Hydrogen Storage: Thermochemical Studies of *N*-Alkylcarbazoles and Their Derivatives as a Potential Liquid Organic Hydrogen Carriers

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Supporting Information

ABSTRACT: Although *N*-ethylcarbazole is considered as a most promising potential liquid organic hydrogen carriers (LOHC) substance, a major drawback for stationary and particularly mobile applications is its high melting point of 343 K. Study of other possible *N*-alkylcarbazole-derivatives having lower melting points but keeping a high storage density is of practical importance. This contribution presents thermochemical properties (enthalpy of formation, enthalpy of vaporization, enthalpy of sublimation, and fusion enthalpy) for *N*-alkylcarbazoles (with alkyl = isopropyl, *n*-propyl, and *n*-butyl) derived from experiments in order to investigate the applicability of the carbazole derivatives as potential LOHCs. Additionally, high-level quantum chemical calculations were applied to determine molar enthalpies of formation of the gaseous carbazole derivatives and thus validated the experimental findings. Using a combination of the quantum-chemical calculations with vaporization enthalpy data measured in this work, the standard molar liquid phase enthalpies of formation were derived for alkylcarbazole derivatives. Results of this study were applied for thermodynamic analysis of the liquid-phase reversible hydrogena



this study were applied for thermodynamic analysis of the liquid-phase reversible hydrogenation/dehydrogenation processes with *N*-alkylcarbazoles.

1. INTRODUCTION

Liquid organic hydrogen carriers (LOHC) are a promising option for the storage of hydrogen. LOHC materials can exist in an hydrogen-lean and hydrogen-rich form. By reversible catalytic hydrogenation the hydrogen-lean carrier is converted into its hydrogen-rich state. The hydrogen-lean form is recovered by a dehydrogenation reaction and hydrogen is released for further utilization. While the exothermic hydrogenation reaction is performed at elevated pressures of 30 to 50 bar, the endothermic dehydrogenation reaction is done at ambient pressure, but requires high temperatures. However, the LOHC substances can be stored under ambient conditions without degradation or loss of hydrogen and can be handled in the existing infrastructure for hydrocarbon fuels. This represents a major advantage compared to other hydrogen storage technologies discussed in the literature.¹

In the last years, *N*-ethylcarbazole has become one of the most intensely investigated LOHCs.^{2–17} Several properties of *N*-ethylcarbazole are beneficial for its use as LOHC, e.g. a high H_2 -storage density (5.8 wt %) and favorable thermophysical as

well as thermochemical properties.^{18–20} The ethyl group in the N-ethylcarbazole molecule lowers the melting point compared to carbazole, but it is still solid at room temperature.²⁰ However, many authors consider the high melting point of Nethylcarbazole of 343.1 K as the major drawback for stationary and particularly mobile applications.²¹⁻²³ It was found out that mixtures consisting of different N-alkylcarbazoles can significantly reduce the melting point.²⁴ Binary mixtures each consisting of two of the three substances N-ethylcarbazole (0H-NEC), N-propylcarbazole (0H-NPC) and N-butylcarbazole (0H-NBC) showed melting points around room temperature. Previous quantum chemical studies indicated that the Gibbs energy change during hydrogenation and thus the equilibrium constants for carbazole and methylcarbazole are similar to that of N-ethylcarbazole.²⁰ Because of their chemical propinquity these substances are supposed to have a similar

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Table 1. N-Alkylcarbazole Derivatives Studied in This Work^a

| substance | Source | Structure | CAS | purity (GC)% |
|---|-------------------|-----------------------------------|--------------|-----------------|
| N-isopropyl-carbazole | Apollo Scientific | | 1484-09-9 | >99.9 |
| N-propyl-carbazole | this work | | 1484-10-2 | >99.9 |
| N-butyl-carbazole | this work | | 1484-08-8 | >99.9 |
| 12H-N-propyl-carbazole (isomeric mixture) ^a | this work | $\langle \langle \rangle \rangle$ | 1612790-27-8 | >98.0 |
| 12H-N-butyl-carbazole (isomeric mixture) ^a | this work | $\langle \rangle$ | 1612790-29-0 | >98.0 |

^aThis hydrogenated product has chiral centers and the mixture of stereoisomers was used in this work.

reaction behavior as *N*-ethylcarbazole. Yang et al.²⁵ reported full hydrogenation of *N*-propylcarbazole at a remarkably fast reaction rate. Therefore, *N*-alkylcarbazole derivatives (alkyl: isopropyl, propyl, butyl) as well as the fully hydrogenated derivatives 12H-*N*-propylcarbazole (12H-NPC) and 12H-*N*butylcarbazole (12H-NBC) were experimentally and computationally studied in this work in order to investigate their applicability as potential LOHCs. This study extends our previous work on the thermodynamic characteristics of carbazole derivatives^{18–20} by the molecules presented in Table 1.

2. MATERIALS AND METHODS

2.1. Materials. The carbazole derivatives 0H-NPC and 0H-NBC were produced by alkylation of carbazole using phase-transfer catalysis. The *n*-propyl iodide (98+%; CAS 107-08-4, purchased from Alfa Aesar) and butyl bromide (99%; CAS 109–65–9, purchased from Sigma-Aldrich) were used as alkylating agents, respectively.²⁶ Carbazole (95%; CAS: 86–74–8, Merck) was dispersed in toluene and heated up to 75 °C. The phase-transfer-catalyst benzyltriethylammonium chloride (99%; CAS 56-37-1, purchased from Alfa Aesar) and the alkylating agent were added and the mixture was stirred for 3 h. The two phases were separated and toluene was removed from the product phase by drying under vacuum. The alkylated carbazole was recrystallized twice from ethanol. Purity was checked using gas chromatography mass spectroscopy (GC–MS).

Hydrogenation was performed in a 300 mL steel autoclave (Parr) equipped with a gas entrainment stirrer. LOHC and cyclohexane as solvent were added to the reactor. Ruthenium on alumina (5 wt % on support) (CAS 7440–18–8, purchased from Alfa Aesar) was used as catalyst ($n_{cat}/n_{LOHC} = 1$ %). The reactor was closed and purged three times with argon. The reactor was then heated up to the reaction temperature of 150 °C and pressurized with 50 bar H₂ gas (Linde, 99.999%). The hydrogenation reaction was started by setting the stirrer to 1200 rpm and the reaction was run for 24 h in fed batch mode and stopped by cooling down the reactor to room temperature. The catalyst was separated by filtration. The hydrogenated LOHC product was isolated from the solvent by rotary

evaporation and dried under vacuum overnight. The hydrogenated product was purified by distillation.

