Comprehensive thermodynamic study of substituted indoles/perhydro indoles as potential Liquid Organic Hydrogen Carrier system

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ABSTRACT

Indole has been proposed as a Liquid Organic Hydrogen Carrier (LOHC) component. Its hydrogenation leads to octahydro indole, which can subsequently release hydrogen again in an endothermic, catalytic dehydrogenation reaction. This reaction requires high temperatures due to limitations by the reaction equilibrium. It is therefore interesting to find derivatives of the carrier molecules with lower enthalpies of reaction, which corresponds to a higher equilibrium constant. In this study, methyl and phenyl substituted derivatives of indole have been examined. Vapor pressures and enthalpies of vaporisation/sublimation have been measured. The standard molar enthalpies of formation in the gas phase have been calculated using quantum chemistry. The liquid phase standard molar enthalpies of formation were derived and used for calculating reaction enthalpies. The results show that methylation lowers the enthalpy of reaction for dehydrogenation. The reduction is not very pronounced in case of single methylation (up to 3.1 kJ mol^{-1}/$_{\mathrm{H2}}$), but can be increased by manifold methylation (*e.g.* 4.6 kJ mol^{-1}/$_{\mathrm{H2}}$ in case of 2,3-dimethyl-H8-indole). Substitution of indole with a phenyl group leads to a corresponding hydrogenated counterpart, that can only be dehydrogenated partially under mild conditions. This is due to the fact that the reducing effect of the nitrogen atom on enthalpy of reaction is only effective in the indole system itself, while the cyclohexyl ring has similar dehydrogenation properties to homocyclic LOHCs.

Keywords: indole derivatives; LOHC; vapour pressure measurements; enthalpy of vaporisation; enthalpy of formation; quantum-chemical calculations

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1 Introduction

The development of improved hydrogen storage technologies is considered crucial for a sustainable future energy system [1]. Hydrogen storage and transportation technologies based on the reversible hydrogenation of liquid organic hydrogen carriers (LOHC) appears highly promising in this regard [2]. In the LOHC approach, hydrogen uptake is realized by catalytic hydrogenation of an aromatic substance. The corresponding hydrogen-rich saturated compound can store large amounts of hydrogen under ambient conditions. For hydrogen release, the saturated compound is dehydrogenated again catalytically, yielding hydrogen and the original hydrogen-lean aromatic substance, which can be utilized in repeated storage cycles [3]. Aromatic substances that can be used as LOHC compounds are, for instance, toluene [4] or (di)benzyl toluene [5].

Homocyclic LOHCs are beneficial in terms of stability. On the other hand, enthalpy of reaction for dehydrogenation is comparatively high (*e.g.* $+64.4 \pm 1.0$ kJ $\text{mol}^{-1}/_{\text{H2}}$ in case of dibenzyl toluene). As a consequence, there is not only a high heat demand for hydrogen release, but also reaction thermodynamics are rather unfavourable (*i.e.* dehydrogenation at ambient pressure requires temperatures of about 300 °C). Some nitrogen-containing heterocycles, on the other hand, exhibit significantly lower enthalpies of reaction (about 15 kJ $\text{mol}^{-1}/_{\text{H2}}$ lower). Thus, hydrogen release can be realized at much lower temperatures. This fact has led to intensified research activities on N-containing heterocycles as LOHCs [6-8]. Two elements are crucial for this type of research: catalyst development and understanding of the reaction thermodynamics. Vapor pressures and vaporisation thermodynamics are also indispensable for the development of process engineering for hydrogenation/dehydrogenation processes.

In this work, we continue a thermochemical study of N-containing heterocyclic compounds [9,10] and indole derivatives in particular [11] with comprehensive experimental and theoretical thermochemical investigation of mono-methyl- (2-methyl-indole, 3-methyl-indole, 5-methyl-indole, 7-methyl-indole) and dimethyl-indoles (2,3-dimethyl-indole) and their perhydrogenated counterparts leading to the determination of the dehydrogenation/hydrogenation reaction enthalpies of these potential LOHC systems. The aim of this work is provision of a consistent data set that allows to compare the different, chemically similar indoles regarding their reaction thermodynamics.

2 Materials and methods

The samples of methyl indoles were of commercial origin (Sigma-Aldrich and TCI) with purities of 98-99 % and used as received. However, before starting the vapor pressure measurements using the transpiration method, the samples were conditioned 'in situ' in the experimental device, as described in the Electronic Supporting Materials (ESI). Final purities were determined using a gas chromatograph equipped with an HP-5 capillary column and a flame ionization detector. The negligible amount of impurities (below 0.004 mass fraction) was found in samples used for vapor pressure measurements.

We used the transpiration method [12,13] to measure the vapor pressure of methyl-indoles at different temperatures. The standard molar enthalpies of sublimation and standard molar enthalpies of vaporisation, $\Delta_{\mathrm{cr,l}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}$, were derived from the temperature dependencies of the vapor pressures. The thermal behavior of 3-methyl-indole was studied using differential scanning calorimetry (DSC) [14]. We used the quantum chemical composite G3MP2 method [15] implemented in the Gaussian 16 software to calculate the H_{298}-values, which were further converted to the standard molar enthalpies of formation $\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\mathrm{o}}(\mathrm{g})$. Brief descriptions of the experimental and computational techniques used in this work are included in the ESI.

3 Results and Discussion

3.1 Vapor pressures of indole derivatives

The temperature dependencies of vapor pressures, p_i, for 2-methyl-, 3-methyl-, 5-methyl-, 7-methyl- and 2,3-dimethylindoles were measured using the transpiration method in the temperature range between 292 K and 377 K. Vapor pressures for 2-methyl-indole and 7-methyl-indole were measured above and below melting points (see Table S1). Measurements on 3-methyl-indole were performed above the solid-solid phase transition T_{tr} = 316.8 K (see Table S1), detected for this compound by DSC. Experimental details and results of the transpiration method for indole derivatives are given in Table 1.

Table 1

Results of transpiration method for indole derivatives: absolute vapor pressures *p*, standard molar vaporisation/sublimation enthalpies and standard molar vaporisation/sublimation entropies.

T/ K[a]	m/ mg[b]	$V(N_2)$[c] / dm^3	T_a/ K[d]	Flow/ dm$^3\cdot$h^{-1}	p/ Pa[e]	$u(p)$/ Pa[f]	$\Delta_{l,cr}^{g}H_m^o(T)$/ kJ·mol^{-1}	$\Delta_{l,cr}^{g}S_m^o(T)$/ J·K^{-1}·mol^{-1}
2-methyl-indole: $\Delta_l^g H_m^o$(298.15 K) = (70.8±0.9) kJ·mol^{-1}								
$\ln(p/p_{ref}) = \frac{302.9}{R} - \frac{91366.5}{RT} - \frac{69.0}{R}\ln\frac{T}{298.15}$; p_{ref} = 1 Pa								
334.2	1.19	1.636	293.2	2.05	13.50	0.36	68.3	130.3
338.2	1.33	1.363	293.2	2.05	18.08	0.48	68.0	129.5
342.2	1.34	1.023	293.2	2.05	24.30	0.63	67.8	128.8
346.2	2.15	1.301	293.2	3.90	30.69	0.79	67.5	127.7
350.4	1.59	0.716	293.2	2.05	41.13	1.05	67.2	127.0
354.2	2.13	0.733	293.2	2.00	53.98	1.37	66.9	126.4
358.2	1.51	0.416	293.2	1.19	67.30	1.71	66.7	125.4

362.2	1.36	0.287	293.2	1.19	87.83	2.22	66.4	124.8
366.2	1.85	0.307	293.2	1.19	111.59	2.81	66.1	124.0
370.2	2.29	0.297	293.2	1.19	142.85	3.60	65.8	123.4

