ K)$ for the structurally related compounds provides a possibility for obtaining the vaporization enthalpy of a compound of interest, provided that the $\Delta_{sol}^g H_m^\circ$ value was measured under the same conditions. The accuracy of the predictions is dependent mostly on the accuracy of the $\Delta_l^g H_m^\circ(298\ K)$ of the reference compounds. The most reliable results are usually derived when the reference compounds are structurally similar and from the same chemical family. The experimental results for the temperature dependence of the corrected retention time in form of equation $\ln(1/t_r) = m + n/T$ for a series of 16 reference aromatic compounds and their derived values of $\Delta_{sol}^g H_m^\circ$ are listed in Table S11. We used only experimental results for $\Delta_l^g H_m^\circ(298\ K)$ on aromatic heterocycles available from the literature (see Table S11). From the correlation of the selected dataset, the following equation for the estimation of vaporization enthalpies was obtained:

$$\Delta_l^g H_m^\circ(298\ K)\ (kJ\ mol^{-1})$$
$$= -20.9 + 1.82 \times \Delta_{sol}^g H_m^\circ\ (r = 0.993) \tag{17}$$

The uncertainty of $\Delta_l^g H_m^\circ(298\ K)$ values derived from eq 17 is assessed to be ±1.5 kJ mol^{-1}. With this correlation and the measured values of $\Delta_{sol}^g H_m^\circ$ for the missing carbazole derivatives, the enthalpies of vaporization were estimated (see column 4 in Table 10). We proved an ability of eq 17 to predict the vaporization enthalpies of carbazole derivatives, using the values of $\Delta_l^g H_m^\circ(298\ K)$ for 4H-carbazole, 12H-carbazole, 4H-NEC, and 8H-NEC measured in this work by the transpiration method. The latter data were excluded from the development of eq 17 deliberately. The results for these four compounds, derived from the CGC method and transpiration method, are in agreement within the limits of their experimental uncertainties (see Table S12 in the Supporting Information).

3.3.4. Combination of QC Calculations and Estimated Vaporization Enthalpies for Prediction of the Liquid Phase Enthalpies of Formation. Having established the ability of the high-level G3MP2 method to predict the reliable gas-phase enthalpies of formation of carbazole derivatives (see column 6 in Table 10), as well as having a self-consistent set of their vaporization enthalpies (see column 4 in Table 10) derived in the current study, we calculated the unavailable $\Delta_f H_m^\circ(liq, 298$ K) values of carbazole derivatives using the basic thermodynamic equation:

$$\Delta_f H_m^\circ(liq, 298\,\mathrm{K}) = \Delta_f H_m^\circ(g, \mathrm{G3MP2})$$
$$- \Delta_l^g H_m^\circ(298\,\mathrm{K, exp}) \qquad (18)$$

Results are given in Table 10 (column 2). These values are required for calculation of enthalpies of (de)hydrogenation reactions that are essential for practical applications of LOHC.

3.4. Thermodynamic Analysis of the Hydrogenation/Dehydrogenation Processes for the Carbazole Derivatives. The thermodynamics of the hydrogenation (or dehydrogenation) reaction (see Figure 9) determine the quality
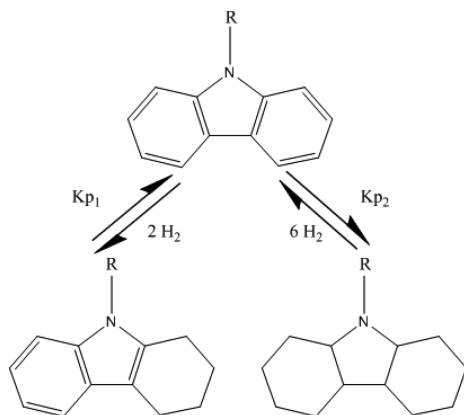
Figure 9. Thermodynamics of the LOHC hydrogenation (or dehydrogenation) process.

and quantity of hydrogen storage. Moreover, reliable values of reaction enthalpies, $\Delta_r H_m^\circ$ are necessary for an efficient heat management in devices using the LOHC.

In this work, we used the G3MP2 method to calculate thermodynamic functions of the hydrogenation reactions presented in Figure 9 for carbazole and its alkyl-substituted (R = Me and Et) derivatives. Results are presented in Table 11.

Analysis of the data presented in Table 11 shows that both reactions are thermodynamically favorable. It turns out that the enthalpies of reaction $\Delta_r H_m^\circ$ within the homologous series 1 and 2 are similar. Thus, the chain length is hardly important as the criterion, in terms of thermodynamics for the selection of the starting carbazole derivative.

When comparing the equilibrium constants of full hydrogenation to that of partial hydrogenation, it seems that the first is highly favored over the latter. However, the different stoichiometry must be taken into consideration. When the change in Gibbs free energy $\Delta_r G_m^\circ$ is divided by the number of moles, it appears that the values are quite similar. Hence, similar thermodynamic driving forces can be considered for both reactions.

Table 11. Thermodynamic Functions of Hydrogenation Reactions of the Carbazole Derivatives in the Gas Phase (at T = 298 K and $p°$ = 0.1 MPa) Calculated with the G3MP2: (a) K_{p1} and (b) K_{p2}

	(a) K_{p1}			
R-	$\Delta_r G_m^\circ$ [kJ mol^{-1}]	$\Delta_r H_m^\circ$ [kJ mol^{-1}]	$\Delta_r S_m^\circ$ [J K^{-1} mol^{-1}]	K_{p1}
H-	−12.0	−123.6	−374.3	1.2×10^2
CH$_3$-	−11.5	−124.6	−379.3	1.0×10^2
C$_2$H$_5$-	−7.2	−118.7	−374.0	18.3
	K_{p2}			
R-	$\Delta_r G_m^\circ$ [kJ mol^{-1}]	$\Delta_r H_m^\circ$ [kJ mol^{-1}]	$\Delta_r S_m^\circ$ [J K^{-1} mol^{-1}]	K_{p2}
H-	−43.9	−265.9	−744.5	5.0×10^7
CH$_3$-	−46.2	−270.4	−752.0	1.3×10^8
C$_2$H$_5$-	−37.4	−259.1	−743.4	3.6×10^6

4. CONCLUSIONS

In this work, we have obtained a consistent set of thermophysical and thermochemical properties of carbazole derivatives considered as potential liquid organic hydrogen carrier (LOHC). These properties are significantly changing upon the degree of hydrogenation. This change of the physicochemical properties of the LOHC should be taken into account, with regard to process design, modeling, and engineering of (de)hydrogenation processes.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.iecr.5b01841.

Auxiliary properties of the materials used in the present study (Table S1); typical results for combustion experiments (Table S2); values of specific energies of combustion for all combustion experiments (Table S3); molar heat capacities measured by the DSC (Table S4); experimental density of the carbazole derivatives at different temperatures (Table S5); experimental results for dynamic viscosities (Table S6); experimental values of surface tension (Table S7); experimental values of refractive indices (Table S8); compilation of data on molar heat capacities at 298 K of the carbazole derivatives (Table S9); the G3MP2 total energies at 0 K, enthalpies at 298 K, and enthalpies of formation calculated by atomization procedure for the molecules studied in this work (Table S10); experimental results from correlation gas-chromatographic method (Table S11); and comparison of vaporization enthalpies of carbazole derivatives derived from the correlation gas chromatography and those measured by the transpiration method (Table S12) (PDF)

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