2.2. Enthalpy of Formation Measurements: Combustion Calorimetry. The standard molar enthalpies of combustion of N-alkylcarbazoles were measured with a static bomb isoperibolic calorimeter at a pressure of 3.04 MPa. A microbalance with a resolution of 10^{-6} g was used to weight pellets of solid samples. In order to achieve complete combustion, small pieces of polyethylene were used as an auxiliary material. The detailed experimental procedure was reported elsewhere.^{18,19} The energy equivalent of the calorimeter ε_{calor} was measured using a certified sample SRM 39j, of benzoic acid from NIST. We applied a conventional procedure²⁷ for reduction to standard states and for conversion of the energy of the actual bomb process to the energy of the isothermal process. The relative atomic masses applied for the elements are C = 12.010600, H = 1.007975 and N = 14.006855, which represent the mean of the interval for each element reported by the IUPAC commission²⁸ in 2011. Energetic correction for the formation of nitric acid in the combustion process was based on titration with 0.1 mol·dm⁻³ NaOH (aq). The mass of sample was reduced to vacuum based on the density (Table S1). Results for the combustion experiments are reported in the Tables S2 and S3.

2.3. Vapor Pressure and Vaporization Enthalpy Measurements. Transpiration Method. Absolute vapor pressures of N-alkylcarbazoles were measured using the transpiration method.^{29,30} The sample under study was solved in acetonitrile and mixed with small glass beads in a beaker. Solvent was evaporated by a gentle heating. A portion of the glass beads covered by the sample was placed in a thermostated U-shaped saturator. At a constant temperature $(\pm 0.1 \text{ K})$ a welldefined nitrogen stream was slow passed through the saturator. At each temperature the saturation of the N2-stream was established. After that, the transported material was collected in a cold trap, within a definite period of time. The amount of the collected sample was measured by using a gas chromatograph (GC) with help of an external standard n-C_nH_{2n+2}. The absolute vapor pressure p_i at each temperature T_i was estimated from the amount of the product collected within a definite period according to equation:

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| Tab | le 2. | Thermoc | hemical | Results | at ' | Г = | 298 | K for | r N-All | kyl-Car | bazoles | (in l | ⟨J•mol⁻¹ |) " |
|-----|-------|---------|---------|---------|------|-----|-----|-------|---------|---------|---------|-------|----------|------------|
|-----|-------|---------|---------|---------|------|-----|-----|-------|---------|---------|---------|-------|----------|------------|

| | compounds | $\Delta_{ m c} H^{\circ}_m({ m cr})$ | $\Delta_{ m f} H^{ m o}_m({ m cr})$ | $\Delta^{\rm g}_{ m cr} H^{\circ}_m {}^{b}$ | $\Delta_{\mathrm{f}} H^{\circ}_{m}(\mathrm{g})_{\mathrm{exp}}$ | $\Delta_{\rm f} H^{\circ}_m({ m g})^c_{ m G3MP2}$ |
|------------------|----------------------------|--------------------------------------|-------------------------------------|---|--|---|
| | N-isopropylcarbazole | -8086.1 ± 3.0 | 39.8 ± 3.6 | 97.7 ± 1.0 | 137.5 ± 3.7 | 139.4 |
| | N-propylcarbazole | -8083.7 ± 2.1 | 37.3 ± 2.9 | 106.6 ± 0.6 | 143.9 ± 3.0 | 141.6 |
| | N-butylcarbazole | -8734.7 ± 2.4 | 9.0 ± 3.2 | 113.5 ± 0.9 | 122.5 ± 3.3 | 120.2 |
| ^a The | e uncertainties correspond | to the expanded uncertai | inties of the mean (0.9 | 5 confidence level). ^b | From Table 4. ^c From | Table 5. |

Table 3. Alkylcarbazoles: Experimental Vapor Pressures p, Standard Molar Enthalpies of Sublimation, $\Delta_{cr}^g H_m^{\circ}$, Standard Molar Entropies of Sublimation, $\Delta_{cr}^g S_m^{\circ}$, Standard Molar Enthalpies of Vaporization, $\Delta_{l}^{g} H_m^{\circ}$, and Standard Molar Entropies of Vaporization, $\Delta_{l}^{g} S_m^{\circ}$, Measured by the Transpiration Method