2-methyl-indole: $\Delta_{\mathrm{cr}}^{\mathrm{g}} H_{\mathrm{m}}^{\mathrm{o}}$(298.15 K) = (85.2±0.4) kJ·mol^{-1}

$$\ln\,(p/p_{ref}) = \frac{305.2}{R} - \frac{93256.1}{RT} - \frac{27.1}{R}\ln\frac{T}{298.15}\;;\; p_{\mathrm{ref}} = 1\ \mathrm{Pa}$$

292.2	0.43	41.34	300.2	2.43	0.20	0.01	85.3	182.9
295.2	0.67	45.37	298.2	3.03	0.28	0.01	85.3	182.5
298.2	0.75	36.00	298.2	2.40	0.40	0.01	85.2	182.2
302.2	0.51	14.95	295.2	4.99	0.64	0.02	85.1	182.1
306.2	0.68	12.90	298.2	4.84	0.99	0.03	85.0	181.7
310.2	0.60	7.478	295.2	4.99	1.51	0.04	84.9	181.3
314.2	0.77	6.221	298.2	5.18	2.34	0.06	84.7	181.1
318.2	0.47	2.568	295.2	3.95	3.40	0.09	84.6	180.5
320.2	0.81	3.600	296.2	5.14	4.21	0.11	84.6	180.4
322.2	0.84	3.110	298.2	5.18	5.11	0.15	84.5	180.2
324.2	0.83	2.486	296.2	5.14	6.30	0.18	84.5	180.2
326.2	0.76	1.906	298.2	3.81	7.50	0.21	84.4	179.9
328.2	0.76	1.582	296.2	4.13	9.06	0.25	84.4	179.7
330.2	0.73	1.271	298.2	3.81	10.83	0.30	84.3	179.4
331.2	0.89	1.376	296.2	4.13	12.11	0.33	84.3	179.5
332.2	0.85	1.207	298.2	3.81	13.34	0.36	84.3	179.5

3-methyl-indole (cr I): $\Delta_{\mathrm{cr}}^{\mathrm{g}} H_{\mathrm{m}}^{\mathrm{o}}$(298.15 K) = (79.3±0.5) kJ·mol^{-1}

$$\ln\,(p/p_{ref}) = \frac{288.8}{R} - \frac{87330.7}{RT} - \frac{27.1}{R}\ln\frac{T}{298.15}\;;\; p_{\mathrm{ref}} = 1\ \mathrm{Pa}$$

317.2	1.32	6.038	296.2	4.03	4.09	0.11	78.7	164.2

321.2	1.73	5.367	296.2	4.03	6.05	0.18	78.6	164.1
324.2	1.69	4.025	296.2	4.03	7.87	0.22	78.5	163.7
328.2	1.63	2.683	296.2	4.03	11.41	0.31	78.4	163.5
332.2	1.67	2.013	296.2	4.03	15.55	0.41	78.3	162.9
336.2	1.59	1.342	296.2	4.03	22.29	0.58	78.2	162.8
340.2	2.14	1.296	296.2	2.88	30.98	0.80	78.1	162.5
342.2	3.28	1.688	295.2	4.05	36.38	0.93	78.1	162.3
344.2	1.80	0.795	296.2	2.38	42.50	1.09	78.0	162.1
346.2	2.78	1.046	295.2	4.05	49.64	1.27	78.0	161.9
348.2	1.92	0.620	298.2	1.18	58.39	1.48	77.9	161.8
352.2	1.61	0.384	298.2	1.18	79.29	2.01	77.8	161.5
356.2	2.42	0.433	298.2	1.18	105.63	2.67	77.7	161.1
360.2	2.14	0.285	298.2	1.18	141.91	3.57	77.6	160.9
364.2	2.68	0.266	298.2	1.18	190.21	4.78	77.5	160.6

5-methyl-indole: $\Delta_{\mathrm{l}}^{\mathrm{g}} H_{\mathrm{m}}^{\mathrm{o}}$(298.15 K) = (70.5±0.7) kJ·mol^{-1}

$$\ln\left(p/p_{ref}\right) = \frac{309.5}{R} - \frac{92077.1}{RT} - \frac{72.3}{R}\ln\frac{T}{298.15}\text{ ; } p_{\mathrm{ref}} = 1\text{ Pa}$$

338.2	2.35	1.473	293.2	2.21	29.66	0.77	67.6	132.5
340.2	1.82	0.992	293.2	2.98	34.08	0.88	67.5	132.0
342.2	1.91	0.920	293.2	2.21	38.45	0.99	67.3	131.4
346.2	1.47	0.539	293.2	2.02	50.69	1.29	67.1	130.6
346.2	1.97	0.718	293.2	2.21	51.05	1.30	67.1	130.7
347.2	2.10	0.727	296.2	2.18	54.11	1.38	67.0	130.4
348.2	2.43	0.773	293.2	2.21	58.29	1.48	66.9	130.3
350.2	1.81	0.512	293.2	1.02	65.85	1.67	66.8	129.8

352.2	1.71	0.435	296.2	1.04	73.71	1.87	66.6	129.2
354.2	1.57	0.341	293.2	1.02	85.50	2.16	66.5	129.0
356.2	1.78	0.338	293.2	1.01	97.85	2.47	66.3	128.6
358.2	2.00	0.341	293.2	1.02	109.12	2.75	66.2	128.1
360.2	2.24	0.330	296.2	1.04	127.00	3.20	66.0	127.9
362.2	2.59	0.341	293.2	1.02	140.71	3.54	65.9	127.4
366.2	2.36	0.245	293.2	1.01	178.30	4.48	65.6	126.5
368.2	2.83	0.261	296.2	1.04	202.99	5.10	65.5	126.3
370.2	3.15	0.256	293.2	1.02	228.24	5.73	65.3	125.9

7-methyl-indole: $\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}$(298.15 K) = (68.4±1.2) kJ·mol^{-1}

$$\ln\left(p/p_{ref}\right) = \frac{303.3}{R} - \frac{89931.9}{RT} - \frac{72.3}{R}\ln\frac{T}{298.15}\text{ ; } p_{\mathrm{ref}} = 1\text{ Pa}$$

357.2	1.86	0.343	293.2	1.03	100.58	2.54	64.1	122.1
359.2	2.14	0.343	293.2	1.03	115.74	2.92	64.0	121.9
361.2	2.43	0.350	293.2	1.05	129.08	3.25	63.8	121.4
363.2	2.01	0.257	293.2	1.03	144.60	3.64	63.7	121.0
365.2	2.39	0.271	293.2	1.05	163.74	4.12	63.5	120.7
367.2	3.33	0.343	293.2	1.03	179.95	4.52	63.4	120.1
369.2	3.86	0.350	293.2	1.05	204.63	5.14	63.2	119.8
371.2	4.44	0.368	293.2	1.05	223.91	5.62	63.1	119.3
373.2	4.80	0.350	293.2	1.05	254.35	6.38	63.0	119.0
375.2	4.30	0.280	293.2	1.05	284.58	7.14	62.8	118.7
377.2	4.77	0.280	293.2	1.05	315.79	7.92	62.7	118.3

7-methyl-indole: $\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}$(298.15 K) = (85.4±0.9) kJ·mol^{-1}

$$\ln\left(p/p_{ref}\right) = \frac{308.0}{R} - \frac{94100.5}{RT} - \frac{29.2}{R}\ln\frac{T}{298.15}\text{ ; } p_{\mathrm{ref}} = 1\text{ Pa}$$

303.2	1.73	45.77	293.2	2.76	0.70	0.02	85.2	182.6
309.2	0.85	11.87	293.2	5.09	1.33	0.04	85.1	181.8
315.2	2.85	20.64	293.2	4.00	2.57	0.07	84.9	181.5
321.2	1.06	4.154	293.2	5.09	4.75	0.12	84.7	181.0
327.2	3.63	7.808	293.2	3.90	8.63	0.24	84.5	180.6
333.2	2.06	2.543	293.2	5.09	15.08	0.40	84.4	180.1
336.2	2.31	2.212	293.2	3.90	19.38	0.51	84.3	179.7
339.2	1.88	1.397	293.2	3.99	25.01	0.65	84.2	179.3
345.2	1.88	0.811	293.2	1.95	42.97	1.10	84.0	179.0
347.2	2.02	0.769	293.2	2.31	48.74	1.24	84.0	178.5
351.2	1.78	0.487	293.2	1.95	67.87	1.72	83.8	178.1

2,3-dimethyl-indole: $\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}$(298.15 K) = (86.2±0.9) kJ·mol^{-1}

$$\ln\,(p/p_{ref}) = \frac{295.2}{R} - \frac{93559.0}{RT} - \frac{24.8}{R}\ln\frac{T}{298.15}\,;\ p_{\mathrm{ref}} = 1\ \mathrm{Pa}$$

318.2	1.68	30.85	293.2	2.06	0.91	0.03	85.7	172.8
323.2	0.95	10.13	293.2	5.06	1.57	0.04	85.5	172.7
326.2	2.24	18.14	293.2	5.06	2.07	0.06	85.5	172.4
330.2	1.88	10.13	293.2	5.06	3.12	0.08	85.4	172.3
334.2	2.11	8.016	293.2	5.06	4.43	0.12	85.3	171.8
338.2	2.00	5.316	293.2	5.06	6.33	0.18	85.2	171.5
342.2	2.00	3.797	293.2	5.06	8.85	0.25	85.1	171.1
346.2	0.49	0.617	293.2	2.06	13.21	0.36	85.0	171.2
350.2	2.33	2.110	293.2	5.06	18.57	0.49	84.9	171.0
354.2	2.42	1.688	296.2	5.06	24.33	0.63	84.8	170.2
358.2	2.21	1.059	293.2	2.12	35.02	0.90	84.7	170.3

362.2	2.00	0.706	293.2	2.12	47.42	1.21	84.6	169.9
366.2	2.64	0.706	293.2	2.12	62.70	1.59	84.5	169.4
370.2	2.66	0.530	293.2	2.12	84.29	2.13	84.4	169.1

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[a] Saturation temperature measured with the standard uncertainty ($u(T)$ = 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. Uncertainties are given as standard uncertainties.

[d] T_a is the temperature of the soap bubble meter used for measurement of the gas flow.

[e] Vapor pressure at temperature T, calculated from the m and the residual vapor pressure at the condensation temperature calculated by an iteration procedure.

[f] Standard uncertainties were calculated with $u(p_i/\mathrm{Pa}) = 0.005 + 0.025(p_i/\mathrm{Pa})$ for pressures below 5 Pa and with $u(p_i/\mathrm{Pa}) = 0.025 + 0.025(p_i/\mathrm{Pa})$ for pressures from 5 to 3000 Pa. The standard uncertainties for T, V, p, m, are standard uncertainties with 0.683 confidence level. Uncertainties of the vaporisation/sublimation enthalpy $U(\Delta_{\mathrm{l,cr}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}})$ are the expanded uncertainty (0.95 level of confidence, k = 2) calculated according to procedures described elsewhere [16,17]. Uncertainties include uncertainties from the experimental conditions and the fitting equation, vapor pressures, and uncertainties from adjustment of vaporisation enthalpies to the reference temperature T = 298.15 K.

Only few vapor pressure studies of methyl-indoles have been found in the literature [9,20,24]. In our recent work, [9] we studied vapor pressures over the crystal sample of 2-methyl-indole to validate the questionable sublimation thermodynamics of this compound. In this work, we repeated the measurement below the melting point in a wider temperature range and additionally measured vapor pressures of 2-methyl-indole over the liquid sample. The new vapor pressures in both regions are in good agreement with previous results (see Fig. S1). In the course of this work, we noticed a misprint in the measurement report for 2,3-dimethyl-indole published earlier [18]: the GC was calibrated correctly, but the calibration coefficients were incorrect. To confirm the published result, we repeated the measurements over solid 2,3-dimethyl-indole and both, the old and the new result, are now in agreement (see Fig. S2). For the solid 3-methyl-indole, coefficients of the linear p-T dependence in the range of 288-333 K were given by Stephenson and Malanowski [19]. The origin of the data is not available, but according to our DSC study (see Table S1), the solid-solid phase transition in 3-methyl-indole is in the middle of the specified temperature range, invalidating the vapor pressure approximation. For liquid 3-methyl-indole, Stull [20] gave boiling temperatures at reduced pressure. Again, the origin of the data from this compilation is not clear.

The experimental vapor pressures at different temperatures were approximated by the following equation [12,13]:

$$\mathrm{R} \times \ln(p_i / p_{ref}) = a + \frac{b}{T} + \Delta_{\mathrm{cr,l}}^{\mathrm{g}} C_{\mathrm{p,m}}^{\mathrm{o}} \times \ln\left(\frac{T}{T_0}\right) \qquad (1),$$

where R = 8.31446 J·K^{-1}·mol^{-1} is the molar gas constant, the reference pressure, $p_{ref} = 1$ Pa, and a and b are adjustable parameters; the arbitrary temperature T_0 applied in Eq. (1) was chosen to be T_0 = 298.15 K and $\Delta_{\mathrm{cr,l}}^{\mathrm{g}} C_{\mathrm{p,m}}^{\mathrm{o}}$ (see Table S2) is the difference of the molar heat capacities of the gas and the crystal (or liquid) phases respectively. Approximation coefficients a and b of Eq. (1) are given in Table 1 and the coefficients b were used to derive vaporisation/sublimation enthalpies of the indole derivatives (see details in ESI). From our experience, Eq. (1) not only works well for interpolating vapor pressures, but also for extrapolating about 30 K above and below the temperature range under study. With this experience, it was reasonable to estimate the absolute vapor pressures of indole derivatives (as the hydrogen-lean form of the LOHC system) at three temperatures (293 K, 323 K, and 373 K) technically relevant for hydrogen storage. The results shown in Table 2 indicate that all investigated methyl-indoles have very low vapor pressures even at 373 K, which is essential for the safe handling of these potentially interesting molecules for H_2 storage.

Table 2

Absolute vapor pressures *p* of indoles at selected temperatures

compound	*p*/Pa at 293 K	*p*/Pa at 323 K	*p*/Pa at 373 K
	hydrogen-lean	*LOHC compound* [a]	
2-methyl-indole (liq)	0.40	5.7	166
2-methyl-indole (cr)	0.22	5.1	
3-methyl-indole (cr)	0.35	7.1	
5-methyl-indole (liq)	0.65	9.4	266
7-methyl-indole (liq)	0.75	9.9	252
7-methyl-indole (cr)	0.22	5.6	
2,3-dimethyl-indole (cr)	0.06	1.5	
	hydrogen-rich	*LOHC compound* [b]	
2-methyl-H8-indole (liq) [c]	61	533	7861
3-methyl-H8-indole (liq)	47	370	4925
5-methyl-H8-indole (liq)	56	418	5285
7-methyl-H8-indole (liq)	70	498	5894
2,3-dimethyl-H8-indole (liq)	1.4	122	3042

[a] Calculated using coefficients of Eq. (1) given in Table 1.

[b] Derived from structure-property correlations (see Table S3).