| T/K^{a} | m/mg^b | $V(N_2)^c/dm^3$ | $T_{\rm a}/{ m K}^d$ | $flow/dm^3{\cdot}h^{-1}$ | p/Pa^{e} | $u(p)/\operatorname{Pa}^{f}$ | $(\Delta^{\rm g}_{\rm cr} H^{\circ}_m/\Delta^{\rm g}_{\rm I} H^{\circ}_m)/{\rm kJ}\cdot{\rm mol}^{-1}$ | $(\Delta^{g}_{cr}S^{\circ}_{m}/\Delta^{g}_{l}S^{\circ}_{m})$ J·K ⁻¹ ·mol ⁻¹ | | | |
|-----------|--------------------------------|-----------------|----------------------|---------------------------------------|---|---------------------------------|--|---|--|--|--|
| | | | N-Iso | propylcarbazole: Δ_{0}^{i} | ${}^{g}_{er}H^{\circ}_{m}(298 \text{ K})$ | $= (97.7 \pm 1.0)$ |) kJ·mol ^{−1} | | | | |
| | | | In | $(n/n^{\circ}) = \frac{315.56}{2}$ | 108954.29 | 37.6 lp | T/K | | | | |
| | | | 111 | $(p/p) = \frac{1}{R}$ | R(T/K) | $=$ $\frac{1}{R}$ $\frac{1}{2}$ | 98.15) | | | | |
| 339.7 | 0.21 | 8.35 | 295.9 | 4.64 | 0.30 | 0.01 | 96.18 | 177.5 | | | |
| 345.7 | 0.43 | 9.33 | 295.9 | 4.91 | 0.54 | 0.02 | 95.96 | 176.8 | | | |
| 348.0 | 0.70 | 12.44 | 295.9 | 4.73 | 0.66 | 0.02 | 95.87 | 176.3 | | | |
| 352.0 | 0.39 | 4.72 | 295.9 | 4.64 | 0.96 | 0.03 | 95.72 | 175.9 | | | |
| 355.9 | 0.48 | 4.25 | 295.9 | 4.64 | 1.32 | 0.04 | 95.57 | 175.2 | | | |
| 359.2 | 0.48 | 3.09 | 295.9 | 4.64 | 1.84 | 0.05 | 95.45 | 175.1 | | | |
| 361.9 | 0.78 | 3.75 | 295.9 | 4.89 | 2.45 | 0.07 | 95.35 | 175.2 | | | |
| 365.2 | 0.86 | 3.09 | 295.9 | 4.64 | 3.27 | 0.09 | 95.22 | 174.9 | | | |
| 367.3 | 1.02 | 3.23 | 295.9 | 4.73 | 3.72 | 0.10 | 95.15 | 174.3 | | | |
| 371.1 | 0.72 | 1.63 | 295.9 | 4.89 | 5.23 | 0.14 | 95.00 | 174.1 | | | |
| 375.1 | 1.11 | 1.81 | 295.9 | 4.73 | 7.23 | 0.18 | 94.85 | 173.6 | | | |
| | | | N-P | ropylcarbazole: $\Delta_l^g H$ | $H_m^{\circ}(298 \text{ K}) =$ | (87.8 ± 0.4) | kJ·mol ^{−1} | | | | |
| | 362.07 119054.90 105.0 (T/K) | | | | | | | | | | |
| | | | In(| p/p) = $\frac{1}{R}$ | R(T/K) | $-\frac{1}{R}$ In (2) | 298.15) | | | | |
| 323.9 | 1.24 | 80.34 | 294.7 | 4.81 | 0.18 | 0.01 | 85.05 | 152.6 | | | |
| 329.8 | 0.66 | 24.30 | 294.7 | 4.81 | 0.32 | 0.01 | 84.43 | 150.9 | | | |
| 335.3 | 0.69 | 15.40 | 294.7 | 4.81 | 0.53 | 0.02 | 83.85 | 149.1 | | | |
| 341.8 | 0.51 | 6.53 | 294.7 | 4.84 | 0.92 | 0.03 | 83.17 | 147.0 | | | |
| 347.5 | 1.06 | 8.30 | 294.7 | 4.84 | 1.49 | 0.04 | 82.57 | 145.2 | | | |
| 353.8 | 0.78 | 3.71 | 294.7 | 4.84 | 2.46 | 0.07 | 81.91 | 143.3 | | | |
| 359.7 | 1.41 | 4.19 | 294.7 | 4.84 | 3.93 | 0.10 | 81.29 | 141.7 | | | |
| 365.6 | 0.95 | 1.88 | 294.7 | 4.69 | 5.94 | 0.15 | 80.67 | 139.8 | | | |
| 371.7 | 0.90 | 1.09 | 294.7 | 4.69 | 9.57 | 0.26 | 80.03 | 138.4 | | | |
| | | | N-H | Butylcarbazole: Δ^{g}_{Γ} | $I_m^{\circ}(298 \text{ K}) =$ | (92.5 ± 0.6) l | kJ·mol ^{−1} | | | | |
| | | | ln(| $n/n^{\circ}) = \frac{377.56}{2}$ | 126238.27 | $-\frac{113.0}{\ln}$ | T/K | | | | |
| | | | m(| R = R | R(T/K) | $R = \frac{1}{2}$ | 298.15) | | | | |
| 331.3 | 0.34 | 23.12 | 295.2 | 4.63 | 0.16 | 0.01 | 88.71 | 156.8 | | | |
| 337.2 | 0.34 | 13.87 | 295.2 | 4.63 | 0.27 | 0.01 | 88.04 | 154.5 | | | |
| 342.5 | 0.34 | 8.40 | 295.2 | 4.63 | 0.44 | 0.02 | 87.44 | 152.8 | | | |
| 349.2 | 0.28 | 3.91 | 295.2 | 4.60 | 0.78 | 0.02 | 86.68 | 150.4 | | | |
| 354.9 | 0.41 | 3.45 | 295.2 | 4.60 | 1.29 | 0.04 | 86.03 | 148.9 | | | |
| 360.8 | 0.56 | 2.99 | 295.2 | 4.60 | 2.07 | 0.06 | 85.36 | 146.9 | | | |
| 367.4 | 0.83 | 2.61 | 295.2 | 4.60 | 3.50 | 0.09 | 84.61 | 145.0 | | | |
| 372.8 | 0.50 | 1.07 | 295.2 | 4.60 | 5.13 | 0.13 | 84.01 | 143.2 | | | |

^aSaturation temperature (u(T) = 0.1 K). ^bMass of sample transferred; condensed at T = 243 K. ^cVolume of nitrogen $(u(V) = 0.005 \text{ dm}^3)$ used to transfer m(u(m) = 0.0001 g) of the sample. ^d T_a is the temperature of the soap bubble meter, which was used for measuring the gas flow. ^cVapor pressure at temperature T, calculated from the mass and the residual vapor pressure at T = 243 K obtained using an iterative procedure. ^fUncertainties were calculated with u(p/Pa) = 0.005 + 0.025(p/Pa) for pressures below 5 Pa and with u(p/Pa) = 0.025 + 0.025(p/Pa) above 5 Pa.

$$p_i = m_i R T_a / V M_i; \quad V = V_{N2} + V_i \quad (V_{N2} \gg V_i)$$
 (1)

where *R* is the gas constant (8.314462 J·K⁻¹·mol⁻¹); m_i is the mass of the compound that is transported, M_i is the molar mass of the compound, and V_i is its contribution to the volume of the gaseous phase. V_{N2} is the volume of the carrier gas, and T_a is the temperature of the soap bubble meter that was used for measuring the gas flow. The volume, V_i of the carrier gas was

derived from the time and the flow rate measurements. Uncertainties of vapor pressures were assessed based on a procedure described elsewhere.³⁰ Validation of the system operation in the range p = 1-500 Pa was performed with the vapor pressure measurements on naphthalene and benzoic acid. Our results for these compounds agree with the literature^{31,32} with a deviation of 0.5–2.5%. An additional check of the

uncertainty estimations was also performed with series of *n*-alkanols³³ and aliphatic esters²⁹ in the range p = 0.1-1000 Pa. It was established that vapor pressures of substance classes like *n*-alkanols and aliphatic esters measured by the transpiration method are comparable to the literature within 1-3%.

2.4. Vaporization Enthalpies: GC-Correlation method. This method is based on the correlation of retention times measured by using the GC^{34,35} with vaporization enthalpies of reference materials of the parent structure. Temperature dependencies of the retention times of carbazole derivatives were measured with the Agilent 7890A equipped with an autosampler and a flame-ionization detector. These lead to enthalpies of transfer, $\Delta_{sol}^{g}H_{m}^{\circ}$, from solution (in the chromatographic phase) to the gas phase. By using an autosampler it was possible to generally achieve reproducible of retention times within 1-3 s. GC-measurements were done isothermally. The temperature of the GC was maintained constant within ± 0.1 K. A HP-5 capillary column (length: 30 m, diameter; 0.25 mm, film thickness: 0.25 μ m) was used. Helium was utilized as a carrier gas and its volume flow rate was pressure controlled (inlet pressure: 104 kPa). Alkylcarbazoles were injected as highly diluted solutions in dichloromethane. The measured retention times at each temperature were corrected with the retention time of a nonretained component (dichloromethane).