[c] Calculated using experimental data from ref. [9].

The absolute vapor pressures of fully hydrogenated indole derivatives are even more important for their practical application since they are directly distributed as H_2-carriers in the liquid fuel infrastructure. The vapor pressures of these compounds at 293 K, 323 K, and 373 K are also given in

Table 2. It is evident that the hydrogen-rich indoles have vapor pressures two orders of magnitude higher, but even at the practically relevant temperature of 323 K, the vapor pressure levels are acceptable for safe LOHC distribution.

Admittedly [21], the dehydrogenation of the LOHC requires temperatures significantly higher than 373 K, so reliable knowledge of the vapor pressures up to the boiling point is of considerable practical interest. However, the transpiration method used in this work is preferably used for measurements of vapor pressures below ≈3000 Pa [13]. As a consequence, for the moderately volatile indole derivatives, reasonable experimental temperatures are below 373 K. To obtain vapor pressures for indole derivatives over a broader temperature range, we combined the transpiration results with very limited boiling point data at different pressures collected from the original literature (see Table S4). The Clarke and Glew equation [22] can more reliably approximate the vapor pressures over the wide temperature range than Eq. (1):

$$R \times \ln(p_{\mathrm{i}}/p^{\mathrm{o}}) = -\frac{\Delta_{\mathrm{l}}^{\mathrm{g}} G_{\mathrm{m}}^{\mathrm{o}}(\theta)}{\theta} + \Delta_{\mathrm{l}}^{\mathrm{g}} H_{\mathrm{m}}^{\mathrm{o}}(\theta) \times \left(\frac{1}{\theta} - \frac{1}{T}\right) - \Delta_{\mathrm{l}}^{\mathrm{g}} C_{\mathrm{p,m}}^{\mathrm{o}}(\theta) \times \left(\frac{\theta}{T} - 1 + \ln\left(\frac{T}{\theta}\right)\right) \quad (2),$$

In this equation p_{i} is the vapor pressure at the temperature T, θ is an arbitrary reference temperature (in this work we used θ = 298.15 K), p^{o} is an arbitrary reference pressure (p^{o} = 1 Pa in this work), R is the molar gas constant; $\Delta_{\mathrm{l}}^{\mathrm{g}} G_{\mathrm{m}}^{\mathrm{o}}(\theta)$, is the differences in the standard molar Gibbs energy of vaporisation, between the liquid and gas phase; $\Delta_{\mathrm{l}}^{\mathrm{g}} H_{\mathrm{m}}^{\mathrm{o}}(\theta)$ is the difference in the standard molar enthalpy of vaporisation between the liquid and gas phase, and $\Delta_{\mathrm{l}}^{\mathrm{g}} C_{\mathrm{p,m}}^{\mathrm{o}}(\theta)$ is the difference in the molar heat capacity at constant pressure between the liquid and gas phase. An advantage of the Clarke and Glew equation is that the fitting coefficients are directly related to the thermodynamic functions of vaporisation. Coefficients of the Clarke and Glew equation (Eq. 2) suitable for estimating vapor pressures up to the boiling point are given in Table 3.

Table 3

Coefficients of the Clarke and Glew equation (Eq. 2) suitable for estimating vapor pressures up to boiling temperatures[a]

Compound	T-range	$\Delta_l^g G_m^o$(298.15 K)	$\Delta_l^g H_m^o$(298.15 K)	$-\Delta_l^g C_{p,m}^o$ [b]
	K	kJ·mol^{-1}	kJ·mol^{-1}	J·K^{-1}·mol^{-1}
2-methyl-indole	334.2-546.4	29.7±0.1	72.5±0.2	69
3-methyl-indole	370.2-539.2	28.7±0.5	70.1±1.3	69
5-methyl-indole	338.2-540.2	28.3±0.1	70.3±0.3	72
7-methyl-indole	357.2-539.2	28.5±0.1	70.8±0.3	72
2,3-dimethyl-indole	382.0-558.2	31.3±0.4	75.9±1.2	84
8H-indole	277.9-458.7	16.6±0.1	52.7±0.5	74
2-methyl-8H-indole	275.1-470.5	17.4±0.1	54.1±0.4	80

[a] Uncertainties of thermodynamic functions are expressed as the standard uncertainty.

[b] From Table S2.

The approximation coefficients of Eq. (2) are given in Table 3 and can be used to obtain vapor pressures of the hydrogen-lean and hydrogen-rich counterparts of the LOHC systems at any temperature relevant for this hydrogen storage technology. Considering that the vapor pressures of fully hydrogenated indole and 2-methyl-indole in general do not differ significantly (see Table 2), the coefficients of *p*-*T* dependencies given in Table 3 for 2-methyl-8H-indole can be propagated to technical vapor pressure calculations for other methyl-8H-indoles.

3.2 Thermodynamics of vaporisation/sublimation processes

The vaporisation/sublimation enthalpies, which are derived from the experimental vapor pressure-temperature dependencies according to the Clausius–Clapeyron relation, are referenced to the average temperature, T_{av}, of the examined interval. For engineering calculations, these enthalpies should be adjusted to any common temperature. For the thermochemical calculations, the enthalpies have to be adjusted to the reference temperature T = 298.15 K. Adjustment details are given in ESI. The thermodynamic properties of vaporisation derived from the Clarke and Glew equation with θ = 298.15 K (see Table 3) generally represent a correct level, but they are considered more as empirical coefficients of approximation to estimate vapor pressures at a desired temperature. Therefore, the $\Delta_{\mathrm{cr,l}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}$(298.15 K)-values from Eq. (2) might be somewhat influenced by the inaccuracy of high-temperature vapor pressures taken from the literature. In contrast, the transpiration results in this work were not measured too far from T = 298.15 K and could provide more accurate values of $\Delta_{\mathrm{cr,l}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}$(298.15 K). Thus, the results from the transpiration method have been treated by using Eq. (1) in order to evaluate enthalpies of sublimation/vaporisation at 298.15 K according to equation:

$$\Delta_{\mathrm{cr,l}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}(298.15\ \mathrm{K}) = -b + \Delta_{\mathrm{cr,l}}^{\mathrm{g}}C_{p,\mathrm{m}}^{\mathrm{o}} \times 298.15 \qquad (3)$$

The original absolute vapor pressures available in the literature have also been treated by using Eqs. (1) and (3). The combined uncertainties of the $\Delta_{\mathrm{cr,l}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}$(298.15 K)-values include uncertainties from the experimental conditions, uncertainties in vapor pressure and uncertainties due to the temperature adjustment to T = 298.15 K as described elsewhere [16,17]. The compilation of the sublimation/vaporisation enthalpies of methyl-indoles derived using Eq. (3) and referenced to T = 298.15 K are given in Table 4, column 5.

As it can be seen from Table 4, a remarkable consistency of the $\Delta_{\mathrm{cr,l}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}$(298.15 K)-values for 2-methyl-indoles is now achieved for this compound for the crystal and for the liquid state. At the reference temperature T = 298.15 K the 3-methyl-indole exist in the crystal modification crII. Above the phase transition temperature T_{tr} = 316.8 K, this compound changes into the crystal modification crI with the phase transition enthalpy of $\Delta_{\mathrm{crII}}^{\mathrm{crI}}H_{\mathrm{m}}^{\mathrm{o}}$ = 2.7±0.6 kJ·mol^{-1}. The transpiration experiments with 3-methylindole were carried out in the crI phase. To derive the $\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}$(298.15 K, crII)-value for this compound, the phase transition enthalpy was adjusted to T = 298.15 K and added to the $\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}$(298.15 K, crI)-value measured by transpiration (see Table S1). The resulting value $\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}$(298.15 K, crII) = 81.2±0.7 kJ·mol^{-1} was used for further thermochemical calculations.