2.5. Theoretical Enthalpies of Formation in the Gas Phase. The Gaussian 09 series software³⁶ and the G3MP2 method³⁷ were used for the quantum chemical calculations of energies of carbazole derivatives. Computational details are reported elsewhere.³⁸ Values of enthalpies, H_{298} , for alkylcarbazoles were calculated by thermodynamic standard procedures.³⁹

3. RESULTS AND DISCUSSION

3.1. Thermochemical Results. 3.1.1. Molar Enthalpies of Formation. Results for the combustion calorimetric experiments with alkylcarbazoles are shown in Table S2. We used the standard specific energies of combustion $\Delta_c u^\circ$ (listed in Table S3) for deriving the standard molar enthalpies of combustion $\Delta_c H_m^\circ$ as well as the standard molar enthalpies of formation in the crystalline $\Delta_f H_m^\circ$ (cr) or liquid state $\Delta_f H_m^\circ$ (liq) which are shown in Table 2. The values of $\Delta_c u^\circ$ and $\Delta_c H_m^\circ$ refer to following reactions:

N - isopropylcarbazole:

$$C_{15}H_{15}N(cr) + 18.75O_2(g) = 15CO_2(g) + 7.5H_2O(liq) + 0.5N_2(g)$$
(2)

N-propylcarbazole:

$$C_{15}H_{15}N(cr) + 18.75O_2(g) = 15CO_2(g) + 7.5H_2O(liq) + 0.5N_2(g)$$
(3)

N - butylcarbazole:

$$C_{16}H_{17}N(liq) + 20.25O_2(g) = 16CO_2(g)$$

+ 8.5H₂O(liq) + 0.5N₂(g) (4)

Values of enthalpies of formation, $\Delta_{\rm f} H^{\circ}_m$ (liq or cr), of alkylcarbazoles were calculated according to the law of Hess applied to eqs 2–4 using the standard molar enthalpies of formation for H₂O(liq) and CO₂(g) assigned by CODATA.⁴⁰ On the basis of the guidelines presented by Olofsson⁴¹ and by Hubbard et al.²⁷ the uncertainties related to the combustion

experiments have been calculated. They correspond to expanded uncertainties of the mean for the standard molar energy and enthalpy of combustion (for the 0.95 confidence level). These uncertainties include contributions by the calibration with benzoic acid as well as by the values used for auxiliary quantities. The uncertainty assigned to the standard molar enthalpy of formation $\Delta_f H_m^{\circ}(cr)$ is twice the overall standard deviation. The latter uncertainty includes contributions from combustion energies of the auxiliary materials and from calibration. Also the uncertainties of enthalpies of formation of H₂O and CO₂ used in eqs 2–4 were taken into account. Combustion energies of *N*-isopropylcarbazole, *N*propylcarbazole, and *N*-butylcarbazole are reported for the first time.

3.1.2. Absolute Vapor Pressures of Alkylcarbazoles. The vapor pressure is a major substance property in LOHC applications because it is significant for the complete removal of LOHC vapor from the hydrogen released in the dehydrogenation reactor. A low vapor pressure is also favorable in terms of safety to minimize the uptake by inhalation. The vapor pressures of *N*-isopropylcarbazole, *N*-propylcarbazole, and *N*-butylcarbazole listed in Table 3 are reported for the first time. Values for the absolute vapor pressures p_i at different temperatures have been fitted with equation:²⁹

$$R \ln p_i = a + \frac{b}{T} + \Delta_1^g C_{p,m}^o \ln\left(\frac{T}{T_0}\right)$$
(5)

with *a* and *b* being adjustable parameters and $\Delta_{\rm gr}^{\rm s}C_{\rm p,m}^{\circ}$ (or $\Delta_{\rm gr}^{\rm g}C_{\rm p,m}^{\circ}$) being the difference between the molar heat capacities in the gaseous and the condensed state, respectively. Value of T_0 appearing in eq 5 is an arbitrarily chosen reference temperature ($T_0 = 298$ K was chosen in this work). We calculated $\Delta_{\rm fr}^{\rm s}C_{\rm p,m}^{\circ}$ or $\Delta_{\rm gr}^{\rm s}C_{\rm p,m}^{\circ}$ in eq 5 (see Table S4) with the procedure suggested by Chickos and Acree.⁴² This procedure is based on the isobaric molar heat capacity $C_{\rm p,m}^{\circ}$ (liq or cr, 298 K), which was estimated by a group-contribution method.⁴³

An increased alkyl chain length helps to reduce the vapor pressure of the investigated *N*-alkylcarbazoles (see Figure S1), making long-chained derivatives more attractive for practical applications.

3.1.3. Vaporization and Sublimation Enthalpies of Alkylcarbazoles. We derived vaporization enthalpies of *N*-propylcarbazole and *N*-butylcarbazole, as well as the sublimation enthalpy for *N*-isopropylcarbazole from the measured temperature dependencies of vapor pressures which were approximated with eq 5. Vaporization enthalpy was calculated with eq 6:

$$\Delta_{\rm l}^{\rm g} H_{\rm m}^{\rm o}({\rm T}) = -b + \Delta_{\rm l}^{\rm g} C_{p,m}^{\rm o} T \tag{6}$$

Experimental results for the transpiration method and the coefficients *a* and *b* of eq 5 are shown in Table 3. Values for the combined uncertainties of vaporization or sublimation enthalpies were calculated according to procedure described elsewhere.³⁰ They include contributions from uncertainties of experimental parameters in the transpiration measurements (temperature, volume, and mass-determination), uncertainties of the measured vapor pressure, as well as uncertainties caused by the temperature adjustment of vaporization enthalpy to T = 298 K. As a rule, low vaporization enthalpies are favorable for practical applications since evaporation during the dehydrogenation reaction negatively influences the overall energy balance. Nevertheless, the measured vaporization enthalpies of *N*-

Table 4. Compilation of Experimental Standard Molar Enthalpies of Fusion, $\Delta_{cr}^{l}H_{m}^{\circ}$, Standard Molar Enthalpies of Sublimation, $\Delta_{cr}^{g}H_{m}^{\circ}$, and Standard Molar Enthalpies of Vaporization, $\Delta_{cr}^{g}H_{m}^{\circ}$, of Alkylcarbazoles Derived in This Work (in kJ·mol⁻¹)

| | | | | 298 K | |
|----------------------|----------------------|--|--------------------------------|-------------------------------------|---|
| compounds | $T_{\rm fus}/{ m K}$ | $\Delta^{\mathrm{l}}_{\mathrm{cr}} H^{\mathrm{o}}_{m}$ at T_{fus} | $\Delta^{l}_{cr}H^{\circ}_{m}$ | $\Delta^{ m g}_{ m cr} H^{\circ}_m$ | $\Delta^{\mathrm{g}}_{\mathrm{f}} H^{\mathrm{o}}_{m}$ |
| N-isopropylcarbazole | 393.9 ± 0.3 | 18.26 ± 0.41^{b} | 12.3 ± 1.9 | 97.7 ± 1.0 | 85.4 ± 2.1^{c} |
| N-propylcarbazole | 320.4 ± 0.3 | 19.57 ± 0.22 | 18.8 ± 0.4 | 106.6 ± 0.6^{d} | 87.8 ± 0.4 |
| N-butylcarbazole | 330.6 ± 0.1 | 22.80 ± 0.33 | 21.0 ± 0.7 | 113.5 ± 0.9^{d} | 92.5 ± 0.6 |
| | | 1 1: (1 (200) | 7 11 | 1 11 CL | $1 1 42 \ b_{\Gamma}$ |