Table 4

Compilation of available enthalpies of sublimation/vaporisation $\Delta_{\mathrm{cr,l}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}$

Compound/CAS	Method[a]	T- range	$\Delta_{\mathrm{cr,l}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}(T_{\mathrm{av}})$	$\Delta_{\mathrm{cr,l}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}$(298.15 K)[b]	Ref.
		K	kJ·mol^{-1}	kJ·mol^{-1}	
2-methyl-indole (cr)	DC	360.1	91.7±1.0	87.6±2.4	[23]
	FT			85.5±1.0	[9]
	T	298.3-330.1	84.7±0.4	85.1±1.2	[9]
	T	292.2-332.2	84.8±0.3	85.2±0.4	Table 1
				85.3±0.4 [c]	average
2-methyl-indole (liq)	IP	340.0-430.0	66.3±0.2	72.1±1.0	[24]
	E	427.3-595.0	58.0±0.2	72.2±2.2	[24]
	FT			71.9±0.6	[9]
	T	334.2-370.2	67.1±0.8	70.8±0.9	Table 1
				71.7±0.4 [c]	average
	J_x			70.0±1.5	Table 5
	J_{Lee}			70.4±1.5	Table 6

3-methyl-indole (cr)	n/a	288-333	83.3±2.0	(83.6±2.1)	[19]
	DC	349.9	83.0±1.9	(90.4±2.4)	[23]
	FT			**81.2±0.7**[c]	Table S1
3-methyl-indole (crI)	T	317.2-364.2	78.0±0.4	79.3±0.5	Table 1
3-methyl-indole (liq)	n/a	368.2-539.4	63.7±1.0	(73.8±1.2)	[20]
	FT			**69.8±1.4**	Table S1
	J_x			70.2±1.5	Table 5
	J_{Lee}			70.2±1.5	Table 6
5-methyl-indole (liq)	BP	378-540	58.0±1.5	69.0±3.0	Table S5
	T	338.2-370.2	66.5±0.6	70.5±0.7	Table 1
				70.4±0.7[c]	average
	J_x			70.3±1.5	Table 5
7-methyl-indole (cr)	T	303.2-351.2	84.6±0.8	85.4±0.9	Table 1
7-methyl-indole (liq)	T	357.2-377.2	63.4±1.0	68.4±1.2	Table 1
	J_x			69.0±1.5	Table 5
	J_{Lee}			69.2±1.5	Table 6
				68.8±0.8[c]	average
2,3-dimethyl-indole (cr)	T	313.2-373.2	84.7±0.8	85.8±0.9	Table S6
	T	318.2-370.2	85.1±0.8	86.2±0.9	Table 1
				86.0±0.6[c]	average
2,3-dimethyl-indole (liq)	BP	396-558	62.2±1.8	76.8±3.4	Table S5
	J_x			75.0±1.5	Table 5
	J_{Lee}			75.1±1.5	Table 6
				75.2±1.0[c]	average

[a] Techniques: DC = drop calorimetry; T = transpiration method; FT = derived as the difference of sublimation and fusion enthalpies (see Table S1); IP = inclined piston method; E = Ebulliometry; J_x - derived from correlation with Kovats´s indices (see Table 5); J_{Lee} - derived from correlation with Lee´s indices (see Table 6); BP = derived from boiling points at reduced pressures found in the literature (Table S5).

[b] Uncertainty of the sublimation/vaporisation enthalpy $U(\Delta_{\mathrm{cr,l}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}})$ is the expanded uncertainty (0.95 level of confidence, k = 2) calculated according to a procedure described elsewhere [16,17]. It includes uncertainties from the experimental conditions, uncertainties of vapor pressure, uncertainties from the fitting equation, and uncertainties from temperature adjustment to T = 298.15 K.

[c] Weighted mean value. Values in parenthesis were excluded from the calculation of the mean. Values in bold are recommended for further thermochemical calculations.

3.3 Evaluation of vaporisation enthalpies of methyl-indoles and methyl-octahydro-indoles

The hydrogenation/dehydrogenation processes happen in a complex, biphasic vapor-liquid system. Hence, vaporisation thermodynamics is needed for engineering calculations. The vaporisation enthalpies of 2-methyl-, 5-methyl-, and 7-methylindoles were derived directly from the vapor pressures (see Table 1). The melting temperatures of 3-methyl-indole and 2,3-dimethyl-indole were too high for the transpiration experiments in this work and we have to obtain their enthalpies of vaporisation by other means. Moreover, the vaporisation enthalpies of hydrogen-rich methyl-octahydro-indoles are also required for engineering calculations. Admittedly, a convenient way to get the missing thermochemical information is to correlate it with measurable physicochemical properties. For example, one of the substance-specific mark is the gas-chromatographic (GC) retention index. The most popular Kovats index [25] is based on the retention times of *n*-alkanes. Collections and compilations of Kovats indices are available and ready to use [26,27]. The retention index is generally related to the vaporisation process as it reflects the intensity of sorption/desorption of a gaseous compound in the GC stationary liquid phase. It is already well-established, that the

$\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}$(298.15 K)-values correlate linearly with Kovats indices in series of structurally similar compounds, *e.g*. homologous series of alkanols, esters, amines *etc*. [28]. In Table 5 we collected similarly shaped aromatic compounds with reliable vaporisation enthalpies and available Kovats indices on the SE-30 [27] and derived a good linear correlation between vaporisation enthalpies $\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}$(298.15 K) and Kovats indices, J_x, for this collection:

$$\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}(298.15\ \mathrm{K})\ /(\mathrm{kJ\cdot mol^{-1}}) = 0.1 + 0.0505\times J_x \qquad \text{with } (R^2 = 0.995) \qquad 4$$

The ‘theoretical’ vaporisation enthalpies derived from Eq. (5) (see Table 5, column 5) agree well with the experimental values measured in this work using the transpiration method (see Table 1 as well as Table 4, column 5). Such good agreement can be considered as validation of the experimental data measured in this work using the transpiration method (see Table 1). Moreover, the missing vaporisation enthalpies of 3-methyl-indole, 2,3-dimethyl-indole and some other indoles were derived from Eq. (4). Results given in Table 5, indicate that differences between experimental vaporisation enthalpies and ‘theoretical’ values calculated according to Eq. (4) are mostly below 1.5 kJ·mol^{-1}. Hence, the uncertainties of enthalpies of vaporisation which are estimated from the correlation of $\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}$(298.15 K) with Kovats indices are evaluated with an uncertainty of ±1.5 kJ·mol^{-1}.

Table 5

Correlation of vaporisation enthalpies, $\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}$(298.15 K), of heterocyclic compounds with their Kovats indices (J_x)

CAS	Compound name	J_x [a]	$\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}(298\ \mathrm{K})_{\mathrm{exp}}$ kJ·mol^{-1}	$\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}(298\ \mathrm{K})_{\mathrm{calc}}$ [b] kJ·mol^{-1}	Δ[c] kJ·mol^{-1}
496-15-1	indoline	1196	60.8±0.9 [9]	60.5	0.3
120-72-9	indole	1296	65.6±0.4 [Table 4]	65.5	0.1
95-20-5	2-methyl-indole	1385	71.7±0.4 [Table 4]	70.0	1.7
83-34-1	3-methyl-indole	1388	69.8±1.4 [Table 4]	**70.2±1.5**	-0.4
614-96-0	5-methyl-indole	1391	70.4±0.7 [Table 4]	70.3	0.1
933-67-5	7-methyl-indole	1365	68.4±1.2 [Table 4]	69.0	-0.6
91-55-4	2,3-dimethyl-indole	1484		**75.0±1.5**	
1196-79-8	2,5-dimethyl-indole	1480		**74.8±1.5**	
21296-92-4	2,3,5-trimethyl-indole	1572		**79.5±1.5**	
948-65-2	2-phenyl-indole	1968	99.4±3.3 [Table S1]	99.5	
4375-15-9	3-methyl-indoline	1330		**67.3±1.5**	
635-46-1	1,2,3,4-tetrahydroquinoline	1318	65.3±0.2 [29]	66.7	-1.4

[a] Kovats indices at 443 K, J_x, on the standard non-polar column SE-30 [27].

[b] Calculated using Eq. (4) with the assessed expanded uncertainty of ±1.5 kJ·mol^{-1} (0.95 level of confidence, k = 2)

[c] Difference between column 4 and 5 in this table.

Additional validation of the $\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}$(298.15 K)-values evaluated in Table 5 was performed in this work using the Lee´s chromatographic retention indices, J_{Lee}, [30] for series of methyl-indoles and similarly shaped compounds collected in Table 6. The following high-quality linear correlation between vaporisation enthalpies and J_{Lee} indices was derived:

$$\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}(298.15\ \mathrm{K})\ /(\mathrm{kJ{\cdot}mol^{-1}}) = 4.8 + 0.2733\times J_{Lee} \quad \text{with } (R^2 = 0.998) \tag{5}$$

Table 6

Correlation of vaporisation enthalpies, $\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}$(298.15 K), of heterocyclic compounds with their Lee´s indices (J_{Lee})

CAS	Compound	J_{Lee} [a]	$\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}(298\ \mathrm{K})_{\mathrm{exp}}$ kJ·mol^{-1}	$\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}(298\ \mathrm{K})_{\mathrm{calc}}$ [b] kJ·mol^{-1}	Δ[c] kJ·mol^{-1}
496-15-1	indoline	204.7	60.8±0.9 [9]	60.7	0.1
120-72-9	indole	222.7	65.6±0.4 [9]	65.7	-0.1
95-20-5	2-methyl-indole	240.1	71.7±0.4 [Table 4]	70.4	1.3
83-34-1	3-methyl-indole	239.2	69.8±1.4 [Table 4]	**70.2±1.5**	-0.4
933-67-5	7-methyl-indole	235.5	68.4±1.2 [Table 4]	69.2	-0.8
91-55-4	2,3-dimethylindole	257.3	-	**75.1±1.5**	
1196-79-8	2,5-dimethylindole	256.7	-	**75.0±1.5**	
21296-92-4	2,3,5-trimethylindole	273.6	-	**79.6±1.5**	
948-65-2	2-phenyl-indole	346.2	99.4±3.3 [Table S1]	99.4	0.0

[a] Lee indices, J_{Lee}, on the standard non-polar column SE-52 [30].

[b] Calculated using Eq. (5) with the assessed expanded uncertainty of ±1.5 kJ·mol^{-1} (0.95 level of confidence, k = 2).

[c] Difference between column 4 and 5 in this table.

The vaporisation enthalpies of 3-methyl-indole and 2,3-dimethyl-indole derived from Eq. (5) are indistinguishable with vaporisation enthalpies derived from the correlations with Kovats indices (see Table 4, column 4). A collection of compounds involved in determining the vaporisation enthalpies of octahydro-indoles is given in Table 7.

Table 7
Correlation of vaporisation enthalpies, $\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}$(298.15 K), of aromatic hydrocarbons and heterocyclic compounds with their Kovats indices (J_x), used to derive enthalpies of vaporisation of octahydro-indoles

compound	J_x [a]	$\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}$(298 K)$_{\mathrm{exp}}$	$\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}$(298 K)$_{\mathrm{calc}}$ [b]	Δ[c]
		kJ·mol^{-1}	kJ·mol^{-1}	kJ·mol^{-1}
1-methyl-pyrrolidine	697	34.2±0.2 [31]	34.2	0.0
toluene	780	38.1±0.2 [31]	38.0	0.1
1,4-dimethylbenzene	876	42.4±0.2 [31]	42.4	0.0
indane	1033	50.6±1.5 [32]	49.6	-0.4
indene	1059	49.2±1.0 [32]	50.8	-0.2
tetrahydro-naphthalene	1164	55.2±1.0 [31]	55.6	-0.4
quinoline	1231	59.3±0.4 [33]	58.7	0.6
2-methyl-quinoline	1294	61.8±0.4 [33]	61.6	0.2
3-methyl-quinoline	1346	63.7±0.4 [33]	64.0	-0.3
4-methyl-quinoline	1357	64.3±0.4 [33]	64.5	-0.2
6-methyl-quinoline	1343	64.0±0.3 [33]	63.9	0.1
7-methyl-quinoline	1338	63.7±0.5 [33]	63.6	0.1
8-methyl-quinoline	1304	62.0±0.3 [33]	62.1	-0.1
2,6-dimethyl-quinoline	1397	65.8±0.4 [33]	66.4	-0.6
1-methyl-indole	1285	61.9±0.3 [34]	61.2	0.7
H8-indole	1140	53.5±0.7 [9]	54.5	-1.0
1-methyl-H8-indole	1125		**53.9±1.0**	
2-methyl-H8-indole	1199	57.8±0.8 [9]	57.3	0.5
3-methyl-H8-indole	1217		**58.1±1.0**	
5-methyl-H8-indole	1204		**57.5±1.0**	
6-methyl-H8-indole	1204		**57.5±1.0**	
7-methyl-H8-indole	1182		**56.5±1.0**	
2,3-dimethyl-H8-indole	1285		**61.2±1.0**	
2-cyclohexyl-H8-indole	1777		**83.8±1.0**	
1-methyl-2-cyclohexyl-H8-indole	1762		**83.2±1.0**	

[a] Kovats indices at 443 K, J_x, on the standard non-polar column SE-30 [27].

[b] Calculated using Eq. (6) with the assessed expanded uncertainty of ±1.0 kJ·mol^{-1} (0.95 level of confidence, k = 2)

[c] Difference between column 4 and 5 in this table.

The following linear correlation between vaporisation enthalpies and J_x indices was derived:

$$\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}(298.15\ \mathrm{K})\ /(\mathrm{kJ\cdot mol^{-1}}) = 2.1 + 0.0460\times J_x \qquad \text{with } (R^2 = 0.9980) \qquad (6)$$

The most important species in this series are H8-indole and 2-methyl-H8-indole, for which reliable vaporisation enthalpies were measured in our recent work [9]. As can be seen from Table 7, these two octahydro-indoles fit well into the correlation according to Eq. (6), giving confidence to the $\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}$(298.15 K)-values derived for other perhydrogenated species in Table 7.

The 'theoretical' results for vaporisation enthalpies derived in Tables 5 and 6 are listed in Table 4 for comparison and denoted as J_x for the Kovats indices and J_{Lee} for the Lee´s indices. These 'theoretical' values are valuable to support the level of enthalpy of vaporisation derived from other methods, especially in cases where data are scarce or absent *(e.g.* for 3-methyl-indole, 2,3-dimethyl-indole, and methyl-octahydro-indoles).

3.4 Standard molar enthalpies of formation of indole derivatives

The standard molar enthalpies of formation, $\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\mathrm{o}}$, are indispensable to estimate reaction enthalpies and optimize heat management in chemical technology. The enthalpies of formation of indole derivatives in the crystal phase, $\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\mathrm{o}}$(cr), and in the liquid phase, $\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\mathrm{o}}$(liq), are collected in Table 5, column 2. These data were used together with the vaporisation/sublimation enthalpies of indoles, which evaluated in Table 4 to derive the experimental gas-phase standard molar enthalpies of formation, $\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\mathrm{o}}(\mathrm{g})_{\mathrm{exp}}$ at 298.15 K (see Table 8, column 4).