^{*a*}Experimental enthalpy of fusion $\Delta_{cr}^{l}H_{m}^{\circ}$ measured at T_{fus} and adjusted to 298 K according to the procedure proposed by Chickos and Acree⁴² ^{*b*}For comparison $\Delta_{cr}^{l}H_{m}^{\circ} = 17.7$ kJ·mol⁻¹at 395.2 K⁴⁵ ^{*c*}Calculated as the difference between the columns 5 and 4. ^{*d*}Calculated as the sum of the columns 4 and 6.

Table 5. Comparison of Theoretical and Experimental Standard Molar Enthalpies of Formation, $\Delta_f H_m^{\circ}(g, 298 \text{ K})$, of Carbazole Derivatives (in kJ·mol⁻¹)

| compounds | $\Delta_{\rm f} H^{\circ}_m({ m g}) \ { m G3MP2}({ m AT})$ | $\Delta_{\mathrm{f}} H^{\circ}_{\mathrm{m}}(g) \operatorname{AT}(\operatorname{corrected})$ | $\Delta_{\mathrm{f}} H^{\circ}_{\mathrm{m}}(\mathrm{g}) \exp$ |
|--------------------------------------|--|--|--|
| 0-H-carbazole | 196.4 | 207.1 | 206.0 ± 2.9^{20} |
| N-methylcarbazole | 185.3 | 196.0 | 196.4 ± 3.1^{20} |
| 1,2,3,4-tetrahydro-N-methylcarbazole | 82.7 | 93.4 | 92.5 ± 1.9^{20} |
| N-ethylcarbazole | 153.2 | 163.9 | 167.7 ± 2.8^{20} |
| N-isopropylcarbazole | 128.7 | 139.4 | 137.5 ± 3.7 |
| N-propylcarbazole | 130.9 | 141.6 | 143.9 ± 3.0 |
| N-butylcarbazole | 109.5 | 120.2 | 122.5 ± 3.3 |
| 12H-isopropylcarbazole | -173.0 | -173.0 | - |
| 12H-N-propylcarbazole | -172.9 | -172.9 | - |
| 12H-N-butylcarbazole | -194.4 | -194.4 | - |

propylcarbazole and *N*-butylcarbazole (see Tables 2 and 3) are somewhat higher in comparison to the enthalpy of vaporization of *N*-ethylcarbazole ($\Delta_1^g H_m^\circ = 83.9 \pm 0.5 \text{ kJ} \cdot \text{mol}^{-1}$ at 298 K),¹⁹ which nowadays is considered as the most promising LOHC.

3.1.4. Enthalpies of Fusion of Alkylcarbazoles. In a series of preliminary experiments we observed that volatility of Npropylcarbazole and N-butylcarbazole was very low in the temperature range below their melting points. In order to avoid time-consuming sublimation experiments we performed transpiration experiments above the melting point instead. In this case vaporization enthalpies derived according to eqs 5 and 6, were combined with values of enthalpy of fusion, derived from the DSC-measurements. Sum of vaporization and fusion enthalpies provide the desired enthalpy of sublimation for the alkylcarbazole. In this work, experimental enthalpies of fusion were used. These have been measured by DSC and have been reported just recently²⁴ (see Table 4). Admittedly, the measured values of $\Delta_{cr}^{l}H_{m}^{\circ}$ are referred to T_{fus} (melting temperature). The adjustment to T = 298 K was performed by equation:⁴²

$$\begin{aligned} \{\Delta_{cr}^{l}H_{m}^{\circ}(T_{fus}/K) &- \Delta_{cr}^{l}H_{m}^{\circ}(298K)\}/(J \cdot mol^{-1}) \\ &= \{(0.75 + 0.15C_{p,m}^{\circ}, cr)[(T_{fus}/K) - 298K]\} \\ &- \{(10.58 + 0.26C_{p,m}^{\circ}, liq)[(T_{fus}/K) - 298K]\} \end{aligned}$$
(7)

with $C_{p,m/cr}^{\circ}$ and $C_{p,m,liq}^{\circ}$ being the molar isobaric heat capacities of the solid respectively liquid alkylcarbazoles (see Table S4). Values of $\Delta_{cr}^{l}H_{m}^{\circ}(298 \text{ K})$ are given in Table 4. Uncertainties of $\Delta_{cr}^{l}H_{m}^{\circ}(298 \text{ K})$ values were assessed to be of 30% of the total temperature adjustment.⁴⁴ The values for the fusion enthalpies adjusted to the reference temperature 298 K were used to derive the required enthalpies of sublimation, $\Delta_{cr}^{g}H_{m}^{\circ}(298 \text{ K})$, or enthalpies of vaporization, $\Delta_{f}^{g}H_{m}^{\circ}(298 \text{ K})$, of alkylcarbazoles shown in Table 2. 3.1.5. Gas-Phase Standard Molar Enthalpies of Formation from Experiment. Results on $\Delta_{cr}^{g}H_m^{\circ}(298 \text{ K})$, $\Delta_{cr}^{g}H_m^{\circ}(298 \text{ K})$ and $\Delta_{cr}^{l}H_m^{\circ}(298 \text{ K})$ for alkylcarbazoles (Tables 2–4) together with the results from combustion calorimetry were used in order to get the experimental standard molar enthalpies of formation, $\Delta_{f}H_m^{\circ}(g)$ at 298 K (see Table 2, column 5). These results based on thermochemical experiments were used for comparison to theoretical results calculated with the high-level quantum-chemical (QC) method G3MP2 (see Table 5).

3.2. Validation and Prediction of the Thermochemical Properties. Structure—property relationships were applied on the series of the *N*-alkylcarbazoles. This kind of study can help to discover general rules for validating experimental property values. Furthermore, they allow for the predicting the properties of intermediate forms that are hardly available.

3.2.1. Gas Phase Enthalpies of Formation from QC. The modern high-level quantum chemical methods become a valuable tool for establishing mutual consistency of theoretical and experimental results.^{46,47} In our previous work^{19,20} we have shown that the composite G3MP2 method can be applied to alkyl substituted carbazoles successfully. In this study we applied the G3MP2 for calculation of $\Delta_f H_m^o(g)$ of alkylcarbazoles for the sake of comparison with the experimental data collected in Table 2.