Table 8

Thermochemical data for indole derivatives at T=298.15 K (p°=0.1 MPa, in kJ·mol^{-1})[a]

compound	$\Delta_f H_m^o$(cr or l)	$\Delta_{cr,l}^{g} H_m^o$	$\Delta_f H_m^o(g)_{exp}$
indole (cr)	87.2±0.9 [9]	75.3±0.4 [Table 4]	162.5±1.0
1-methyl-indole (liq)	93.6±2.3 [23]	61.9±0.3 [34]	155.5±2.3
2-methyl-indole (cr)	36.1±1.3 [9]	85.3±0.4 [Table 4]	121.4±1.4
3-methyl-indole (cr)	47.4±2.3 [23]	81.2±0.7 [Table 4]	128.6±2.4
2,3-dimethyl-indole (cr)	4.2±1.0 [35]	86.0±0.6 [Table 4]	90.2±1.2
1-methyl-2-phenyl-indole (cr) [36]	131.0±3.1	111.1±0.7	242.1±3.2
2-phenyl-indole (cr) [36]	140.1±3.5	114.4±0.8	254.5±3.6
indoline (liq) [9]	60.0±0.9	60.8±0.9	120.8±1.3
H8-indole (liq) [9]	-117.5±1.8	53.5±0.7	-64.0±1.9
2-methyl-indoline [9]	17.2±1.9	63.0±0.4	80.2±1.9
2-methyl-H8-indole [9]	-157.1±2.1	57.8±0.8	-99.3±2.2

[a] Uncertainties in this table are expressed as two times the standard deviation.

However, not all enthalpies of formation of methyl-indoles and methyl-octahydro-indoles required for the thermodynamic analysis are experimentally available. The missing values were calculated using the high-level G3MP2 method.

Stable conformers were found by using a computer code named CREST (conformer-rotamer ensemble sampling tool) [37] and optimised with the B3LYP/6-31g(d,p) method [38]. The energies E_0 and the enthalpies H_{298} of the most stable conformers were finaly calculated by using the G3MP2 method.

The enthalpies H_{298} were converted to the *theoretical* gas-phase enthalpies of formation of indoles using an atomisation reaction [39]. The G3MP2 atomization procedure requires correction [18]. The latter correction was derived from correlation between experimental enthalpies of formation and the $\Delta_f H_m^o(\text{g, AT})_{G3MP2}$-values directly calculated via atomisation reaction:

$$\Delta_f H_m^o(g)_{theor}/\text{ kJ·mol}^{-1} = 1.047 \times \Delta_f H_m^o(\text{g, AT})_{G3MP2} - 1.1 \qquad \text{with } R^2 = 0.9996 \qquad (7)$$

The data used to establish this correlation are given in Table 9.

The *theoretical* $\Delta_f H_m^o(g)_{theor}$ values of indoles ‘corrected’ in this way agree well with the experimental values (see Table 9, column 5). It should be emphasized that the correlation included both saturated and unsaturated indoles and that the *theoretical* enthalpies of formation of octahydro-indoles are fairly consistent with experimental values within the limits of experimental uncertainties. This fact is important in order to consider the theoretical gas phase formation enthalpies of the methyl- and cyclohexyl-octahydro-indoles as reliable and to use these values to derive the energetics of hydrogenation/dehydrogenation reactions, as shown in Section 3.5.

Table 9

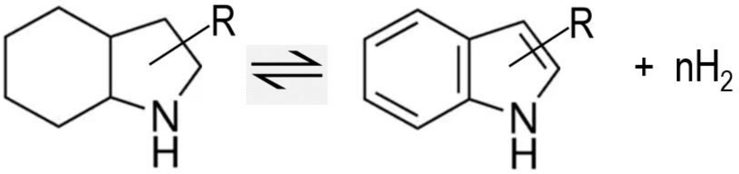
Correlation of the G3MP2(atomization) gas-phase enthalpies of formation with the experimental values for indole derivatives (at T = 298.15 K, $p°$ = 0.1 MPa, in kJ·mol^{-1}).

compound	$\Delta_f H^o_m(g)_{G3MP2}$ [a]	$\Delta_f H^o_m(g)_{exp}$ [b]	$\Delta_f H^o_m(g)_{theor}$ [c]	Δ [d]
indole	158.8	162.5±1.0	165.2	-2.7
1-methylindole	149.1	155.5±2.3	155.1	0.4
2-methylindole	118.9	121.4±1.4	123.5	-2.1
3-methylindole	125.1	127.8±2.4	130.0	-2.2
5-methylindole	128.1	-	133.1	
6-methylindole	127.5	-	132.5	
7-methylindole	122.7	-	127.5	
2,3-dimethylindole	86.2	90.2±1.2	89.3	0.9
1-methyl-2-phenyl-indole	233.6	242.1±3.2	243.6	-1.5
2-phenyl-indole	239.1	254.5±3.6	249.3	5.2
indoline	115.9	120.8±1.3	120.3	0.5
H8-indole	-60.5	-64.0±1.9	-64.3	0.3
2-methyl-indoline	78.0	80.3±1.9	80.7	-0.4
2-methyl-H8-indole	-95.2	-99.3±2.2	-100.7	1.4
3-methyl-H8-indole	-89.4		-94.6	
5-methyl-H8-indole	-89.8		-95.0	
6-methyl-H8-indole	-90.1		-95.3	
7-methyl-H8-indole	-90.4		-95.6	
2,3-dimethyl-H8-indole	-117.9		-124.4	
2-cyclohexyl-H8-indole	-169.0		-177.9	
1-methyl-2-cyclohexyl-H8-indole	-167.4		-176.3	

[a] Calculated by G3MP2 and atomization reaction.
[b] From Table 8.
[c] Calculated according to Eq. (7).
[d] Difference between column 3 and column 4.

3.5 Thermodynamic analysis of the dehydrogenation/hydrogenation LOHC systems

The liquid-phase enthalpy of the reversible dehydrogenation/hydrogenation reaction, $\Delta_r H_m^o$(liq), according to Eq. (8) is an important parameter to optimize the conditions for hydrogen storage using indoles as the LOHC system (with n = 2, 3 or 4 in Eq. (9) for gradual or complete dehydration).



(8)

The liquid-phase enthalpies of formation for the participants of the reaction were obtained according to the general thermochemical relation:

$$\Delta_f H_m^o(\text{liq, 298.15 K}) = \Delta_f H_m^o(\text{g, 298.15 K}) - \Delta_l^g H_m^o(\text{298.15 K}) \qquad (9)$$

Thermochemical data required for these calculations are given in Table 10 for the hydrogen-rich (HR) species and in Table 11 for their hydrogen-lean (HL) counter-parts. The enthalpies of the dehydrogenation/hydrogenation reaction of the R-octahydro-indole/R-indole LOHC system (see Eq. 8) were derived according to the Hess´s Law, using the standard molar enthalpies of formation of the reaction participants evaluated in Tables 10 and 11 and listed in Table 12.

Table 10

Calculation of the liquid phase enthalpies of formation, $\Delta_f H_m^o$(liq), of the hydrogen-reach counter-parts, at T = 298.15 K (p°=0.1 MPa, in kJ·mol^{-1})[a]

compound	$\Delta_f H_m^o(\text{gas})_{\text{HR}}$[a]	$\Delta_l^g H_m^o$[b]	$\Delta_f H_m^o(\text{liq})_{\text{HR}}$[c]
H8-indole [9]	-64.0±1.9	53.5±0.7	-117.5±2.0
2-methyl-H8-indole [9]	-99.3±2.2	57.8±0.8	-157.1±2.3
3-methyl-H8-indole	-94.6±4.1	58.1±1.0	-152.7±4.2
5-methyl-H8-indole	-95.0±4.1	57.5±1.0	-152.5±4.2
6-methyl-H8-indole	-95.3±4.1	57.5±1.0	-152.8±4.2
7-methyl-H8-indole	-95.6±4.1	56.5±1.0	-152.1±4.2
2,3-dimethyl-H8-indole	-124.4±4.1	61.2±1.0	-185.6±4.2
2-cyclohexyl-H8-indole	-177.9±4.1	83.7±1.0	-261.6±4.2
1-methyl-2-cyclohexyl-H8-indole	-176.3±4.1	83.0±1.0	-259.3±4.2

[a] Gas-phase enthalpies of formation of the fully hydrogenated molecules (HR = “hydrogen-rich”) from Table 9, column 4.

[b] Evaluated in Table 7.

[c] Calculated according to Eq. (9).

Table 11

Calculation of the liquid phase enthalpies of formation, $\Delta_f H_m^o$(liq), of the hydrogen-lean counter-parts, at T = 298.15 K (p°=0.1 MPa, in kJ·mol^{-1})[a]

compound	$\Delta_f H_m^o$(gas)$_{HL}$ [a]	$\Delta_l^g H_m^o$ [b]	$\Delta_f H_m^o$(liq)$_{HL}$ [c]
indole	162.5±1.0	60.8±0.9	101.7±1.3
2-methyl-indole	121.4±1.4	71.7±0.4	49.7±1.5
3-methyl-indole	128.6±2.4	69.8±1.4	58.8±2.8
5-methylindole	133.2±4.1	70.4±0.7	62.8±4.2
6-methylindole	127.6±4.1	70.4±0.7	57.2±4.2
7-methylindole	132.6±4.1	68.8±0.8	63.8±4.2
2,3-dimethyl-indole	90.2±1.2	75.2±1.0	15.0±1.6
2-phenyl-indole	254.5±3.6	99.4±3.3	155.1±4.9
1-methyl-2-phenyl-indole	242.1±3.2	98.3±1.2	143.8±3.4

[a] Gas-phase enthalpies of formation of the fully dehydrogenated molecules (HL = “hydrogen-lean”) from Table 9, column 4.

[b] Evaluated in Table 7.

[c] Calculated according to Eq. (9).

Table 12

Calculation of the liquid phase reaction enthalpies, $\Delta_r H_m^o$(liq), of the dehydrogenation of perhydro-indoles (reaction according to Eq. 8), at T = 298.15 K (p°=0.1 MPa, in kJ·mol^{-1})

compound	$\Delta_f H_m^o$(liq)$_{HR}$[a]	$\Delta_f H_m^o$(liq)$_{HL}$[b]	$\Delta_r H_m^o$(liq)[c]	$\Delta_r H_m^o$(liq)/H$_2$ [d]
H8-indole	-117.5±2.0	101.7±1.3	219.2±2.4	54.8
2-methyl-H8-indole	-157.1±2.3	49.7±1.5	206.8±2.8	51.7
3-methyl-H8-indole	-152.7±4.2	58.8±2.8	211.5±5.1	52.9
5-methyl-H8-indole	-152.5±4.2	62.8±4.2	215.3±5.9	53.8
6-methyl-H8-indole	-152.8±4.2	57.2±4.2	210.0±5.9	52.5
7-methyl-H8-indole	-152.1±4.2	63.8±4.2	215.9±5.9	54.0
2,3-dimethyl-H8-indole	-185.6±4.2	15.0±1.6	200.6±4.5	50.2
2-cyclohexyl-H8-indole	-261.6±4.2	155.1±4.9	416.7±6.5	59.5
1-methyl-2-cyclohexyl-H8-indole	-259.3±4.2	143.8±3.4	403.1±5.4	57.6

[a] From Table 10.

[b] From Table 11.

[c] Calculated according to the Hess´s Law applied to the reaction 9.

[d] Reaction enthalpy per mole H$_2$

From a practical point of view, relating the enthalpy of reaction to the amount of hydrogen released (kJ·mol^{-1}/$_{H2}$) allows a comparison of the enthalpy values of LOHC systems with different stoichiometries. In these units the enthalpies of reaction for the dehydrogenation of mono-methylated octahydro-indoles range between +51.7 and +54.0 kJ·mol^{-1}/$_{H2.}$ The lowest value for a mono-methylated indole is observed for 2-methyl-indole, which has the methyl group directly next to the nitrogen group. However, there is no clear trend observable regarding the position of methylation.

Furthermore, the difference between the highest and lowest enthalpy of reaction for mono-methylated indoles is only 2.3 kJ·mol^{-1}/$_{H2}$, which is only about two times more than the uncertainty. Hence, it can be concluded that the effect of the position of the methyl group might be negligible for most calculations regarding process design. However, it provides interesting insides for mechanistic studies.

These values for the dehydrogenation of the methylated H8-indoles are slightly lower than for H8-indole itself (not substituted) with an enthalpy of reaction of +54.8 kJ·mol^{-1}/$_{H2}$. The double methylated 2,3-dimethyl-H8-indole has an even lower enthalpy of reaction for dehydrogenation than the mono-methylated forms (+50.2 kJ·mol^{-1}/$_{H2}$).

Substitution with a cyclohexyl ring (2-cyclohexyl-H8-indole and 1-methyl-2-cyclohexyl-H8-indole), in contrast, leads to a strong increase in enthalpy of reaction. Yet, it should to be kept in mind that the cyclohexyl ring is dehydrogenated itself, as a homocyclic ring, which does not benefit from the effect of the nitrogen atom. Hence, it is likely that that the H8-indole system is dehydrogenated easily as a first reaction step, while the subsequent dehydrogenation of the cyclohexyl ring is less favorable and would require high temperatures like it is the case for the dehydrogenation of methyl cyclohexane.

Interesting in the context of the dehydrogenation reaction are the findings for the indoline species. Indoline might be expected as an intermediate product in the dehydrogenation of H8-indole. The reaction of H8-indole to indoline is thermodynamically slightly favored compared to the dehydrogenation of homocycles (+59.2 kJ·mol^{-1}/$_{H2}$ compared to +65.4 kJ·mol^{-1}/$_{H2}$ for dibenzyl toluene). However, the second reaction step (indoline to indole) is thermodynamically highly favored (+27.2 kJ·mol^{-1}/$_{H2}$) as only one hydrogen molecule has to be released to create an aromatic system in the N-containing, five-membered ring. It can therefore be expected that the accumulation of significant amounts of indoline in the reaction mixture is highly unlikely.

4 Conclusions

Indole and its derivatives with methyl and phenyl substitution in different positions have been studied, utilizing methods such as combustion calorimetry, differential scanning calorimetry and the transpiration method, regarding their thermochemical properties. High level computational methods based on the DFT approach have been applied for validation. Vapor pressures and enthalpies of sublimation, vaporisation and formation have been derived. The results are relevant, for instance, for the design of novel LOHC-based hydrogen storage processes. The findings reported in this study show, that alkyl substitution of indole lowers the enthalpy of reaction for dehydrogenation by 1 to 3 $\text{kJ·mol}^{-1}/_{\text{H2}}$ (depending on the position of substitution). Multiple substitution enhances this effect. This observation is relevant as lower enthalpy of reaction does not only lower the heat demand for hydrogen release, but also shifts the reaction equilibrium of the hydrogen release reaction towards the products. This allows dehydrogenation at lower temperatures and increases overall energy efficiency.

Declaration of Competing Interest

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

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi

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