Admittedly, in the QC calculations, the molecular conformations would sensitively affect the accuracy of the computed enthalpies. In our previous work we have shown that alkyl-substituted carbazoles have a rigid structure.²⁰ Other than the flat and rigid structures of *N*-alkylcarbazoles the hydrogenated intermediates become more flexible. For the accurate calculation of the theoretical $\Delta_f H_m^o(g)$ value for any flexible molecule, the energetics of all possible conformers have to be calculated and taken into account. However, for relatively large molecules like hydrogenated alkylcarbazoles, it seems to be very time-consuming task. Results of our recent work^{19,20} for similarly shaped molecules helps to save the computational

| Table 6. Experimental Enthalpies of Transfer from the Solution to the Vapor $\Delta_{sol}^{g} H_{m}^{\circ}$ derived from Correlation Gas- | |
|--|--------------|
| Chromatography. Comparison of the Experimental Enthalpies of Vaporization with Values Calculated by eq 9 (in kJ:r | nol^{-1}) |

| | coefficients ^a | | | | $\Delta_1^{g} H_m^{\circ}(298 \text{ K})$ | |
|---|----------------------------|----------------------|--------------------------------------|--------------------------------|---|-----------------|
| compounds | m | п | $\Delta^{ m g}_{ m sol} H^{\circ}_m$ | exp | eq 9 | Δ |
| N-isopropylcarbazole | 12.86 | -7032.7 | 58.5 | 85.4 ± 2.1 | 85.6 | -0.2 |
| N-propylcarbazole | 13.25 | -7253.0 | 60.3 | 87.8 ± 0.4 | 88.8 | -1.0 |
| N-butylcarbazole | 13.53 | -7538.4 | 62.7 | 92.5 ± 0.6 | 93.3 | -0.8 |
| 12H-N-isopropylcarbazole | - | - | - | - | 71.4 ^b | _ |
| 12H-N-propylcarbazole | 11.19 | -6228.2 | 51.8 | - | 73.4 | - |
| 12H-N-butylcarbazole | 11.81 | -6513.9 | 54.1 | - | 77.6 | - |
| ^{<i>a</i>} Coefficients of equation $\ln(1/t_r) =$ | m + n/T and ^b C | alculated from entha | lpy of vaporization | n of 12H- <i>N</i> -ethylcarba | zole ¹⁸ and increm | ents from Table |

7.

time. It has turned out that in many cases only a small number of the most stable conformers have a significant contribution to the theoretical $\Delta_{f}H_{m}^{\circ}(g)$ value. We observed that conformers with energies of about 10 kJ·mol⁻¹ larger than those for the most stable conformer are basically absent in the gas phase and they can be omitted by calculation of the theoretical $\Delta_{\rm f} H^{\circ}_m({\rm g})$ value. This simplification is often applied with sufficient accuracy for large molecules showing abundant flexibility.²⁰ An analysis of the stable conformations of the hydrogenated molecule 12H-N-propylcarbazole has shown that the collection of stable conformers exhibits similar energetics and the differences between them does not exceed 1-5 kJ·mol⁻¹ as calculated by DFT. A similar distribution of the most stable conformers could be observed for 12H-N-butylcarbazole. Thus, we used the high-level and the time-consuming G3MP2 method only for calculations of the most stable conformer for each alkylcarbazole under study.

Enthalpies of formation $\Delta_{\rm f} H^{\circ}_{m}({\rm g}, 298 {\rm K})$ of alkylcarbazoles were derived from enthalpies H_{298} using the well-established atomization procedure (AT).¹⁹ However, our previous studies^{18–20} have shown, that $\Delta_{\rm f} H^{\circ}_{m}({\rm g}, 298 {\rm K})$ values for aromatic molecules calculated with the standard atomization reaction deviate from the experimental results systematically. In order to overcome shortcomings of this simple and attractive atomization procedure, we suggested to modify the AT method by using an empirical linear correlation (see eq 8) between experimental and AT-calculated gas-phase enthalpies of formation. We used the reliable experimental data available for similarly shaped aromatic compounds^{18–20} (Table 5, column 4) to derive the following equation:

$$\Delta_{\rm f} H_m^{\circ}({\rm g})({\rm exp})/{\rm kJ} \cdot {\rm mol}^{-1} = 1.00 \times \Delta_{\rm f} H_m^{\circ}({\rm g})({\rm AT}) + 10.7$$
(8)

This correlation is now developed especially for the alkylcarbazoles. Correlation 8 we used to calculate the AT "corrected" theoretical enthalpies of formation of the isopropyl-, propyl-, and butylcarbazole (Table 5, column 3). We observed a good agreement between experimental and theoretical values for the alkylcarbazoles (Table 5), taking into account that uncertainties associated with the G3MP2 method usually are about 2-4 kJ·mol⁻¹. This good agreement could serve as a prove of the reliability of theoretical and experimental results presented in this work. Moreover, we have in demonstrated in our previous work,^{19,20} that the composite G3MP2 method is capable of reproducing experimental values for fully hydrogenated carbazole derivatives within the uncertainties of the experimental values (about 3 to 4 kJ mol^{-1}) by using the AT procedure without any "correction". The fully hydrogenated derivatives of iso-propyl carbazole

(12H-isopropylcarbazole), propylcarbazole (12H-propylcarbazole), and butylcarbazole (12H-butylcarbazole) are of interest for the current study. Thus, we calculated their $\Delta_f H^\circ_m(g)$ at 298 K (Table 5, column 2) for the energetic balancing of the hydrogenation/dehydrogenation process with these LOHCs.

As a matter of fact, a large amount of highly pure samples are usually required for the experimental thermochemical studies. Within of the time frame of the current study we were not able to produce a sufficient amount of pure samples of fully hydrogenated alkylcarbazoles 12H-isopropylcarbazole, 12Hpropylcarbazole, and 12H-butylcarbazole. Nevertheless, it is possible to assess their properties using well established empirical procedure (e.g., group additivity^{20,48}) or halfempirical structure–property correlations as follows.

3.2.2. Vaporization Enthalpies From the Correlation-GC Analysis. The correlation GC-method (CGC) can be used to obtain a reliable assessment of the vaporization enthalpies.^{34,35} In the CGC-method, we correlate the retention time t_r of a alkylcarbazole of interest with the net values measured for a number of parent compounds where the enthalpies of vaporization are well established. For each alkylcarbazole, the retention times have been used for calculating the transfer enthalpies from the solution to the gas phase $(\Delta_{sol}^g H_m^\circ)$ by plotting $\ln(1/t_r)$ vs 1/T. The slope of this linear correlation $\ln(1/t_r) = m + n \cdot T^{-1}$ when multiplied by the gas constant, R, affords $\Delta_{sol}^{g}H_{m}^{\circ}$. The empirical linear relationship between $\Delta_{sol}^{g}H_{m}^{\circ}$ and $\Delta_{s}^{g}H_{m}^{\circ}(298 \text{ K})$ are often observed for the structurally related compounds. This linear dependence can be further used for estimation of the vaporization enthalpy for a compound of interest with a similarly shape, if the experimental $\Delta_{sol}^{g}H_{m}^{\circ}$ value has been measured under the same conditions. In our previous study,²⁰ we correlated experimental $\Delta_{sol}^g H_m^{\circ}$ values for series of 16 N-containing heterocyclic compounds and developed the following equation:

$$\Delta_{1}^{g} H_{m}^{\circ}(298 \text{ K})/\text{kJ} \cdot \text{mol}^{-1} = -20.9 + 1.82 \times \Delta_{\text{sol}}^{g} H_{m}^{\circ}$$
$$(R^{2} = 0.993) \tag{9}$$

This correlation together with $\Delta_{sol}^{g}H_{m}^{\circ}$ values measured in this work we used for calculation of $\Delta_{l}^{g}H_{m}^{\circ}(298 \text{ K})$ for alkylcarbazoles (see Table 6, column 6). The uncertainty of vaporization enthalpies values was estimated with eq 9 as $\pm 1.5 \text{ kJ} \cdot \text{mol}^{-1}$.

It was reasonable to validate vaporization enthalpies $\Delta_{\Gamma}^{s}H_{m}^{\circ}(298 \text{ K})$ of alkylcarbazole derived from eq 9 using the vaporization enthalpies obtained from the transpiration method. $\Delta_{\Gamma}^{s}H_{m}^{\circ}(298 \text{ K})$ values for iso-propyl, propyl and butyl carbazoles measured by CGC and the transpiration method agree with each other within the range of their experimental

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uncertainties (see Table 6). Such a good agreement has allowed estimating reliable vaporization enthalpies also for fully hydrogenated alkylcarbazoles, required for further analysis of the thermodynamic characteristics of the (de)hydrogenation reactions. It has turned out, that vaporization enthalpies of the hydrogenated species 12H-*N*-propylcarbazole and 12H-*N*-butylcarbazole are lower than their dehydrogenated counterparts. However, the similar behavior was previously observed¹⁹ for the pair 12H-*N*-ethylcarbazole and *N*-ethylcarbazole.

3.2.3. Validation of Vaporization Enthalpies and Gas Phase Enthalpies of Formation based on GA. Groupadditivity (GA) procedure is a valuable tool for validation as well as for predicting thermochemical properties of organic compounds.⁴⁸ A very simple procedure for predicting enthalpies of formation in the gas-phase of the substituted benzenes was suggested by Cox and Pilcher⁴⁹ in 1970. This scheme is based on a starting molecule benzene and a consequent exchange of *H*-atoms from the benzene ring by any substituent *R* with a contribution $\Delta H(H \rightarrow R)$, specific for the type of *R*. We decided to reshape this substitution procedure for prediction of thermochemical properties of the carbazole derivatives in combination with the group additivity procedure proposed in our recent work.¹⁸ The group-additivity values (GAVs) used in this work are given in Table 7.

Table 7. GAVs for Estimation of Standard Molar Enthalpies of Vaporization, $\Delta_{\rm f}^{\rm g} {\rm H}_m^{\rm o}(298~{\rm K})$ and Standard Molar Enthalpies of Formation, $\Delta_{\rm f} {\rm H}_m^{\rm o}({\rm g}, 298~{\rm K})$, of Carbazole Derivatives (in kJ·mol⁻¹)

| GAV | $\Delta^{\mathrm{g}}_{\mathrm{I}} H^{\circ}_{m}$ | $\Delta_{\mathrm{f}} H^{\circ}_m(\mathrm{g})$ |
|--------------------------|--|---|
| N-carbazole ^a | 74.9 | 236.7 |
| $C - (C)(H)_{3}$ | 6.33 | -42.05 |
| $C - (C)_2(H)_2$ | 4.52 | -21.46 |
| $C - (C)_3(H)$ | 1.24 | -9.04 |
| $C - (C)_4$ | -2.69 | -1.26 |
| $C - (N)(C)(H)_2$ | 2.9 | -26.9 |
| $C - (N)(C)_2(H)$ | -2.0 | -20.0 |
| $C - (N)(C)_{3}$ | -7.7 | -16.1 |
| | | |

^{*a*}Derived from experimental data¹⁸ $\Delta_1^{g} H_m^{\circ} = 84.1 \pm 1.3 \text{ kJ} \cdot \text{mol}^{-1}$ and $\Delta_f H_m^{\circ}(g) = 167.7 \pm 2.8 \text{ kJ} \cdot \text{mol}^{-1}$ for *N*-ethylcarbazole by subtracting of increments $C-(C)(H)_3$ and $C-(N)(C)(H)_2$

For the sake of simplicity, we decided to use *N*-ethylcarbazole as the starting molecule. Indeed, by a subtraction of contribution for increments $C-(C)(H)_3$ and $C-(N)(C)(H)_2$ from a thermochemical property $(\Delta_f^{B}H_m^{\circ} \text{ or } \Delta_f H_m^{\circ})$ of *N*ethylcarbazole, the contribution for the unsubstituted carbazole moiety was derived (see Table 7). Thus, other alkylsubstituents (isopropyl, propyl, butyl, etc.) can be now constructed from GAVs given in Table 7 and combined with the contribution for the *N*-carbazole unity in order to estimate the required property for any similarly shaped molecule. This procedure is very practical for the quick appraisal of the $\Delta_{\rm f}^{\rm g} H_m^{\circ}(298 \text{ K})$ and $\Delta_{\rm f} H_m^{\circ}({\rm g}, 298 \text{ K})$ of the alkyl substituted carbazoles. Enthalpies of vaporization as well as the gas phase enthalpies of formation of the alkylcarbazoles estimated by using GA are given in Table 8. As can be seen from this table, the estimated vaporization enthalpies are in agreement with the experimental values within $\pm 1 \text{ kJ} \cdot \text{mol}^{-1}$. Estimated gas phase enthalpies of formation are in agreement with the experiment within the boundaries of experimental uncertainties of \pm (2–3) $kJ \cdot mol^{-1}$, except for N-isopropylcarbazole, where the larger disagreement of 5.9 kJ·mol⁻¹ is caused by an additional strain interaction of the iso-propyl substituent with the carbazole ring. The latter interaction is absent as a parameter in Table 7, but it can be easy assessed from the similarly shaped strain pattern present in 2,3-dimetylbutane (see Figure S2 in supporting materials). Strain interactions of the two iso-propyl moieties in the 2,3-dimethylbutane of 8.5 kJ·mol⁻¹ (given in Table 8, column 7) are on the same level as those in the Nisopropylcarbazole. Good agreement between experiment and results from GA calculations can serve as a valuable test for internal consistency of the vaporization and formation enthalpies measured in this work.

3.2.4. Prediction of Enthalpies of Formation in the Liquid Phase. The reliable set of vaporization enthalpies of alkylcarbazoles and their hydrogenated derivatives have been measured and evaluated in the current study. Together with theoretical $\Delta_{\rm f} H^{\circ}_m(g, 298 \text{ K})$ values calculated with the high-level G3MP2-method we are able now to estimate the missing data for the thermodynamic calculations standard molar enthalpies of formation in the liquid phase $\Delta_{\rm f} H^{\circ}_m(\text{liq}, 298 \text{ K})$ of alkylcarbazoles and their hydrogenated derivatives (see Table 9, column 4) using the thermodynamic equation:

$$\Delta_{f}H_{m}^{\circ}(\text{liq, 298 K}) = \Delta_{f}H_{m}^{\circ}(\text{g, G3MP2}) - \Delta_{I}^{g}H_{m}^{\circ}(298$$

K, exp) (10)

Table 9. Liquid Phase Standard Molar Enthalpies of Formation of Carbazole Derivatives at 298 K (in kJ·mol⁻¹)

| | compounds | $\Delta_{\mathrm{f}} H^{\circ}_{\mathrm{m}}(\mathrm{g})$ | $\Delta^{\mathrm{g}}_{\mathrm{I}} H^{\mathrm{o}}_{m}$ | $\Delta_{\mathrm{f}} H^{\circ}_{m}(\mathrm{liq})$ | | | | | |
|----------------|---|--|---|---|--|--|--|--|--|
| | N-isopropylcarbazole | 137.5 ^a | 85.4 ^a | 52.1 | | | | | |
| | N-propylcarbazole | 143.9 ^a | 87.8 ^a | 56.1 | | | | | |
| | N-butylcarbazole | 122.5 ^a | 92.5 ^a | 30.0 | | | | | |
| | 12H-N-isopropylcarbazole | -173.0 ^b | 71.4 ^c | -244.4 | | | | | |
| | 12H-N-propylcarbazole | -172.9 ^b | 73.4 ^c | -246.3 | | | | | |
| | 12H-N-butylcarbazole | -194.4 ^b | 77.6 [°] | -272.0 | | | | | |
| ^a I | From Table 2. ^b From Table 5. ^c From Table 6. | | | | | | | | |

Table 8. Comparison of Experimental and Estimated (GA Method) Values of Vaporization Enthalpies as well as Gas Phase Enthalpies of Formation at 298 K (in kJ·mol⁻¹)

| compounds | $\Delta_l^g H_m^{\circ a} \exp$ | GA | exp-GA | $\Delta_{\mathrm{f}} H^{\circ}_{m}(\mathrm{g})^{a} \exp$ | GA | exp-GA |
|----------------------|---------------------------------|------|--------|--|--------|--------|
| N-isopropylcarbazole | 85.4 | 85.5 | -0.1 | 137.5 | 131.7 | 5.8 |
| N-propylcarbazole | 87.8 | 88.6 | -0.8 | 143.9 | 146.3 | -2.4 |
| N-butylcarbazole | 92.5 | 93.1 | -0.6 | 122.5 | 124.8 | -2.3 |
| 2,3-dimethylbutane | 29.3 ^b | 27.8 | 1.5 | -177.8 ^b | -186.3 | 8.5 |

^{*a*}From Table 2. ^{*b*}From ref 49.

These values were further applied for calculating the enthalpies of reaction for (de)hydrogenation required for the detailed design of LOHC processes.

3.3. Calculation of the Enthalpies of Reaction for (De)Hydrogenation. The enthalpy of reaction is a crucial parameter for hydrogen storage based on the LOHC technology. Enthalpies of reaction, $\Delta_r H_m^\circ$ at 298 K for the hydrogenation/dehydrogenation reactions:

N-isopropylcarbazole:

$$C_{15}H_{15}N(\text{liq}) + 6H_2(g) = C_{15}H_{27}N(\text{liq}) \text{ with } \Delta_r H_m^\circ$$

= -296.5 kJ·mol⁻¹ (11)

N-propylcarbazole:

$$C_{15}H_{15}N(\text{liq}) + 6H_2(g) = C_{15}H_{27}N(\text{liq}) \text{ with } \Delta_r H_m^\circ$$

= -302.4 kJ·mol⁻¹ (12)

N-butylcarbazole:

$$C_{16}H_{17}N(\text{liq}) + 6H_2(g) = C_{16}H_{29}N(\text{liq}) \text{ with } \Delta_r H_m^\circ$$

= -302.0 kJ·mol⁻¹ (13)

were calculated using the liquid phase enthalpies of formation of carbazole derivatives from Table 9 according to Hess law. The values of the reaction enthalpy calculated per mol of the hydrogen are very similar (-49.4, -50.4, and -50.4 kJ·mol⁻¹-H₂, respectively). For comparison, we adjusted the gas phase enthalpy of hydrogenation of acenaphthene to perhydroacenaphthene reported by Frye and Weitkamp⁴⁹ to the liquid phase (see ESI) using the thermochemical data for acenaphthene evaluated by Roux et al.:⁵⁰

$$C_{12}H_{10}(\text{liq}) + 6H_2(g) = C_{12}H_{20}(\text{liq}) \text{ with } \Delta_r H_m^\circ$$

= -52.4 kJ·mol⁻¹ (14)

The reaction with acenaphthene liberates significantly lower energy -10.5 kJ·mol⁻¹-H₂. At the similar level were found⁴⁹ to be the enthalpies of hydrogenation of fluorene, indene and indole. In contrast the LOHC *N*-ethylcarbazole liberates by hydrogenation to the dodecahydro-*N*-ethylcarbazole $-50.5 \pm$ 0.8 kJ·mol⁻¹-H₂, which is equal to values obtained in this study. This similarity make *N*-alkylcarabazoles attractive for the practical application.

CONCLUSIONS

The self-consistent set of thermochemical properties for alkylcarbazoles and their fully hydrogenated derivatives was measured and critically evaluated in this work. On the basis of the measured property data *N*-isopropylcarbazole, *N*-propylcarbazole, and *N*-butylcarbazole seem to be promising LOHC candidates. The rather low enthalpies of reaction will allow for rather low temperatures in hydrogen release, which is beneficial for the energy balance of most hydrogen storage processes. Together with their generally low vapor pressures this favors their use as hydrogen carrier materials.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.5b10392.

Auxiliary properties for the materials used in this work (Table S1); typical results of combustion experiments

(Table S2); values for specific energies of combustion of all combustion experiments (Table S3); compilation of molar heat capacities (Table S4); Comparison of vapor pressures of the carbazole derivatives (Figure S1); Comparison of strain patterns (Figure S2); data evaluation discussion (PDF)

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Notes

The authors declare no competing financial interest.

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